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Theoretical and Experimental Investigations of Diradicals, Pyramidalized Alkenes, and Bent Alkynes

Rebecca Lee Hoenigman

A dissertation submitted in partial fulfillment of the requirements for the degree of

Doctor of Philosophy

University of Washington

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Abstract

Theoretical and Experimental Investigations of Diradicals, Pyramidalized Alkenes, and Bent Alkynes

Rebecca Lee Hoenigman

Chair of the Supervisory Committee:
Professor Weston Thatcher Borden
Department of Chemistry

Radical anions have been generated in the gas-phase as potential precursors of diradicals, pyramidalized alkenes, and bent alkynes. The radical anions were studied by gas-phase ion experiments and by density functional theory (DFT) and *ab initio* calculations. The reaction of cyclopentanone with $O^{\bullet-}$ produced three isomers -- the radical anions of cyclopentanone-2,5-diyl (**3**$^{\bullet-}$), cyclopentanone-2,4-diyl, and 2-carbenacyclopentanone. The proton affinity (PA) and electron affinity (EA) of **3**$^{\bullet-}$ were determined by bracketing experiments to be, respectively, 361.6 ± 4.8 kcal/mol and *ca.* 0.5 eV. Although the experimental PA of **3**$^{\bullet-}$ is consistent with the calculated values, both DFT and *ab initio* calculations predict an EA that is 1.0 eV higher than the experimental value. The apparent conflict between the calculated and experimental EA values is resolved by proposing that adiabatic electron transfer leads, not to cyclopentanone-2,5-diyl, but to 1,4-pentadien-3-one. Preliminary negative ion photoelectron spectroscopy experiments support this hypothesis.

The radical anions of 1,5-dehydroquadricyclane (**6**$^{\bullet-}$), norbornyne (**16**$^{\bullet-}$), and norbornenyne (**17**$^{\bullet-}$) were generated from the Squires reaction of, respectively, 1,5-bis(trimethylsilyl)quadricyclane, 2,3-bis(trimethylsilyl)norbornene, and 2,3-bis(trimethylsilyl)norbornadiene. The PAs and EAs of these ions were measured by bracketing experiments and the experimental values were compared with those predicted by calculations. The PA and EA of **6**$^{\bullet-}$ were found to be, respectively, 385.6 ± 5.1 kcal/mol and *ca.* 0.6 eV, in good agreement with the predicted values, and lead to an experimental heat of hydrogenation (ΔH_{H2}) of 91.0 ± 5.1 kcal/mol for 1,5-dehydroquadricyclane. The PA and EA of **17**$^{\bullet-}$ were measured to be, respectively, 377.5 ± 3.0 kcal/mol and 0.81 ± 0.29 eV, again in good agreement with calculated values, leading to ΔH_{H2} = 93.9 ± 11.6 kcal/mol for norbornenyne. The PA and EA of **16**$^{\bullet-}$ were determined to be, respectively, 372.9 ± 3.0 kcal/mol and 0.68 ± 0.1 eV. The experimental EA of **16**$^{\bullet-}$ is in good agreement with the predicted values; but the experimental PA is *ca.* 10 kcal/mol lower than the values predicted by *ab initio* and DFT calculations. The discrepancy between the measured and predicted PAs is resolved by proposing that adiabatic proton transfer occurs through rearrangement of **16**$^{\bullet-}$ to cyclopentylacetylide radical anion.

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Acknowledgements

I would like to thank Professor Weston T. Borden, not only for his support, guidance, and encouragement throughout the years, but also for the opportunities to pursue research at the University of Colorado during my graduate career. I would also like to thank Professors Veronica Bierbaum and Carl Lineberger for productive collaborations and their hospitality at the University of Colorado. Much of this work would not have been completed without the patience and skill of Dr. Shuji Kato, to whom I am in debt for many late night emails and last minute experiments. I would also like to thank the past and present members of the Borden Group for encouraging discussions and commiseration. Last, but certainly not least, I would like to thank my family for their unending love and support.

Introduction

Chemistry is the transformation of one structure of matter into another structure of matter.[1] The study of chemistry seeks to understand and explain these transformations, many of which involve short-lived intermediates. Intermediates, such as diradicals, carbenes, and compounds containing strained π bonds, are short-lived because they are highly reactive. Therefore, it has been difficult to study these compounds.

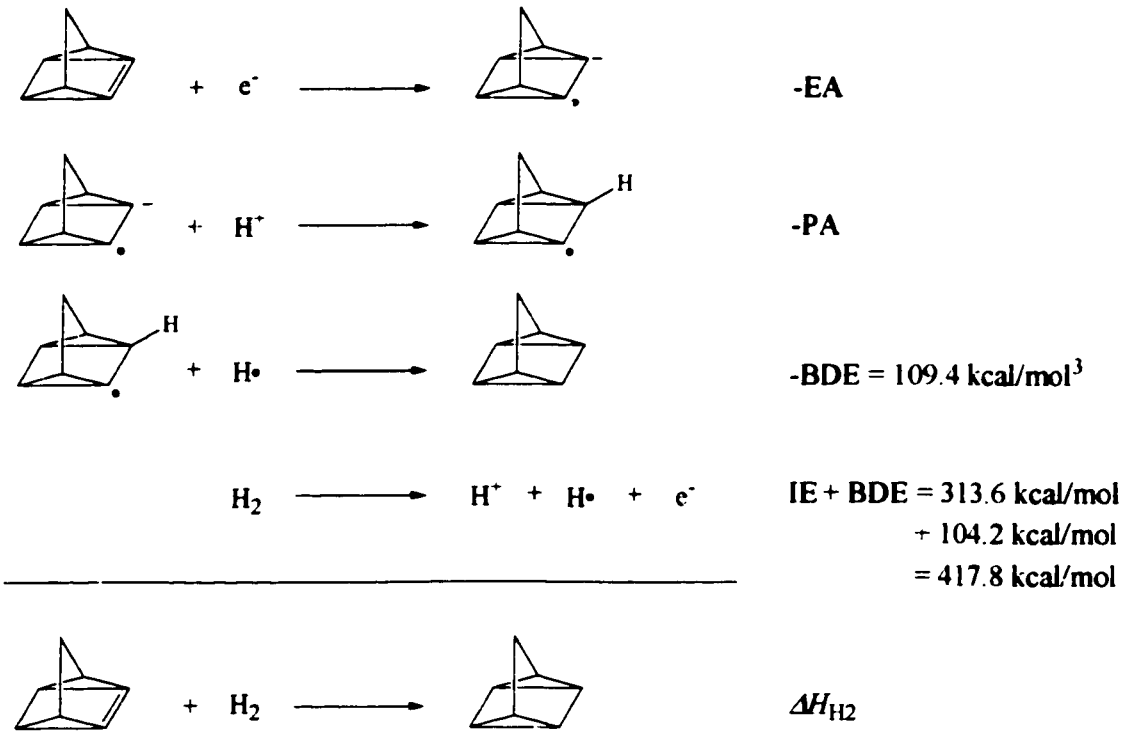
One useful method of studying reactive intermediates is via gas-phase ion chemistry. Gas-phase ion chemistry can provide thermodynamic information about cations and anions, which can in turn lead to information about neutral compounds. For example, if the electron affinity (EA) and proton affinity (PA) of an anion can be measured, these values can be combined in a thermocycle with the ionization potential (IP) of hydrogen to yield the bond dissociation energy (BDE) of the corresponding neutral (Equation 1). The BDE of cubane[2] and quadricyclane,[3] among others, have been measured by this method.

RH	$\rightarrow$	$R^- + H^+$	PA
R^-	$\rightarrow$	$R\cdot + e^-$	EA
$H^+ + e^-$	$\rightarrow$	$H\cdot$	-IP
RH	$\rightarrow$	$R\cdot + H\cdot$	BDE

$$BDE(R\text{-}H) = PA(R^-) + EA(R\cdot) - IP(H\cdot) \qquad \text{(Eq. 1)}$$

Experiments with gas-phase ions can also provide the heat of hydrogenation (ΔH_{H2}) of a pyramidalized alkene or bent alkyne. As shown in Scheme 1 for quadricycl-1(5)-ene, the EA and PA of a radical anion can be combined in a thermocycle with the BDE of the saturated hydrocarbon, the BDE of H_2 and the IP of hydrogen to yield ΔH_{H2}. The heats of hydrogenation of cubene[2,4] and bicyclo[1.1.0]but-1(3)-ene[5] have been measured by this method. Quadricyclene, cubene, and bicyclo[1.1.0]but-1(3)-ene are all far too reactive to allow direct measurements of their heats of hydrogenation in solution.

Scheme 1:



$$\Delta H_{H2}(\text{quadricycl-1(5)-ene}) = 308.4 \text{ kcal/mol} - EA - PA \qquad \text{(Eq. 2)}$$

In addition, gas-phase ion chemistry can provide information about the ground and excited states of reactive intermediates. Negative ion photoelectron spectroscopy (NIPES) is quite likely the best method to measure the singlet-triplet splitting (ΔE_{ST}) of compounds such as diradicals and carbenes.[6] NIPES can also provide information about the frequencies of some of the vibrations in each of these states.

In order to perform gas-phase experiments on radical anions, a method for generating radical anions in the gas-phase is, of course, required. Perhaps the most common method is to allow a neutral compound to react with atomic oxygen radical anion ($O^{\bullet-}$). This reaction results in net H_2^+ abstraction from the neutral, thus producing a hydrocarbon radical anion and H_2O.[7]

Reaction with $O^{\bullet-}$ has been used to generate a variety of carbene and distonic radical anions.[8] However, $O^{\bullet-}$ is a highly reactive and, hence, unselective reagent. A method for regiospecifically generating radical anions in the gas-phase is to allow a disilane to react with F^-, followed by F_2 (the Squires reaction).[9] Both of these methods have been used to generate the radical anions studied in this dissertation.

This dissertation describes six collaborative studies of reactive intermediates by gas-phase ion chemistry. Calculations and syntheses were performed at the University of Washington, and studies of gas-phase ions were performed at either the University of Colorado or the University of Minnesota. Flowing afterglow-selected ion flow tube (FA-SIFT) experiments were performed in collaboration with Professor Veronica Bierbaum and Dr. Shuji Kato at the University of Colorado. Fourier transform ion cyclotron resonance (FT-ICR) experiments were done in collaboration

with Professor Steve Kass at the University of Minnesota. NIPES experiments were carried out in collaboration with the group of Professor Carl Lineberger at the University of Colorado.

Two types of reactive intermediates were studied. The first chapter of this dissertation describes theoretical and experimental work pertaining to diradicals, in particular, cyclopentanone-2,5-diyl. The second chapter is concerned with studies of compounds containing strained π bonds, both pyramidalized alkenes (*e.g.* quadricyclenes) and bent alkynes (*e.g.* norbornyne).

Notes to Introduction:

1. Paraphrased from Prof. Weston T. Borden.

2. Hare, M.; Emrick, T.; Eaton, P. E.; Kass, S. R. *J. Am. Chem. Soc.* **1997**, *119*, 237.

3. Lee, H. S.; DePuy, C. H.; Bierbaum, V. M. *J. Am. Chem. Soc.* **1996**, *118*, 5068.

4. Staneke, P. O.; Ingemann, S.; Eaton, P. E.; Nibbering, N. M. M.; Kass, S. R. *J. Am. Chem. Soc.* **1994**, *116*, 6445.

5. Chou, P. K.; Kass, S. R. *J. Am. Chem. Soc.* **1991**, *113*, 697.

6. Ervin, K. M.; Lineberger, W. C. In *Advances in Gas Phase Ion Chemistry*, Vol. 1, Adams, N. G.; Babcock, L. M., Eds.; JAI Press: Greenwich, CT, 1992.

7. Lee, J.; Grabowski, J. J. *Chem. Rev.* **1992**, *92*, 1611.

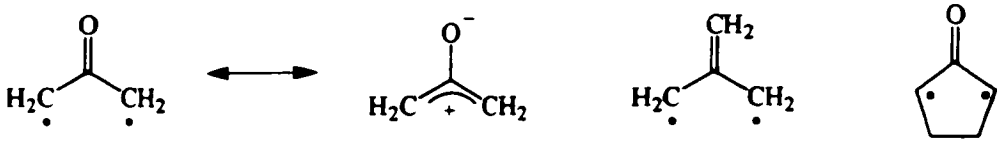
8. See, for example: Born, M.; Ingemann, S.; Nibbering, N. M. M. *Mass Spectrom. Rev.* **1997**, *16*, 181.

9. (a) Wenthold, P. G.; Hu, J.; Squires, R. R. *J. Am. Chem. Soc.* **1994**, *116*, 6961. (b) Wenthold, P. G.; Hu, J.; Squires, R. R. *J. Am. Chem. Soc.* **1996**, *118*, 11865.

Chapter 1: Cyclopentanone-2,5-diyl

Introduction

Oxyallyl (**1**) has been postulated to be an intermediate in many reactions, such as the Favorskii rearrangement,[1] the photochemical rearrangement of 2,5-cyclohexadienones,[2] and the rearrangement of allene oxides to cyclopropanones.[3]



1 **2** **3**

Oxyallyl can be thought of as a heteroatom derivative of trimethylenemethane (**2**), the best-studied non-Kekulé hydrocarbon diradical.[4] As expected from both qualitative considerations and quantitative calculations,[5] electron paramagnetic resonance (EPR)[6] and negative ion photoelectron spectroscopy (NIPES)[7] experiments have both found **2** to have a triplet ground state. The NIPES experiments found the energy difference between the singlet and triplet to be ΔE_{ST} = 16.1 kcal/mol,[7] which is in good agreement with the results of the best calculations.[5]

If oxygen is substituted for a methylene group in **2**, the resulting diradical (**1**) is predicted to have nearly degenerate singlet and triplet states.[5,8] If alkyl substituents are added to **1** the singlet is predicted to be the ground state.[5,8b,9]

Organic chemists typically think of **1** as having a zwitterionic structure, since this is an attractive way of explaining the stabilization of singlet **1**. However,

electronic structure calculations have shown that singlet **1** is predominantly a diradical species, with a strong C=O bond.[8a,9,10] For example, despite the fact that in cyclopentanone-2,5-diyl (**3**) the singlet is predicted to be lower than the triplet by 7.0 kcal/mol, $\nu_{C=O}$ = 1736 cm^{-1} has been predicted.[9b] This prediction is very close to the value of $\nu_{C=O}$ = 1740 cm^{-1} found for cyclopentanone.[11]

Experimental evidence suggests that a singlet really is the ground state of oxyallyl derivatives.[12] However, ΔE_{ST} has not yet been experimentally determined in the parent oxyallyl (**1**), in **3**, or in any other derivative of **1**.

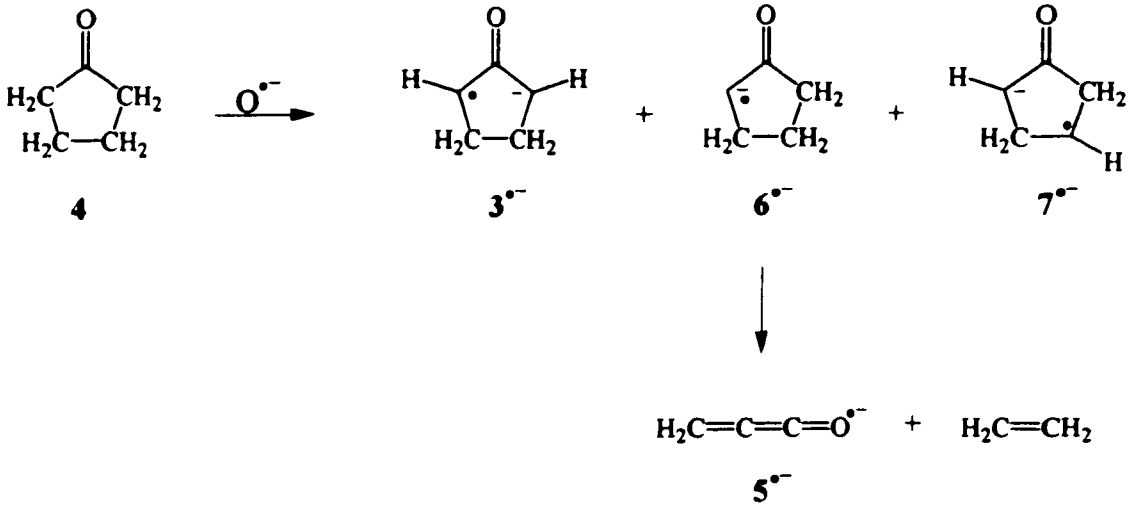
As noted in the Introduction to this dissertation, perhaps the best way to measure the ΔE_{ST} in a diradical is to utilize NIPES.[13] We hoped to employ NIPES to determine experimentally ΔE_{ST} in **3** and also to compare the C=O stretching frequencies in the singlet and triplet states of this diradical with the predicted frequencies.[9b]

Obtaining a NIPE spectrum requires a beam of radical anions. Therefore, in order to obtain the NIPE spectrum of **3**, we need to generate cyclopentanone-2,5-diyl radical anion (**3**$^{\bullet-}$). As discussed in the Introduction to this dissertation, one of the most common ways to generate radical anions in the gas-phase is to allow a neutral compound to react with atomic oxygen radical anion ($O^{\bullet-}$).[14] Thus, a promising route to **3**$^{\bullet-}$ would be to allow cyclopentanone (**4**) to react with $O^{\bullet-}$.

Relatively little is known about the gas-phase ion chemistry that occurs when **4** is allowed to react with $O^{\bullet-}$. Harrison and Jennings have shown that $C_5H_7O^-$, $C_5H_6O^{\bullet-}$, and $C_3H_2O^{\bullet-}$ are produced, but these anions were not characterized.[15]

However, the $C_3H_2O^{\bullet-}$ ion was shown to contain no hydrogen from the carbon that is α to the carbonyl group in **4**. On this basis it was suggested that this radical anion is most likely methylene ketene radical anion ($\mathbf{5}^{\bullet-}$), formed by loss of ethylene from 2-carbenacyclopentanone radical anion ($\mathbf{6}^{\bullet-}$), as shown in Scheme 1.

Scheme 1:



This chapter describes the results of several flowing afterglow-selected ion flow tube (FA-SIFT) experiments on the reaction of **4** and various derivatives of **4** with $O^{\bullet-}$. The products formed in this reaction have been characterized, and the first NIPE spectrum of $\mathbf{3}^{-}$ has been obtained. In addition, density functional theory (DFT) and *ab initio* calculations have been performed in order to aid in the interpretation of the studies of the gas-phase ion chemistry.

Discussion and Results

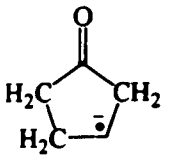
FA-SIFT Experiments: The reaction of **4** with $O^{\bullet-}$ was found to be fairly rapid ($k = 2.94 \times 10^{-9} \pm 0.25$ cm^3 molecule^{-1} s^{-1}, efficiency = 63%) and to generate four primary anions: $C_5H_7O^-$, $C_5H_6O^{\bullet-}$, $C_3H_2O^{\bullet-}$, and HO^- in an approximate ratio of 1 : 4 : 2 : 5. Both HO^- and $C_5H_6O^{\bullet-}$ undergo a secondary reaction with **4** to give $C_5H_7O^-$. The former reaction is calculated to be very exothermic; whereas, the latter is computed to be slightly endothermic (*vide infra*). Finally, electron loss was found to be a major pathway in the reaction of **4** with $O^{\bullet-}$, as an 80% loss of signal was observed.

The $C_5H_7O^-$ ion was determined to be the enolate anion of cyclopentanone by proton affinity (PA)[16] and electron affinity (EA) bracketing experiments.[17] Proton transfer was observed with CHF_2CH_2OH (ΔH_{acid} = 366.4 kcal/mol) and CH_3SH (ΔH_{acid} = 356.8 kcal/mol), while no proton transfer was observed with PhCCH (ΔH_{acid} = 370.6 kcal/mol) or *i*-PrOH (ΔH_{acid} = 375.9 kcal/mol), leading to an assigned PA of 368.5 ± 2.1 kcal/mol for $C_5H_7O^-$. In addition, no electron transfer was observed in the reaction of $C_5H_7O^-$ with SO_2 (EA = 1.107 eV), so the EA of the ion is greater than 1.1 eV. These values are consistent with the formation of cyclopentanone enolate anion (ΔH_{acid} = 368.0 ± 4.2 kcal/mol,[17] EA = 1.598 ± 0.007 eV[18]).

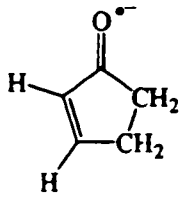
Confirmation that the $C_5H_7O^-$ ion is, in fact, the enolate ion of cyclopentanone came from generating the enolate anion independently by allowing **4** to react with HO^-. The resulting $C_5H_7O^-$ ion showed the same reactivity as the $C_5H_7O^-$ ion generated in the reaction of **4** with $O^{\bullet-}$.

There are six $C_5H_6O^{\bullet-}$ isomers that might be formed from the reaction of **4** with $O^{\bullet-}$. If $O^{\bullet-}$ abstracts a proton from C-2 and a hydrogen atom from C-5 of **4** the desired radical anion, $\mathbf{3}^{\bullet-}$, would be generated. However, $H_2^{\bullet}$ abstraction could also occur from C-2 and C-4 to generate distonic radical anion $\mathbf{7}^{\bullet-}$.

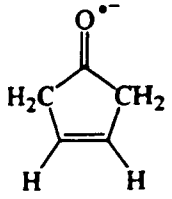
Two carbene radical anions are also possible. If 2,2-$H_2^{\bullet}$ abstraction occurs carbene radical anion $\mathbf{6}^{\bullet-}$ would be formed; whereas, 3,3-$H_2^{\bullet}$ abstraction would lead to carbene radical anion $\mathbf{8}^{\bullet-}$.



$\mathbf{8}^{\bullet-}$



$\mathbf{9}^{\bullet-}$



$\mathbf{10}^{\bullet-}$

In principle, 2,3-$H_2^{\bullet}$ abstraction could also occur to produce the radical anion of 2-cyclopentenone ($\mathbf{9}^{\bullet-}$), while 3,4-$H_2^{\bullet}$ abstraction would lead to the radical anion of 3-cyclopentenone ($\mathbf{10}^{\bullet-}$). However, both of these radical anions are predicted (*vide infra*) to lose an electron spontaneously. Therefore, although $\mathbf{9}^{\bullet-}$ and $\mathbf{10}^{\bullet-}$ might have a transient existence, they are unlikely to be among the $C_5H_6O^{\bullet-}$ radical anions observed. Nevertheless, formation of both $\mathbf{9}^{\bullet-}$ and $\mathbf{10}^{\bullet-}$ could be the source of the electron loss that is observed.

DFT calculations are known to calculate the thermodynamic properties of radical anions well,[19] when unrestricted Hartree-Fock calculations are performed with

the B3LYP functional[20] and the 6-31+G* basis set.[21] Therefore, in order to aid in the structural assignment of the $C_5H_6O^{\bullet-}$ anion(s) formed in the reaction of **4** with $O^{\bullet-}$, (U)B3LYP/6-31+G* calculations were performed on the six possible radical anion products. The results are summarized in Table 1.1.

Table 1.1: (U)B3LYP/6-31+G* Thermochemical Data for $C_5H_6O^{\bullet-}$ at 298 K.

Anion	**3**$^{\bullet-}$	**6**$^{\bullet-}$	**7**$^{\bullet-}$	**8**$^{\bullet-}$	**9**$^{\bullet-}$	**10**$^{\bullet-}$
Relative Enthalpy (kcal/mol)	0	23.4	9.0	40.4	-8.9	11.9
Proton Affinity (kcal/mol)	363.2	386.6	372.2	395.9	n/a	N/a
Electron Affinity (eV)	1.66[a]	1.63	1.56	0.91	-0.03	-0.72

(a) Corrected EA = 1.48 eV using the UB3LYP/6-31+G* EA of the triplet and ΔE_{ST} from CASPT2 (see text).

Although isomer **9**$^{\bullet-}$ is computed to be the radical anion of lowest enthalpy, the extra electron in it is predicted to be unbound, and so **9**$^{\bullet-}$ should not be observed. Similarly, **10**$^{\bullet-}$ is also predicted to be unbound and is unlikely to be observed. However, as already noted, formation of **9**$^{\bullet-}$ and **10**$^{\bullet-}$ could be the reason that 80% signal loss is observed in the reaction of **4** with $O^{\bullet-}$.

The extra electron in all four of the remaining isomers is computed to be strongly bound. Isomer **3**$^{\bullet-}$ is predicted to be lowest in enthalpy by 9.0 kcal/mol. Both **6**$^{\bullet-}$ and **7**$^{\bullet-}$ are computed to be energetically accessible in the reaction of **4** with $O^{\bullet-}$ but carbene radical anion **8**$^{\bullet-}$ is not. The reaction of **4** with $O^{\bullet-}$ to produce **8**$^{\bullet-}$ and H_2O

is predicted at the (U)B3LYP/6-31+G* level of theory to be 3.4 kcal/mol endothermic and is thus unlikely to occur.

The results of the UB3LYP calculations limit the $C_5H_6O^{\bullet-}$ isomers formed in the reaction of **4** with $O^{\bullet-}$ to three possible radical anions -- **3**$^{\bullet-}$, **6**$^{\bullet-}$, or **7**$^{\bullet-}$. As shown in Table 1.1, although these ions are predicted to have similar EAs, their PAs are computed to be significantly different. Distonic radical anion **3**$^{\bullet-}$ is predicted to be the most acidic isomer (PA = 363.2 kcal/mol), while distonic ion **7**$^{\bullet-}$ is computed to be more basic than **3**$^{\bullet-}$ by 9 kcal/mol (PA = 372.2 kcal/mol). Of the three possible radical anions, carbene **6**$^{\bullet-}$ is predicted to be the most basic (PA = 386.6 kcal/mol).

There are a variety of neutral compounds available in the predicted acidity range for **3**$^{\bullet-}$- **7**$^{\bullet-}$ to be able to distinguish between compounds with ΔPA = 10 kcal/mol. As shown in Table 1.2, proton transfer to $C_5H_6O^{\bullet-}$ was observed upon reaction of the $C_5H_6O^{\bullet-}$ ion(s) with *t*-BuSH (ΔH_{acid} = 352.5 kcal/mol) and CH_3SH (ΔH_{acid} = 356.8 kcal/mol). The reaction of CF_3CH_2OH (ΔH_{acid} = 361.9 kcal/mol) with $C_5H_6O^{\bullet-}$ was inconclusive. Although a small amount of proton transfer was observed, loss of $C_5H_6O^{\bullet-}$ due to clustering with CF_3CH_2OH made this experiment inconclusive as to whether proton transfer is actually favorable. Therefore, a conservative lower limit of the PA of $C_5H_6O^{\bullet-}$ is 356.8 kcal/mol, the ΔH_{acid} of CH_3SH. No proton transfer was observed in the reaction of $C_5H_6O^{\bullet-}$ with *i*-PrOH, PhCCH, or CHF_2CH_2OH; and neither proton abstraction, nor H/D exchange occurred upon reaction with CD_3OD (ΔH_{acid} = 381.8 kcal/mol) or CH_3CH_2OD (ΔH_{acid} = 372.4 kcal/mol).

Table 1.2: Results for the Proton Affinity Bracketing Experiments of $C_5H_6O^{\bullet-}$.

Acid	ΔH_{acid} (kcal/mol)	Proton Transfer?
t-BuSH	352.5	Yes
CH_3SH	356.8	Yes
CF_3CH_2OH	361.9	Maybe
CHF_2CH_2OH	366.4	No
PhCCH	370.6	No
i-PrOH	375.9	No
CH_3CH_2OD	372.4	No
CD_3OD	381.8	No

The results of the bracketing experiments place the PA of $C_5H_6O^{\bullet-}$ between those of CH_3SH and CHF_2CH_2OH and thus lead to PA = 361.6 ± 4.8 kcal/mol for $C_5H_6O^{\bullet-}$. This experimental PA is in excellent agreement with the UB3LYP/6-31+G* value of PA = 363.2 kcal/mol for ion $\mathbf{3}^{\bullet-}$.[22] CASPT2 calculations predict $\mathbf{3}^{\bullet-}$ to have a PA of 357.0 kcal/mol, which is also within the error limits of the experimental value. Nevertheless, is it possible for $C_5H_6O^{\bullet-}$ to consist of a mixture of isomers?

Dawson, *et. al.*, observed both 1,1-H_2^+ and 1,3-HD^+ abstraction products when acetone-1,1,1-d_3 was allowed to react with $O^{\bullet-}$, although a slight preference for 1,3-HD^+ abstraction (56%) was noted.[23] Presumably, both oxyallyl radical anion ($\mathbf{1}^{\bullet-}$) and the isomeric carbene radical anion are formed in this reaction. Based on this observation, it seems likely that **4** (an ethano-bridged derivative of acetone) should produce not only distonic radical anion $\mathbf{3}^{\bullet-}$, but also carbene radical anion $\mathbf{6}^{\bullet-}$.

As already noted, it has been proposed that formation of the $C_3H_2O^{\bullet-}$ ion in the reaction of **4** with $O^{\bullet-}$ indicates that $\mathbf{6}^{\bullet-}$ is, in fact, generated in this reaction but subsequently fragments to methylene ketene radical anion ($\mathbf{5}^{\bullet-}$) and ethylene. The fragmentation of $\mathbf{6}^{\bullet-}$ to form $\mathbf{5}^{\bullet-}$ and ethylene is computed to be a stepwise reaction

with a net activation barrier of 14.5 kcal/mol at the (U)B3LYP/6-31+G* level of theory (Figure 1.1). The energy liberated by formation of the ion-dipole complex between $\mathbf{6}^{\bullet-}$ and H_2O in the reaction of **4** with $O^{\bullet-}$ should be enough to overcome this activation barrier and allow carbene $\mathbf{6}^{\bullet-}$ to fragment.

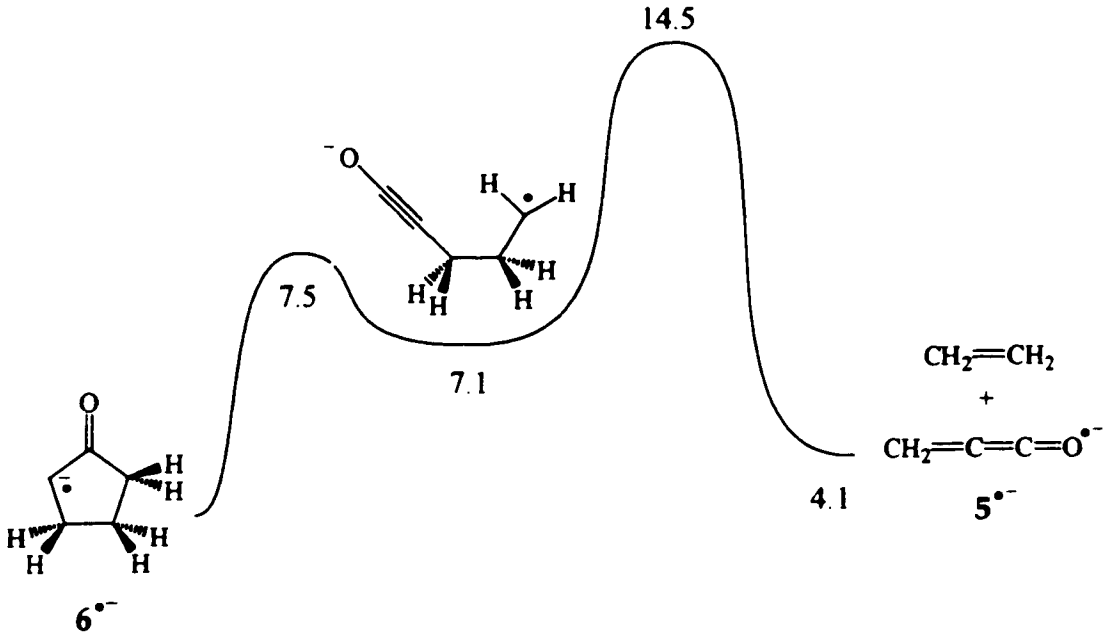


Figure 1.1: Relative Enthalpies (kcal/mol) of Stationary Points Along the Reaction Pathway for the Fragmentation of $\mathbf{6}^{\bullet-}$ to $\mathbf{5}^{\bullet-}$ and Ethylene, computed by (U)B3LYP/6-31+G* .

(U)B3LYP/6-31+G* predicts an EA of 1.03 eV and a PA of 351.1 kcal/mol for $\mathbf{5}^{\bullet-}$. Electron transfer was observed when $C_3H_2O^{\bullet-}$ was allowed to react with SO_2 (EA = 1.107 eV), but no electron transfer was observed upon reaction with CS_2 (EA =

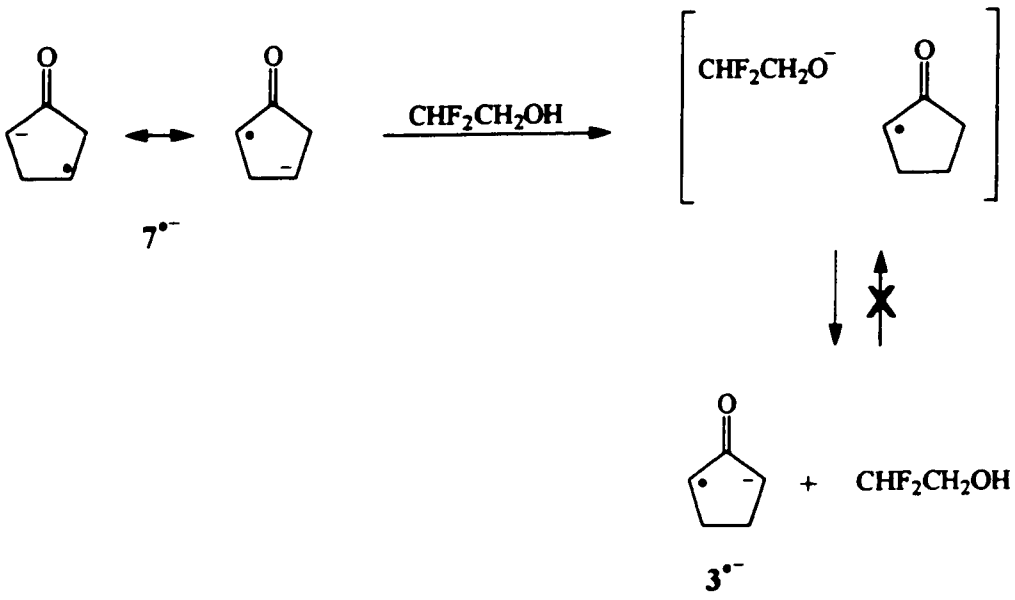
0.52 eV). The EA of $C_3H_2O^{\bullet-}$, thus bracketed, is 0.81 ± 0.29 eV, which is consistent with the calculated value of EA = 1.03 eV for **5**$^{\bullet-}$.

Proton transfer was observed when $C_3H_2O^{\bullet-}$ was allowed to react with CH_3SH, but no proton transfer was observed upon reaction of $C_3H_2O^{\bullet-}$ with CF_3CH_2OH, thus giving an assigned PA of 359.5 ± 2.6 kcal/mol. In this case, UB3LYP/6-31+G* underestimates the PA of **5**$^{\bullet-}$. However, B3LYP calculations seem to overestimate the stability of cumulenes.[24] Therefore, it is perhaps not surprising that UB3LYP calculations underestimate the PA of **5**$^{\bullet-}$.

Since it appears that the reaction of **4** with $O^{\bullet-}$ produces both distonic radical anion **3**$^{\bullet-}$ and carbene radical anion **6**$^{\bullet-}$, and since UB3LYP/6-31+G* calculations predict distonic ion **7**$^{\bullet-}$ to be 14.4 kcal/mol lower in energy than **6**$^{\bullet-}$, if **6**$^{\bullet-}$ is generated in the reaction of **4** with $O^{\bullet-}$, it is reasonable to expect ion **7**$^{\bullet-}$ to be generated as well. However, based on the measured PA of 361.6 ± 4.8 kcal/mol, the resulting $C_5H_6O^{\bullet-}$ anion appears to consist entirely of isomer **3**$^{\bullet-}$, since the PA of **7**$^{\bullet-}$ is computed to be 372.2 kcal/mol.

If **7**$^{\bullet-}$ is formed in the reaction of **4** with $O^{\bullet-}$, why does the observed PA for the $C_5H_6O^{\bullet-}$ radical anion appear to be that of pure **3**$^{\bullet-}$? A possible explanation is that isomerization of **7**$^{\bullet-}$ to **3**$^{\bullet-}$ through multiple proton exchanges could occur in the ion-dipole complex of **7**$^{\bullet-}$ with a neutral acid, as shown in Scheme 2 for CHF_2CH_2OH. For example, if $C_5H_6O^{\bullet-}$ contains isomer **7**$^{\bullet-}$ (predicted PA = 372.2 kcal/mol), proton transfer is expected to occur upon reaction with the more acidic CHF_2CH_2OH (ΔH_{acid} = 366.4 kcal/mol). The $CHF_2CH_2O^-$ formed can migrate to C-5 of the

Scheme 2:



cyclopentanone-2-yl radical, which is also formed, and then abstract an α-hydrogen to generate the more stable ion $\mathbf{3}^{\bullet-}$. The ion-dipole complex can then dissociate to give $\mathbf{3}^{\bullet-}$ and CHF_2CH_2OH, with no observable proton transfer.[25]

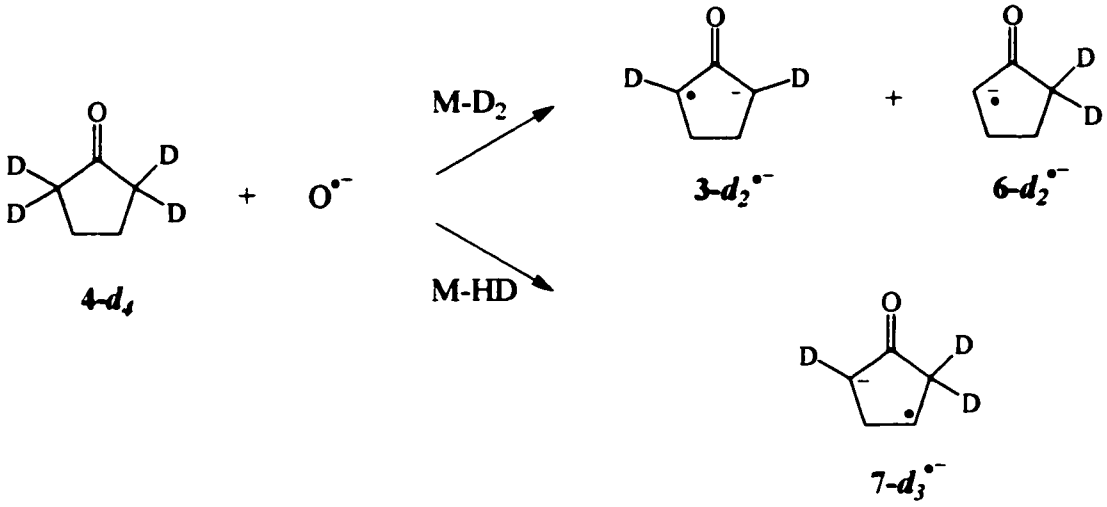
Similarly, the low PA observed for $C_5H_6O^{\bullet-}$ does not rule out the presence of $\mathbf{6}^{\bullet-}$. Although it is possible that all the carbene radical anion $\mathbf{6}^{\bullet-}$ that is formed initially fragments to $\mathbf{5}^{-}$ plus ethylene, if some $\mathbf{6}^{\bullet-}$ persisted, it could, like $\mathbf{7}^{\bullet-}$, isomerize to $\mathbf{3}^{\bullet-}$ when treated with CHF_2CH_2OH. Wenthold and Squires have observed isomerizations, similar to those proposed for $\mathbf{6}^{\bullet-}$ and $\mathbf{7}^{\bullet-}$, in attempting to bracket the PA of the *meta*- and *para*-bromophenyl anions with methanol and water.[26]

In an effort to determine whether distonic radical anion $\mathbf{7}^{\bullet-}$ is formed in the reaction of **4** with $O^{\bullet-}$, a sample of cyclopentanone-2,2,5,5-d_4 (**4**-d_4) was prepared by University of Washington undergraduate Jennie Thomas for FA-SIFT experiments.

The reaction of **4-d_4** with $O^{\bullet-}$ resulted in six primary products, $C_5H_4D_3O^-$, $C_5H_3D_3O^{\bullet-}$, $C_5H_4D_2O^{\bullet-}$, m/z 54, DO^-, and HO^- in an approximate ratio of 0.9 : 1.8 : 4 : 1.1 : 3.7 : 4.6. Both HO^- and DO^- react with **4-d_4** to generate $C_5H_4D_3O^-$ in secondary reactions. The m/z 54 ion did not appear to undergo any secondary reactions, while both the $C_5H_4D_2O^{\bullet-}$ and $C_5H_3D_3O^{\bullet-}$ ions appeared to react with **4-d_4** in slow, slightly endothermic secondary reactions to produce $C_5H_4D_3O^-$.

The formation of the M-HD ion ($C_5H_3D_3O^{\bullet-}$) is presumably due to 2,4-DH^+ abstraction to generate anion **7-$d_3^{\bullet-}$** (Scheme 3). 2,3-DH^+ abstraction would also form an M-HD radical anion (**9-$d_3^{\bullet-}$**), but this radical anion should not bind an electron (Table 1.1). It is, in principle, possible that the formation of $C_5H_3D_3O^{\bullet-}$ could be due to initial formation of **7-$d_3^{\bullet-}$**, but followed by H/D scrambling in the ion-dipole complex and isomerization of **7-$d_3^{\bullet-}$** to **3-$d_3^{\bullet-}$**.[27] However, $C_5H_3D_3O^{\bullet-}$ has different reactivity than $C_5H_4D_2O^{\bullet-}$. For example, upon reaction with NO, $C_5H_3D_3O^{\bullet-}$ forms an

Scheme 3:



adduct much more efficiently than $C_5H_4D_2O^{\bullet-}$. In addition, $C_5H_3D_3O^{\bullet-}$ is more reactive with CS_2 than $C_5H_4D_2O^{\bullet-}$. If $C_5H_3D_3O^{\bullet-}$ was **3-*d*$_3^{\bullet-}$**, rather than **7-*d*$_3^{\bullet-}$**, then both ions would be expected to have the same reactivity.

The simplest explanation for the formation of HO^- is that, instead of abstracting an α-deuterium atom from **4-*d*$_4$**, $O^{\bullet-}$ abstracts a β-hydrogen atom to generate cyclopentanone-3-yl and HO^-. Although the C-H bond dissociation energy (BDE) of **4** is computed to be 7.8 kcal/mol higher at the β-site, hydrogen abstraction by $O^{\bullet-}$ at the β-site is calculated to be exothermic by 6.6 kcal/mol at (U)B3LYP/6-31+G*. Therefore, direct β-hydrogen abstraction appears to be a possible route for formation HO^-.

The observed M-D_2 radical anion ($C_5H_4D_2O^{\bullet-}$) could be due to either 2,5-D_2 abstraction to form distonic ion **3-*d*$_2^{\bullet-}$**, to 2,2-D_2 abstraction to generate carbene **6-*d*$_2^{\bullet-}$**, or to formation of a mixture of **3-*d*$_2^{\bullet-}$** and **6-*d*$_2^{\bullet-}$**. However, some or all of the latter radical anion would be expected to fragment, by loss of ethylene-d_2, to form **5**$^{\bullet-}$.

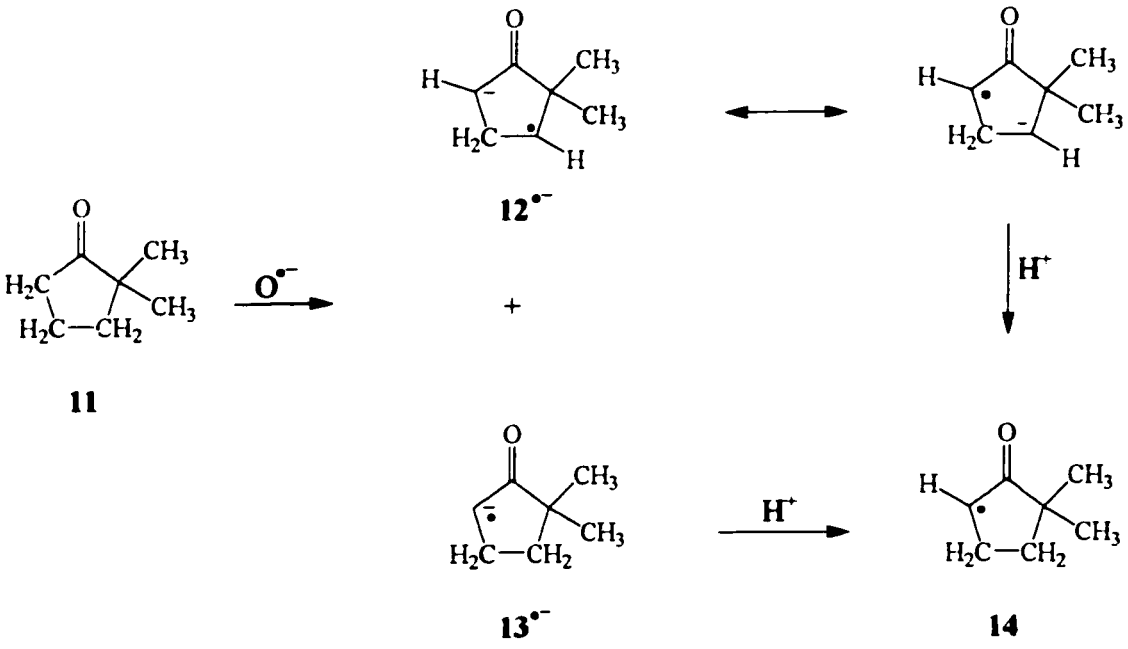
In the reaction of **4-*d*$_4$** with $O^{\bullet-}$ an m/z 54 ion ($C_3H_2O^{\bullet-}$) was detected. Since **5**$^{\bullet-}$ does not have any hydrogens α to the carbonyl group, it would not contain any deuterium. In fact, no ions were observed at either m/z 55 or m/z 56, thus supporting the hypothesis that the $C_3H_2O^{\bullet-}$ ion is **5**$^{\bullet-}$.

The results of the $O^{\bullet-}$ FA-SIFT experiments with both **4** and **4-*d*$_4$** support the generation of **3**$^{\bullet-}$, **6**$^{\bullet-}$, **3-*d*$_2^{\bullet-}$**, and **6-*d*$_2^{\bullet-}$** respectively. In addition, the reaction of **4-*d*$_4$** with $O^{\bullet-}$ suggests that **7-*d*$_3^{\bullet-}$** may also be generated in this reaction. In order to

investigate this possibility further, we attempted to generate a dimethyl derivative of $7^{\bullet-}$, under conditions where a dimethyl derivative of $3^{\bullet-}$ cannot also be formed.

