I. The Synthesis and Spectroscopy of a Series of 1,3-Diaryl-1,3-cyclopentadiyls and 1,4-Diarylbicyclo[2.1.0]pentanes

II. Progress Toward the Synthesis of Non-Kekulé Naphthalene, a Series of Tetramethyleneethanes, and Bi(cyclobutadienyl)

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To ra loo ra loo ra loo

Acknowledgement

It is a truism that no scientific work is independently created. All those who have preceded our efforts with their own have helped to create the environment in which our work is done. Our thought process is shaped and guided by the things we study, and the things we study are the works of others. Likewise, a key article, an insightful explanation, or even an offhand remark at the right moment can cause the pieces of one's personal puzzle to fall into place and a greater picture to be revealed. It is often only in retrospect that the true value of any particular contribution can be appreciated; even intangibles such as a favorite piece of music or a friend's bad joke can be of inestimable worth. Therefore no list of acknowledgements will ever be complete. To those not named specifically below, my thanks to you for anything and everything you have done. I only hope that my (inadvertent) omissions can be forgiven. Then again, if Elvis isn't going to complain, should you?

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Abstract

1,4-Diarylbicyclo[2.1.0]pentanes **6-XY** were prepared from the corresponding diazenes by thermolysis. Variable temperature NMR reveals that *para* substituents have only small effects on the free energies of activation at coalescence in the bridge-flip reaction. The effects correlate with the Hammett parameters derived from the thermolysis of *para*-substituted dibenzyl mercurials, $\sigma_J^{\bullet}$. The reduced magnitude of substituent effects observed in these compounds was attributed to the incomplete formation of radical character at the transition state and to its cumyl radical nature.

1,3-Diaryl-1,3-cyclopentadiyls **7-XY** prepared by low-temperature photolysis of the same diazenes have triplet grounds states. The zfs parameter |*E*/hc| is constant for the series, indicating *para* substituents cause no substantial change in molecular symmetry. The zfs parameter |*D*/hc| correlates extremely well with the general Hammett parameter for *para* groups, σ_p, which allows the separation of observed |*D*/hc| values for bromine-containing members of the series into contributions from spin-orbit coupling and from inductive and resonance effects of the substituents. Spin-orbit coupling effects of the bromines on |*D*/hc| are small relative to the system's hyperfine couplings and estimated spin-orbit effects based on interactions without heavy atoms.

Phenylsulfonyl-containing members of this series undergo significant unimolecular decay at 77 K. The relative decay rates correlate well with a decrease in the exchange energy (as implied by smaller |*D*/hc| values), which decreases the singlet-triplet gap.

Linear free-energy relationships for these systems depend on both substituents present. A sum of the two individual substituent constants was used because each radical unit contributes equally to the observed properties. This is the first reported correlation of biradical properties with *para*-substituent effects determined in other systems.

Significant progress toward the syntheses of non-Kekulé naphthalene, a series of tetramethyleneethanes, and bi(cyclobutadienyl) was made. The reactivity of precursors to these compounds has been explored, and routes for future efforts have been charted.

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Chapter 1

The Synthesis and Spectroscopy of a Series of 1,3-Diaryl-1,3-cyclopentadiyls and 1,4-Diarylbicyclo[2.1.0]pentanes

Introduction

Organic systems with unpaired electrons are conventionally considered to be highly reactive species that are but intermediates on the paths of numerous photochemical and thermal processes.[1] Their study can offer insight into the fundamental chemical processes of bond formation and bond breakage. Due to their high reactivity, they are compounds whose preparation and study present considerable challenges.

In recent years, extended organic systems (such as polymers) with unpaired electrons have caught the interest of researchers as sources of new materials with unusual magnetic and electrical properties.[2] If the spins of the unpaired electrons can be made to align in a parallel fashion throughout the material, they would be ferromagnetically coupled and the organic substance might then exhibit magnetic properties typically only found in inorganic materials.

Before any attempt to rationally design an extended organic system with ferromagnetically coupled electrons can be made, a fundamental understanding of unpaired electrons in small, discrete organic systems must be obtained. The knowledge acquired can then be applied to the design of macromolecules with novel properties. The study of biradicals, molecules which have one bond fewer than allowed by the standard rules of valence,[3] offers opportunities to gain the insight necessary to give the design process a sound chemical foundation on which to build.

A biradical can have its two unpaired electrons aligned with the spins antiparallel (S = 0, the singlet) or with the spins parallel (S = 1, the triplet). It is therefore the triplet state which has ferromagnetically coupled electrons. A thorough understanding of what effects cause two electrons to couple ferromagnetically must be obtained before one can expect to be able to design a system with a large number of unpaired, ferromagnetically coupled, electrons.

Biradicals can be divided into two classes, delocalized, in which the unpaired electrons are in classical π conjugation,[4] and localized, in which the unpaired electrons are not in

classical π conjugation.[5] It is important to note that localized biradicals can have delocalizing substituents, *i.e.*, the radical centers themselves may be part of a classical π system, such as allyl or benzyl. Delocalized biradicals are the main focus of Chapter 2; the discussion here is tailored toward localized biradicals.

A biradical can be defined in valence bond terms as a molecule with an even number of electrons with two distinct radical centers. In their seminal work on the theoretical description of biradicals,[1fg] Salem and Rowland described the orbital properties of such a system when the radical centers were two homosymmetric *p* orbitals, which is when the *p* orbitals are related by a symmetry axis or plane (Figure 1-1a). From these *p* orbitals, two formally non-bonding molecular orbitals (NBMOs) can be constructed (Figure 1-1b). The in-phase combination (appropriately weighted by overlap and normalization factors) is symmetric with respect to the mirror plane passing between the *p* orbitals and will be the source of bonding interactions between the radical centers. The out-of-phase combination, (also appropriately weighted by overlap and normalization factors) is antisymmetric with respect to the mirror plane passing between the *p* orbitals and will be the source of anti-bonding interactions between the radical centers. When the overlap between the centers is zero, the two NBMOs are degenerate. From this arises the definition of a biradical in molecular orbital terminology as a molecule which has two electrons in two degenerate (or nearly degenerate) NBMOs.[1fg]

The analysis by Salem and Rowland continued by assessing the covalent and ionic contributions to the triplet and singlet states. Because the spins in a triplet are parallel, they will not be found in the same orbital (Pauli exclusion principle).[6] The triplet is therefore best described by a purely covalent wavefunction. Because the spins in a singlet are anti-parallel, the electrons can be found in the same orbital and ionic terms contribute. Some ionic character is present in the singlet whenever there is non-zero overlap between the radical centers. However, when the overlap between the two radical centers is zero, a purely covalent wavefunction describes the situation well. In the case of zero overlap,

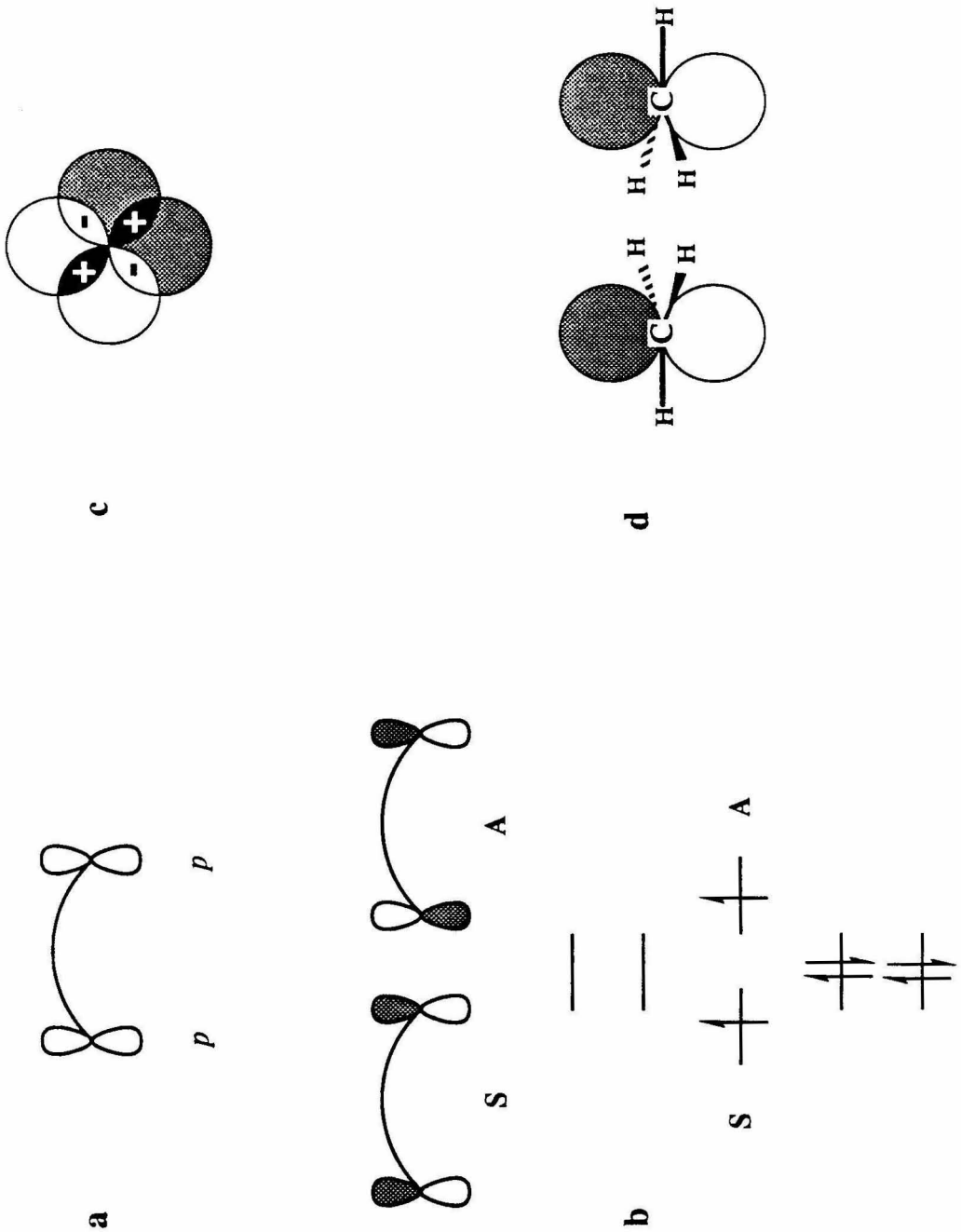


Figure 1-1: Orbital representations and models of homosymmetric biradicals.

which is the usual situation for biradicals, the ionic terms are too energetically unfavorable to contribute significantly to the singlet wavefunction. For this reason, the ionic states are typically omitted in discussions of the chemically relevant states of homosymmetric biradicals.[1fg,7]

Large overlap between the radical centers corresponds to strong bonding interactions and a lower energy of the symmetric combination of *p* orbitals, which lifts the degeneracy of the NBMOs and favors the singlet. One key to achieving a biradical with a triplet ground state is reduction of overlap.[8,9] When overlap is zero or nearly so, the NBMOs are degenerate and exchange energy makes the triplet configuration more favorable.

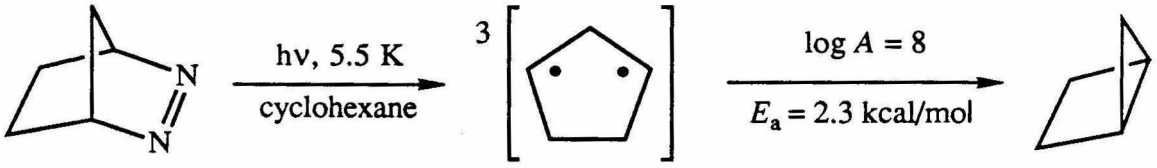
The other key to a triplet ground state is to maximize exchange interactions.[8,10] This can be accomplished by keeping the radical centers close together (in the exchange operator, the distance between the electrons appears in the denominator). Because the spatial portion of the wavefunction for a singlet is symmetric, the sign of the exchange integral is positive, and exchange energy is added to the overall energy of the singlet. The spatial portion of a triplet wavefunction is antisymmetric, the sign of the exchange intergral is negative, and exchange energy is subtracted from the overall energy of the triplet.

At first inspection, the two keys seem to be in contradiction: the minimization of overlap generally requires an increased separation between the radical centers, and maximization of exchange requires the radical centers to be in close proximity. One way in which this can be overcome is shown in Figure 1-1c. If two *p* orbitals are on the same atomic center, they have large overlap, but the overlap integral is zero because the overlap between regions of positive and negative spin density cancels. The exchange interactions are large because the orbitals are spatially coextensive. For this reason, methylene and most simple carbenes have triplet ground states.[11] The balance of interactions in this system can be construed as the physical underpinning of Hund's rule.

In contrast, when two *p* orbitals on two isolated atomic centers (such as two methyl radicals; Figure 1-1d) interact in a π fashion, the singlet is the ground state at all

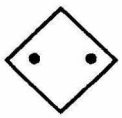
internuclear separations.[8] This is primarily an indication of the tendency of through-space effects to stabilize bonding interactions. For example, at a distance of 2.1 Å, there is large overlap between the two methyl radicals (a π bond), and the singlet lies 15 kcal/mol below the triplet. The exchange interactions present in this system clearly do not overcome this large singlet preference.

Buchwalter and Closs were the first to experimentally show that the interactions of two localized radical centers can lead to a biradical with a triplet ground state. 1,3-Cyclopentadiyl **1** was generated from the corresponding diazene by photolysis at cryogenic temperatures in frozen organic matrices and was determined to have a triplet ground state.[12] **1** decays *via* heavy-atom tunnelling to bicyclo[2.1.0]pentane with an activation energy of 2.3 kcal/mol. *Ab initio* studies placed the singlet-triplet gap at 900 cal/mol (calculated at the planar geometry) and found the distance between the radical centers to be 2.37 Å.[7]

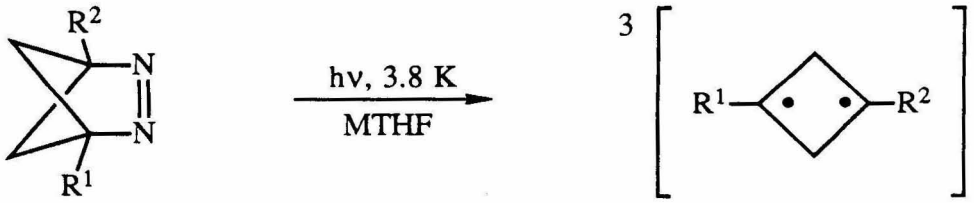


1

These results were followed by *ab initio* studies on 1,3-cyclobutadiyl **2** by Goldberg and Dougherty.[8] **2**, which has a distance of 2.11 Å between the radical centers, was calculated to have a triplet ground state with a singlet-triplet gap of 1.7 kcal/mol, roughly twice that of **1**. However, 1,3-cyclobutadiyl could not be observed by electron paramagnetic resonance (EPR) spectroscopy.[13] This has since been determined to be due to the very short triplet lifetimes of 1,3-cyclobutadiyl, which tunnels to the singlet state too rapidly to be observed.[14]



2



R^1, R^2 = Me, Et, Ph, CH_2=CH- **3**

Success was achieved in observing 1,3-disubstituted-1,3-cyclobutadiyls **3**.[5,15] These compounds have triplet ground states and decay to bicyclobutanes. Substitution of alkyl groups at the radical centers increases the mass of the tunnelling moieties , which slows the tunnelling rate, increases the lifetime of the triplet, and allows the EPR observation of the biradicals. The ring-closure activation energies for these compounds are less than the singlet-triplet gaps. Substitution of delocalizing groups (vinyl and phenyl) at the radical centers stabilizes the radicals, shuts down the tunnelling mechanism, and causes more conventional thermal (Arrhenius) behavior. The ring-closure activation energies for the vinyl- and phenyl-substituted biradicals are greater than the singlet-triplet gaps.

The interactions of two methyl radicals do not explain these results, but a model which also takes into account through-bond coupling does (Figure 1-2).[8] The 1,3-trimethylene unit in cyclopentadiyls and cyclobutadiyls is a homosymmetric biradical. The two *p* orbitals can be combined in-phase and out-of-phase to form, respectively, a symmetric orbital (S) and an antisymmetric orbital (A) with respect to the mirror-plane separating them. These radical orbitals, S and A, will have higher energies than the fully bonding π-CH_2 orbitals, and the S orbital will have a lower energy than the A (the through-space effect). Only the S combination has the proper symmetry to mix with the π-CH_2 orbitals.

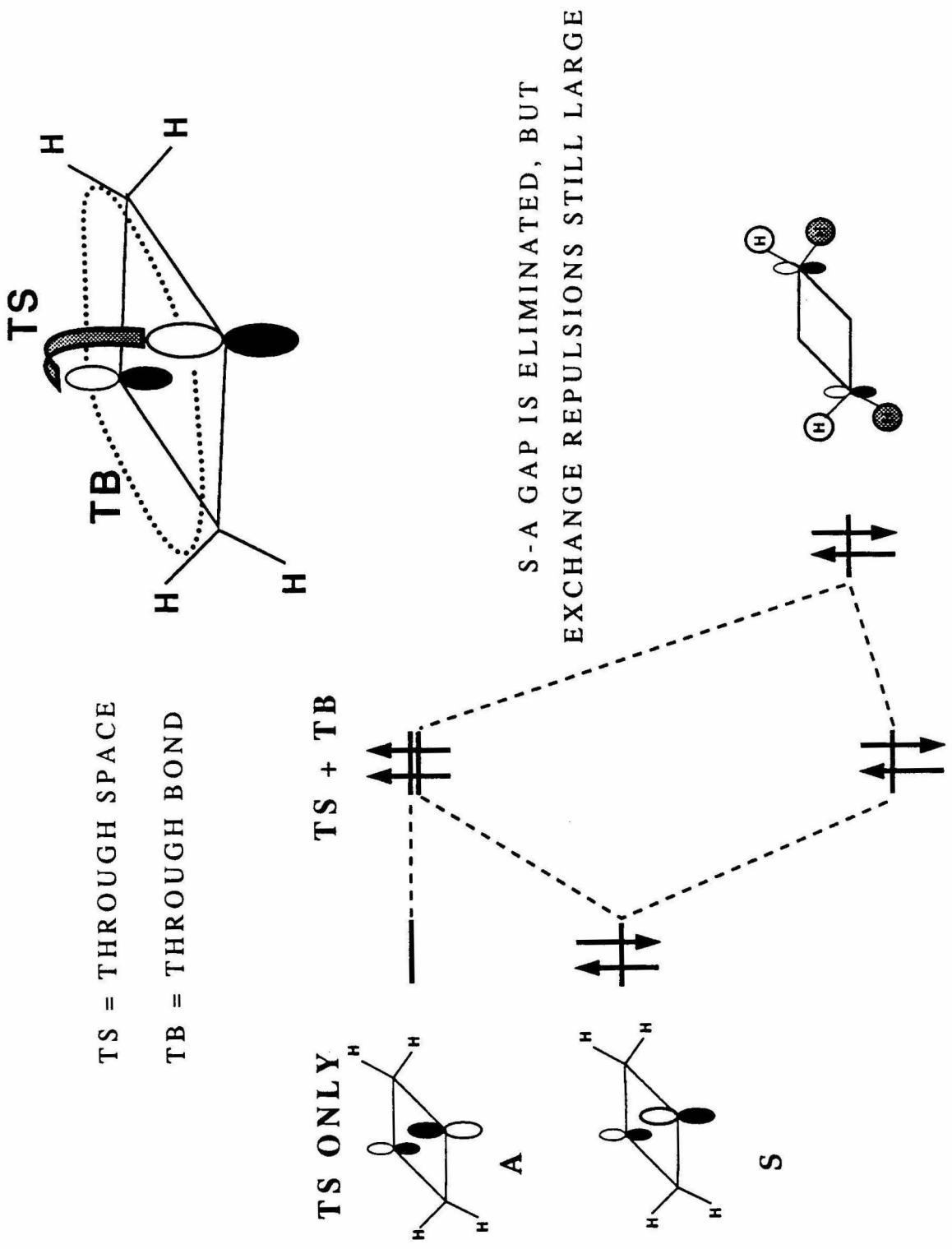


Figure 1-2: Through-bond and through-space effects in 1,3-cyclobutadiyls and 1,3-cyclopentadiyls.

This mixing lowers the energy of the π-CH_2 orbitals and raises the energy of the S combination to a point where it is degenerate or nearly degenerate with the A combination. The degeneracy (or near-degeneracy) of the S and A orbitals allows the exchange interactions to dominate and thereby causes the triplet to be the ground state. The greater singlet-triplet gap in cyclobutadiyls relative to cyclopentadiyls (about double) can be attributed to the presence of two through-bond coupling units rather than one.

The effect of stabilizing substituents which causes the change in ring-closure mechanism from tunnelling to Arrhenius behavior in the 1,3-cyclobutadiyl system can be explained by examining the diagrams in Figure 1-3.[15] In the absence of stabilizing groups, a singlet biradical is not expected to be a true intermediate on the singlet surface but only, in effect, a transition state.[1fg] No energy well is expected on the singlet surface (recent work[14] contradicts this notion, but the arguments also apply if a shallow well exists on the singlet surface). The stability of a triplet biradical is primarily due to the spin-forbiddenness of ring closure. Intersystem crossing requires a near degeneracy of the singlet (S) and triplet (T) surfaces, which is brought about by geometric distortion. Hence the transition state for surface crossing is approximated by the S-T crossing point. The activation energy for ring closure will be less than the singlet-triplet gap, and a narrow barrier results.

In all tunnelling models, barrier width is the most important parameter. Narrow barriers facilitate tunnelling, wide barriers make tunnelling infeasible. Introduction of stabilizing substituents at the radical centers introduces an energy well (or deepens an existing well) on the singlet surface and would be expected to deepen the well on the triplet surface to a similar extent. The S-T crossing-point moves to a different position and the barrier width becomes too wide for tunnelling. In this way, the activation energy also becomes greater than the singlet-triplet gap.

The understanding gained from these models of 1,3-disubstituted-1,3-cyclobutadiyl behavior was applied to the cyclopentadiyl system. **1** had been found to be unstable at all temperatures;[12] tunnelling is very efficient. Simple methyl substitutions led to compounds

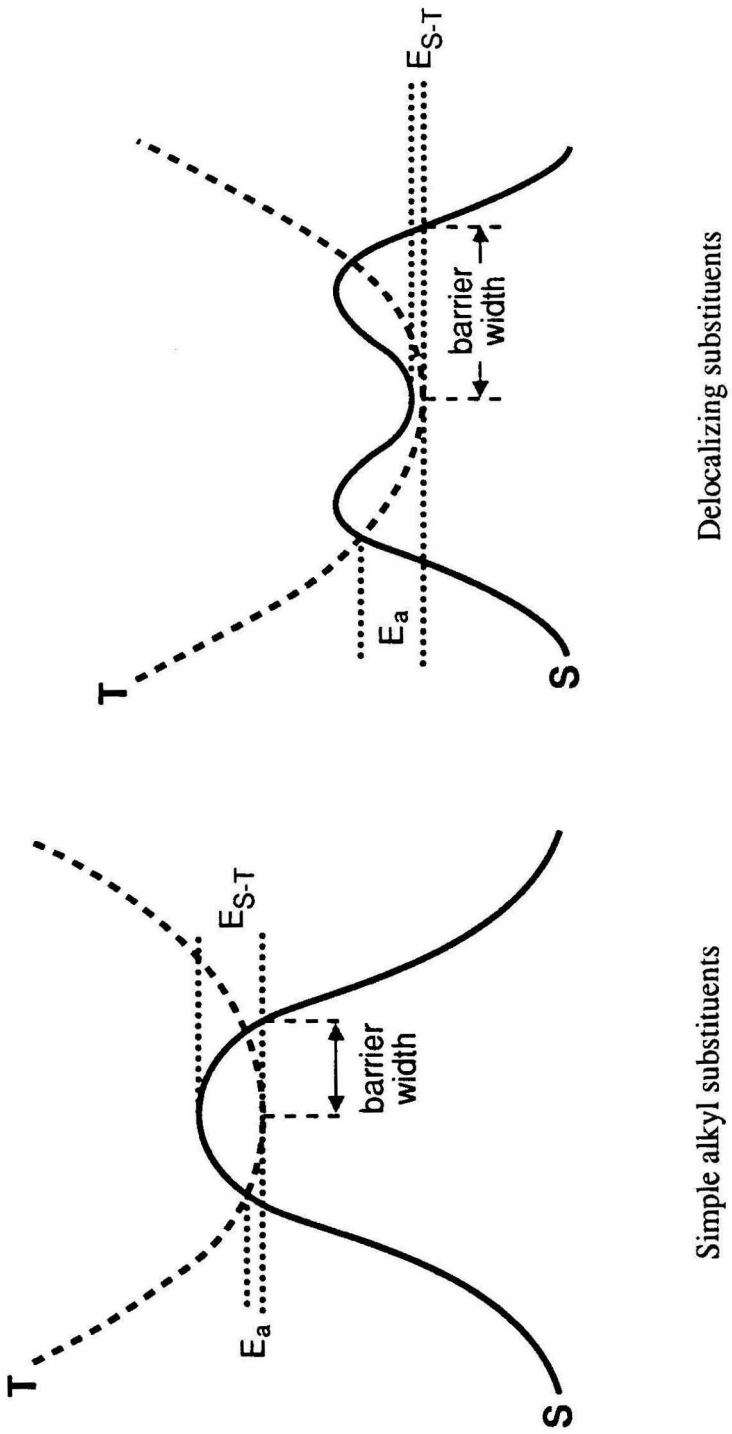
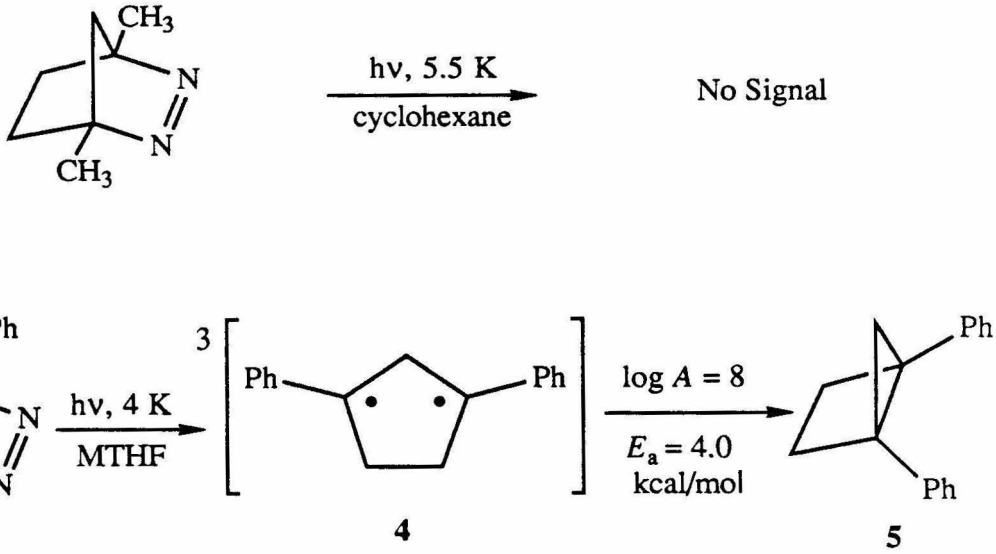


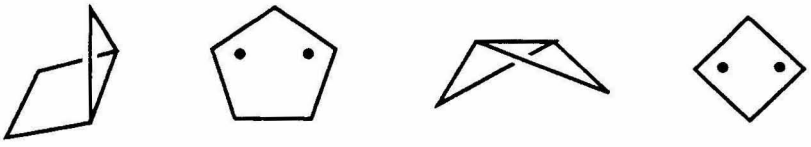
Figure 1-3: Effect of substituents on 1,3-cyclobutadiyl decay mechanisms.

that gave weak or no EPR signals,[12] and therefore the cyclopentadiyl framework appeared too sensitive to substitution to allow for comprehensive examination of substituent effects.



However, upon the introduction of phenyl groups into the cyclopentadiyl system, Coms and Dougherty observed tremendous changes.[16] 1,3-Diphenyl-1,3-cyclopentadiyl **4** was found to be a biradical with a triplet ground state which is stable at 77 K. In contrast, 1,3-diphenyl-1,3-cyclobutadiyl (**3**, $R^1 = R^2 = Ph$) is only marginally observable at 60 K.[17] As in the cyclobutadiyl system, the phenyl groups shut down the tunnelling mechanism. **4** decays to 1,4-diphenylbicyclo[2.1.0]pentane **5** with an activation energy of 4.0 kcal/mol.

The increased stability of **4** relative to 1,3-diphenyl-1,3-cyclobutadiyl was ascribed primarily to the differences in ring strain present in the two systems. Bicyclo[2.1.0]-pentane has a strain energy of 55 kcal/mol and **1** has a strain energy of only 5 kcal/mol.[18] By comparison, bicyclobutane has a strain energy of 64 kcal/mol, and **2** has a strain energy of 25 kcal/mol.[17] Thus there is 11 kcal/mol less driving force for reaction in the cyclo-pentadiyl system than in the cyclobutadiyl system. Undoubtedly the greater distance between the radical centers and greater geometric distortions required to achieve ring closure also contribute.[17]

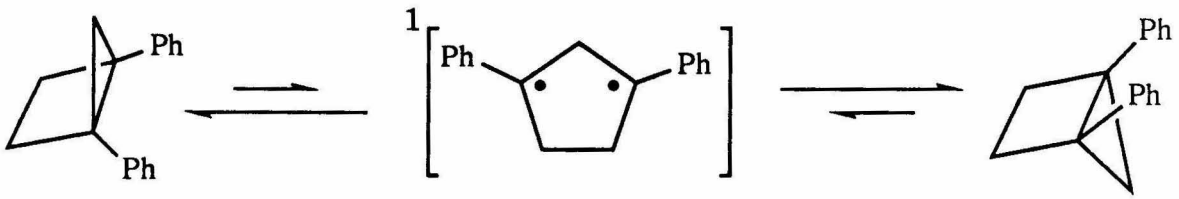


1 **2**

Strain energies (kcal/mol):

55	5	64	35

Figure 1-4 shows the EPR spectrum of **4**, which was thoroughly studied.[16,17,19] This system proved to be unique because both the triplet and the singlet states were readily accessible to experimental examination. A complete lineshape dynamic nuclear magnetic resonance spectroscopy (NMR) analysis and a magnetization transfer study were performed on the bridge-flip reaction of its closed-shell isomer **5**. This molecule was found to have a bridgehead carbon-bridgehead carbon bond with a strength of no more than 12 kcal/mol.



5 **4**

With these results before us, we found ourselves presented with an ideal opportunity to conduct a kind of study that had not been previously performed on biradical systems. The 1,3-diaryl-1,3-cyclopentadiyl/1,4-diarylbicyclo[2.1.0]pentane system provides a way to evaluate the effects of *para* substituents on both the singlet and triplet states of a biradical system. Both states are readily accessible: 77 K EPR studies of the triplet, dynamic NMR studies of the singlet near 100 °C. How would *para* substituents affect the singlet-triplet gap and the kinetic stability of triplet **4**? How would they affect the strength of the

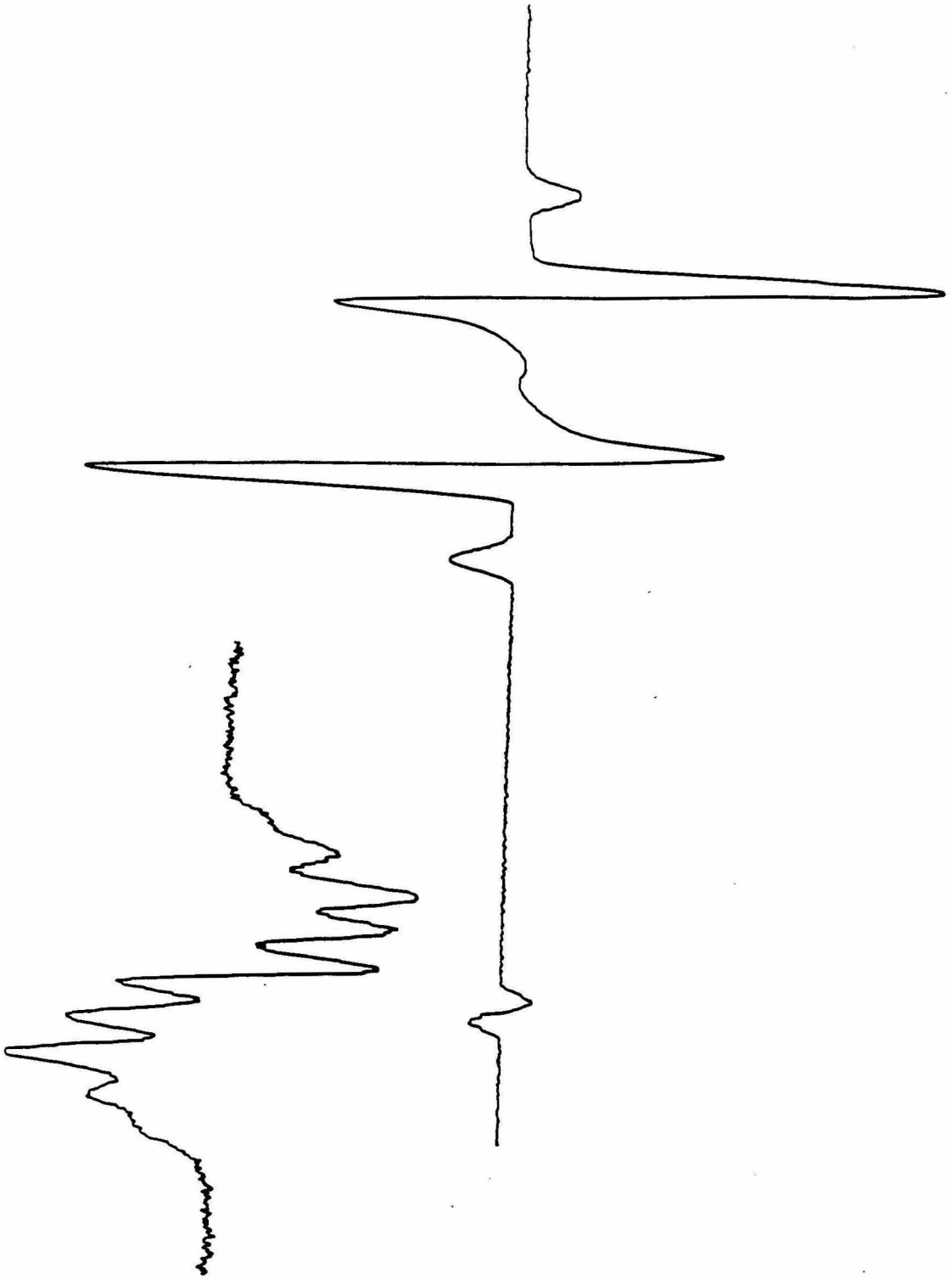
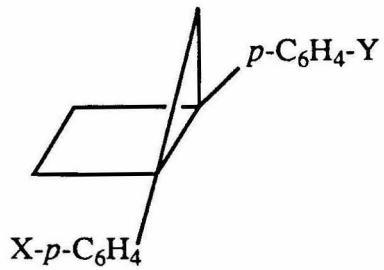
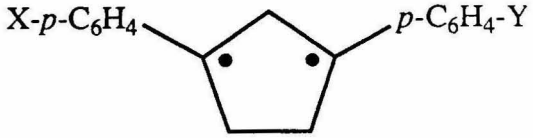


Figure 1-4: EPR of **4**; $|D/hc| = 0.045\ cm^{-1}$, $|E/hc| = 0.001\ cm^{-1}$.

bridgehead carbon-bridgehead carbon bond in **5**? Are the effects of substituents in closed-shell and monoradical species applicable to biradical species? If so, which property correlates with which substituent constant? The answers to these questions are of interest at a basic level, as well as from the standpoint of being better able to engineer novel organic materials.



6-XY



7-XY

Label	X	Y
6-MeMe	Me	Me
6-MeOMeO	MeO	MeO
6-BrBr	Br	Br
6-MePhSO$_2$	Me	PhSO$_2$
6-MeOPhSO$_2$	MeO	PhSO$_2$
6-PhSO$_2$PhSO$_2$	PhSO$_2$	PhSO$_2$

Label	X	Y
7-MeMe	Me	Me
7-MeOMeO	MeO	MeO
7-BrBr	Br	Br
7-MePhSO$_2$	Me	PhSO$_2$
7-MeOPhSO$_2$	MeO	PhSO$_2$
7-PhSO$_2$PhSO$_2$	PhSO$_2$	PhSO$_2$
7-MeBr	Me	Br
7-MeOBr	MeO	Br

By examining the free energies of activation of the bridge-flip reaction of 1,4-diaryl-bicyclo[2.1.0]pentanes **6-XY** and the triplet EPR of 1,3-diaryl-1,3-cyclopentadiyls **7-XY**, we have been able to compile data which answer these questions and that have allowed the construction of linear free-energy relationships, a classical tool of physical organic chemistry which relates structure and reactivity.[20] We chose as *para* substituents for study the strongly electron-donating methoxy (donation of a lone pair from oxygen), the weakly electron-donating methyl (donation by hyperconjugation), the weakly electron-withdrawing bromine (donation of a lone pair, but electronegative), and the strongly

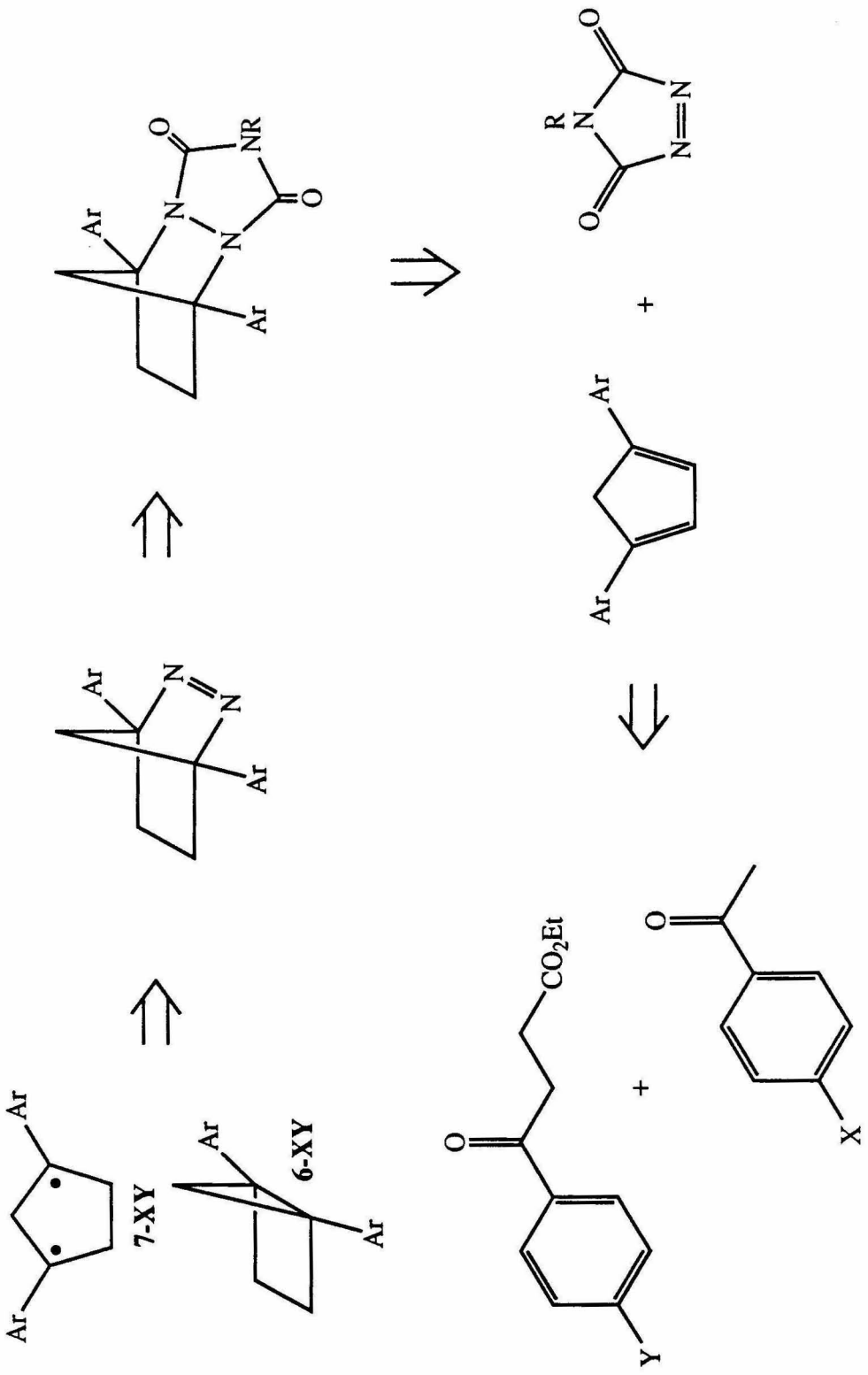
electron-withdrawing phenylsulfonyl group (which acts primarily through inductive, not resonance effects[21]).

Synthesis and Discussion

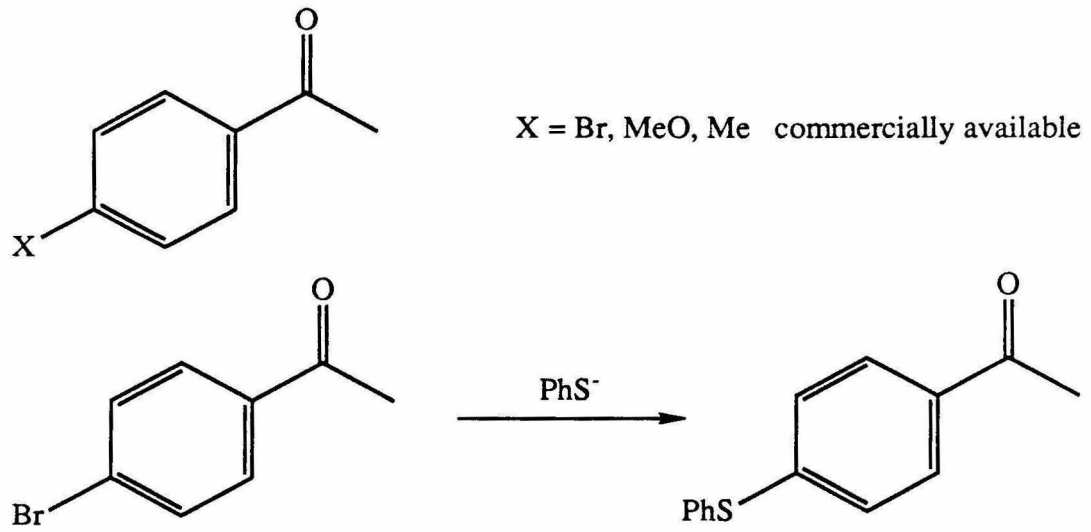
A retrosynthetic overview of the preparations of 1,3-diaryl-1,3-cyclopentadiyls **7-XY** and 1,4-diarylbicyclo[2.1.0]pentanes **6-XY** is outlined in Scheme 1-1. The analysis is based on the preparations[16,17] of **4** and **5**; the steps are discussed in detail below. The bicyclopentanes can be prepared by thermolysis of a diazene precursor; the cyclopentadiyls can be produced by photolysis of the same diazenes. Diazenes are readily obtained from urazoles by hydrolysis or hydrazinolysis followed by oxidation. The urazoles are available from the Diels-Alder cycloadditon of N-substituted 1,2,4-triazoline-3,5-diones with 1,4-diaryl-1,3-cyclopentadienes, followed by reduction of the double bond. The cyclopentadienes can be produced by condensing *para*-substituted acetophenones and β–benzoyl-propionate esters.

The *para*-methoxy-, bromo-, and methylacetophenones are commercially available.[22] *p*-Methylacetophenone comes as a wet and discolored mixture of compounds. Distillation at atmospheric pressure under argon provided *p*-methylacetophenone in a 9:1 mixture with the *ortho* isomer. The mixture of acetophenones was reacted with semicarbazide hydrochloride, and the semicarbazone mixture obtained was repeatedly recrystallized from water.[23] The acetophenones were regenerated by acidic hydrolysis. NMR and gas chromatography/mass spectroscopy (GCMS) revealed a 24:1 ratio of *para* to *ortho* isomers. Final purification of the *para* isomer was accomplished by recrystallization from pentane-dichloromethane at -78 °C[24] (100% pure by GCMS). Displacement of bromide from *p*-bromoacetophenone by thiophenoxide anion generated from thiophenol and potassium hydroxide provided *p*-thiophenoxyacetophenone in good yield (Scheme 1-2).[25]

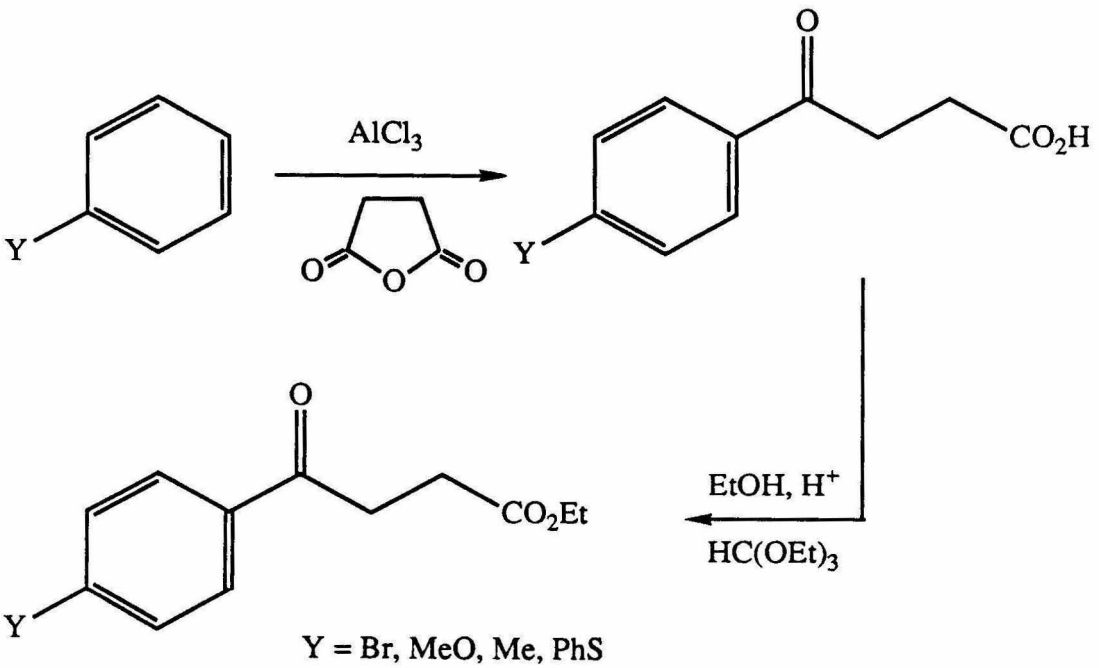
Scheme 1-1



Scheme 1-2

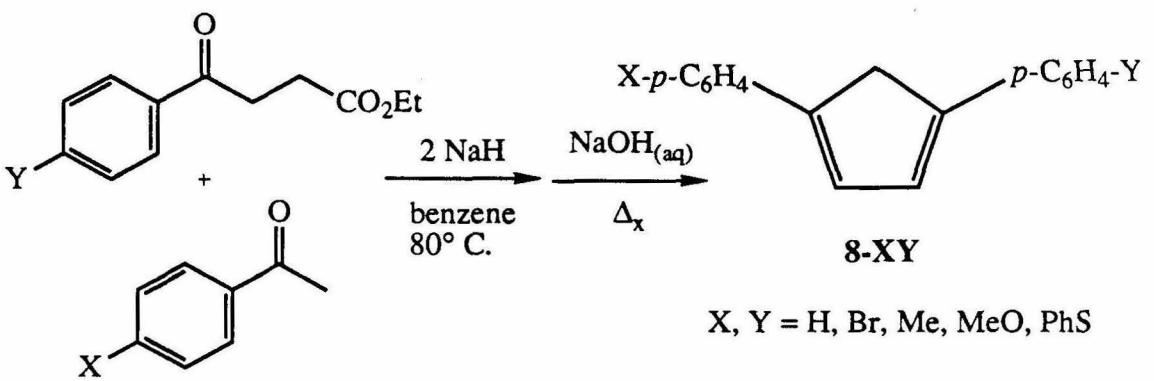


Scheme 1-3



The *para*-substituted β–benzoylpropionate esters were readily obtained by the methodology in Scheme 1-3. Friedel-Crafts acylation of the appropriate benzene derivatives with succinic anhydride and aluminum trichloride affords the propionic acids.[26] These were esterified by acid-catalyzed reaction with ethanol and triethylorthoformate.

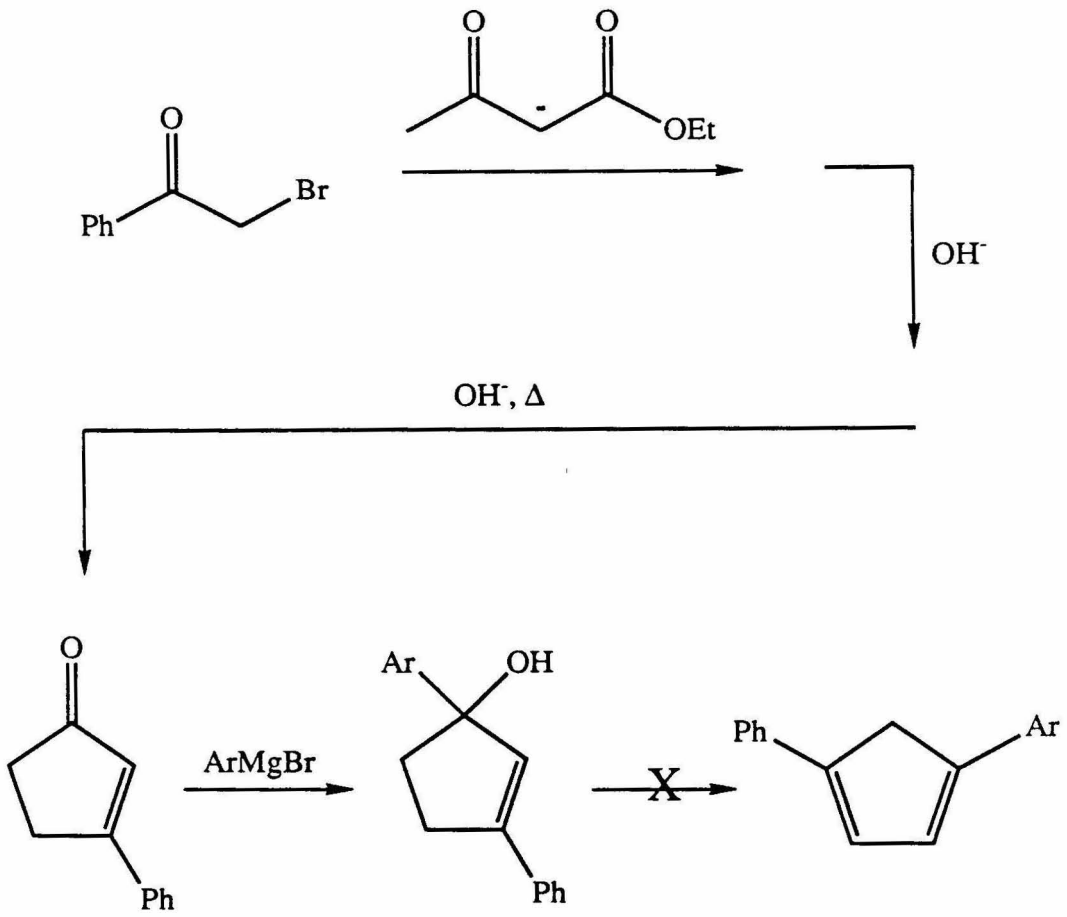
The reaction which produces the 1,4-diaryl-1,3-cyclopentadienes **8-XY** occurs under harsh conditions and is sensitive to changes in the reactants.[27] Electron-donating substituents and weakly electron-withdrawing substituents on the acetophenones and esters are tolerated, strongly electron-withdrawing substituents are not.[27d] This sensitivity was also verified in this laboratory (*e.g.*, *p*-nitro-acetopheneone does not react successfully).



This reaction is virtually the only useful route to these compounds. Alternatives, such as the one illustrated in Scheme 1-4, have failed for previous researchers.[27d] These factors exerted a profound influence on our choice of substituents and on the methods and timing of their introduction. (See Appendix A for a discussion of another route and for the details of efforts to prepare diarylcyclopentadienes and urazoles functionalized differently from those discussed in this chapter.)

A plausible mechanism which leads to the desired product is shown in Scheme 1-5.[27cd] The first step is deprotonation α to the ester, then the anion produced undergoes condensation with the acetophenone. Dehydration produces a new set of protons whose acidity is due to the ester functionality, and another deprotonation-condensation-dehydration

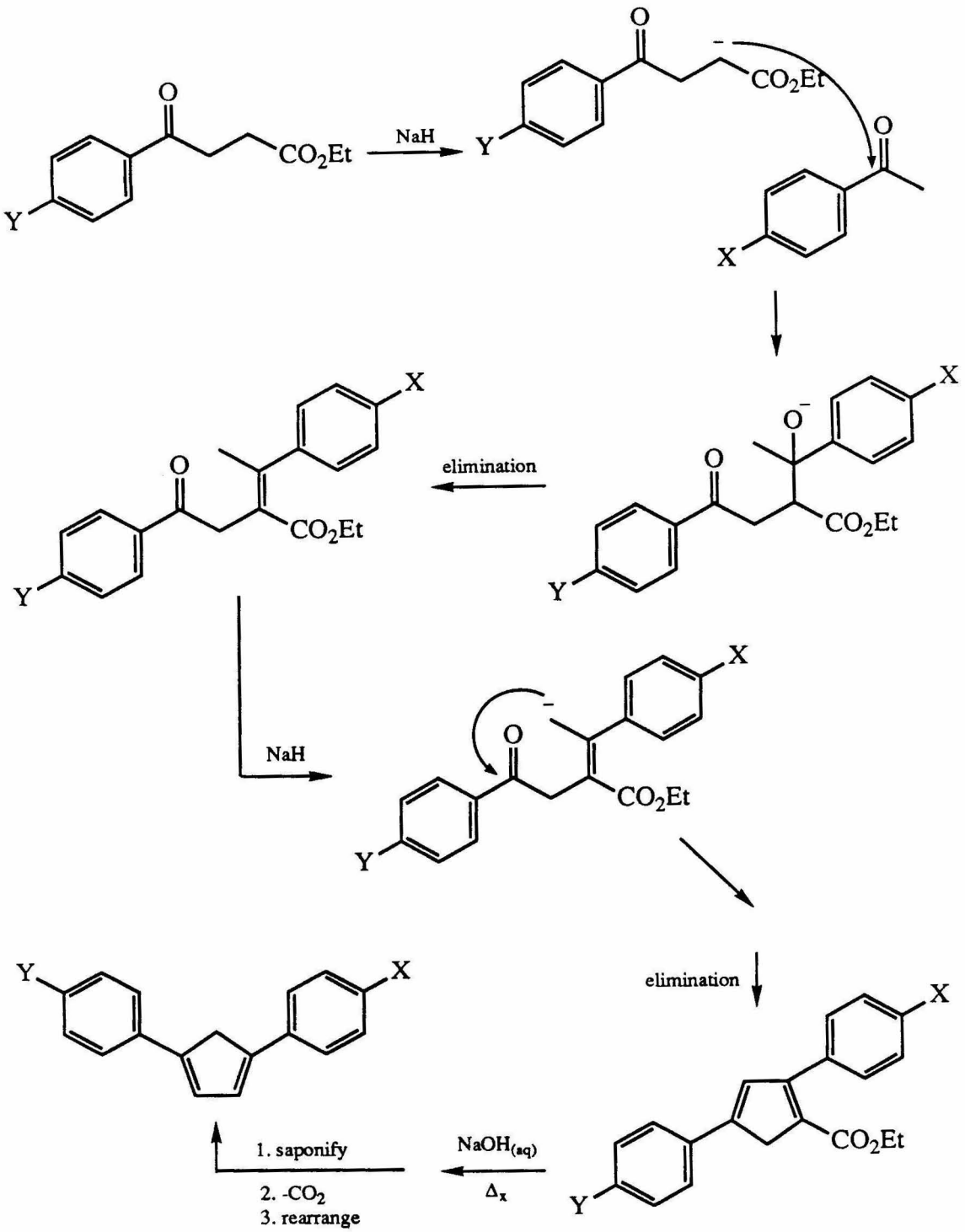
Scheme 1-4



sequence provides the ring-closed ester derivative. Reflux with concentrated aqueous base saponifies the ester, induces decarboxylation, and rearranges the diarylcyclopentadiene to the most stable, fully conjugated, form.

There are three different carbonyl moieties and a strong base involved; this produces a complex and counterintuitive interplay of acidities. Normally, protons α to ketones are more acidic than those α to esters.[28] In these cases, that greater acidity should be enhanced by the presence of the phenyl rings, even though they are only cross-conjugated with the position of the acidic ketone protons.[29] Clearly, however, deprotonation α to the ester and

Scheme 1-5


NaH
elimination
NaH
elimination
NaOH(aq)
Δx
1. saponify
2. -CO2
3. rearrange

subsequent nucleophilic attack of the anion so formed on the acetophenone carbonyl are at least kinetically favored. The effect of strongly electron-withdrawing substituents may then be rationalized as increasing the acidities of the protons α to the acetophenone carbonyls to the point where proton transfer to the anion α to the ester dominates or to the point where that anion is no longer formed (deprotonation occurs exclusively α to the acetophenone carbonyls).[27d] The ready availablility of competing, non-produtive, reaction paths may help explain the relatively low yields (which generally range from 15 to 30%).

Using the methodology of Greifenstein, *et al.*,[27d] in which two equivalents of sodium hydride in refluxing benzene are used, one sees immediate gas evolution upon mixing of the reagents. About two hours after completion of the first gas evolution phase, a second one ensues. The reaction changes from an initially clear yellow (or orange) solution to a progressively darker brown, inhomogeneous mixture. The inhomogeneity is due to a viscous dark brown oil. Ironically, the absence of this oil is almost a sure sign that the reaction failed. By starting with eight to ten grams of both the acetophenone and the ester, one to three grams of product cyclopentadiene can be obtained.

Diels-Alder cycloaddition and hydrogenation of a double bond constitute a two-step sequence which is usually expected to produce high yields of product in a straightforward manner. The 1,4-diaryl-1,3-cyclopentadiene system is not, however, a typical Diels-Alder diene moiety. It is sufficiently sterically hindered to resist undergoing cycloaddition with itself, unlike unsubstituted cyclopentadiene. Cycloaddition of diarylcyclopentadienes also requires the unfavorable interruption of extended systems of π conjugation. Lastly, the 1,4-diaryl-1,3-cyclopentadienes are rigid, high-melting solids which are only sparingly soluble in many organic solvents. *Para*-substitution generally detracts from their solubility. For example, the parent **8-HH** is soluble in hexanes, but **8-MeMe** is not to any useful extent.

Nor are the N-substituted 1,2,4-triazoline-3,5-diones typical Diels-Alder dienophiles. They decompose in polar solvents[30] and readily undergo 1,4-addition (they are potent

Michael acceptors).[30b,31] However, weaker dienophiles, such as diethyl azodicarboxylate,[27b] dimethyl azodicarboxylate, and di(2,2,2-trichloroethyl) azodicarboxylate, would not react with the 1,4-diaryl-1,3-cyclopentadienes.

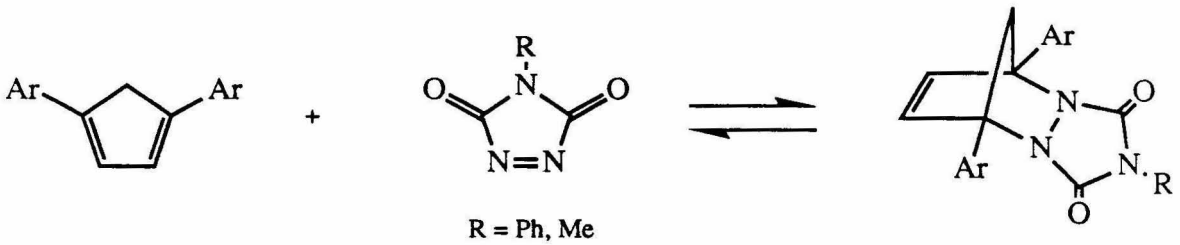
Once cycloaddition is accomplished, two more problems are encountered.[17] The adducts readily undergo retro-Diels-Alder reaction in polar solvents, which are the only type in which they are soluble. The adducts are also subject to hydrogenolysis of the bridgehead carbon-nitrogen bond when catalytic hydrogenation is used to reduce the double bond.

The overall situation is that summarized in Scheme 1-6. The Diels-Alder reaction between the diarylcyclopentadiene and triazolinedione is an equilibrium reaction which can be forced to completion by the addition of excess triazolinedione. In the polar solvents necessary to dissolve the adduct for reduction of the double bond, the Diels-Alder adduct begins to dissociate back to diarylcyclopentadiene and triazolinedione. This effect is worsened because the diarylcyclopentadiene is typically only sparingly soluble and begins to precipitate, the triazolinedione decomposes in polar solvents, and catalytic hydrogenation reduces the diarylcyclopentadiene to the diarylcyclopentane and the triazolinedione to the N-substituted urazole. All three factors siphon away reactants and shift the equilibrium to the left, which, by Le Chatlier's principle, causes even more adduct to dissociate. Hydrogenolysis of the bridgehead carbon-nitrogen bond in both the reduced and unreduced adducts serves to further reduce yields.

The outcome is a complex mixture of compounds from which the desired reduced adduct urazole can only be isolated after difficult and exacting flash column chromatography. The reported yield for this sequence (Scheme 1-7) performed on **8-HH** with MTAD and 5% Rh/Al_2O_3 catalyst[32] under three atmospheres of hydrogen gas in weakly acidified ethyl acetate at 0 °C is 67%.[17] For the di(4-bromophenyl) and di(4-methoxyphenyl) derivatives under the same conditions, yields were about one-third to one-half that

amount (≈20-35%). The reduced yields are due, at least in part, to the significantly lower solubility of the *para*-substituted species.

Scheme 1-6

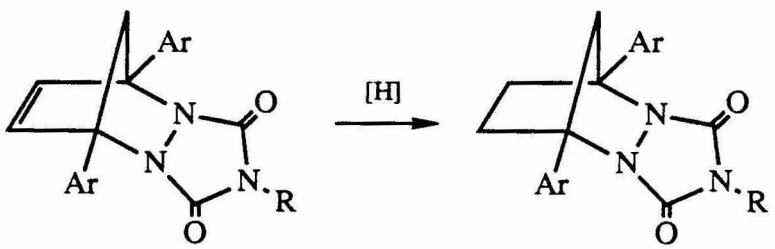


stable, sterically hindered diene

decomposes in polar solvents

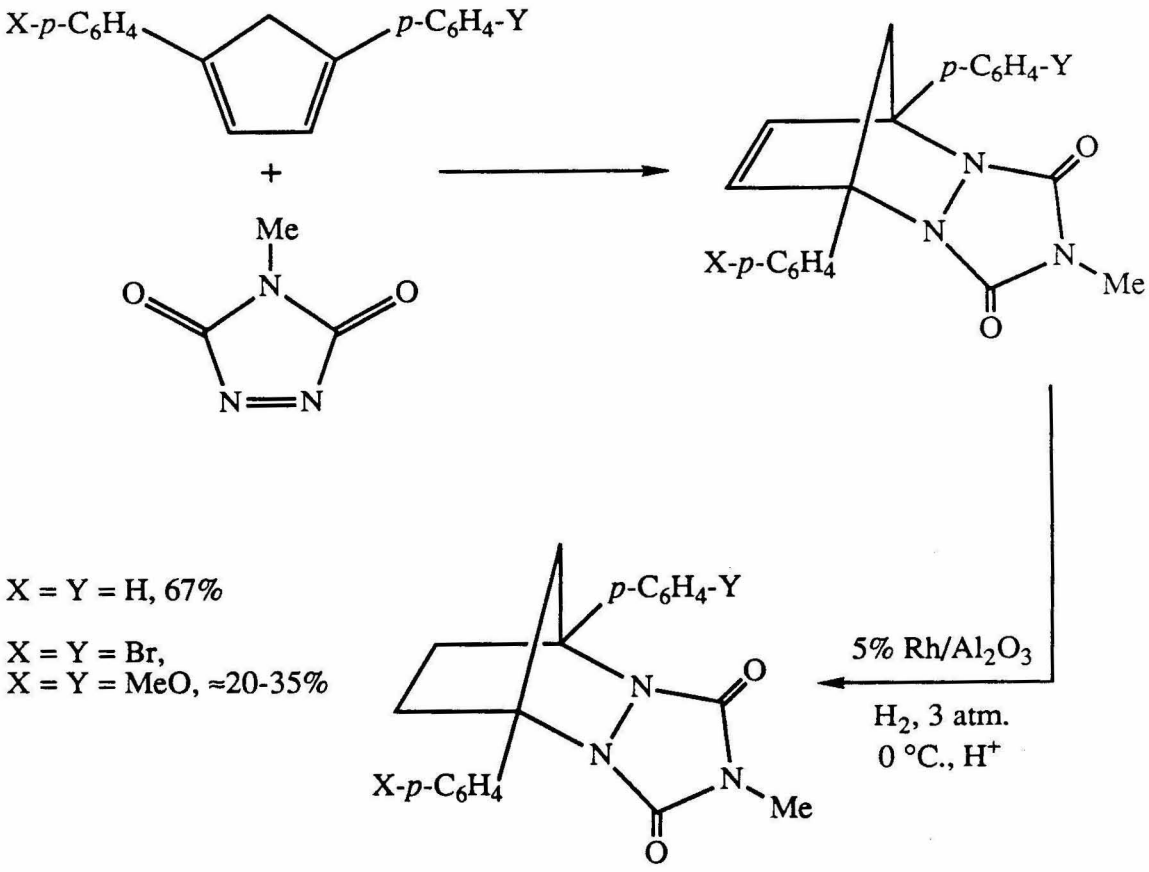
only soluble in polar solvents; retro Diels-Alder facile in polar solvents

- low temperatures (0°C.) and a large excess of PTAD favor adduct



Pd/C, 1 atm. H_2	too slow, retro, reduction of diene
Pd/C, 3 atm. H_2	low yields; retro, reduction of diene, hydrogenolysis of bridgehead C-N bond
Rh/Al_2O_3, 3 atm. H_2	somewhat better yields; retro, reduction of diene, hydrogenolysis still problems
diimide, HN=NH, from $KO_2CN=NCO_2K$ and AcOH in glyme at 0°C.	fair yields; some retro, no diene reduction or hydrogenolysis

Scheme 1-7

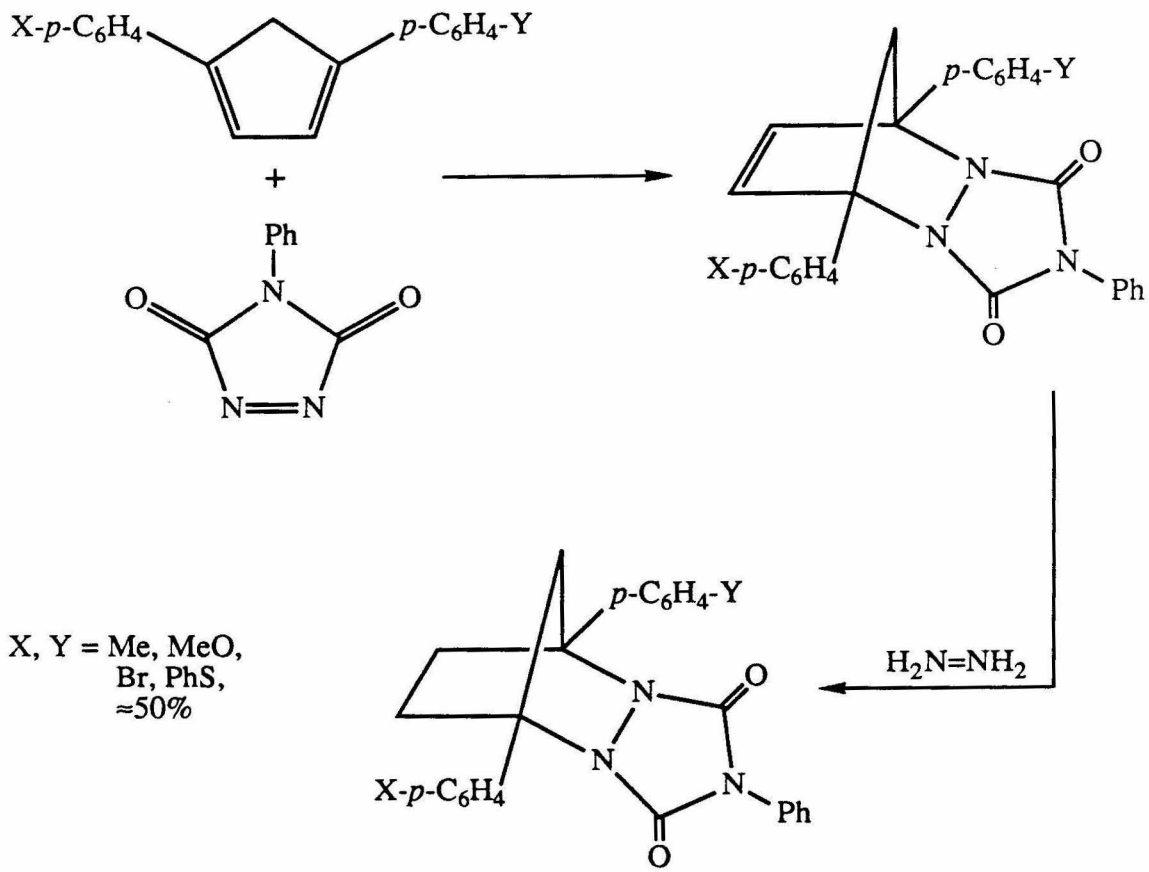


Variations on the catalytic hydrogenation theme were attempted. Rhodium had already been found to give less hydrogenolysis than palladium.[17] Lower hydrogen gas pressures resulted in a rate of double bond reduction so slow that almost no saturated adduct was obtained due to faster adduct dissociation.