Toward this end, a sample of 2,2-dimethylcyclopentanone (**11**) was synthesized by the method of Conia, *et. al.*[28] and allowed to react with $O^{\bullet-}$. The geminal α-methyl groups in **11** preclude formation of an oxyallyl radical anion. However, two different H_2^+ abstraction products are still possible from the reaction of **11** with $O^{\bullet-}$ (Scheme 4).[29] If 3,5-H_2^+ abstraction occurs, distonic radical anion $\mathbf{12}^{\bullet-}$ would be formed, while 5,5-H_2^+ abstraction from **11** would lead to carbene radical anion $\mathbf{13}^{\bullet-}$.

Scheme 4:



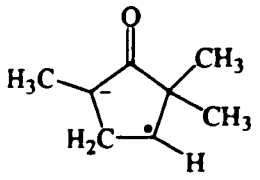
The reaction of **11** with $O^{\bullet-}$ produced an M-H ion ($C_7H_{11}O^-$), an M-H_2 ion ($C_7H_{10}O^{\bullet-}$), and $C_3H_2O^{\bullet-}$ in an apparent ratio of 3 : 2 : 3.[30] The generation of $C_3H_2O^{\bullet-}$ suggests that carbene radical anion **13**$^{\bullet-}$ is formed and, like **6**$^{\bullet-}$, then fragments to methylene ketene radical anion (**5**$^{\bullet-}$), in this case by loss of isobutylene.

The structure of $C_7H_{10}O^{\bullet-}$ was investigated by combining DFT calculations with PA bracketing experiments. UB3LYP calculations predict distonic radical anion **12**$^{\bullet-}$ to be 15.1 kcal/mol lower in energy than carbene radical anion **13**$^{\bullet-}$. Since both **12**$^{\bullet-}$ and **13**$^{\bullet-}$ would form radical **14** upon protonation, **12**$^{\bullet-}$ is computed to be less basic than **13**$^{\bullet-}$ by this amount. The calculated PAs are 370.4 kcal/mol and 385.5 kcal/mol, respectively.

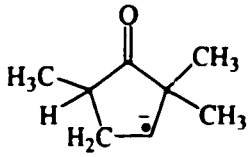
The proton affinity bracketing experiments give an upper limit of 370.6 kcal/mol for the PA of $C_7H_{10}O^{\bullet-}$, since no proton transfer was observed upon reaction of $C_7H_{10}O^{\bullet-}$ with EtOH (ΔH_{acid} = 378.3 kcal/mol) or PhCCH (ΔH_{acid} = 370.6 kcal/mol). In addition, proton transfer was observed when $C_7H_{10}O^{\bullet-}$ was allowed to react with CHF_2CH_2OH, giving a lower limit of ΔH_{acid} = 366.4 kcal/mol. These limits lead to an assigned PA of 368.5 ± 2.1 kcal/mol for this radical anion. The experimental PA is too low for $C_7H_{10}O^{\bullet-}$ to be carbene radical anion **13**$^{\bullet-}$, thus suggesting that all of the carbene radical anion **13**$^{\bullet-}$ that is formed either fragments to **5**$^{\bullet-}$ and isobutylene, or isomerizes to the more stable distonic radical anion **12**$^{\bullet-}$ in the ion-dipole complex with proton transfer reagents.

Further evidence supporting the formation of cyclopentanone-2,4-diyl radical anion (**7**$^{\bullet-}$) in the reaction of **4** with $O^{\bullet-}$ comes from the reaction of 2,2,5-

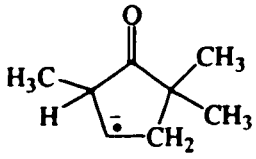
trimethylcyclopentanone (**15**) with $O^{\bullet-}$. There are five possible M-H_2 radical anions that can be formed in this reaction.[31] If $H_2^{\bullet}$ abstraction occurs from C-3 and C-5, distonic radical anion **16**$^{\bullet-}$ would be generated. 3,3-$H_2^{\bullet}$ abstraction leads to carbene radical anion **17**$^{\bullet-}$, while $H_2^{\bullet}$ abstraction could also occur from C-4 leading to carbene radical anion **18**$^{\bullet-}$ In principle, 4,5-$H_2^{\bullet}$ abstraction would lead to **19**$^{\bullet-}$, while 3,4-$H_2^{\bullet}$ abstraction would lead to **20**$^{\bullet-}$.



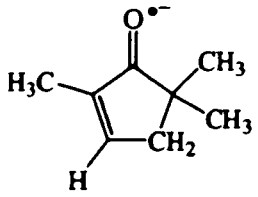
16$^{\bullet-}$



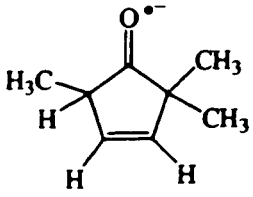
17$^{\bullet-}$



18$^{\bullet-}$



19$^{\bullet-}$



20$^{\bullet-}$

Although, **19**$^{\bullet-}$ is calculated to be the radical anion of lowest enthalpy, like its protio analog (**9**$^{\bullet-}$), both it and **20**$^{\bullet-}$ are not predicted to bind an electron. Of the isomers that are predicted to bind an electron, distonic radical anion **16**$^{\bullet-}$ is computed to be lowest in enthalpy. Carbene radical anions **17**$^{\bullet-}$ and **18**$^{\bullet-}$ are predicted by UB3LYP to be, respectively, 35.8 kcal/mol and 37.3 kcal/mol higher in enthalpy than **16**$^{\bullet-}$.

Only two ions were observed when **15** was allowed to react with $O^{\bullet-}$, an M-H ion and an M-H_2 ion. No $C_3H_2O^{\bullet-}$ ion was detected. The formation of the M-H ion is due to enolate anion formation, while the M-H_2 ion can only be due to the generation of $\mathbf{16}^{\bullet-}$.

The fact that an M-H_2 ion is observed in this reaction supports the formation of unsubstituted radical anion $\mathbf{7}^{\bullet-}$ in the reaction of **4** with $O^{\bullet-}$, and the formation of $\mathbf{7}$-$\boldsymbol{d_3}^{\bullet-}$ in the reaction of $\mathbf{4}$-$\boldsymbol{d_4}$ with $O^{\bullet-}$. The absence of any fragmentation is consistent with $\mathbf{6}^{\bullet-}$, $\mathbf{6}$-$\boldsymbol{d_2}^{\bullet-}$, and $\mathbf{13}^{\bullet-}$, being the precursor of the $C_3H_2O^{\bullet-}$ ion in the reactions of, respectively, **4**, $\mathbf{4}$-$\boldsymbol{d_4}$, and **11** with $O^{\bullet-}$. Thus, the $C_5H_6O^{\bullet-}$ formed in the reaction of **4** with $O^{\bullet-}$ most likely consists, at least initially, of a mixture of isomers -- $\mathbf{3}^{\bullet-}$, $\mathbf{6}^{\bullet-}$, and $\mathbf{7}^{\bullet-}$. Carbene radical anion $\mathbf{6}^{\bullet-}$ fragments to $\mathbf{5}^{\bullet-}$ plus ethylene, but we cannot completely rule out the possibility that some $\mathbf{6}^{\bullet-}$ survives long enough to be among the $C_5H_6O^{\bullet-}$ ions detected.

EA of $C_5H_6O^{\bullet-}$: In order to investigate further the nature of the $C_5H_6O^{\bullet-}$ radical anion formed in the reaction of $O^{\bullet-}$ with cyclopentanone, electron affinity bracketing experiments were completed. When $C_5H_6O^{\bullet-}$ was allowed to react with SO_2, electron transfer was observed (k = 1.433 x $10^{-9} \pm 0.12$ cm^3 $molecule^{-1}$ s^{-1}, efficiency = 93%). Some electron transfer was also observed upon reaction of $C_5H_6O^{\bullet-}$ with CS_2 (k = 2.93 x $10^{-10} \pm 0.23$ cm^3 $molecule^{-1}$ s^{-1}, efficiency = 27%); in addition, clustering [*i.e.* formation of $(C_5H_6O^{\bullet-} \bullet CS_2)$] was also observed. Similarly, when $C_5H_6O^{\bullet-}$ was allowed to react with O_2, the major product was electron transfer

($k = 1.69 \times 10^{-10} \pm 0.13$ cm^3 molecule^{-1} s^{-1}, efficiency = 28%), but a small amount of clustering was observed.

The clustering products observed when $C_5H_6O^{\bullet-}$ was allowed to react with CS_2 (EA = 0.52 eV) and O_2 (EA = 0.45 eV) are the result of endothermic electron transfer.[32] This suggests that the experimental EA for $C_5H_6O^{\bullet-}$ is close to 0.5 eV. However, as shown in Table 1.1, the predicted EAs for all three possible $C_5H_6O^{\bullet-}$ isomers are about 1.6 eV at (U)B3LYP/6-31+G*. Thus, the calculations appear to be in error by *ca.* 1.1 eV.

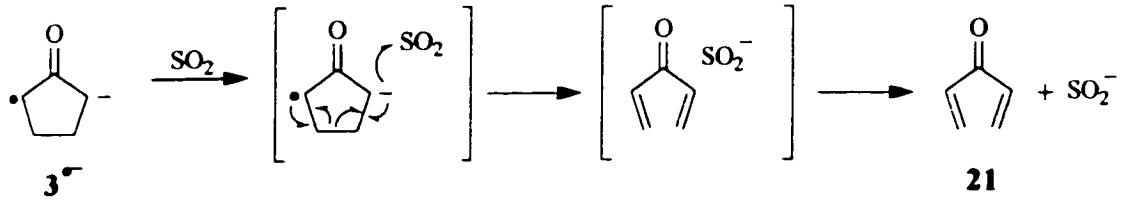
Although B3LYP usually does a good job of calculating EAs,[19] it is a single determinant method and therefore does less well in calculating the energies of singlet diradicals.[33] For example, Powell and Borden predicted the ΔE_{ST} = –7.0 kcal/mol in **3** at CASPT2N/6-311G(2d,p).[9b] Using B3LYP/6-31+G*, ΔE_{ST} = –2.8 kcal/mol is obtained, because the energy of the singlet is overestimated. In order to describe accurately singlet **3**, a multi-reference method should be used.

One computationally cheap method around this failure of B3LYP to compute the energy of singlet **3** accurately is to calculate the energy difference between radical anion $\mathbf{3}^{\bullet-}$ and triplet **3**, using UB3LYP, and then to subtract ΔE_{ST} computed by CASPT2. In this case, using EA = 1.78 eV for forming triplet **3** and ΔE_{ST} = -7.0 kcal/mol, a value of EA = 1.48 eV is obtained for $\mathbf{3}^{\bullet-}$.[34] This value is 0.18 eV lower than the value computed by B3LYP as the difference between $\mathbf{3}^{\bullet-}$ and singlet **3**.

Even though the corrected EA of $\mathbf{3}^{\bullet-}$, and the EAs of isomers $\mathbf{6}^{\bullet-}$ and $\mathbf{7}^{\bullet-}$, are predicted to be *ca.* 1.5 eV, the experimental EA of the $C_5H_6O^{\bullet-}$ ion was measured to

be only 0.5 eV. The most likely explanation for this 1 eV discrepancy is that, in the adiabatic electron transfer process, $\mathbf{3}^{\bullet-}$ undergoes cleavage of the C_3-C_4 σ-bond to generate 1,4-pentadien-3-one (**21**) either in concert with, or prior to electron transfer. This process is shown in Scheme 5 for SO_2.[35]

Scheme 5:



The postulated reaction forms a lower energy neutral than **3**.[36] In fact, using the corrected energy for singlet **3**, **21** is computed to be 21.6 kcal/mol lower in energy. Thus, the adiabatic EA computed for $\mathbf{3}^{\bullet-} \rightarrow \mathbf{21}$ is 0.54 eV, a value that is in excellent agreement with the experimentally determined EA for $C_5H_6O^{\bullet-}$.

It is unlikely that the radical anion of 1,4-pentadien-3-one ($\mathbf{21}^{\bullet-}$) is generated directly from the reaction of **4** with $O^{\bullet-}$, since $\mathbf{21}^{\bullet-}$ is predicted to have a PA of 347.5 kcal/mol, a value which is much lower than the observed value of PA = 361.6 ± 4.8 kcal/mol. However, some rearrangement of $\mathbf{3}^{\bullet-}$ to $\mathbf{21}^{\bullet-}$ apparently does occur in the ion-dipole complexes formed with all three of the electron acceptor reagents used in this study, and it is only when this rearrangement occurs that the electron transfer to the acceptor can take place.[37]

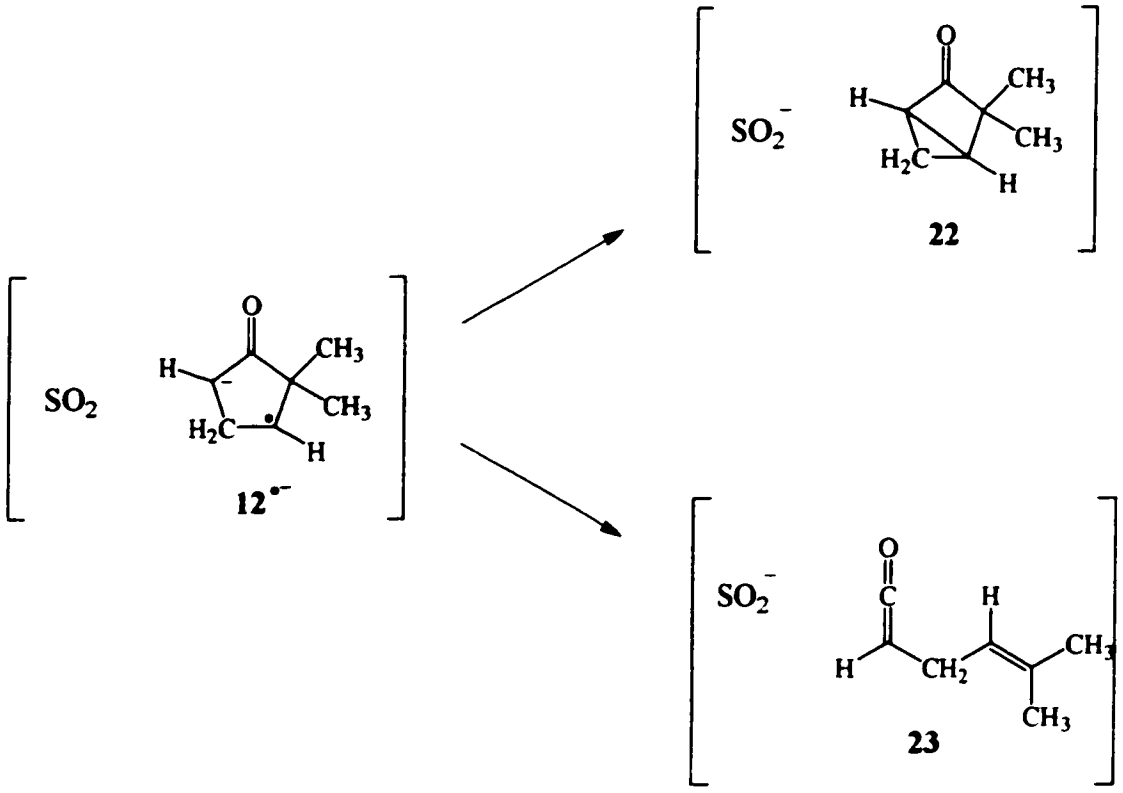
An experimental test of the hypothesis, that the adiabatic EA measured for **3**$^{\bullet-}$ involves formation of **21**, and not **3**, is to measure the EA of $C_5H_6O^{\bullet-}$ by NIPES. Whereas bracketing experiments measure adiabatic EAs, NIPES measures vertical EAs. If the $C_5H_6O^{\bullet-}$ radical anion is **3**$^{\bullet-}$, the vertical EA found by NIPES should be *ca.* 1.5 eV, and not the 0.5 eV that is measured by the EA bracketing experiments. Data from preliminary NIPES experiments are discussed after the following section.

EA of $C_7H_{10}O^{\bullet-}$: Distonic anion **12**$^{\bullet-}$ is predicted by (U)B3LYP/6-31+G* to form a neutral that has a triplet ground state (ΔE_{ST} = 21.2 kcal/mol) with EA = 1.65 eV.

Electron transfer was detected when $C_7H_{10}O^{\bullet-}$ was allowed to react with SO_2, leading to an experimental EA of less than 1.1 eV for distonic radical anion **12**$^{\bullet-}$. This is the second example where there is a large discrepancy between the predicted vertical EA (1.65 eV) and the experimental adiabatic EA (<1.1 eV). Once again, this discrepancy can be explained by rearrangement of the neutral diradical to a more stable closed-shell species upon adiabatic loss of an electron from the radical anion. As illustrated in Scheme 6, distonic radical anion **12**$^{\bullet-}$ can rearrange, either in a stepwise process or in concert with electron transfer, to generate bicyclic ketone **22** or ketene **23**.

The neutral diradical, triplet **12**, is computed to be 23.4 kcal/mol higher in enthalpy than **22**, and 30.3 kcal/mol higher in energy than **23**. The adiabatic EA for **12**$^{\bullet-}$ → **22** is thus predicted to be 0.63 eV, and the adiabatic EA for **12**$^{\bullet-}$ → **23** is predicted to be 0.33 eV. Both of these adiabatic EAs that are computed for **12**$^{\bullet-}$ are

Scheme 6:



consistent with the experimental EA of less than 1.1 eV, but formation of the lower energy product (**23**) would be favored. Additional bracketing experiments, using electron transfer acceptors with low EAs (*e.g.* CS_2 and O_2) are clearly warranted.

NIPES Experiments: Our experiments on the gas-phase ion chemistry of **3**$^{\bullet-}$ piqued our desire to obtain its NIPE spectrum. Not only should the NIPE spectrum of **3**$^{\bullet-}$ provide a value for ΔE_{ST} in cyclopentanone-2,5-diyl (**3**) but it would provide a test of the hypothesis that the adiabatic EA measured for **3**$^{\bullet-}$ involves formation of **21**.

Unfortunately, under the reaction conditions employed in the first NIPES experiments on the ions formed by the reaction of cyclopentanone (**4**) with $O^{\bullet-}$, the enolate ion ($C_5H_7O^-$) was the major product. Moreover, the mass selection capabilities of the NIPE spectrometer cannot distinguish ions separated by 1 amu in the region of m/z 82.[38] However, a NIPE spectrum of the mixture of $C_5H_6O^{\bullet-}$ and $C_5H_7O^-$, formed in the reaction of **4** with $O^{\bullet-}$, was obtained (Figure 1.2). A NIPE spectrum of $C_5H_7O^-$, formed by reaction of **4** with HO^-, was obtained separately (Figure 1.3) and then subtracted from the spectrum of the mixture of anions. The resulting spectrum of the $C_5H_6O^{\bullet-}$ ion is shown in Figure 1.4.

The most obvious feature of this first NIPE spectrum of $C_5H_6O^{\bullet-}$ in Figure 1.4 is that the signal to noise ratio is quite poor. However, there does appear to be at least two electronic states (one at approximately eBE = 1.45 eV and a second at approximately eBE = 1.90 eV) of the neutral formed by electron detachment. Intriguingly, the peaks around 1.90 eV are more intense than those around 1.45 eV, as would be expected if the former belonged to the triplet state of **3** (three spin components), and the latter belonged to singlet state (one spin component). If this interpretation were correct, the ground state of **3** would, as predicted, be a singlet and ΔE_{ST} would be ~ 0.45 eV = 10.35 kcal/mol, 3.35 kcal/mol larger than the calculated value.[9b]

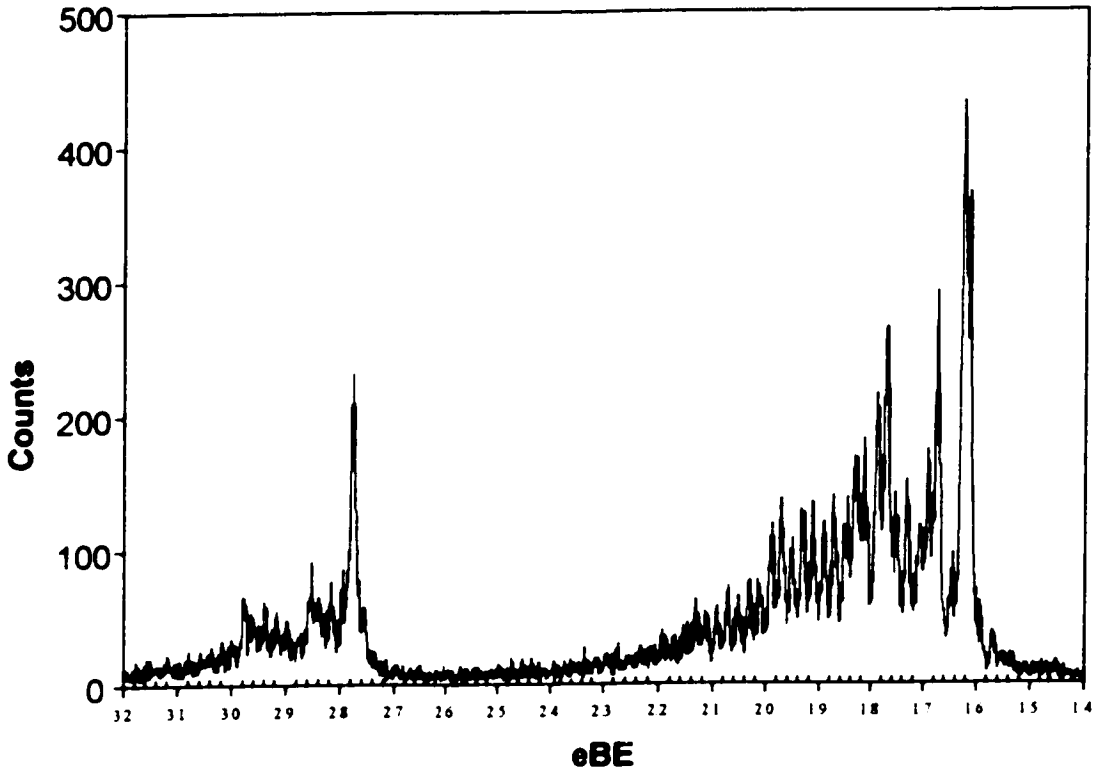


Figure 1.2: Negative ion photoelectron spectrum of the mixture of $C_5H_6O^{\bullet-}$ and $C_5H_7O^-$ ions formed in the reaction of cyclopentanone with $O^{\bullet-}$. eBE is the electron binding energy of the radical anion, which is the difference between the energy used to effect photodetachment (3.408 eV) and the kinetic energy of the photoelectrons detached.

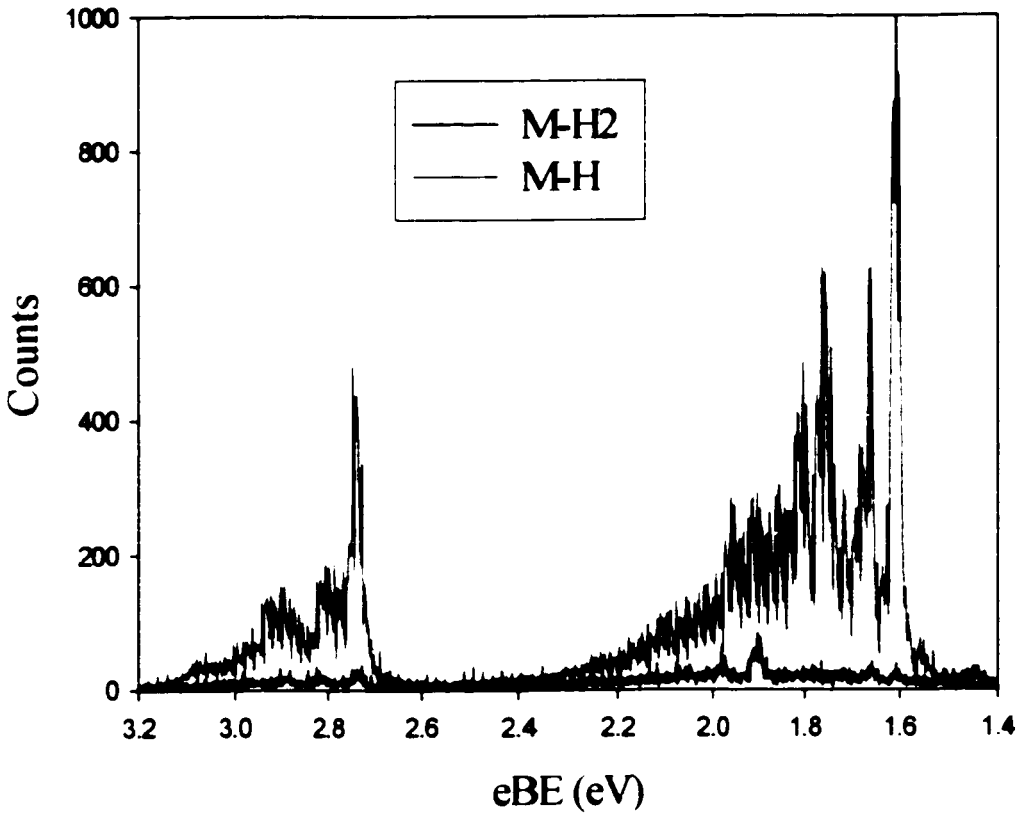


Figure 1.3: Negative ion photoelectron spectrum of the $C_5H_7O^-$ ion formed from the reaction of cyclopentanone with HO^-.

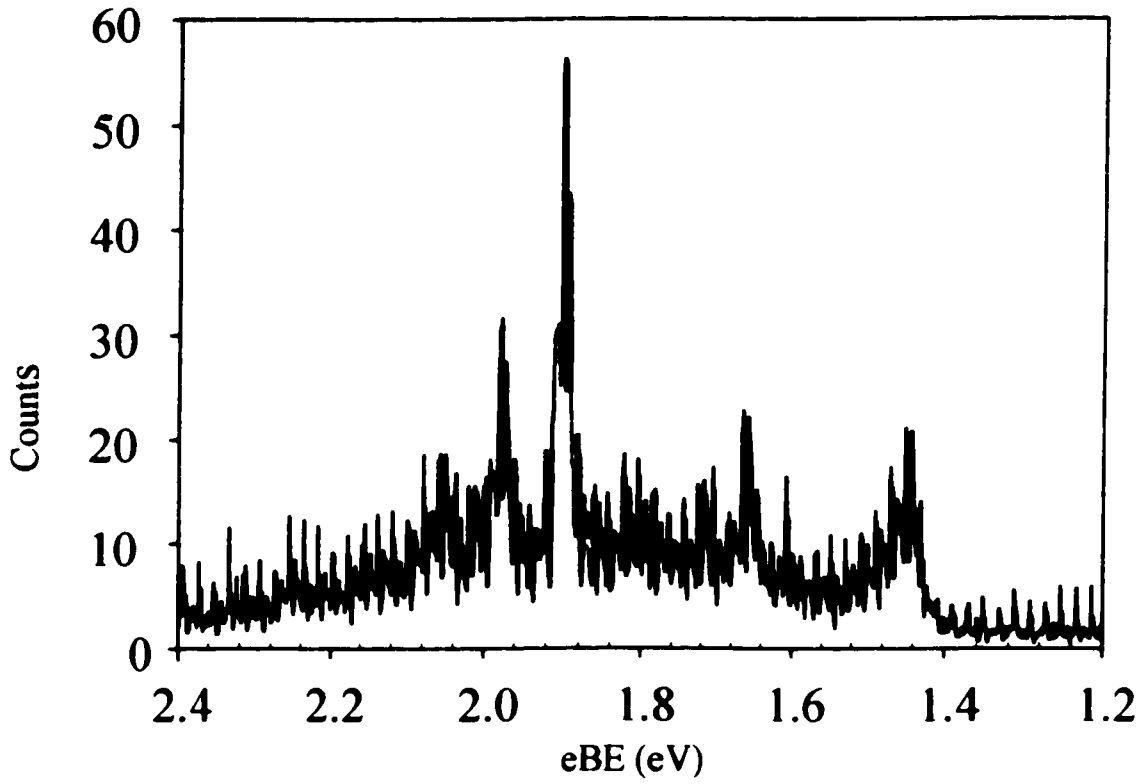


Figure 1.4: Negative ion photoelectron spectrum of the $C_5H_6O^{\bullet-}$ ion formed in the reaction of cyclopentanone with $O^{\bullet-}$. This spectrum is the result of subtracting the NIPE spectrum of $C_5H_7O^-$, shown in Figure 1.3, from the spectrum of the mixture of ions shown in Figure 1.2.

A very clear feature of the NIPE spectrum of $C_5H_6O^{\bullet-}$ in Figure 1.4 is that there is no signal below eBE = 1.4 eV. The first peak, possibly the (0←0) transition of **3**$^{\bullet-}$ to **3**, appears at eBE = 1.45 eV. If further experiments do lead to the assignment of this peak as belonging to vertical formation of singlet **3**, it supports our hypothesis that the adiabatic EA of **3**$^{\bullet-}$ involves rearrangement to a more stable neutral (*i.e.* **21**). Moreover, the position of this peak in the NIPE spectrum at eBE = 1.45 eV is in excellent agreement with the (U)B3LYP EA of 1.48 eV, calculated for **3**$^{\bullet-}$.

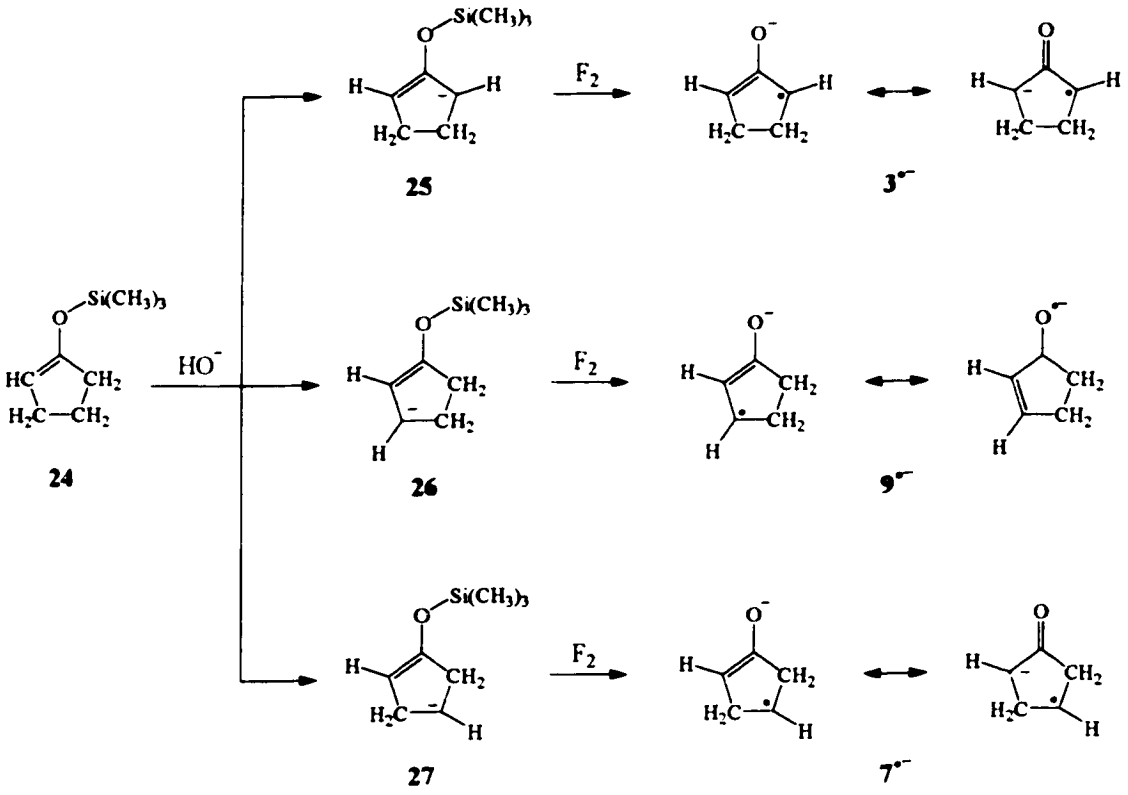
Although a better quality NIPE spectrum is needed, the preliminary NIPES data is consistent with the formation of **3**$^{\bullet-}$ as the major product from the reaction of **4** with $O^{\bullet-}$ and with the predictions that **3** has a singlet ground state. If the spectrum in Figure 1.4 does belong to **3**$^{\bullet-}$, it provides strong support for our hypothesis that, although the adiabatic EA of **3**$^{\bullet-}$ is ~ 0.5 eV, the vertical EA of **3**$^{\bullet-}$ is 1.0 eV higher.

Alternative Routes to 3$^{\bullet-}$: Since the reaction of $O^{\bullet-}$ with **4** does not cleanly produce **3**$^{\bullet-}$, a method for independently generating this radical anion is desirable. As discussed in the Introduction to this dissertation, the Squires reaction of a bis(trimethyl)silane with F^-/F_2 is one way to regiospecifically generate a radical anion.[39] An alternative method, described by Wenthold, *et. al.*, is a modification of the Squires reaction.[27a,40] This method is similar to the Squires reaction in that the second step involves the reaction of a mono(trimethylsilyl) anion with F_2. The modification, however, is that this anion is generated by reaction of HO^- with a mono(trimethylsilyl) precursor, in contrast to the Squires reaction where the mono(trimethylsilyl) anion is generated from reaction of F^- with a bis(trimethylsilyl)

precursor. For example, Wenthold, *et. al.*, used this method to regiospecifically generate oxyallyl radical anion (**1**$^{\bullet-}$) from 2-(trimethylsiloxy)propene.[27a]

With this precedent in mind, 1-(trimethylsiloxy)cyclopentene (**24**) was explored as a potential precursor to **3**$^{\bullet-}$. If allylic anion **25** is generated in the reaction of **24** with HO^-, upon reaction with F_2, this ion would lead to **3**$^{\bullet-}$. However, as shown in Scheme 7, **24** can conceivably generate three anions upon reaction with HO^-.[41]

Scheme 7:



In order to determine which products might be generated in this reaction, DFT calculations were performed on these anions, substituting the $Si(CH_3)_3$ groups in **25** - **27** with SiH_3 groups. Unfortunately, the desired allylic anion **25** is predicted by UB3LYP/6-31+G* to be 3.9 kcal/mol higher in enthalpy than allylic anion **26**. Anion **27** is predicted to be 28.7 kcal/mol higher in enthalpy than **26**, and moreover, **27** is predicted to not bind an electron. Therefore, it should not be observed.

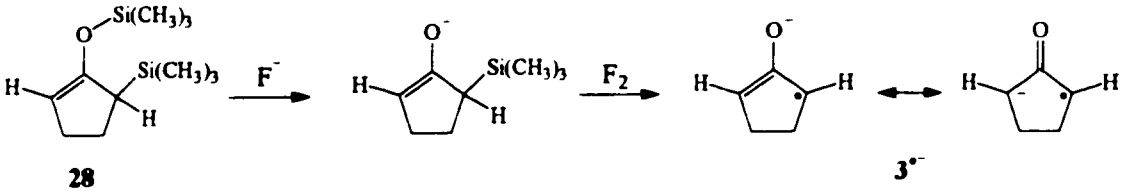
If allylic anion **26** were generated and then allowed to react with F_2, the resulting radical anion should be $\mathbf{9}^{\bullet-}$, which is predicted to not bind an electron. Thus, if the reaction of **24** with HO^- leads to a mixture of **25** and **26**, once this mixture of ions is allowed to react with F_2, any $C_5H_6O^{\bullet-}$ formed should consist entirely of $\mathbf{3}^{\bullet-}$. **24** was synthesized as described by Cazeau, *et. al.*[42] and then allowed to react with HO^-. This reaction generated three products. The major product was cyclopentanone enolate anion ($C_5H_7O^-$, 87.3%), while minor products were trimethylsiloxide ($C_3H_9SiO^-$, 10.3%) and $C_8H_{15}SiO^-$ (*i.e.* M-H, 2.4%). Thus, it appears that direct proton abstraction from **24** is not competitive with the O-Si cleavage reaction.[43]

Further reaction of this mixture of ions with F_2 did yield $C_5H_6O^{\bullet-}$. However, given the very small amount of $C_8H_{15}SiO^-$ formed in the reaction of **24** with HO^-, it is not surprising that the yield of $C_5H_6O^{\bullet-}$ (presumably $\mathbf{3}^{\bullet-}$) was quite low. Thus, the reaction sequence shown in Scheme 7 is not a suitable route for the regiospecific generation of $\mathbf{3}^{\bullet-}$.

Perhaps the most promising method to regiospecifically generate $\mathbf{3}^{\bullet-}$ would be to utilize the Squires reaction of 2-(trimethylsiloxy)-3-(trimethylsilyl)cyclopentene

(**28**) with F^-/F_2 (Scheme 8). This method has been used successfully to generate many distonic radical anions.[39,44] However, this method involves the preparation of the unknown disilane **28**.

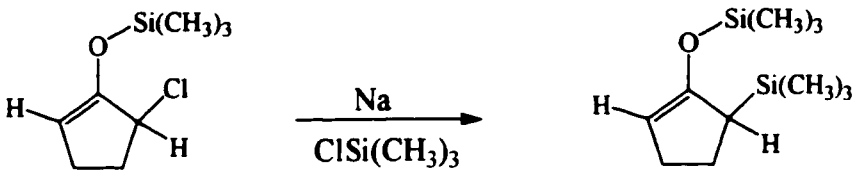
Scheme 8:



28 **3**•⁻

The synthesis of **28** was first attempted by the route shown in Scheme 9. 3-Chloro-2-(trimethylsiloxy)cyclopentene (**29**) was synthesized as described by Miller and McKean.[45] However repeated attempts to metallate **29** with sodium in the presence of chlorotrimethylsilane were unsuccessful. Instead of generating disilane **28**, 2-chlorocyclopentanone was produced.

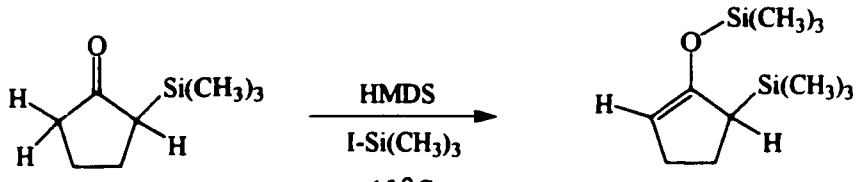
Scheme 9:



29 **28**

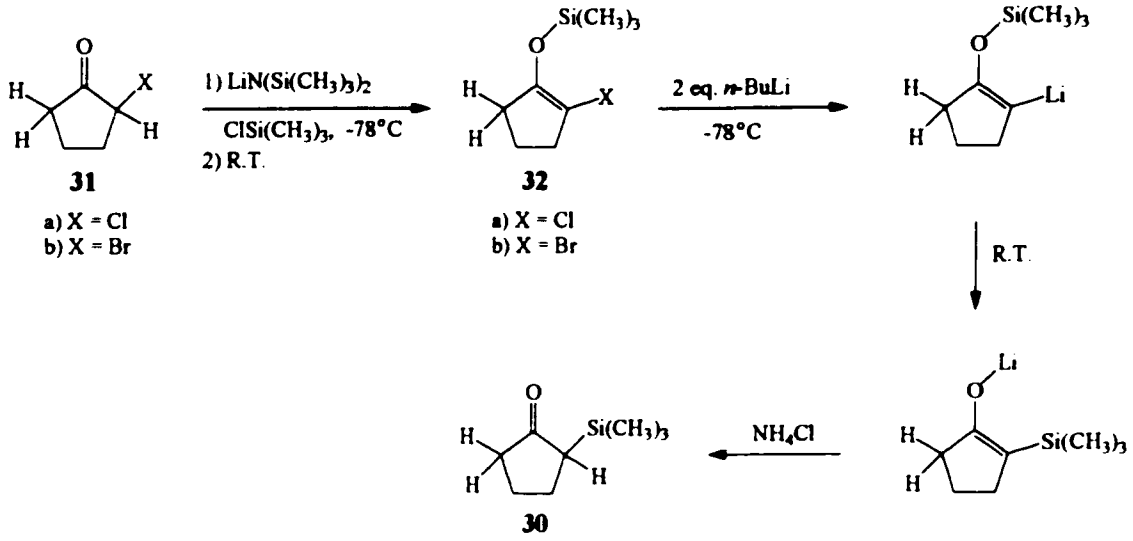
However, modification of Miller and McKean's method might generate **28**. If 2-trimethylsilylcyclopentanone (**30**) were allowed to react with iodotrimethylsilane in the presence of hexamethyldisilazane (HMDS) at –15 °C, it might be possible to generate disilane **28** (Scheme 10). Wiemer has shown that α-trimethylsilyl ketones, like **30**, can be synthesized from α-bromoketones (Scheme 11).[46] The first step in this reaction is to allow an α-bromoketone to react with lithium hexamethyldisilazide at –78 °C in the presence of chlorotrimethylsilane. Upon warming to room temperature, a (trimethylsiloxy)vinyl bromide is generated. The reaction mixture is then cooled to –78 °C and metallated with two equivalents of *n*-butyllithium. Upon warming to room temperature, O to C silyl migration occurs and the desired α-trimethylsilyl ketone is obtained.

Scheme 10:



30 **28**

Scheme 11:



The reaction sequence, outlined in Scheme 11, was first attempted with 2-chlorocyclopentanone (**31a**), since this reagent is commercially available. Although the intermediate chloro(trimethylsilyl)enol ether **32a** was successfully generated in this reaction, subsequent metallation with *n*-butyllithium at –78 °C was unsuccessful.

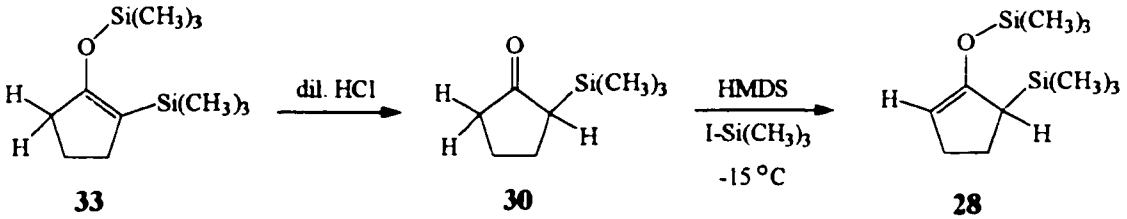
The reaction was then attempted starting with 2-bromocyclopentanone (**31b**), synthesized as described by Baasou and Sheves.[47] Although **31b** was not always purified before reaction, this reagent was found to be easier to handle if washed with $NaHCO_3$ before use. Pure **31b** proved to be stable for weeks if stored in the freezer in CCl_4.

The reaction of **31b** with lithium hexamethyldisilazide at –78 °C, followed by reaction with chlorotrimethylsilane, did not generate enol ether **32b**. Only very minor cyclopentanone products were observed by GCMS analysis (less the 1%). This reaction was attempted both with lithium hexamethyldisilazide generated *in situ* from

HMDS and *n*-butyllithium, and also with commercially available lithium hexamethyldisilazide. In both cases, very little **32b** were obtained (>1% by GC analysis). In an attempt to improve the yield of this reaction, the reaction temperature was varied between −78 °C and room temperature. However, temperature variation had no effect on the products of the reaction. It seems unlikely that this will be a useful route for the synthesis of **30**.

A third route to α-trimethylsilyl ketone **30** is shown in Scheme 12. The unknown trimethylsilyl enol ether, 1-(trimethylsiloxy)-2-(trimethylsilyl)cyclopentene (**33**), could be synthesized by the method of Kowalski, *et. al.*[48] The trimethylsilyl enol ether **33** could be cleaved by reaction with dilute hydrogen chloride to yield **30**. Reaction of **30** with iodotrimethylsilane in the presence of HMDS at −15 °C should afford trimethylsilyl enol ether **28**. Trimethylsilyl enol ether **33**, another possible product of silylation of **30**, should not be formed since Miller and McKean have shown that α substituted ketones form the less substituted trimethylsilyl enol ether when allowed to react with commercially available iodotrimethylsilane in the presence of HMDS.[45]

Scheme 12:



33 **30** **28**

One attractive feature of the route shown in Scheme 12 is that the Squires reaction of the starting trimethylsilyl enol ether **33** could be used to generate carbene radical anion $\mathbf{6}^{\bullet-}$. Thus, this route would yield the bis(trimethylsilyl) precursors, **28** and **33**, of two isomeric $C_5H_6O^{\bullet-}$ radical anions, respectively, $\mathbf{3}^{\bullet-}$ and $\mathbf{6}^{\bullet-}$.

As already noted, independent generation of carbene radical anion $\mathbf{6}^{\bullet-}$ would allow the determination of whether all of $\mathbf{6}^{\bullet-}$, generated in the reaction of **4** with $O^{\bullet-}$, fragments to $\mathbf{5}^{\bullet-}$ and ethylene. If this fragmentation were incomplete, any $C_5H_6O^{\bullet-}$ generated from the Squires reaction of **33** would be carbene radical anion $\mathbf{6}^{\bullet-}$.

Conclusion

The reaction of cyclopentanone (**4**) with $O^{\bullet-}$ generates three isomeric radical anions, $\mathbf{3}^{\bullet-}$, $\mathbf{6}^{\bullet-}$, and $\mathbf{7}^{\bullet-}$. The most abundant radical anion formed in the reaction of **4** with $O^{\bullet-}$ is $\mathbf{3}^{\bullet-}$. This ion was found to have a PA of 361.6 ± 4.8 kcal/mol and an adiabatic EA of 0.5 eV. Although loss of an electron from $\mathbf{3}^{\bullet-}$ to form cyclopentanone-2,5-diyl (**3**) is predicted to require 1.5 eV, the very large discrepancy between the measured and computed EA can be rationalized by proposing that the adiabatic electron transfer process leads not to **3**, but to 1,4-pentadien-3-one (**21**). Divinyl ketone **21** is computed to be 1.0 eV lower in enthalpy than **3**.

Experimental evidence supporting this hypothesis comes from preliminary NIPES experiments on $\mathbf{3}^{\bullet-}$, generated from reaction of **4** with $O^{\bullet-}$. The NIPE spectrum indicates that the vertical EA of $\mathbf{3}^{\bullet-}$ is 1.45 eV, not 0.5 eV. In addition, the preliminary NIPES data suggest that **3** is indeed a singlet diradical with $\Delta E_{ST} \sim 10.35$

kcal/mol. However, further NIPES experiments are needed to provide a better quality spectrum and verify these initial results.