Two primary changes were made to address the miserable results obtained with the "standard" methodology (Scheme 1-8). The first was to switch to the use of PTAD, a stronger dieneophile than MTAD.[33] This afforded a more stable unsaturated adduct. The second alteration was to use diimide[34] instead of catalytic hydrogenation to reduce the double bond in the unsaturated adduct. Diimide does not cause hydrogenolysis of the

bridgehead carbon-nitrogen bond and does not reduce the stable extended π system of the diarylcyclo-pentadienes.

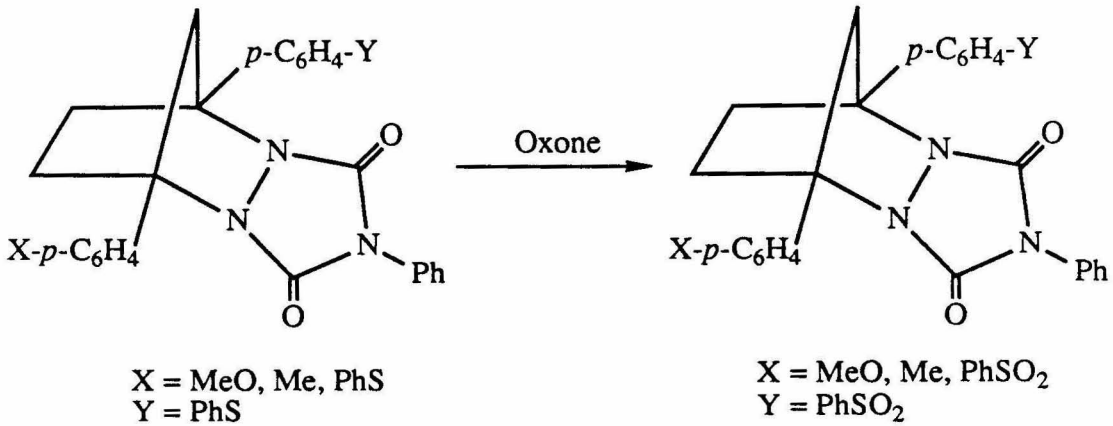
Scheme 1-8



An "innocent" and convenient source of diimide (as compared to bubbling air through a solution which contains hydrazine hydrate) is the slow addition of acetic acid to a vigorously stirred 0 °C suspension of dipotassium azodicarboxylate[34a] in a glyme solution[35] of the unsaturated adduct. Because of the lack of diarylcyclopentadiene reduction and the lack of hydrogenolysis, the crude reaction mixture is much cleaner and results in an almost trivial separation of three components: recovered diarylcyclo-pentadiene, desired reduced adduct urazole, and PTAD reduction and decomposition

products (generally characterizable as high R_f, low R_f, and baseline materials, respectively). Yields of purified N-phenyl urazoles obtained in this manner were consistently on the order of 50%, without taking into account recovered diarylcyclopentadiene.

While at the N-phenyl urazole stage, the thiophenoxy derivatives were oxidized with potassium hydrogen persulfate, $KHSO_5$, commercially available as "Oxone"[22] (a mixture of potassium hydrogen persulfate, potassium hydrogen sulfate, and potassium sulfate).[36] This easily and quantitatively produced the phenylsulfonyl derivatives.

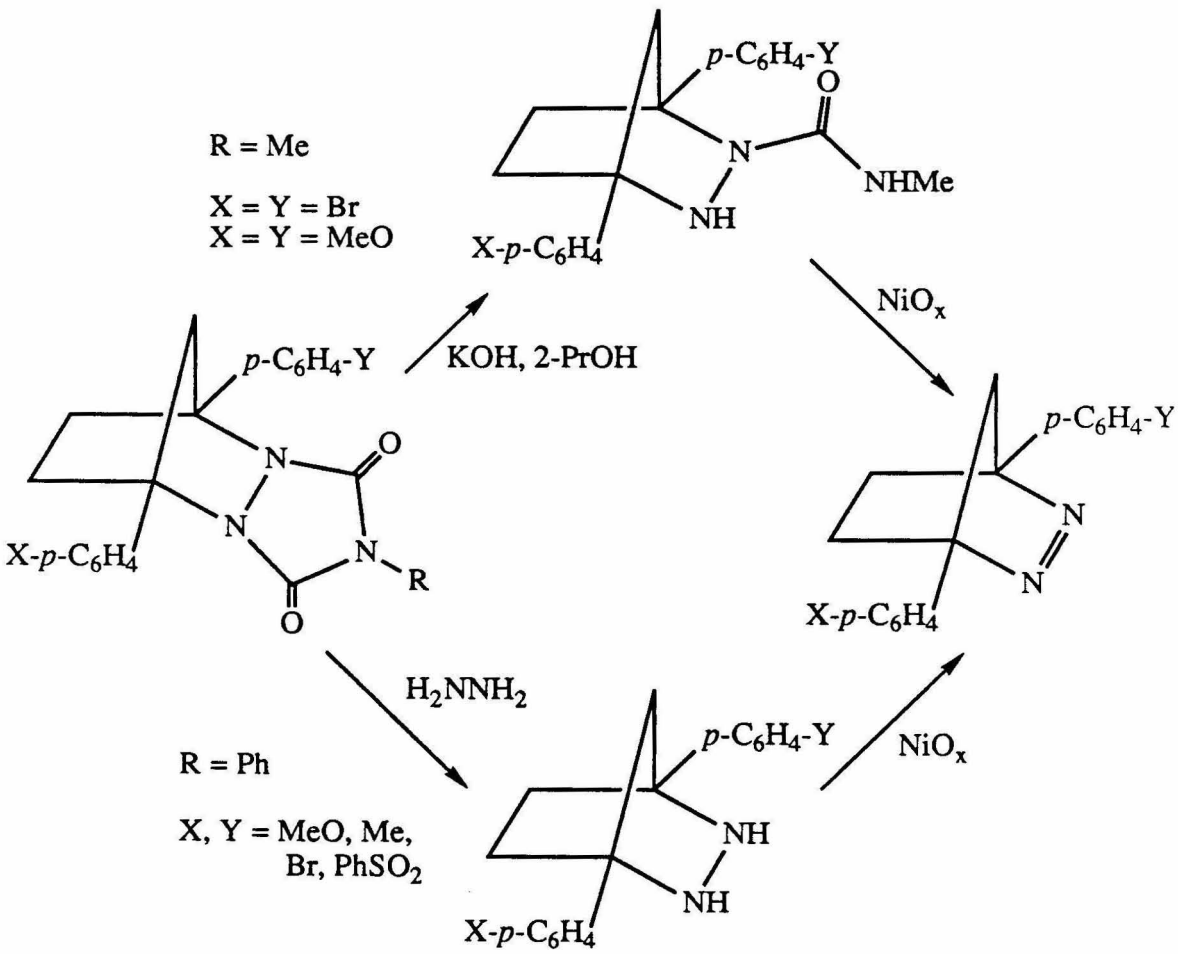


As with the parent diphenyl N-methyl urazole, both the di(4-methoxyphenyl) and di(4-bromophenyl) N-methyl urazoles were transformed into stable, easily purified, semicarbazides by basic hydrolysis (Scheme 1-9).[16] Attempts to perform this well-precedented reaction[5,15,16,17,37] on the N-phenyl urazoles resulted in material which gave virtually no diazene after nickel peroxide oxidation. This necessitated the use of hydrazinolysis followed by nickel peroxide oxidation.

Existing hydrazinolysis methodology for N-phenyl urazoles stipulates the use of an excess of hydrazine hydrate in refluxing 95% ethanol.[38] Under these conditions, it took six days for the N-phenyl urazoles to be converted to hydrazines. However, by using refluxing 2-propanol instead of ethanol, formation of the hydrazines occurred in six to nine hours (the longer reaction times correspond to the phenylsulfonyl derviatives, which

required the use of tetrahydrofuran, THF, as a co-solvent in order to dissolve the urazoles and were therefore less concentrated). The use of anhydrous hydrazine instead of hydrazine hydrate or the use of glyme instead of THF as a co-solvent did not noticeably improve the reaction.

Scheme 1-9

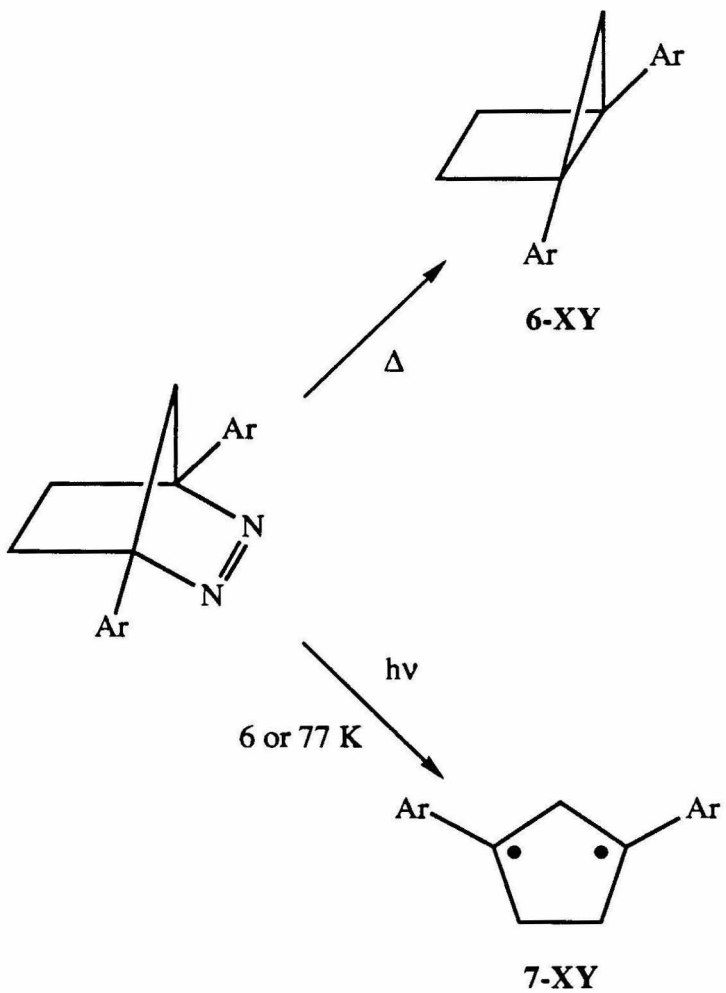


To convert the di(4-methoxyphenyl) and di(4-bromophenyl) N-methyl urazoles to the corresponding hydrazines required five days of reflux in a mixture of anhydrous hydrazine,

hydrazine hydrate, 2-propanol, and glyme (for solubility; the N-methyl urazoles are less soluble than the N-phenyl urazoles). Though the hydrazines were produced cleanly, there is little or no reason to recommend the use of this route over the formation of semicarbazides for these N-methyl urazoles.

Both semicarbazides and hydrazines were oxidized by nickel peroxide[5,15,16,17,39] to the diazenes at 0 °C in dichloromethane (Scheme 1-9). The diazenes (Scheme 1-10) were photolyzed at low temperatures (6 or 77 K) to provide the 1,3-diaryl-1,3-cyclopentadiyls **7-XY**.[16,17] Thermolysis at 60 °C in degassed solutions gave the 1,4-diarylbicyclo[2.1.0]-pentanes **6-XY**.[16,17]

Scheme 1-10



NMR Spectroscopy and Discussion

In order to investigate the effects of the *para* substituents on the strength of the bridgehead carbon-bridgehead carbon bond in the 1,4-diarylbicyclopentanes, variable temperature NMR studies of six compounds were conducted. The work was carried out similarly to that performed previously on **5**,[16,17] though it did not include complete lineshape analysis or magnetization transfer studies. Our intent was to determine the magnitude of any changes in the free energy of activation of the bridge-flip reaction and assess thereby the effects of *para* substituents on the strength of the bridgehead carbon-bridgehead carbon bond (Figure 1-5).

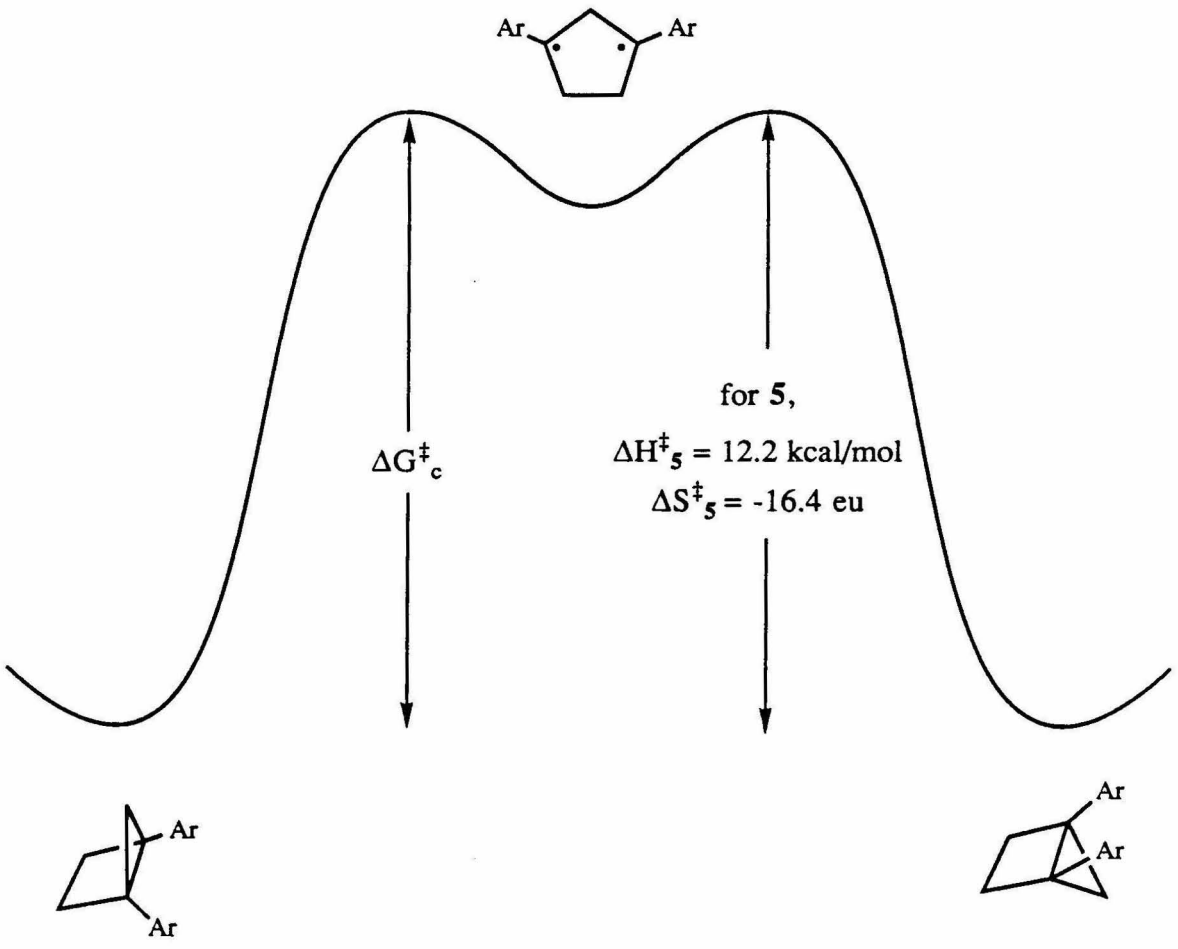


Figure 1-5: Schematic of bridge-flip reaction for **6-XY**

The corresponding diazenes were dissolved in vacuum-transferred deuterochloroform in medium-walled NMR tubes. The solutions were then degassed and the tubes sealed. Thermolysis of the diazenes at 60 °C for one hour afforded the bicyclopentanes. A representative NMR is that of 1,4-di(4-methylphenyl)bicyclo[2.1.0]pentane **6-MeMe** taken at 20 °C on a 300-MHz spectrometer (Figure 1-6; the protons responsible for the observed signals are as shown). The sharpness of the lines indicates that the bridge-flip reaction is slow at this temperature. This was the case for all six bicyclopentanes studied.

Upon warming, the signals due to the *exo* and *endo* protons at the 5-position first broaden, then coalesce as the exchange process accelerates (Figure 1-7). For our purposes of determining the free energies of activation at the coalescence temperatures, it was critical to be able to measure these temperatures as accurately as possible.[40] Use of a 300-MHz spectrometer allowed observation of the actual coalescence of the signals at temperatures below the onset of decomposition of the bicyclopentanes *via* 1,2-hydrogen shift to the cyclopentenes, the onset of which occurs at ≈110 °C in **5**.

The data collected from the coalescence studies are shown in Table 1-1. The trends in chemical shift (reported as frequencies) are not surprising; electron-withdrawing substituents shift the proton signals downfield (higher frequencies). The coupling between the 5_x and 5_n (5_{exo} and 5_{endo}, respectively) protons remains relatively constant. The free energies of activation at coalescence ($\Delta G^{\ddagger}_c$, in kcal/mol) were determined from eq. 1-1,[42] which relates the coalescence temperature (T_c, in Kelvin), the separation between the two proton signals at the slow-exchange limit ($\Delta\nu$, in Hertz), and the coupling constant between the two protons ($J_{5n,5x}$, also in Hertz).

$$\Delta G^{\ddagger}_c = (4.575 \times 10^{-3}) \times T_c \times [9.972 + \log(T_c \div [\Delta\nu^2 + 6J^2_{5n,5x}]^{1/2})] \qquad (1\text{-}1)$$

Use of eq. 1-1 requires that the long-range W-coupling between the $2,3_x$ and 5_x protons be ignored. The coupling constant is ≈2 Hz, and the extra splitting of the 5_x proton signal it causes is quickly lost in the signal broadening which occurs as the sample

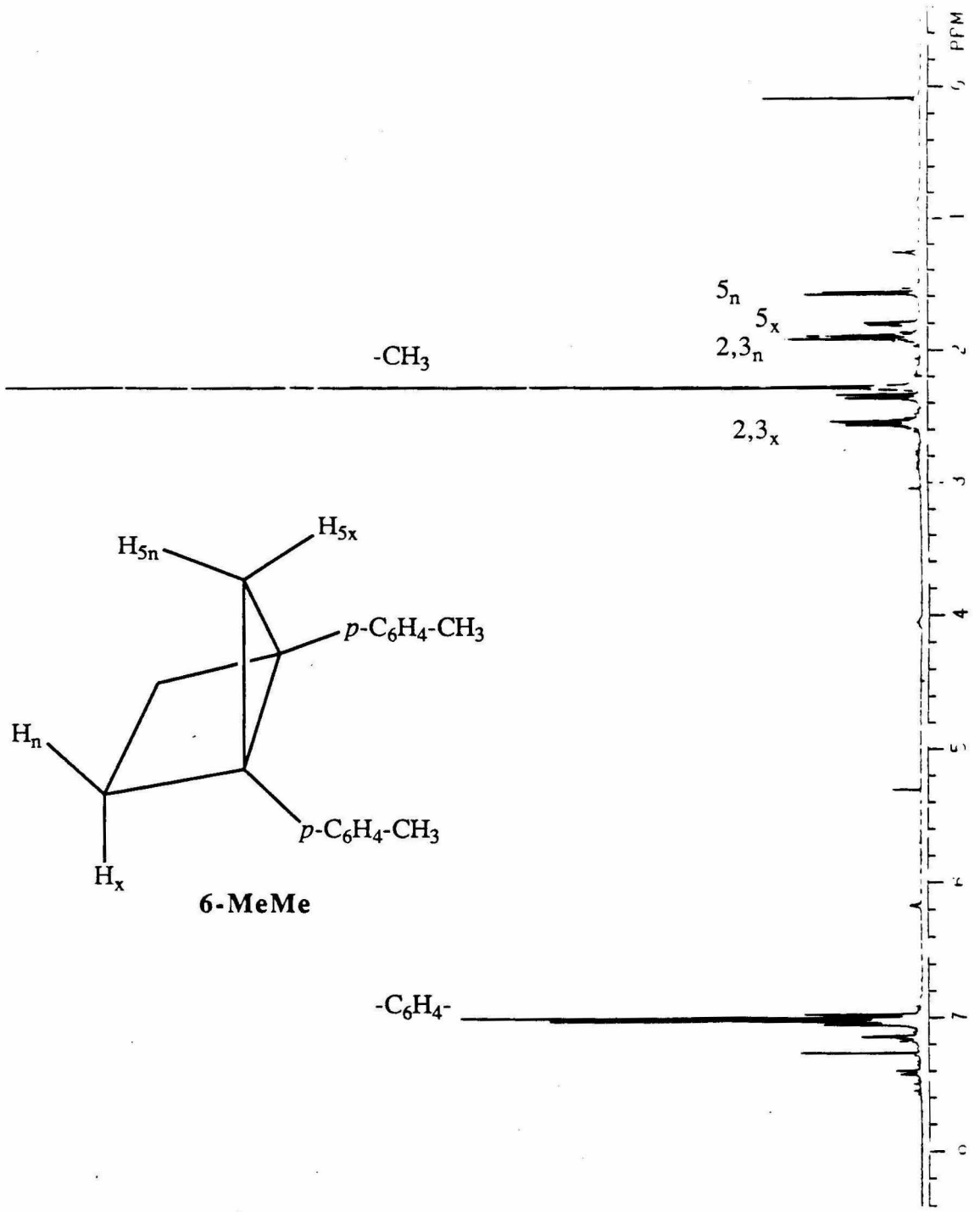


Figure 1-6: 300-MHz NMR of **6-MeMe**.

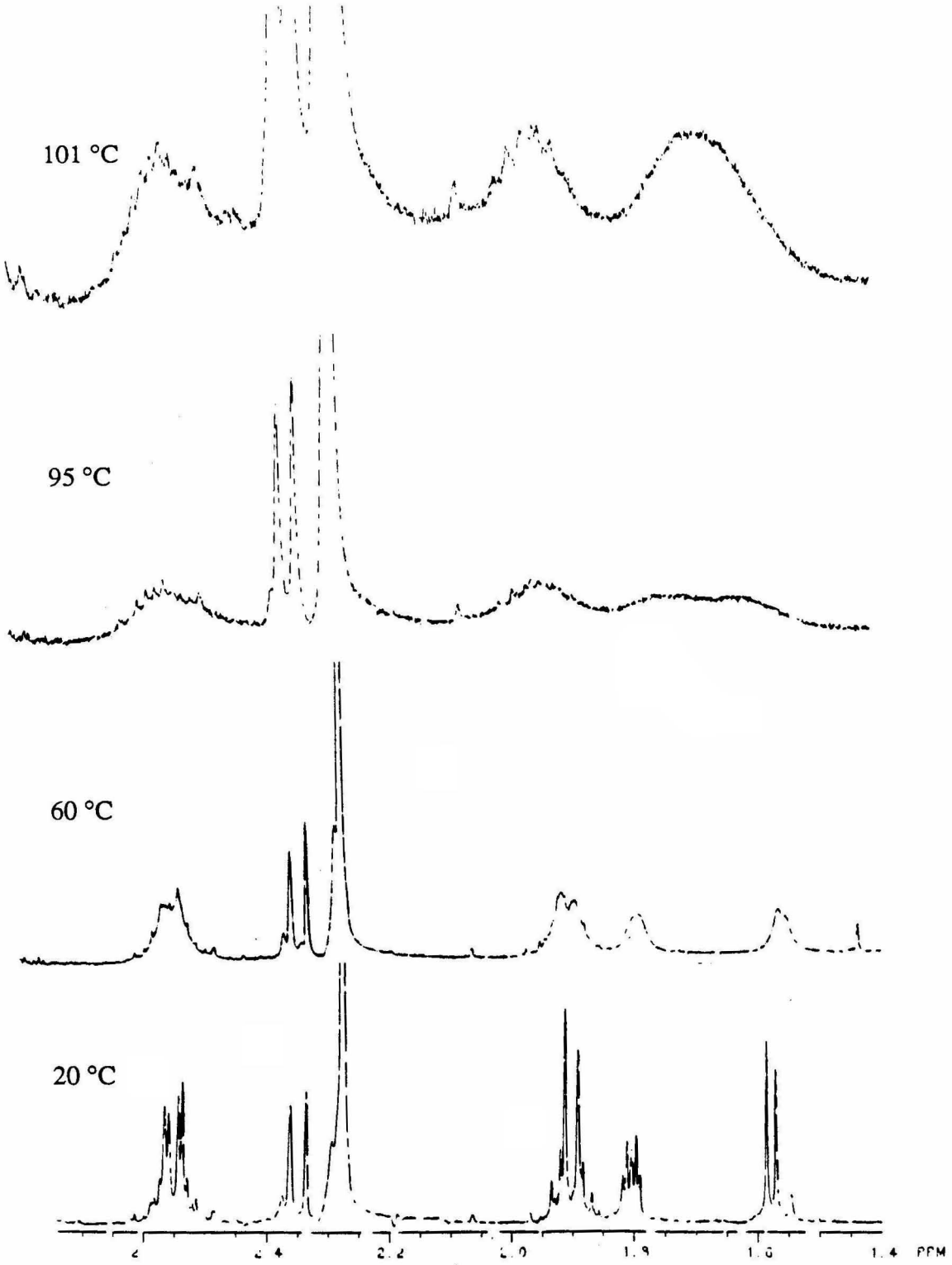


Figure 1-7: Coalescence of 5_x and 5_n proton signals in **6-MeMe**.

is warmed. This coupling was also ignored in the complete lineshape analysis of **5** without detriment to the activation parameters derived.[17] The temperatures were calibrated with an ethylene glycol standard,[41] and the error limits of ±0.2 kcal/mol are those suggested for this overall method.[42] Given the relative simplicity of the method used to study these compounds, they compare favorably with the ±0.1 kcal/mole obtained in the more exacting complete lineshape analysis/magnetization transfer study performed on **5**.

The bridge-flip reaction has a large negative entropy of activation which is due to the necessity of moving the aryl groups into transition-state geometries which begin to resemble that of the planar singlet biradical (so that the stabilizing benzylic radical character is available to the bridgehead carbons).[16,17] The methoxy, methyl, and bromo groups are of roughly similar size[42] and would be expected to have similar entropies of activation which would not differ greatly from the entropy of activation for the bridge-flip reaction of **5**. Any changes in $\Delta G^{\ddagger}_{c}$ should therefore primarily reflect changes in the enthalpy of activation and hence in the bridgehead carbon-bridgehead carbon bond strength.

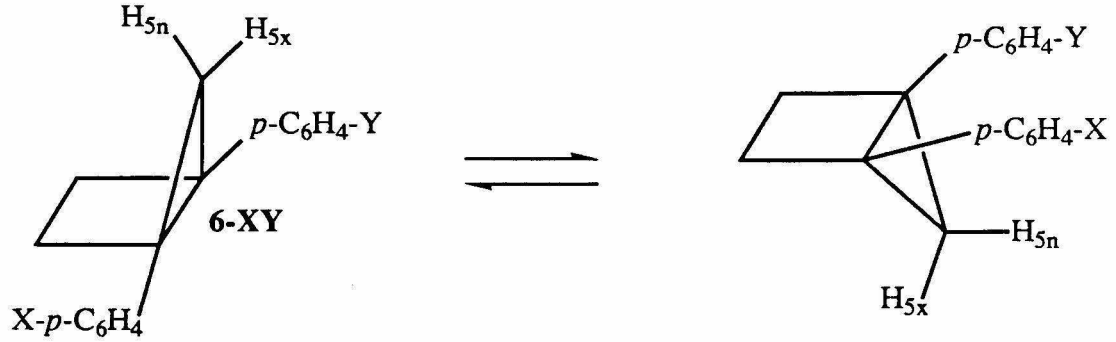
The movements of the larger phenylsulfonyl group will encounter more resistance from solvent than the other groups. The effect of the greater "extensivity" of the phenylsulfonyl groups should be to increase the free energy of activation observed for the reaction (it requires more energy to move these groups into position).[43] The larger amount of energy required to move the phenylsulfonyl groups may mask this group's effect on the bridgehead carbon-bridgehead carbon bond strength to some degree. That is, the actual reduction of bond strength in **6-MePhSO$_2$**, **6-MeOPhSO$_2$**, and **6-PhSO$_2$PhSO$_2$** may be greater than that implied by the observed $\Delta G^{\ddagger}_{c}$ value.

The $\Delta G^{\ddagger}_{5}$ column in Table 1-1 contains the free energy of activation for the bridge-flip reaction of **5** calculated at each of the coalescence temperatures of the other diarylbicyclopentanes. These values were obtained by using eq. 1-2 with $\Delta H^{\ddagger}_{5}$ = 12.2 kcal/mol,[16,17] $\Delta S^{\ddagger}_{5}$ = -16.4 cal/mol•K,[16,17] and by assuming that both $\Delta H^{\ddagger}_{5}$ and $\Delta S^{\ddagger}_{5}$ were

temperature invariant (which is not unreasonable over this temperature range and is necessary due to the lack of heat capacity data).

$$\Delta G^{\ddagger}_{5} = \Delta H^{\ddagger}_{5} - (T_c \times \Delta S^{\ddagger}_{5}) \qquad (1\text{-}2)$$

Table 1-1: NMR data at slow exchange (293 K), coalescence temperatures, and free energies of activation at coalescence for 1,4-diarylbicyclo[2.1.0]pentanes.



6-XY	ν_{5n} (Hz)	ν_{5x} (Hz)	$\Delta\nu$ (Hz)	$J_{5n,5x}$ (Hz)	T_c (K)	$\Delta G^{\ddagger}_c$ (kcal/mol) (±0.2)	$\Delta G^{\ddagger}_5$ (kcal/mol) (±0.2)
6-MeMe	473.05	541.55	68.50	4.51	374.0	18.3	18.3
6-MeOMeO	465.01	522.46	57.45	4.49	367.1	18.1	18.2
6-BrBr	503.62	544.85	41.23	4.78	366.1	18.3	18.2
6-MePhSO$_2$	520.43	571.47	51.04	4.79	365.1	18.1	18.2
6-MeOPhSO$_2$	518.09	560.08	41.99	4.80	360.0	17.9	18.1
6-PhSO$_2$PhSO$_2$	549.83	588.46	38.63	4.99	349.2	17.4	17.9

Qualitatively, it appears that methoxy and phenylsulfonyl groups facilitate the reaction (presumably by stabilizing any radical character which develops in the transition state), the methyl group has no effect, and bromine retards the reaction (presumably by destabilizing any radical character which develops in the transition state). These effects are small, and with the exception of **6-PhSO$_2$PhSO$_2$**, the free energies of activation are within

experimental error of each other and the free energy values for the bridge-flip reaction of **5**. Only the phenylsulfonyl group can be said to have significantly altered the energy of the transition state for this reaction and, by extension, to have lessened the strength of the bridgehead carbon-bridgehead carbon bond.

However, though the differences are small, the $\Delta G^{\ddagger}_{c}$ data in Table 1-1 are internally consistent. The higher $\Delta G^{\ddagger}_{c}$ for **6-MeMe** *vs.* that of **6-MeOMeO** is repeated when the methyl and methoxy groups are paired with phenylsulfonyl groups in **6-MePhSO$_2$** and **6-MeOPhSO$_2$**. This consistency suggested that an attempt to correlate these $\Delta G^{\ddagger}_{c}$ values with known Hammett substituent constants could yield interesting information, even with the understanding that, due to the uncertainties in the measurements, the information gleaned would necessarily be more qualitative than quantitative in nature.

The appropriate linear free-energy relationship is given by eq. 1-3, in which σ_x and σ_y are the substituent constants for each X and Y from Table 1-1, respectively, and ρ is the slope of the line obtained and indicates the sensitivity of the bridge-flip reaction to substituent effects relative to the system from which σ_x and σ_y were determined.[20] The bridge-flip reaction is a homolytic bond-breaking process and creates two radical centers in the same way and at the same time. Each radical can be expected to affect the course of the reaction equally, and any effects on free energy should therefore be directly related to the substituent constant for each *para* substituent of the two benzylic systems.

$$(\Delta G^{\ddagger}_{\mathbf{5}} - \Delta G^{\ddagger}_{c})/(2.303\ RT_c) = \rho\sigma = \rho(\sigma_x + \sigma_y) \qquad (1\text{–}3)$$

Table 1-2 presents various Hammett substituent constants and Swain-Lupton field and resonance parameters fot the methoxy, methyl, bromo, and phenylsulfonyl substituents.[44] The σ_p constants are the standard Hammett parameters for *para* substituents and have their origins in the studies of the acidities of substituted benzoic acids.[20] The Swain-Lupton F parameter represents that part of σ_p caused by the inductive (field) effects of a substituent,

and the Swain-Lupton R parameter represents that part of σ_p caused by the resonance capabilities of a substituent.[20] These parameters have been used to successfully correlate the free energies and rates for a wide variety of reactions, though they have not been particularly useful for reactions in which radicals are involved.

Table 1-2: Hammett and Swain-Lupton substituent constants for *para* substituents.

X, Y	σ_p[a]	F [a]	R [a]	$\sigma_\alpha^{\bullet}$[b]	$\sigma_C^{\bullet}$[c]	$\sigma_F^{\bullet}$[d]	$\sigma_J^{\bullet}$[e]
MeO	-0.27	0.29	-0.56	0.018	0.24	-0.12	0.42
Me	-0.17	0.01	-0.18	0.015	0.11	-0.02	0.39
Br	0.23	0.45	-0.22	[f]	0.13	0.17	0.13
$PhSO_2$	0.68	0.58	0.10	0.018	[f]	[f]	0.92 [g]

[a] Hansch, C.; Leo, A.; Taft, R. W. *Chem. Rev.* **1991**, *91*, 165-195. [b] Wayner, D. D. M.; Arnold, D. R. *Can. J. Chem.* **1984**, *62*, 1164-1168. [c] Creary, X.; Mehrsheikh-Mohammadi, M. E.; McDonald, S. *J. Org. Chem.* **1987**, *52*, 3254-3263. [d] Fisher, T. H.; Meierhoefer, A. W. *J. Org. Chem.* **1978**, *43*, 224-228. [e] Dinçtürk, S.; Jackson, R. A. *J. Chem. Soc., Perk. Trans. II* **1981**, 1127-1131. [f] Substituent not studied. [g] Calculated value from equation given in ref. [e] and the values in ref. [a].

The Swain-Lupton parameters were originally created to provide a flexibility not afforded by the use of σ_p alone. Their use entails breaking down the σ for a system into components due to inductive and resonance effects, each weighted for its contribution to the reaction being studied: $\sigma = fF + rR$. When $f = r = 1$, σ_p is recovered.[20] The R parameter has been criticized for not allowing for a substituent's different abilities to stabilize by resonance under different conditions. Four other resonance parameters have been suggested and are used: σ_R°, for unperturbed systems; $\sigma_{R(BA)}$, for substituted benzoic acids; σ_R^{+}, for electron-poor benzene rings; σ_R^{-}, for electron-rich benzene rings.[20] Though the values of these four change as compared to R and to each other, the relative ordering and magnitudes do not. In other words, the effect of a methoxy group is always much larger than that of either a methyl or bromo group, the effects of methyl and bromo groups are about the same, and the bromo group consistently has a slightly larger effect

than the methyl. For these reasons, the R parameter was chosen as being representative of resonance constants in general for the substituents in this study.

The other four Hammett constants in Table 1-2 are the existing parameters which are intended to allow correlation of rates and equilibria for *para*-substituted benzylic radical systems. The $\sigma_\alpha^\bullet$ scale was derived from the changes in spin density reflected by the changes in hyperfine coupling constants in substituted benzyl radicals.[45] The $\sigma_C^\bullet$ scale arose from Creary's studies of the rearrangement of 2-aryl-3,3-dimethylmethylene-cyclopropanes.[46] Fisher developed $\sigma_F^\bullet$ constants from the radical brominations of 4-substituted-3-cyanotoluenes with N-bromosuccinimide.[47] The $\sigma_J^\bullet$ parameters were determined by Jackson by examination of the rates of formation of *para*-substituted benzyl radicals produced by the thermolysis of *para*-substituted dibenzyl mercurials.[48]

Recent work has found a good correlation between the $\sigma_F^\bullet$ scale and the reactivities of *para*-substituted benzyl radicals toward molecular oxygen.[49] However, Fisher[50] has recently derided the $\sigma_F^\bullet$ scale (developed in his laboratories) for not being sufficiently comprehensive and for not accounting for polar effects properly, which has been a significant challenge in the development of $\sigma^\bullet$ scales in general. Fisher also points out that the $\sigma_J^\bullet$ parameters are not comprehensive and were based on the (incorrect[50]) assumption that *meta* substituents have no effect on the stabilities of benzyl radicals. He concludes that the $\sigma_\alpha^\bullet$ scale, though comprehensive, suffers from a limited range of values and from a lack of normalization to other Hammett parameters, and that the $\sigma_C^\bullet$ scale is the most comprehensive and has the most "positive features."

Figures 1-8 through 1-14 show the plots of $(\Delta G^{\ddagger}_{5} - \Delta G^{\ddagger}_{c})/(2.303\ RT_c)$ *vs.* $(\sigma_x + \sigma_y)$ for the compounds studied. The plots made use of the data Table 1-1 and in Table 1-2. It is readily noted that the free energies are not well-correlated with the standard Hammett parameter for *para* substituents, σ_p (Figure 1-8), or with field (Figure 1-10) or resonance (Figure 1-11) effects alone. Similarly, the $\sigma_\alpha^\bullet$ (Figure 1-14) and $\sigma_C^\bullet$ (Figure 1-13) scales fail to account for the observed changes in $\Delta G^{\ddagger}_{c}$. A tantalizingly good fit is obtained from

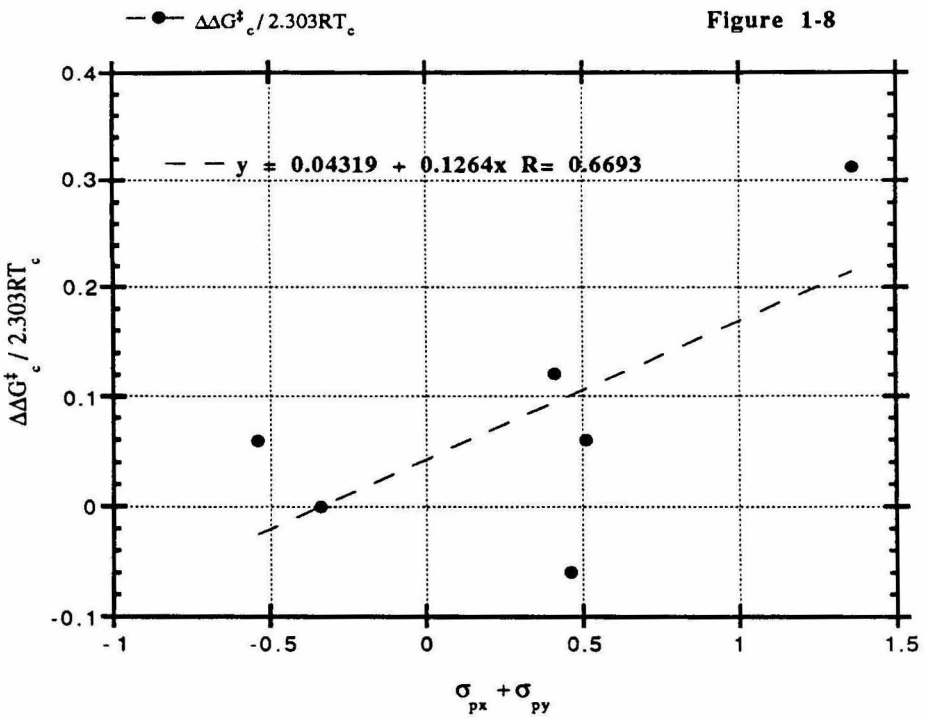


Figure 1-8

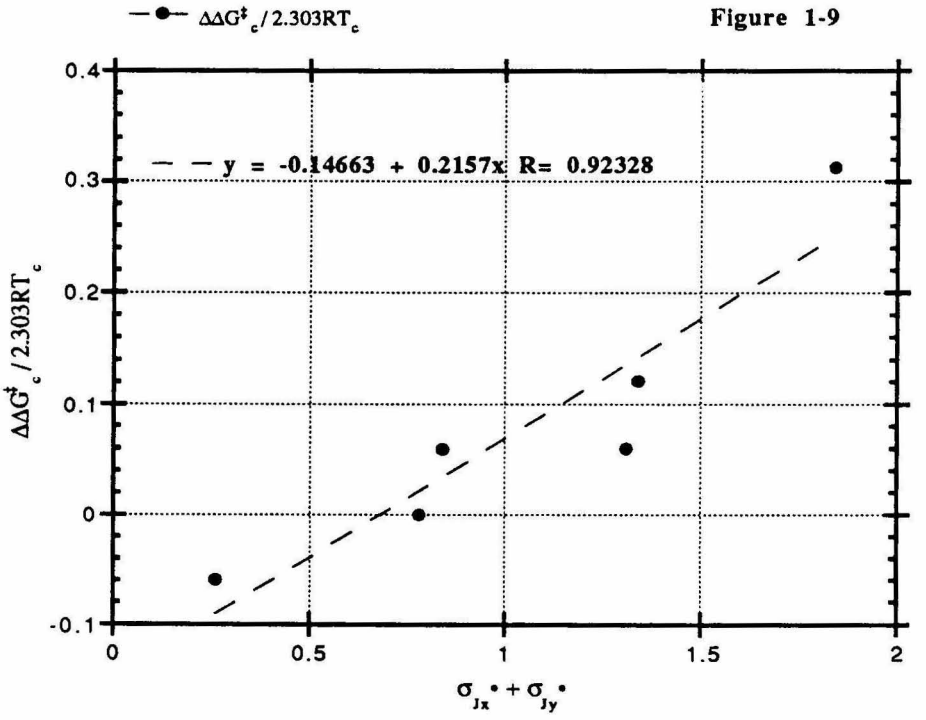


Figure 1-9

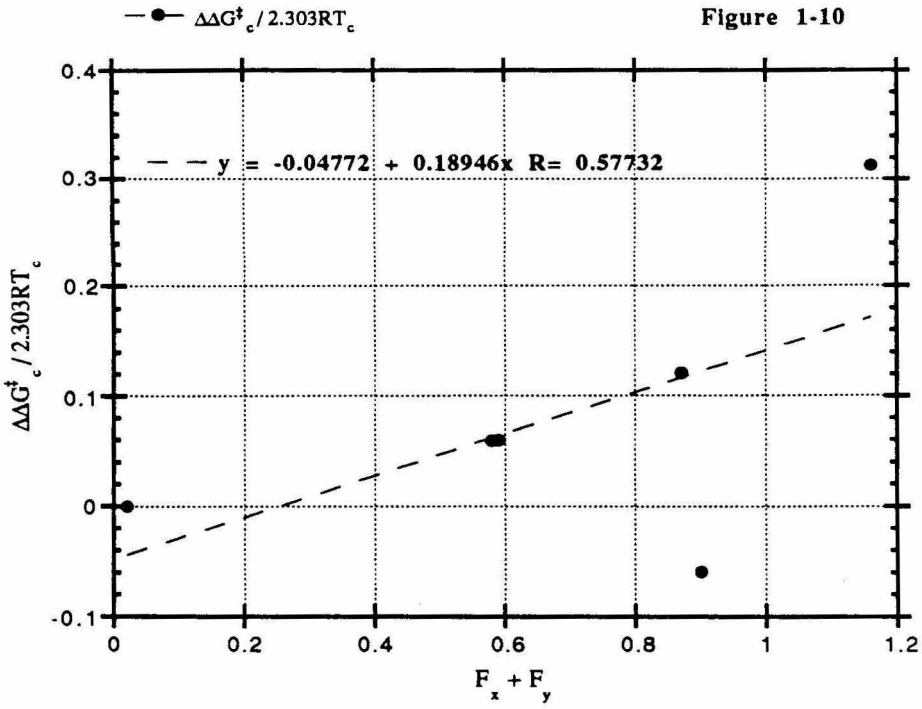


Figure 1-10

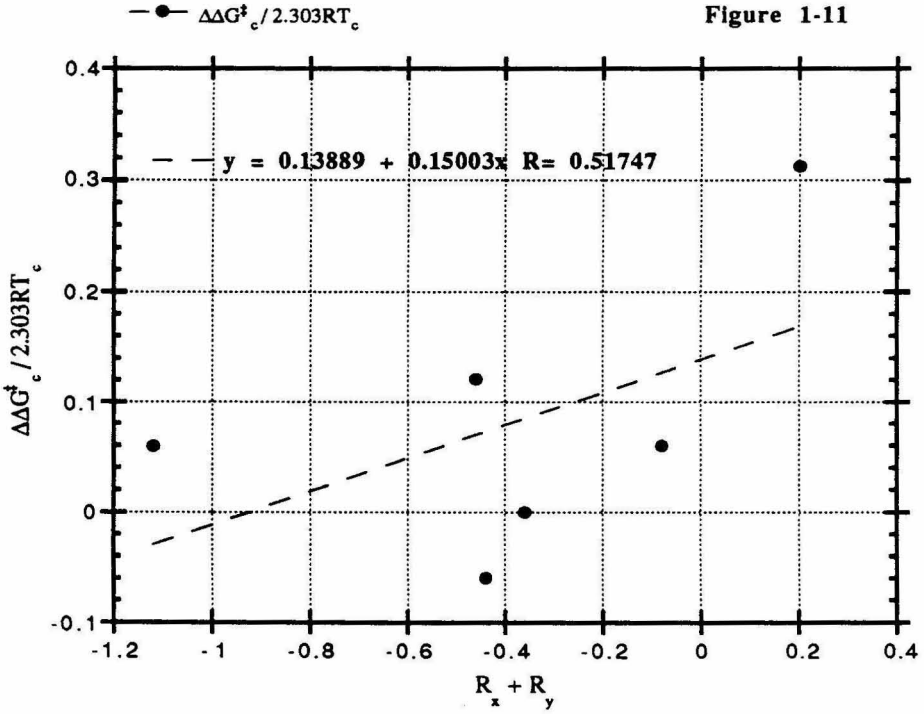


Figure 1-11

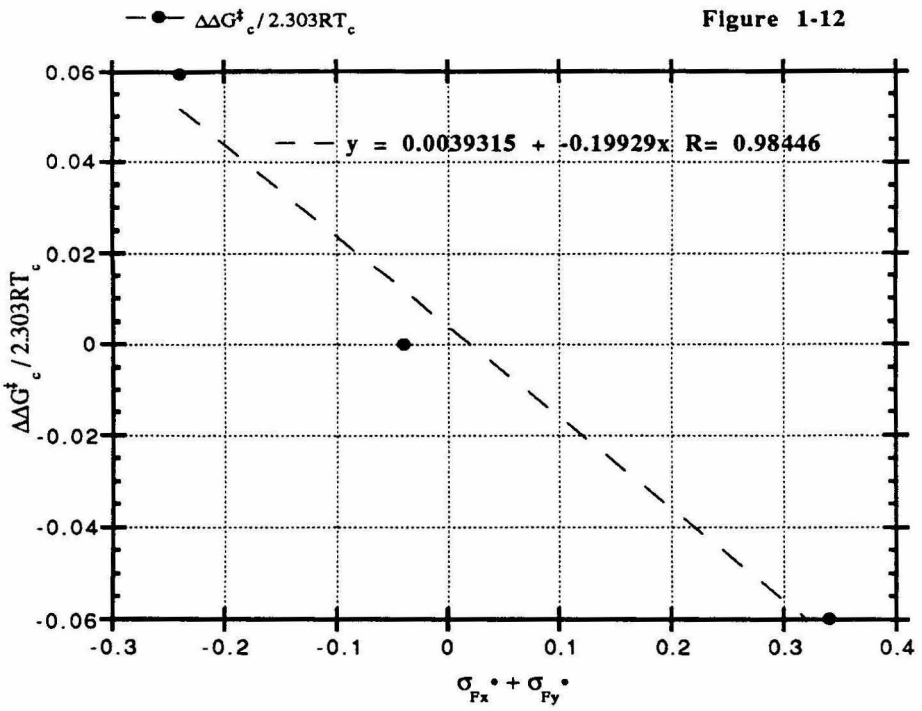


Figure 1-12

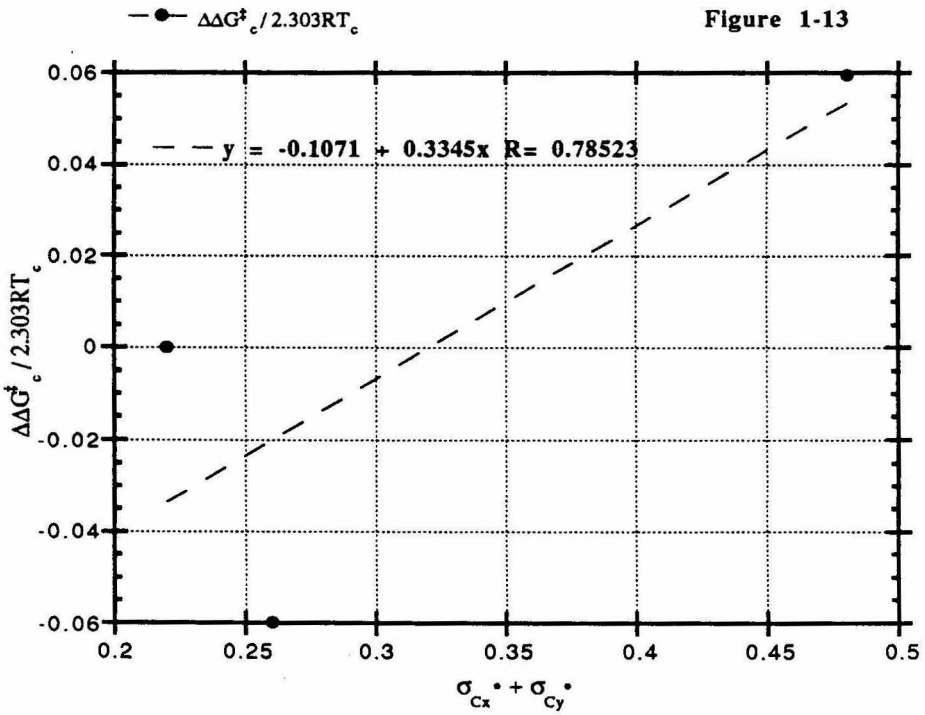


Figure 1-13

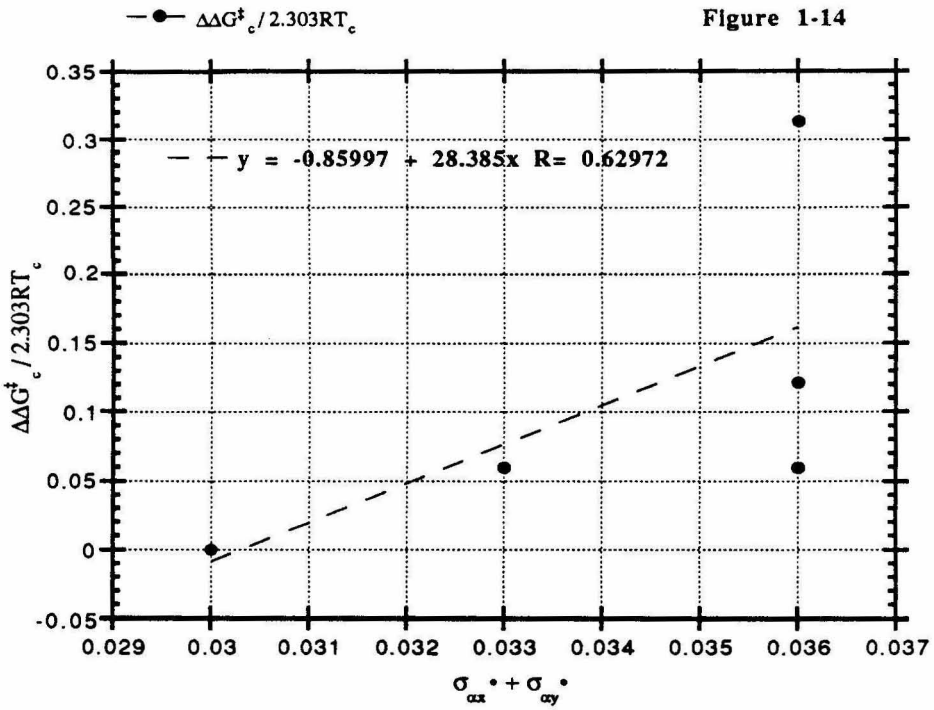


Figure 1-14

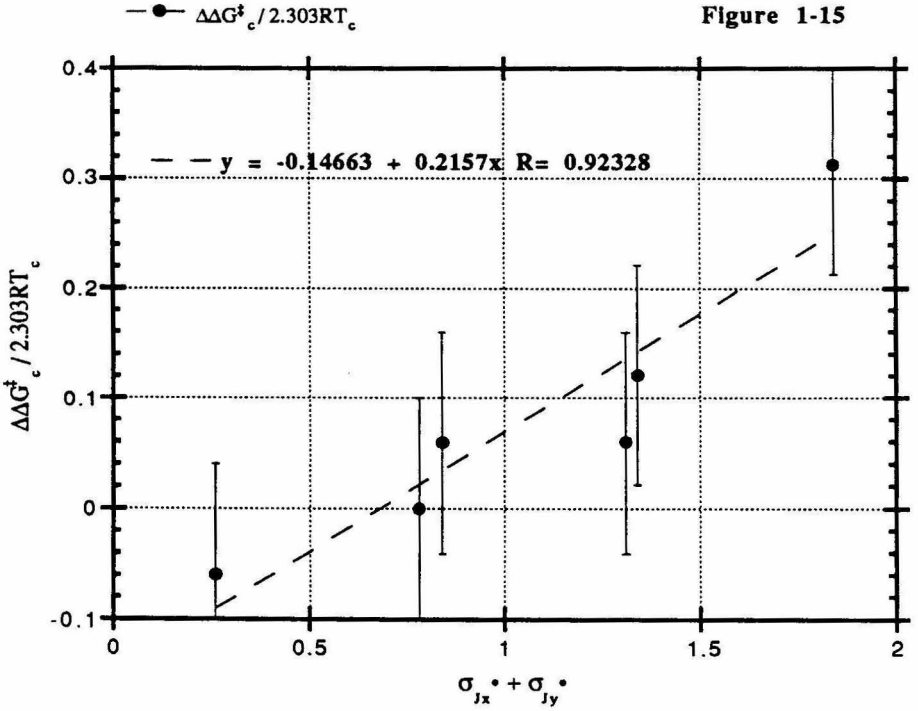


Figure 1-15

the $\sigma_F^\bullet$ scale (Figure 1-12), but closer scrutiny strongly suggests that this is simply a fortuitous artifact of the errors in the data.

The $\sigma_F^\bullet$ scale does not have a value for the phenylsulfonyl group, which was observed to be the cause of the largest lowering of $\Delta G^\ddagger_c$ in the series (**6-PhSO$_2$PhSO$_2$**). For compounds **6-MePhSO$_2$**, **6-MeOPhSO$_2$**, and **6-PhSO$_2$PhSO$_2$** to be on the same line as the other three compounds, the $\sigma_F^\bullet$ constant for the phenylsulfonyl group would have to be more negative than that for the methoxy group. In the $\sigma_F^\bullet$ scale,[47] only fluorine (an electron-acceptor by induction, an electron-donor by resonance) has a more negative value than methoxy (-0.25). Groups such as nitro, cyano, and acetyl (all strong electron-withdrawing substituents which resemble phenylsulfonyl far more than fluorine does) all have large positive $\sigma_F^\bullet$ values (0.27, 0.34, and 0.53, respectively). It is difficult to find any legitimate physical grounds which would enable cogent rationalization of such contradictory relationships.

The $\sigma_J^\bullet$ scale (Figure 1-9) does provide a fair correlation for all the compounds and substituents (correlation coefficient = 0.92). A comment on the source of the $\sigma_J^\bullet$ constant for the phenylsulfonyl group is now in order. In addition to $\sigma_J^\bullet$ values for substituents which were directly determined in the studies of the homolyses of the dibenzyl mercurials,[48] an empirical relationship between the $\sigma_J^\bullet$ constants and other, previously determined, Hammett parameters was elucidated. This allows calculation of $\sigma_J^\bullet$ values for substituent groups which were not directly studied. This dramaticially enhances the scope and utility of the $\sigma_J^\bullet$ scale. This empirical relationship was used to calculate the $\sigma_J^\bullet$ value of 0.92 for phenylsulfonyl. Taking into account the error limits of the $\Delta G^\ddagger_c$ values and the empirical origin of the phenylsulfonyl $\sigma_J^\bullet$ parameter, the quality of the fit is not too bad.

Figure 1-15 is a plot of $(\Delta G^\ddagger_5 - \Delta G^\ddagger_c)/(2.303\ RT_c)$ *vs.* $(\sigma_{Jx}^\bullet + \sigma_{Jy}^\bullet)$ with error bars derived from the propagation of the ±0.2 kcal/mole in the $\Delta G^\ddagger_c$ values. That the bridge-flip reaction should correlate with the thermal generation of benzyl radicals is not unreason-

able because that is what happens during the bridge-flip process. With the error bars as shown in Figure 1-15, it is obvious that no meaningful quantitative relationship between substituents and bridgehead carbon-bridgehead carbon bond strengths can be determined from this study. It does seem safe to conclude, however, that the bridge-flip reaction is facilitated by *para* substituents in the order phenylsulfonyl > methoxy > methyl > bromo.

Further insight into the nature of the bridge-flip process is revealed by the value of ρ ($\approx$0.22) obtained from the plot *vs.* ($\sigma_{Jx}^{\bullet} + \sigma_{Jy}^{\bullet}$). This value is the slope of the line in the plot and provides information relative to the dibenzyl mercurial thermolysis reaction which defines the $\sigma_J^{\bullet}$ scale (for which ρ=1).[48] The slopes are both positive which indicates that they are affected by electron-withdrawing and electron-donating factors in the same (undoubtedly complicated) way.[20] The much smaller magnitude of the ρ value for the bridge-flip process implies that the bridge-flip reaction system is much less susceptible to substituents effects.[20] The small changes in $\Delta G^{\ddagger}_c$ observed for this series of compounds is evidence of this.

To begin to rationalize the relative insensitivity of the bridge-flip reaction to *para*-substituent effects (as evidenced by the small magnitude of ρ), an examination of the schematic for the reaction shown in Figure 1-5 is necessary. It has been determined that for **5** the reaction involves only the singlet state and that the singlet biradical is a true intermediate, not a transition state, for the reaction.[16,17,19] The $\Delta G^{\ddagger}_c$ measured is the free energy change required to attain the transition state that leads to the formation of the singlet biradical, not to attain the singlet biradical itself. It is only at the singlet biradical stage that the full benzylic radical character of the bridgehead carbons is completely developed (it is this stabilizing benzylic character which creates or deepens the energy well in which the singlet biradical resides[1fg]). The transition state which corresponds to the measured $\Delta G^{\ddagger}_c$ has only partial benzylic radical character at the bridgehead carbons, and an implication of this data is that the amount of benzylic character is far less than that of the transition state for the homolysis of dibenzyl mercurials.

Another factor in the decreased sensitivity of the bridge-flip reaction is that the radical centers are technically cumyl radicals, not benzyl radicals. Cumyl radicals have been shown to be less sensitive to *para*-substituent effects than benzyl radicals in electrochemical oxidation and reduction studies.[51] Those same studies and others[52] also showed that diphenylmethyl radicals are even less sensitive than cumyl radicals. (The decreased sensitivity of the diphenylmethyl system as compared to the cumyl system has been reiterated by solvolysis studies.[53])

These trends suggest that, for the benzylic radical family, the more stable the parent radical, the less susceptible to *para*-substituent effects it is. Tertiary radicals are more stable than primary ones,[54] and so cumyl radicals, which have tertiary benzylic positions, are more stable than benzyl radicals, which have primary benzylic positions. A benzyl radical is more stable than a tertiary alkyl radical,[54] and so the diphenylmethyl radical, which has a phenyl substituent rather than two methyl substituents, is more stable than a cumyl radical. The electrochemical studies imply that the trends are unlikely to be due to steric considerations because the (essentially) planar radicals, which should have similar steric requirements for interaction with an electrode, are the starting compounds for the oxidations and reductions. It is therefore reasonable to assume that part of the insensitivity to *para*-substituent effects observed in the bridge-flip reaction is because a cumyl system is being analyzed with parameters derived from the study of a benzyl system (the dibenzyl mercurials).

An important feature of the data in Table 1-1 is that the value of $\Delta G^{\ddagger}_{c}$ observed for **6-BrBr** is not in need of a separate explanation; it is consistent with the other values. No heavy-atom effect[55] was detected. The heavy-atom effect arises because actual molecules do not contain pure spin states. A singlet has some triplet character, and a triplet has some singlet character. The mixing between singlet and triplet is due to spin-orbit coupling. The presence of a "heavy atom" in a molecule increases the spin-orbit coupling as follows: An electron spinning about a nucleus can be viewed as the nucleus spinning about the electron

(by the theory of relativity). The magnetic field produced by the spinning nucleus applies a torque on the electron, which may cause it to undergo a "spin-flip" (go from α spin to β spin or from β spin to α spin). The heavier the nucleus is, the greater is the magnetic field which it creates by its motion relative to the electron, and the more likely it is to cause an electron to change spin states.[56] Heavy-atom effects have been observed in both delocalized and localized biradical systems.[57]

The lack of anomaly for the dibromo compound supports the conclusion that the bridge-flip reaction occurs entirely on the singlet surface. If the triplet surface were involved, intersystem crossing from the initial singlet state (closed-shell bicyclopentane) to the triplet state and back to the singlet state would be required. Because of greatly improved spin-orbit coupling, a heavy atom such as bromine can be expected to increase intersystem crossing rates.[55,56,57] Such an increase would have been reflected by a lower $\Delta G^{\ddagger}_{c}$ for the bridge-flip reaction of **6-BrBr**. In fact, the $\Delta G^{\ddagger}_{c}$ observed for **6-BrBr** was the only one of the series to be greater than that for **5** at the corresponding coalescence temperature.

Finally, despite the "push-pull" appearance of a compound such as **6-MeOPhSO$_2$**, the diarylbicyclopentane system and bridge-flip reaction will not be susceptible to capto-dative effects.[58] Stabilization of radicals by the captodative effect occurs when both an electron donor and an electron acceptor can act in concert upon a radical center. The presence of both a donor and an acceptor allow the inclusion of extra resonance structures in the representation of the radical. These resonance structures contain a positive charge on the donor and a negative charge on the acceptor and hence are not available to a radical substituted with two electron-donating or two electron-withdrawing groups.[58]

The singlet biradical in the bridge-flip process possesses two localized benzylic radicals, each with one *para* substituent acting directly upon it. The methylene groups are not capable of the direct resonance associated with the captodative effect (*i.e.*, they have no lone pairs to donate to an adjacent electron-deficient carbon).[58ac] Because of the planar

ring geometry,[16,17] the carbon-hydrogen bonds are not aligned in a position conducive to hyperconjugation,[59] which, in any case, is not generally sufficient to enable the captodative effect (compare the greater activation of phenyl rings by methoxy groups relative to that provided by methyl groups).[20] In the absence of possiblities for direct resonance, it is no surprise that captodative effects are unobserved.