Carbene radical anion $\mathbf{6}^{\bullet-}$ undergoes fragmentation to generate methylene ketene radical anion ($\mathbf{5}^{\bullet-}$) and ethylene. Experiments with 2,2-dimethylcyclopentanone (**11**) suggest that almost all of the carbene radical anion $\mathbf{13}^{\bullet-}$ formed from **11** undergoes either fragmentation to $\mathbf{5}^{\bullet-}$ or isomerization to distonic anion $\mathbf{12}^{\bullet-}$.

Formation of $\mathbf{7}^{\bullet-}$, which is calculated to be 9.0 kcal/mol higher in enthalpy than $\mathbf{3}^{\bullet-}$, is indicated by the fact that reaction of cyclopentanone-2,2,5,5-d_4 with $O^{\bullet-}$ produces $C_5H_3D_3O^{\bullet-}$. This M-HD radical anion was shown to have different reactivity than $C_5H_4D_2O^{\bullet-}$, the M-D_2 radical anion that is also formed in this reaction.

In addition, reaction of 2,2-dimethylcyclopentanone (**11**) with $O^{\bullet-}$ generates an M-H_2 ion. Although the PA measured for this ion is consistent with DFT calculations for the PA of distonic radical anion $\mathbf{12}^{\bullet-}$, there is a large discrepancy between the measured EA and that computed for the formation of the corresponding diradical. This difference can be explained by proposing that, when $\mathbf{12}^{\bullet-}$ loses an electron in the ion-dipole complex with electron acceptors, adiabatic electron transfer leads to either bicyclic ketone **22** or ketene **23** rather than to diradical **12**.

Experimental

Calculations. Density functional theory (DFT) geometry optimizations were carried out with Becke's hybrid, three-parameter, functional[20a] and the correlation functional of Lee, Yang, and Parr[20a] (B3LYP). A vibrational analysis was performed

at each stationary point in order to confirm its identity as a minimum energy structure (no vibrational modes with an imaginary frequency) or as a transition state (one vibrational mode with an imaginary frequency). The vibrational analyses also provide the zero-point and thermal energy corrections that are necessary to convert the B3LYP electronic energies to enthalpies at 298 K. For this purpose the vibrational frequencies were used without scaling.

Geometry optimizations were also performed with (4/4)CASSCF for neutral structures and (5/4)CASSCF for radical anions. The active electrons were distributed among four π molecular orbitals. CASSCF vibrational analyses were carried out in order to establish the nature of each stationary point found and to obtain zero-point and thermal corrections to its energy. In order to include the effects of dynamic electron correlation,[49] CASPT2[50] single-point calculations were performed at CASSCF geometries. The CASSCF zero-point and thermal corrections were used to convert the CASPT2 electronic energies to enthalpies.

All calculations were performed using the 6-31+G* basis set.[21] All (U)B3LYP, and CASSCF calculations were carried out using the Gaussian 98 suite of programs,[51] while all CASPT2 calculations were performed using the MOLCAS package of programs.[52]

Gas-phase Experiments. All NIPES experiments were carried out in collaboration with Prof. Carl Lineberger at the University of Colorado, and all FA-SIFT experiments were carried out in collaboration with Prof. Veronica Bierbaum and Dr. Shuji Kato at the University of Colorado, using a tandem flowing afterglow-

selected ion flow tube (FA-SIFT) instrument that has been described previously.[53] Proton affinity and electron affinity bracketing experiments were performed by allowing neutrals with known acidity and electron affinity to react with the mass selected ion of interest (*e.g.* $C_5H_7O^-$ or $C_5H_6O^{\bullet-}$).[17] Reagents used for gas-phase experiments were synthesized as described below, with the exception of cyclopentanone, which was obtained from Aldrich (99+ %) and used as received.

Synthesis. Benzene and ether solvents were dried over and distilled from Na/benzophenone. All other reagents were used as received, unless otherwise noted. Alkoxides were purchased from Aldrich and stored and handled in a glovebox. Glassware was flame dried under vacuum, and all reactions were performed under argon, unless otherwise noted.

Gas chromatographic analyses were done on a Hewlett Packard 5890 series II gas chromatograph equipped with an Alltech Econo-Cap 30 m x 0.25 mm SE-54 capillary column (0.25 μm film thickness). Mass spectra were obtained on a Hewlett Packard 5890 gas chromatograph coupled to a Hewlett Packard 5971A mass selective detector and equipped with a Supel Co. 30 m x 0.2 μm SPB-1 capillary column (0.2 μm film thickness). ^1H and ^{13}C NMR spectra were recorded in chloroform-d_1 on a Brucker AF 300 and referenced to residual $CHCl_3$ in the sample, unless otherwise noted.

Cyclopentanone-2,2,5,5-d_4 (4-d_4):[54] Distilled cyclopentanone (20 ml, 0.226 mol) was added to 80 ml of D_2O. Sodium deuterioxide was added (0.25 ml, 40 % by weight in D_2O) and the solution was stirred for one hour and then extracted with

methylene chloride (4 x 100 ml). The organic layers were combined, dried over $MgSO_4$, and concentrated by rotary evaporation. The process was repeated five times, each with fresh D_2O. Purification by vacuum fractional distillation with a 4" vigreux column (40 - 45 °C, water aspirator) gave 5.7 g (0.065 mol, 28.7 % yield) of clear liquid. The deuterium incorporation was 96 % as determined by GCMS and ^1H NMR analysis. ^1H NMR (300 MHz) δ 1.87 (s, 4H). MS (EI) 89, 88 (M^+), 87, 86, 60, 59, 57, 56 (100%), 55, 54, 52.

2,2-Dimethylcyclopentanone (11) and 2,2,5-trimethylcyclopentanone (15):[28] A solution of sodium *tert*-pentoxide (28.3 g, 0.257 mol) in 100 ml of benzene was added over 1 hour to a cooled (0 °C) solution of cyclopentanone (10.2 ml, 0.115 mol) and dimethylsulfate (23.8 ml, 0.252 mol) in 226 ml of ether. The reaction mixture was refluxed for 2 hours and 100 ml of water was added. The layers were separated and the benzene layer was washed with water (4 x 100 ml) and dried over $MgSO_4$. To remove the excess dimethylsulfate, 5% aqueous NaOH (200 ml) was added to the benzene layer and the solution was stirred for 2 hours. The layers were separated and the organic layer was washed with water until neutral (4 x 400 ml). The unreacted cyclopentanone and methylcyclopentanone were removed by converting them to bisulfite addition products: saturated sodium bisulfite (200 ml) was added to the benzene layer and the solution was stirred for 2 hours at room temperature. Water (100 ml) was added and the layers were separated. The aqueous layer was washed with ether (3 x 100 ml). The organic layers were combined, dried over $MgSO_4$, and

the pale yellow solution was concentrated by rotary evaporation. Distillation (50 – 70 °C, 8" vigreux) gave 4.24 g of a clear liquid consisting of **11**, **15**, and 2,2,5,5-tetramethylcyclopentanone. **11** was isolated from this mixture by converting it to a formic ester. In a typical reaction, a solution of the ketone mixture (1.6 g) and ethyl formate (1.9 ml, 0.024 mol) was added over 30 – 60 minutes to a solution of sodium methoxide (5.47 g, 0.101 mol) in 45 ml of benzene. The reaction mixture was allowed to stir overnight and ice was added (10 g). The ice was allowed to melt and the layers were then separated. The benzene layer was washed with water (2 x 10 ml) and dried over $MgSO_4$. The benzene layer was saved, as it consisted of **15** and 2,2,5,5-tetramethylcyclopentanone. **15** was not separated from the tetramethyl impurity. The aqueous layers were combined, acidified with 30 % aqueous HCl, and extracted with ether (4 x 10 ml). The organic layers were combined, dried over $MgSO_4$, and concentrated by rotary evaporation to give 511 mg of a clear liquid (98 % pure by GC). ^{1}H NMR (300 MHz) δ 0.96 (s, 6H), 1.75 (m, 4H), 2.18 (m, 2H). MS (EI) 112 (M^+), 97, 79, 69, 56 (100 %) 41, 39.

1-(Trimethylsiloxy)cyclopentene (24):[42] Cyclopentanone (4.4 ml, 49.8 mmol) was added to a solution of pre-dried sodium iodide (9.3 g, 62.0 mmol) in 62 ml of acetonitrile. Triethylamine (8.7 ml, 62.4 mmol) was slowly added, followed by addition of chlorotrimethylsilane (7.9 mol, 62.3 mmol). The solution was stirred for 30 minutes at room temperature, upon which time 100 ml each of cold pentane and saturated NH_4Cl were added. Cold water (50 ml) was added to dissolve all salts and

the layers were separated. The aqueous layers were washed with pentane (3 x 50 ml). The organic layers were combined and washed with water (1 x 50 ml) and saturated NH4Cl (1 x 50 ml) and then dried over $MgSO_4$. The solvent was removed by rotary evaporation. Purification by vacuum fractional distillation (4" vigreux, water aspirator) gave 3.96 g (25.4 mmol, 51.0 % yield) of a colorless liquid. ^{1}H NMR (300 MHz) δ 0.22 (s, 9H), 1.87 (m, J = 1.0 Hz, 7.3 Hz, 2H), 2.28 (m, J = 1.5 Hz, 7.3 Hz, 4H), 4.64 (app. s, 1H). MS (EI) 156 (M^+), 155, 141, 127, 99, 75 (100 %), 73, 59, 45.

3-Chloro-2-(trimethylsiloxy)cyclopentene (29):[45,55] Hexamethyldisilazane (0.51 ml, 2.42 mmol) and iodotrimethylsilane (0.32 ml, 2.24 ml) were added subsequently to a cooled (-20 °C) solution of 2-chlorocyclopentanone (0.20 ml, 1.99 mmol) in 5 ml of CCl_4. The solution was stirred at –20 °C for 30 minutes, then warmed to 10 °C and stirred for an additional 3 hours. The solution was diluted with 20 ml of pentane and subsequently washed with saturated $NaHCO_3$ (3 x 10 ml), 10 % aqueous sodium thiosulfate (3 x 10 ml), and water (1 x 10 ml). The organic layer was dried over $MgSO_4$ and concentrated by rotary evaporation to yield 361 mg (1.89 mmol, 95.1 % yield) of dark orange liquid (~ 90% pure by GCMS). ^{1}H NMR (300 MHz) δ 0.25 (s, 9H), 2.29 (m, J = 2.0 Hz, 8.0 Hz, 4H), 4.65 (dt, J = 2.0 Hz, 2.6 Hz, 1H), 4.89 (dt, J = 2.0 Hz, 2.6 Hz, 1H). ^{13}C NMR (300 MHz) δ 0.06, 26.79, 33.04, 65.32, 107.52, 154.73. MS (EI) 192, 190 (M^+), 177, 175, 155, 139, 95, 93, 81, 73 (100 %), 65.

2-Bromocyclopentanone (31b):[47] A solution of cyclopentanone (17.5 ml, 0.198 mol) and N-bromosuccinimide (35.6 g, 0.200 mol) in 200 ml of CCl_4 was refluxed for 3 hours in the presence of a catalytic amount of benzoyl peroxide. The solution was cooled and the solids were filtered. The organic layer was washed with water (3 x 100 ml) and saturated $NaHCO_3$ (2 x 100 ml) and then dried over $MgSO_4$. The solvent was removed by rotary evaporation and purification by vacuum fractional distillation (80 – 90 °C, 0.65 – 0.85 Torr) gave 6.03 g (0.037 mol, 18.7 % yield) of clear liquid (90 % pure by GC). ^{1}H NMR (300 MHz) δ 2.02 (m, 6H), 3.92 (s, 1H). MS (EI) 164, 162 (M^+), 108, 106, 83 (100 %), 55, 39.

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16. The proton affinity (PA) of an anion is equivalent to the gas phase acidity (ΔH_{acid}) of the corresponding neutral.

17. Unless otherwise noted, all thermochemical data come from: (a) Lias, S. G.; Bartmess, J. E.; Liebman, J. F.; Holmes, J. L.; Levin, R. D.; Mallard, W. G. *J. Phys. Chem. Ref. Data* **1988**, *17*, Suppl. No. 1. These data are available in updated form from: (b) Linstrom, P. J.; Mallard, W. G., Eds.; **NIST Chemistry WebBook, NIST Standard Reference Database Number 69**, July 2001, National Institute of Standards and Technology, Gaithersburg, MD, 20899 (http://webbook.nist.gov).

18. Brauman has revised the EA of the enolate anion of cyclopentanone from 1.617 ± 0.056 eV which is currently listed on the NIST WebBook[17b] to 1.598 ± 0.007 eV. Brinkman, E. A.; Berger, S.; Marks, J.; Brauman, J. I. *J. Chem. Phys.* **1993**, *99*, 7586.

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22. (U)B3LYP/6-31+G* predicts the reaction of **3**$^{\bullet-}$ with **4** to yield $C_5H_7O^-$ and cyclopentanone-2-yl to be endothermic by 3.6 kcal/mol, while the reaction of **7**$^{\bullet-}$ with **4** to yield cyclopentanone-3-yl and $C_5H_7O^-$ is predicted to be endothermic by 2.2 kcal/mol. However, if **7**$^{\bullet-}$ reacts with **4** to generate the more stable cyclopentanone-2-yl and $C_5H_7O^-$, the reaction is predicted to be exothermic by 5.6 kcal/mol. Likewise, carbene radical anion **6**$^{\bullet-}$ is predicted to react in an exothermic manner with **4** to give $C_5H_7O^-$ and cyclopentanone-2-yl (ΔH = -19.6 kcal/mol).

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24. (a) Plattner, D. A.; Houk, K. N. *J. Am. Chem. Soc.* **1995**, *117*, 4405. (b) Woodcock, H. L.; Schaefer, H. F., III; Schreiner, P. R. *J. Phys. Chem. A* **2002**, ACS ASAP.

25. In principle, this mechanism could be tested by allowing $C_5H_6O^{\bullet-}$ to react with CHF_2CH_2OD. If isomer **7**$^{\bullet-}$ is present, it would be expected to abstract D^+ from CHF_2CH_2OD. Upon isomerization, **3-*d*$_1$**$^{\bullet-}$ (*i.e.* $C_5H_5DO^{\bullet-}$) should be observed. However, due to the similar acidities of **3**$^{\bullet-}$ and CHF_2CH_2OD, any **3-*d*$_1$**$^{\bullet-}$ formed might be expected to undergo 2 H/D exchanges with CHF_2CH_2OD to form, ultimately, **3-*d*$_3$**$^{\bullet-}$. In practice, the use of CHF_2CH_2OD induces large signal loss due to clustering. Therefore, observation of any **3-*d*$_3$**$^{\bullet-}$ that may be formed would be difficult.

26. Wenthold, P. G.; Squires, R. R. *J. Am. Chem. Soc.* **1994**, *116*, 6401.

27. Squires has noted that the reaction of deuterated hydrocarbons with $O^{\bullet-}$ does not necessarily give reliable ratios of the relative yields of M-H_2, M-HD, and M-D_2, as the nascent radical anion can undergo H/D exchange with the water molecule in the ion-dipole complex before dissociation. (a) Wenthold, P. G.; Hu, J.; Hill, B. T.; Squires, R. R. *Int. J. Mass Spectrom.* **1998**, *179/180*, 173. (b) Ref. 18a.

28. (a) Gault, F. G.; Germain, J. E.; Conia, J. M. *Bull. Soc. Chim. France* **1957**, 1064. (b) Conia, J. M. *Bull. Soc. Chim. France* **1950**, 547. (c) House, H. O.; Trost, B. M. *J. Org. Chem.* **1965**, *30*, 2502.

29. There are two possible radical anions that can be formed if H_2^+ abstraction occurs from only the methyl substituents. However, both of these radical anions are predicted to be ≥ 30 kcal/mol higher in enthalpy than **12**$^{\bullet-}$. Likewise, 4-carbena-2,2-dimethylcyclopentanone radical anion is predicted to be 33 kcal/mol higher in enthalpy than **12**$^{\bullet-}$.

30. Due to discrimination against the higher masses, the ratios are not quantitative.

31. It is conceivable that H_2^+ abstraction could also occur in a number of combinations from the three methyl groups. However, the relative enthalpy for these isomers is predicted to be well over 30 kcal/mol relative to **16**$^{\bullet-}$ at UB3LYP/6-31+G*.

32. The endothermic nature of these reactions can also be inferred from the slow rates of reaction and poor efficiencies.

33. Bally, T.; Borden, W. T. In *Reviews in Computational Chemistry*, Vol. 13, Lipkowitz, K. B.; Boyd, D. B., Eds.; John Wiley and Sons: New York, 1999.

34. At CASPT2/6-31+G* EA = 1.32 eV was obtained for singlet **3**. However, in our experience CASPT2 is more likely than B3LYP to underestimate EAs.

35. Rearrangement to a more stable neutral could, at least in principle, explain the large discrepancy between the computed vertical EA for acenaphthyne radical anion and the experimental adiabatic value. Broadus, K. M.; Kass, S. R. *J. Am. Chem. Soc.* **2001**, *123*, 4189.

36. Closure of **3** to form bicyclo[2.1.0]pentan-5-one is highly unlikely since the bicyclic ketone is computed to be 27.5 kcal/mol higher in enthalpy than **21**.

37. It has been postulated that a carbocation rearrangement is responsible for the anomalously high PA found for protonation of a pyramidalized olefin. Cleven, C. D.; Hoke, S. H.; Cooks, R. G.; Hrovat, D. A.; Smith, J. M.; Lee, M.-S.; Borden, W. T. *J. Am. Chem. Soc.* **1996**, *118*, 10872.

38. The NIPE spectrometer employs a Wein filter for mass resolution. At low masses the mass resolution is ~1-2 amu (*i.e.* $O^{\bullet-}$ can be distinguished from HO^-), but for higher masses the resolution is ~2-3 amu.

39. (a) Wenthold, P. G.; Hu, J.; Squires, R. R. *J. Am. Chem. Soc.* **1994**, *116*, 6961. (b) Wenthold, P. G.; Hu, J.; Squires, R. R. *J. Am. Chem. Soc.* **1996**, *118*, 11865.

40. Prof. Wenthold later informed me that this method does not give high yields of the desired radical anions. For the oxyallyl case, Wenthold observed an approximate 1:1 ratio of oxyallyl radical anion (m/z 56) to enolate anion (m/z 57).

41. Although it is possible that a vinyl anion could also be generated, attempts to find a stationary point for 1-siloxycyclopentene-2-yl anion were unsuccessful and lead to 2-silylcyclopentanone-2-yl enolate anion.

42. (a) Cazeau, P.; Duboudin, F.; Moulines, F.; Babot, O.; Dunogues, J. *Tetrahedron*, **1987**, *43*, 2075. (b) Spectral comparison with: Rathore, R.; Kochi, J. K. *J. Org. Chem.* **1996**, *61*, 627.

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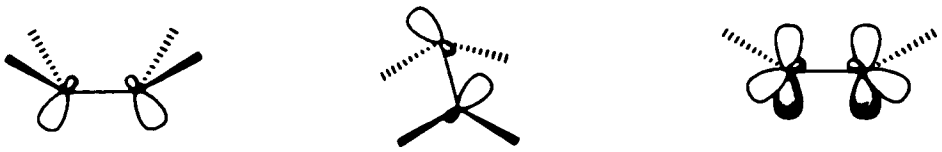
Chapter 2: Strained π-Bonds

Introduction

For over a century, chemists have been interested in strained molecules.[1] More recently, pyramidalized alkenes[2], twisted alkenes,[3] and bent alkynes[4] have been the subject of both theoretical and experimental studies. In pyramidalized alkenes the doubly bonded carbons and the four carbons attached to them do not lie in the same plane (Figure. 2.1). Similarly, a bent alkyne contains a triple bond in which the two sp hybridized carbons are not collinear with the two attached carbons. In order to restore some of the overlap between the atomic orbitals that form the π bond lost upon twisting, the olefinic carbons in twisted alkenes also tend to pyramidalize.

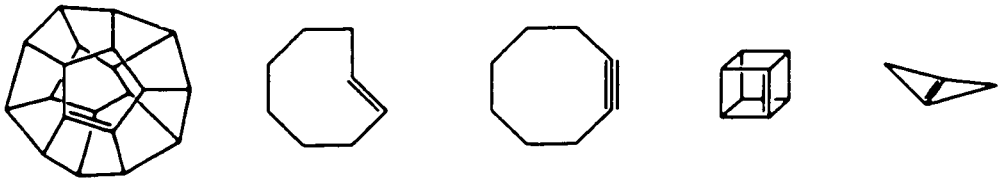


Pyramidalized Alkene Twisted Alkene Bent Alkyne

Figure 2.1: Orbital Diagram of Compounds Containing Strained π Bonds.

In pyramidalized alkenes, twisted alkenes, and bent alkynes the overlap between the 2p atomic orbitals that form π bonds is reduced. Consequently, all three types of molecules tend to be highly reactive and difficult to isolate.

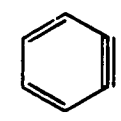
Some pyramidalized alkenes, twisted alkenes, and bent alkynes, such as dodecahedrene (**1**),[5] *trans*-cyclooctene (**2**),[6] and cyclooctyne (**3**),[7] are isolable. However, the most interesting examples of each of these types of compounds only have a fleeting existence. Nevertheless, as mentioned in the Introduction to this dissertation, two highly pyramidalized alkenes, cubene[8] (**4**) and bicyclo[1.1.0]but-1(3)-ene[9] (**5**), have been formed and studied in the gas-phase. In addition, quadricyclenes **6** – **8** have been generated and trapped in solution.[10] However, there is, as yet, no experimental evidence for the existence of the twisted alkene, quadricyclene **9**.



1 **2** **3** **4** **5**

6 **7** **8** **9**

Perhaps the most studied bent alkyne is *ortho*-benzyne (**10**).[11] Although **10** is not isolable, it has been both generated and trapped in solution[11i-l] as well as studied in the gas-phase.[11a-e] The electron affinity (EA),[11a,b] gas phase acidity (ΔH_{acid}),[11c] and singlet-triplet splitting (ΔE_{ST})[11a,b] in **10** have been experimentally measured.



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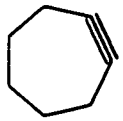

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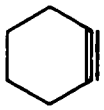

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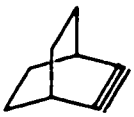

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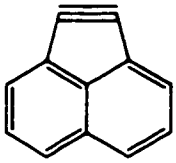

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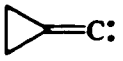
One intriguing question about cycloalkynes is: what is the smallest size ring that can contain a triple bond? Although cycloheptyne (**11**) is not isolable, **11** has been generated and trapped in solution.[12] Both cyclohexyne (**12**)[13] and cyclopentyne (**13**)[14] have also been generated and trapped in solution. In addition, bicyclic analogs of **12** and **13** have been observed. For example, bicyclo[2.2.2]octyne (**14**),[15] acenaphthyne (**15**),[16] norbornyne (**16**),[17] and norbornenyne (**17**)[18] have all been generated and trapped in solution.

18



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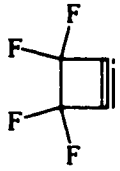


20

To date, cyclopentyne is the smallest cycloalkyne that has been experimentally observed, but is it possible to place a triple bond in a three- or four-membered ring? Thus far, efforts to trap cyclobutyne (**18**) in solution have been unsuccessful.[19] A computational study by Johnson and Daoust predicted **18** would

rearrange with little to no barrier to cyclopropylidenecarbene (**19**) in an exothermic reaction (ΔH = -20.9 kcal/mol).[20] Although **18** may be inaccessible, Johnson and Daoust suggested that perfluorocyclobutyne (**20**) might be stable to rearrangement.[20] A recent computational study has confirmed this prediction,[21] and there is some evidence that **20** has been generated and trapped in solution.[22]

Although many pyramidalized alkenes and bent alkynes have been generated and chemically trapped, for most of these molecules little thermodynamic information has been gathered for these species. As discussed in the Introduction to this dissertation, perhaps the best way to measure the thermodynamic properties of reactive intermediates is via gas-phase ion chemistry. However, in order to perform gas-phase ion experiments, one must, of course, be able to generate the ion of interest. Unfortunately, most alkene and alkyne radical anions have very short lifetimes because loss of an electron is exothermic (*i.e.* the EA is negative).[23]

It has been shown that pyramidalization of a π bond effectively lowers the energy of the lowest unoccupied molecular orbital (LUMO) (Figure 2.2).[24] Thus, the EA of an alkene is effectively increased (*i.e.* made more positive) by pyramidalization, and the EA of an alkyne is increased by bending. Although this effect is not large enough to allow cyclooctyne (**3**) to bind an electron,[25] *ortho*-benzyne (**10**) has been found to have a positive EA.[11a,b] It should therefore be possible to generate radical anions of many highly pyramidalized alkenes and bent alkynes for gas-phase studies.

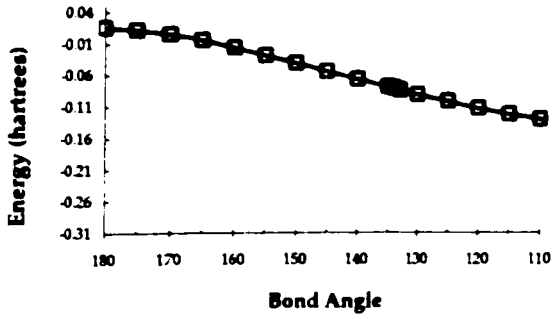


Figure 2.2: Effect of Pyramidalization of Ethylene on the LUMO Energies, Calculated at (U)B3LYP/6-31+G*

This chapter consists of five sections; each describing a collaborative project designed to explore the chemistry of pyramidalized alkenes and bent alkynes. The first section describes a theoretical and experimental study of the four quadricyclene isomers (**6-9**). The second section is concerned with research directed towards the generation of norbornenyne radical anion (**17**$^{\bullet-}$). The third section is devoted to theoretical and experimental studies of norbornyne radical anion (**16**$^{\bullet-}$). The fourth section describes a study of the gas-phase ion chemistry of cyclopentene, while the last section of this chapter discusses attempts to generate perfluorocyclobutyne radical anion (**20**$^{\bullet-}$).

2.1 Quadricyclene

Quadricyclenes **6**, **7**, and **8** have been generated and trapped in solution.[10] Although these experiments have given some insight into the relative energies of these three isomers,[10c] thermochemical data has not been obtained for these

pyramidalized alkenes. However, *ab initio* calculations have provided some predictions about quadricyclenes **6** - **9**.

6 **7** **8** **9**

Table 2.1: TCSCF/6-31G* Calculated Data for Quadricyclenes **6** – **9**.[10a]

Isomer	**6**	**7**	**8**	**9**
Relative Energy (kcal/mol)	11.8	0	4.0	14.5
Olefin Strain Energy (kcal/mol)	79	67	71	81

The relative energies and the olefin strain energies (OSEs) of **6** – **9**, computed by Szeimies at the TCSCF/6-31G* level, are shown in Table 2.1.[10a] The range of OSEs computed for the quadricyclenes (67 – 81 kcal/mol) is similar to that of 70.6 kcal/mol predicted for tricyclo[3.3.0.$0^{3,7}$]oct-1(5)-ene (**21**).[26] Isomer **7** is calculated to be more stable than isomer **6** by 11.8 kcal/mol. Analogously, prismene **22** is computed to be 10.4 kcal/mol more stable than prismene **23**.[27] Experimental evidence has been obtained that the relative energies predicted for quadricyclenes **6** and **7** is correct.[10c]

21 **22** **23**

Szeimies has also reported values of ΔE_{ST} for **6** – **9** at the TCSCF/6-31G* level.[10a] However, by performing RHF/6-31G* calculations, we discovered that the triplet states were actually calculated with UHF wavefunctions. The use of unrestricted Hartree-Fock wavefunctions for the triplets makes the ΔE_{ST} values computed by Szeimies smaller than the actual TCSCF values, which should properly use ROHF wavefunctions for the triplets. In order to obtain more accurate values for ΔE_{ST}, and to predict the relative enthalpies of **6** – **9**, and the electron affinities (EAs) and proton affinities (PAs) of the radical anions of **6** – **9** for possible comparison with the values obtained from future experiments, (U)B3LYP, CASSCF, and CASPT2 calculations were performed with the 6-31+G* basis set (Table 2.2). All three levels of theory predict isomer **7** to be the most stable quadricyclene, while isomer **9** is predicted to be the highest energy isomer. All four isomers are predicted to bind an electron. Therefore, it should be possible to generate **6**$^{\bullet-}$ – **9**$^{\bullet-}$ for gas-phase experiments

The predicted UB3LYP/6-31+G* PAs of isomers **6**$^{\bullet-}$ – **9**$^{\bullet-}$ (386.0 – 400.1 kcal/mol) are similar to the experimental PAs of the radical anions of cubene (**4**, PA = 392 ± 3 kcal/mol)[8] and bicyclo[1.1.0]but-1(3)-ene (**5**, PA = 386 ± 5 kcal/mol).[9] The CASPT2/6-31+G* PAs are lower than the UB3LYP values.

As mentioned in Chapter 1, (U)B3LYP/6-31+G* has been found usually to calculate the thermodynamic properties of radical anions well.[28] However, alkenes **6** – **9** can be expected to have some diradical character. Although (U)B3LYP usually

Table 2.2: Calculated Thermochemical Data for Quadricyclenes **6** – **9** at 298 K.

Isomer	**6**	**7**	**8**	**9**
Relative Enthalpy (kcal/mol)				
(U)B3LYP[a]	4.3	0	3.0	n/a[d]
CASSCF[b]	11.6	0	4.0	13.3
CASPT2[c]	5.0	0	3.4	15.6
Electron Affinity (eV)				
(U)B3LYP	0.75	0.65	0.75	1.04[e]
(U)B3LYP corrected[f]	0.61	0.42	0.57	0.97
CASPT2	0.54	0.19	0.30	0.69
Proton Affinity (kcal/mol)				
UB3LYP	388.1	386.0	386.8	400.1
CASPT2	378.9	381.8	382.7	396.3
Singlet-Triplet Splitting (kcal/mol)				
(U)B3LYP	20.3	18.6	24.1	n/a
CASSCF[g]	14.7	26.5	23.7	0.3
CASPT2	23.5	24.0	28.2	1.7
Relative Enthalpies of the Radical Anions (kcal/mol)				
UB3LYP	2.1	0	0.8	3.3
CASPT2	0	2.9	3.8	7.0

(a) (U)B3LYP/6-31+G* optimized geometries. (b) CASSCF(2,2)/6-31+G* optimized geometries. (c) CASPT2/6-31+G*//CASSCF(2,2)/6-31+G*, CASPT2 electronic energies were converted to enthalpies with the CASSCF zero point energies and thermal corrections. (d) Attempts to locate a B3LYP optimized geometry for singlet **9** lead to a rearranged carbene singlet. (e) EA calculated for triplet **9**. (f) EA = $EA_{Triplet} - \Delta E_{ST}$(CASPT2), see text. (g) Quadricyclene triplets were optimized at ROHF/6-31+G*.

does a good job of calculating EAs,[28] it is a single determinant method and therefore does less well in calculating the energies of singlet diradicals.[29] Therefore the (U)B3LYP EAs of $\mathbf{6}^{\bullet-}$ – $\mathbf{9}^{\bullet-}$ are likely to be too low. Indeed, (U)B3LYP underestimates the EA of $\mathbf{4}^{\bullet-}$ by 0.47 eV.

In order to take account of the diradical character of these species, a CASSCF wavefunction should be used.[29] However, CASSCF does not include dynamic electron correlation and therefore does a poor job of calculating the energies of radical anions.[30] CASPT2, which is based on CASSCF wavefunctions but which also contains dynamic electron correlation, is likely to give the more reliable numbers for

the EAs of these species. However, like most *ab initio* methods, CASPT2 is more likely than (U)B3LYP to underestimate EAs.

As discussed in Chapter 1, a method to correct the EAs computed by (U)B3LYP for its failure to calculate the energies of singlet diradicals accurately is to compute the energy difference between the radical anion and the triplet, using UB3LYP, and then to subtract the ΔE_{ST} value obtained from CASPT2. Applying this method to the EAs of $\mathbf{6}^{\bullet-}$ – $\mathbf{9}^{\bullet-}$ gives values which, as expected, are still higher than the CASPT2 EAs, but lower than the uncorrected (U)B3LYP values.[31]

Another difference between the various types of calculations can be seen in the relative energies of isomers **6** and **7**. B3LYP and CASPT2 predict the energy difference between these two isomers to be about half that computed by CASSCF. The reason for this difference is that the double bond in **6** interacts with the cyclopropane bonds distal to it in a manner that would eventually lead to a retro-Diels Alder reaction (Figure 2.3). Since CASSCF does not include dynamic electron correlation, it does not describe this orbital interaction well.

Evidence for this interaction in alkene **6** comes from comparing the bond lengths in the B3LYP and (2/2)CASSCF optimized geometries (Figure 2.4). Although the double bond length in both geometries is essentially the same, the C2-C7 (C4-C6) bond length of 1.668 Å in the B3LYP optimized geometry is considerably longer than the value of 1.581 Å in the CASSCF optimized geometry. In addition, the C6-C7 bond length is 1.476 Å in the B3LYP optimized geometry, which is nearly 0.04 Å shorter than in the CASSCF optimized geometry.

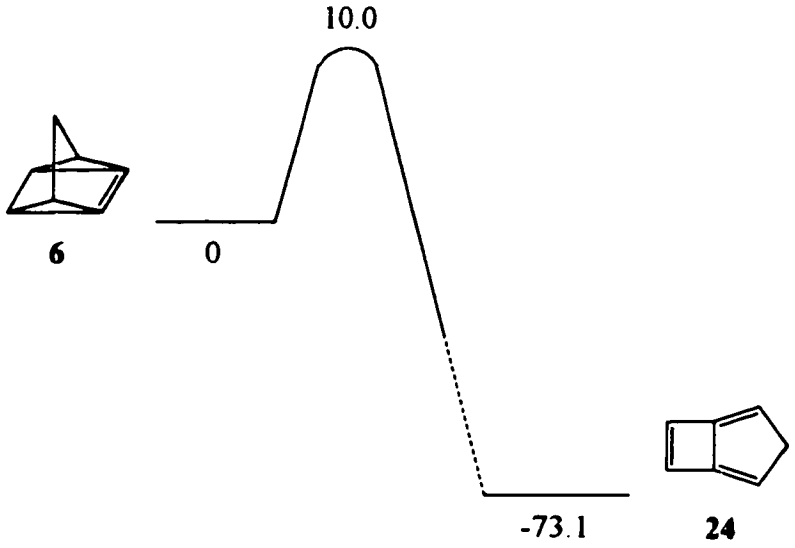
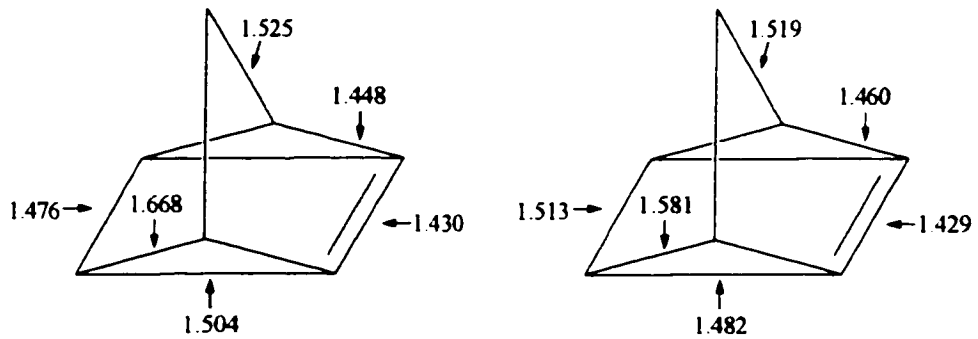


Figure 2.3: Retro-Diels Alder Reaction of Quadricyclene **6** to form Bicyclo[3.2.0]hepta-1(2),4(5),6(7)-triene (**24**) (Relative B3LYP/6-31+G* Enthalpies Given in kcal/mol).



B3LYP optimized geometry

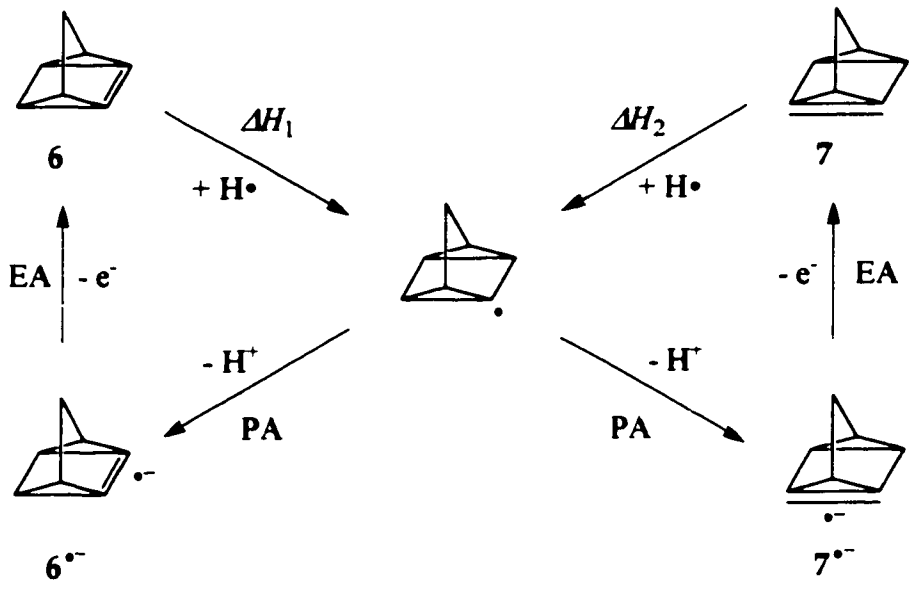
CASSCF optimized geometry

Figure 2.4: Comparison of the Bond Lengths in the B3LYP/6-31+G* and (2/2)CASSCF/6-31+G* Optimized Geometries of **6**.

These differences in geometry suggest that the ability to calculate the interaction of the double bond with the distal cyclopropane bonds is important to obtaining accurate energies for **6**. Thus, measurement of the experimental energy difference between **6** and **7** would be particularly interesting, since we believe it would show that the B3LYP and CASPT2 values are in better agreement with experiment than the value provided by CASSCF.

Addition of a hydrogen atom to **6** and **7** would furnish the same radical. As shown in Scheme 1, measurement of the EAs and PAs of $\mathbf{6}^{\bullet-}$ and $\mathbf{7}^{\bullet-}$ would give the enthalpy changes on formation of this radical (Equation 1), and the difference

Scheme 1:



between these enthalpy changes is equal to the enthalpy difference between these two pyramidalized alkenes (Equation 2).

$$\Delta H_1 = IP(H^{\cdot}) - PA(\mathbf{6}^{\cdot-}) - EA(\mathbf{6}^{\cdot-}) \qquad \text{(Eq. 1)}$$

$$\Delta\Delta H = PA(\mathbf{7}^{\cdot-}) + EA(\mathbf{7}^{\cdot-}) - PA(\mathbf{6}^{\cdot-}) - EA(\mathbf{6}^{\cdot-}) \qquad \text{(Eq. 2)}$$

In order to obtain experimental values for the EAs and PAs of quadricyclene isomers $\mathbf{6}^{\cdot-}$ – $\mathbf{9}^{\cdot-}$, it is necessary to generate their radical anions in the gas-phase. If appropriate precursors of these radical anions could be formed, negative ion photoelectron spectroscopy (NIPES) could be used to obtain not only the EAs, but also the ΔE_{ST} values for the alkenes. Therefore, we sought a method that would allow the regiospecific formation of $\mathbf{6}^{\cdot-}$ – $\mathbf{9}^{\cdot-}$.

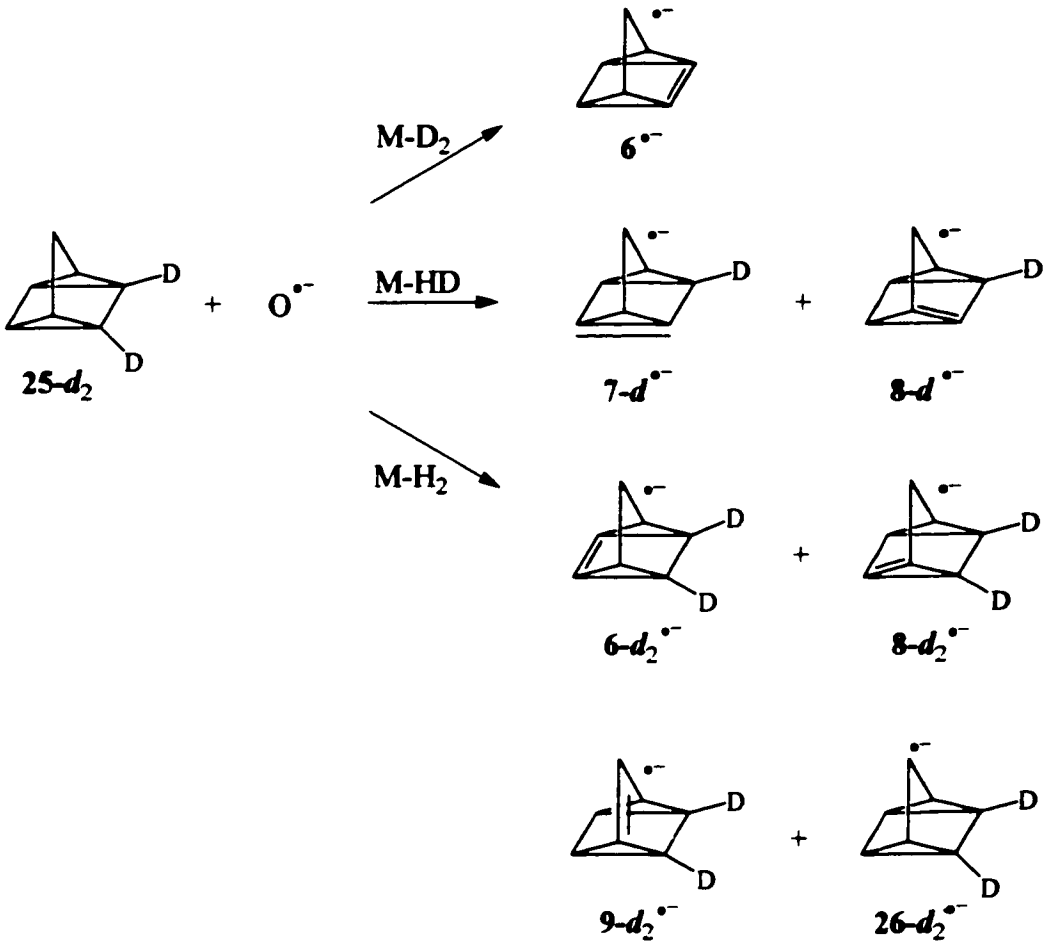
As discussed in the Introduction to this dissertation, one of the most common ways to generate a radical anion in the gas-phase is to allow atomic oxygen radical anion ($O^{\cdot-}$) to react with a hydrocarbon, resulting in net $H_2^{\cdot}$ abstraction from the hydrocarbon.[32] Unfortunately, as exemplified in the previous chapter of this dissertation, $O^{\cdot-}$ is a notoriously unselective reagent and a mixture of quadricyclene isomers would be expected to be formed from reaction of quadricyclane (**25**) with $O^{\cdot-}$.

Indeed, based on results in the last two lines of Table 2.2, the radical anions of **6 – 9** are predicted to have similar enthalpies. Therefore, the results of calculations predict that, upon reaction with $O^{\bullet-}$, **25** will produce a $C_7H_6^{\bullet-}$ ion that will consist of a nearly equal mixture of the four isomeric quadricyclene radical anions.

In addition, the radical anion of 7-carbenaquadricyclane (**26**$^{\bullet-}$) could also be generated by the reaction of **25** with $O^{\bullet-}$ and **26**$^{\bullet-}$ is actually predicted to be 7.1 kcal/mol lower in enthalpy than **6**$^{\bullet-}$ by UB3LYP/6-31+G*. Therefore, it is highly likely that this ion would also be formed in the reaction of **25** with $O^{\bullet-}$ and thus further complicate the NIPE spectrum of the mixture of radical anions formed by this reaction.

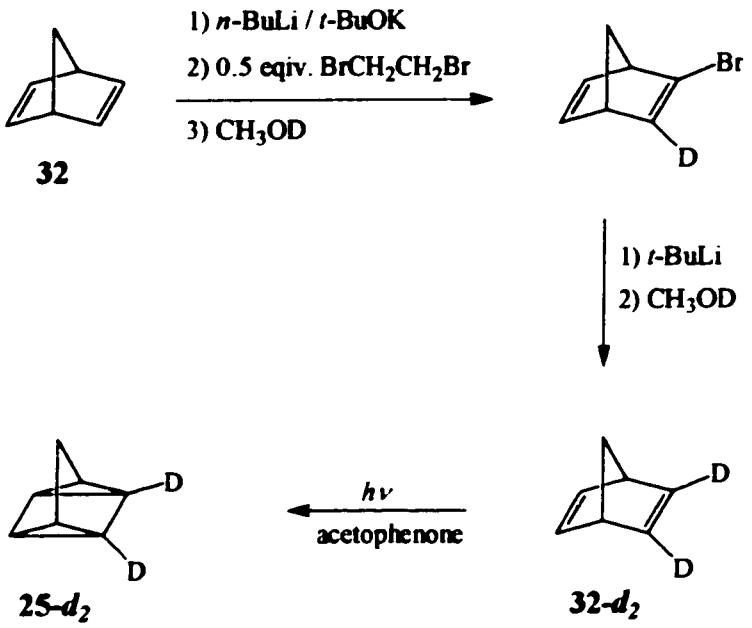
In principle, separate NIPE spectra of the four quadricyclene isomers could be obtained by preparing quadricyclane-1,5-d_2 (**25-d_2**), using mass selection (Scheme 2) and spectral subtraction. The formation of carbene radical anion **26-d_2**$^{\bullet-}$ among the M-H_2 ions would complicate the interpretation of the spectra, but at least the NIPE spectra of some of the quadricyclene isomers could be obtained. Toward this end, a sample of **25-d_2** was synthesized as shown in Scheme 3.