EPR Spectroscopy and Discussion

Thorough discussions of triplet EPR have been presented elsewhere,[5,15,17,60] and only a review of the salient points will be presented here. EPR spectroscopy of triplet-state organic compounds differs from the more commonly encounterd EPR of doublet compounds (monoradicals). A fundamental difference is the nature of the energy level patterns. The two spin states of a doublet ($\Delta m_s = \pm 1/2$) are degenerate in the absence of an externally applied magnetic field. In a triplet, the three spin states ($\Delta m_s = 0, \pm 1$) are not degenerate. The two electrons interact *via* a dipolar coupling of the spins to create an internal magnetic field which causes a splitting of the energy levels. This "zero-field" splitting (zfs) is characterized by the two zfs parameters *D* and *E* as shown in Figure 1-16. Because zfs arises primarily from dipolar coupling, the magnitude of *D* is proportional to r^{-3}, where *r* is the average distance between the spins.[60a] In cases when there is significant spin-orbit coupling in addition to the spin-dipolar interaction, the value of *D* is less indicative of the mean separation of the electrons.[60b] *E* reflects the molecular symmetry of the triplet system. In structures with threefold or higher symmetry, *E* will be zero because two of the triplet sublevels will be degenerate.[60a]

Another basic difference between triplet and doublet EPR spectroscopy is the nature of the samples typically used for studies. EPR of monoradicals is usually performed on samples in fluid media, and the spectra obtained are therefore nicely isotropic.[60a] For a doublet, application of an external magnetic field splits the two levels and allows observation of the allowed $\Delta m_s = 1$ transition.

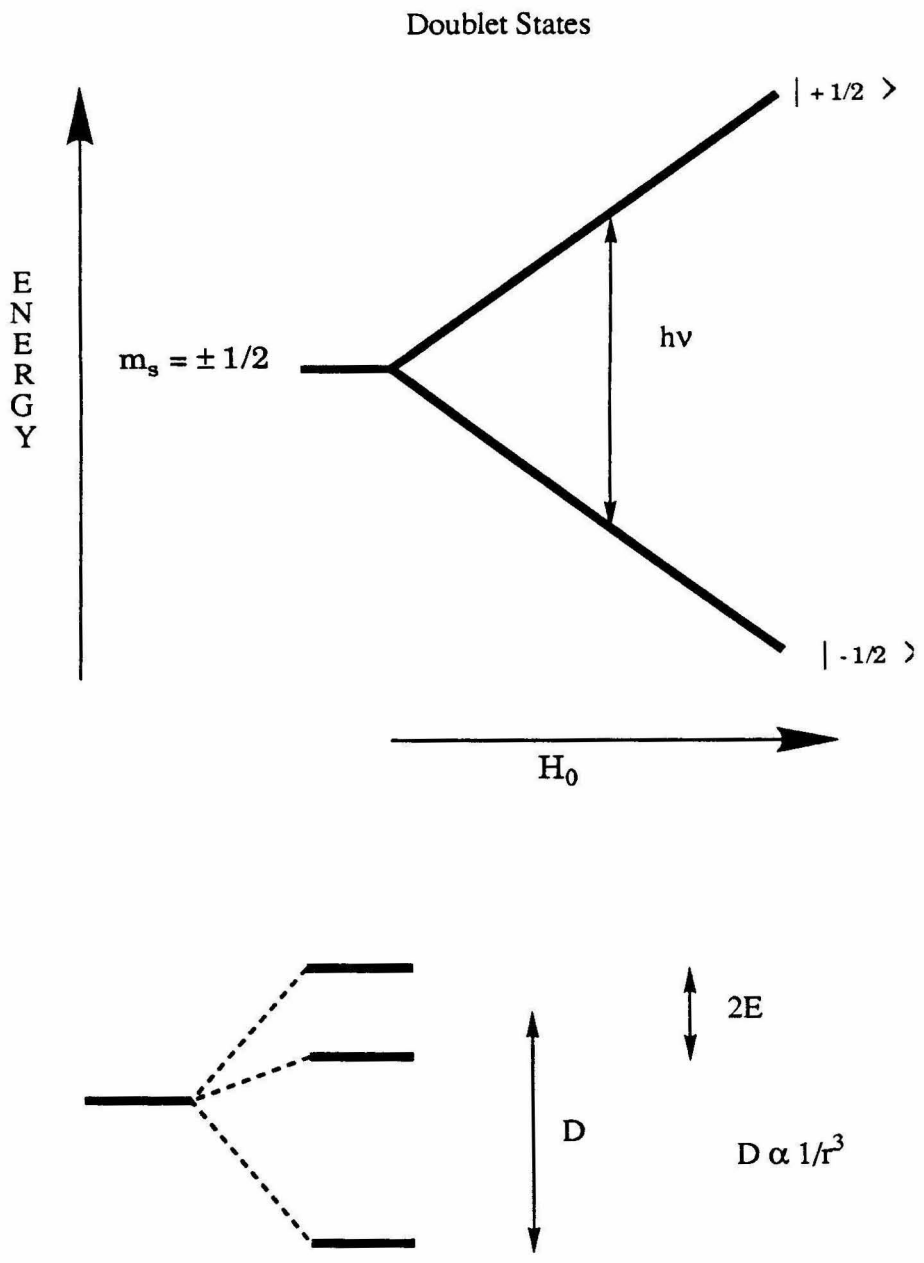


Figure 1-16: Doublet state and triplet sublevel splitting

The spectra of triplet species are commonly obtained from samples in rigid media. The rigid medium often used is a frozen solvent glass which causes the samples, which are

suspended in the glass, to be randomly oriented but non-reorienting (powder samples). Because there are three triplet sublevels and the selection rule for allowed transitions is $\Delta m_s = 1$, one would expect two EPR transitions for a triplet. However, the exact transitions observed will depend on the orientation of the internal principal magnetic axes of the biradical (as created by the dipolar coupling between the spins) relative to the external magnetic field.[60a] Fortunately, only the structures with one of their principal magnetic axes nearly aligned with the external field (the canonical orientations) are observed, otherwise an infinite number of observed transistions could be expected. Because there are three magnetic axes and two transitions for each canonical orientation, a typical first-derivative triplet spectrum has six lines (Figure 1-17b; 1-17a is the integral of 1-17b). For highly symmetric triplet species (small values of E or $E = 0$) the middle four lines collapse and a four-line spectrum results.[60a] In addition to the six allowed transitions, another is ususally observed at lower frequencies. This is the "forbidden," $\Delta m_s = 2$, transistion seen at "half-field." The presence of this line is diagnostic for the triplet state; it cannot be seen in doublets.

By performing EPR studies on the 1,3-diaryl-1,3-cyclopentadiyls, we hoped to determine the effects of *para* substituents on the kinetic stabilities, on the spin distribution, and on the ground-state multiplicicty of the biradicals. No systematic studies of *para* substituent effects on biradicals with phenyl groups have been previously conducted. It was our hope to bring these compounds into the fold of traditional physical organic chemistry.

The diazene samples were dissolved in vacuum-transferred 2-methyltetrahydrofuran (MTHF) in thin-walled quartz EPR tubes, the solutions were degassed, and the tubes were cooled to 77 K (liquid nitrogen) or 6 K (liquid helium) in the cavity of an EPR spectrometer. The diazenes were irradiated with either a 500 or 1000 watt mercury arc lamp through filters which restricted transmitted wavelengths to $305 \leq \lambda \leq 386$ nm.

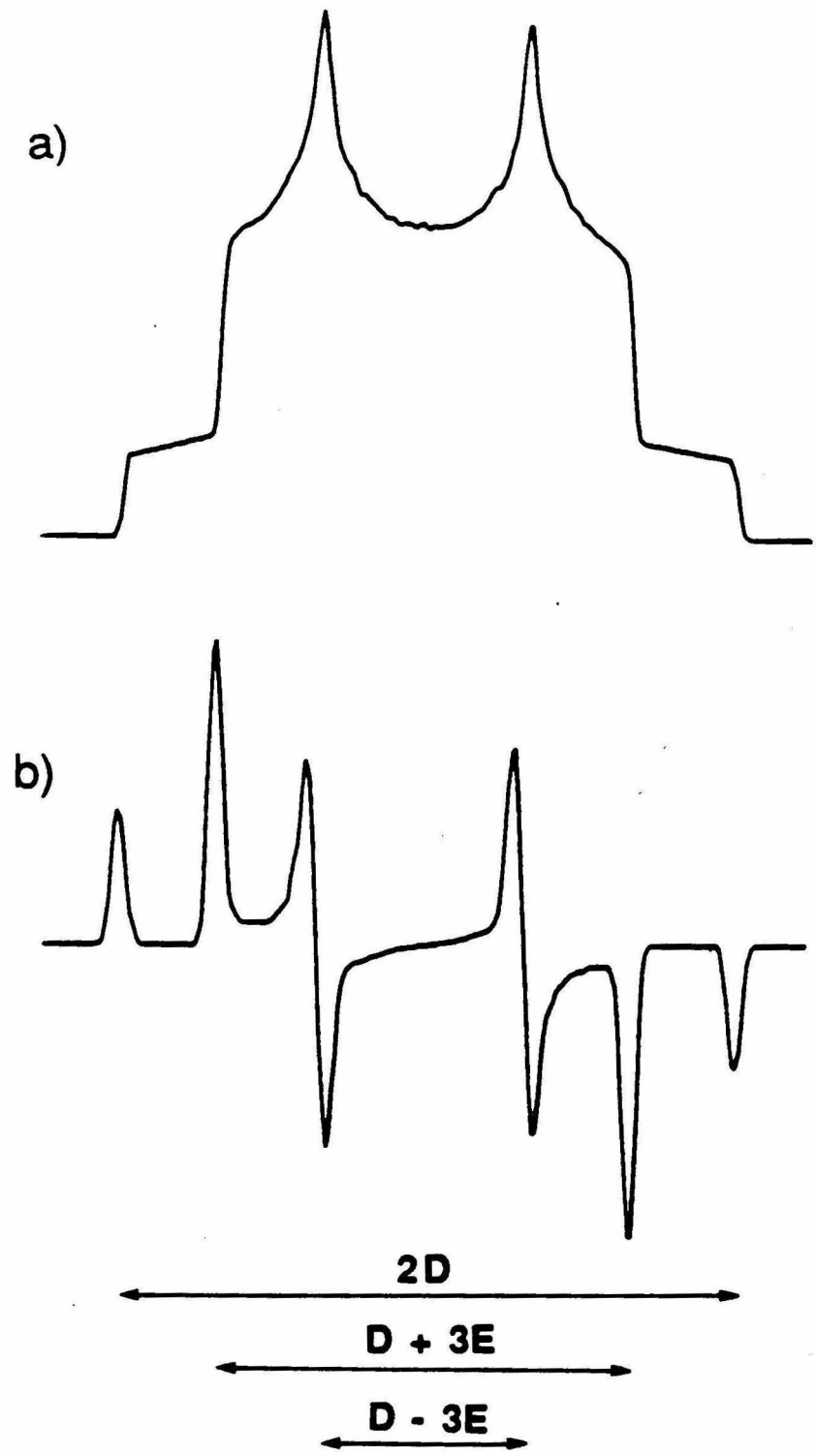


Figure 1-17: Typical first-derivative triplet EPR spectrum (b) and its integral (a).

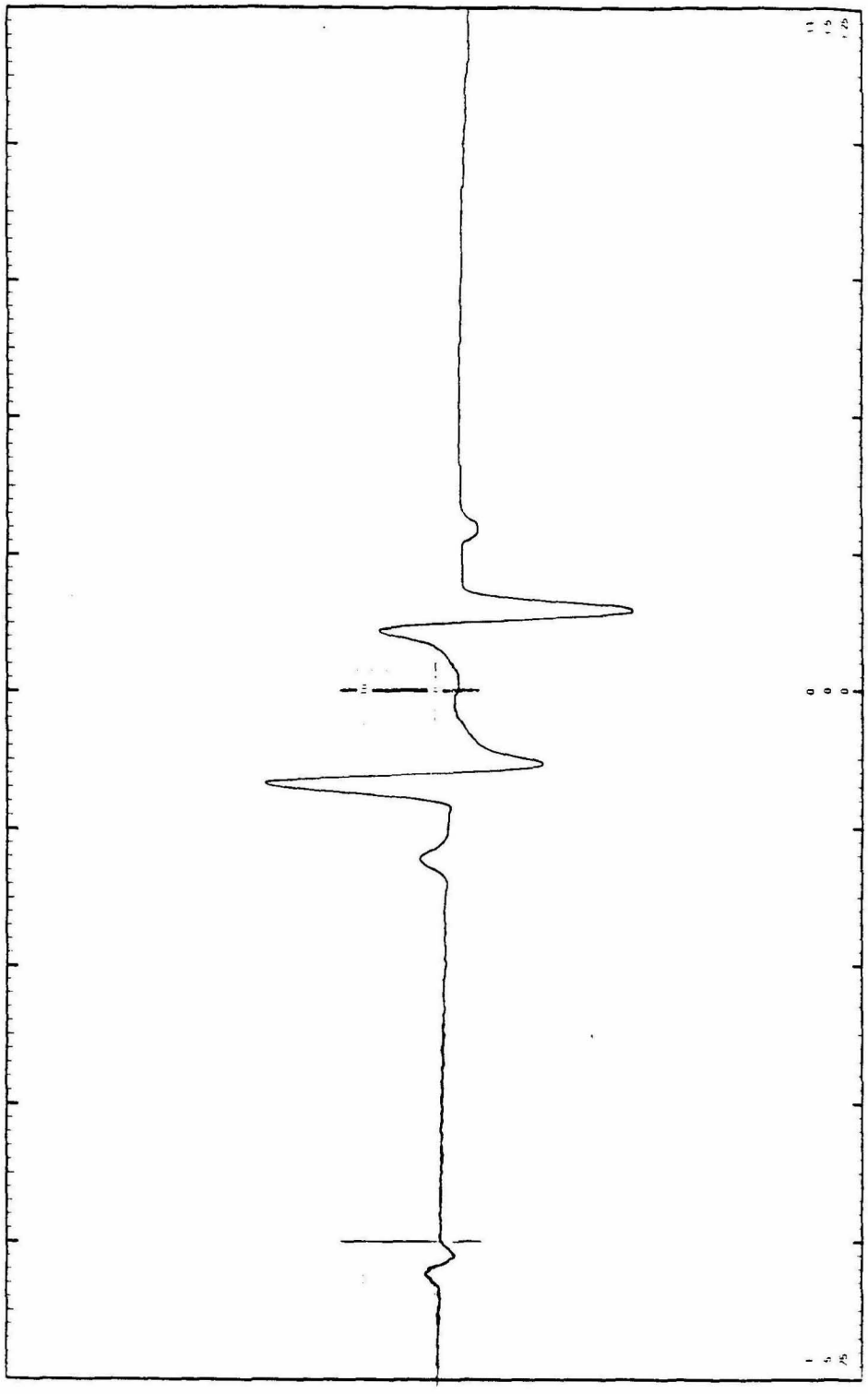


Figure 1-18: Triplet EPR spectrum of **7-MeOMeO** at 77 K.

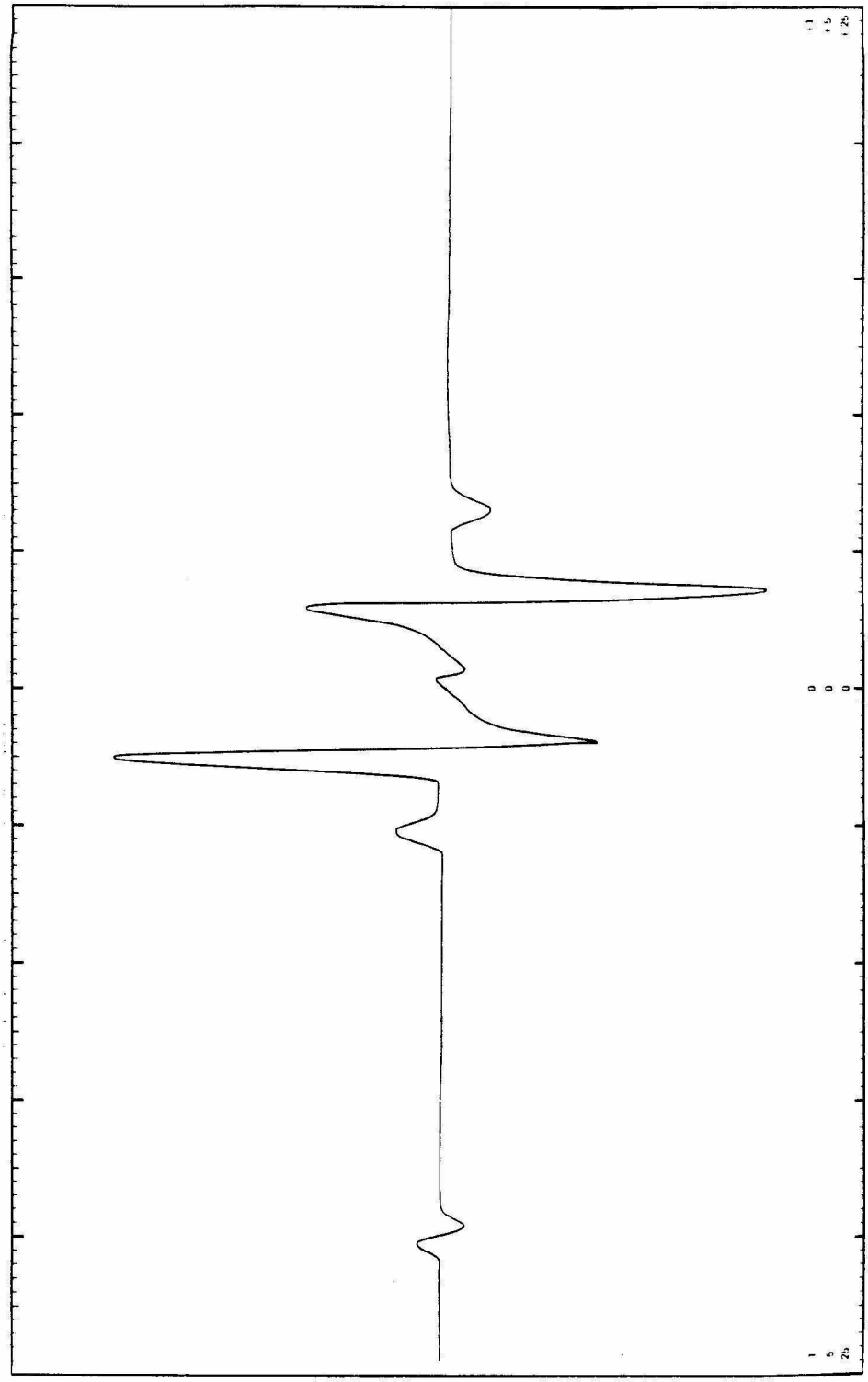


Figure 1-19: Triplet EPR spectrum of **7-MeMe** at 77 K.

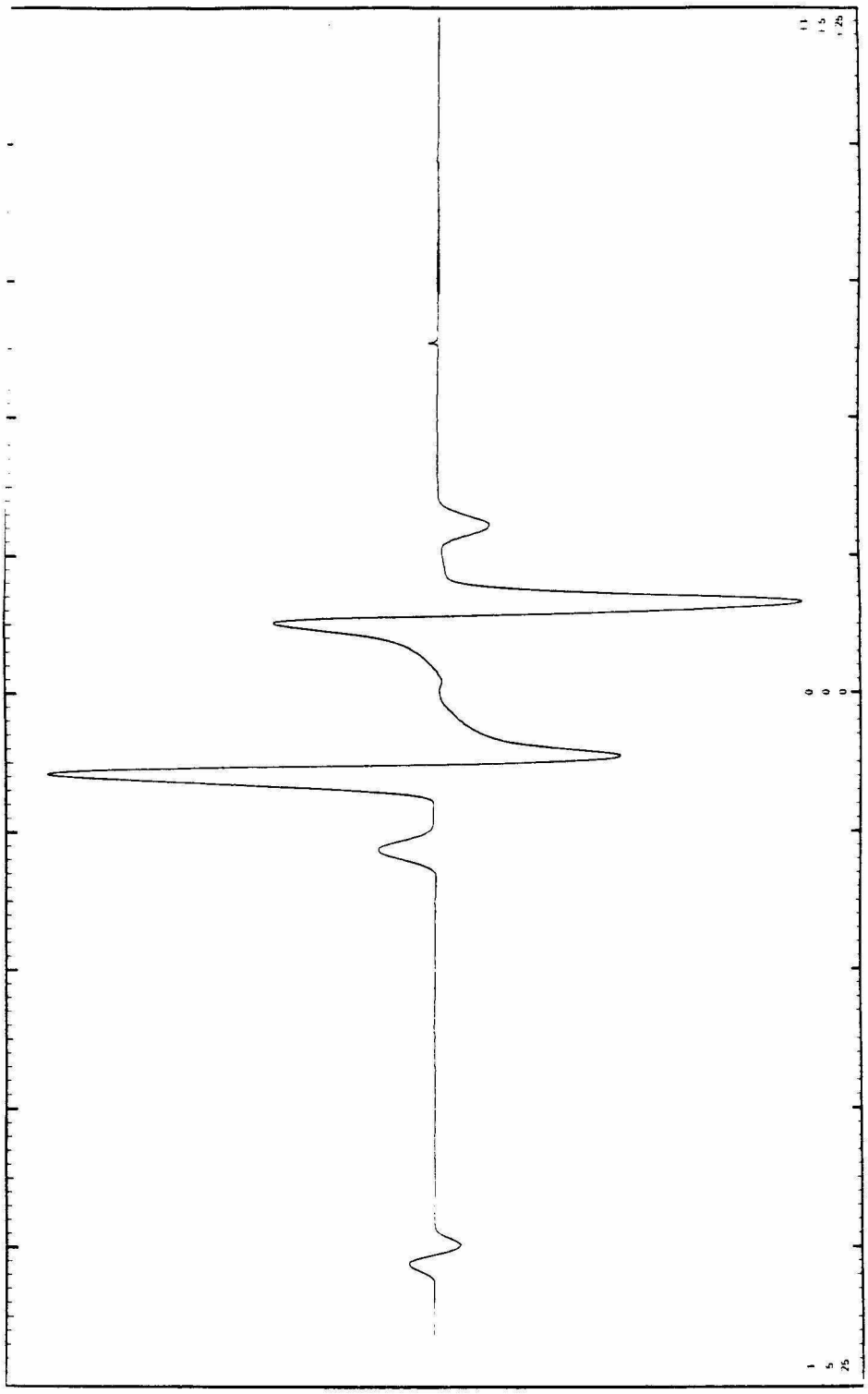


Figure 1-20: Triplet EPR spectrum of **7-MeOBr** at 77 K.

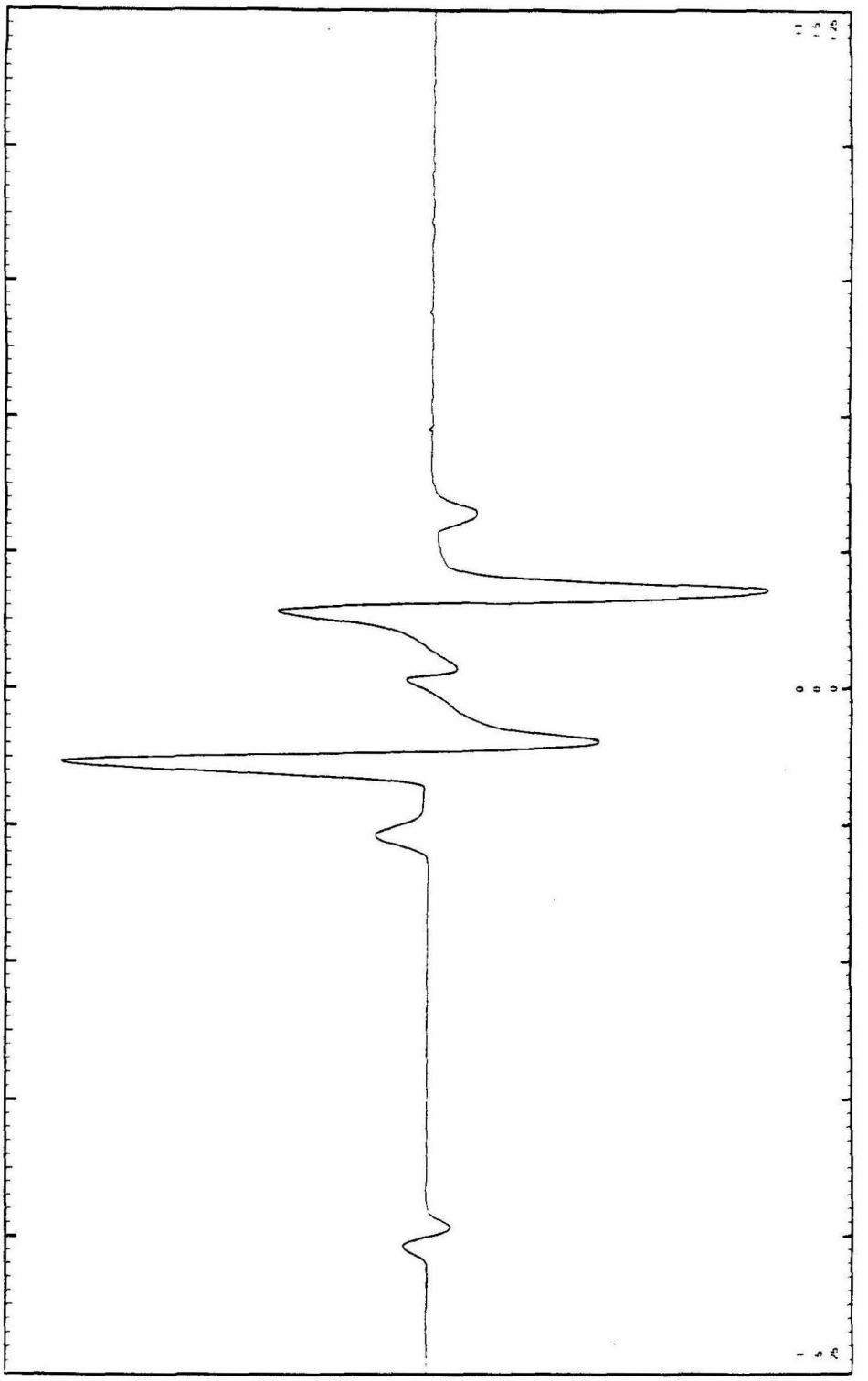


Figure 1-21: Triplet EPR spectrum of **7-MeBr** at 77 K.

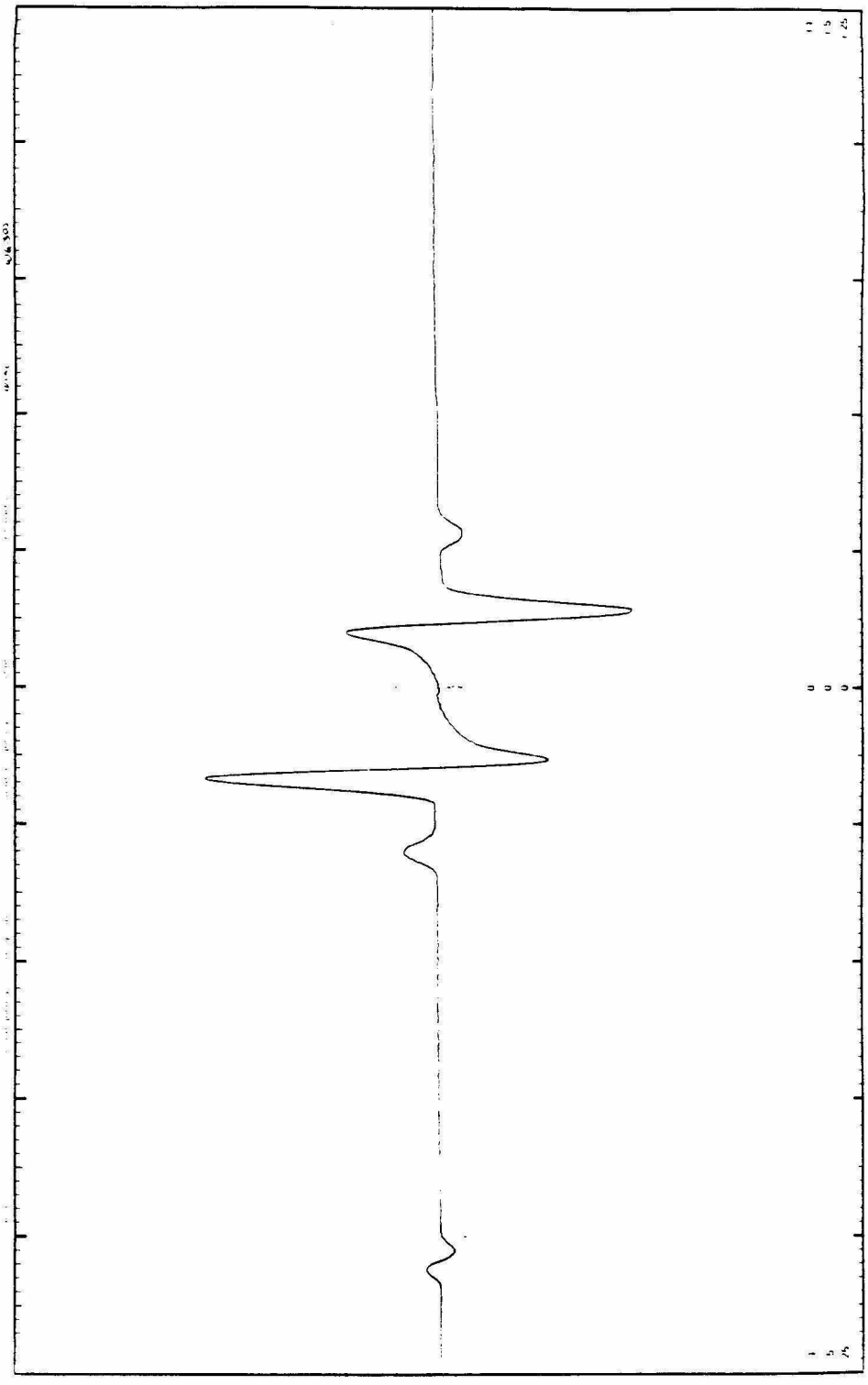


Figure 1-22: Triplet EPR spectrum of **7-BrBr** at 77 K.

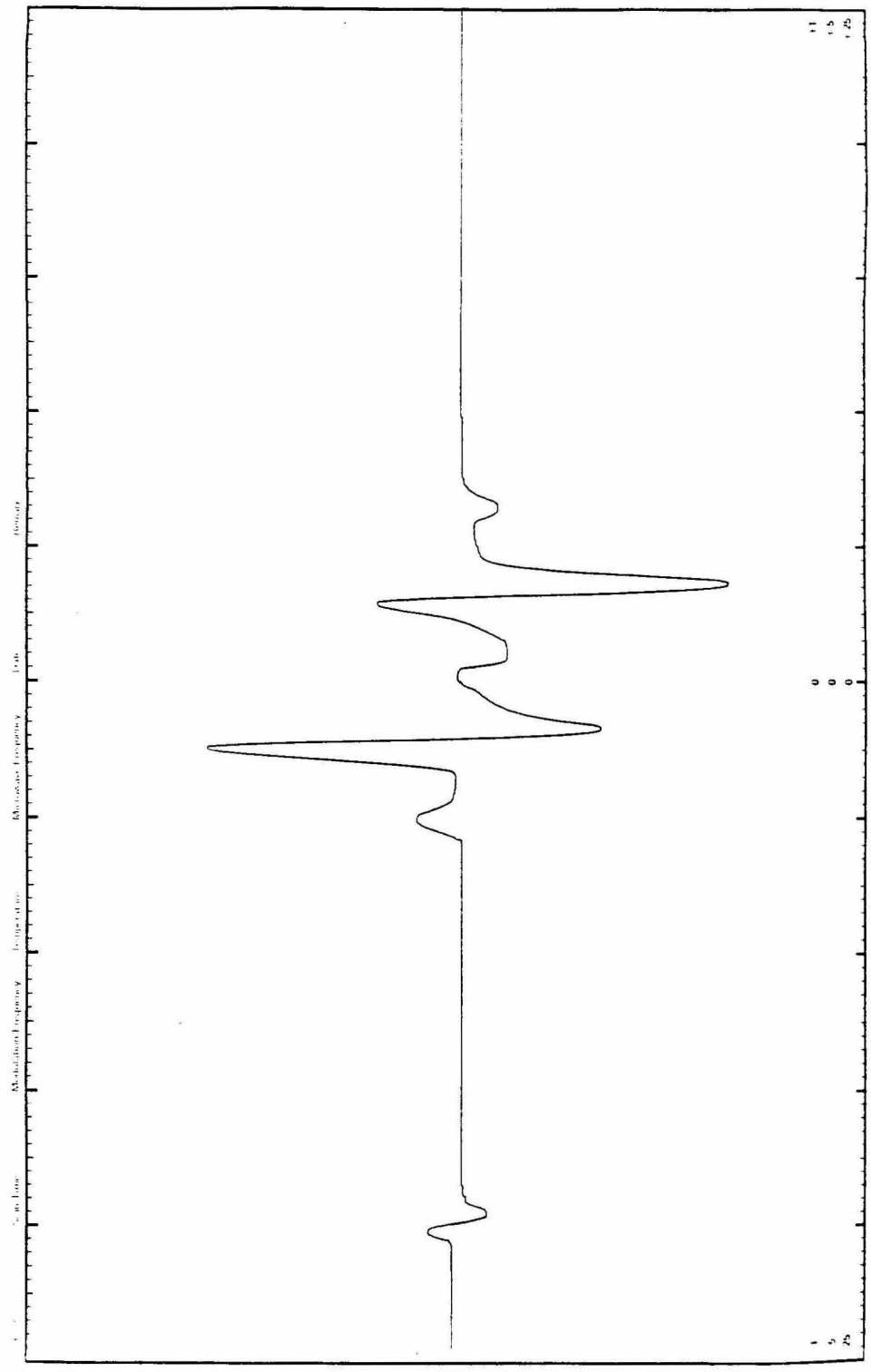


Figure 1-23: Triplet EPR spectrum of **7-MeOPhSO$_2$** at 6 K.

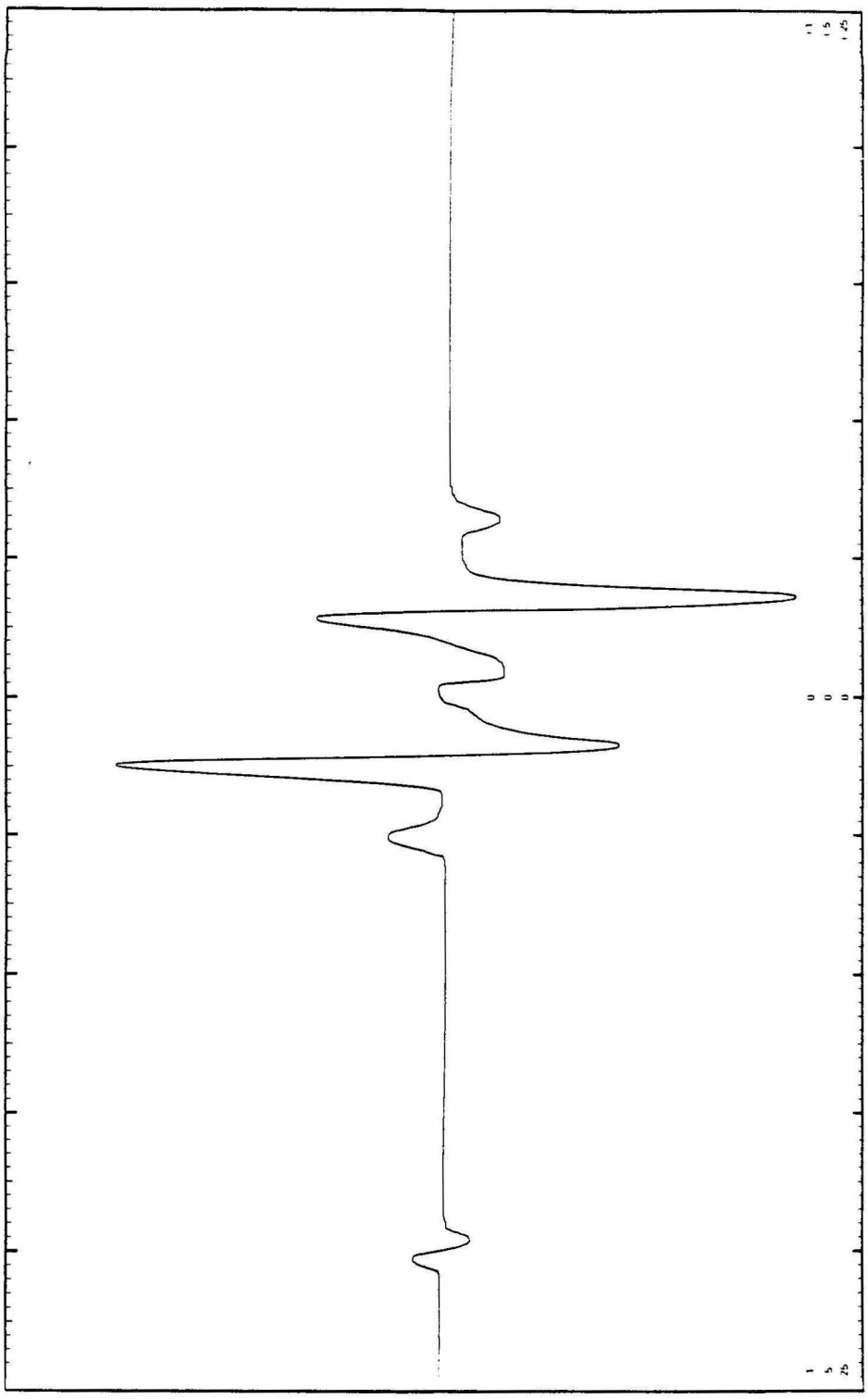


Figure 1-24: Triplet EPR spectrum of **7-MePhSO$_2$** at 6 K.

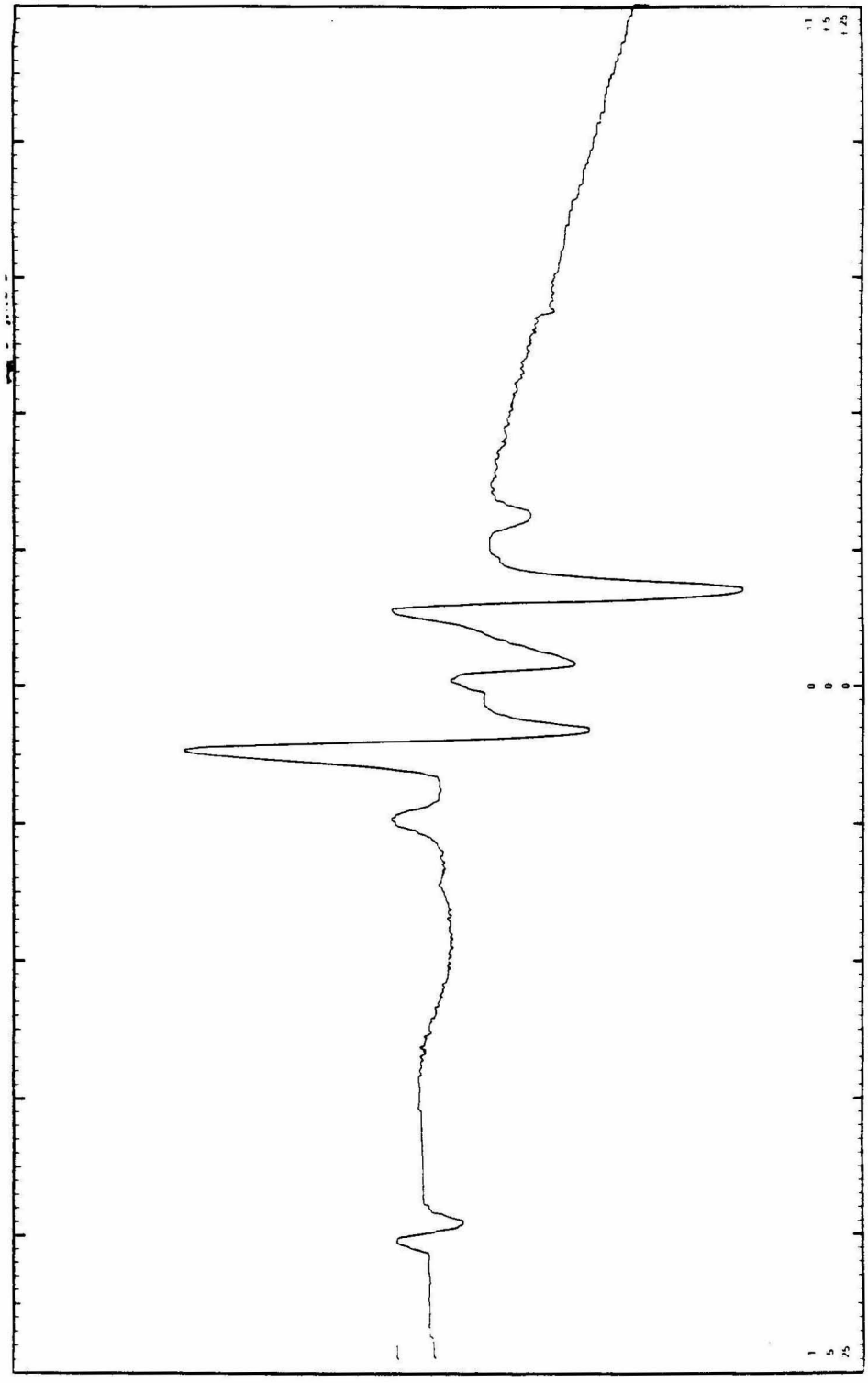
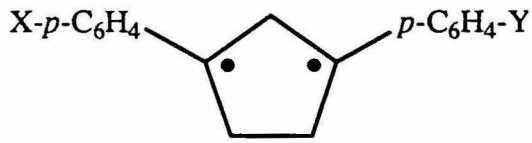


Figure 1-25: Triplet EPR spectrum of **7-PhSO$_2$PhSO$_2$** at 6 K.

The EPR spectra are shown in Figures 1-18 to 1-25. Each spectrum is centered at 3300 Gauss and is 4000 Gauss wide. The spectrum of **7-MeOMeO** is essentially an exact match of that of **4**;[16,17] the spectra are superimposible without discernible difference in spectral features. In analogy to **4**, we assume that the 1,3-diaryl-1,3-cyclopentadiyls are ground state triplets because the triplet signals are readily observable at 6 K. Table 1-3 lists the values of 2 x |*D*| measured from the triplet spectra and the outcome of their conversion into |*D*/hc| values. The values for |*E*/hc| are also listed.

Table 1-3: Zfs parameters |*D*/hc| and |*E*/hc| for the 1,3-diaryl-1,3-cyclopentadiyls.



7-XY

7-XY	2 x |*D*| (Gauss) (±5)	|*D*/hc| (cm^{-1}) (±0.00023)	|*E*/hc| (cm^{-1})
7-MeOMeO	960	0.0449	0.001
7-MeMe	950	0.0444	0.001
7-MeOBr	945	0.0442	0.001
7-MeBr	940	0.0439	0.001
7-BrBr	930	0.0435	0.001
7-MeOPhSO$_2$	920	0.0430	0.001
7-MePhSO$_2$	915	0.0428	0.001
7-PhSO$_2$PhSO$_2$	880	0.0411	0.001

It is readily observed from Table 1-3 that the |*D*/hc| values decrease more as the *para* substituent becomes more strongly electron-withdrawing. In general, a decrease in the magnitude of |*D*/hc| means that, on average, the two spin-parallel electrons are separated by a greater distance.[60ab] The observed trend in |*D*/hc| values corresponds well with the intuitive notion that a strongly electron-withdrawing group will shift electron density from the benzylic position into the phenyl ring. The consistency of the |*E*/hc| values, which are all equal and the same as that of **4**,[16,17] implies that the *para* substitution, even with two different groups in the same molecule, does not affect the molecular or orbital symmetry of the biradicals in any overt manner.

As with the free energies of activation for the bridge-flip reaction, we sought to correlate the observed trends in |*D*/hc| with known Hammett substituent parameters. Figures 1-26 to 1-32 show the results of a linear free-energy relationship analysis of the |*D*/hc| values for the 1,3-diaryl-1,3-cyclopentadiyls. Eq. 1-4 was used to make the plots. |*D*/hc| is as in Table 1-3, $|D_H/hc|$ is the value for **4** (the same as that of **7-MeOMeO**), and the values of $\sigma = (\sigma_x + \sigma_y)$ are from Table1-2.

$$\log[|D/hc|/|D_H/hc|] = \rho\sigma = \rho(\sigma_x + \sigma_y) \qquad (1\text{-}4)$$

Again, as for the plots of the data from the NMR study of the bridge-flip reaction of the 1,4-diarylbicyclo[2.1.0]pentanes, the $\sigma_F^\bullet$ scale provides a very good correlation for the substituent groups for which it has values (Figure 1-30). Unlike the results for the plot of NMR data *vs.* $(\sigma_{Fx}^\bullet + \sigma_{Fy}^\bullet)$, the magnitude of the $\sigma_F^\bullet$ constant for the phenylsulfonyl group implied by the fit is more in accord with the values the $\sigma_F^\bullet$ scale has for other strongly electron-withdrawing groups (*vide supra*). There is, however, no compelling interpretation of the the radical bromination reaction of 4-substituted-3-cyanotoluenes which makes one expect that it would provide substituent constants which correlate with |*D*/hc| values from triplet EPR spectra. Without a value for the phenylsulfonyl group, even if only empirically derived, it is difficult to meaningfully assess the general utility of this scale.

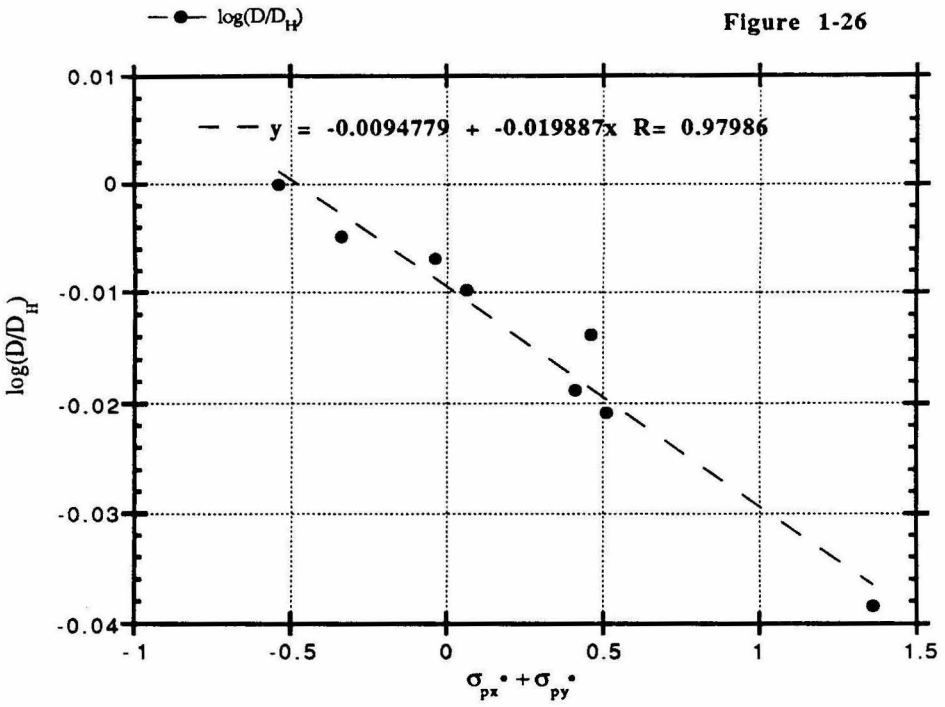


Figure 1-26

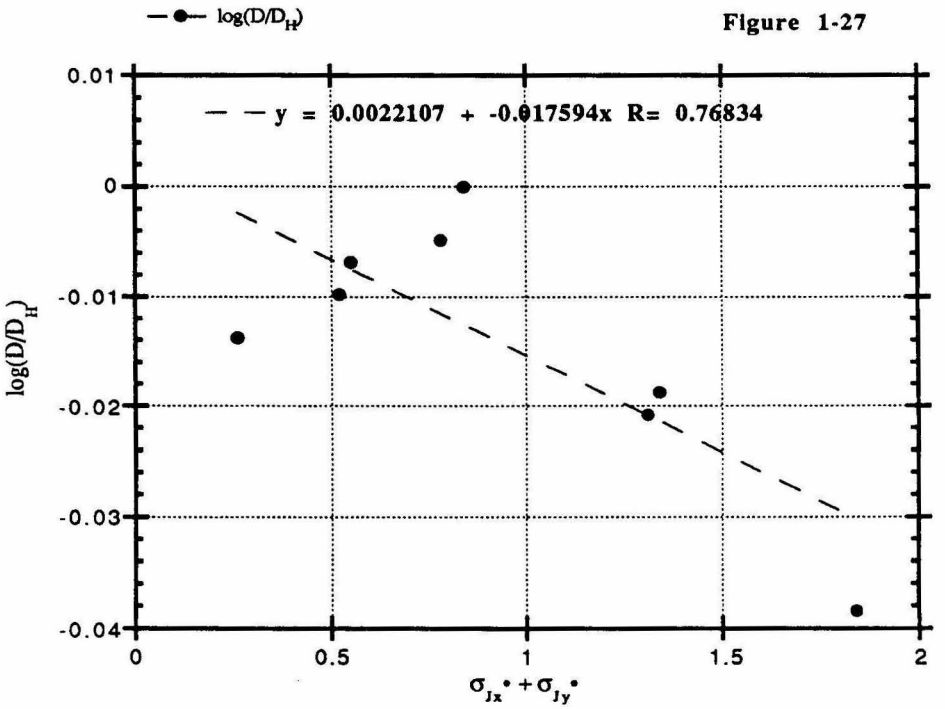


Figure 1-27

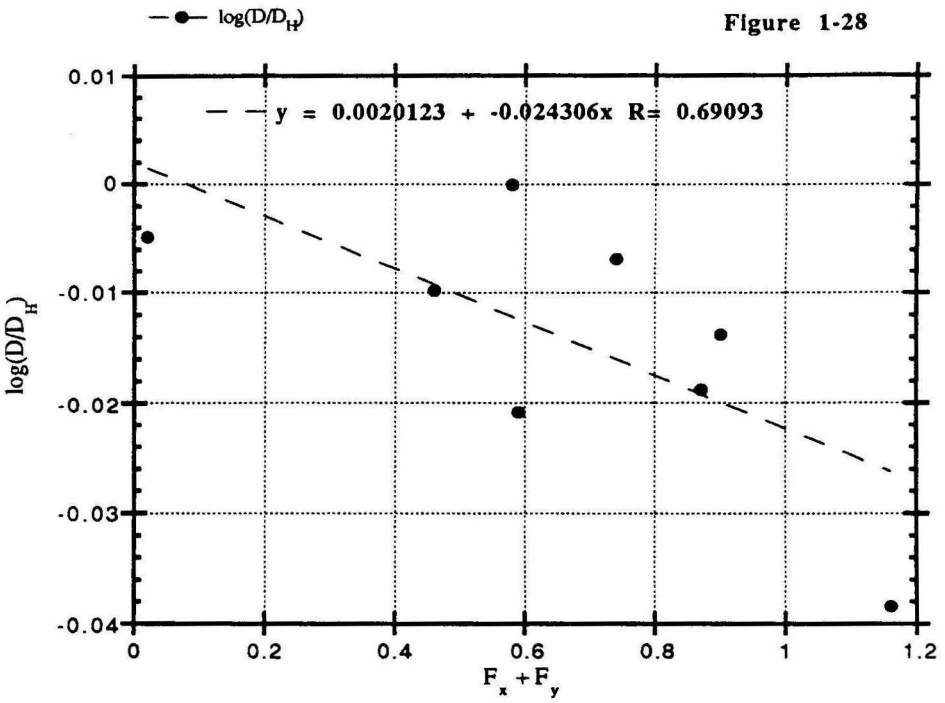


Figure 1-28

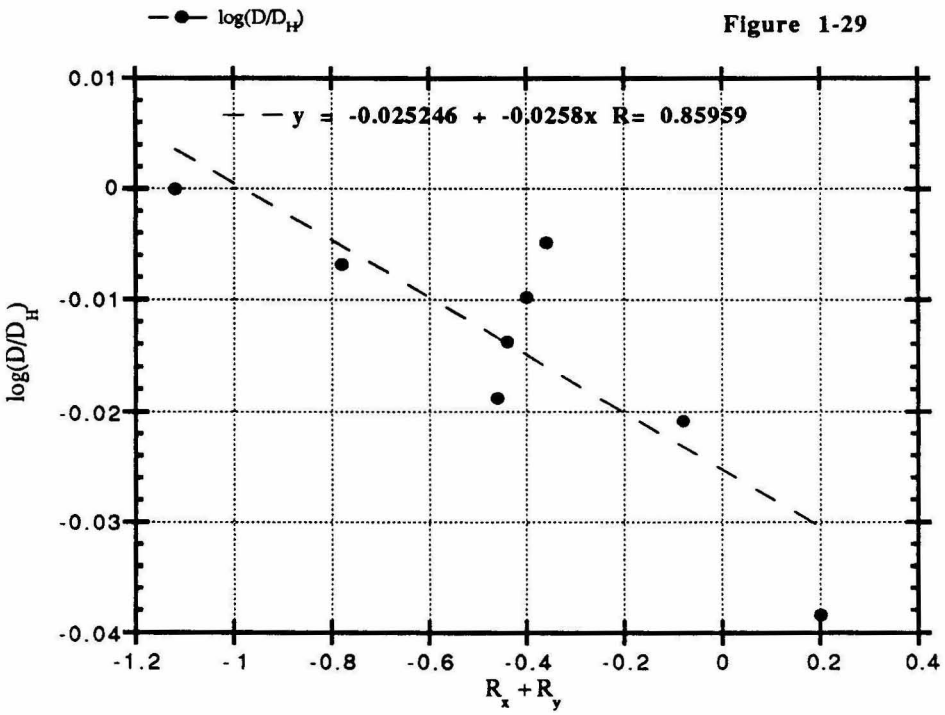


Figure 1-29

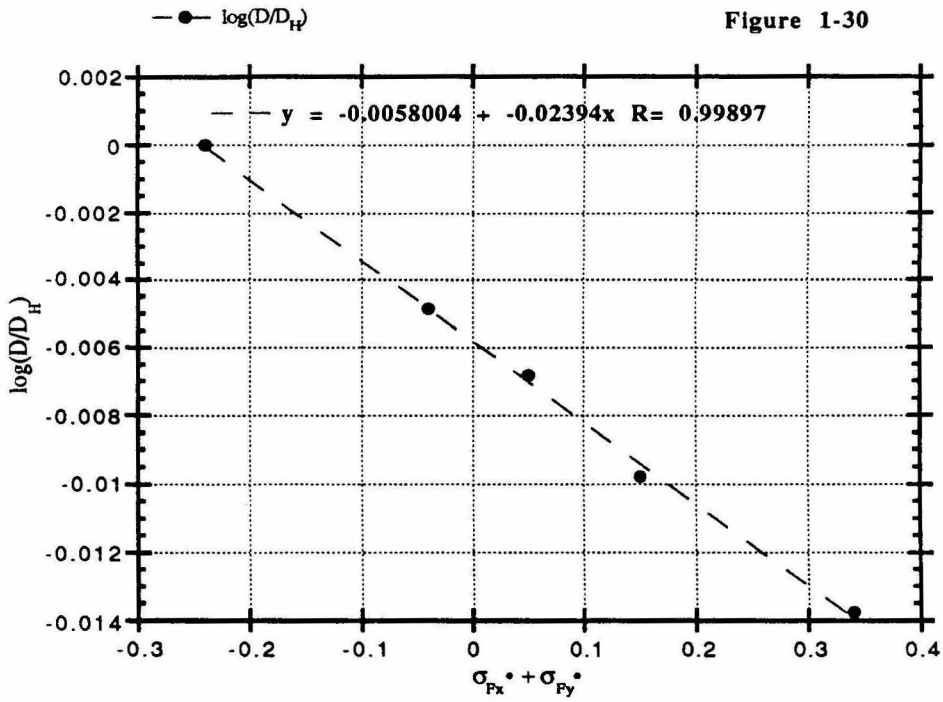


Figure 1-30

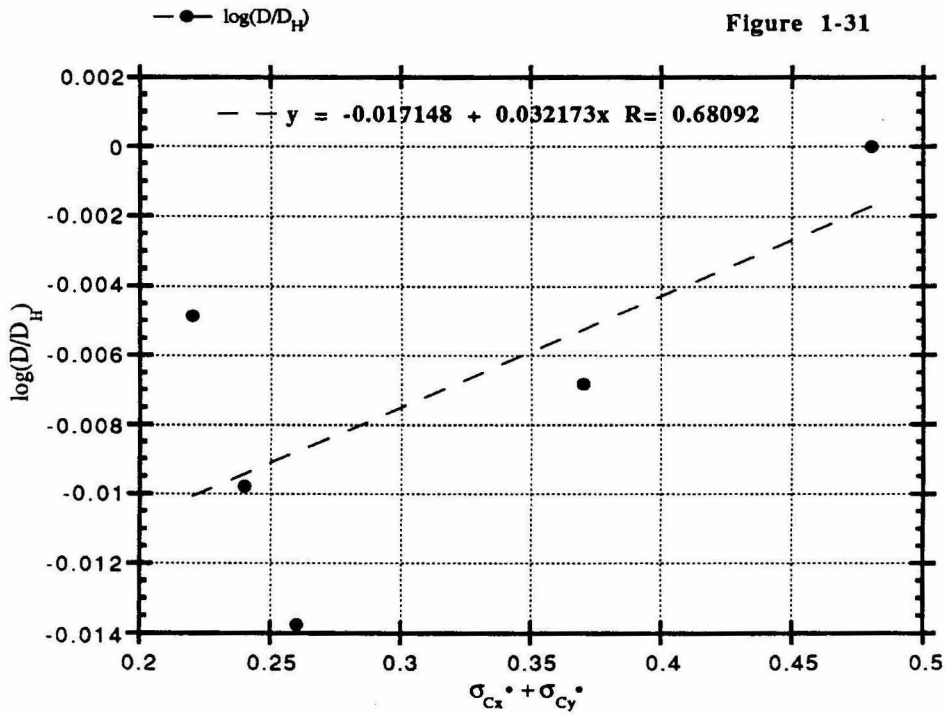


Figure 1-31

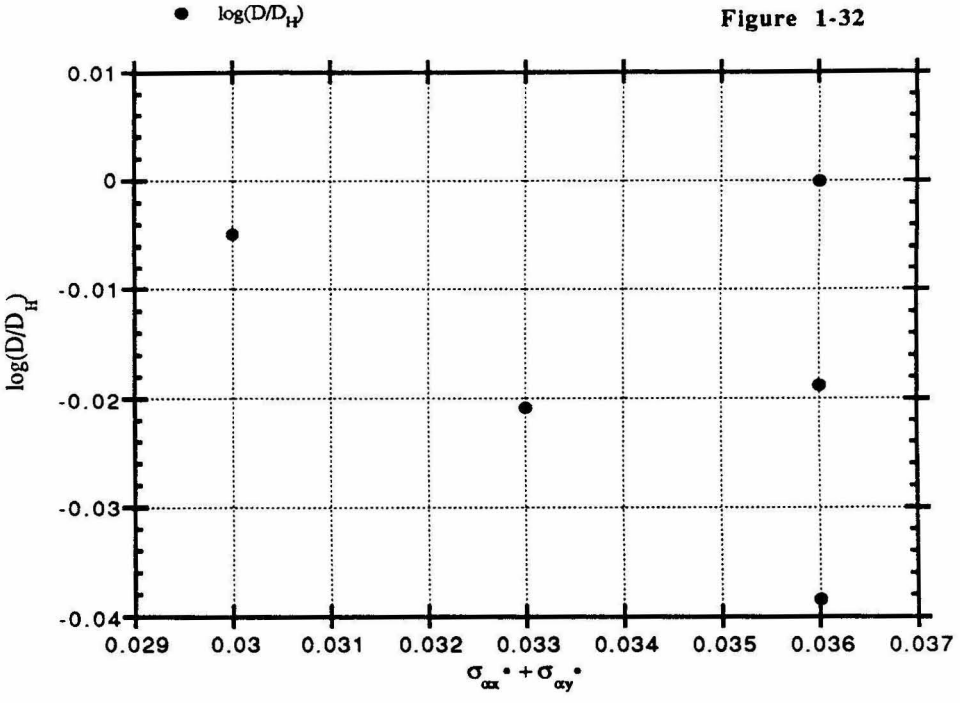


Figure 1-32

An examination of the other plots indicates that only one other scale, the standard Hammett substituent constant for *para* substituents, σ_p, provides a good fit to the observed EPR data (Figure 1-26). **7-MeOMeO** and **4** have essentially the same EPR spectrum, which indicates that methoxy and hydrogen have the same effect in this system. Methoxy is an inductive electron-withdrawing group because of the electronegative oxygen and is also a resonance electron donor (of oxygen lone pairs). These properties appear to cancel each other in this system. The only parameter of those in Table 1-2 which is known to take into account both inductive and resonance properties of substituent groups to achieve a balanced assessment of those effects on chemical properties is σ_p. However, that σ_p should correlate well with a non-kinetic and temperature-independent property of biradicals such as |*D*/hc|, which reflects electron distribution, is quite surprising, if for no other reason than the σ_p scale has not previously correlated well with radical reactions.[20]

An anecdotal observation is that in plots of data *vs.* σ_p, small values of ρ often mean a radical intermediate is involved (clearly the case in this system).[20] The ρ value obtained in the plot *vs.* σ_p here is ≈-0.02. Also, in correlations *vs.* σ_p, negative values of ρ mean that electron-donating groups cause an increase in the property being studied.[20] That groups which increase the electron density of the phenyl rings cause the benzylic radical electrons to be less delocalized into the phenyl rings (as is plainly the case in this system) seems reasonable.

An *a priori* expectation, simply based upon its origin in the EPR studies of the effects of *para* substituents on the electon-nuclear hyperfine coupling (referred to as hyperfine coupling hereafter) observed in substituted benzyl radicals, would logically have been that the $\sigma_\alpha^\bullet$ scale would have accounted for the EPR results observed for the 1,3-diaryl-1,3-cyclopentadiyls.[45] It is noted that a common application of the $\sigma_\alpha^\bullet$ scale is its use as a second fitting parameter in linear free-energy equations.[61] Due to their small magnitudes in comparison with other substituent constants, the $\sigma_\alpha^\bullet$ constants function as "correction factors" to improve the quality of the fits obtained in plots *vs.* other substituent constants. The equations then take the form $\log[K/K_0] = \rho_\alpha\sigma_\alpha^\bullet + \rho\sigma$.[61] It is further noted that the inclusion of extra fitting parameters with their own weighting coefficients (in this case ρ_α) will generally improve the quality of any attempted correlation.[20]

The σ_p scale can be used to factor the observed |*D*/hc| values into contributions from electronic and spin-orbit effects. Figure 1-33 is a plot of $\log[|D/hc|/|D_H/hc|]$ *vs.* $(\sigma_{px} + \sigma_{py})$ for only the biradicals which do not contain bromine. The fit obtained can be seen to be excellent. Why is there improvement when |*D*/hc| values for bromine-containing 1,3-diaryl-1,3-cyclopentadiyls **7-MeOBr**, **7-MeBr**, and **7-BrBr** are excluded? From studies on the halogen-substituted trimethylenemethane (TMM) derivatives **9-HBr**, **9-BrBr**, and **9-HI**, it was determined that the presence of a heavy atom such as bromine or iodine greatly increases the |*D*/hc| values as compared to the |*D*/hc| value of the unsubstituted

derivative **9-HH** (Table 1-4).[62] The value of |*D*/hc| was found to no longer be solely dependent on the separation of the electrons, but also on spin-orbit coupling.[60b,62]

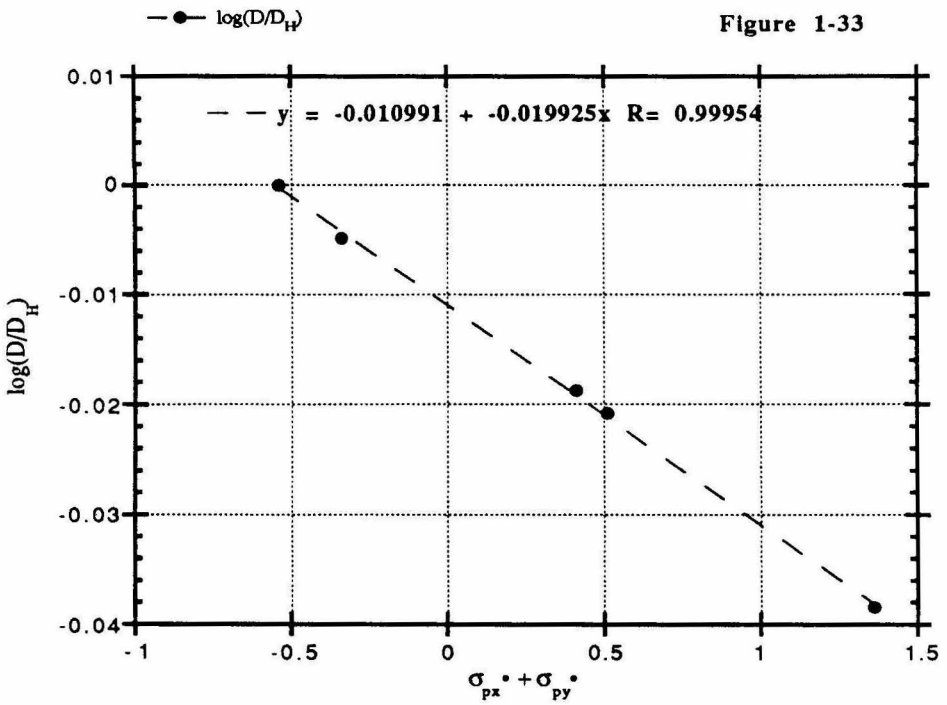
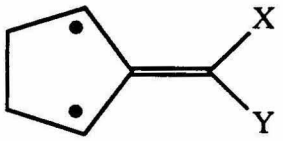


Figure 1-33

Table 1-4: Heavy-atom effects on |*D*/hc| values for TMM derivatives.[a]



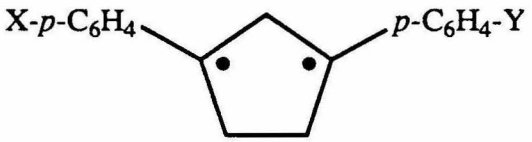
9-XY

9-XY	|*D*/hc| (cm^{-1})
9-HH	0.0265
9-HBr	0.0529
9-BrBr	0.0873
9-HI	0.2637

[a] Hilinski, E. F.; Ph. D. Thesis; Yale University; 1982.