Scheme 2:



The synthesis of **25-*d*$_2$** was modeled after Szeimies synthesis of 1,5-dibromoquadricyclane.[10b] Metallation of norbornadiene by a mixture of *n*-butyllithium and potassium *tert*-butoxide, followed by bromination with 1,2-dibromoethane, and quenching with methanol-O-*d* afforded 2-bromo-3-deuterionorbornadiene. Metallation of this norbornadiene derivative with *tert*-butyllithium, followed by reaction with methanol-O-*d* gave norbornadiene-2,3-d_2. Sensitized photolysis of norbornadiene-2,3-d_2 produced **25-*d*$_2$**.[33]

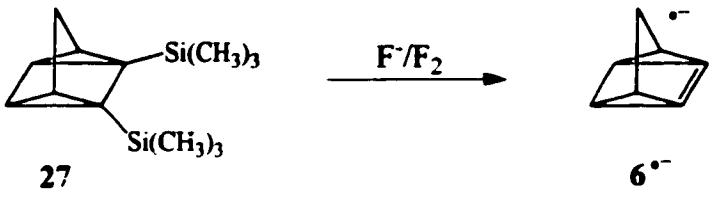
Scheme 3:



As expected from experiments on the reaction of $O^{\bullet-}$ with undeuterated **25**, the same reaction with **25-*d*$_2$** did, in fact, produce radical anions.[34] Unfortunately, poor mass resolution in Professor Lineberger's NIPES instrument failed to separate the M-D_2, M-HD, and M-H_2 radical anions before obtaining the NIPE spectra and the same NIPE spectrum was obtained regardless of the ion for which mass selection was attempted.

As discussed in the Introduction and previous chapter of this dissertation, another method for generating radical anions in the gas-phase is to react a disilane with F^-/F_2 (the Squires reaction).[35] This method has the advantage over the reaction of a hydrocarbon with $O^{\bullet-}$ of introducing the double bond regiospecifically. For example, as shown in Scheme 4, synthesis of 1,5-bis(trimethylsilyl)quadricyclane (**27**) should allow generation of the radical anion of 1,5-dehydroquadricyclane (**6**$^{\bullet-}$).

Scheme 4:



27 **6**$^{\bullet-}$

Modifying the synthetic route shown in Scheme 3 by quenching the carbanions generated in both reactions with chlorotrimethylsilane instead of with methanol-O-*d*, afforded a sample of **27**. As expected, the Squires reaction of **27** did generate a $C_7H_6^{\bullet-}$ ion, albeit in poor yield.[36] Flowing afterglow-selected ion flow tube (FA-SIFT) experiments were performed in order to characterize the $C_7H_6^{\bullet-}$ ion generated from the Squires reaction of **27**. The PA of $C_7H_6^{\bullet-}$ was bracketed to be between MeOH (ΔH_{acid} = 380.5 kcal/mol)[37] and H_2O (ΔH_{acid} = 390.8 kcal/mol), giving PA = 385.6 ± 5.1 kcal/mol. This experimental value for $C_7H_6^{\bullet-}$ is in excellent agreement with the UB3LYP/6-31+G* predicted value of PA = 388.1 kcal/mol for **6**$^{\bullet-}$.

Electron transfer was observed when $C_7H_6^{\bullet-}$ was allowed to react with SO_2 (EA = 1.107 eV). Slow electron transfer was observed upon reaction of $C_7H_6^{\bullet-}$ with CS_2 (EA = 0.52 eV), suggesting that this is an endothermic process. No electron transfer was observed when $C_7H_6^{\bullet-}$ was allowed to react with O_2 (EA = 0.42 eV). The results of the EA bracketing experiments suggest that the $C_7H_6^{\bullet-}$ ion has an experimental EA near 0.6 eV. This value is in good agreement with both the corrected

B3LYP/6-31+G* EA of 0.61 eV and the CASPT2/6-31+G* value of 0.54 eV predicted for $\mathbf{6}^{\bullet-}$.

As discussed in the Introduction (see page 2, Scheme 1), the EA and PA of $\mathbf{6}^{\bullet-}$ can be combined with the ionization potential (IP) of hydrogen (313.6 kcal/mol), the bond dissociation energy (BDE) of H_2 (104.2 kcal/mol), and the BDE of **25** (109.4 kcal/mol)[38] to give the heat of hydrogenation (ΔH_{H2}) for alkene **6** (Equation 3).

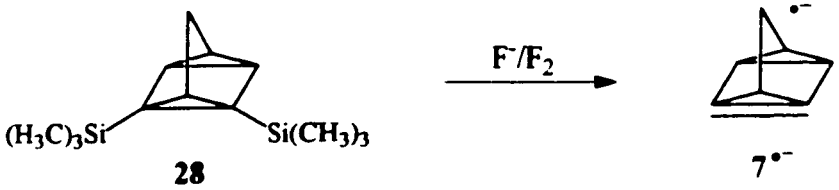
$$\Delta H_{H2}(\mathbf{6}) = IP(H^{\bullet}) + BDE(H_2) - EA(\mathbf{6}^{\bullet}) - PA(\mathbf{6}^{\bullet}) - BDE(\mathbf{25}) \qquad \text{(Eq. 3)}$$

Given PA = 385.6 ± 5.1 kcal/mol and EA ~ 0.6 eV, an approximate value of ΔH_{H2} = 91.0 ± 5.1 kcal/mol can be obtained for **6**. These experimental values for **6** compare favorably with cubene (**4**), where ΔH_{H2} = 88 ± 5 kcal/mol, based on EA($\mathbf{4}^{\bullet}$) = 0.50 ± 0.1 eV, and PA($\mathbf{4}^{\bullet}$) = 392 ± 3 kcal/mol.[8]

Since the results of FA-SIFT experiments were consistent with the $C_7H_6^{\bullet-}$ ion, formed from the Squires reaction of **27**, being $\mathbf{6}^{\bullet-}$, NIPES experiments on this ion were attempted. Unfortunately, the Squires reaction of **27** generates $\mathbf{6}^{\bullet-}$ in such poor yield that it has thus far been difficult to obtain a NIPE spectrum. However, further attempts to increase the efficiency of the reaction of **27** with F^-/F_2 are certainly warranted. Alternatively, with better mass resolution, the reaction of **25-*d*$_2$** with $O^{\bullet-}$ could be used to generate $\mathbf{6}^{\bullet-}$ for NIPES; since, as shown in Scheme 2, the only M-D_2 ion that can be formed from this reaction of **25-*d*$_2$** is $\mathbf{6}^{\bullet-}$.

Although NIPES experiments on $\mathbf{6}^{\bullet-}$, generated from the Squires reaction of **27**, were unsuccessful, we decided to investigate whether reaction of 1,7-bis(trimethylsilyl)quadricyclane (**28**) with F^-/F_2 would generate $\mathbf{7}^{\bullet-}$ (Scheme 5) in sufficiently high yield to allow a NIPE spectrum of this isomer of $\mathbf{6}^{\bullet-}$ to be obtained.

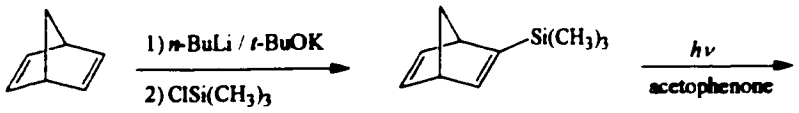
Scheme 5:

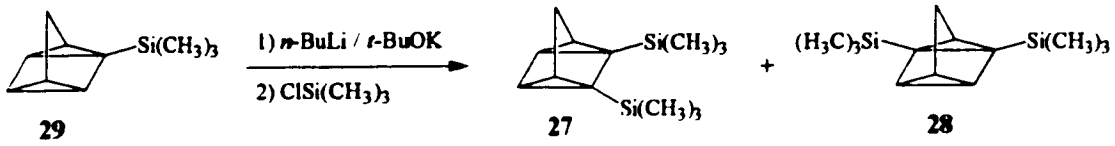


The synthesis of **28** was first attempted as outlined in Scheme 6. Metallation of norbornadiene with *n*-butyllithium and potassium *tert*-butoxide followed by reaction with chlorotrimethylsilane gave 2-(trimethylsilyl)norbornadiene. Photolysis of this substituted norbornadiene in the presence of acetophenone afforded 1-(trimethylsilyl)quadricyclane (**29**).

Metallation of **29** with *n*-butyllithium and potassium *tert*-butoxide might be expected to give a mixture of two carbanions, which should react with chlorotrimethylsilane to give **27** and **28**. RHF/6-31+G* calculations predict the carbanion that would lead to **28** is 0.5 kcal/mol lower in energy than the carbanion that would lead to **27**. Therefore, it seems likely that **28** would be the major product formed by the last two reactions in Scheme 6.

Scheme 6:





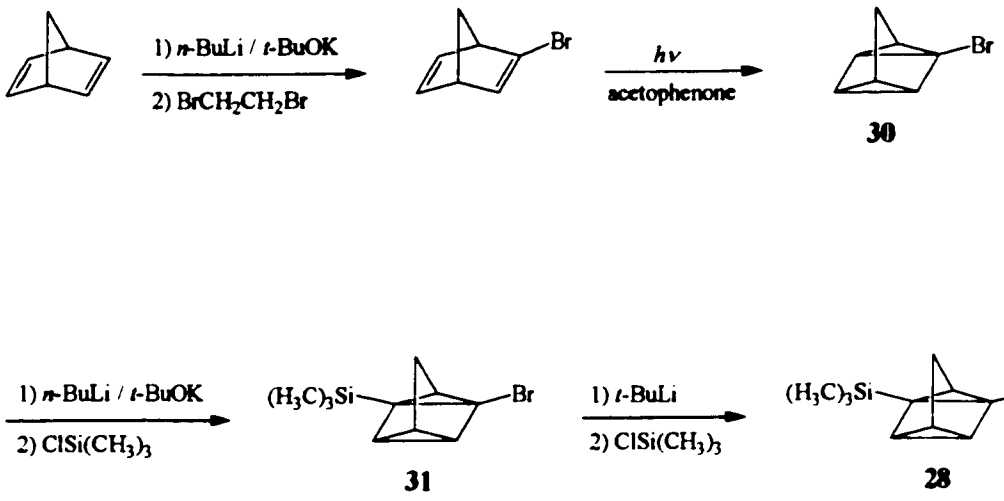
29 27 28

Unfortunately, deprotonation of **29** with *n*-butyllithium and potassium *tert*-butoxide does not occur at room temperature after three days. Metallation of **29** with *n*-butyllithium and tetramethylethylenediamine (TMEDA) also failed. Therefore an alternate route to the synthesis of **28** was devised.

Szeimies has shown that elimination of LiBr from 1-bromo-5-lithioquadricyclane does not occur at –78 °C.[10b] Therefore, it is reasonable to expect that 1-bromo-7-lithioquadricyclane, if generated from 1-bromoquadricyclane (**30**) at –78 °C, would survive long enough to react with chlorotrimethylsilane at this temperature to form 1-bromo-7-(trimethylsilyl)quadricyclane (**31**) (Scheme 7). Metallation of **31** with *tert*-butyllithium, followed by reaction with chlorotrimethylsilane, should then give **28**.

In order to prepare **30**, the carbanion generated from reaction of norbornadiene with *n*-butyllithium and potassium *tert*-butoxide was quenched with

Scheme 7:

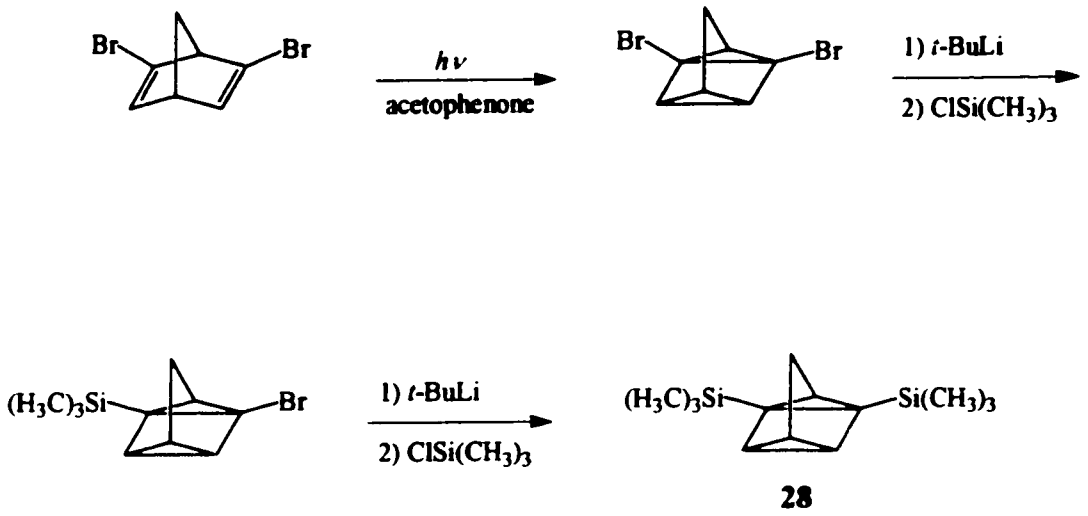


1,2-dibromoethane. The 2-bromonorbornadiene formed was photolyzed in the presence of acetophenone to give **30**.

A sample of **30** was synthesized and allowed to react with *n*-butyllithium and potassium *tert*-butoxide. Unfortunately, the desired deprotonation at C7 did not take place. Instead, metal-halogen exchange apparently occurred; since, after quenching with chlorotrimethylsilane, 1-(trimethylsilyl)quadricyclane (**29**) was obtained.

It might be possible to synthesize **28** via the route shown in Scheme 8. However, this synthetic route is not appealing, given the high toxicity of the starting dibromonorbornadiene.[39] Therefore, further attempts to prepare **28** as a precursor to 7^{-} were not under taken.

Scheme 8:



28

2.2 Norbornenyne

Much of the literature on quadricyclane (**25**) is linked with the literature on norbornadiene (**32**). As mentioned above, photolysis of **32** generates **25**, and **25** reverts to **32** when heated to 140 °C.[33] This pair of reactions was explored as a potential method of converting solar energy to thermal energy.[40] In this dissertation, **25** and **32** are also linked, in this case, as potential precursors to two different types of compounds containing pyramidalized π bonds.

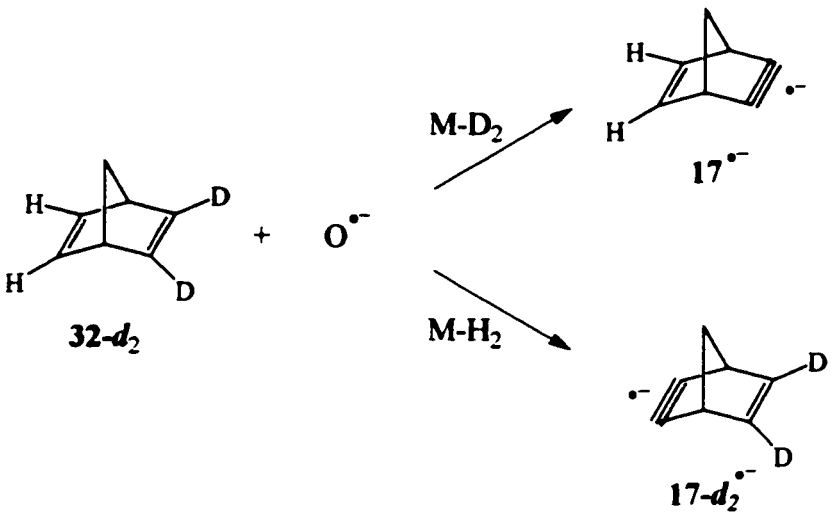
Kitamura and coworkers have generated and trapped norbornenyne (**17**) in solution.[18] However, very little is known about this strained cycloalkyne. Computational studies have predicted the strain in the in plane π bond of norbornenyne to be 72.7 kcal/mol.[18] This value is greater than the strain in the in

plane π bond of cyclopentyne (69.5 kcal/mol), but less than the strain in the in plane π bond of cyclobutyne (74.6 kcal/mol).[20]

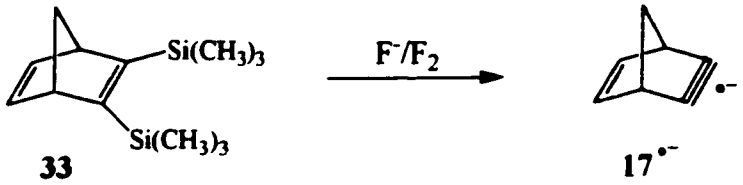
Obtaining experimental thermochemical data (*e.g.* ΔE_{ST} and ΔH_{H2}) for **17** is highly desirable. Data is available for the $C_7H_7^-$ ion formed from **32**,[41] but there is almost no literature on the $C_7H_6^{\bullet-}$ ion formed from **32** by reaction with $O^{\bullet-}$. Although Grabowski did observe a peak corresponding to $C_7H_6^{\bullet-}$, when **32** was allowed to react with $O^{\bullet-}$, this ion was not characterized.[42]

If the radical anion of norbornenyne ($\mathbf{17}^{\bullet-}$) is the only ion formed in the reaction of **32** with $O^{\bullet-}$, preparing norbornadiene-2,3-d_2 (**32**-d_2) and allowing it to react with $O^{\bullet-}$ would generate a mixture of M-H_2 and M-D_2, but no M-HD radical anions (Scheme 9). On the other hand, if the reaction of **32** with $O^{\bullet-}$ does produce a mixture of isomers, $\mathbf{17}^{\bullet-}$ might be generated regiospecifically via the Squires reaction of 2,3-bis(trimethylsilyl)norbornadiene (**33**) (Scheme 10).

Scheme 9:



Scheme 10:



In order to aid in the characterization of the $C_7H_6^{\bullet-}$ ions that we might observe from the reactions shown in Schemes 9 and 10, the EA and PA of $17^{\bullet-}$ and ΔE_{ST} in **17** were calculated at a variety of theoretical levels with the 6-31+G* basis set (Table 2.3). As discussed in the previous section of this chapter, CASPT2 is most likely to give the most reliable value for the predicted EA of $17^{\bullet-}$. Since CCSD(T) is a single determinant method, it may not accurately calculate the singlet bent alkyne. However,

Table 2.3: Calculated Thermochemical Data for Norbornenyne (**17**) at 298 K.

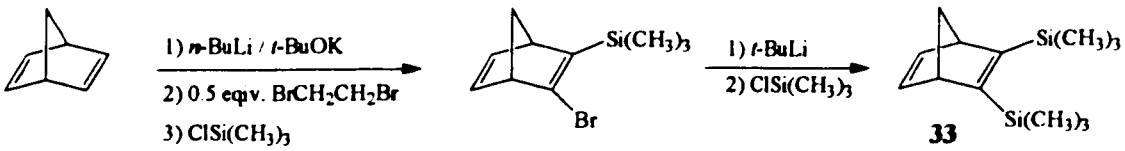
Electron Affinity (eV)	
(U)B3LYP[a]	1.50
(U)B3LYP corrected[b]	1.24
CASPT2[c]	0.91
CCSD(T)[d]	0.83
Proton Affinity (kcal/mol)	
UB3LYP	384.6
CASPT2	379.5
CCSD(T)	384.2
Singlet-Triplet Splitting (kcal/mol)	
(U)B3LYP	13.0
CASSCF[e]	23.6
CASPT2	18.8
CCSD(T)	19.6

(a) (U)B3LYP/6-31+G* optimized geometries. (b) EA = $EA_{Triplet} - \Delta E_{ST}$(CASPT2), see text. (c) CASPT2/6-31+G*//CASSCF(6,6)/6-31+G*. (d) CCSD(T)/6-31+G*//(U)B3LYP/6-31+G*. (e) CASSCF(6,6)/6-31+G* optimized geometries.

a comparison of the ΔE_{ST} values computed at the CASPT2 and CCSD(T) levels of theory suggests that, at least in the case of **17**, CCSD(T) appears to describe accurately the singlet alkyne. In contrast, the (U)B3LYP value of ΔE_{ST} appears to be too small by *ca.* 6 kcal/mol.

We first attempted to generate **17**$^{\bullet-}$ from the Squires reaction of **33**. A sample of **33** was prepared as outlined in Scheme 11. Using the FA-SIFT technique, the Squires reaction was found to be successful in generating a $C_7H_6^{\bullet-}$ ion from **33**, albeit in low yield. This ion was characterized by bracketing the EA and PA values and comparing the experimental results with predicted values.

Scheme 11:



33

Proton transfer was observed when the $C_7H_6^{\bullet-}$ ion was allowed to react with *t*-BuOH (ΔH_{acid} = 374.5 kcal/mol). Upon reaction with MeOH (ΔH_{acid} = 380.5 kcal/mol) only clustering products were observed, suggesting an endothermic reaction. In addition, no proton transfer was observed when $C_7H_6^{\bullet-}$ was allowed to react with EtOH (ΔH_{acid} = 378.3 kcal/mol). The lack of proton transfer to EtOH, and the formation of clustering products upon reaction with MeOH suggest that the PA of $C_7H_6^{\bullet-}$ is close to that of EtOH. However, a conservative bracket is PA = 377.5 ± 3.0 kcal/mol for $C_7H_6^{\bullet-}$. This value compares favorably with the CASPT2 predicted

value, PA = 379.5 kcal/mol. The UB3LYP value (PA = 384.6 kcal/mol) appears to overestimate the PA of **17**$^{\bullet-}$, as it did for quadricyclene **6**$^{\bullet-}$ above. Surprisingly, the CCSD(T) value also appears to be too high.

Electron transfer was observed when $C_7H_6^{\bullet-}$ was allowed to react with SO_2 (EA = 1.107 eV). In addition, some electron transfer was observed upon reaction with CS_2 (EA = 0.52 eV). However, the results of the CS_2 reaction were inconclusive due to additional reactions (discussed below). No charge transfer was observed upon reaction with O_2 (EA = 0.45 eV). Therefore EA bracketing experiments suggest that the $C_7H_6^{\bullet-}$ ion formed from the Squires reaction of **33** has a conservative EA of 0.78 ± 0.33 eV. This experimental value is in good agreement with the values predicted at CASPT2 (EA = 0.91 eV) and CCSD(T) (EA = 0.83 eV). Again, (U)B3LYP/6-31+G* overestimates the EA of **17**$^{\bullet-}$, even after correction for its overestimation of the energy of the singlet state of **17**.

In order to judge how accurate our calculations for **17**$^{\bullet-}$ are likely to be, the ΔE_{ST} for *ortho*-benzyne (**10**) and the PA and EA of the radical anion of *ortho*-benzyne (**10**$^{\bullet-}$) were calculated at the various levels of theory with the 6-31+G* basis set and compared to the experimental values for this bent alkyne (Table 2.4). As in the case of **17**$^{\bullet-}$, (U)B3LYP significantly overestimates the EA of **10**$^{\bullet-}$. However, both CASPT2 and CCSD(T) slightly underestimate the EA of **10**$^{\bullet-}$. The PAs predicted by UB3LYP and CASPT2 appear to bracket the experimental PA of **10**$^{\bullet-}$, with the UB3LYP value on the high side and CASPT2 on the low side, while CCSD(T) accurately reproduces the experimental value. All four methods in Table 2.4

Table 2.4: Calculated Thermochemical Data for *ortho*-Benzyne (**10**) at 298 K.

Electron Affinity (eV)		Experimental[f]
(U)B3LYP[a]	0.89	
(U)B3LYP corrected[b]	0.79	
CASPT2[c]	0.44	0.564 ± 0.007
CCSD(T)[d]	0.31	
Proton Affinity (kcal/mol)		
UB3LYP	381.2	
CASPT2	376.3	378.7 ± 3.1
CCSD(T)	379.7	
Singlet-Triplet Splitting (kcal/mol)		
(U)B3LYP	29.8	
CASSCF[e]	34.0	
CASPT	32.1	37.5 ± 0.3
CCSD(T)	33.8	

(a) (U)B3LYP/6-31+G* optimized geometries. (b) EA = $EA_{Triplet} - \Delta E_{ST}$(CASPT2), see text. (c) CASPT2/6-31+G*//CASSCF(8,8)/6-31+G*. (d) CCSD(T)/6-31+G*//(U)B3LYP/6-31+G*. (e) CASSCF(8,8)/6-31+G* optimized geometries. (f) EA and ΔE_{ST} are from Ref. 11b, PA is from Ref. 11e.

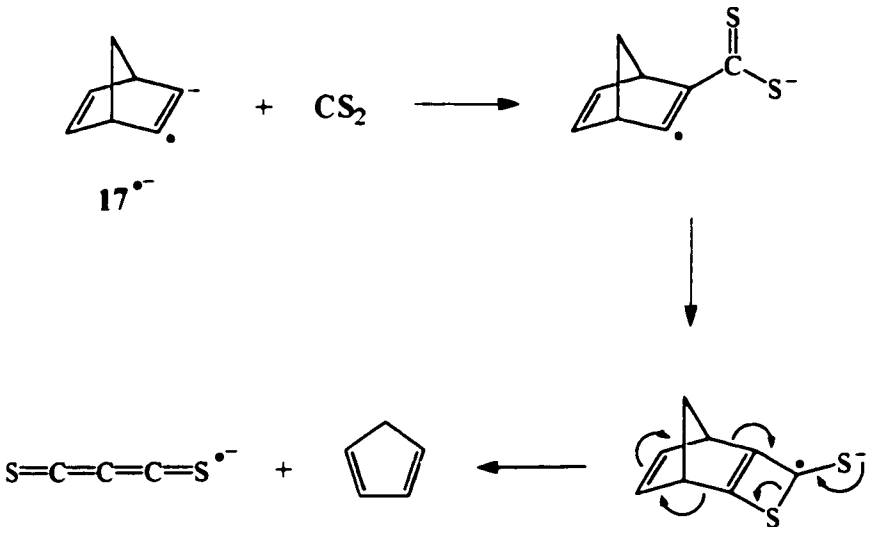
underestimate ΔE_{ST} for **10**. Performing CCSD(T) and CASPT2 calculations with a larger basis set might be expected to more accurately reproduce the experimental values. However, we did not undertake these calculations.

The EA and PA values in Table 2.4 indicate that our CASPT2 and CCSD(T) calculations can be expected to predict fairly accurately the thermochemical data for **17**$^{\bullet-}$. The agreement between the experimental EA and PA values for the $C_7H_6^{\bullet-}$ ion, formed from the Squires reaction of **33**, and the calculated values for **17**$^{\bullet-}$ make it seem likely that the product of the Squires reaction of **33** is indeed **17**$^{\bullet-}$.

Additional evidence for assigning **17**$^{\bullet-}$ to the structure of the $C_7H_6^{\bullet-}$ ion comes from the reaction of this radical anion with CS_2. The major product (95%) of this reaction is $C_3S_2^{\bullet-}$. This ion was assigned as $SCCCS^{\bullet-}$ based collision-induced

dissociation (CID) experiments.[43] The formation of this product can be rationalized as involving the addition of CS_2 to $\mathbf{17}^{\bullet-}$, followed by fragmentation to form cyclopentadiene and $SCCCS^{\bullet-}$ (Scheme 12).

Scheme 12:



In order to obtain a more accurate value for the EA of $\mathbf{17}^{\bullet-}$, and to measure ΔE_{ST} of **17**, we wanted to obtain a NIPE spectrum. Unfortunately, as in the case of quadricyclene $\mathbf{6}^{\bullet-}$, the Squires reaction of **33** does not generate enough $\mathbf{17}^{\bullet-}$ for NIPES experiments to be successful. Therefore, the reaction of **32** with $O^{\bullet-}$ was explored. If this reaction generates only $\mathbf{17}^{\bullet-}$, then, as shown in Scheme 9, the reaction of **32-*d*$_2$** should produce only $C_7H_6^{\bullet-}$ and $C_7H_4D_2^{\bullet-}$.

Since **32-*d*$_2$** had already been prepared (Scheme 3), this deuterated norbornadiene was readily available for gas-phase studies. The reaction of **32-*d*$_2$** with $O^{\bullet-}$ produced $C_7H_6^{\bullet-}$ (M-D_2), $C_7H_5D^{\bullet-}$ (M-HD), and $C_7H_4D_2^{\bullet-}$ (M-H_2). Since the

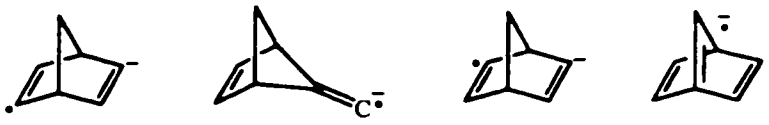
sample used was 93 % **32-d_2** and 7% **32-2-d_1**, if **17**$^{\bullet-}$ was the only $C_7H_6^{\bullet-}$ isomer formed, a 0.93 : 0.07 : 1 mixture of $C_7H_6^{\bullet-}$, $C_7H_5D^{\bullet-}$, and $C_7H_4D_2^{\bullet-}$ should have been observed. However, the ratio of $C_7H_6^{\bullet-}$: $C_7H_5D^{\bullet-}$: $C_7H_4D_2^{\bullet-}$ actually formed upon reaction of **32-d_2** with $O^{\bullet-}$ was 1 : 2.6 : 1.4.

This ratio is quite far from the ratio expected if just **17**$^{\bullet-}$ formed. The large amount of $C_7H_5D^{\bullet-}$ observed indicates that at least one radical anion is generated by abstraction of a hydrogen that is not vinylic.

Figure 2.5 shows some possible $C_7H_6^{\bullet-}$ isomers that could be formed in the reaction of undeuterated **32** with $O^{\bullet-}$ and gives their relative enthalpies calculated at the UB3LYP/6-31+G* level of theory. At this level of theory, **17**$^{\bullet-}$ is actually calculated to be 4.2 kcal/mol higher in enthalpy than the radical anion of 2,7-dehydronorbornadiene (**34**$^{\bullet-}$) and 1.9 kcal/mol higher in enthalpy than the radical anion of the bent allene, norborna-1(2),2(3),5(6)-triene (**35**$^{\bullet-}$). Although, CCSD(T) and CASPT2 calculations predict **17**$^{\bullet-}$ to be lower in enthalpy than **35**$^{\bullet-}$ by 0.2 and 3.9 kcal/mol, respectively, CCSD(T) predicts distonic ion **34**$^{\bullet-}$ to be 3.1 kcal/mol more stable than **17**$^{\bullet-}$. Nevertheless, since **17**$^{\bullet-}$, **34**$^{\bullet-}$ and **35**$^{\bullet-}$ are predicted to be close in energy at both UB3LYP and CCSD(T), all three isomers are likely to be formed in the reaction of **32-d_2** with $O^{\bullet-}$.

In addition, both 7-carbenanorbornadiene radical anion (**36**$^{\bullet-}$) and 1,3-dehydronorbornadiene radical anion (**37**$^{\bullet-}$) are predicted to bind the extra electron. Since these isomers are predicted to be, respectively, 0.6 and 0.8 kcal/mol higher in

	17$^{\bullet-}$	**34**$^{\bullet-}$	**35**$^{\bullet-}$	**36**$^{\bullet-}$	**37**$^{\bullet-}$
Relative Enthalpy (kcal/mol)	0	- 4.2	- 1.9	0.6	0.8
Electron Affinity (eV)	1.50	1.52	1.23	1.22	1.32



	38$^{\bullet-}$	**39**$^{\bullet-}$	**40**$^{\bullet-}$	**41**$^{\bullet-}$
Relative Enthalpy (kcal/mol)	3.4	4.9	5.7	6.7
Electron Affinity (eV)	1.71	1.15	1.60	-1.92

Figure 2.5: Relative Enthalpies of Possible $C_7H_6^{\bullet-}$ Isomers Formed from the Reaction of **32** with $O^{\bullet-}$, Calculated at UB3LYP/6-31+G*.

enthalpy than **17**$^{\bullet-}$, **36**$^{\bullet-}$ and **37**$^{\bullet-}$ might also be generated in the reaction of **32-*d*$_2$** with $O^{\bullet-}$.

As mentioned in the Introduction to this chapter, there is a close relationship between bent alkynes and vinylidenes. Therefore, a discussion of the isomers of $C_7H_6^{\bullet-}$ would not be complete without mention of vinylidene **39**$^{\bullet-}$. As in the case of cyclopentyne,[20] vinylidene **39**$^{\bullet-}$ is predicted by UB3LYP to be 4.9 kcal/mol higher in enthalpy than **17**$^{\bullet-}$. This difference is predicted to be even greater at CCSD(T) (ΔE = 7.5 kcal/mol) and CASPT2 (ΔE = 11.7 kcal/mol). Therefore, it seems unlikely that

39$^{\bullet-}$ would be an observed product in the reaction of **32** with $O^{\bullet-}$, since it cannot be formed directly, and rearrangement of **17**$^{\bullet-}$ to **39**$^{\bullet-}$ is calculated to be endothermic.

Although the results of the UB3LYP calculations make it seem very plausible that the $C_7H_5D^{\bullet-}$ ion formed in the reaction of ***32-d₂*** with $O^{\bullet-}$ comes from abstraction of either a CH_2 hydrogen to form **34**$^{\bullet-}$ or a bridgehead hydrogen to form **35**$^{\bullet-}$, formation of these two ions, plus **17**$^{\bullet-}$ cannot explain the product ratios observed. Suppose that the mole fraction of **17**$^{\bullet-}$ formed from **32** is X and that the sum of the mole fractions of **34**$^{\bullet-}$ and **35**$^{\bullet-}$ is 1-X. Ignoring possible isotope effects, reaction of ***32-d₂*** with $O^{\bullet-}$ should afford X/2 moles of both **17**$^{\bullet-}$ and ***17-d₂***$^{\bullet-}$, plus1-X moles of a mixture of **34**$^{\bullet-}$ and **35**$^{\bullet-}$ that is half d_1 ($C_7H_5D^{\bullet-}$) and half d_2 ($C_7H_4D_2^{\bullet-}$). Thus, the product ratios of $C_7H_6^{\bullet-}$: $C_7H_5D^{\bullet-}$: $C_7H_4D_2^{\bullet-}$ formed should be (X/2) : ((1-X)/2) : (X/2 + (1-X)/2) = X : 1-X : 1. Experimentally, the ratio of $C_7H_6^{\bullet-}$ to $C_7H_4D_2^{\bullet-}$ ions is 1.4, and from this ratio X = 0.7. Thus, according to the above analysis, 1-X = 0.3. However, the experimental ratios are not 0.7 : 0.3 : 1 = 1 : 0.4 : 1.4 but 1 : 2.6 :1.4.

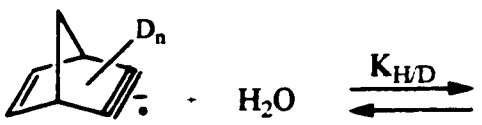
A kinetic isotope effect would favor loss of hydrogen, rather than deuterium, in the formation of the products. For example, k_H/k_D = 1.4 for formation of **17**$^{\bullet-}$ would result in a ratio of $C_7H_6^{\bullet-}$ to $C_7H_4D_2^{\bullet-}$ ions of 1 : 1.4. This would imply X = 1, meaning no $C_7H_5D^{\bullet-}$ should have been formed. However, experimentally, $C_7H_5D^{\bullet-}$ ions are the most abundant.

In order to determine whether the experimental ratios of radical anions formed from ***32-d₂*** could be due to equilibrium isotope effects, the Bigeleisen equation[44] was used to calculate the equilibrium isotope effects expected for the reaction of ***32-d₂***

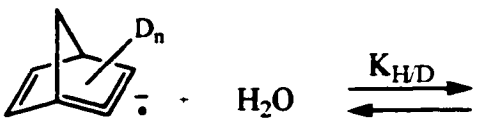
with $O^{\bullet-}$ to form $\mathbf{17}^{\bullet-}$ and $\mathbf{35}^{\bullet-}$. The isotope effects ranged from 1.0 to 1.4 for $\mathbf{17}^{\bullet-}$ and from 1.1 to 1.6 for $\mathbf{35}^{\bullet-}$ (Table 2.5) and in each case favored loss of deuterium from **32-d_2**. Having protium attached to carbon, rather than to oxygen, minimizes the zero-point vibrational energies, and this effect is largest when protium is attached to an sp^2 carbon.

Table 2.5: Calculated UB3LYP/6-31+G* Equilibrium Isotope Effects for the Radical Anions of Norbornenyne ($\mathbf{17}^{\bullet-}$) and Norborna-1(2),2(3),5(6)-triene ($\mathbf{35}^{\bullet-}$).

Compound	**17-1-d_1**$^{\bullet-}$	**17-6-d_1**$^{\bullet-}$	**17-1,5-d_2**$^{\bullet-}$	**17-1,6-d_2**$^{\bullet-}$	**17-5,6-d_2**$^{\bullet-}$
$K_{H/D}$	0.97	1.18	1.19	1.19	1.44
Compound	**35-3-d_1**$^{\bullet-}$	**35-4-d_1**$^{\bullet-}$	**35-5-d_1**$^{\bullet-}$	**35-6-d_1**$^{\bullet-}$	**35-3,4-d_2**$^{\bullet-}$
$K_{H/D}$	1.24	1.05	1.22	1.17	1.35
Compound	**35-3,5-d_2**$^{\bullet-}$	**35-3,6-d_2**$^{\bullet-}$	**35-4,5-d_2**$^{\bullet-}$	**35-4,6-d_2**$^{\bullet-}$	**35-5,6-d_2**$^{\bullet-}$
$K_{H/D}$	1.57	1.50	1.33	1.27	1.48



17-d_n $^{\bullet-}$ **17-d_0**$^{\bullet-}$ (Eq. 4)



35-d_n $^{\bullet-}$ **35-d_0**$^{\bullet-}$ (Eq. 5)

From Table 2.5 the equilibrium isotope effect favoring formation of **17-*d*$_0$**$^{\bullet-}$ over **17-5,6-*d*$_2$**$^{\bullet-}$ is calculated to be 1.44, and that favoring formation of **35-3-*d*$_1$**$^{\bullet-}$ over **35-5,6-d$_2$**$^{\bullet-}$ is 1.48/1.24 = 1.19. Using these equilibrium isotope effects, the previously calculated ratios of $C_7H_6^{\bullet-}$, $C_7H_5D^{\bullet-}$, and $C_7H_4D_2^{\bullet-}$ products becomes (1.44(X)/2.44) : (1.19(1-X)/2.19) : (X/2.44 + (1-X)/2.19) = (0.59X) : (0.54(1-X)) : (0.46 – 0.05X). From the experimental ratio of $C_7H_4D_2^{\bullet-}$: $C_7H_6^{\bullet-}$ = 1.44, X = 0.52. Therefore, the predicted ratios of $C_7H_6^{\bullet-}$: $C_7H_5D^{\bullet-}$: $C_7H_4D_2^{\bullet-}$ are 0.31 : 0.26 : 0.43 = 1 : 0.8 : 1.4.

Thus, inclusion of an equilibrium isotope effect does increase the relative amount of $C_7H_5D^{\bullet-}$ that is expected to be formed. However, if the only ions present are **17**$^{\bullet-}$ and **35**$^{\bullet-}$, the predicted ratio of 1 : 0.8 for $C_7H_6^{\bullet-}$: $C_7H_5D^{\bullet-}$ is still very far from the measured ratio of 1 : 2.6. Clearly, at least one other ion must be formed in the reaction of **32** with $O^{\bullet-}$, and, when formed from **32-*d*$_2$**, this ion must preferentially be formed with loss of just one deuterium.

Formation of ions **38**$^{\bullet-}$ and **40**$^{\bullet-}$ from **32-*d*$_2$** would, perforce, proceed with loss of just one deuterium. However, they are computed to be sufficiently high in energy that formation of them in significant amounts seems unlikely. Nevertheless, their reversible formation from **17**$^{\bullet-}$ by proton exchange with H_2O/D_2O in the ion-dipole complex would result in **17-*d*$_0$**$^{\bullet-}$ and **17-*d*$_2$**$^{\bullet-}$ being accompanied by **17-*d*$_1$**$^{\bullet-}$. Statistically, it is four times more probable for **17-*d*$_1$**$^{\bullet-}$ than for either **17-*d*$_0$**$^{\bullet-}$ or **17-*d*$_2$**$^{\bullet-}$ to be formed, so the presence of large amounts of $C_7H_5D^{\bullet-}$ can be accommodated without invoking formation of any **34**$^{\bullet-}$ or **35**$^{\bullet-}$.

Although the ratios of $C_7H_6^{\bullet-}$, $C_7H_5D^{\bullet-}$, and $C_7H_4D_2^{\bullet-}$ formed from the reaction of **32**-d_2 with $O^{\bullet-}$ do not demand formation of **34**$^{\bullet-}$ or **35**$^{\bullet-}$, our calculations certainly lead us to expect that one, or both, of these ions, as well as **17**$^{\bullet-}$, should be generated by reaction of **32**-d_2 with $O^{\bullet-}$. In fact, further FA-SIFT experiments, carried out with unlabelled **32** provided evidence that the $C_7H_6^{\bullet-}$ ion, formed on reaction with $O^{\bullet-}$, is comprised of two components. One component behaves similarly to the radial anion generated by the Squires reaction with **33**. This component was found to have a bracketed EA of 0.81 ± 0.29 (between CS_2 and SO_2) and PA close to that of EtOH (ΔH_{acid} = 378.3 kcal/mol). In addition, upon reaction with CS_2, this component generated $SCCCS^{\bullet-}$. Thus, this radical anion is most likely the desired norbornenyne radical anion (**17**$^{\bullet-}$).

The second $C_7H_6^{\bullet-}$ ion is more basic than the first. The PA of the second ion was found to be close to that of H_2O (ΔE_{ST} = 390.8 kcal/mol).[45] In addition, the EA of the second $C_7H_6^{\bullet-}$ ion appears to be slightly less than that of the first.[46]

The assignment of the structure of **34**$^{\bullet-}$ to the second ion is consistent with not only the similar enthalpies calculated for **17**$^{\bullet-}$ and **34**$^{\bullet-}$, but also with the additional computational result that the PA of **34**$^{\bullet-}$ is computed to be 6.9 kcal/mol higher than the PA of **17**$^{\bullet-}$ at the UB3LYP level of theory (Table 2.6). In addition, the adiabatic EA of **34**$^{\bullet-}$ is predicted to be lower than that of **17**$^{\bullet-}$, consistent with experimental observations.

However, the structure of the second $C_7H_6^{\bullet-}$ component cannot be unequivocally assigned, since like **34**$^{\bullet-}$, bent allene **35**$^{\bullet-}$ is also predicted to be more

basic and less bound than **17**$^{\bullet-}$ (Table 2.6). Since isomer **35**$^{\bullet-}$ is predicted to be 1.9 kcal/mol lower in enthalpy by UB3LYP, and 3.9 kcal/mol higher in enthalpy by CASPT2, the second $C_7H_6^{\bullet-}$ ion could either be allene radical anion **35**$^{\bullet-}$, distonic radical anion **34**$^{\bullet-}$, or, more likely, a mixture of both.

Table 2.6: Comparison of the Radical Anions of Norbornenyne (**17**$^{\bullet-}$), 2,7-Dehydronorbornadiene (**34**$^{\bullet-}$), and Norborna-1(2),2(3),5(6)-triene (**35**$^{\bullet-}$) at 298 K.

Isomer	**17**$^{\bullet-}$	**34**$^{\bullet-}$	**35**$^{\bullet-}$
Proton Affinity (kcal/mol)			
UB3LYP[a]	384.6	391.5	389.0
Electron Affinity (eV)			
(U)B3LYP	1.50	0.11[b]	1.23

(a) (U)B3LYP/6-31+G* optimized geometries. (b) Adiabatic EA to form tricyco[3.2.0.0^{2,7}]hepta-3(4),6(7)-diene.

Regardless of the structural assignment of the second $C_7H_6^{\bullet-}$ ion, the large difference in basicity between it and **17**$^{\bullet-}$ should enable us to obtain the NIPE spectrum of **17**$^{\bullet-}$ by protonating the second ion with an acid too weak to protonate **17**$^{\bullet-}$. The NIPE spectrum of the mixture of the two radical anions could also be obtained, and the spectrum of **17**$^{\bullet-}$ subtracted from that of the mixture, to give the NIPE spectrum of the second component.

As mentioned above, the Squires reaction of **33** does not generate enough **17**$^{\bullet-}$ to make it possible to obtain a NIPE spectrum. Unfortunately, preliminary attempts to obtain the NIPE spectrum of **17**$^{\bullet-}$ by allowing **32** to react with $O^{\bullet-}$ in the NIPE spectrometer were also unsuccessful. Additional attempts to obtain the NIPE spectrum of **17**$^{\bullet-}$ are certainly warranted.

Although we do not yet have an accurate value for the EA of **17**$^{\bullet}$, we can nonetheless use the experimental data we do have to obtain an approximate value for the ΔH_{H2} of **17**. Applying Equation 3, using PA = 377.5 ± 3.0 kcal/mol, EA = 0.81 ± 0.29 eV, and BDE(**32**) = 115 6 ± 1.9 kcal/mol,[38] gives ΔH_{H2} = 93.9 ± 11.6 kcal/mol. This value compares favorably with the values of ΔH_{H2} = 88 ± 5 kcal/mol for cubene (**4**),[8] ΔH_{H2} = 91.0 ± 5.1 kcal/mol for 1,5-dehydroquadricyclane (**6**), and ΔH_{H2} = 87.4 ± 3.8 kcal/mol for *ortho*-benzyne (**10**).[47]

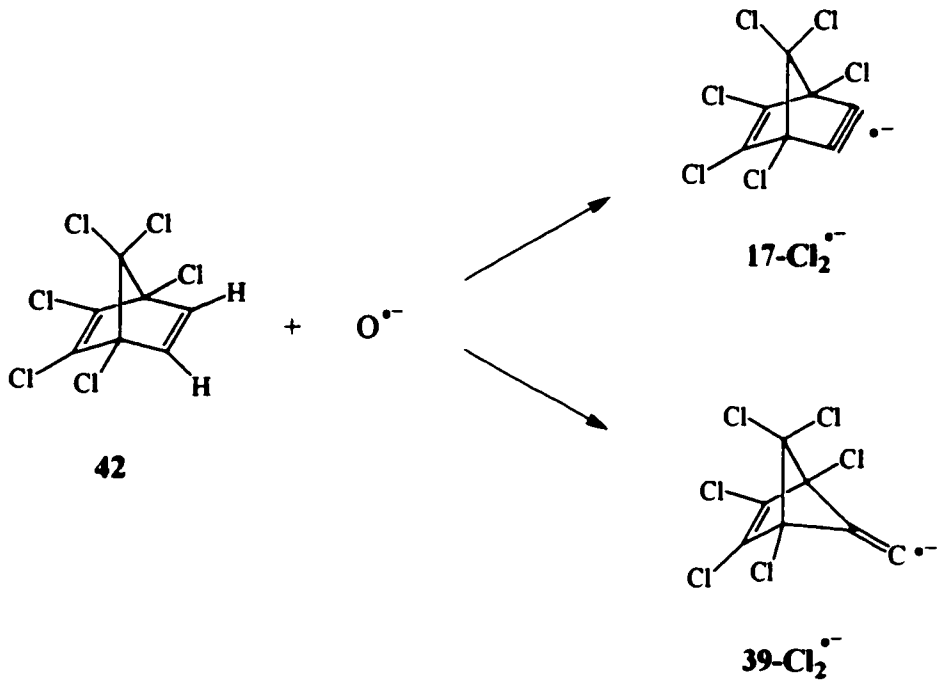
Although attempts to obtain a NIPE spectrum of **17**$^{\bullet}$ have been unsuccessful, it might be possible to obtain the NIPE spectrum of a derivative. For example, 1,2,3,4,7,7-hexachloronorbornadiene (**42**), upon reaction with O$^{\bullet}$, can give as the only M-H_2 product the hexachloro derivative of the norbornenyne radical anion (**17-Cl$_6$**$^{\bullet}$) (Scheme 13). Of course it is possible that **17-Cl$_6$**$^{\bullet}$ might rearrange to **39-Cl$_6$**$^{\bullet}$. However, as in the case of parent **17**$^{\bullet}$, vinylidene **39-Cl$_6$**$^{\bullet}$ is predicted to be 10.7 kcal/mol higher in enthalpy than **17-Cl$_6$**$^{\bullet}$ at UB3LYP/6-31+G*. Thus it appears likely that any $C_7Cl_6^{\bullet}$ formed from the reaction of **42** with O$^{\bullet}$ would be **17-Cl$_6$**$^{\bullet}$.

A sample of **42** was prepared for FA-SIFT experiments by Dr. Bongjin Park, a visiting scientist in the Borden group. Paquette's synthetic route to **42**[48] proved to be extremely inefficient and **42** was only prepared in low purity.

When this sample of **42** was allowed to react with O$^{\bullet}$, only very small amounts of $C_7HCl_6^{\bullet}$ and $C_7Cl_6^{\bullet}$ were observed. The major product from this reaction appeared to be Cl$^-$. However, the Cl$^-$ peak was observed to decrease with time, suggesting that it may be due to an impurity in the sample. Nevertheless, this

preliminary experiment suggests that the reaction of **42** with $O^{\bullet-}$ is unlikely to be useful for obtaining a NIPE spectrum of **17**-$Cl_6^{\bullet-}$.

Scheme 13:



42

17-$Cl_2^{\bullet-}$

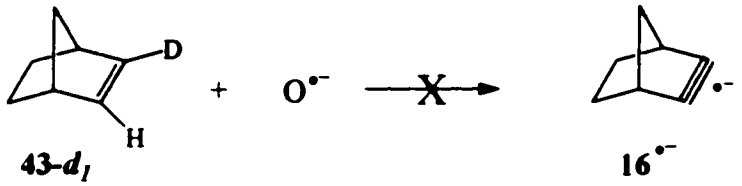
39-$Cl_2^{\bullet-}$

2.3 Norbornyne

Since it appears that we were able to generate the radical anion of norbornenyne (**17**$^{\bullet-}$) in the gas-phase, the next logical goal in our quest for strained alkenes was to generate the radical anion of norbornyne (**16**$^{\bullet-}$). There is evidence that **16** has been generated and trapped in solution,[17] however, nothing is known about the thermochemistry of this bent alkyne.

As with norbornadiene, the gas-phase ion chemistry of norbornene (**43**) has been mostly focused on the $C_7H_9^-$ ion formed from the reaction of **43** with HO^-.[41b] Very little is known about the $C_7H_8^{\bullet-}$ ion formed from the reaction of **43** with $O^{\bullet-}$. Kass has explored the reaction of norbornene-2-*d*$_1$ (**43-*d*$_1$**) with $O^{\bullet-}$.[49] Although the deuterium content of the sample was low (~30 % d_1), this reaction produced no detectable M-HD ion (Scheme 14). If **16**$^{\bullet-}$ is generated in this reaction, it appears to be a minor product.

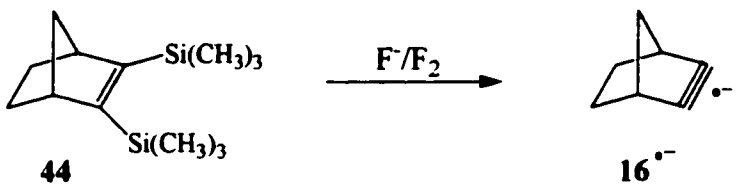
Scheme 14:



43-*d*$_1$ **16**$^{\bullet-}$

Based on Kass's observations, it seems unlikely that **43** is a suitable precursor to **16**$^{\bullet-}$ for NIPES experiments. Therefore, the Squires reaction of 2,3-bis(trimethylsilyl)norbornene (**44**) was explored as a potential route to **16**$^{\bullet-}$ (Scheme 15). The synthesis of **44** was carried out in collaboration with University of Washington undergraduate Lani V. Lockett.

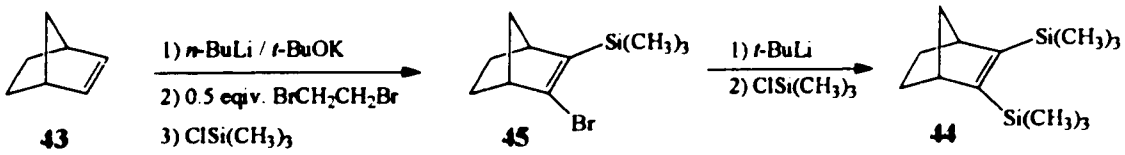
Scheme 15:



44 **16**$^{\bullet-}$

The synthesis of **44** was first attempted by the modification shown in Scheme 16, of the synthesis of 2,3-bis(trimethylsilyl)norbornadiene (**33**). Metallation of **43** with *n*-butyllithium and potassium *tert*-butoxide, followed by bromination with 1,2-dibromoethane and quenching with chlorotrimethylsilane, should afford 2-bromo-3-(trimethylsilyl)norbornene (**45**). Metallation of **45** with *tert*-butyllithium and quenching the anion with chlorotrimethylsilane should then give **44**.

Scheme 16:

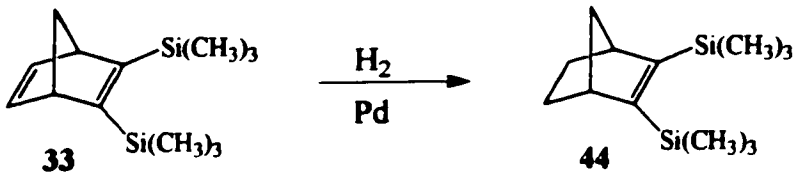


43 **45** **44**

Unfortunately, metallation of **43** proved difficult.[50] Instead of **45**, the first step of this reaction produced only small amounts of 2-(trimethylsilyl)norbornene. Metallation was attempted at various temperatures between –78 °C and –20 °C,[51] but satisfactory conditions for this reaction were not found.

An alternative synthesis of **44** is outlined in Scheme 17. Hydrogenation of the unsubstituted double bond in **33** should give **44**. A sample of **44** was successfully prepared by this route and mailed to Professor Steve Kass for Fourier transform ion cyclotron resonance (FT-ICR) experiments.

Scheme 17:



33 **44**

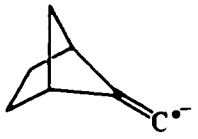
Kass found that the Squires reaction of **44** does produce a $C_7H_8^{\bullet-}$ ion. The EA of this ion was measured by bracketing experiments to be 0.68 eV ± 0.1 eV, while the PA, also measured by bracketing experiments, was found to be 372.9 ± 3.0 kcal/mol.

The EA of **16**$^{\bullet-}$ is predicted to be 1.19 eV at (U)B3LYP/6-31+G*. However, as mentioned above, B3LYP is not expected to calculate accurately the singlet state of the bent alkyne. Therefore, the (U)B3LYP value should provide an upper limit of the EA of **16**$^{\bullet-}$.

As shown in Table 2.4, CASPT2/6-31+G* does a better job than (U)B3LYP of predicting the EA of *ortho*-benzyne (**10**$^{\bullet-}$). CASPT2 calculations predict **16**$^{\bullet-}$ should have EA = 0.57 eV. This predicted value is in excellent agreement with the experimental value, suggesting that the $C_7H_8^{\bullet-}$ ion formed from the Squires reaction of **44** is indeed **16**$^{\bullet-}$.

The proton affinity of **16**$^{\bullet-}$ was also computed by both UB3LYP and CASPT2 calculations, since these two methods were found to bracket the PA of **10**$^{\bullet-}$. UB3LYP calculations predict PA = 386.6 kcal/mol and CASPT2 calculations predict PA = 383.6 kcal/mol. In this case, the experimental PA is almost 10 kcal/mol lower than the predicted values.

This large discrepancy could be due to rearrangement of **16**$^{\bullet-}$. For example, **16**$^{\bullet-}$ might rearrange to 5-methylenebicyclo[2.1.1]heptane radical anion (**46**$^{\bullet-}$).[52] Vinylidene **46**$^{\bullet-}$ is predicted by (U)B3LYP/6-31+G* to have EA = 0.78 eV and PA = 377.9 kcal/mol. The predicted EA of **46**$^{\bullet-}$ is within the error limits of the experimental value. Although the PA of this species is still higher than the experimental value, it is computed to be much less basic than **16**$^{\bullet-}$. Therefore, **46**$^{\bullet-}$ should at least be considered as a possible product of the Squires reaction of **44**.

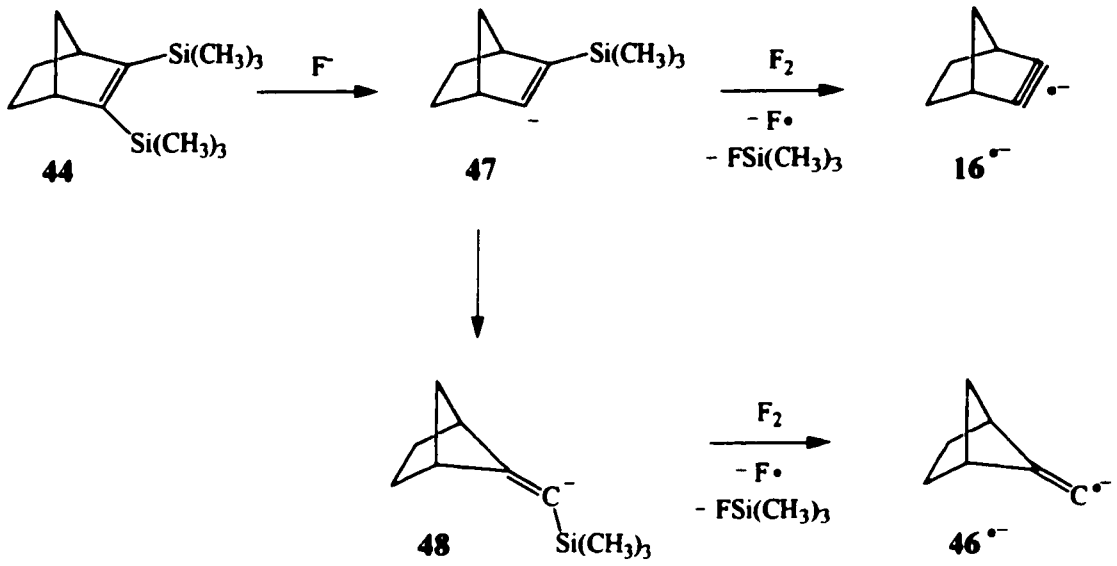


46$^{\bullet-}$

However, similar to the case in the norbornadiene radical anion, **46**$^{\bullet-}$ is predicted to be 5.5 kcal/mol higher in enthalpy than **16**$^{\bullet-}$ at UB3LYP/6-31+G*. Increasing the size of the basis set actually increases the difference between the relative enthalpies of these two species. At UB3LYP/6-311+G*, **46**$^{\bullet-}$ is predicted to be 6.7 kcal/mol higher in enthalpy than **16**$^{\bullet-}$, while at the CCSD(T)/6-31+G* level of theory **46**$^{\bullet-}$ is predicted to be 6.4 kcal/mol higher in enthalpy than **16**$^{\bullet-}$. Thus **46**$^{\bullet-}$ is an unlikely structure for the $C_7H_8^{\bullet-}$ ion, at least if generated from rearrangement of **16**$^{\bullet-}$.

The Squires reaction of **44** is a stepwise process. The first step involves reaction of **44** with F^- to form vinyl anion **47** (Scheme 18). After dissociative electron transfer to F_2 to generate F^- and a vinyl radical, **47** then loses its second trimethylsilyl

Scheme 18:



group to form, presumably, **16**$^{\bullet-}$. Although, based on relative enthalpies, it seems unlikely that **16**$^{\bullet-}$ directly rearranges to **46**$^{\bullet-}$, it might be possible for vinyl anion **47** to rearrange to vinylidene anion **48**. If this rearrangement were to occur, the discrepancy between the measured and predicted PA values could be explained by the formation of **46**$^{\bullet-}$ via the rearrangement of **47**, as opposed to **16**$^{\bullet-}$. However, not only would this pathway involve a 1,2-shift in a carbanion, which would be a very high energy process, but also anion **48** is computed to be 13.2 kcal/mol higher in enthalpy than anion **47** at UB3LYP/6-31+G*. Therefore, this rearrangement pathway is even less likely to form vinylidene radical anion **46**$^{\bullet-}$ than direct rearrangement of **16**$^{\bullet-}$ to **46**$^{\bullet-}$.

Another possible explanation for the observed discrepancy between the experimental PA (372.9 ± 3.0 kcal/mol) and that predicted for **16**$^{\bullet-}$ (PA_{CASPT2} = 383.6

kcal/mol) is that **16**$^{\bullet-}$ undergoes ring opening to cyclopentylacetylide **49**$^{\bullet-}$. As shown in Figure 2.6, **49**$^{\bullet-}$ is predicted by UB3LYP to be 10.2 kcal/mol lower in enthalpy than **16**$^{\bullet-}$ and the rearrangement has a calculated barrier of 13.8 kcal/mol. In addition, **49**$^{\bullet-}$ is predicted to have PA = 377.2 kcal/mol, which is within the experimental limits of the PA measured for $C_7H_8^{\bullet-}$.

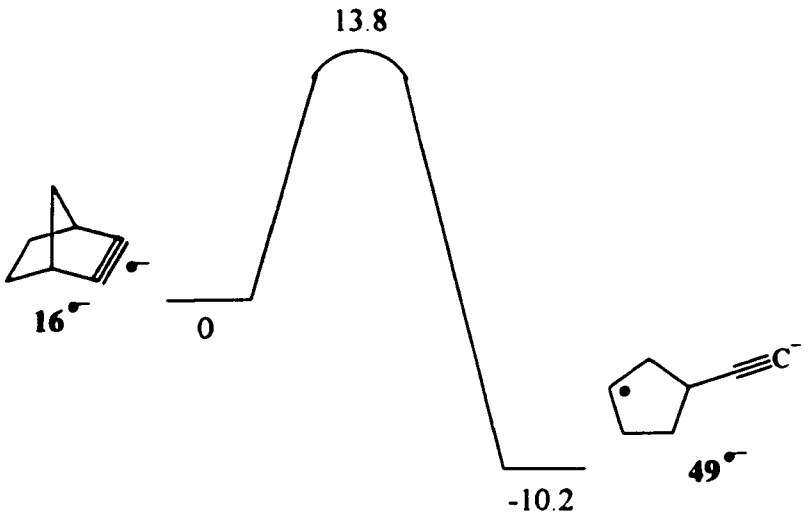


Figure 2.6: Rearrangement of Norbornyne Radical Anion (**16**$^{\bullet-}$), Calculated at (U)B3LYP/6-31+G* (all values in kcal/mol).

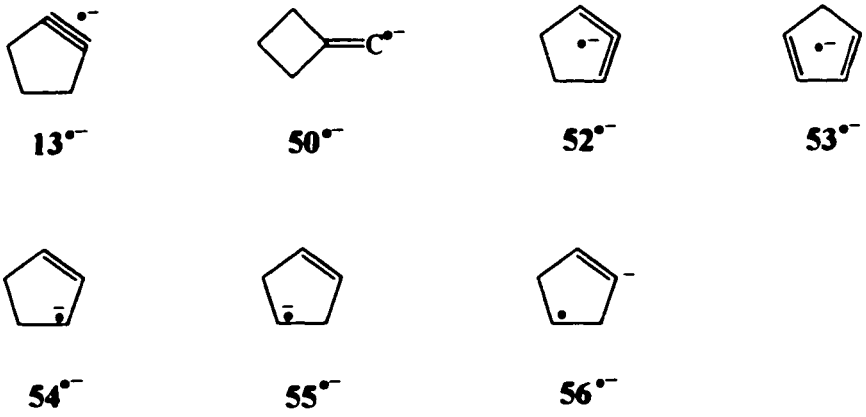
However, it is unlikely that **49**$^{\bullet-}$ is formed directly from the Squires reaction of **44**, since this isomer is predicted to have an EA of 1.56 eV, which is nearly double the experimental value. However, some rearrangement of **16**$^{\bullet-}$ to **49**$^{\bullet-}$ apparently could occur in the ion-dipole complex of $C_7H_8^{\bullet-}$ with weak acids, because it is only when this rearrangement occurs that proton transfer can take place.

2.4 Cyclopentyne

Our success in generating norbornenyne radical anion (**17**$^{\bullet-}$) also triggered our interest in using gas-phase ion chemistry to form cyclopentyne radical anion (**13**$^{\bullet-}$). Since norbornenyne is an ethenyl-bridged cyclopentyne derivative, we were hopeful that we could also generate **13**$^{\bullet-}$ and use EA and PA bracketing experiments to obtain the ΔH_{H2} of cyclopentyne (**13**).

As discussed in the Introduction to this chapter, **13** has been generated and trapped in solution.[14] Unlike cyclobutyne (**18**), **13** is stable toward rearrangement to cyclobutylidenecarbene (**50**).[20] In fact, **13** is often generated from **50** in solution.[14b,d,f]

Upon reaction with $O^{\bullet-}$, cyclopentene (**51**) might be expected to form **13**$^{\bullet-}$. However, as discussed in the previous sections, $O^{\bullet-}$ is a highly unselective reagent and it is possible that a variety of $C_5H_6^{\bullet-}$ isomers could be generated by the reaction of **51** with $O^{\bullet-}$. For instance, 1,2-H_2^+ abstraction would generate the desired **13**$^{\bullet-}$, but 2,3-H_2^+ abstraction would lead to formation of the radical anion of 1,2-cyclopentadiene (**52**$^{\bullet-}$), and 3,4 -H_2^+ abstraction would generate 1,3-cyclopentadiene radical anion (**53**$^{\bullet-}$). There are also two carbene radical anions that could be generated in the reaction of $O^{\bullet-}$ with **51**. 3,3-H_2^+ abstraction would lead to conjugated carbene radical anion **54**$^{\bullet-}$; whereas 4,4-H_2^+ abstraction would lead to unconjugated carbene radical anion **55**$^{\bullet-}$. In addition, distonic radical anion **56**$^{\bullet-}$ could be generated by 1,4-H_2^+ abstraction.



13$^{\bullet-}$ **50**$^{\bullet-}$ **52**$^{\bullet-}$ **53**$^{\bullet-}$

54$^{\bullet-}$ **55**$^{\bullet-}$ **56**$^{\bullet-}$

Allene radical anion **52**$^{\bullet-}$ and carbene radical anion **54**$^{\bullet-}$ are predicted to nearly degenerate in enthalpy and be the most stable, bound, $C_5H_6^{\bullet-}$ isomers by UB3LYP/6-31+G* calculations (Table 2.7). Although cyclopentadiene radical anion **53**$^{\bullet-}$ is predicted to be 19.8 kcal/mol lower in enthalpy than **52**$^{\bullet-}$, the extra electron in **53**$^{\bullet-}$ is not predicted to be bound, and therefore, **53**$^{\bullet-}$ should not be an observable $C_5H_6^{\bullet-}$ isomer.

Table 2.7: (U)B3LYP/6-31+G* Thermochemical data for $C_5H_6^{\bullet-}$ at 298 K.

Anion	**13**$^{\bullet-}$	**50**$^{\bullet-}$	**52**$^{\bullet-}$	**53**$^{\bullet-}$	**54**$^{\bullet-}$	**55**$^{\bullet-}$	**56**$^{\bullet-}$
Relative Enthalpy (kcal/mol)	19.3	23.4	0	-19.8	0	19.1	13.8
Proton Affinity (kcal/mol)	390.3	378.6	402.1	n/a	402.1	407.9	402.6
Electron Affinity (eV)	1.11[a]	0.83	1.09	-0.91	0.79	0.34	1.01

(a) $EA_{Corrected}$ = 0.87 eV, calculated from $EA_{Triplet} - \Delta E_{ST}$(CASPT2), with $EA_{Triplet}$ = 1.79 eV and ΔE_{ST}(CASPT2) = 21.1 kcal/mol.

Unfortunately, the desired radical anion, **13**$^{\bullet-}$, is predicted to be 19.3 kcal/mol higher in enthalpy than allene radical anion **52**$^{\bullet-}$. Consistent with previous

predictions[20] and experimental observations[14b,d,f] for the neutral species, cyclobutylidenecarbene radical anion **50**$^{\bullet-}$ is predicted to be 4.1 kcal/mol higher in enthalpy than **13**$^{\bullet-}$. Distonic radical anion **56**$^{\bullet-}$ is predicted to be 13.8 kcal/mol higher in enthalpy than **52**$^{\bullet-}$.

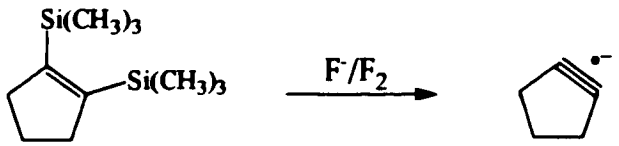
Although **13**$^{\bullet-}$ is not predicted to be the most stable $C_5H_6^{\bullet-}$ isomer, the reaction of **51** with $O^{\bullet-}$ was nonetheless explored. When **51** was allowed to react with $O^{\bullet-}$, three products were observed. The major product was HO^- (85.5 %) while minor products were $C_5H_7^-$ (0.9 %) and $C_5H_6^{\bullet-}$ (13.6 %).

Electron transfer was observed when $C_5H_6^{\bullet-}$ was allowed to react with SO_2, thus providing an upper limit of 1.107 eV for the EA of $C_5H_6^{\bullet-}$. As shown in Table 2.7, this value is consistent with all of the possible $C_5H_6^{\bullet-}$ isomers and therefore does not provide much insight into the structure of this ion. A lower bracket was not determined for this ion.

No proton transfer was observed when $C_5H_6^{\bullet-}$ was allowed to react with H_2O (ΔH_{acid} = 390.8 kcal/mol), thus making **13**$^{\bullet-}$ (PA predicted to be 390.3 kcal/mol) an unlikely contributor to $C_5H_6^{\bullet-}$. The reaction of $C_5H_6^{\bullet-}$ with NH_3 (ΔH_{acid} = 403.7 kcal/mol) was inconclusive. The $C_5H_6^{\bullet-}$ ion count depleted upon reaction with NH_3, however, no NH_2^- was observed. Thus, a lower bracket for the PA of $C_5H_6^{\bullet-}$ is 390.8 kcal/mol, but the PA could be much higher. This finding is consistent with the prediction that this $C_5H_6^{\bullet-}$ ion consists of **52**$^{\bullet-}$ and/or **54**$^{\bullet-}$. Both, coincidently, are predicted to have PA = 402.1 kcal/mol.

Perhaps the Squires reaction of 1,2-bis(trimethylsilyl)cyclopentene (**57**) would prove to be a more successful method of generating **13**$^{\bullet-}$ (Scheme 19). However, the synthesis of **57** is likely to prove more challenging than the preparation of either **33** or **44**.

Scheme 19:

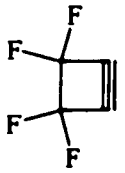


57 **13**$^{\bullet-}$

2.5 Perfluorocyclobutyne

As noted in the Introduction to this chapter, perfluorocyclobutyne (**20**) is predicted to be stable towards rearrangement to perfluorocyclopropylidenecarbene (**58**).[20,21] In fact, there is some evidence that **20** has been generated and trapped in solution.[22] However, to date there is no thermochemical data for this highly strained alkyne.

We sought to generate **20**$^{\bullet-}$ in the gas-phase and to measure its PA and EA. The experimental EA and PA of **20**$^{\bullet-}$ could then be compared to the predicted values of EA = 2.96 eV and PA = 352.0 kcal/mol.[21]



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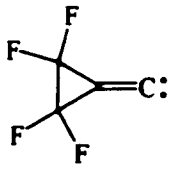
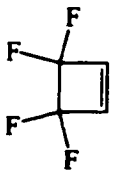


58



59

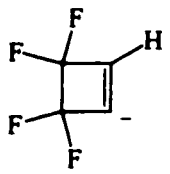
A sample of 3,3,4,4-tetrafluorocyclobutene (**59**) was prepared by Kevin Bartlett.[21] Preliminary gas-phase experiments by Professor Paul Wenthold on the reaction of **59** with $O^{\bullet-}$ did not produce a $C_4F_4^{\bullet-}$ ion.[21] However, in our FA-SIFT experiments, we did observe $C_4F_4^{\bullet-}$, although the yield was quite poor.

When **59** was allowed to react with $O^{\bullet-}$, seven products were observed. The major products of the reaction were m/z 125 (28.4%, $C_4HF_4^-$), m/z 121 (38.2%, $C_4HF_4^-$ + $O^{\bullet-}$ - HF), and m/z 74 (13.7%), while minor products were m/z 124 (2.7%, $C_4F_4^{\bullet-}$), m/z 141 (5.3%, $C_4HF_4^-$ + $O^{\bullet-}$), m/z 102 (5.5%), and m/z 39 (6.2%, HF + F^-). Although a $C_4F_4^{\bullet-}$ ion (presumably **20**$^{\bullet-}$) is generated in this reaction, it is not a suitable method to prepare **20**$^{\bullet-}$, since the yields of $C_4F_4^{\bullet-}$ were too low to characterize this ion.

The $C_4HF_4^-$ ion, formed in the reaction of **59** with $O^{\bullet-}$, was generated independently by allowing **59** to react with HO^-. No proton transfer was observed upon reaction of the $C_4HF_4^-$ ion with EtOH (ΔH_{acid} = 378.3 kcal/mol), PhCCH (ΔH_{acid} = 370.6 kcal/mol), or acetone (ΔH_{acid} = 369.0 kcal/mol). Proton transfer was observed when the $C_4HF_4^-$ ion was allowed to react with *t*-BuSH (ΔH_{acid} = 352.5 kcal/mol), CH_3SH (ΔH_{acid} = 356.8 kcal/mol), and CF_3CH_2OH (ΔH_{acid} = 361.9 kcal/mol), thus

leading to an assigned proton affinity of 365.5 ± 3.5 kcal/mol for $C_4HF_4^-$. This value compares quite well with the predicted value of ΔH_{acid} = 364.5 kcal/mol for perfluorocyclobutenyl anion (**60**).[53]

Since the reaction of **59** with $O^{\bullet-}$ does not produce useful quantities of **20**$^{\bullet-}$, the Squires reaction of 1,2-bis(trimethylsilyl)-3,3,4,4-tetrafluorocyclobutene (**61**) was explored. A sample of **61** was prepared by Kevin Bartlett.[21] The first step of the Squires reaction -- formation of vinyl anion **62** by reaction of **61** with F^- -- was successful. However, upon reaction of **62** with F_2, only a very small amount of $C_4F_4^{\bullet-}$ was observed. Attempts to bracket the proton affinity of this ion were unsuccessful.



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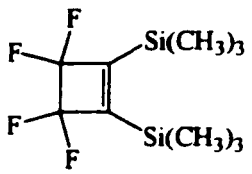
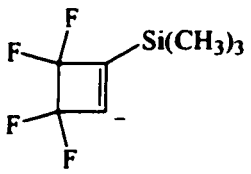


61



62

In this case, the Squires reaction does not appear to generate substantial quantities of $C_4F_4^{\bullet-}$. It is possible that the second step of the Squires reaction, which involves dissociative electron transfer from **62** to F_2, is unfavorable, due to the similar electron affinities of **62** (EA calculated to be 2.93 eV)[21] and F_2 (EA = 3.1 eV). Whatever the reason, like the reaction of **59** with $O^{\bullet-}$, the reaction of **61** with F^-/F_2 does not produce enough $C_4F_4^{\bullet-}$ to allow the PA and EA of this radical anion to be measured.

Summary and Conclusions

The radical anions of 1,5-dehydroquadricyclane (**6**$^{\bullet-}$) norbornyne (**16**$^{\bullet-}$) and norbornenyne (**17**$^{\bullet-}$) have been generated in the gas-phase. However, attempts to generate the radical anions for cyclopentyne (**13**$^{\bullet-}$) and perfluorocyclobutyne (**20**$^{\bullet-}$) were unsuccessful.

The reaction of $O^{\bullet-}$ with quadricyclane (**25**) produced a mixture of quadricyclene radical anions. 1,5-dehydroquadricyclane (**6**$^{\bullet-}$) was generated independently of the three other isomeric quadricyclenes via the Squires reaction of **27**. The resulting $C_7H_6^{\bullet-}$ ion was found to have EA ~ 0.6 eV and PA = 385.6 ± 5.1 kcal/mol. These experimental values are in excellent agreement with the values predicted for **6**$^{\bullet-}$ at both (U)B3LYP/6-31+G* and CASPT2/6-31+G*. Thus, the $C_7H_6^{\bullet-}$ ion formed by reaction of **27** with F^-/F_2 is assigned as **6**$^{\bullet-}$, and an approximate ΔH_{H2} = 91.0 ± 5.1 kcal/mol was obtained for the pyramidalized alkene, 1,5-dehydroquadricyclene (**6**).

The Squires reaction of 2,3-bis(trimethylsilyl)norbornadiene (**33**) also produced a $C_7H_6^{\bullet-}$ ion, which had EA = 0.78 ± 0.33 eV and PA = 377.5 ± 3.0 kcal/mol. These experimental values are in good agreement with those predicted by (U)B3LYP/6-31+G*, CASPT2/6-31+G*, and CCSD(T)/6-31+G*. This ion was assigned as the radical anion of norbornenyne (**17**$^{\bullet-}$).

The reaction of norbornadiene (**32**) with $O^{\bullet-}$ generated a $C_7H_6^{\bullet-}$ ion that appears to be comprised of two components. The first component has identical reactivity to the $C_7H_6^{\bullet-}$ ion generated from the Squires reaction of **33** and is assigned

as **17**$^{\bullet-}$. The second component was found to have a PA ~ 10 kcal/mol higher than **17**$^{\bullet-}$.

Calculations were carried out to aid in the assignment of the structure of the latter $C_7H_6^{\bullet-}$ ion. The radical anions of 2,7-dehydronorbornadiene (**34**$^{\bullet-}$) and norborna-1(2),2(3),5(6)-triene (**35**$^{\bullet-}$) are predicted to have enthalpies similar to that of **17**$^{\bullet-}$. In addition, each of these anions is predicted to have a PA ~ 10 kcal/mol higher in enthalpy than that of **17**$^{\bullet-}$. Thus the second $C_7H_6^{\bullet-}$ isomer, formed from reaction of **32** with $O^{\bullet-}$, could either be distonic radical anion **34**$^{\bullet-}$, allene radical anion **35**$^{\bullet-}$, or a mixture of **34**$^{\bullet-}$ and **35**$^{\bullet-}$.

Combining the experimental EA and PA of **17**$^{\bullet-}$ in a thermocycle gives an experimental ΔH_{H2} of 93.9 ± 11.6 kcal/mol for **17**. A more accurate EA for **17**$^{\bullet-}$, would substantially reduce the uncertainty in the value of ΔH_{H2} for **17**. Unfortunately, NIPES experiments on **17**$^{\bullet-}$, generated either by the reaction of **32** with $O^{\bullet-}$ or **33** with F^-/F_2, have not yet been successful.

The Squires reaction of 2,3-bis(trimethylsilyl)norbornene (**44**) generates a $C_7H_8^{\bullet-}$ ion that was found to have EA = 0.68 ± 0.1 eV and PA = 372.9 ± 3.0 kcal/mol. The experimental EA is in excellent agreement with the CASPT2 predicted value of EA = 0.57 eV for the radical anion of norbornyne (**16**$^{\bullet-}$). However, the predicted PA of **16**$^{\bullet-}$ is *ca.* 10 kcal/mol higher than the experimental value. This discrepancy can be explained by proposing that, in the ion-dipole complexes with acids, **16**$^{\bullet-}$ rearranges to a cyclopentylacetylide radical anion (**49**$^{\bullet-}$). The PA calculated for **49**$^{\bullet-}$ is in good agreement with the value measured.

The reaction of cyclopentene (**51**) with $O^{\bullet-}$ was explored as a possible method for generating the radical anion of cyclopentyne (**13**$^{\bullet-}$). When **51** was allowed to react with $O^{\bullet-}$, a $C_5H_6^{\bullet-}$ ion was observed. However, it seems unlikely that this ion is **13**$^{\bullet-}$. Instead, based on UB3LYP/6-31+G* calculations and PA bracketing experiments, the $C_5H_6^{\bullet-}$ ion generated in this reaction is most likely a mixture of the radical anions of 1,2-cyclopentadiene (**52**$^{\bullet-}$) and 3-carbenacyclopentene (**54**$^{\bullet-}$).

Finally, the Squires reaction of 1,2-bis(trimethylsilyl)-3,3,4,4-tetrafluorocyclobutene (**61**) and the reaction of 3,3,4,4-tetrafluorocyclobutene (**59**) with $O^{\bullet-}$ were both explored as potential methods for generating the radical anion of perfluorocyclobutyne (**20**$^{\bullet-}$). Although both of these reactions did produce a $C_4F_4^{\bullet-}$ ion, the yields were too low to allow for its characterization.

In our experience, the reaction of $O^{\bullet-}$ proved to be too unselective to be useful for the regiospecific generation of the radical anions of pyramidalized alkenes and bent alkynes. The reaction of $O^{\bullet-}$ produced, not only the desired radical anion, but also unwanted isomeric products.

The Squires reaction of bis(trimethyl)silanes, does indeed generate regiospecific pyramidalized alkene and bent alkyne radical anions. Unfortunately, the yields of radical anions produced by the Squires reaction were too low to allow for successful NIPES experiments. However, further work on optimizing the conditions of the Squires reaction is necessary. Alternatively, a new method for regiospecific generation of radical anions in high yield is desirable.

Experimental

Calculations. Density functional theory (DFT) calculations were carried out with Becke's hybrid, three-parameter, functional[54] and the correlation functional of Lee, Yang, and Parr[55] (B3LYP). Geometries were optimized at this level of theory, and a B3LYP vibrational analysis was performed at each stationary point found, in order to confirm its identity as an energy minimum (no vibrational modes with an imaginary frequency) or as a transition state (one vibrational mode with an imaginary frequency). The vibrational analyses also provided the zero-point and thermal energy corrections necessary to convert the B3LYP electronic energies to enthalpies at 298 K. For this purpose the B3LYP vibrational frequencies were used without scaling.

Single-point coupled cluster calculations, which include single and double excitations[56] and a noniterative estimate of the effects of triple excitations[57] (CCSD(T)), were performed at the B3LYP optimized geometries. The B3LYP zero-point and thermal energy corrections were used, without scaling, to convert the CCSD(T) electronic energies to enthalpies at 298 K.

Geometry optimizations were also performed with CASSCF. The active spaces used were (6/6) for norbornenyne, (4/4) for norbornyne, and (2/2) for quadricyclenes **6** – **9** For the radical anions the CASSCF active spaces were (7/6) for norbornenyne radical anion, (5/4) for norbornyne radical anion, and (3/2) for the four quadricyclene radical anions (*i.e.* ROHF). The active electrons were distributed among the π or π–like molecular orbitals. CASSCF vibrational analyses were carried

out to establish the nature of each stationary point found and to obtain zero-point and thermal corrections to its energy.

In order to include the effects of dynamic electron correlation,[30] CASPT2[58] single-point calculations were performed at CASSCF geometries. The CASSCF zero-point and thermal corrections were used to convert the CASPT2 electronic energies to enthalpies.

All calculations were performed using the 6-31+G* basis set.[59] All (U)B3LYP, CASSCF, and CCSD(T) calculations were carried out using the Gaussian 98 suite of programs,[60] while all CASPT2 calculations were performed using the MOLCAS package of programs.[61]

Gas-phase Experiments. FT-ICR experiments were performed at the University of Minnesota, in collaboration with Professor Steve Kass. FA-SIFT experiments were carried out in collaboration with Professor Veronica Bierbaum and Dr. Shuji Kato at the University of Colorado, using a tandem flowing afterglow-selected ion flow tube (FA-SIFT) instrument that has been described previously.[62] Proton affinity and electron affinity bracketing experiments were carried out by allowing neutrals with known acidity and electron affinity to react with the ion of interest.[37] Reagents used for gas-phase experiments were either obtained from Aldrich or synthesized as described below, with the exception of 3,3,4,4-tetrafluorocyclobutene (**59**) and 1,2-bis(trimethylsilyl)-3,3,4,4-tetrafluorocyclobutene (**61**), which were provided by Kevin Bartlett,[21] and 1,2,3,4,7,7-hexachloronorbornadiene (**42**) which was prepared by Dr. Bongjin Park.

Synthesis. Ether solvents were dried over and distilled from Na/benzophenone. All other reagents were used as received, unless otherwise noted. Alkoxides were purchased from Aldrich and handled and stored in a glovebox. Column chromatography was performed using Silica Gel 60 (230 - 410 mesh, 0.04 - 0.063 mm). Thin layer chromatography was performed on aluminum supported Silica Gel 60 plates (0.2 mm thick, F254). Photolysis was carried out with a 200-wt Ace-Hanovia high-pressure quartz mercury vapor lamp in a water bath. Hydrogenations were performed on a Parr hydrogenator. Glassware was flame dried under vacuum, and all reactions were carried out under argon, unless otherwise noted.

Gas chromatographic analyses were done either on a Hewlett Packard 5790A series gas chromatograph, equipped with an Alltech Econo-Cap 30 m x 0.25 mm EC-5 capillary column (0.25 μm film thickness) and coupled to a Hewlett Packard 3390A integrator, or on a Hewlett Packard 5890 series II gas chromatograph, equipped with an Alltech Econo-Cap 30 m x 0.25 mm SE-54 capillary column (0.25 μm film thickness). Mass spectra were obtained on a Hewlett Packard 5890 gas chromatograph, coupled to a Hewlett Packard 5971A mass selective detector and equipped with a Supel Co. 30 m x 0.2 μm SPB-1 capillary column (0.2 μm film thickness). ^{1}H and ^{13}C NMR spectra were recorded in chloroform-d_1 on a Brucker AF 300 and referenced to residual $CHCl_3$ in the sample, unless otherwise noted. Preparative gas chromatography was completed on a Gow-Mac gas chromatograph series 350 with a thermal conductivity detector coupled to a Gow-Mac model 70-150 recorder.

2-Bromo-3-deuterionorbornadiene: Norbornadiene (18 ml, 0.167 mol) was dissolved in 50 ml of THF and cooled to –78 °C under an argon atmosphere. Potassium *tert*-butoxide (12.9 g, 0.115 mol) was dissolved in 100 ml of THF and added to the reaction mixture. *n*-Butyllithium (50 ml, 0.125 mol, 2.5 M in hexanes) was added dropwise over 30 minutes. The solution was stirred for 1 hour at –78 °C and then a solution of 1,2-dibromoethane (4.6 ml, 0.054 mol) in 20 ml of THF was added over 20 minutes. The reaction mixture was warmed to –40 °C and stirred for 1 hour. Methanol-O-*d* (20 ml, 0.493 mol) was added and the solution was warmed to room temperature over 1.5 hours. Saturated NH_4Cl (75 ml) and water (75 ml) were added and the layers were separated. The water layer was extracted with ether (3 x 100 ml), and the organic layers were combined and dried over $MgSO_4$. The solvent was removed by rotary evaporation. Purification by vacuum fractional distillation (44 – 50 °C, 4" vigreux column, water aspirator) gave 3.48 g (0.020 mol, 38.2 % yield) of clear liquid (96.0 % pure by GC). The deuterium incorporation was determined by GCMS and ^{1}H NMR to be 88.8 % d_1. ^{1}H NMR (300 MHz) δ 2.05 (dt, J = 1.5 Hz, 5.9 Hz, 1H), 2.27 (dt, J = 1.5 Hz, 5.9 Hz, 1H), 3.48 (m, 1H), 3.61 (m, 1H), 6.78 (dd, J = 2.9 Hz, 5.4 Hz, 1H), 6.90 (dd, J = 3.9 Hz, 5.4 Hz, 1H). MS (EI) 173, 172, 171 (M^+), 170, 147, 145, 92, 91, 66, 39.

Norbornadiene-2,3-d_2 (32-d_2): A solution of 2-bromo-3-deuterionorbornadiene (5.33 g, 0.031 mol) in 30 ml of ether was cooled to –78 °C under an argon atmosphere. *tert*-Butyllithium (40 ml, 0.068 mol, 1.7 M in pentane) was added dropwise over 30

minutes. The solution was stirred at –78 °C for 1.5 hours and methanol-O-*d* (11.5 ml, 0.283 mol) was added. The reaction mixture was warmed to room temperature over 3 hours, then saturated NH_4Cl (50 ml) and water (50 ml) were added, and the layers were separated. The water layer was extracted with ether (3 x 75 ml), and the organic layers were combined and dried over $MgSO_4$. The solvent was removed by distillation through an 8" vigreux column to yield 5 ml of crude material. Preparative GC on a 4' x 1/4" 20% DC-200 on Chrom -P 80/100 mesh column (column temperature: 38 °C, injection port: 85 °C, detector: 89 °C) yielded 0.858 g (9.1 mmol, 29.4 % yield) of clear liquid (99.6 % pure by GC). The deuterium incorporation was 93.0 % d_2, as determined by GCMS and ^{1}H NMR. ^{1}H NMR (300 MHz) δ 1.97 (app. t, J = 1.5 Hz, 2H), 3.56 (m, J = 1.5 Hz, 2.0 Hz, 2H), 6.76 (t, J = 2.0 Hz, 2H). ^{13}C NMR (300 MHz) δ 50.21, 75.48, 143.55. MS (EI) 94 (M^+), 93 (100 %), 92, 67, 66.

Quadricyclane-1,5-*d*$_2$ (25-*d*$_2$): Acetophenone (0.2 ml, 1.7 mmol), ether (10 ml), and norbornadiene-2,3-*d*$_2$ (19 mmol) were placed into a 25 x 200 mm Pyrex tube and degassed with argon. The solution was irradiated for 7 hours. The solvent was removed by rotary evaporation, and preparative GC on an 8' x 1/4" 20% Carb on Chrom -P 20M 80/100 mesh column yielded 0.19 g (2.03 mol, 10.7 % yield) of clear liquid (92.0 % pure by GC). ^{1}H NMR (300 MHz) δ 1.35 (d, J = 4.4 Hz, 2H), 1.48 (d, J = 4.4 Hz, 2H), 2.02 (t, J = 1.5 Hz, 2H). MS (EI) 94 (M^+), 93 (100 %), 92, 67, 66.

2-Bromo-3-(trimethylsilyl)norbornadiene: A solution of potassium *tert*-butoxide (14.4 g, 0.128 mol) in 114 ml of THF was added to a cooled solution (–78 °C) of norbornadiene (18.5 ml, 0.171 mol) in 36 ml of THF under an atmosphere of argon. *n*-Butyllithium (47 ml, 0.118 mol, 2.5 M in hexanes) was added dropwise over 20 minutes. The solution was stirred for 30 minutes at –78 °C, and a solution of 1,2-dibromoethane (4.6 ml, 0.053 mol) in 20 ml of THF was added dropwise over 20 minutes. The solution was warmed to –40 °C and stirred for 1 hour. Chlorotrimethylsilane (30 ml, 0.236 mol) was added and the reaction mixture was warmed to room temperature over 1 hour. Saturated NH_4Cl (100 ml) and water (100 ml) were added and the layers were separated. The water layer was extracted with ether (3 x 100 ml), and the organic layers were combined and dried over $MgSO_4$. The solvent was removed by rotary evaporation. Purification by vacuum fractional distillation with an 8" vigreux column (81 – 87 °C, water aspirator) gave 9.0 g (0.037 mol, 69.8 % yield) of clear liquid (98.2 % pure by GC). ^{1}H NMR (300 MHz) δ 0.13 (s, 9H), 1.92 (dt, J = 1.6 Hz, 6.2 Hz, 1H), 2.11 (dt, J = 1.6 Hz, 6.2 Hz, 1H), 3.51 (m, 1H), 3.17 (m, 1H), 6.69 (ddd, J = 2.0 Hz, 5.2 Hz, 0.8 Hz, 1H), 6.81 (ddd, J = 3.0 Hz, 5.2 Hz, 0.2 Hz, 1H). ^{13}C NMR (300 MHz) δ -1.36, 56.05, 61.80, 72.74, 141.49, 143.24, 147.67, 148.15. MS (EI) 244, 242 (M^+), 199, 197, 163, 147, 97, 73 (100 %).

2,3-Bis(trimethylsilyl)norbornadiene (33): *tert*-Butyllithium (50 ml, 0.085 mol, 1.7 M in pentane) was added slowly over 10 minutes to a cooled (–78 °C) solution of 2-bromo-3-(trimethylsilyl)norbornadiene (9.0 g, 0.037 mol) in 40 ml of ether under an

argon atmosphere. The reaction mixture was stirred for 1 hour at -78 °C, after which chlorotrimethylsilane (28 ml, 0.221 mol) was added. The solution was warmed to room temperature over 3.5 hours, saturated NH_4Cl (50 ml) and water (50 ml) were added, and the layers were separated. The water layer was extracted with ether (3 x 100 ml), and the organic layers were combined and dried over $MgSO_4$. The solvent was removed by rotary evaporation. Purification by column chromatography (1: silica, 19.5 cm x 2 cm, hexanes, 2: silica, 24 cm x 4 cm, hexanes) gave 7.1 g (0.03 mol, 81.3 % yield) of clear liquid (96.2 % pure by GC). ^{1}H NMR (300 MHz) δ 0.11 (s, 18H) 1.59 (app. t, J = 1.5 Hz, 2H), 3.88 (m, J = 1.5 Hz, 2.0 Hz, 2H), 6.56 (t, J = 2.0 Hz, 2H). ^{13}C NMR (300 MHz) δ 0.80, 58.74, 72.18, 143.59, 165.69. MS (EI) 236 (M^+), 221, 162 (100 %), 155, 133, 97, 73.

1,5-Bis(trimethylsilyl)quadricyclane (27): A solution of 2,3-bis(trimethylsilyl)norbornadiene (2.23 g, 9.45 mmol) and acetophenone (0.049 ml, 0.43 mmol) in 25 ml of ether was degassed for 5 minutes under argon and then irradiated for 18 hours. The solvent was removed by rotary evaporation to yield 2.03 g (8.6 mmol, 91.0 % yield) of clear liquid. ^{1}H NMR (300 MHz) δ -0.06 (s, 18H), 1.24 (dt, J = 1.5 Hz, 3.9 Hz, 2H), 1.44 (d, J = 4.4 Hz, 2H), 1.97 (dt, J = 1.5 Hz, 11.23 Hz, 1H), 2.12 (dt, J = 1.5 Hz, 11.23 Hz, 1H). ^{13}C NMR (300 MHz) δ -1.10, 13.09, 19.12, 27.71, 32.76. MS (EI) 236 (M^+), 221, 162, 155, 133, 73, 66 (100 %).