Because it does not include the data from the bromine-containing biradicals, the plot in Figure 1-33 correlates only inductive and resonance effects of substituents with the distribution of electrons in the 1,3-diaryl-1,3-cyclopentadiyl system. Thus the use of the σ_p scale allows the |*D*/hc| values for the bromine-containing biradicals to be factored into contributions from field and resonance effects and from spin-orbit coupling. Accordingly, by using the values for $(\sigma_{px} + \sigma_{py})$ obtained from Table 1-2 and the equation of the line for the fit in Figure 1-33, the data in Table 1-5 can be derived. $|D/hc|_{observed}$ are the observed values from Table1-3. $|D/hc|_{calculated}$ are the values predicted by $(\sigma_{px} + \sigma_{py})$ and the fit of Figure 1-33. They represent the contribution to $|D/hc|_{observed}$ due to the field and resonance effects of the *para* substituents. The $\Delta|D/hc|$ values are the differences between observed and predicted |*D*/hc| values ($|D/hc|_{observed} - |D/hc|_{calculated}$) and represent the spin-orbit coupling contributions to $|D/hc|_{observed}$ provided by the bromine atoms.

Table 1-5: Spin-orbit contributions to |*D*/hc| for bromine-substituted 1,3-diaryl-1,3-cyclopentadiyls.

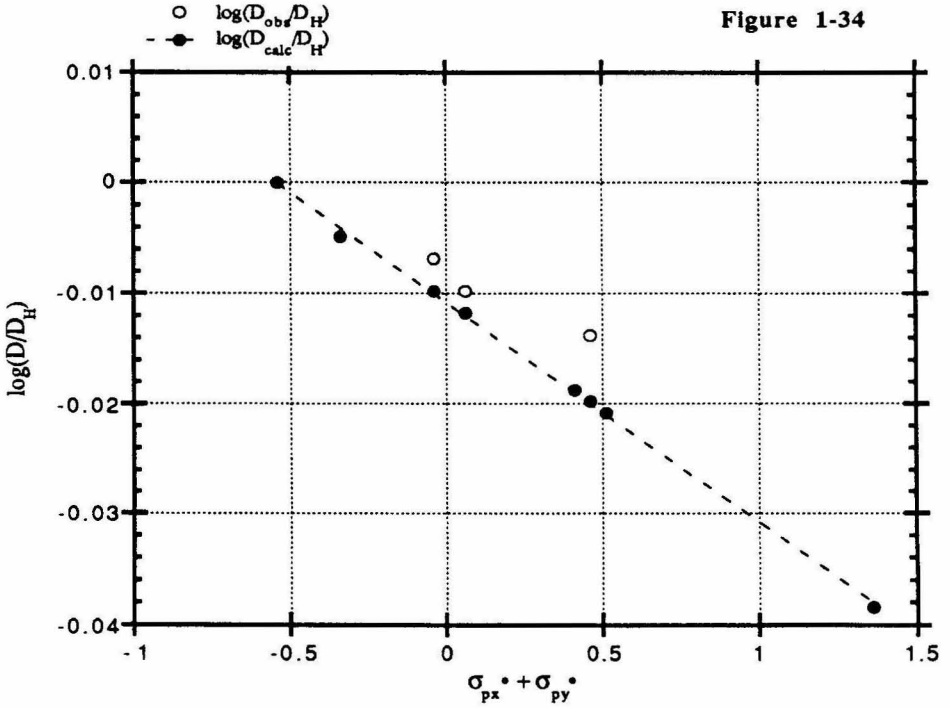


7-XY

7-XY	$\|D/hc\|_{observed}$ (cm^{-1})	$\|D/hc\|_{calculated}$ (cm^{-1})	$\Delta\|D/hc\|$ (cm^{-1})
7-MeOBr	0.0442	0.0439	0.0003
7-MeBr	0.0439	0.0437	0.0002
7-BrBr	0.0435	0.0429	0.0006

The presence of a bromine atom can be seen to be consistently worth an increase in |*D*/hc| of about 0.0003 cm^{-1}. Also, the direction of the effect is consistent with that observed in the TMM derivatives (an increase in |*D*/hc|). The effect is greatly attenuated as compared to the TMM system, but that would be expected: the heavy atoms are substituted directly on a radical center for the TMMs,[62] but are much more remote from the radical centers (the benzylic positions) in the 1,3-diaryl-1,3-cyclopentadiyls. The effect of the bromines is admittedly small in the 1,3-diaryl-1,3-cyclopentadiyl system, but it is significant given the limits of ±0.00023 cm^{-1} on the observed |*D*/hc| values in Table 1-3.

The change in |*D*/hc| values for the bromine-containing biradicals is most easily visualized graphically. Figure 1-34 plots the |*D*/hc| values for the biradicals without bromines (Table 1-3) and the $|D/hc|_{calculated}$ values (Table 1-5) for the bromine-containing biradicals on one line. It also shows the three $|D/hc|_{observed}$ values (Tables 1-3 and 1-5), which plainly lie above the line.



That the bromines do interact with the unpaired electrons is further evidenced by the appearance of the half-field transitions in the EPR spectra. The $\Delta m_s = 2$ region of triplet biradicals is a useful source of information about hyperfine coupling because, for values of $|D/hc| < 0.06$ cm^{-1}, this transition is only minimally anisotropic and straightforward patterns can be seen.[60a] Hyperfine coupling is in turn an indication of the interaction of nuclear spins with the unpaired electrons of the triplet.[5,16,17] The EPR spectra of the $\Delta m_s = 2$ regions for the eight triplet biradicals are shown in Figures 1-35 to 1-42. Each spectrum is centered at 1650 Gauss and is 400 Gauss wide. As for the $\Delta m_s = 1$ region, the hyperfine coupling pattern seen in **7-MeOMeO** is quite similar to that of **4**.[16,17] Discernible structure can be observed in the spectra for the biradicals with methoxy or phenylsulfonyl substituents. When the substituents are methyl or bromo, the transition is much smoother in appearance and much of the fine structure is lost. Qualitative simulations of this region for these compounds indicated that the additional coupling from the three hydrogens (nuclear spin = 1/2) of the methyl groups and from the bromine atoms (nuclear spin = 3/2) accounts for this loss of structure. The additional splittings which result broaden the patterns beyond the ability of the instrument to resolve them and smoother lines are observed.

In general, the resolution of these triplet spectra is not sufficient to allow quantification of the changes in hyperfine coupling constants caused by the introduction of *para* substituents. Anisotropy of the actual couplings and the simplifying assumption of uniform transition probabilities necessary to the simulation process also serve to act against efforts to extract meaningful information.[17] The changes are slight, as is expected from the small values of the $\sigma_\alpha^\bullet$ constants in Table 1-2. Because these constants were derived from changes in the hyperfine coupling of benzyl radicals, they would be expected to accurately predict the hyperfine coupling in these biradicals.[45,61] On a qualitative level, they do agree with the hyperfine structure observed. The $\sigma_\alpha^\bullet$ constants are the same for methoxy and

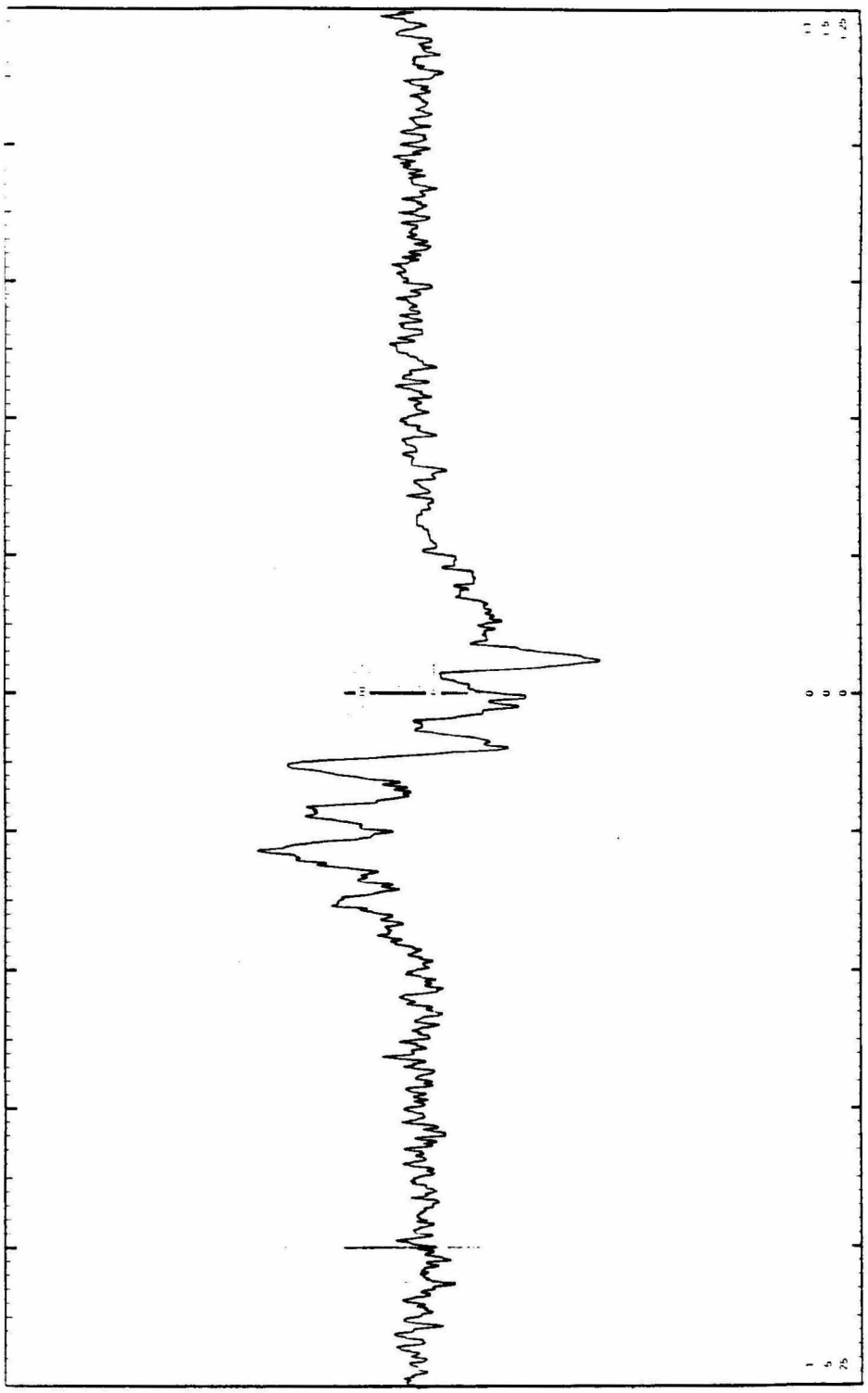


Figure 1-35: EPR spectrum of $\Delta m_s = 2$ region for **7-MeOMeO** at 77 K.

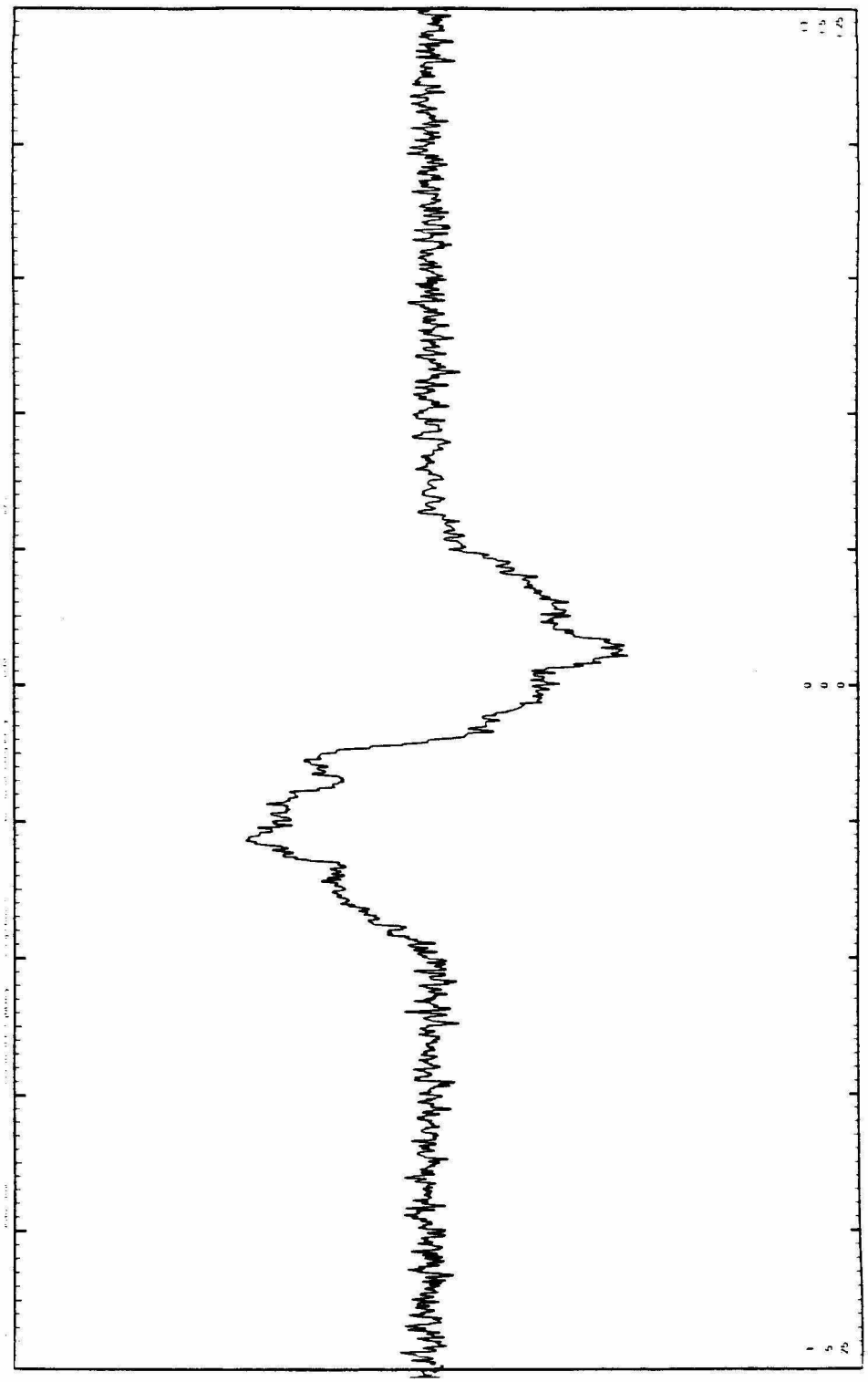


Figure 1-36: EPR spectrum of $\Delta m_s = 2$ region for **7-MeMe** at 77 K.

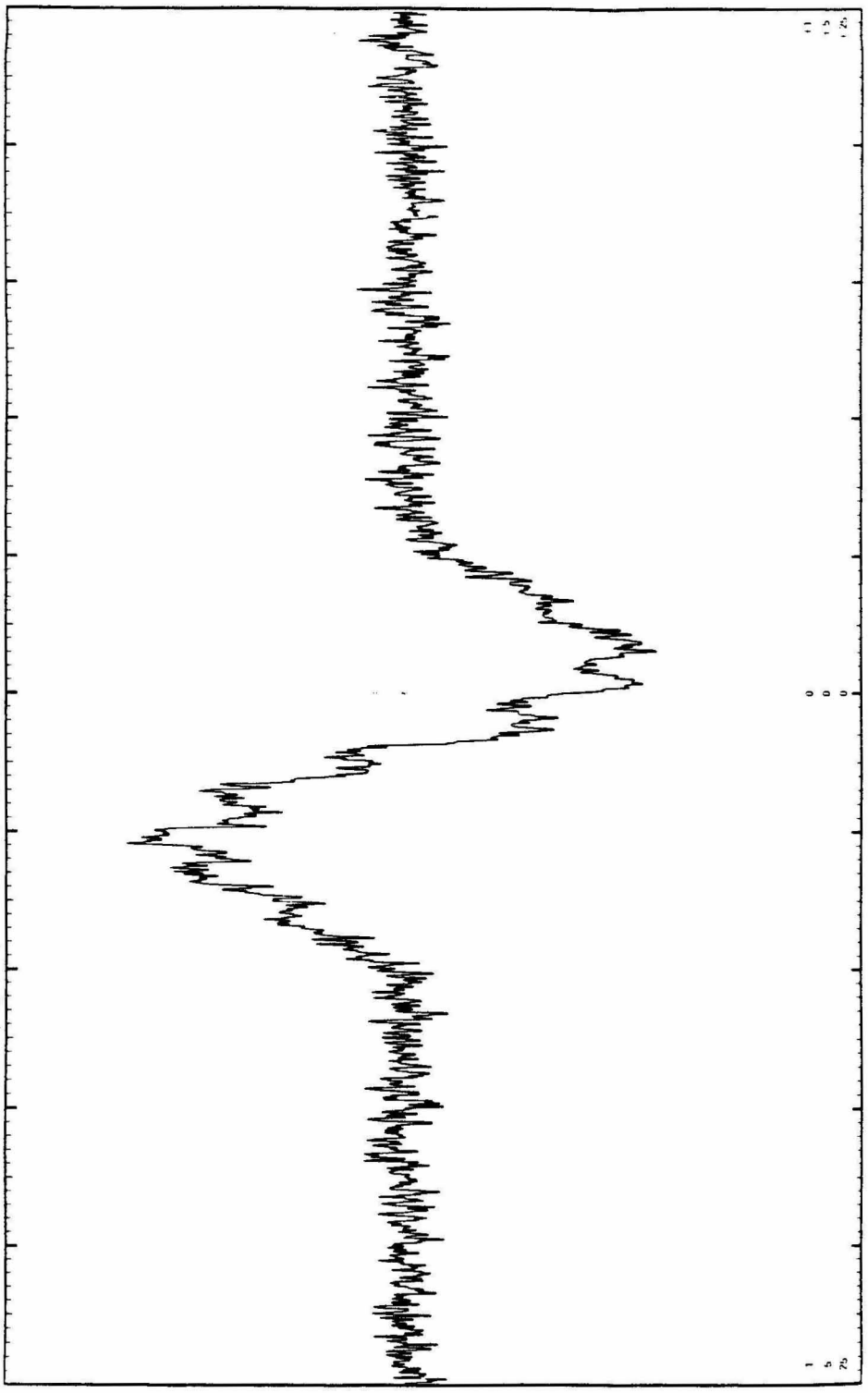


Figure 1-37: EPR spectrum of $\Delta m_s = 2$ region for **7-MeOBr** at 77 K.

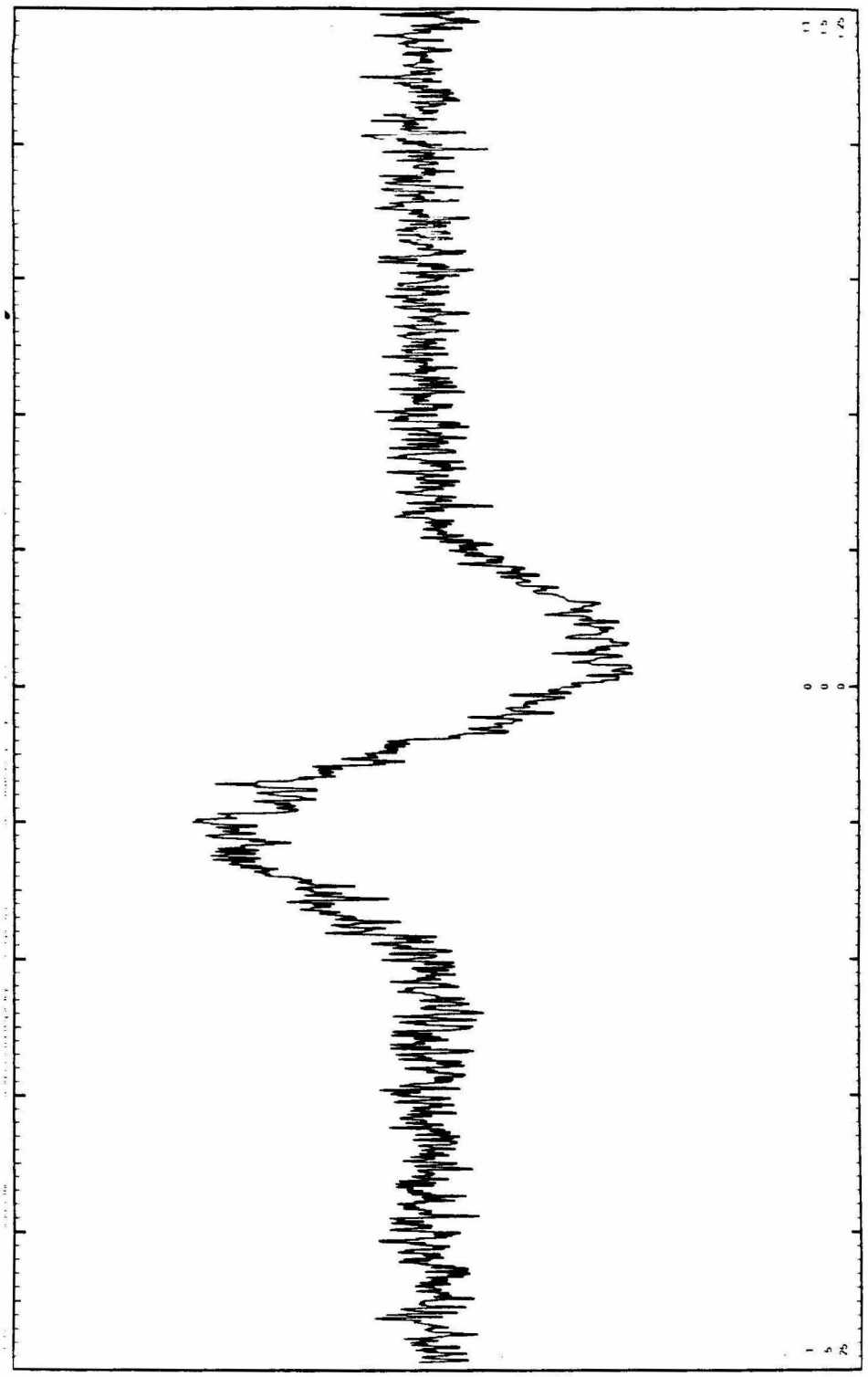


Figure 1-38: EPR spectrum of $\Delta m_s = 2$ region for **7-MeBr** at 77 K.

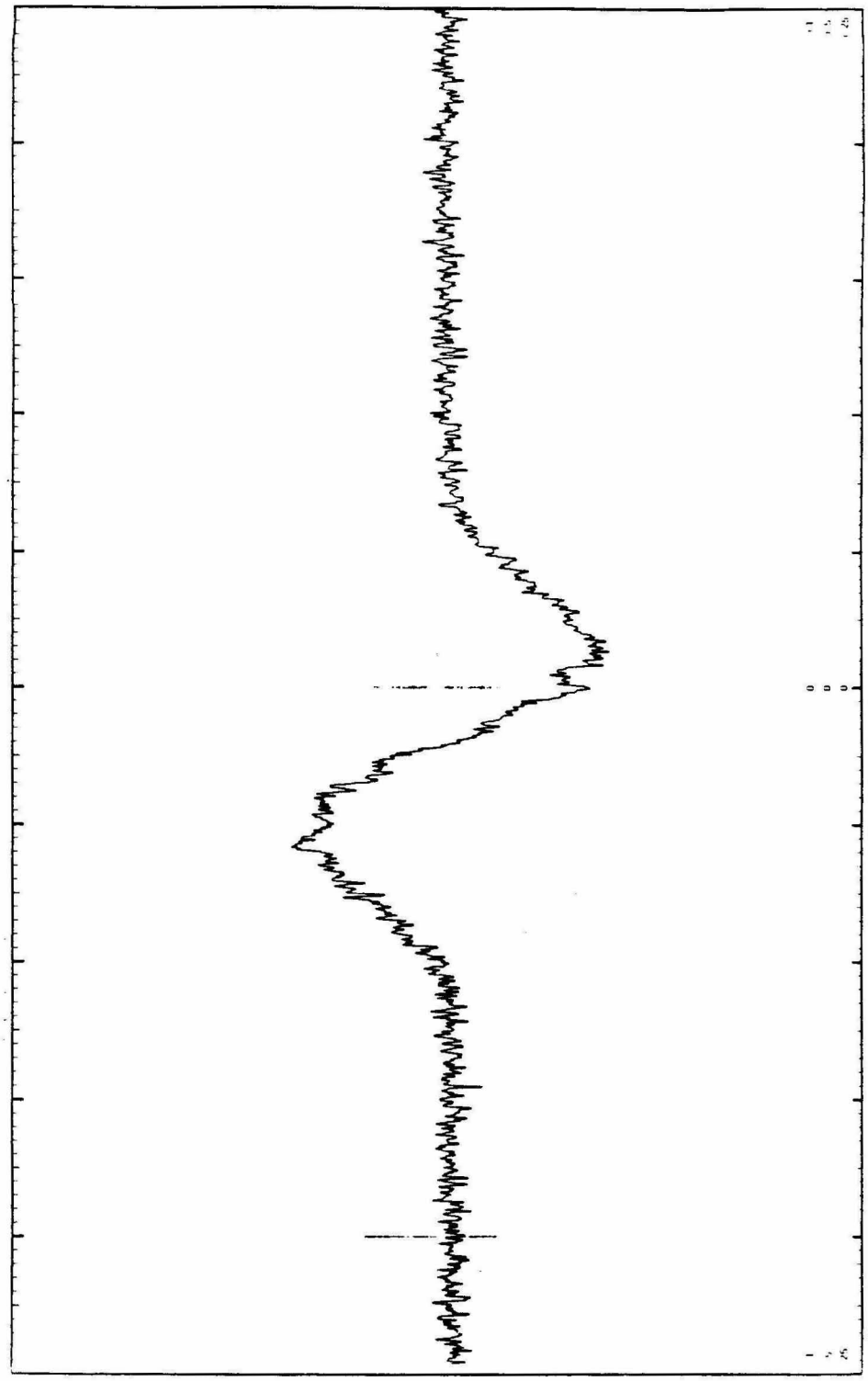


Figure 1-39: EPR spectrum of $\Delta m_s = 2$ region for **7-BrBr** at 77 K.

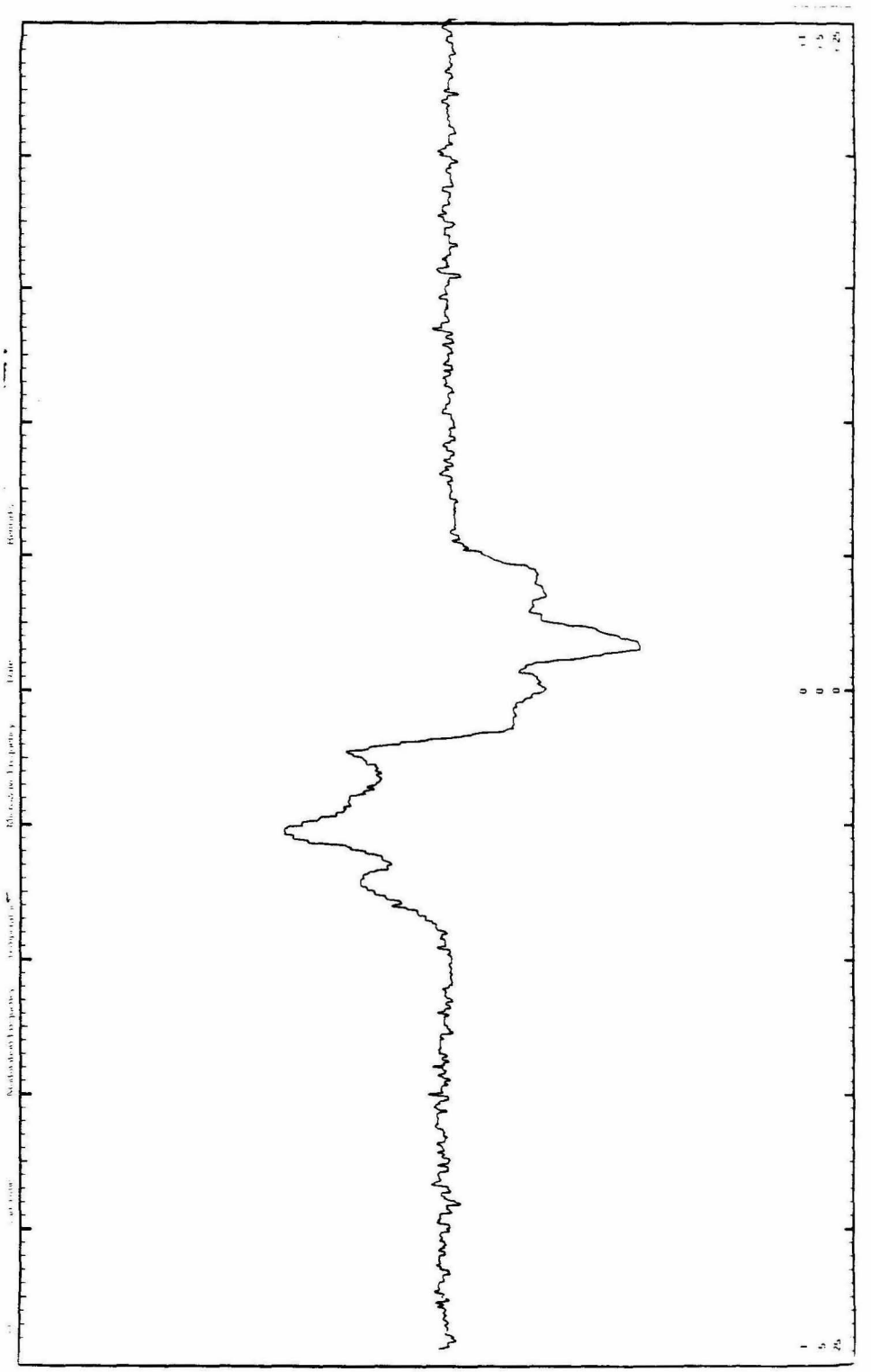


Figure 1-40: EPR spectrum of $\Delta m_S = 2$ region for **7-MeOPhSO$_2$** at 6 K.

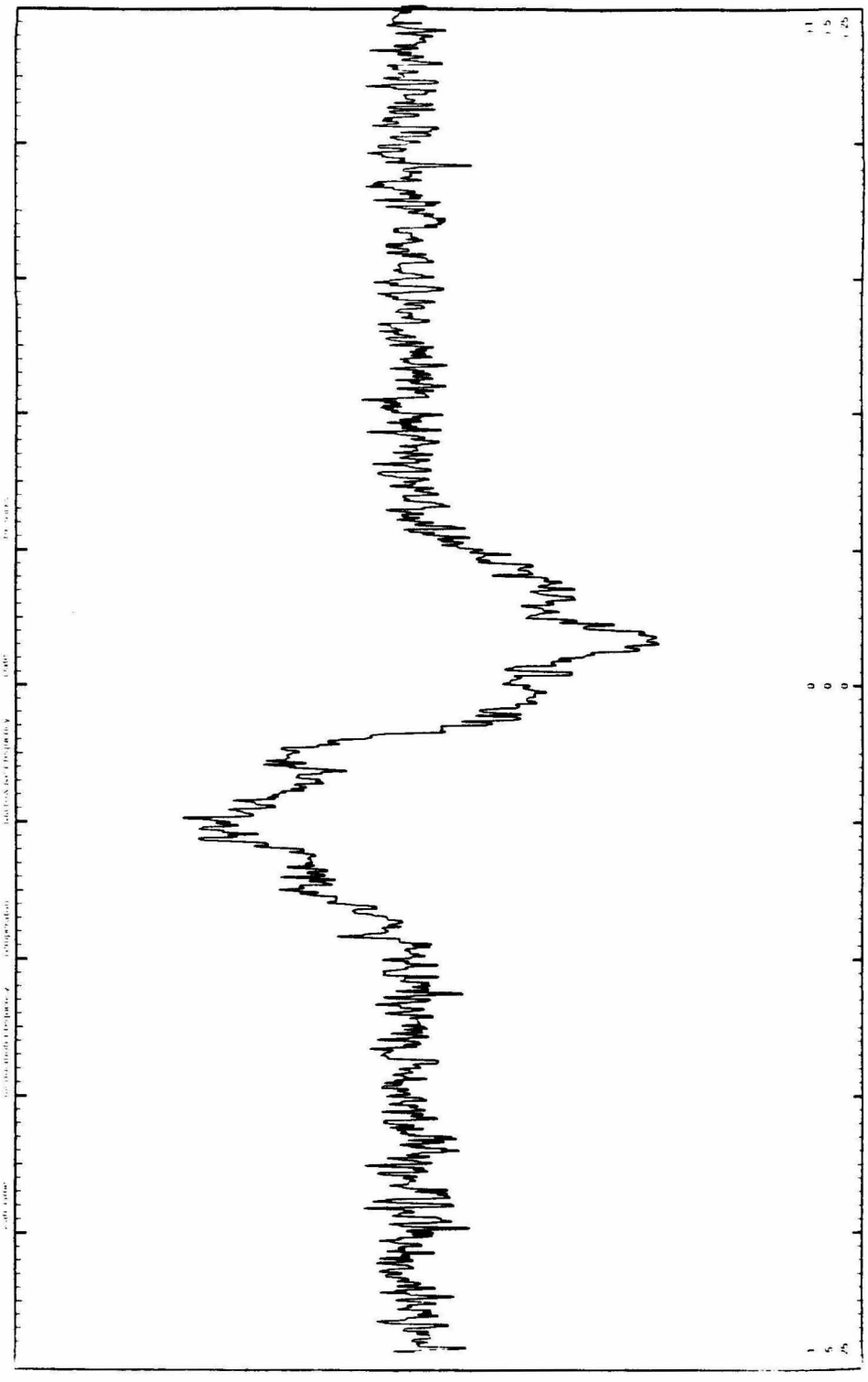


Figure 1-41: EPR spectrum of $\Delta m_S = 2$ region for **7-MePhSO$_2$** at 6 K.