2-(Trimethylsilyl)norbornadiene: A solution of potassium *tert*-butoxide (6.8 g, 0.061 mol) in 20 ml of THF was added to a cooled solution (–78 °C) of norbornadiene (6.0 ml, 0.056 mol) in 25 ml of THF under an atmosphere of argon. *n*-Butyllithium (24 ml, 0.06 mol, 2.5 M in hexanes) was added dropwise over 10 minutes. The solution was stirred for 45 minutes at –78 °C and chlorotrimethylsilane (20 ml, 0.158 mol) was added. The reaction mixture was warmed to room temperature over 1 hour. Saturated NH_4Cl (50 ml) and water (50 ml) were added and the layers were separated. The water layer was extracted with ether (3 x 100 ml), and the organic layers were combined and dried over $MgSO_4$. The solvent was removed by rotary evaporation. Purification by column chromatography (silica, 15 cm x 6 cm, hexanes) gave 5.21 g (0.032 mol, 57.1 % yield) of clear liquid (99.1 % pure by GC). ^1H NMR (300 MHz) δ 0.04 (s, 9H), 1.82 (dt, J = 1.5 Hz, 5.9 Hz, 2H), 3.62 (m, 1H), 3.67 (m, 1H), 6.66 (t, J = 1.8 Hz, 2H), 6.99 (d, J = 2.9 Hz, 1H). MS (EI) 164 (M+), 149, 121, 83, 73, 66 (100 %), 43.

1-(Trimethylsilyl)quadricyclane (29): A solution of 2-(trimethylsilyl)norbornadiene (2.46 g, 15.0 mmol) and acetophenone (0.09 ml, 0.75 mmol) in 38 ml of benzene was degassed for 5 minutes under argon and then irradiated for 4 hours. The solvent was removed by rotary evaporation to yield 2.25 g (13.7 mmol, 91.5 % yield) of clear liquid. ^1H NMR (300 MHz) δ –0.06 (s, 9H), 1.29 (dt, J = 1.5 Hz, 4.9 Hz, 2H), 1.43 (m, 3H), 1.99 (dt, J = 1.5 Hz, 10.7 Hz, 1H), 2.09 (dt, J = 1.5 Hz, 10.7 Hz, 1H). MS (EI) 164 (M+), 149, 121, 83, 73, 66 (100 %), 43.

2-Bromonorbornadiene: Norbornadiene (20 ml, 0.186 mol) in 50 ml of THF was added to a cooled (–78 °C) solution of potassium *tert*-butoxide (14.1 g, 0.125 mol) in 100 ml of THF under an argon atmosphere. *n*-Butyllithium (61 ml, 0.098 mol, 1.6 M in hexanes) was added dropwise over 20 minutes. The solution was stirred at –78 °C for 1 hour and then 1,2-dibromoethane (9 ml, 0.104 mol) in 40 ml of THF was added dropwise over 45 minutes. The solution was warmed to room temperature over 1.5 hours and saturated NH_4Cl (75 ml) and water (75 ml) were added and the layers were separated. The water layer was extracted with ether (3 x 100 ml), and the organic layers were combined and dried over $MgSO_4$. The solvent was removed by rotary evaporation. Purification by vacuum fractional distillation through a 4" vigreux column (34 – 38 °C, water aspirator) gave 4.1 g (0.024 mol, 24.5 % yield) of clear liquid (97.6 % pure by GC). ^{1}H NMR (300 MHz) δ 2.03 (dt, J = 1.5 Hz, 6.4 Hz, 1H), 2.22 (dt, J = 1.5 Hz, 6.4 Hz, 1H), 3.44 (app. s, 1H), 3.56 (app. s, 1H), 6.60 (d, J = 2.9 Hz, 1H), 6.73 (dd, J = 2.9 Hz, 4.9 Hz, 1H), 6.85 (dd, J = 2.9 Hz, 4.9 Hz, 1H). MS (EI) 172, 170 (M^+), 146, 144, 91 (100 %), 65, 39.

1-Bromoquadricyclane (30): A solution of 2-bromonorbornadiene (4.0 g, 23.4 mmol) and acetophenone (0.14 ml, 1.2 mmol) in 50 ml of benzene was irradiated for 4 hours. The solvent was removed by rotary evaporation. Purification by column chromatography (alumina, 17 cm x 4 cm, hexanes) gave 0.65 g (3.8 mmol, 16.2 % yield) of clear liquid. ^{1}H NMR (300 MHz) δ 1.51 (tq, J = 1.5 Hz, 4.8 Hz, 1H), 1.75 (dddd, J = 2.6 Hz, 4.8 Hz, 1H), 1.82 (dq, J = 1.5 Hz, 5.5 Hz, 1H), 1.92 (dt, J = 1.5 Hz,

11.4 Hz, 1H), 2.01 (m, J = 1.8 Hz, 2.2 Hz, 1H), 2.05 (m, J = 2.2 Hz, 2.6 Hz, 1H), 2.19 (dt, J = 1.5 Hz, 11.4 Hz, 1H).

2,3-Bis(trimethylsilyl)norbornene (44):[63] A solution of 2,3-bis(trimethylsilyl)norbornadiene (0.281 g, 1.1 mmol) and 5% palladium on carbon (0.046 g) in 15 ml of methanol was hydrogenated for 4 minutes (14 psi). The palladium was filtered and the product was extracted with pentane (3 x 35 ml). The pentane extract was dried over $MgSO_4$, and the solvent was removed by distillation through an 8" vigreux column. Residual pentane was removed under vacuum at -30 °C to yield 0.14 g (0.59 mmol, 49.2 % yield) of clear liquid (99.8 % pure by GC). ^1H NMR (200 MHz) δ 0.12 (s, 18H), 0.79 (m, 2H), 0.99 (dt, J = 1.3 Hz, 8 2 Hz, 1H), 1.11 (dq, J = 2.0 Hz, 8.2 Hz, 1H), 1.52 (m, 2H), 3.03 (q, J = 1.6 Hz, 2H). MS (EI) 238 (M+), 134, 121 (100%), 95, 79, 66.

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46. The amount of the second $C_7H_6^{\bullet -}$ component decreased as the injection energy (E_{inj}) during CID experiments on the mixture of $C_7H_6^{\bullet -}$ ions was increased. This suggests that the second component is less bound than the first component.

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GETTING AWAY FROM REACTION TIME:

HEMISPHERIC DIFFERENCES ON AN IMPLICIT MEMORY TASK

by

ELIZABETH M. SOETY

A dissertation submitted in partial fulfillment
of the requirements for the degree of
Doctor of Philosophy
Department of Psychology
College of Arts and Sciences
University of South Florida

August 2002

Major Professor: Cynthia R. Cimino, Ph.D.

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An Abstract

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Research over the past thirty years has revealed a unique contribution of the right hemisphere (RH) to language processing. However, methodological difficulties, such as definition of relatedness and variability in reaction time have interfered with clearer understanding of this contribution. In this study, normal subjects completed a lateralized implicit memory task. Memory pairs varied by strength of associative relationship (weak or strong) and direction of relationship (forward, backward, or forward and backward). Stimuli characteristics including prime and target set size, connectivity, frequency, imageability, number of overlaps and mediators, in addition to mediator and overlap strength were held constant. Analysis of the priming data revealed main effects of visual field, strength and direction in addition to a strength x direction interaction. Thus, when stimuli characteristics are controlled, the left hemisphere processes information more efficiently than the right hemisphere, regardless of word pair relationship.

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Introduction

Brain-behavior research during the past several decades has revealed an overall lateralization of functioning. Specifically, verbal and other sequential processes are preferentially mediated by the left hemisphere whereas spatial and other non-sequential processes are preferentially mediated by the right hemisphere. Thus, language, one of the most highly lateralized functions, appears to be more easily processed by the left hemisphere while analysis and synthesis of visual information appears to be better performed by the right hemisphere, particularly in right handed individuals.

Much evidence has accumulated in support of the right hemisphere's contribution to language processes. For example, many patients with right hemisphere lesions display deficits in the conveyance and/or comprehension of emotionally laden speech (Heilman, Bowers, & Valenstein, 1993). Moreover, such patients display poorly organized, tangential speech and focus on insignificant details during a conversation (Gardner, 1975; Wapner, Hamby, & Gardner, 1981; Foldi, Cicone, & Gardner, 1983). Additionally, fMRI imaging revealed bilateral activation during language tasks, suggesting that both hemisphere's contribute to information processing (Kiehl, Liddle, Smith, Mendrek, Forster, & Hare, 1999; Springer, Binder, Hammeke, Swanson, Frost, Bellgowan, Brewer, Perry, Morris, & Mueller, 1999; St George, Kutas, Martinez, & Sereno, 1999).

Several areas of research have also pointed toward right hemispheric involvement

with comprehension of word meanings. For example, left-hemisphere damaged (LHD) patients, even those with large lesions, retain the ability to articulate some thoughts and understand a portion of incoming messages (Wepman, J. M. 1951; Gardner, 1975; Rosenbeck, LaPointe, Wertz 1989). Moreover, split-brain patients, whose damaged corpus callosum has eliminated communication between the two hemispheres, demonstrate that the right hemisphere is capable of some linguistic functions, including an extensive reading vocabulary (Zaidel, 1990). Moreover, evidence of the right hemisphere's ability to assume language functioning following hemidecortication has been documented (Dennis & Whitaker, 1976). Finally, within the field of cognitive neuropsychology, a right hemisphere advantage has been demonstrated in numerous priming studies (Burgess & Simpson, 1988; Chiarello, 1985; Chiarello, Burgess, Richards & Pollock, 1990; Koivisto,1997, 1998, 1999).

Priming is one effective paradigm frequently utilized to examine language processing. Essentially, it is believed that once the first stimulus (e.g., prime) is presented, either with or without subject's awareness, activation of related words (e.g., nodes) occurs immediately and automatically (Collins & Loftus, 1975). This activation allows for faster identification of a second word (e.g., target) when the prime and target are related (Meyer & Schvaneveldt, 1971). Thus, once a word is perceived, access to subsequent words can be facilitated when the subsequent words are related orthographically, phonetically, or semantically to the initial word (Chiarello, 1985; Abernathy & Coney, 1990; Neely, 1991). Repetition priming is one example of a priming task. Specifically, information acquired during a learning episode can result in enhanced

performance on various tasks following the learning episode, such as stem completion and word identification (For review, see Schacter, 1987).

Though studied for nearly two decades, understanding of the right hemisphere's contribution to language processing remains unclear. Within the priming literature, several researchers have found a right hemisphere advantage in certain conditions (Atchley, Burgess, & Keeney,1998, Atchley and Burgess,1998; Abernathy & Coney, 1993; Chiarello, 1985, Chiarello, Burgess, Richards & Pollock,1990; Chiarello, Richards, & Pollock,1992; Koivisto & Laine,1995; Koivisto,1997, 1998, 1999; Walker and Ceci 1985), yet in similar conditions, no right hemisphere advantage is detected (Abernathy & Coney, 1990, 1996; Audet, Driessen & Burgess,1998; Audet, Burgess, & Driessen, 1999; Atchley, Keeney, & Burgess, 1999; Chiarello, 1985; Chiarello, Burgess, Richards, & Pollock,1990; Chiarello, Richards, & Pollock,1992; Collins, 1999; Richards and Chiarello, 1995; Koivisto, 1997, 1998).

One major issue in the priming research has been the question of what type of information is better processed by the right hemisphere. Some researchers have found a right hemisphere advantage when the words share a strong association (i.e., frequently co-occur in speech) (Atchley, 1998; Koivisto, 1995; Abernathy & Coney, 1993) while others have found the advantage with word pairs sharing primarily a categorical relationship (Chiarello, 1990; Chiarello, 1992; Koivisto, 1997), and still others have found the advantage with word pairs sharing both a categorical and associative relationship (Chiarello, 1985; Walker and Ceci, 1985). Thus, it remains quite unclear as to the type of information that is preferentially processed by the right hemisphere.

The task type within this literature also varies. Tasks include but are not limited to pronunciation (subject is asked to pronounce displayed word), lexical decision (subject is asked to report if series of letters is an English word), judgements (are words related in meaning?). For example, Audet, et al., (1998) and Richards and Chiarello (1995) employed a pronunciation task, Audet, et al., (1999) used a relatedness judgement task, while in the remaining studies mentioned above, a lexical decision task was adopted. Moreover, Chiarello, et al., (1990 & 1992) used both a pronunciation and a lexical decision paradigm and obtained similar results in both. However, reaction time and error rates tend to yield inconsistent and conflicting results. Thus, it is possible that use of other methodologies may provide more reliable and meaningful results. For example, Koivisto and Laine (1995) found hemispheric differences with an implicit memory task. Therefore, use of a priming task that is not reliant upon reaction time, such as an implicit memory task, may be well advised.

In conclusion, several areas of experimentation have pointed toward right hemispheric involvement in comprehension of single word meanings including work with brain-damaged patients, split-brain patients, and neurologically intact individuals. However, the precise nature of this involvement has not been clearly delineated. It is anticipated that presenting word pairs sharing varying strengths and types of associative relationships in an alternative priming paradigm, the right hemisphere's contribution to language processing will be better understood.

Patient Studies

As mentioned earlier, brain-injured patients have added to our understanding of hemispheric differences. Winner and Gardner (1977) found that right-hemisphere damaged (RHD) patients possess the ability to comprehend the literal meaning of language but are less able to determine the context in which metaphoric or nonliteral language might be used. Fiore and Schooler (1998) concluded that these patients have difficulty matching the language to its appropriate context and suggested that they have lost the use of surrounding, pragmatic features. In addition, Weylman, Brownell, Roman, and Gardner (1989) found differences in correct interpretations of indirect requests. Specifically, left-hemisphere damaged (LHD) patients choose contextually appropriate but factually incorrect responses, whereas RHD patients ignore the contextual cues and choose factually correct but contextually inappropriate responses. For example, when asked "can you open the door for me," LHD patients will open the door (i.e., contextually correct but factually incorrect) whereas RHD patients will not open the door and will instead reply "yes, I am physically able to open the door" (i.e., contexually incorrect but factually correct). Based on these findings, Beeman (1998) concluded that "the patients with LHD had difficulty comprehending the elements of the discourse, whereas patients with RHD comprehended the elements but could not integrate them into the context as a whole" (p. 272).

Beeman (1998) also cites hemispheric differences regarding joke interpretation and suggests that patients with RHD miss the point of jokes because they do not integrate the punch line with the previous context. For example, Birhle and colleagues (1986)

found that RHD and LHD patients performed more poorly than controls on a nonverbal cartoon completion task; whereas RHD patients choose surprising, incoherent endings, LHD patients choose the straightforward endings that are coherent, but not surprising. In drawing inferences, a necessary step inherent in the understanding of humor, Beeman states "the RH may activate predictive inferences, whereas the LH selects and incorporates coherent inferences" (p. 276). This debility extends to visual material with verbal captions. Gardner, Ling, Flamm, and Silverman (1975) found that RHD patients could not appreciate the point of a cartoon when no caption was provided. In addition, RHD patients have been noted to exhibit bizarre humorous responses and respond differently to items than do LHD patients or normal controls. In general, RHD patients seem to be characterized by an inappropriate sense of humor, make inappropriate jokes, and do so in inappropriate contexts (Foldi, Cicone, & Gardner, 1983; Wapner, Hamby & Gardner, 1981).

Split-brain patients also provide a unique model for examining hemispheric differences across a wide range of tasks. In 1967, Sperry and Gazzaniga described their experience with commissurotomized patients who maintained the ability to comprehend words presented both visually and auditorily to the right hemisphere. Since that time, Zaidel and colleagues (1990) have examined performance on reading tasks in these patients and have found that whereas the right hemisphere has an extensive reading vocabulary, it is less impaired relative to the left at processing concrete nouns as opposed to function words, does not benefit from grapheme-to-phoneme conversion rules, and has a tendency to confuse words closely related in meanings (see Zaidel, 1990, for a summary

of this work). Banich & Nicholas (1998) concluded "Although the relatively fine semantic coding by the left hemisphere may underlie integration of information that occurs within a narrow temporal sequence (e.g., words occurring close to one another in a sentence), the coarser and more diffuse semantic processing of the right hemisphere has been suggested to play an important role in integrating information over larger linguistic expanses" (p. 55).

Thus, based on the research with brain-damaged patients, some authors have hypothesized that the right hemisphere activates a broader array of meanings to allow for processing of multiple connotations in jokes and to relate the appropriate meaning to the context during conversations enabling both comprehension of metaphoric language and processing indirect requests (Beeman, Friedman, Grafman, Perez, Diamond, & Lindsay, 1994; Richards & Chiarello, 1995). Moreover, within the split-brain literature, this confusion of words close in meaning is consistent with poorer processing of closely related word meanings and enhanced performance with more distantly related meanings.

Non Patient Studies

Some researchers have found support for the presence of a different pattern of activation in the right hemisphere as compared with the left hemisphere. For example, Chiarello and colleagues posit that the right hemisphere advantage in language processing occurs as a result of the greater spread of activation in the right hemisphere as compared with the left hemisphere. They suggest that instead of being a degraded version of the left hemisphere, that more distantly related words are activated in the right hemisphere

whereas in the left hemisphere a smaller network of words is activated. (See Figure 1 and 2 in Appendix A).

Rodel, Cook, Regard, & Landis (1992) also hypothesize that a different pattern of activation occurs in the right and left hemispheres and have posited that the hemispheres process language in a different yet complementary fashion. Specifically, they predicted that the right hemisphere might show a processing advantage with more distantly related words whereas the left hemisphere's advantage would occur with more closely related prime-target pairs. Their results indicated that words presented to the right visual field (LH) were more frequently judged as semantically close in meaning than words presented to the left visual field (RH).

Additionally, Beeman et al (1994) hypothesized that the right hemisphere processes words more "coarsely" (i.e., distantly related information is activated more strongly) than the left hemisphere. Thus, the right hemisphere would benefit more from the presentation of weakly related primes whereas the left would show greater benefit with one strongly related prime. They found the participants benefitted more from summation primes presented to the left visual field (lvf-RH) than when presented to the right visual field (rvf-LH). Moreover, in the second part of their experiment, when a strong associate was flanked by two unrelated words, for rvf-LH targets, participants benefitted more from this direct prime than from the summation primes. Thus, these results were consistent with the notion that the left hemisphere processes closely related material while the right hemisphere more coarsely processes information and therefore can benefit from the presentation of more distantly related word primes.

Others theorize that the right hemisphere not only processes different types of information but that processing in the right hemisphere is dependent upon certain conditions. For example, Koivisto (1997) proposed that instead of a hemispheric processing difference, the right hemisphere advantage observed in past studies is due to a time course disparity between the hemispheres. Specifically, it was posited that the left hemisphere would benefit instantly from the prime whereas the activation in the right hemisphere would occur more slowly. Thus, at a longer interstimulus interval, the right hemisphere is able to benefit from primes whereas the left hemisphere does not require the delay and is, in fact, hindered by the delay due to subsequent inhibition of more distantly related words. According to this hypothesis, the difference in priming at the longer interstimulus interval is a result of post lexical processes, as the right hemisphere advantage does not occur at short interstimulus intervals. In fact, they found the right hemisphere advantage to occur when the participants' attention was drawn to the primes in addition to the target, encouraging post-lexical comparison of the word pairs. Therefore, they attributed the right hemisphere advantage to post lexical processes rather than a different pattern of activation in the right versus the left hemisphere.

The Priming Paradigm

In order to understand the priming literature to date, an understanding of the relevant variables is first necessary. Within priming studies, there are several relevant variables, including position of prime presentation, length of interval between prime and target, type and operationalization of relatedness, proportion of related trials, type of task

and dependent variable. A brief review of these variables will set the stage for this investigation.

Automatic Versus Controlled Processing

One crucial factor influencing the inconsistencies in the literature is the issue of automatic (i.e., unconscious) versus controlled (i.e., conscious) processes. In a purely automatic paradigm, there is shorter presentation of both prime and target (i.e., under 200 msec), the interval between the prime onset and target onset (i.e., stimulus onset asynchrony or SOA) is brief (typically less than 500 msec), and there is a low proportion of related trials (typically 20% or less). However, few studies employ consistently automatic or controlled conditions, thereby interfering with detection of consistent hemispheric differences. Based on the studies reviewed here, it appears that some degree of controlled processing must occur for a right hemisphere advantage to be detected. For example, Atchley (1998) had subjects view the prime for 750 msec, allowing for conscious encoding of the information. Chiarello's studies (1985, 1990, 1992) all employed SOA's of 500 or greater. Moreover, when Koivisto (1998) modified a purely automatic study by presenting a higher proportion of related trials and directing the subjects to pay attention to the prime, a right hemisphere advantage emerged.

Prime Position

The position of the prime has been found to make a substantial difference in results (Chiarello, 1990, 1992; Walker and Ceci, 1985) and is assumed to relate to

whether one or both hemisphere's are provided with the information and thus can contribute to the processing. It is theorized that lateralized primes may initiate different processes than centrally presented primes. For example, Chiarello, et al., (1992) manipulated prime location and found larger priming overall with centrally presented primes, but found priming asymmetry only with lateralized primes. Reduced priming in the lateralized condition is consistent with the literature on presentation of degraded stimuli. Specifically, when stimulus presentation is less distinct (as in the case of lateral presentation), less priming can occur. By presenting stimuli in a lateralized visual field as opposed to central visual field, the stimuli appears away from the point of greatest acuity (i.e., foveal vison). Additionally, the subject is provided with only a brief exposure to the word, thus it is degraded.

Chiarello concluded that the lateralized prime presentation produces more selective rather than smaller effects. This conclusion is based on the finding of greater priming with categorically - weakly associated word pairs in the right hemisphere compared to the left only with lateralized primes. Thus, she concluded that presentation of lateralized rather than centralized primes to the right hemisphere allowed for detection of a unique spread of activation in the right hemisphere. Moreover, because lateralized and centralized priming effects were equivalent, she concluded that both presentation types provided equal opportunity to access language processing.

Thus, when the purpose is to identify one hemisphere's contribution to processing independently from the other, a lateralized prime is employed. Otherwise, a central presentation of the prime is employed.

Though numerous studies have found equivalent hemispheric priming with central prime presentation, few have found a right hemisphere advantage. Atchley et al (1998) found that when the prime is presented centrally for 750 msec, a right hemisphere advantage can be found with word pairs that are associated, but whose targets represent subordinate perceptual features of the noun prime (i.e., lamb - ears rather than lamb - chops). Koivisto and Laine (1995) also found a right hemisphere advantage when associated prime - target pairs (e.g., bear - forest) were centrally presented in a study phase of a memory task. However, during the lateralized implicit phase, (i.e., generate an associate following presentation of a prime), greater priming was found with the purely associatively related primes that were presented to the right hemisphere than to the left. Equivalent priming was found with categorically and associated word pairs (e.g., saw - axe). Noteworthy, both of these experiments employed purely controlled methodology, allowing conscious processing by both hemispheres of the primes.

In contrast with central presentation studies, many investigations employing a lateralized prime have detected a right hemisphere advantage. Only two studies employed a short SOA. Walker and Ceci (1985) presented prime - target pairs for 100 msec (0 SOA) that were related either categorically and associatively (e.g., rain - snow) or only shared an associative relationship (e.g., dog - bark) and used a high relatedness proportion (66% of word trials). They found accuracy priming in the right hemisphere with the categorical and associated word pairs but did not find priming in the left. Koivisto also employed a short SOA (165 msec), reportedly used word pairs that were related categorically only (however association between several word pairs existed, such

as river - pond, rock - sand, and guitar - cello), used a high proportion of related trials (50% of word trials), and encouraged subjects' conscious processing of the prime. A priming effect was found in the right hemisphere and not in the left. Again, with high relatedness proportions, both studies most likely allowed for a degree of controlled processing, which then allowed for detection of a right hemisphere advantage.

In the remaining lateralized experiments that found a right hemisphere advantage, a longer SOA was employed. Chiarello (1985) used a low relatedness proportion (20% word trials) and categorically and associated prime - target pairs and found priming to be greater in the right than in the left hemisphere. In 1990, Chiarello and colleagues again employed a low relatedness proportion and found categorical priming in the right hemisphere and not in the left. Though their "categorical-only" pairs shared a much weaker associative relationship than the word pairs that they defined as categorically and associatively related, (e.g., doctor - nurse), these word pairs do share an associative relationship (e.g., sugar - salt and oak - maple) based on association norms (Nelson, McEvoy, & Schreiber, 1994). Chiarello and Richards (1992) also used a low relatedness proportion and word pairs that were related categorically but were weakly associated. Again right hemisphere priming was obtained without left hemisphere priming. Koivisto (1997) employed similar methodology (i.e., low relatedness proportion of categorically and weakly associated word pairs) and found priming in both hemispheres, with greater priming in the right than left. Finally, Abernathy and Coney (1993) found right hemisphere, not left hemisphere, priming with associatively related word pairs (e.g., bowl - fruit, sky - blue).

Word Pair Relationship

The type of word pair relationship preferentially processed by the right hemisphere remains unclear. Typically in priming studies, word pairs are related by association (i.e., probability of co-occurrence in speech) and/or are from the same semantic category (i.e., fruits, animals, household items). One problem in the literature is the varied operationalization of associative and categorical relatedness. Periodically published norms are utilized, but more often than not separate groups of subjects are asked to categorize or generate associates which are then included or rejected as stimuli pairs.

The type of relationship in which the right hemisphere advantage has been found has varied. For example, while Abernathy and Coney (1993) found the advantage with strongly associated word pairs, Atchley et al (1998) found the advantage with weakly associated word pairs, and both Chiarello (1985, 1990) and Koivisto (1997, 1998) found the advantage with categorically but weakly associated word pairs. Thus, it appears that some degree of association is necessary, but the strength to which and the direction of association (e.g., forward, backward, mediators, overlaps) remains unclear.

Association. With regard to associative relationship, not only do associative norms exist, but also a mathematical method of measuring the *strength of association* has been developed. Strength of relationship has been operationalized primarily in terms of word association such that words that are more or less commonly produced in a free association task are defined as strongly (i.e., closely) or weakly (i.e., distantly) related, respectively.

The associative relationship may be such that the prime is likely to produce the target in a word association task (i.e., forward strength) or the target may produce the prime in a word association task (i.e., backward strength).

In addition to direct connections, prime target pairs may have indirect connections. Specifically, word pairs can also be connected by mediators (e.g., crayon produces yellow which produces sun) or can share connections (e.g., crayon and painting both produce color). Therefore, in approximating strength of relatedness within a semantic category, indirect connections must be included. Nelson, Bennett, & Leibert, (1997) describe the use of an algorithm for calculating indirect connections. By use of this algorithm, it is possible to quantify the strength of direct and indirect associations.

Associative and categorical relationships. In contrast with association, though category norms exist, no adequate way of measuring the strength of categorical relationships has been established to date. Specifically, category norms do provide high and low dominance exemplars based on the typicality of an item within a category, but the categories differ to a great degree between category norm studies. For example, both Rosch (1975) and Battig and Montague (1969) used "fruit" as one category, whereas Shapiro and Palermo (1970) used "citrus fruit" as a category. This inconsistency between category norms interferes with use of more than one category normative set. Moreover, category sizes vary substantially, ranging from four members to greater than sixty, further complicating the issue of finding pairs with equivalent categorical relationships.

In one study, Koivisto and Laine (1995) classified words as sharing a categorical relationship (which they refer to as coordinate) if the words come from the same semantic category. Additionally, they classify words as sharing a locative relationship if the words frequently occur within the same context. Finally, within each category (i.e., coordinate and locative), they specify how words can share an associative relationship, thus, the degree to which they co-occur in speech. This latter associative relationship is based on subject ratings. They hypothesize that the right hemisphere preferentially processes words that share a locative relationship. This word pair type they describe as being interconceptual pairs as they have no properties in common and instead are linked by world knowledge or unity within scenes or events. For example coffin - grave share context, but Koivisto and Laine propose that they do not share other features or properties. In contrast, they theorize that the left hemisphere preferentially processes word pairs that share a categorical relationship. This word pair type they describe as being intraconceptual pairs as the word pairs are linked by a similarity of properties or internal logical analysis. For example bus - train share both a categorical relationship and share many properties or features in common (i.e., shape, speed, etc.). Taken in a broad sense, this classification system is consistent with the preference for visuospatial processing in the right hemisphere, but is not consistent with the idea that the right hemisphere activities a larger network of meanings, a conclusion drawn from patient-language studies.

Chiarello et al. (1992) classifies word relationships into "similar only," word pairs that share a categorical relationship but are not considered to share an associative

relationship (i.e., do not co-occur in speech), "associative only," word pairs that share only an associative relationship, (i.e., do co-occur in speech), and "similar and associated," word pairs that share category membership and frequently co-occur in speech. Theoretically, Chiarello posits that the right hemisphere's advantage emerges when word pairs share category membership but only share few features. The left hemisphere, on the other hand, is speculated to show greater activation with word pairs that share more features in common. For example, she posits that activation will be maintained longer in the left hemisphere with prime-target pairs sharing a greater number of semantic features (e.g., doctor-nurse share such features as working in a hospital, wearing white uniform, providing medical treatment) than for those sharing few semantic features (e.g., lawyer-nurse who have less in common). In contrast, the right hemisphere uses less selective methods, allowing priming between items with little feature overlap. This model is consistent with the activation of larger meanings based on brain-damaged patient studies mentioned earlier.

The classification system by Chiarello is similar to Koivisto's locative/coordinate classification system with regard to the categorically related word pairs, though Chiarello separates the weakly associated from the strongly associated to form the "similar only" word pairs. Moreover, Chiarello's hypothesis is similar to Koivisto's in that they both postulate that the left hemisphere is more efficient in processing word pairs that share features or properties. Where the two differ is their belief in the degree and type of feature or properties linking the word pairs that allows for greater spread of activation in the right hemisphere. Specifically, Chiarello proposes that the word pairs share only few

features or properties inherent in the category membership while Koivisto suggests that the word pairs do not share properties or features, but are linked instead by "world knowledge" or "unity of scenes and events." One might argue that this linkage proposed by Koivisto is a type of feature or property, thereby allowing for a similarity between the two hypotheses.

Feature overlap. Feature overlap, however, as with other methods used to estimate strength of relationship, has not been well defined. Moreover, feature overlap, when investigated further, may actually reflect indirect associative relationships, such as the number of mediators and/or overlaping words between the prime-target pair.

McRae and Boisvert (1998) also propose that priming with weakly associated prime-target pairs is the result of featural overlap between the words. For example, they site McRae, de Sa, and Seidenberg's (1997) study as support for priming based on featural overlap. In this study, the researchers collected semantic feature norms for 190 object concepts and used them to construct semantic representations in terms of individual features and correlated feature pairs. Individual features included perceptual, functional, contextual, in addition to co-occurance (e.g., what a shirt is typically worn with). Correlated features are individual features shared by members in the same basic-level concept. For example, "has fur" and "has whiskers" are significantly correlated because living things like dogs and lions that have fur also tend to have whiskers. Through regression analysis, they found that individual features predicted priming for non living things and correlated features predicted priming effects for living things. Thus,

greater priming was found if non living things shared individual features (e.g., found in bedrooms) whereas greater priming was found if living things shared correlated features (e.g., has feathers). Based on these results, they concluded the featural representations are accessed in the initial detection of word meaning and therefore account for priming effects found with categorically related words in past priming studies. However, the possibility of priming through associative mediators and overlaps is not addressed. McRae and Boisvert do point out the variety of feature types and need for further delineation in terms of type of feature. Thus, to further pursue feature overlap as a method of measuring relationship strength, it will be necessary to specify what features are relevant and specifically how feature overlap is measured.

Janczura and Nelson addressed this issue more recently (1999). They began by discounting the featural hypothesis with two main arguments; first, the vagueness of what can be counted as a feature, and second, the inability of featural representations to account for the variability in typicality effects. As mentioned earlier, typicality relates to the degree that a category member is more or less representative of a category. The problem is that typicality ratings are greatly affected by both previous and recent learning. In fact, by manipulating the frequency a category name/category-exemplar pair was presented, they were able to influence judgements of category-exemplars as more or less typical of a category. Thus, category typicality is influenced by many variables and is not solely due to featural commonalties.

The question of how to define categorical relatedness remains. One method involves determination of the featural aspects of category members. This is based on the

belief that members of a given category share common features (e.g., flowers have petals, stems, etc.). Thus, the presentation of one category member (e.g., tulip) may be more or less likely to spread activation along similar features to another category member (e.g., daisy). Yet if typicality ratings can be influenced, featural representations cannot solely account for categorical relatedness. However, our representations of category members and strength of association between category members fluctuates over time. This fluctuation also prohibits reliance on typicality as a method of determining strength of categorical relatedness.

Therefore, several researchers have viewed frequency of feature overlap as a way of classifying relatedness. However, the lack of adequate methods to measure degree of feature overlap and the inconsistencies in the featural overlap literature interfere with it's use at this time. Morever, it may come to pass that featural overlap instead reflects a degree of association, rather than being a novel concept. Therefore, association, for which published norms exist, provides a more reliable form of relatedness measurement at this time.

Direction of association. In an earlier study, Koivisto (1998) looked at word pairs sharing either a forward or backward association. In the forward association pairs, the target was associated with the prime but the prime was not necessarily associated with the target (e.g, beaver - tail). Backward association pairs were comprised of word pairs in which the prime was associated with the target, but the target was not necessarily associated with the prime (e.g., tail - beaver). The results indicated that a forward

priming advantage occurred in the left hemisphere while a backward priming advantage occurred only in the right hemisphere. Interestingly, Koivisto concluded that the backward priming was the result of post-lexical semantic integration in the right hemisphere while Chiarello (2000) concluded that the backward priming was an indication of the right hemisphere's activation of weaker semantic relationships. Thus, it is unclear as to whether the right hemisphere advantage with this word pair type is due to the strength of association or the direction of association.

Stimulus characteristics. An additional problem within the relatedness issue has been the poor control of related variables such as prime and target set size (i.e., the number of forward, backward, overlaps, and mediators associated with the word), connectivity, frequency, and number of overlaps and mediators, in addition to forward, backward, mediator and overlap strength within the priming research. It is well known that many of these features affect memory performance, such as concreteness (Nelson & Schreiber, 1992), printed frequency (Nelson & Xu, 1995), and set size (Nelson, Bennett, & Leibert, 1997). Additionally, the hemisphere's differ in their ability to process word pair types with varying degrees of concreteness (Chiarello, Senehi, & Nuding, 1987; Deloche, 1987) and word length (Young & Ellis; Ellis, Young, & Anderson, 1988). Yet often these variables are not held constant. For example, when these variables were analyzed, Koivisto's locative targets had a significantly greater frequency of occurrence in printed text than the coordinate targets ($t = -2.53$, $p = .015$; locative $M = 102.64$ and

coordinate M = 45.32). Thus, future control of these related variables will allow for more consistency of results.

Task Type

One additional variable influencing the inconsistencies within the priming literature is the type of task employed. Several different task types have been utilized including pronunciation, lexical decision, judgements (i.e., are they related in meaning?), generation of associates, and even implicit and explicit memory tasks. One major drawback of the majority of these tasks is the instability of the dependent variables analyzed in these paradigms (i.e., accuracy and reaction time). For example, Walker and Ceci (1985) found equivalent priming in the right and left hemispheres using reaction time, yet found hemispheric differences in the accuracy data. In contrast, many other researchers have found reaction time to be a more sensitive measure of hemispheric differences than accuracy (Audet, Burgess and Driessen, 1999; Koivisto, 1998, 1999; Chiarello, 1992; Chiarello and Richards, 1992). There is a fine balance between accuracy and reaction time such that if accuracies are too high (95% and above), the lack of variability interferes with detection of condition differences. Thus, reaction time becomes a more sensitive dependent variable. However, if accuracies are too low (less than 80%), reaction time is compromised and is a less reliable dependent measure.

Another major weakness inherent in the lexical decision task is the use of neutral trials. Typically, priming is defined as the difference in reaction time or accuracy between the unrelated or neutral trials and the related trials. However, to date there is

much controversy in the use of neutral trials, as the definition of what constitutes a "neutral" prime remains unclear. Some researchers have used "BLANK" as the neutral prime, yet this word has semantic meaning, so it could actually be considered a type of unrelated trial. Others have used a series of symbols, such as "XXXXX" or "******," yet even this choice remains controversial given the possible effects on the subjects decision making process (De Groot, Thomassen, & Hudson, 1982). Specifically, subjects may discount or cease attending to the prime with this type of neutral prime as it provides no assistance with the task at hand. In doing so, they may also fail to attend to the primes of interest (i.e., unrelated and related primes). One solution to this difficulty is to exclude neutral trials. However, by doing so, it eliminates the possibility of detecting inhibition (i.e., when reaction time or accuracy worsens with unrelated trials as compared with neutral trials).

Though the pronunciation and lexical decision are more commonly used, it is presumed that use of other methodologies may provide more meaningful results, particularly given the inconsistencies found within pronunciation and lexical decision studies. Therefore, because of the difficulties inherent in the more commonly used methodologies (e.g., pronunciation, lexical decision, judgement), use of a priming task that is not reliant upon reaction time and/or accuracy is indicated.

Koivisto and Laine (1995) employed implicit and explicit memory tasks instead of pronunciation or lexical decision. As mentioned earlier, they displayed word pairs that were related either categorically and associatively or pairs that were related only by association. They then presented the first word of the study pairs and non studied pairs

laterally and asked the subject to generate either the first word that came to their mind (i.e. implicit task) or to respond with the second word from the studied pair (i.e., explicit task). They defined priming as the difference between the probability of producing an unstudied word (i.e., similar to the unrelated or neutral condition) and the probability of producing the studied word (i.e., similar to the related condition). Though no hemispheric differences were detected on the explicit task, a right hemisphere advantage was seen with the associatively but not categorically related word pairs in the implicit task.

It is well known that information acquired during a specific learning session can facilitate subsequent processing of that same information without making explicit reference to the study period. This facilitation, also called repetition priming, occurs automatically and does not require deliberate recollection of the prior learning episode. This type of priming is reflected in the implicit memory task and is dependent upon the automatic activation of preexisting memory representations, such as familiar words. Moreover, it has been argued that this activation occurs independently of the type of processing performed by the individual during the study task (Schacter, 1987). Thus, implicit memory allows for examination of automatic processing of stimuli, hypothetically the same processes tapped by the lexical decision and pronunciation studies.

One drawback of this type of study in hemispheric studies is the issue of both hemisphere's having access to the information during the study period. However, during the test phase, when automatic processes are activated, only one hemisphere is

predominately exposed to the material. Thus, this lateralized free association phase allows for access of the semantic organization of each hemisphere independently. Moreover, hemispheric differences have been detected in the past with use of this paradigm (Koivisto and Laine, 1995).

Predominant Hypotheses

Within both the patient and nonpatient literature, studies show that the right hemisphere appears to preferentially process context and multiple meanings, in addition to providing organization and maintenance of relevant speech during conversations and in other behaviors. In order to perform these functions, it has been proposed that the right hemisphere activates a broader field of meanings and related nodes during processing than does the left hemisphere. This pattern of activation would translate within the priming paradigm into greater priming with word pairs that are not as closely related. However, as mentioned earlier, this has not always been the case in the priming literature. One reason for this inconsistency may be limitations of the dependent variables analyzed in these studies. Another contributing factor may be the way in which word relationships have been defined.

As mentioned earlier, Koivisto and Laine (1995) classify words as either sharing a categorical relationship (which they refer to as coordinate), or as sharing a locative relationship (i.e., if the words frequently occur within the same context). Though they attempted to control for association, strength of association was based on subject ratings by a small group of individuals who did not participate in the study (n = 18) and not by

published association norms. They hypothesize that the right hemisphere preferentially processes words that share a locative relationship. In contrast, they postulate that left hemisphere preferentially processes word pairs that share a categorical relationship.

Chiarello et al. (1992) classifies word relationships into word pairs that share a categorical relationship but are not believed to share an associative relationship, word pairs that share only an associative relationship, and word pairs that share category membership and frequently co-occur in speech. Theoretically, Chiarello maintains that the right hemisphere preferentially processes word pairs sharing few features while the left hemisphere preferentially processes words sharing many features. This hypothesis is similar to Koivisto's in that they both conclude that the left hemisphere is more efficient in processing word pairs that share features or properties. Where the two differ is their belief in the degree and type of feature or properties linking the word pairs that allows for greater spread of activation in the right hemisphere.

The problem with this classification system is that the concept of feature overlap remains poorly defined and unoperationalized. As mentioned earlier, feature overlap, may with future research, be shown to be a reflection of association as opposed to being a distinct type of relatedness. Thus, association remains a better definition of relatedness because there is a well developed normative base and consensus of agreement regarding the definition of association. There are different directions of association. As mentioned earlier, Koivisto (1998) found a left hemisphere priming advantage with word pairs sharing only a forward association while a right hemisphere advantage has been found with word pairs sharing a backward association. They concluded that this advantage

occurred as the result of post-lexical processing rather than an advantage with this word pair type. Because she posits that the right hemisphere activates a larger array of meanings, Chiarello (2000) concluded that the advantage occurred as a result of the right hemisphere's advantage with weakly related word pairs. Thus, it is unclear as to whether the right hemisphere advantage with this word pair type is due to the *strength* of association or the *direction* of associative relationship.

Purpose and Rationale

Work with brain-damaged patients, split-brain patients, and neurologically intact individuals has pointed toward right hemispheric involvement in comprehension of single word meanings. However, it remains unclear as to the type of information preferentially processed by the right hemisphere. Moreover, use of a variety of priming task types has failed to clarify this issue. Problems with past research include failure to use a purely automatic or controlled paradigm, poor definition of word pair relationship, poor control of other related variables (i.e., prime and target set size, frequency, connectivity, etc.), and employment of tasks that use reaction time and accuracy as dependent variables.

The first goal of this study was to examine hemispheric priming using a different kind of priming task; an implicit free association paradigm was employed. Though the time course of this spread of activation has been under debate (Koivisto, 1998), based on the studies of this nature, it appears that the right hemisphere activation is dependent upon some degree of controlled processing. Thus, deliberate processing of the information at some point may be necessary for the right hemisphere advantage to occur.

By using an implicit memory paradigm, the subjects consciously processed the word pairs during the initial presentation period, then the free association phase allowed for access of semantic organization of each hemisphere independently.

The second goal of the study was to examine hemispheric priming with different word pair types in order to delineate which relationships are preferentially processed by the right hemisphere. As mentioned earlier, it is unclear as to the strength and direction of relationship necessary for the right hemisphere advantage to occur. Given the problems with feature overlap described in detail above, strength and direction of associative relationship was manipulated. Thus, word pairs sharing (1) forward - only association, (2) backward - only association, or (3) forward and backward association were included. Half of each word pair group shared a weak associative relationship and half shared a strong associative relationship based on the normative probability of the prime predicting the target (Nelson, McEvoy, & Schreiber,1999). Prime and target set size, connectivity, and frequency, imageability, number of overlaps and mediators, in addition to mediator and overlap strength were held constant. Varying both the direction and the strength of the association made it possible to determine if the right hemisphere advantage occurs only with weak association, regardless of direction of association, or if the right hemisphere advantage occurs instead as a result of the direction of association, not strength of association.

To meet these goals, the methodology used by Koivisto and Laine (1995) was employed, including central presentation of word pairs during a study period, followed by an implicit memory task in which subjects were asked to generate the first word that

comes to mind when presented with new and old laterally presented primes. An explicit memory phase was added to Koiviso's methodology to address possible problems with subject's questioning about the fact that they were not asked to recall the word pairs, though they were told that they would be prior to the study phase of the experiment.

Hypotheses and Predictions

Based on a review of the priming literature, the right hemisphere advantage appears to be dependent upon the presence of some degree of associative relationship between the word pairs. It has been proposed that the right hemisphere activates a larger array of meanings than the left hemisphere. Thus, it is suggested that the right hemisphere advantage would be detected with word pairs sharing a weak associative relationship. Though forward priming has been found in the left hemisphere with backward priming in the right, it remains to be seen if this varies by strength of association. Thus, this hypothesis predicts a right hemisphere advantage in all three weak association conditions (i.e., forward, backward, and both). Additionally, since backward association is presumed to be a type of weak association, the right hemisphere advantage will also occur in the strong backward association condition in addition to the three weak conditions mentioned above. In contrast, if the hemisphere advantage only occurs with the direction of association, the right hemisphere advantage will occur in both the strong and weak backward association conditions only. Thus, the two hypotheses differ in their predictions in the left and both association conditions (See Table 1). Specifically, while the strength of association hypothesis predicts a right hemisphere advantage with in the

weak conditions in both the forward and both conditions, the direction of association hypothesis does not predict a right hemisphere advantage in these conditions.

Table 1

Direction and Strength of Association Hypotheses

	Forward		Backward		Both	
Association	Weak	Strong	Weak	Strong	Weak	Strong
Direction	*No**	No	Yes	Yes	*No*	No
Strength	*Yes*	No	Yes	Yes	*Yes*	No

* RH Advantage predicted

Methods

Participants

One hundred and eighty-six participants (141 females, 45 males) were recruited from the undergraduate subject pool at the University of South Florida to participate in this study. All showed right-handed dominance as evidenced by a score of at least 9 points on the Briggs and Nebes (1975) Handedness Questionnaire (range 9-24, M = 20.18, SD = 3.92), and no familial sinistrality. All participants were native English speakers between the ages of 18 and 52 (M = 21.56, SD = 4.71), with normal or corrected to normal vision. Participation was voluntary and students received extra credit points towards final course grades in return for participation in the experiment.

Stimuli

Critical stimuli consisted of 120 associatively related word pairs determined by association norms (Nelson, et al., 1999). Forty word pairs shared only a forward connection, 40 shared only a backward connection, and 40 shared both a forward and backward connection. Words sharing a forward only association were comprised of prime - target pairs in which the target is produced in response to the prime in a word association task. In contrast, word pairs sharing a backward only association were comprised of pairs in which the target is *not* produced in response to the prime, yet the

prime is produced in response to the presentation of the target during a word association task. Finally, word pairs sharing both a forward and backward association in this study share equal likely hood of being produced on a word association task. Half of each association group shared a strong associative relationship (i.e., mean normative probability of the prime producing the target of .30) (see Nelson, Bennett, & Leibert, 1997 for explanation of this algorithm) and half of each group shared a weak associative relationship (i.e., mean normative probability of the prime producing the target of .08). For word pairs sharing both forward and backward association, the combined probabilities of the prime producing the target and the target producing the prime totaled either .30 in the strong condition or .08 in the weak condition. Prime and target set size were held constant across all conditions (Prime M = 15.53, SD = 4.34; Target M = 14.94, SD = 4.46). Additionally, stimuli were relatively concrete (Prime M = 4.71, SD = 1.24; Target M = 4.89, SD = 1.20), moderately frequent (Prime M = 82.28, SD = 80.70; Target M = 86.01, SD = 79.67), and moderately interconnected (Prime M = 1.57, SD = 0.63; Target M = 1.47, SD = 0.61). Indirect relationships were also held constant (overlap M = 0.025, SD = 0.02; mediator M = 0.011, SD = 0.02; indirect total M = 0.023, SD = 0.03), as was the length of both the primes and the targets (Prime M = 4.75, SD = 0.95; Target M = 4.69, SD = 1.00). Stimuli are presented in Appendix B.

Design and Procedure

Factors in this study included one within subjects factor: Visual Field (right, left) and three between-subject factors: Gender (Male, Female), Direction of Associative

Relationship (forward, backward, and forward-backward), and Strength of Associative Relationship (weak, strong). Stimuli were presented to participants on a Dell computer using the SuperLab software. After completing a consent form and a handedness questionnaire, participants were seated approximately 45 centimeters from the screen with head placed in chin rest to maintain central presentation at this distance. Verbal and written directions were included to assure that participants comprehended task instructions. At the beginning of the study phase, participants were told that they would be shown word pairs and that their memory for these pairs will be tested later. The study phase began with a 500 millisecond second warning tone. Each of the twenty word pairs were then presented centrally for three thousand milliseconds with an interval of 150 milliseconds between pairs. The implicit memory phase immediately followed the study phase, beginning with 16 practice trials. Each implicit memory trial began with a 500 millisecond second warning tone that was followed by a centrally fixation cross which remained on the screen throughout the trial. One test word was then presented for 200 milliseconds in either the left or right visual field 2° eccentric from the center of the screen. For the first eight trials, the participant was asked to simply name the word. In the remaining practice trials, the participant was then asked to produce the first word that comes to his or her mind. The examiner paced the practice and test items and pressed a key to proceed to the next item. During the practice and test phases, participants were also told to maintain their focus on the cross positioned in the center of the screen and the importance of not looking to the right or left was emphasized. Eye movement was monitored by the examiner through videocamera focused on the participant's face during

the session using a Sony Handycam Video Camera Recorder 8, model CCD-F70, a technique recommended by McKeever (1986). When an eye movement was detected by the examiner during the trial, a notation was made of this movement.

Following the practice trials, the test portion of the implicit memory phase began with three filler primes that were not analyzed but will be included to allow the subject to adjust to the test situation. None of the practice or filler primes appeared in the critical group. Immediately after the filler words, 40 words were presented (20 primes from the word pairs presented during the memory phase and 20 primes from the nonstudied pairs). For each direction of associative relationship (i.e., forward, backward or both forward and backward), strength of association was varied (strong or weak), resulting in six different relatedness conditions. Each participant viewed only one of the six relatedness types due to time and memory constraints. Therefore, Strength and Direction were between subject conditions. In order to balance lists by studied/unstudied presentation, two versions of each word pair type was created. Specifically, for each relatedness type (e.g., forward-strong), half of the 40-word pairs was seen in the studied condition in one list and half was seen in the unstudied presentation in a second list. Participants were randomly assigned to receive one of the twelve lists (see Table 2).

The explicit memory phase followed the implicit memory phase. Stimuli presentation was identical to the implicit memory phase in that each trial began with a 500 millisecond second warning tone that was followed by a centrally fixation cross that remained on the screen throughout the trial. Primes from the study pairs were then presented for 200 milliseconds one at a time in either the left or right visual field 2°

eccentric from the center of the screen. The participant was asked to say the word that went with it from the memory pairs that they were asked to remember at the start of the experiment. The examiner again paced the test items by pressing a key to proceed to the next item. Additionally, participants were reminded to maintain their focus on the cross positioned in the center of the screen and the importance of not looking to the right or left was emphasized.

Table 2

Diagram of List Versions by Direction and Strength of Association

	Direction of Association		
Strength of Association	Forward	Backward	Forward & Backward
Weak	Lists 1 & 2	Lists 5 & 6	Lists 9 & 10
Strong	Lists 3 & 4	Lists 7 & 8	Lists 11& 12

Results

Of the 186 participants, one subject was removed due to misunderstanding of the task that was revealed at experiment completion. An additional subject was removed due to an administration error of the examiner. Of the remaining 184 subjects, descriptive statistics were calculated for each of the twelve conditions (i.e., Visual Field (2) x Strength (2) x Direction (3)). Ten subjects were discarded due to at least one recall cell $\pm$ 2 standard deviations from the total participant cell mean, leaving a total of 174 subjects (134 females and 42 males) included in the final target recovery analysis.

Eye Movements Included

In this study, data were analyzed including and excluding trials in which the participant's eyes moved. Eye movement trials are typically removed to insure that the stimuli was presented initially to one hemisphere only. If the subject fails to keep his or her eyes on the fixation mark throughout the trial, it is unclear if the stimuli appeared solely in his or her visual field. In this experiment, only one word was presented during each trial and the presentation time was only 200 milliseconds, shorter than the time necessary for an individual to move his or her eyes to a new location. Thus, if the subject's eyes did move when the stimuli initially appeared, the stimuli would have disappeared by the time that the eyes had focused upon the area. Consequently, including

the eye movement trials should not have greatly affected the validity of the visual field presentation.

Priming Analysis

Using the probability of producing the target word (i.e., the second word of the word pair) without having seen the word pair during the study phase as the baseline probability and the probability of producing the target word after having seen the word pair during the study phase as the priming probability, priming was calculated by subtracting the baseline probability from the priming probability.

A Mixed design ANOVA analysis was conducted with priming as the dependent variable. This analysis included one within subjects factor: Visual Field (right, left) and three between-subject factors: Gender (Male, Female), Direction of Associative Relationship (forward, backward, and forward-backward), and Strength of Associative Relationship (weak, strong). ANOVA summary table is presented in Appendix E.

Analysis of priming data did not reveal a main effect of gender, nor did gender interact with any other variable, thus the following analysis was calculated without gender. Mean probabilities of target recovery as a function of word pair association, hemisphere and prior study are presented in Table 3. The main effect of Visual Field approached significance ($F(1,168) = 2.80$, $p = .096$). The left hemisphere advantage was observed such that overall, priming probability scores were higher in the left hemisphere (LH) ($M = 0.28$, $SD = .02$) than in the right hemisphere (RH) ($M = 0.25$, $SD = .02$) (Figure 3). Main effects of both Strength ($F(1,168) = 11.33$, $p = .001$) and Direction (F

(2,168) = 8.35, p <.0001) were found. Specifically, priming probability was greater when primes and targets shared a strong relationship (M = 0.30, SD = .02) than when word pairs shared a weak relationship (M = .02, SD = .02) (Figure 4). Use of Fisher's Least Significant Difference (LSD) revealed that priming probability was greater when the association between the prime - target pairs was forward and backward (M = 0.31, SD = .02) or forward only direction (M = 0.29, SD = .02) than when the association between the prime - target pairs was in the backward direction (M = 0.19, SD = .02) (Figure 5). The interaction between Strength and Direction was also significant (F (2,168) = 3.25, p = .041). LSD testing revealed priming probability was greatest when words shared a strong forward - backward association (M = 0.39, SD = .03) or a strong forward association (M =0.33, SD = .03), and was least when words shared a weak forward (M = 0.25, SD = .03), a weak forward - backward (M = 0.23, SD = .03), a strong backward (M = 0.19, SD = .03) or a weak backward relationship (M = 0.19, SD = .03) (Figure 6). Neither the interaction between Visual Field and Strength or the interaction of interest, (i.e., Visual Field x Strength x Direction) were significant.

Table 3

Priming as a Function of Word Pair Association, Hemisphere and Prior Study

	Forward Only		Forward Only		Backward Only		Backward Only		Forward & Backward		Forward & Backward	
	Strong		Weak		Strong		Weak		Strong		Weak	
	LH	RH	LH	RH	LH	RH	LH	RH	LH	RH	LH	RH
Studied	.60	.46	.28	.30	.23	.19	.19	.19	.51	.46	.29	.22
Non-Studied	.25	.15	.06	.03	.02	.01	.00	.07	.08	.10	.03	.03
Priming	.35	.31	.22	.27	.21	.18	.19	.18	.43	.35	.26	.20

Implicit Studied Pair Analysis

A Mixed design ANOVA analysis was conducted on the number of target words produced in the implicit memory phase. Thus, number correct responses (i.e., number of target words from the studied prime-target pairs) served as the dependent measure. This analysis included one within subjects factor: Visual Field (right, left) and three between-subject factors: Gender (Male, Female), Direction of Associative Relationship (forward, backward, and forward-backward), and Strength of Associative Relationship (weak, strong). ANOVA summary table is presented in Appendix E.

Analysis of target recovery data did not reveal a main effect of gender, nor did gender interact with any other variable, thus the following analysis was calculated without gender. See Table 3 for mean probabilities of target recovery as a function of word pair association, hemisphere and prior study. The main effect of Visual Field was significant ($F(1,168) = 8.60$, $p = .004$). A left hemisphere advantage was observed such that overall, studied target words were produced most often in response to studied primes presented to

the right visual field (LH) (M = .35, SD = .015) than to primes presented to the left visual field (RH) (M = .30, SD = .015). Main effects of both Strength (F (1,168) = 41.18, p < .0001) and Direction (F (2,168) = 25.91, p < .0001) were also found. Specifically, studied target words were produced most often in response to studied primes when primes and targets shared a strong relationship (M = .41, SD = .02) than when word pairs shared a weak relationship (M = .26, SD = .02). Additionally, LSD testing revealed that studied target words were produced most often in response to studied primes when the association between the prime - target pairs was in the forward direction (M = .41, SD = .02) than when the association between the prime - target pairs was in the backward direction (M = .20, SD = .02). Interestingly, target words from prime - target pairs sharing a forward and backward relationship (M = .37, SD = .02) were produced more than those sharing a backward relationship, but did not differ significantly from those sharing a forward connection.

The interaction between Strength and Direction was significant (F (2,168) = 7.88, p = .001) such that target recovery was greatest when words shared a strong forward association (M =.53, SD = .03) or a strong forward - backward association (M = .48, SD = .03), and was least when words shared a weak forward (M = .29, SD = .03), a weak forward - backward (M = .25, SD = .03), a strong backward (M = .21, SD = .03) or a weak backward relationship (M = .19, SD = .03). The interaction between Visual Field and Strength was also significant (F (1,168) = 4.36, p = .04). LSD testing revealed that number of studied targets did not differ with primes presented in the right or left visual field for word pairs sharing a weak relationship (LH M = .25, SD = .21; RH M = .23, SD

= .21). Yet when word pairs shared a strong associative relationship, studied targets were produced most often to primes presented in the right visual field (LH) (M = .45, SD = .02) than to primes presented in the left visual field (RH) (M = .36, SD = .02).

The interaction of interest, (i.e., Visual Field x Strength x Direction) indicated a trend toward significance (F (2,168) = 2.82, p = .06). LSD testing showed that targets were produced more often to primes presented in the right visual field (LH) than in the left visual field (RH) when studied pairs shared a strong forward relationship (LH M = .60, SD = .04; RH M = .46, SD = .04). However, no other visual field comparisons were significant. The only condition in which the mean of the RH trials exceeded the mean of the LH trials was with the word pairs sharing a weak forward association (RH M = .30, SD = .03; LH M = .28, SD = .04), though this difference was not statistically significant (p = .599).

Implicit Unstudied Pair Analysis

A Mixed design ANOVA analysis was conducted on the number of target words produced in response to the unstudied primes during the implicit memory phase. Thus, number correct responses (i.e., number of target words from the unstudied prime-target pairs) served as the dependent measure. This analysis included one within subjects factor: Visual Field (right, left) and three between-subject factors: Gender (Male, Female), Direction of Associative Relationship (forward, backward, and forward-backward), and Strength of Associative Relationship (weak, strong). ANOVA summary table is presented in Appendix E.

Analysis of target recovery data for the unstudied targets did not reveal a main effect of gender, nor did gender interact with any other variable, thus the following analysis was calculated without gender. Mean probabilities of target recovery as a function of word pair association, hemisphere and prior study are presented in Table 3. The main effect of Visual Field was significant ($F(1,168) = 4.651$ $p = .032$). A left hemisphere advantage was observed such that overall, the probability of producing target words was greatest in response to unstudied primes presented to the right visual field (LH) ($M = .07$, $SD = .01$) than to unstudied primes presented to the left visual field (RH) ($M = .06$, $SD = .01$). Main effects of both Strength ($F(1,168) = 66.89$, $p < .0001$) and Direction ($F(2,168) = 49.03$, $p < .0001$) were also found. Specifically, the probability of producing unstudied target words in response to unstudied primes was greater when primes and targets shared a strong relationship ($M = .10$, $SD = .01$) than when word pairs shared a weak relationship ($M = .03$, $SD = .01$). Additionally, the probability of producing unstudied target words in response to unstudied primes was greatest when the association between the prime - target pairs was in the forward direction ($M = .13$, $SD = .01$) than when the association between the prime - target pairs was in the backward direction ($M = .01$, $SD = .01$). Target words from prime - target pairs sharing a forward and backward relationship ($M = .06$, $SD = .01$) were produced more than those sharing a backward relationship, and less often than those sharing a forward connection.

The interaction between Strength and Direction was significant ($F(2,168) = 19.55$, $p = .001$) such that target recovery to be greatest when words shared a strong forward association ($M = .20$, $SD = .01$) or a strong forward - backward association ($M =$

.09, SD = .01), and was least when words shared a weak forward (M = .05, SD = .01), a weak forward - backward (M = .03, SD = .01), a strong backward (M = .02, SD = .01) or a weak backward relationship (M = .03, SD = .01). Interestingly, the interaction between Visual Field and Direction was also significant (F (2,168) = 8.23, $p < .0001$. LSD testing revealed that number of studied targets did not differ with primes presented in the right or left visual field for word pairs sharing a backward relationship (LH M = .01, SD = .01; RH M = .01, SD = .01) or a forward and backward relationship (LH M = .05, SD = .01; RH M = .07, SD = .01). Yet when word pairs shared a forward associative relationship, studied targets were produced most often to primes presented in the right visual field (LH) (M = .16, SD = .01) than to primes presented in the left visual field (RH) (M = .09, SD = .01).

The interaction of interest, (i.e., Visual Field x Strength x Direction) was not significant.

Explicit Studied Pair Analysis

A Mixed design ANOVA analysis was conducted using the number of target words produced in the explicit memory phase as the dependent measure. As with the implicit analysis, this analysis included one within subjects factor: Visual Field (right, left) and three between-subject factors: Gender (Male, Female), Direction of Associative Relationship (forward, backward, and forward-backward), and Strength of Associative Relationship (weak, strong). ANOVA summary table is presented in Appendix E.

Analysis of target recovery data did not reveal a main effect of gender, nor did gender interact with any other variable, thus the following analysis was calculated without the variable gender. The main effect of Visual Field was significant ($F(1,168) = 5.20$, $p = .024$). Consistent with the implicit results, a left hemisphere advantage was again observed such that overall, studied target words were produced most often in response to studied primes presented to the right visual field (LH) ($M = .492$, $SD = .015$) than to primes presented to the left visual field (RH) ($M = .454$, $SD = .015$). Main effects of both Strength ($F(1,168) = 57.20$, $p < .0001$) and Direction ($F(2,168) = 21.39$, $p < .0001$) were also found. Specifically, studied target words were produced most often in response to studied primes when primes and targets shared a strong relationship ($M = .567$, $SD = .018$) than when word pairs shared a weak relationship ($M = .379$, $SD = .018$). Additionally, studied target words were produced most often in response to studied primes when the association between the prime - target pairs was in the forward direction ($M = .551$, $SD = .022$) when the association between the prime - target pairs was in the backward direction ($M = .360$, $SD = .022$). As with the implicit analysis, target words from prime - target pairs sharing a forward and backward relationship ($M = .507$, $SD = .022$) were produced more than those sharing a backward relationship, but did not differ significantly from those sharing a forward connection.

The interaction between Strength and Direction was again significant ($F(2,168) = 14.49$, $p < .0001$) such that target recovery to be greatest when word pairs shared a strong forward association ($M = .657$, $SD = .031$) or a strong forward - backward association ($M = .677$, $SD = .030$), and was least when words shared a weak forward - backward (M

= .337, *SD* = .032), a strong backward (*M* = .367, *SD* = .031) or a weak backward relationship (*M* = .353, *SD* = .031). Target recovery was moderate when words shared a weak forward association (*M* = .445, *SD* = .030). The interaction between Visual Field and Strength was not significant, nor was the interaction of interest, (i.e., Visual Field x Strength x Direction).

Eye Movements Removed

Priming Analysis

Priming analysis with eye movements deleted again revealed main effects of Visual Field ($F(1,168) = 7.18$, $p=.008$), Strength ($F(1,168) = 9.76$, $p=.002$) and Direction ($F(2,168) = 8.92$, $p<.0001$), and an interaction between Strength and Direction ($F(2,168) = 3.35$, $p=.037$). No other significant effects were found. ANOVA summary table is presented in Appendix E.

Implicit Studied Pair Analysis

Analysis of the implicit trials again revealed a main effect of Visual Field ($F(1,168) = 17.48$, $p<.0001$), such that participants produced studied targets to primes presented in the right visual field (LH) more often than to the left visual field (RH). Also consistent with the analysis when eye movements were included were the main effects of Strength ($F(1,168) = 25.25$, $p<.0001$) and Direction ($F(2,168) = 15.98$, $p<.0001$), and the interaction between Strength and Direction ($F(2,168) = 4.97$, $p=.008$). No other significant effects were found. ANOVA summary table is presented in Appendix E.

Implicit Unstudied Pair Analysis

Analysis of the number of target words from the unstudied prime-target pairs on the implicit trials again revealed a main effect trend of Visual Field ($F(1,168) = 3.316$, $p = .070$), such that participants produced unstudied targets to primes presented in the right visual field (LH) more often than to the left visual field (RH). Also consistent with the analysis when eye movements were included were the main effects of Strength ($F(1,168) = 47.637$, $p < .0001$) and Direction ($F(2,168) = 30.689$, $p < .0001$), and the interaction between Strength and Direction ($F(2,168) = 11.246$, $p < .0001$). The interaction between Visual Field and Direction was also significant ($F(2,168) = 5.938$, $p = .003$ such that when word pairs shared a forward associative relationship, studied targets were produced most often to primes presented in the right visual field (LH) ($M = .12$, $SD = .01$) than to primes presented in the left visual field (RH) ($M = .07$, $SD = .01$). The interaction of interest, (i.e., Visual Field x Strength x Direction) indicated was significant ($F(2,168) = 4.216$, $p = .02$). LSD testing showed that targets were produced more often to primes presented in the right visual field (LH) than in the left visual field (RH) when studied pairs shared a strong forward relationship (LH $M = .21$, $SD = .02$; RH $M = .11$, $SD = .01$). However, no other visual field comparisons were significant. No other significant effects were found. ANOVA summary table is presented in Appendix E.

Explicit Studied Pair Analysis

Analysis of the explicit trials with eye movements deleted revealed a Visual Field trend ($F(1,168) = 3.71$, $p = .056$), main effects of Strength ($F(1,168) = 23.00$, $p < .0001$)

and Direction ($F(2,168) = 7.05$, $p = .001$), and an interaction between Strength and Direction ($F(2,168) = 6.89$, $p = .001$). No other significant effects were found. ANOVA summary table is presented in Appendix E.

Analysis of Eye Movement Response Bias

A two-way ANOVA was performed with the number of eye movements per cell as the dependent variable in order to determine if eye movements differed between conditions. The variables were all within-subject and included Memory Condition (Implicit New, Implicit Old, Explicit Old) and Visual Field.

ANOVA results indicated a significant main effect of Memory Condition ($F(2,368) = 43.97$, $p < .0001$), such that subjects moved their eyes most often to the explicit memory stimuli ($M = 0.754$, $SD = .09$), next often to the old implicit memory stimuli (i.e., primes from the memory pairs) ($M = 0.50$, $SD = .07$), and least often to the new implicit memory stimuli (i.e., primes that participants have not seen before) ($M = 0.12$, $SD = .03$). No other effects were found.

Discussion

Numerous patient and non-patient studies have pointed toward a right hemisphere language superiority with certain types of material. However, it remains unclear as to the type of information preferentially processed by the right hemisphere. It has been proposed that the right hemisphere activates a larger array of meanings than the left hemisphere. Thus, it is suggested that the right hemisphere advantage occurs when word pairs share a weak associative relationship. In this study, all three weak association conditions (i.e., forward, backward, and both) in addition to both the strong backward condition fall into this category. In contrast, a second hypothesis posits that the hemisphere advantage is dependent upon the direction of association, such that the right hemisphere advantage should occur with word pairs sharing either a strong and or a weak backward association.

The first goal of this study was to address past research problems. Toward this end, hemispheric priming was examined using a different kind of priming task; an implicit memory paradigm was employed. This was done to eliminate difficulties associated with paradigms in which reaction time is the dependent variable. Additionally, word pairs were equated for frequency, concreteness, set size, and word length, a procedure seldom executed in prior studies. The strength of the indirect relationships was

also held constant. Thus, the word pairs only differed in the direct strength and the direction of the associative relationship.

The second goal of this study was to delineate which relationships are preferentially processed by the right hemisphere, thus word pairs sharing weak or strong forward, backward, or forward and backward association were included in this experiment. This was accomplished in order to test whether the right hemisphere advantage emerges with word pairs sharing a weak associative relationship (as predicted by the depth of activation hypothesis) or if the right hemisphere advantage is dependent upon the direction of the association between the word pairs (backward versus forward or forward and backward).

Though the explicit phase of the study was mainly included to address potential participant problems (i.e. asking participants to remember word pairs but never asking them to recall this information), the explicit data was very consistent with the implicit results. Moreover, the fact that the explicit target recovery was greater than implicit target recovery suggests that different aspects of processing were accessed with the two tasks.

A main effect of Visual Field in favor of the right visual field (LH) was found in all analyses, including the baseline probability analysis. Main effects of both Strength and Direction of association were also consistently found such that the probability of target recovery was greater for strongly related primes than for weakly related primes and was greater when the association was in the forward or forward and backward direction versus the backward only direction, consistent with past research in this area (Bahrick,

1970; Nelson & McEvoy,1979; Nelson, Bennett, & Leibert, 1997; Nelson, McKinney, Gee, & Janczura, 1998). Additionally, the expected interaction between Direction and Strength of association was found such that target recovery was best when word pairs shared strong forward association or a strong forward - backward association and was least when words shared a weak or strong backward association. Thus, when all word pair characteristics and association were controlled for, the main effects of hemisphere and association remain the most salient findings.

The only interactions observed between visual field and association were found with the unstudied and studied pairs on the implicit task. The Strength x Visual Field interaction was observed with studied pairs on the implicit task when eye movements were included such that target recovery for word pairs sharing a strong associative relationship was greater for primes presented in the right visual field (LH) than in the left visual field (RH). For unstudied pairs, the Direction x Visual Field was significant such that target recovery for word pairs sharing a forward associative relationship was greater for primes presented in the right visual field (LH) than in the left visual field (RH). Together, these results continue to support the superiority of the left hemisphere's ability to process verbal information, particularly with word pairs sharing a strong forward association.

Most importantly, the interaction of interest (Strength x Direction x Visual Field) was significant in the analysis of the unstudied pairs when eye movements were removed. A trend toward significance was also noted in the analysis of studied pairs on the implicit task when eye movement trials were included. As predicted by both the strength and the

direction hypothesis, a right visual field (LH) advantage with word pairs sharing a strong forward association was noted. No other visual field differences were statistically significant. Noteworthy, target recovery was slightly greater for primes presented to the left visual field (RH) than to the right visual field (LH) for studied word pairs sharing a weak forward association, yet this advantage was not statistically significant. Thus, the predicted right hemisphere advantage was not found with any of word pairs in any analysis.

Overall, the results do not support or reject either hypothesis. When stimuli characteristics are controlled for, on an implicit memory task, the left hemisphere's superior efficiency in processing verbal information continues to be the predominate finding.

Both hypotheses also predicted a left hemisphere advantage with word pairs sharing a strong forward and backward association, though this was not found. One explanation might relate to the fact that the forward and backward association pairs have the same total association strength, but this strength is a combination of the forward strength plus the backward strength. For example, one forward-backward pair, blue - green, has a forward strength of .135 and a backward strength of .118 for a total strength of .253. In contrast, one word pair sharing only a forward connection, plant - green has a forward strength only of .256. Thus, the total direct connection of the pairs is equivalent. However, since a forward connection is more powerful than a backward connection, the forward only condition may have been a stronger condition overall.

One explanation for the lack of a left visual field (RH) advantage is the observation that target recovery in both backward conditions was quite low when participants were asked to generate the first word that came to his or her mind (i.e., implicit memory phase of the experiment). For the group of subjects that were asked to remember the word pairs sharing a weak backward association, twenty-four percent of the participants did not produce any of the target words when primes from these word pairs were presented to the left visual field (RH). Additionally, twenty-eight percent of the participants who viewed the same word pairs (i.e., weak backward) failed to produce any targets in response to primes presented to the right visual field (LH). As with the weak backward condition, as many as thirty-five percent of the participants who viewed word pairs sharing a strong backward relationship failed to produce correct targets in response to primes presented to the RH during the implicit memory phase. Twenty-one percent of the same participants failed to produce correct targets to primes presented to the LH.

In contrast to the participants who viewed the backwardly associated word pairs, participants who viewed word pairs sharing a forward or a forward and backward condition performed much better. Few individuals (≤ 3 in each condition) failed to produce any correct targets when presented with the lateralized primes during the implicit memory trials.

In this study, data were analyzed including and excluding trials in which the participant's eyes moved. In this investigation, the data with the eye movements included revealed one of the more interesting findings (i.e., the interaction between Visual Field and Strength), though the results did not differ markedly with or without eye movement

trials. Eye movement trials are typically removed to insure that the stimuli was presented initially to one hemisphere only. If the subject fails to keep his or her eyes on the fixation mark throughout the trial, it is unclear if the stimuli appeared solely in his or her visual field. In this experiment, only one word was presented during each trial and the presentation time was only 200 milliseconds, shorter than the time necessary for an individual to move his or her eyes to a new location. Thus, if the subject's eyes did move when the stimuli initially appeared, the stimuli would have disappeared by the time that the eyes had focused upon the area. Therefore, including the eye movement trials should not have greatly affected the validity of the visual field presentation.

Results of the eye movement response bias analysis revealed significantly more eye movements on explicit trials compared to implicit trials. This finding is consistent with the notion that participants should be more motivated to respond correctly to the explicit trials as they recognize that there are correct answers to the explicit trials and thus have increased incentive to obtain the best view possible of the prime. In contrast, participants are told simply to say the first word that comes to their mind on the implicit trials. Thus, participants do not believe that there are right or wrong answers on the implicit trials and are therefore do not have the same incentive to obtain the best view possible of the implicit primes and are less likely to move their eyes on these trials.

It is unclear as to whether the implicit task is an improvement upon the lexical decision and pronunciation studies. Cronin-Golomb et al (1996) found implicit target recovery to occur intrahemispherically in two patients who's forebrain commisures have been severed, suggesting that implicit processing can occur within one hemisphere.

Additionally, it does appear that overall, participants did not use explicit strategies during the implicit phase as their target recovery was greater for the explicit than the implicit trials. Thus, the goal of tapping automatic processing appears to have been met. However, a right hemisphere advantage was not found with any of the word pairs, suggesting that use of an implicit memory task may be a less sensitive measure of hemispheric differences. Zeelenberg et al (1999) did not find backward priming on an implicit memory task. Yet in this study, participants did provide targets to primes in all word pair conditions, including those word pairs sharing only a backward association. Noteworthy, target recovery in the backward conditions was quite poor, suggesting that performance in the backward conditions may have been too low to detect significance in these conditions.

Irrespective of methodological differences (e.g., controlled versus automatic conditions, different paradigms, and different stimuli type), the right hemisphere advantage in language studies has been inconsistent at best. For example, while Chiarello and colleagues (1985, 1990, 1992) have frequently found a right hemisphere advantage with word pairs sharing what they believed were non associated stimuli (word association norms reveal a weak association between many of their word pairs), other researchers have found the equivalent or LH advantage with similar stimuli (Abernathy & Coney, 1996; Atchley, et al, 1998; Koivisto, 1995; Walker & Ceci, 1985). Moreover, in some laboratories, the right hemisphere has been found to occur with highly associated stimuli (Abernathey & Coney, 1993; Collins, 1999; Koivisto, 1995) in contrast with Chiarello and colleagues (1985, 1990, 1992) who found equivalent or a LH advantage with such

word pairs sharing a strong association. Thus, researchers have yet to define conditions in which the RH advantage consistently emerges.

First, I believe that the difficulty exists in finding examples of the right hemisphere's unique language processing capabilities at the single word level. Banich and Heller (1998) discuss the difference between the right and left hemisphere lies not with the material itself, but rather the processing style of the material. Specifically, they describe the left hemisphere's better ability to process information in a "piecemeal, analytic, and sequential manner" which of course is a better approach to processing verbal information while the right hemisphere excels in the processing in an "integrative and holistic manner," thus better allowing for processing of spatial information. Therefore, investigation of the right hemisphere's processing superiority may be difficult to detect at the single word level.

Second, activation-inhibition mechanisms may be interfering with detection of hemispheric processing differences. Querne, Eustache, and Faure (2000) describe how, when there is a particular task that needs to be accomplished, the hemisphere most competent to perform the task will be activated while the other hemisphere will be inhibited. Yet when two tasks are presented, the hemisphere most competent to perform the tasks will attempt to perform both tasks, while the inhibition of the contralateral hemisphere will be released if the first hemisphere becomes overloaded by the two tasks. Thus, by employing a verbal memory paradigm in conjunction with a lexical decision task, they were able to reduce the inhibition of the right hemisphere on the lexical decision task. Specifically, they found that when the memory load upon the left

hemisphere was light (i.e., participants were presented with only two words to remember prior to the lexical decision task), accuracy on the lexical decision task for words presented to the right hemisphere was comparable to previous studies (i.e., accuracy was better for imageable words than for nonimageable words). However, when the memory load upon the left hemisphere was increased (i.e., participants were presented with six words to remember), right hemisphere performance on the lexical decision task improved (i.e., performance was equivalent for imageable and non imageable words). This suggests that during a typical language task, such as a lexical decision or implicit language memory task, the right hemisphere's performance may be inhibited to some extent, preventing detection of differences in hemispheric processing on these simple tasks.

It may be of benefit to utilize imaging techniques to further understand the right hemisphere's language processing strengths. Seger et al (2000) employed a noun-verb generation task such that seven adults generated either the first verb that came to mind (usual verb) or an unusual verb in response to a noun prime. They found that when participants generated an unusual verb there was increased activation in the right middle and superior frontal gyri, left middle frontal gyri, and bilateral cerebellum yet no activation in the left inferior prefrontal cortex. Yet when participants generated a usual verb, this latter area, the left inferior prefrontal cortex was activated. This pattern of activation suggests that the right hemisphere is involved in the processing of less typical information and is consistent with the hypothesis that the right hemisphere is involved in the processing of distant associations and is therefore more involved in maintaining multiple meanings.

In conclusion, an attempt was made to resolve the inconsistencies in the literature by employing a new task not dependent upon reaction time and by controlling stimuli variables typically not held constant in prior studies. In this study, the data were generally consistent with prior association studies (i.e., greater target recovery with word pairs sharing a strong rather than weak associative connection and greater target recovery with word pairs sharing a forward or forward and backward condition versus a backward only association) and with predicted explicit versus implicit target recovery discrepancies (i.e., explicit target recovery exceeding implicit target recovery), suggesting that these results are valid. However, neither hypothesis was supported or rejected. This lack of RH advantage in any condition is not too surprising given the inconsistencies in this area of research to date. The difficulty with detection of the right hemisphere language advantage may lie in the experimental condition. Use of a single word paradigm may not allow for the right hemisphere specialization to be detected consistently. Future research focusing on the use of dual tasks (i.e., memory together with lexical decision) and/or imaging techniques may elucidate the unique contribution of the right hemisphere to language processing, as it most definitely does exist.

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Appendices

Appendix A: Spread of Activation Diagrams

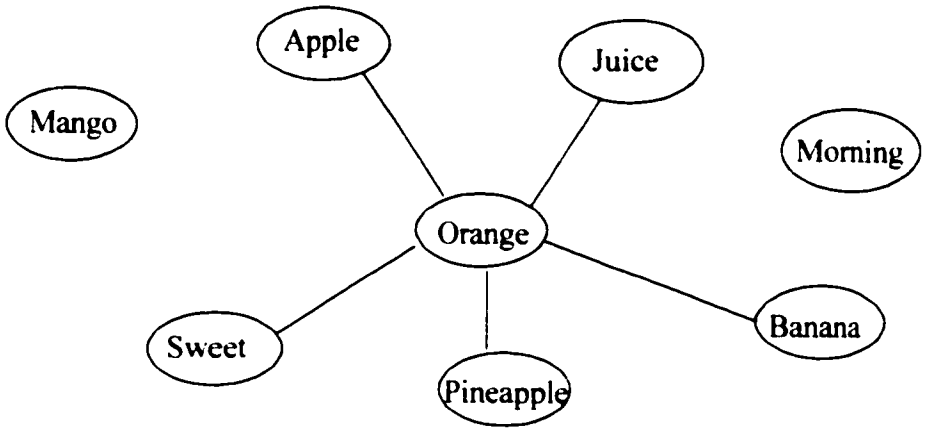

Figure 1. Spread of Activation in the Left Hemisphere

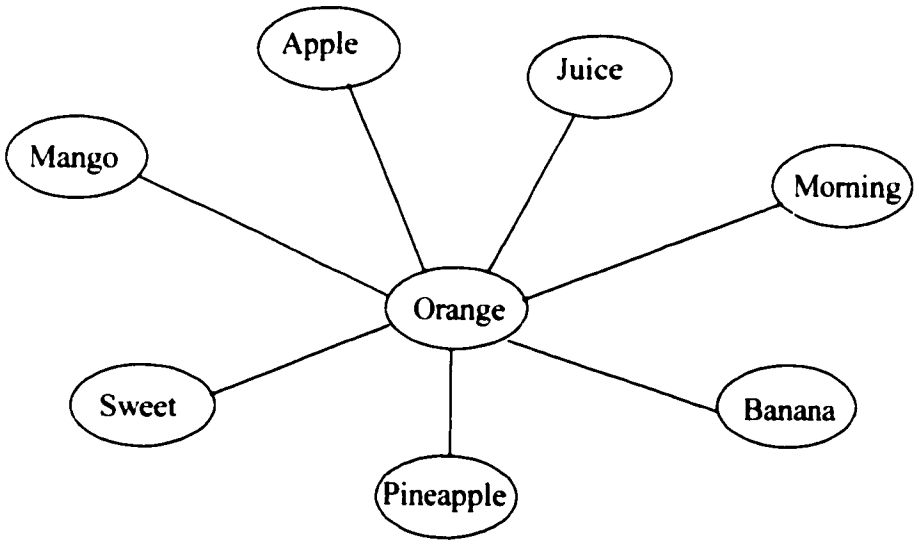

Figure 2. Spread of Activation in the Right Hemisphere

Appendix B: Priming Results

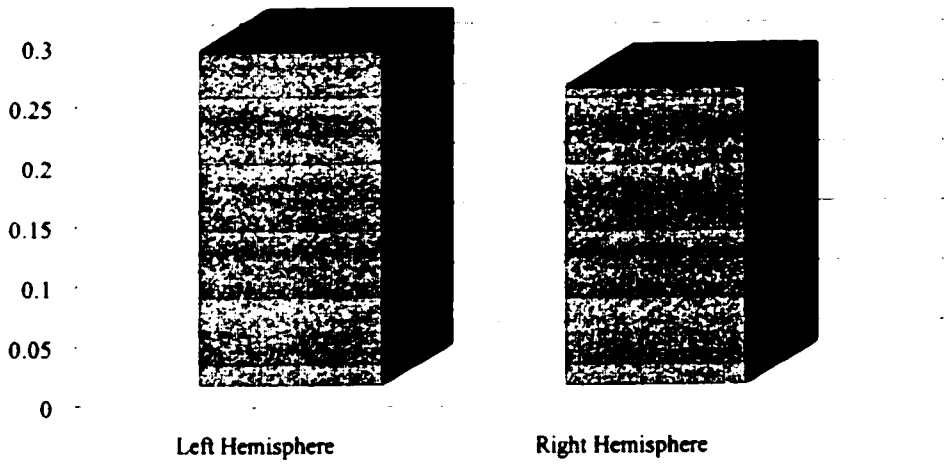

Figure 3. Mean Priming Probability by Hemisphere

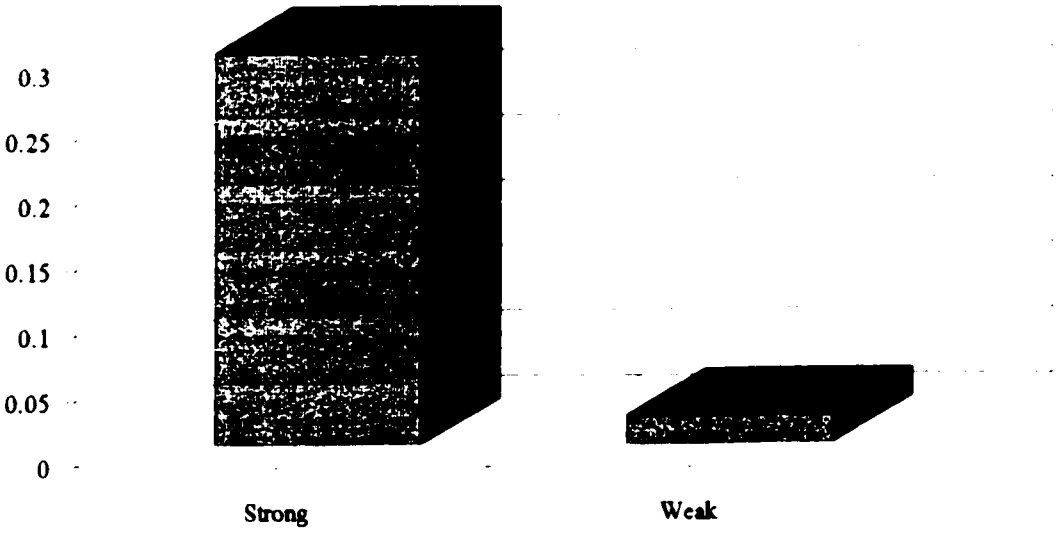

Figure 4. Mean Priming Probability by Strength of Association

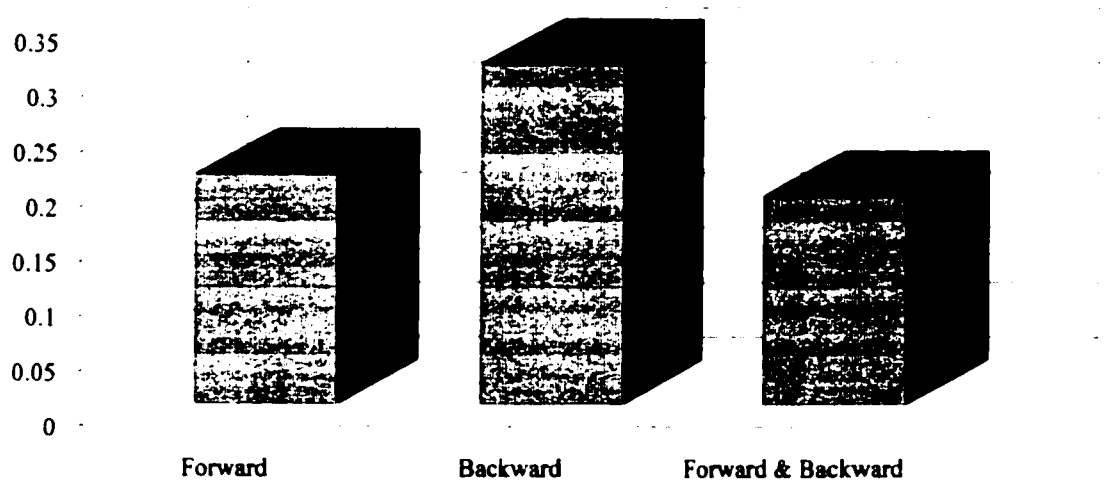

Figure 5. Mean Priming Probability by Direction of Association

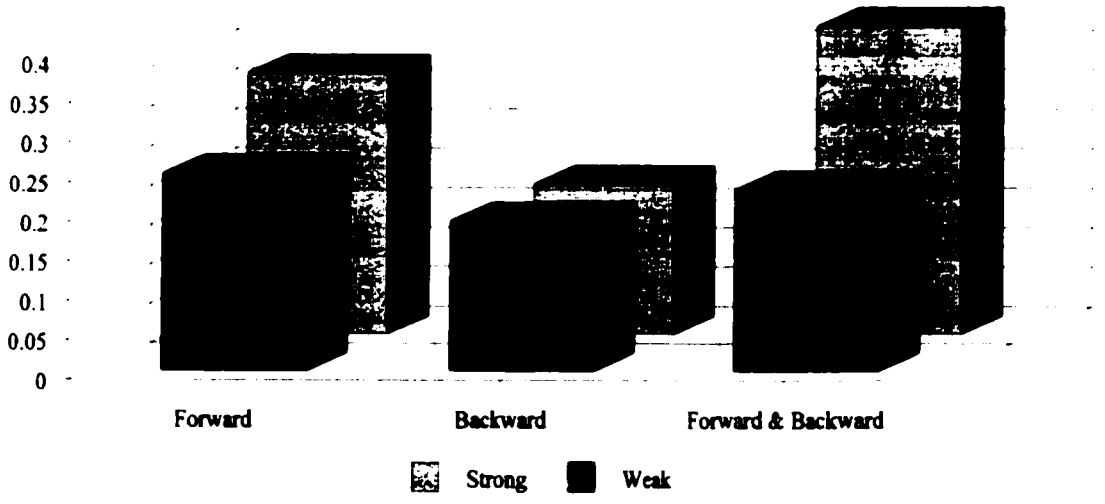

Figure 6. Mean Priming Probability by Strength and Direction of Association

Appendix C: Stimuli Lists

Table 4

Word Pairs Sharing a Weak Forward and Backward Association

Cue	Conn	Conc	WF	Set	Length	Target	Conn	Conc	WF	Set	Length
Church	2.14	5.82	348	15	6	Bell	0.6	6.52	18	11	4
Police	0.89	6.69	155	19	6	Force	0.60	2.92	230	17	5
Height	0.67	3.85	35	6	6	Length	2.38	3.75	116	13	6
Game	1.62	4.72	123	13	4	Board	0.63	6.87	239	21	5
Rain	1.65	5.77	70	18	4	Drop	0.75	3.16	59	16	4
Body	2.03	6.58	276	31	4	Soul	1.37	1.87	47	20	4
Bubble	1.12	5.39	12	8	6	Soap	1.76	5.77	22	22	4
Shy	1.57		13	16	3	Bold	1.53		21	20	4
Yarn	2.56	5.82	14	17	4	String	1.12	5.40	19	17	5
Grade	1.00	3.70	35	14	5	Mark	2.24	4.60	83	18	4
Fit	1.11	3.45	75	21	3	Exercise	3.12	4.62	58	28	7
Snap	0.80	4.11	12	16	4	Twig	1.83	5.47	1	6	4
Cowboy	0.70	5.68	16	10	6	West	0.67	4.03	235	6	4
Study	3.55	4.10	246	20	5	Class	2.83	5.03	207	23	5
Leaf	2.30	5.89	12	10	4	Plant	1.86	5.98	125	14	5
Angel	1.29	3.41	18	14	5	Wings	1.38	5.82	27	8	5
Load	1.53	4.35	45	16	4	Carry	1.50	3.93	88	19	5
Color	3.08	4.45	414	12	5	Green	1.19	5.46	116	17	5
Awake	1.11	4.40	20	9	5	Tired	1.79	3.04	48	14	5
Silk	2.61	5.26	12	18	4	Cloth	2.90	5.76	40	21	5

Note Conn = connectivity, connection strength of word.
Conc = concreteness, scale = 1 - 7, with 1 - 3 = abstract and 4 - 7 = concrete.
WF = word frequency, scale = # of words/million.
Set = set size, number of associates for word

Table 5

Word Pairs Sharing a Weak Forward and Backward Association

Cue	Conn	Conc	WF	Set	Length	Target	Conn	Conc	WF	Set	Length
Paper	1.07	5.96	157	15	5	Book	1.57	6.09	193	15	4
Collar	1.50	6.09	17	14	6	Neck	1.61	5.83	81	19	4
Fame	1.75	2.21	18	13	4	Glory	1.28	3.53	21	19	5
Sound	2.50	5.28	204	10	5	Ear	0.85	6.26	29	14	3
Point	1.70	4.54	395	24	5	Aim	1.08	3.40	37	13	3
Humble	1.06	2.27	18	18	6	Proud	1.33	3.22	50	22	5
Jungle	1.81	6.28	20	21	6	Africa	1.07	5.92	45	16	6
Pipe	0.86	6.90	20	15	4	Lead	1.00	4.98	129	14	4
Talent	1.75	2.88	40	16	6	Ability	2.00	2.03	74	22	6
Peace	0.67	2.98	198	19	5	Quiet	0.50	3.70	76	12	5
Pot	1.47	5.30	33	15	3	Flower	1.62	5.62	23	21	6
Pin	1.14	5.81	16	15	3	Safety	1.18	4.27	48	19	6
Attic	1.32		16	21	5	Cellar	1.20	6.83	26	10	6
Wild	1.17	3.72	56	15	4	Calm	1.62	3.56	35	14	4
Plate	3.42	5.74	22	12	5	Bowl	1.68	5.26	23	22	4
Social	0.83	2.33	380	15	6	Status	1.10		97	22	6
Kiss	1.75	5.78	17	13	4	Mouth	1.58	5.47	103	19	5
Sheet	1.38	5.46	45	8	5	Blanket	1.67	6.21	30	9	7
Lake	2.50	5.70	54	15	4	Fishing	2.00	5.05	32	15	7
Era	0.80		30	16	3	Period	1.10	3.92	265	12	6

Note. Conn = connectivity, connection strength of word.
Conc = concreteness, scale = 1 - 7, with 1 - 3 = abstract and 4 - 7 = concrete.
WF = word frequency, scale = # of words/million.
Set = set size, number of associates for word

Table 6

Word Pairs Sharing a Strong Forward and Backward Association

Cue	Conn	Conc	WF	Set	Length	Target	Conn	Conc	WF	Set	Length
Accept	1.94		72	18	6	Reject	2.00	2.82	10	18	6
Sun	2.36	6.23	112	14	3	Tan	1.38	4.18	9	13	3
Blame	1.20	2.15	34	22	5	Accuse	2.40		10	20	6
Blow	0.74	3.88	33	23	4	Wind	1.50	5.40	63	19	4
Blue	1.69	4.49	143	14	4	Green	1.19	5.46	116	17	5
Coat	1.56	5.83	43	17	4	Hat	0.83	5.97	56	12	3
Doctor	2.24	5.75	100	19	6	Lawyer	2.23	5.58	43	13	6
Drink	2.58	4.95	82	20	5	Water	2.00	6.27	442	18	5
Earth	1.92	5.77	150	12	5	Ground	1.00	5.44	186	14	6
Foot	1.11	3.46	70	9	4	Hand	0.94	5.60	431	16	4
Gear	0.88		26	21	4	Shift	1.10		41	10	5
Heavy	1.33	4.09	110	16	5	Weight	1.23	1.34	91	14	6
Jury	1.45	6.19	67	11	4	Trial	2.62	4.92	134	14	5
Lift	1.70	3.70	23	21	4	Raise	1.86	3.17	52	14	5
Red	2.31	4.97	197	14	3	Rose	0.78	5.86	86	10	4
Smell	1.54	4.40	34	13	5	Taste	2.27	4.53	59	15	5
Worth	1.92	2.63	94	13	5	Value	2.47	2.15	200	17	5
Dig	2.12	4.22	10	8	3	Ditch	1.54	5.28	10	14	5
Above	1.44		188	9	5	Beyond	1.00		175	20	6
Star	2.50	5.59	25	16	4	Moon	1.90	5.68	60	10	4

Note. Conn = connectivity, connection strength of word.
Conc = concreteness, scale = 1 - 7, with 1 - 3 = abstract and 4 - 7 = concrete.
WF = word frequency, scale = # of words/million.
Set = set size, number of associates for word

Table 7

Word Pairs Sharing a Strong Forward and Backward Association

Cue	Conn	Conc	WF	Set	Length	Target	Conn	Conc	WF	Set	Length
Fruit	1.47	6.00	35	17	5	Orange	2.15	5.74	23	14	6
Cliff	1.83	5.98	11	12	5	Edge	1.81	4.28	78	17	4
Hear	2.82	3.90	153	11	4	Sound	2.50	5.28	204	10	5
Cry	1.69	4.32	48	14	3	Baby	2.05	5.77	62	19	4
Public	0.47		438	21	6	Private	1.06	3.46	191	18	7
Paper	1.07	5.96	157	15	5	Write	2.25	4.42	106	16	5
Potato	1.71	7.00	15	23	6	Chip	0.71	5.30	17	15	4
Lake	2.50	5.70	54	15	4	River	2.29	5.83	165	20	5
Award	2.74	4.58	46	24	5	Trophy	2.22	6.29	8	9	6
Garden	1.23	5.92	60	14	6	Hose	0.55	6.39	9	13	4
Flat	1.05	4.26	67	19	4	Tire	0.70	5.51	22	10	4
Dull	1.20	3.08	27	11	4	Sharp	2.24	4.12	72	18	5
Draw	1.53	4.32	56	15	4	Paint	1.62	5.73	37	16	5
Cut	1.36	4.15	192	21	3	Knife	1.46	6.08	76	13	5
Cup	2.50	5.35	45	10	3	Glass	1.55	6.31	99	21	5
Camera	0.71	6.23	36	8	6	Film	2.00	5.91	96	12	4
Blind	1.61	4.39	47	19	5	Deaf	1.86	4.29	12	16	4
Aware	1.47		84	18	5	Alert	0.82	3.96	33	13	5
Angel	1.29	3.41	18	14	5	Devil	1.70	2.13	25	11	5
Flag	0.73	6.20	18	12	4	Pole	0.50	5.59	16	14	4

Note. Conn = connectivity, connection strength of word.
Conc = concreteness, scale = 1 - 7, with 1 - 3 = abstract and 4 - 7 = concrete.
WF = word frequency, scale = # of words/million.
Set = set size, number of associates for word

Table 8

Word Pairs Sharing a Weak Forward Association

Cue	Conn	Conc	WF	Set	Length	Target	Conn	Conc	WF	Set	Length
Bit	1.43	3.88	101	14	3	Horse	1.15	6.03	117	16	5
Bridge	0.60	6.36	98	10	6	Cross	2.00	5.10	55	18	5
Camp	0.83	5.69	75	19	4	Fun	2.13	2.45	44	15	3
Chief	0.80	4.82	119	10	5	Fire	2.06	6.13	187	18	4
Expert	2.29	3.87	30	18	6	Smart	2.00	3.00	21	14	5
Flower	1.62	5.62	23	21	6	Smell	1.54	4.40	34	13	5
Ground	1.00	5.44	186	14	6	Beef	1.80	6.23	32	10	4
Guess	1.67	3.27	56	20	5	Think	2.85	3.38	433	22	5
Matter	1.30		342	25	6	Atom	2.50	4.77	37	12	4
Pot	1.47	5.30	33	15	3	Stove	1.80	5.75	15	11	5
Toes	0.56		19	11	4	Shoe	0.64	5.96	14	14	4
Dry	0.83	3.36	68	18	3	Clean	1.83	3.82	70	13	5
Alone	1.44	3.81	195	19	5	Sad	1.14	3.52	35	7	3
Argue	1.40	3.23	29	10	5	Agree	0.43		51	11	5
Broke	1.07	3.90	72	18	5	Poor	0.73	3.00	113	11	4
Fight	2.05	4.16	98	24	5	Box	0.73	5.91	70	15	3
Wide	1.47	3.44	125	15	4	Thin	1.40	3.82	92	5	4
Grain	1.36	5.63	27	11	5	Rice	1.69	6.04	33	19	4
Guilty	2.00	2.49	29	18	6	Wrong	0.67	2.60	129	6	5
Lawyer	2.23	5.58	43	13	6	Money	1.39	5.77	265	19	5

Note Conn = connectivity, connection strength of word.
Conc = concreteness, scale = 1 - 7, with 1 - 3 = abstract and 4 - 7 = concrete.
WF = word frequency, scale = # of words/million.
Set = set size, number of associates for word

Table 9

Word Pairs Sharing a Weak Forward Association

Cue	Conn	Conc	WF	Set	Length	Target	Conn	Conc	WF	Set	Length
Letter	1.27	5.16	145	15	6	Opener	0.25		6	4	6
Claim	0.81		98	22	5	Check	1.00	4.38	88	13	5
Press	1.06		127	17	5	Push	0.50	4.12	37	10	4
Truth	1.75	2.72	126	17	5	Justice	1.50	2.18	114	15	6
Mass	1.41	4.09	110	19	4	Weight	1.23	4.35	91	14	6
Marine	2.81	5.95	55	17	6	Fish	1.26	5.84	35	24	4
Pat	1.37	3.80	35	19	3	Tap	0.72	4.95	18	19	3
Fell	1.35	4.03	92	18	4	Trip	1.40	4.39	81	10	4
Shape	1.67	4.22	85	18	5	Round	0.43	4.34	81	7	5
Mark	2.24	4.60	83	18	4	Spot	1.25	4.71	57	12	4
Tea	0.80	6.05	28	11	3	Ice	1.29	6.51	45	18	3
Weapon	1.57	6.38	42	7	6	Knife	1.46	6.08	76	13	5
Active	1.50		88	21	6	Busy	1.91	3.21	58	24	4
Formal	1.67		48	17	6	Dance	1.47	4.98	90	19	5
File	1.19	4.63	81	16	4	Paper	1.07	5.96	157	15	5
Pure	1.50	2.68	56	18	4	Gold	2.31	5.68	52	16	4
Sight	2.12	3.84	86	18	5	Sound	2.50	5.28	204	10	5
Draw	1.53	4.32	56	15	4	Pencil	0.75	7.00	34	9	6
Coast	2.52	5.51	61	22	5	Ocean	2.31	5.63	34	17	5
Worry	1.65	2.80	55	24	5	Happy	1.29	3.51	98	8	5

Note. Conn = connectivity, connection strength of word.
Conc = concreteness, scale = 1 - 7, with 1 - 3 = abstract and 4 - 7 = concrete.
WF = word frequency, scale = # of words/million.
Set = set size, number of associates for word

Table 10

Word Pairs Sharing a Weak Backward Association

Cue	Conn	Conc	WF	Set	Length	Target	Conn	Conc	WF	Set	Length
Horse	1.15	6.03	117	16	5	Bit	1.43	3.88	101	14	3
Cross	2.00	5.10	55	18	5	Bridge	0.60	6.36	98	10	6
Fun	2.13	2.45	44	15	3	Camp	0.83	5.69	75	19	4
Fire	2.06	6.13	187	18	4	Chief	0.80	4.82	119	10	5
Smart	2.00	3.00	21	14	5	Expert	2.29	3.87	30	18	6
Smell	1.54	4.40	34	13	5	Flower	1.62	5.62	23	21	6
Beef	1.80	6.23	32	10	4	Ground	1.00	5.44	186	14	6
Think	2.85	3.38	433	22	5	Guess	1.67	3.27	56	20	5
Atom	2.50	4.77	37	12	4	Matter	1.30		342	25	6
Stove	1.80	5.75	15	11	5	Pot	1.47	5.30	33	15	3
Shoe	0.64	5.96	14	14	4	Toes	0.56		19	11	4
Clean	1.83	3.82	70	13	5	Dry	0.83	3.36	68	18	3
Sad	1.14	3.52	35	7	3	Alone	1.44	3.81	195	19	5
Agree	0.43		51	11	5	Argue	1.40	3.23	29	10	5
Poor	0.73	3.00	113	11	4	Broke	1.07	3.90	72	18	5
Box	0.73	5.91	70	15	3	Fight	2.05	4.16	98	24	5
Thin	1.40	3.82	92	5	4	Wide	1.47	3.44	125	15	4
Rice	1.69	6.04	33	19	4	Grain	1.36	5.63	27	11	5
Wrong	0.67	2.60	129	6	5	Guilty	2.00	2.49	29	18	6
Money	1.39	5.77	265	19	5	Lawyer	2.23	5.58	43	13	6

Note. Conn = connectivity, connection strength of word.
Conc = concreteness, scale = 1 - 7, with 1 - 3 = abstract and 4 - 7 = concrete.
WF = word frequency, scale = # of words/million.
Set = set size, number of associates for word

Table 11

Word Pairs Sharing a Weak Backward Association

Cue	Conn	Conc	WF	Set	Length	Target	Conn	Conc	WF	Set	Length
Opener	0.25		6	4	6	Letter	1.27	5.16	145	15	6
Check	1.00	4.38	88	13	5	Claim	0.81		98	22	5
Push	0.50	4.12	37	10	4	Press	1.06		127	17	5
Justice	1.50	2.18	114	15	6	Truth	1.75	2.72	126	17	5
Weight	1.23	4.35	91	14	6	Mass	1.41	4.09	110	19	4
Fish	1.26	5.84	35	24	4	Marine	2.81	5.95	55	17	6
Tap	0.72	4.95	18	19	3	Pat	1.37	3.80	35	19	3
Trip	1.40	4.39	81	10	4	Fell	1.35	4.03	92	18	4
Round	0.43	4.34	81	7	5	Shape	1.67	4.22	85	18	5
Spot	1.25	4.71	57	12	4	Mark	2.24	4.60	83	18	4
Ice	1.29	6.51	45	18	3	Tea	0.80	6.05	28	11	3
Knife	1.46	6.08	76	13	5	Weapon	1.57	6.38	42	7	6
Busy	1.91	3.21	58	24	4	Active	1.50		88	21	6
Dance	1.47	4.98	90	19	5	Formal	1.67		48	17	6
Paper	1.07	5.96	157	15	5	File	1.19	4.63	81	16	4
Gold	2.31	5.68	52	16	4	Pure	1.50	2.68	56	18	4
Sound	2.50	5.28	204	10	5	Sight	2.12	3.84	86	18	5
Pencil	0.75	7.00	34	9	6	Draw	1.53	4.32	56	15	4
Ocean	2.31	5.63	34	17	5	Coast	2.52	5.51	61	22	5
Happy	1.29	3.51	98	8	5	Worry	1.65	2.80	55	24	5

Note Conn = connectivity, connection strength of word.
Conc = concreteness, scale = 1 - 7, with 1 - 3 = abstract and 4 - 7 = concrete.
WF = word frequency, scale = # of words/million.
Set = set size, number of associates for word

Table 12

Word Pairs Sharing a Strong Forward Association

Cue	Conn	Conc	WF	Set	Length	Target	Conn	Conc	WF	Set	Length
Artery	1.25	6.28	46	8	6	Heart	1.40	6.02	173	16	5
Birds	0.73	5.94	57	21	5	Fly	1.42	5.14	33	19	3
Basic	1.50		171	20	5	Simple	1.14	2.98	161	7	6
Decade	1.14	3.35	46	7	6	Ten	1.75	4.92	165	20	3
Dust	1.00	6.67	70	16	4	Dirt	1.94	5.51	43	18	4
Eyes	2.08		394	15	4	Blue	1.69	4.49	143	14	4
Bound	1.00		42	15	5	Tie	5.55	1.14	23	17	3
Gain	1.20	3.21	74	10	64	Weight	1.23	4.35	91	14	6
Harbor	3.44		37	9	6	Boat	1.62	6.33	72	16	4
Living	2.18	3.98	194	11	6	Dead	1.41	4.25	174	18	4
Pieces	0.78	3.75	92	14	6	Puzzle	0.64	5.81	10	13	6
Please	1.41	2.08	62	19	6	Thanks	0.22	2.63	37	14	6
Bone	1.53	5.75	33	19	4	Dog	0.40	5.75	75	5	3
Snake	0.95	6.48	44	21	5	Bite	1.28	4.32	10	19	4
Suite	1.36		27	13	5	Hotel	1.27	6.80	126	16	5
Volume	1.89	5.14	135	18	6	Loud	1.78	3.93	20	11	4
Verse	2.54		28	16	5	Song	1.57	5.04	70	16	4
Spare	0.33		23	11	5	Extra	1.14		50	18	5
Cafe	1.92	5.64	20	15	4	Coffee	1.08	6.43	78	13	6
Trial	2.62	4.92	134	14	5	Court	1.40	5.05	230	17	5

Note. Conn = connectivity, connection strength of word.
Conc = concreteness, scale = 1 - 7, with 1 - 3 = abstract and 4 - 7 = concrete.
WF = word frequency, scale = # of words/million.
Set = set size, number of associates for word

Table 13

Word Pairs Sharing a Strong Forward Association

Cue	Conn	Conc	WF	Set	Length	Target	Conn	Conc	WF	Set	Length
Beef	1.80	6.23	32	10	4	Cow	1.50	6.12	29	10	3
Fellow	2.31		63	17	46	Friend	2.05	4.40	133	22	6
Deal	0.93	3.21	142	19	4	Cards	0.79	5.61	26	18	5
Drama	1.80	3.66	43	11	5	Play	1.30	4.22	200	21	4
Duty	1.92	2.32	61	15	4	Job	1.86	4.11	238	7	3
Factor	1.33		71	15	6	Math	2.26	3.78	4	19	4
Fire	2.06	6.13	187	18	4	Hot	1.12	5.03	130	8	3
Games	0.92		55	13	5	Fun	2.13	2.45	44	15	3
Impact	0.91	3.32	67	12	6	Crash	1.29	4.28	20	16	5
Opera	2.29		47	16	5	Sing	2.69	4.12	34	17	4
Plant	1.86	5.98	125	14	5	Green	1.19	5.46	116	17	5
Race	1.20	4.46	103	17	4	Color	3.08	4.45	141	12	5
Sheet	1.38	5.46	45	8	5	Bed	1.45	6.59	127	11	3
Stars	1.62	5.59	29	18	5	Sky	1.18	5.32	58	12	3
Tissue	1.83		41	12	6	Paper	1.07	5.96	157	15	5
Root	0.70	5.54	30	10	4	Tree	0.76	6.62	59	21	4
Baker	2.45		36	14	5	Bread	1.20	6.18	41	15	5
Spread	0.64	3.22	83	15	6	Butter	1.00	6.24	27	15	6
Brown	2.20	4.63	176	20	5	Black	0.50	4.66	203	10	5
Buck	1.00		20	11	4	Dollar	1.38	5.68	46	9	6

Note. Conn = connectivity, connection strength of word.
Conc = concreteness, scale = 1 - 7, with 1 - 3 = abstract and 4 - 7 = concrete.
WF = word frequency, scale = # of words/million.
Set = set size, number of associates for word

Table 14

Word Pairs Sharing a Strong Backward Association

Cue	Conn	Conc	WF	Set	Length	Target	Conn	Conc	WF	Set	Length
Heart	1.40	6.02	173	16	5	Artery	1.25	6.28	46	8	6
Fly	1.42	5.14	33	19	3	Birds	0.73	5.94	57	21	5
Simple	1.14	2.98	161	7	6	Basic	1.50		171	20	5
Ten	1.75	4.92	165	20	3	Decade	1.14	3.35	46	7	6
Dirt	1.94	5.51	43	18	4	Dust	1.00	6.67	70	16	4
Blue	1.69	4.49	143	14	4	Eyes	2.08		394	15	4
Tie	5.55	1.14	23	17	3	Bound	1.00		42	15	5
Weight	1.23	4.35	91	14	6	Gain	1.20	3.21	74	10	64
Boat	1.62	6.33	72	16	4	Harbor	3.44		37	9	6
Dead	1.41	4.25	174	18	4	Living	2.18	3.98	194	11	6
Puzzle	0.64	5.81	10	13	6	Pieces	0.78	3.75	92	14	6
Thanks	0.22	2.63	37	14	6	Please	1.41	2.08	62	19	6
Dog	0.40	5.75	75	5	3	Bone	1.53	5.75	33	19	4
Bite	1.28	4.32	10	19	4	Snake	0.95	6.48	44	21	5
Hotel	1.27	6.80	126	16	5	Suite	1.36		27	13	5
Loud	1.78	3.93	20	11	4	Volume	1.89	5.14	135	18	6
Song	1.57	5.04	70	16	4	Verse	2.54		28	16	5
Extra	1.14		50	18	5	Spare	0.33		23	11	5
Coffee	1.08	6.43	78	13	6	Cafe	1.92	5.64	20	15	4
Court	1.40	5.05	230	17	5	Trial	2.62	4.92	134	14	5

Note. Conn = connectivity, connection strength of word.
Conc = concreteness, scale = 1 - 7, with 1 - 3 = abstract and 4 - 7 = concrete.
WF = word frequency, scale = # of words/million.
Set = set size, number of associates for word

Table 15

Word Pairs Sharing a Strong Backward Association

Cue	Conn	Conc	WF	Set	Length	Target	Conn	Conc	WF	Set	Length
Cow	1.50	6.12	29	10	3	Beef	1.80	6.23	32	10	4
Friend	2.05	4.40	133	22	6	Fellow	2.31		63	17	46
Cards	0.79	5.61	26	18	5	Deal	0.93	3.21	142	19	4
Play	1.30	4.22	200	21	4	Drama	1.80	3.66	43	11	5
Job	1.86	4.11	238	7	3	Duty	1.92	2.32	61	15	4
Math	2.26	3.78	4	19	4	Factor	1.33		71	15	6
Hot	1.12	5.03	130	8	3	Fire	2.06	6.13	187	18	4
Fun	2.13	2.45	44	15	3	Games	0.92		55	13	5
Crash	1.29	4.28	20	16	5	Impact	0.91	3.32	67	12	6
Sing	2.69	4.12	34	17	4	Opera	2.29		47	16	5
Green	1.19	5.46	116	17	5	Plant	1.86	5.98	125	14	5
Color	3.08	4.45	141	12	5	Race	1.20	4.46	103	17	4
Bed	1.45	6.59	127	11	3	Sheet	1.38	5.46	45	8	5
Sky	1.18	5.32	58	12	3	Stars	1.62	5.59	29	18	5
Paper	1.07	5.96	157	15	5	Tissue	1.83		41	12	6
Tree	0.76	6.62	59	21	4	Root	0.70	5.54	30	10	4
Bread	1.20	6.18	41	15	5	Baker	2.45		36	14	5
Butter	1.00	6.24	27	15	6	Spread	0.64	3.22	83	15	6
Black	0.50	4.66	203	10	5	Brown	2.20	4.63	176	20	5
Dollar	1.38	5.68	46	9	6	Buck	1.00		20	11	4

Note Conn = connectivity, connection strength of word.
Conc = concreteness, scale = 1 - 7, with 1 - 3 = abstract and 4 - 7 = concrete.
WF = word frequency, scale = # of words/million.
Set = set size, number of associates for word

Appendix D: Stimuli Strength

Table 16

Strength of Word Pairs Sharing a Weak Forward and Backward Association

Cue	Target	FSG	BSG	Total Direct	OSG	MSG	Total Indirect
Church	Bell	.031	.047	.078	.0000	.0000	.0000
Police	Force	.031	.030	.061	.0000	.0000	.0000
Height	Length	.030	.035	.065	.0029	.00000	.0029
Game	Board	.034	.033	.067	.0030	.0010	.0040
Rain	Drop	.032	.036	.068	.0034	.0008	.0042
Body	Soul	.034	.034	.068	.0008	.00000	.0008
Bubble	Soap	.036	.033	.069	.0033	.0040	.0073
Shy	Bold	.035	.034	.069	.0031	.00000	.0031
Yarn	String	.031	.039	.070	.0095	.0041	.0136
Grade	Mark	.034	.036	.070	.0000	.0000	.0000
Fit	Exercise	.048	.034	.082	.0046	.0030	.0076
Snap	Twig	.038	.034	.072	.0039	.0000	.0039
Cowboy	West	.042	.031	.073	.0000	.0000	.0000
Study	Class	.040	.034	.074	.0288	.0089	.0377
Leaf	Plant	.042	.033	.075	.0946	.0016	.0962
Angel	Wings	.041	.034	.075	.0000	.0000	.0000
Load	Carry	.041	.034	.075	.0150	.0045	.0195
Color	Green	.040	.035	.075	.0355	.0440	.0795
Awake	Tired	.042	.034	.076	.0078	.0890	.0977
Silk	Cloth	.047	.030	.077	.0183	.0236	.0419

Note. FSG = direct forward strength.
BSG = direct backward strength.
OSG = indirect strength of overlaps.
MSG = indirect strength of mediators.

Table 17

Strength of Word Pairs Sharing a Weak Forward and Backward Association

Cue	Target	FSG	BSG	Total Direct	OSG	MSG	Total Indirect
Paper	Book	.039	.039	.078	.0009	.0012	.0021
Collar	Neck	.043	.036	.079	.0067	.0030	.0097
Fame	Glory	.046	.033	.079	.0000	.0000	.0000
Sound	Ear	.031	.049	.080	.0287	.0418	.0705
Point	Aim	.048	.034	.082	.0046	.0030	.0076
Humble	Proud	.034	.048	.082	.0031	.0000	.0031
Jungle	Africa	.034	.048	.082	.0013	.0036	.0049
Pipe	Lead	.047	.036	.083	.0003	.0000	.0003
Talent	Ability	.048	.035	.083	.0050	.0092	.0142
Peace	Quiet	.049	.034	.083	.0000	.0062	.0062
Pot	Flower	.036	.048	.084	.0043	.0091	.0134
Pin	Safety	.050	.036	.086	.0000	.0000	.0000
Attic	Cellar	.040	.047	.087	.0610	.0150	.0760
Wild	Calm	.048	.040	.088	.0020	.0067	.0087
Plate	Bowl	.042	.050	.092	.0349	.0336	.0685
Social	Status	.034	.034	.068	.0000	.0000	.0000
Kiss	Mouth	.045	.049	.094	.0066	.0308	.0374
Sheet	Blanket	.034	.047	.081	.0356	.0025	.0381
Lake	Fishing	.031	.030	.061	.0110	.0000	.0110
Era	Period	0.50	.048	.098	.0686	.0000	.0686

Note. FSG = direct forward strength.
BSG = direct backward strength.
OSG = indirect strength of overlaps.
MSG = indirect strength of mediators.

Table 18

Strength of Word Pairs Sharing a Strong Forward and Backward Association

Cue	Target	FSG	BSG	Total Direct	OSG	MSG	Total Indirect
Accept	Reject	.107	.169	.276	.0100	.0040	.0140
Sun	Tan	.173	.162	.335	.0060	.0000	.0060
Blame	Accuse	.185	.159	.344	.0040	.0000	.0040
Blow	Wind	.058	.169	.327	.0040	.0010	.0050
Blue	Green	.135	.118	.253	.0050	.0040	.0090
Coat	Hat	.162	.103	.265	.0000	.0000	.0000
Doctor	Lawyer	.101	.149	.250	.0000	.0000	.0000
Drink	Water	.152	.167	.319	.0060	.0390	.0450
Earth	Ground	.174	.152	.326	.0120	.0020	.0140
Foot	Hand	.122	.158	.280	.0020	.0000	.0020
Gear	Shift	.131	.182	.313	.0200	.0000	.0200
Heavy	Weight	.104	.190	.294	.0080	.0020	.0100
Jury	Trial	.171	.160	.331	.0790	.0007	.0797
Lift	Raise	.100	.178	.278	.0160	.0000	.0160
Red	Rose	.102	.171	.273	.0000	.0003	.0003
Smell	Taste	.181	.142	.323	.0040	.0008	.0048
Worth	Value	.171	.144	.315	.0790	.0010	.0800
Dig	Ditch	.113	.102	.215	.0660	.0000	.0660
Above	Beyond	.114	.111	.225	.0040	.0000	.0040
Star	Moon	.115	.118	.233	.0460	.0170	.0630

Note. FSG = direct forward strength.
BSG = direct backward strength.
OSG = indirect strength of overlaps.
MSG = indirect strength of mediators.

Table 19

Strength of Word Pair Sharing a Strong Forward and Backward Association

Cue	Target	FSG	BSG	Total Direct	OSG	MSG	Total Indirect
Fruit	Orange	.174	.194	.368	.0260	.0600	.0860
Cliff	Edge	.104	.182	.286	.0100	.0050	.0150
Hear	Sound	.122	.110	.232	.0220	.0200	.0420
Cry	Baby	.109	.115	.224	.0000	.0010	.0010
Public	Private	.136	.144	.280	.0020	.0000	.0020
Paper	Write	.144	.106	.250	.0420	.0310	.0730
Potato	Chip	.140	.190	.330	.0000	.0000	.0000
Lake	River	.142	.118	.260	.0220	.0050	.0270
Award	Trophy	.117	.182	.299	.0180	.0070	.0250
Garden	Hose	.132	.176	.308	.0000	.0000	.0000
Flat	Tire	.150	.117	.267	.0000	.0000	.0000
Dull	Sharp	.148	.158	.306	.0060	.0090	.0150
Draw	Paint	.120	.127	.247	.0150	.0120	.0270
Cut	Knife	.101	.1179	.280	.0007	.001	.0017
Cup	Glass	.148	.133	.281	.0060	.0040	.0100
Camera	Film	.166	.116	.282	.0290	.0000	.0290
Blind	Deaf	.114	.171	.285	.0002	.0000	.0002
Aware	Alert	.137	.118	.255	.0180	.0070	.0250
Angel	Devil	.150	.181	.331	.0070	.0010	.0080
Flag	Pole	.193	.157	.276	.0000	.0000	.0000

Note. FSG = direct forward strength.
BSG = direct backward strength.
OSG = indirect strength of overlaps.
MSG = indirect strength of mediators.

Table 20

Strength of Word Pairs Sharing a Weak Forward Association

Cue	Target	FSG	BSG	Total Direct	OSG	MSG	Total Indirect
Bit	Horse	.079	0	.079	.0009	.0000	.0009
Bridge	Cross	.079	0	.079	.0020	.0000	.0020
Camp	Fun	.079	0	.079	.0004	.0020	.0024
Chief	Fire	.079	0	.079	.0000	.0000	.0000
Expert	Smart	.079	0	079	.0034	.0300	.0334
Flower	Smell	.079	0	.079	.0004	.0130	.0134
Ground	Beef	.079	0	.079	.0000	.0000	.0000
Guess	Think	.079	0	.079	.0011	.0050	.0061
Matter	Atom	.079	0	.079	.0010	.0003	.0013
Pot	Stove	.079	0	.079	.0156	.0143	.0299
Toes	Shoe	.079	0	.079	.0047	.0136	.0183
Dry	Clean	.076	0	.076	.0000	.0010	.0010
Alone	Sad	.081	0	.081	.0000	.0440	.0400
Argue	Agree	.081	0	.081	.0079	.0050	.0129
Broke	Poor	.081	0	.081	.0018	.0000	.0018
Fight	Box	.081	0	.081	.0000	.0000	.0000
Wide	Thin	.076	0	.076	.0546	.0396	.0942
Grain	Rice	.081	0	.081	.0077	.0000	.0077
Guilty	Wrong	.081	0	.081	.0008	.0040	.0048
Lawyer	Money	.081	0	.081	.0024	.0101	.0125

Note. FSG = direct forward strength.
BSG = direct backward strength.
OSG = indirect strength of overlaps.
MSG = indirect strength of mediators.

Table 21

Strength of Word Pairs Sharing a Weak Forward Association

Cue	Target	FSG	BSG	Total Direct	OSG	MSG	Total Indirect
Letter	Opener	.081	0	.081	.0000	.0000	.0000
Claim	Check	.078	0	078	.0078	.0010	.0088
Press	Push	.078	0	.078	.0110	.0169	.0279
Truth	Justice	.082	0	.082	.0009	.0002	.0011
Mass	Weight	.083	0	.083	.0000	.0006	.0006
Marine	Fish	.078	0	.078	.0383	.0089	.0472
Pat	Tap	.081	0	.081	.0119	.0000	.0119
Fell	Trip	.083	0	083	.0695	.0060	.0755
Shape	Round	.083	0	.083	.0168	.0105	.0273
Mark	Spot	.086	0	.086	.0039	.0090	.0129
Tea	Ice	.081	0	.081	.0014	0000	.0014
Weapon	Knife	.075	0	.075	.0077	.0010	.0087
Active	Busy	.080	0	.080	.0020	.0000	.0020
Formal	Dance	.081	0	.081	.0014	0140	.0154
File	Paper	.077	0	.077	.0000	.0260	.0260
Pure	Gold	.077	0	.077	.0000	.0015	.0015
Sight	Sound	.083	0	.083	.0000	.0013	.0013
Draw	Pencil	.084	0	.084	.0080	.0060	.0140
Coast	Ocean	.085	0	.085	.0388	.0430	.0818
Worry	Happy	.085	0	.085	.0176	.0237	.0413

Note. FSG = direct forward strength.
BSG = direct backward strength.
OSG = indirect strength of overlaps.
MSG = indirect strength of mediators.

Table 22

Strength of Word Pairs Sharing a Weak Backward Association

Cue	Target	FSG	BSG	Total Direct	OSG	MSG	Total Indirect
Horse	Bit	0	.079	.079	.0009	.0000	.0009
Cross	Bridge	0	.079	.079	.0020	.0000	.0020
Fun	Camp	0	.079	.079	.0004	.0020	.0024
Fire	Chief	0	.079	.079	.0000	.0000	.0000
Smart	Expert	0	.079	.079	.0034	.0300	.0334
Smell	Flower	0	.079	.079	.0004	.0130	.0134
Beef	Ground	0	.079	.079	.0000	.0000	.0000
Think	Guess	0	.079	.079	.0011	.0050	.0061
Atom	Matter	0	.079	.079	.0010	.0003	.0013
Stove	Pot	0	.079	.079	.0156	.0143	.0299
Shoe	Toes	0	.079	.079	.0047	.0136	.0183
Clean	Dry	0	.076	.076	.0000	.0010	.0010
Sad	Alone	0	.081	.081	.0000	.0440	.0400
Agree	Argue	0	.081	.081	.0079	.0050	.0129
Poor	Broke	0	.081	.081	.0018	.0000	.0018
Box	Fight	0	.081	.081	.0000	.0000	.0000
Thin	Wide	0	.076	.076	.0546	.0396	.0942
Rice	Grain	0	.081	.081	.0077	.0000	.0077
Wrong	Guilty	0	.081	.081	.0008	.0040	.0048
Money	Lawyer	0	.081	.081	.0024	.0101	.0125

Note. FSG = direct forward strength.
BSG = direct backward strength.
OSG = indirect strength of overlaps.
MSG = indirect strength of mediators.

Table 23

Strength of Word Pairs Sharing a Weak Backward Association

Cue	Target	FSG	BSG	Total Direct	OSG	MSG	Total Indirect
Opener	Letter	0	.081	.081	.0000	.0000	.0000
Check	Claim	0	.078	.078	.0078	.0010	.0088
Push	Press	0	.078	.078	.0110	.0169	.0279
Justice	Truth	0	.082	.082	.0009	.0002	.0011
Weight	Mass	0	.083	.083	.0000	.0006	.0006
Fish	Marine	0	.078	.078	.0383	.0089	.0472
Tap	Pat	0	.081	.081	.0119	.0000	.0119
Trip	Fell	0	.083	.083	.0695	.0060	.0755
Round	Shape	0	.083	.083	.0168	.0105	.0273
Spot	Mark	0	.086	.086	.0039	.0090	.0129
Ice	Tea	0	.081	.081	.0014	.0000	.0014
Knife	Weapon	0	.075	.075	.0077	.0010	.0087
Busy	Active	0	.080	.080	.0020	.0000	.0020
Dance	Formal	0	.081	.081	.0014	.0140	.0154
Paper	File	0	.077	.077	.0000	.0260	.0260
Gold	Pure	0	.077	.077	.0000	.0015	.0015
Sound	Sight	0	.083	.083	.0000	.0013	.0013
Pencil	Draw	0	.084	.084	.0080	.0060	.0140
Ocean	Coast	0	.085	.085	.0388	.0430	.0818
Happy	Worry	0	.085	.085	.0176	.0237	.0413

Note. FSG = direct forward strength.
BSG = direct backward strength.
OSG = indirect strength of overlaps.
MSG = indirect strength of mediators.

Table 24

Strength of Word Pairs Sharing a Strong Forward Association

Cue	Target	FSG	BSG	Total Direct	OSG	MSG	Total Indirect
Artery	Heart	.273	0	.273	.0117	.0120	.0237
Birds	Fly	.320	0	.320	.0002	.0050	.0052
Basic	Simple	.203	0	.203	.0708	.0240	.0948
Decade	Ten	.338	0	.338	.0000	.0030	.0030
Dust	Dirt	.284	0	.284	.0092	.0030	.0122
Eyes	Blue	.257	0	.257	.0025	.0110	.0135
Bound	Tie	.235		.235	.0000	.0040	.0040
Gain	Weight	.260	0	.260	.0119	.0370	.0489
Harbor	Boat	.317	0	.317	.0319	.0480	.0798
Living	Dead	.255	0	.255	.0305	.0539	.0844
Pieces	Puzzle	.336	0	.336	.0006	.0000	.0006
Please	Thanks	.291	0	.291	.0008	.0006	.0014
Bone	Dog	.255	0	0.255	.0000	.0000	.0000
Snake	Bite	.279	0	.279	.0000	.0000	.0000
Suite	Hotel	.356	0	.356	.0272	.0000	.0272
Volume	Loud	.277	0	.277	.0124	.0265	.0389
Verse	Song	.231	0	.231	.0140	.0280	.0420
Spare	Extra	.270	0	.270	.0000	.0000	.0000
Cafe	Coffee	.324	0	.324	.0000	.0000	.0000
Trial	Court	.250	0	.250	.0265	.0864	.1129

Note. FSG = direct forward strength.
BSG = direct backward strength.
OSG = indirect strength of overlaps.
MSG = indirect strength of mediators.

Table 25

Strength of Word Pairs Sharing a Strong Forward Association

Cue	Target	FSG	BSG	Total Direct	OSG	MSG	Total Indirect
Beef	Cow	.291	0	.291	.0000	.0450	.0450
Fellow	Friend	.269	0	.269	.0049	.0450	.0499
Deal	Cards	.275	0	.275	.0045	.0000	.0045
Drama	Play	.283	0	.283	.0015	.0570	.0585
Duty	Job	.320	0	.320	.0469	.0250	.0719
Factor	Math	.279	0	.279	.0170	.0440	.0610
Fire	Hot	.285	0	.285	.0023	.0190	.0213
Games	Fun	.270	0	.270	.0132	.0290	.0422
Impact	Crash	.257	0	.257	.0438	.0087	.0525
Opera	Sing	.257	0	.257	.0170	.0169	.0339
Plant	Green	.256	0	.256	.0027	.0074	.0101
Race	Color	.254	0	.254	.0061	.0050	.0111
Sheet	Bed	.276	0	.276	.0004	.0075	.0079
Stars	Sky	.268	0	.268	.0012	.0066	.0078
Tissue	Paper	.285	0	.285	.0000	.0037	.0037
Root	Tree	.353	0	.353	.0000	.0305	.0305
Baker	Bread	.230	0	.230	.0032	.0050	.0082
Spread	Butter	.246	0	.246	.0047	.0139	.0186
Brown	Black	.338	0	.338	.0447	.0580	.1027
Buck	Dollar	.377	0	.377	.0449	.0080	.0529

Note. FSG = direct forward strength.
BSG = direct backward strength.
OSG = indirect strength of overlaps.
MSG = indirect strength of mediators.

Table 26

Strength of Word Pairs Sharing a Strong Backward Association

Cue	Target	FSG	BSG	Total Direct	OSG	MSG	Total Indirect
Heart	Artery	0	.273	.273	.0117	.0120	.0237
Fly	Birds	0	.320	.320	.0002	.0050	.0052
Simple	Basic	0	.203	.203	.0708	.0240	.0948
Ten	Decade	0	.338	.338	.0000	.0030	.0030
Dirt	Dust	0	.284	.284	.0092	.0030	.0122
Blue	Eyes	0	.257	.257	.0025	.0110	.0135
Tie	Bound	0	.235	.235	.0000	.0040	.0040
Weight	Gain	0	.260	.260	.0119	.0370	.0489
Boat	Harbor	0	.317	.317	.0319	.0480	.0798
Dead	Living	0	.255	.255	.0305	.0539	.0844
Puzzle	Pieces	0	.336	.336	.0006	.0000	.0006
Thanks	Please	0	.291	.291	.0008	.0006	.0014
Dog	Bone	0	.255	.255	.0000	.0000	.0000
Bite	Snake	0	.279	.279	.0000	.0000	.0000
Hotel	Suite	0	.356	.356	.0272	.0000	.0272
Loud	Volume	0	.277	.277	.0124	.0265	.0389
Song	Verse	0	.231	.231	.0140	.0280	.0420
Extra	Spare	0	.270	.270	.0000	.0000	.0000
Coffee	Cafe	0	.324	.324	.0000	.0000	.0000
Court	Trial	0	.250	.250	.0265	.0864	.1129

Note. FSG = direct forward strength.
BSG = direct backward strength.
OSG = indirect strength of overlaps.
MSG = indirect strength of mediators.

Table 27

Strength of Word Pairs Sharing a Strong Backward Association

Cue	Target	FSG	BSG	Total Direct	OSG	MSG	Total Indirect
Cow	Beef	0	.291	.291	.0000	.0450	.0450
Friend	Fellow	0	.269	.269	.0049	.0450	.0499
Cards	Deal	0	.275	.275	.0045	.0000	.0045
Play	Drama	0	.283	.283	.0015	.0570	.0585
Job	Duty	0	.320	.320	.0469	.0250	.0719
Math	Factor	0	.279	.279	.0170	.0440	.0610
Hot	Fire	0	.285	.285	.0023	.0190	.0213
Fun	Games	0	.270	.270	.0132	.0290	.0422
Crash	Impact	0	.257	.257	.0438	.0087	.0525
Sing	Opera	0	.257	.257	.0170	.0169	.0339
Green	Plant	0	.256	.256	.0027	.0074	.0101
Color	Race	0	.254	.254	.0061	.0050	.0111
Bed	Sheet	0	.276	.276	.0004	.0075	.0079
Sky	Stars	0	.268	.268	.0012	.0066	.0078
Paper	Tissue	0	.285	.285	.0000	.0037	.0037
Tree	Root	0	.353	.353	.0000	.0305	.0305
Bread	Baker	0	.230	.230	.0032	.0050	.0082
Butter	Spread	0	.246	.246	.0047	.0139	.0186
Black	Brown	0	.338	.338	.0447	.0580	.1027
Dollar	Buck	0	.377	.377	.0449	.0080	.0529

Note. FSG = direct forward strength.
BSG = direct backward strength.
OSG = indirect strength of overlaps.
MSG = indirect strength of mediators.

Appendix E: ANOVA Summary Tables

Table 28

Priming Analysis With Eye Movement Trials Included

Source of Variation	df	Sum of Squares	Mean Square	F	p
Strength	1	.627	.627	11.330	.001
Direction	2	.924	.462	8.351	.000
Direction x Strength	2	.359	.179	3.245	.041
Error	168	9.292	.05531		
Visual Field	1	.07046	.07046	2.796	.096
Visual Field x Strength	1	.04633	.04633	1.839	.177
Visual Field x Direction	2	.07737	.03869	1.535	.218
Visual Field x Strength x Direction	2	.02395	.01197	.475	.623
(VF) Error	168	4.234	.02520		

Table 29

Implicit Studied Pair Analysis With Eye Movement Trials Included

Source of Variation	df	Sum of Squares	Mean Square	F	p
Strength	1	229.850	229.850	41.182	.000
Direction	2	289.233	144.617	25.911	.000
Direction x Strength	2	87.917	43.958	7.876	.001
Error	168	937.660	5.581		
Visual Field	1	18.303	18.303	8.598	.004
Visual Field x Strength	1	9.286	9.286	4.362	.038
Visual Field x Direction	2	2.774	1.387	.652	.523
Visual Field x Strength x Direction	2	12.025	6.012	2.824	.062
(VF) Error	168	357.648	2.129		

Table 30

Implicit Unstudied Pair Analysis With Eye Movement Trials Included

Source of Variation	df	Sum of Squares	Mean Square	F	p
Strength	1	229.850	229.850	41.182	.000
Direction	2	289.233	144.617	25.911	.000
Direction x Strength	2	87.917	43.958	7.876	.001
Error	168	937.660	5.581		
Visual Field	1	18.303	18.303	8.598	.004
Visual Field x Strength	1	9.286	9.286	4.362	.038
Visual Field x Direction	2	2.774	1.387	.652	.523
Visual Field x Strength x Direction	2	12.025	6.012	2.824	.062
(VF) Error	168	357.648	2.129		

Table 31

Explicit Studied Pair Analysis With Eye Movement Trials Included

Source of Variation	df	Sum of Squares	Mean Square	F	p
Strength	1	309.410	309.410	57.203	.000
Direction	2	231.362	115.681	21.387	.000
Direction x Strength	2	156.714	78.357	14.487	.000
Error	168	908.702	5.409		
Visual Field	1	12.382	12.382	5.202	.024
Visual Field x Strength	1	2.050	2.050	.861	.355
Visual Field x Direction	2	3.522	1.761	.740	.479
Visual Field x Strength x Direction	2	4.623	2.312	.971	.381
(VF) Error	168	399.886	2.380		

Table 32

Priming Analysis With Eye Movement Trials Deleted

Source of Variation	df	Sum of Squares	Mean Square	F	p
Strength	1	.558	.558	9.764	.002
Direction	2	1.019	.509	8.919	.000
Direction x Strength	2	.383	.192	3.53	.037
Error	168	9.595	.05711		
Visual Field	1	.168	.168	7.177	.008
Visual Field x Strength	1	.01118	.01118	.477	.491
Visual Field x Direction	2	.05587	.02794	1.192	.306
Visual Field x Strength x Direction	2	.01087	.05435	.232	.793
(VF) Error	168	3.936	.02343		

Table 33

Implicit Studied Pair Analysis With Eye Movement Trials Deleted

Source of Variation	df	Sum of Squares	Mean Square	F	p
Strength	1	156.653	156.653	25.250	.000
Direction	2	198.312	99.156	15.982	.000
Direction x Strength	2	61.615	30.807	4.966	.008
Error	168	1042.294	6.204		
Visual Field	1	31.094	31.094	17.476	.000
Visual Field x Strength	1	3.583	3.583	2.014	.158
Visual Field x Direction	2	4.086	2.043	1.148	.320
Visual Field x Strength x Direction	2	5.556	2.778	1.561	.213
(VF) Error	168	298.915	1.779		

Table 34

Implicit Unstudied Pair Analysis With Eye Movement Trials Deleted

Source of Variation	df	Sum of Squares	Mean Square	F	p
Strength	1	32.028	32.028	47.637	.000
Direction	2	41.609	20.805	30.689	.000
Direction x Strength	2	14.536	7.268	11.246	.000
Error	168	118.517	.705		
Visual Field	1	1.849	1.849	3.316	.070
Visual Field x Strength	1	1.319	1.319	2.344	.128
Visual Field x Direction	2	6.605	3.302	5.938	.003
Visual Field x Strength x Direction	2	4.721	2.361	4.216	.016
(VF) Error	168	85.885	.511		

Table 35

Explicit Studied Pair Analysis With Eye Movement Trials Deleted

Source of Variation	df	Sum of Squares	Mean Square	F	p
Strength	1	191.002	191.002	22.998	.000
Direction	2	117.156	58.578	7.053	.001
Direction x Strength	2	114.481	57.240	6.892	.001
Error	168	1395.290	8.305		
Visual Field	1	8.841	8.841	3.705	.056
Visual Field x Strength	1	2.967	2.967	1.244	.266
Visual Field x Direction	2	8.331	4.165	1.746	.178
Visual Field x Strength x Direction	2	4.079	2.039	.855	.427
(VF) Error	168	400.859	2.386		

About the Author

Elizabeth Soety received a Bachelor's Degree in Psychology from the University of Florida in 1989 and a M.S. in Clinical Psychology from the University of Texas at Tyler in 1992. Prior to entering the University of South Florida's Clinical Psychology Ph.D. program in 1997, she worked in the private practice setting in Orlando, Florida and at the Neuropsychiatry Program at Western Psychiatric Institute in Pittsburgh, Pennsylvania.

While in the Ph.D. program at the University of South Florida, Mrs. Soety received specialized training in neuropsychology under the supervision of Cynthia R. Cimino, Ph.D., and was involved in a variety of research projects in the areas of cancer, stroke, Parkinson's disease, and dementia. Her master's and dissertation research involved exploring the right hemisphere's contribution to language processing.