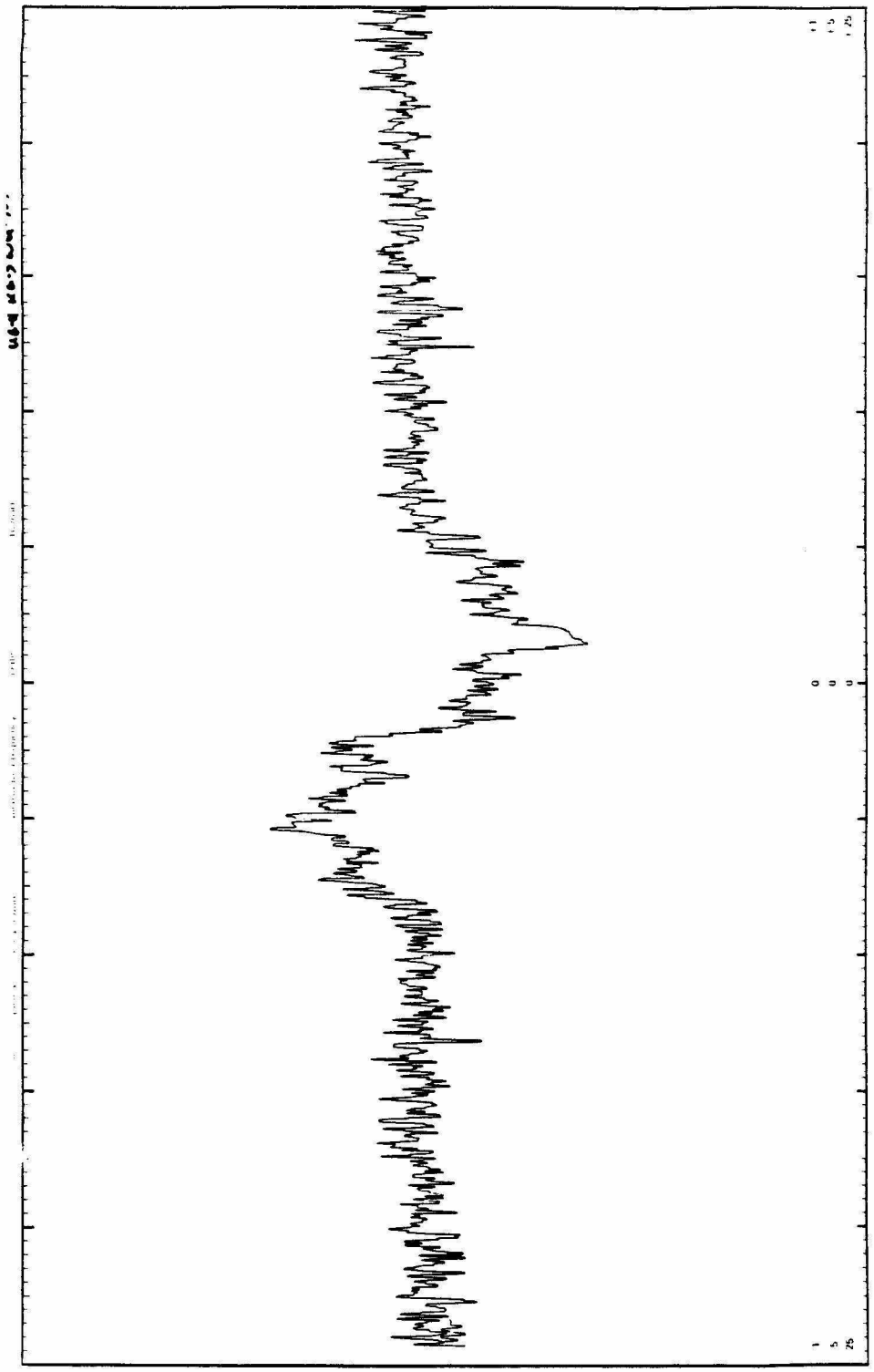


Figure 1-42: EPR spectrum of $\Delta m_s = 2$ region for **7-PhSO$_2$PhSO$_2$** at 6 K.

phenylsulfonyl substituents, and examination of the corresponding spectra for compounds with these groups shows that the hyperfine structure in the $\Delta m_s = 2$ region which arises from them is similar.

The biradicals without phenylsulfonyl substituents are all persistent at 77 K and exhibit little decay in signal intensity over the time span of the EPR experiments (≈1/2 hr.). Their decay behavior at this temperature is qualitatively the same as that displayed by **4**.[17] Figures 1-43 to 1-45 show decay traces of the phenyl-sulfonyl-substituted biradicals **7-MeOPhSO$_2$**, **7-MePhSO$_2$**, and **7-PhSO$_2$PhSO$_2$** at 77 K. Each trace was obtained by irradiating ($305 \leq \lambda \leq 386$ nm) the corresponding diazene sample in an MTHF glass at 77 K for ten minutes and observing the signal intensity increase. After the ten-minute photolysis, the lamp was turned off and the signal allowed to decrease for fifty minutes. The signals for **7-MeOPhSO$_2$** and **7-MePhSO$_2$** were monitored at 3040 G, and the signal for **7-PhSO$_2$PhSO$_2$** was monitored at 3055 G.

1,3-Cyclopentadiyls,[12,16,17] like 1,3-cyclobutadiyls,[15] undergo unimolecular decay to the ring-closed, bicyclic compounds under matrix isolation conditions. The decay rates are non-exponential and are strongly dependent on matrix site effects, but no reaction with the matrix solvent (such as hydrogen abstraction) is observed.[15,16,17] Meaningful kinetic analysis of such systems is complicated. It has been found that a model which has a Gaussian distribution of E_a values and one log A value fits the observed decay data well.[15,17] A most probable rate (k^0) can then be determined from the most probable E_a value (E_a^0). Because of the distribution over E_a, there will be a corresponding distribution of rates. In this way, standard Arrhenius considerations can still apply (eq. 1-5), but instead of one rate equation which describes the entire reaction system, each matrix site has its own rate and E_a.[15] The observed non-exponential decay traces are superpositions of the individual exponential decay traces for each matrix site.

$$k = A \exp(-E_a/RT) \qquad (1\text{-}5)$$

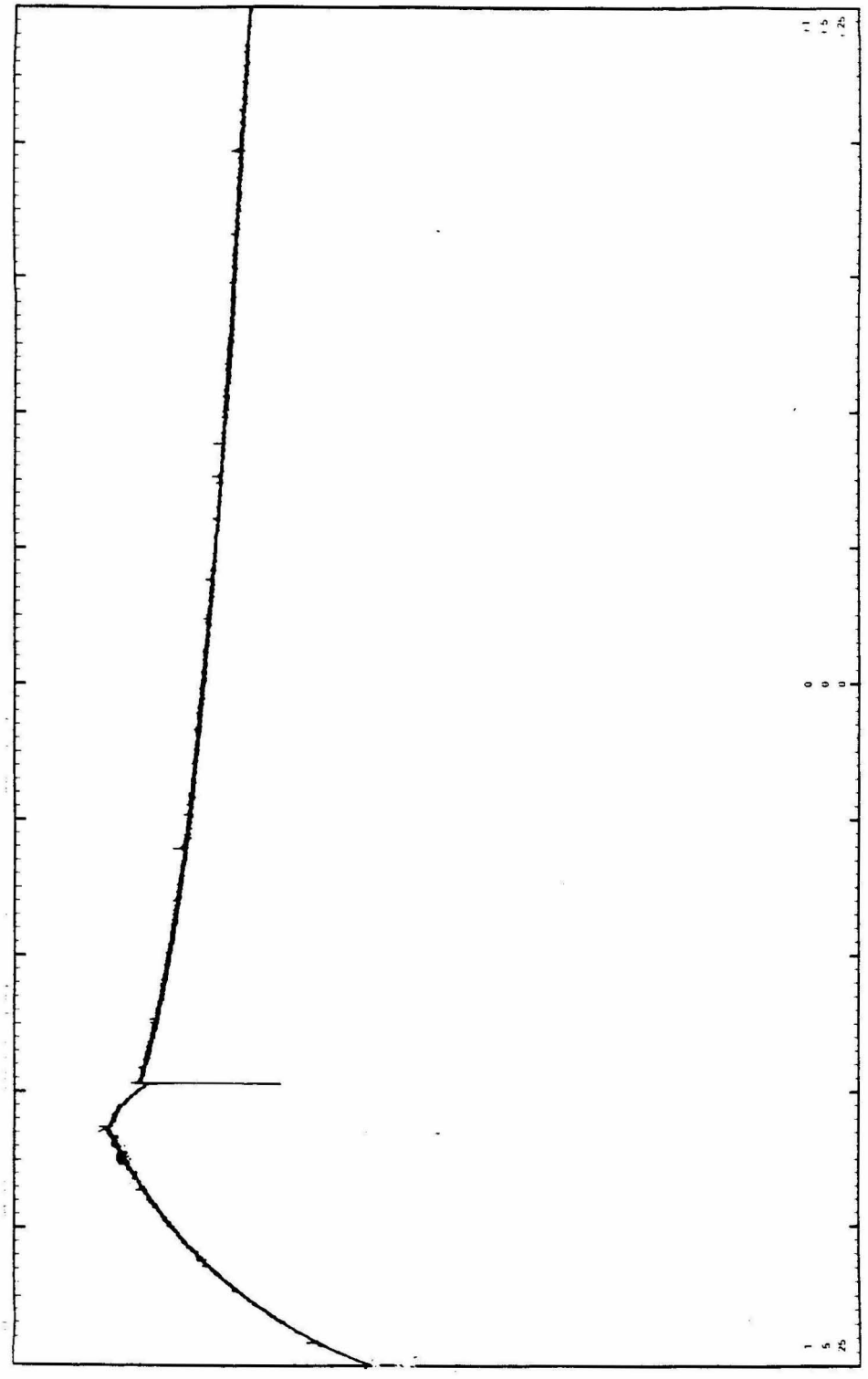


Figure 1-43: Decay trace of **7-MeOPhSO$_2$** at 77 K.

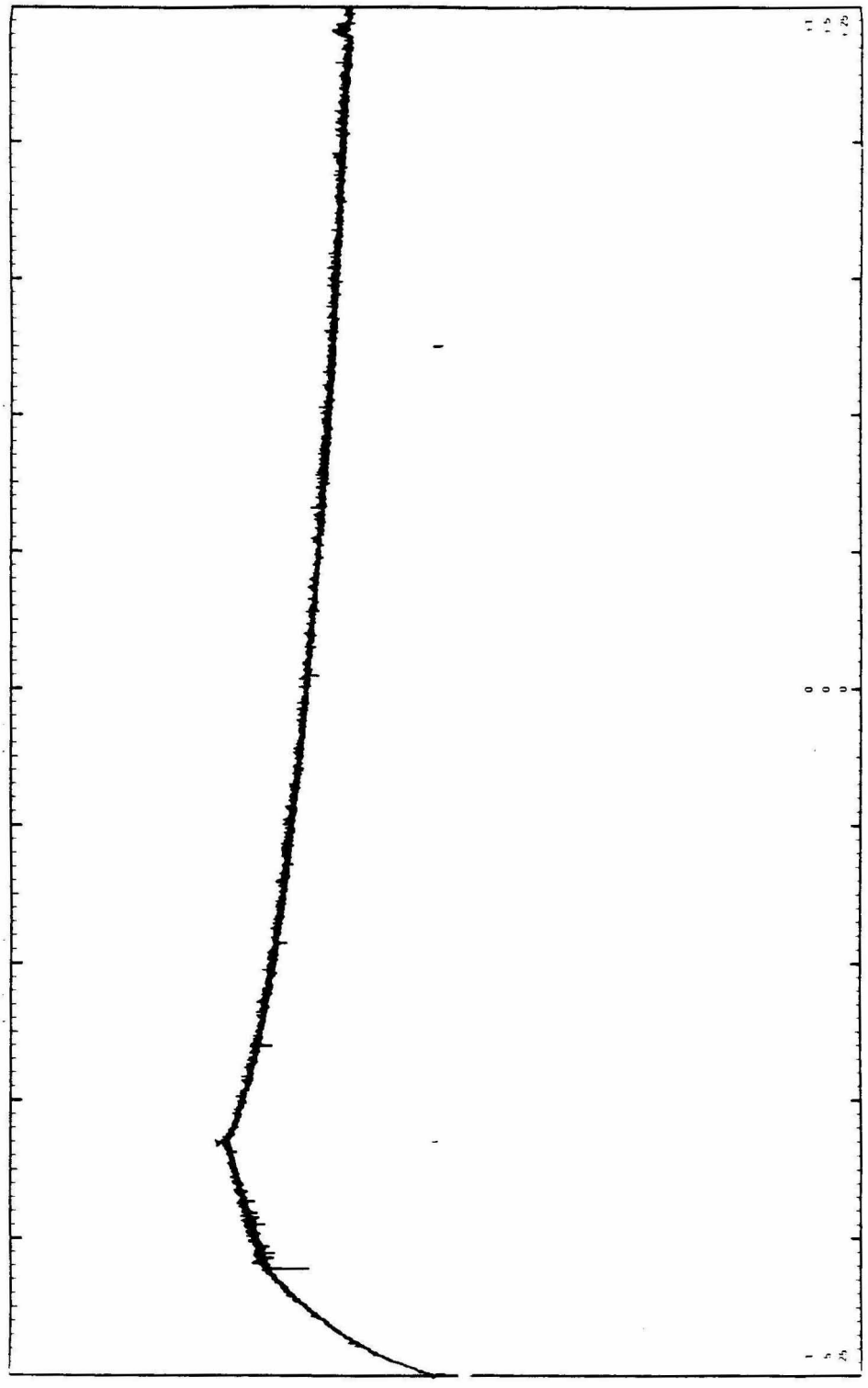


Figure 1-44: Decay trace of **7-MePhSO$_2$** at 77 K.

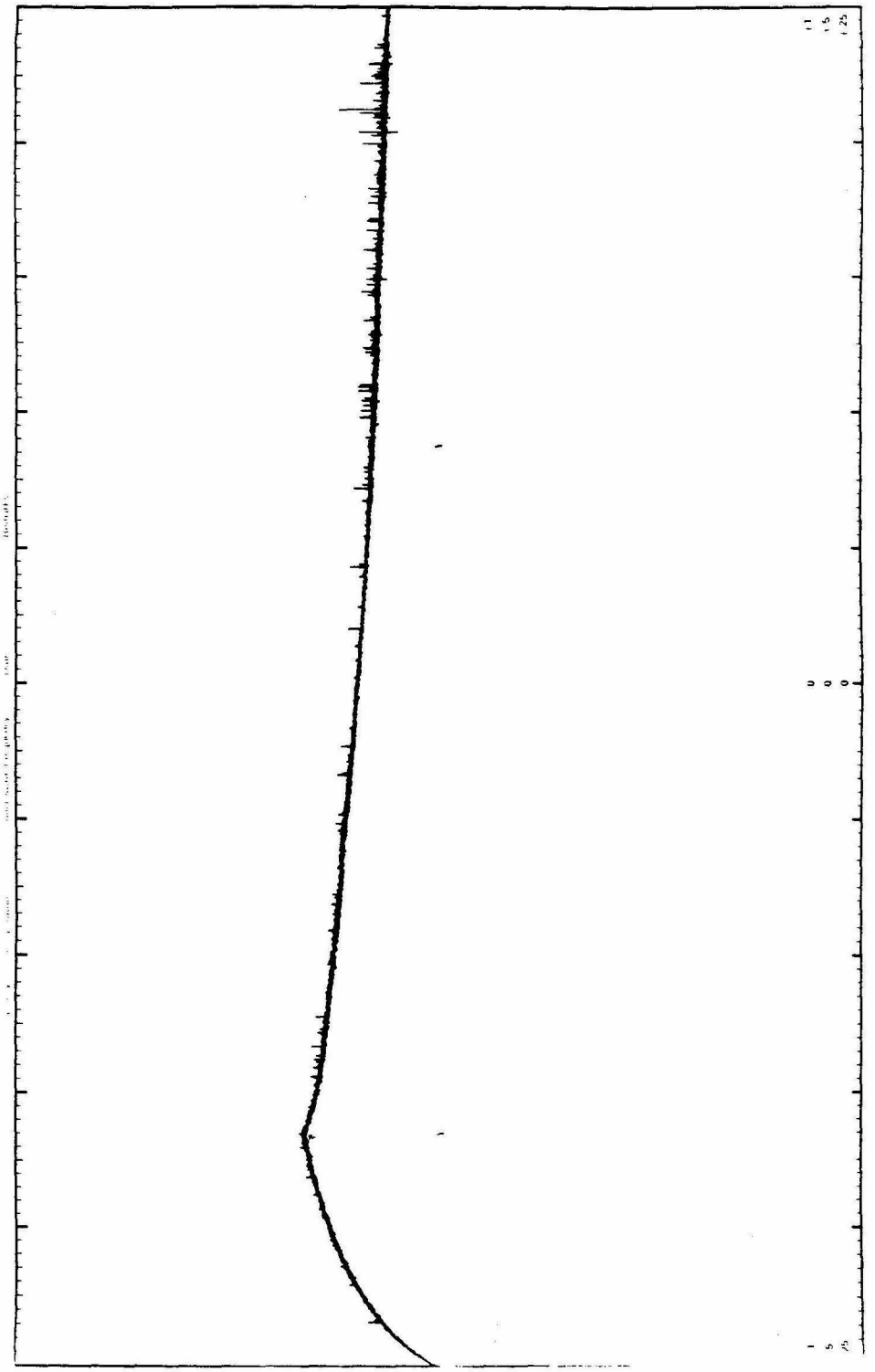


Figure 1-45: Decay trace of **7-PhSO$_2$PhSO$_2$** at 77 K.

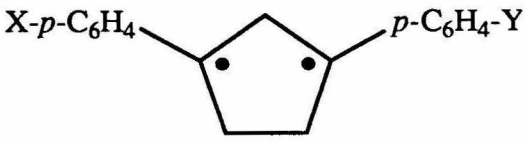
The traces in Figures 1-43 to 1-45 do not feature the careful experimental detail required for such a full kinetic analysis. However, useful qualitative information can still be derived from them. Under the conditions in which these traces were obtained, decay of the "fast" matrix sites (those with small values of E_a in the E_a distribution)[15] will have occurerd during photolysis. The decays observed after the lamp is off will mostly correspond to the decays of "slow" sites (large values of E_a).[15]

Table 1-6 compiles the relevant data taken from the decay traces in Figures 1-43 to 1-45. I_{max} is the relative maximum intensity (that measured at "lamp off"), and $t_{1/2}$ is the time it then takes for the signal to decay to half the value of I_{max}. Modelling the decay observed with one exponential rate law allows use of the half-life relationship[63] in eq. 1-6

$$k_{calc} = (\ln 2) \div t_{1/2} \qquad (1\text{-}6)$$

to obtain decay rates, k_{calc}. It is absolutely vital to stress that these rates have almost no real significance with respect to the actual rates of the reaction. This is because the decay traces are non-exponential, and these numbers were obtained from an explicitly exponential method. These experiments were not performed as, and cannot be compared to, the "distribution-slicing" kinetics performed on 1,3-cyclobutadiyls.[15] For comparison, the most probable rate constant for decay at 77 K was determined to be 4.8×10^{-4} s^{-1} for **4**.[17] The rates listed in Table 1-6 are slower for these phenylsulfonyl-containing compounds, which actually decay more quickly than **4**. Clearly, the most favorable interpretation that can be put on the values of k_{calc} is that they give a rough idea of the decay rates in the "slow" decay region and are only useful for relative comparisons of **7-MeOPhSO$_2$**, **7-MePhSO$_2$**, and **7-PhSO$_2$PhSO$_2$**.

Table 1-6: Qualitative kinetic parameters for the 77 K decay of phenylsulfonyl-substituted triplet 1,3-diaryl-1,3-cyclopentadiyls.



7-XY

7-XY	I_{max}	$t_{1/2}$ (min.)	k_{calc} (s^{-1})
7-MeOPhSO$_2$	37	40	2.8×10^{-4}
7-MePhSO$_2$	30	35	3.3×10^{-4}
7-PhSO$_2$PhSO$_2$	19	30	3.9×10^{-4}

Each trace has its maximum value at the ten-minute mark; each signal grows in as long as the lamp is on and begins to decay as soon as the lamp is off. For the same time period of irradiation (ten minutes), the maximum intensity of the signal which grows in increases in the following order: **7-PhSO$_2$PhSO$_2$ < 7-MePhSO$_2$ < 7-MeOPhSO$_2$**. Given that the efficiency of the photolyses and the initial diazene concentrations are similar for the three compounds, the maximum intensity attained should be about the the same if the compounds decay at the same rate. The relative maximum signal intensities observed imply that the decay rates (of the "fast" sites[15]) decrease in the order **7-PhSO$_2$PhSO$_2$ > 7-MePhSO$_2$ > 7-MeOPhSO$_2$**. The time it takes for the signal to decay to half its maximum intensity once the lamp is turned off increases in the order **7-PhSO$_2$PhSO$_2$ < 7-MePhSO$_2$ < 7-MeOPhSO$_2$**. This suggests that the decay rates (of the "slow" sites[15]) decrease in the order **7-PhSO$_2$PhSO$_2$ > 7-MePhSO$_2$ > 7-MeOPhSO$_2$**.

The consistency of the analyses of the decay traces is encouraging and allows the development of a coherent picture of the effects *para* substituents have on the kinetic

stabilities of 1,3-diaryl-1,3-cyclopentadiyls. The increase in decay rates is mirrored by the decrease in $|D/hc|$ values for **7-MeOPhSO$_2$**, **7-MePhSO$_2$**, and **7-PhSO$_2$PhSO$_2$** (Table 1-3). As $|D/hc|$ decreases, the average separation of the electrons in the triplet increases.[60ab] As the electrons move farther apart, the exchange interactions they experience diminish.[1fg,8,10] Recall that it is the exchange energy that causes the singlet state to be higher than the triplet in planar 1,3-trimethylene biradicals because through-space and through-bond interactions are balanced to give nearly degenerate NBMOs.[8] Separating the electrons by a larger amount causes them to more closely resemble two isolated radicals. Exchange interactions decrease, the singlet-triplet gap narrows, and the kinetic stability of the triplet-ground state biradical is reduced because the singlet state is more thermally accessible (once the singlet state is attained, decay to the bicyclopentane follows).[15,16,17]

Other cogent explanations for the lack of persistence of the phenylsulfonyl-substituted biradicals are not forthcoming. Changes in the geometry of the five-membered ring could lift the approximate degeneracy of the NMBOs, which would result in an increased preference for the singlet state and a decrease in the singlet-triplet gap. There is no evidence for this as the source of the decreased kinetic stability of the phenylsulfonyl-containing 1,3-diaryl-1,3-cyclopentadiyls. Hyperfine coupling constants are sensitive to geometry and would be expected to change noticeably if there were major changes in the conformation of the five-membered ring.[17,59,60] Based on the similarity of the hyperfine structure in the $\Delta m_s = 2$ regions of the EPR spectra for the 1,3-diaryl-1,3-cyclopentadiyls which have methoxy and phenylsulfonyl substituents, and based on the similarity of the hyperfine structure in the $\Delta m_s = 2$ regions of **7-MeOMeO** and **4**, it is reasonable to assume that no significant geometrical changes in the five-membered ring take place upon the introduction of *para* substituents onto the phenyl rings.

If such a conformational effect were important, the phenylsulfonyl-containing biradicals would have been expected to experience it the most because they are the largest substituents

studied and would be expected to cause the greatest geometric distortion. Actually, the most likely conformational effect of the large phenylsulfonyl groups would be to firmly anchor the planar triplet biradical in the matrix and thereby hinder its movement to the conformation necessary for intersystem crossing to the singlet surface.

Another means by which the singlet could be preferentially stabilized relative to the triplet, and hence the singlet-triplet gap decreased, is the lowering of the energies of the zwitterionic portions to the singlet wavefunction.[1cfg] The triplet state is necessarily covalent in nature, but the singlet state (with two antiparallel spins) can simultaneously have both electrons in one of the two NBMOs. In the 1,3-diaryl-1,3-cyclopentadiyl system, this is equivalent to forming a benzyl cation and a benzyl anion. If this were responsible for the decrease in the singlet-triplet gaps, it would be reasonable to expect that **7-MeOPhSO$_2$**, which is ideally substituted to stabilize both a benzyl cation (the electron-donating methoxy group) and a benzyl anion (the electron-withdrawing phenylsulfonyl group), would provide the greatest stabilization of the zwitterionic contribution to the singlet state and would therefore have the fastest decay at 77 K. This is not the case. It should also be recalled that in discussions of the chemically relevant states of a biradical, the zwitterionic states are usually omitted because they are too energetically unfavorable to play significant roles.[1fg,7]

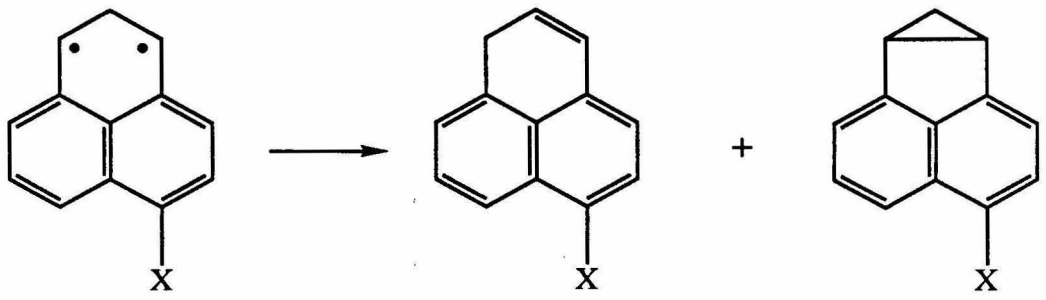
In the absence of zwitterionic stabilization, the stabilizing or destabilizing effect, if any, a substituent has on a benzylic radical unit will be the same whether that benzylic radical is part of the triplet or singlet state biradical.[64] Additional evidence against the preferential stabilization of the singlet state (other than the reduction of exchange energy) is provided by the lack of correlation of the decay rates with the free energy of activation data determined in the NMR studies. Though **6-MeOPhSO$_2$** undergoes the bridge-flip reaction more readily than does **6-MePhSO$_2$**, the EPR signal of **7-MeOPhSO$_2$** does not decay more rapidly than that of **7-MePhSO$_2$**.

If, as it seems from the available data, the occurrence of significant decay of the triplet EPR signals observed at 77 K for the phenylsulfonyl-substituted 1,3-diaryl-1,3-cyclopentadiyls is caused by a narrowing of the singlet-triplet gap brought about by reduction of exchange energy due to the increased average separation of the unpaired electrons, **7-BrBr** should exhibit a noticeable increase in decay rate at only slightly higher temperatures. At 77 K, **7-BrBr** decays no more noticeably than the other non-phenylsulfonyl-containing 1,3-diaryl-1,3-cyclopentadiyls, including **4**. The value of $|D/hc|$ for **7-BrBr** is the lowest of the non-phenylsulfonyl-containing 1,3-diaryl-1,3-cyclopentadiyls studied (Table 1-3), so it would be expected to be the one to exhibit the onset of marked decay at the lowest temperature.

The bromine-containing triplet 1,3-diaryl-1,3-cyclopentadiyls are perplexing entities. Normally, when a heavy atom such as bromine is present, intersystem-crossing rates are increased.[55,56,57] This is typically seen as an increase in the pre-exponential factor A in the Arrhenius equation (eq. 1-5). Thus once enough energy (E_a) has been applied to a triplet-ground state compound to raise it to a point where the triplet and singlet surfaces intersect, the efficiency of the crossing to the singlet surface from the triplet surface is increased and a larger reaction rate is observed. From the changes in hyperfine structure in the $\Delta m_s = 2$ region, we know the bromine nuclei interact with the electrons of the triplet (*vide supra*). Based on the analysis of the decay of phenylsulfonyl-containing 1,3-diaryl-1,3-cyclopentadienes at 77 K as due to a decrease in exchange energy, and the correlation of the decay rates with $|D/hc|$ values, **7-BrBr** should be on the brink of observable decay at 77 K, and an increased rate of intersystem crossing would have been expected to push it over the edge.

Fisher and Michl observed a sixfold increase in the rate of the 2,1-hydrogen shift reaction which forms phenalene **11** from triplet 1,3-perinaphthadiyl **10** upon the substitution of bromine for hydrogen at the 6-position.[57a] An external heavy-atom effect was also observed (at 10 K, the use of krypton as the solid matrix instead of polyethylene

resulted in essentially the same rate increase in the 2,1-hydrogen shift reaction for the unsubstituted compound as the bromine-containing molecule experienced while in a polyethylene matrix). A similar rate increase in the decay of a 1,3-diaryl-1,3-cyclopentadiyl would have been readily detected in the EPR studies performed (smaller rate changes were discerned for the phenylsulfonyl-containing triplet biradicals; *vide supra*).

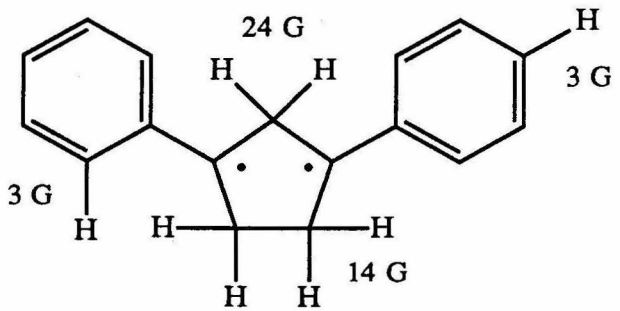


10 **11** X = H, Br

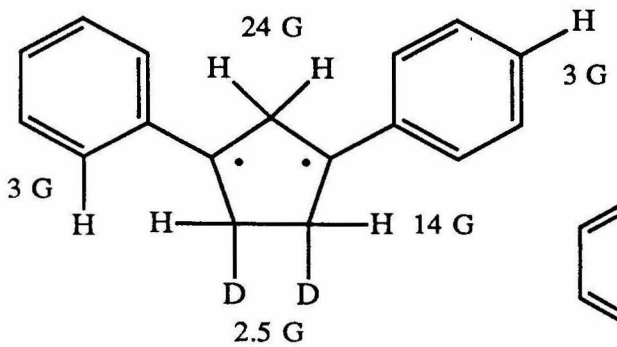
The analysis which leads to the data in Table 1-5 attaches only a small value of energy to the effect of spin-orbit coupling on |*D*/hc|, ≈0.0003 cm^{-1} (≈0.0009 cal/mol) per bromine. This number is not directly related to the spin-orbit matrix element which relates to intersystem crossing, but if it is a reasonable qualitative indicator of the magnitude of heavy-atom spin-orbit coupling in these systems, heavy-atom spin-orbit coupling might be insignificant compared to other mechanisms for intersystem crossing, such as hyperfine coupling. In a discussion of the sources of intersystem-crossing rates in 1,3-trimethylene, Carlacci and Doubleday, *et al.*,[65] determined the average magnitude of the total hyperfine coupling to be ≈0.01 cm^{-1}. They interpreted this as a "natural boundary between 'large' and 'small' values of" spin-orbit coupling, and concluded that small spin-orbit coupling "(< *ca.* 0.001 cm^{-1}) is negligible compared to" hyperfine coupling. In **4**, the hyperfine coupling constants were determined to be as shown below.[17] The total of these coupling

constants is 122 G (0.011 cm^{-1}); a number on the order of 0.0003 cm^{-1} would certainly be small in comparison.

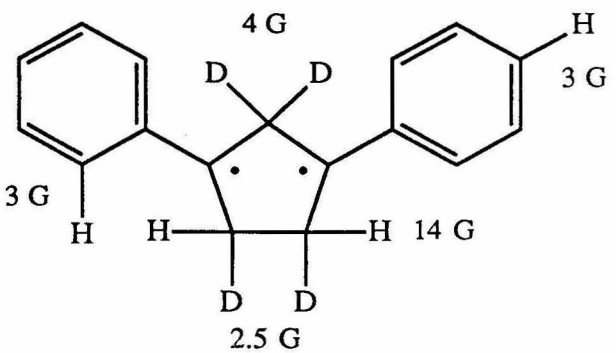
Assignment of hyperfine coupling as an important contribution to intersystem crossing might account for two previously insufficiently explained observations. From a comparison of the decay rates of **4**, 4,5-dideutero-**4**, **4-d_2**, and 2,2,4,5-tetradeutero-**4**, **4-d_4**, the data in Table 1-7 was obtained.[17] |*D*/hc| and |*E*/hc| are the zfs parameters, k^0 values are the most probable decay rates, the E_a values were obtained by assuming the same pre-exponential *A* factor of $10^{8.0}$, and HFC_{tot} values are the sum of the hyperfine coupling constants for each compound. The results of the evaluation of the hyperfine coupling constants are as shown below.[17]



4



4-d_2



4-d_4

Table 1-7: Zfs and kinetic parameters for **4**, **4-d_2**,, and **4-d_4**.[a]

	|D/hc| (cm^{-1})	|E/hc| (cm^{-1})	k^0 (s^{-1})	E_a[b] (kcal/mol)	HFC_{tot} (G)	HFC_{tot} (cm^{-1})
4	0.045	0.001	4.8×10^{-4}	4.0	122	0.011
4-d_2	0.045	0.001	4.2×10^{-4}	4.0	99	0.009
4-d_4	0.045	0.001	8.8×10^{-5}	4.25	59	0.006

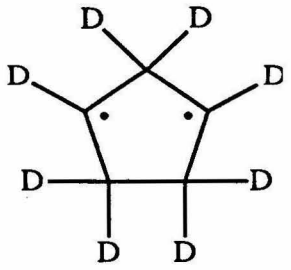
[a] Coms, F. D.; Ph. D. Thesis; California Institute of Technology; 1989. [b] Calculated with log$A$ = 8.0.

The three compounds were found to give the same ratio of decay products (cyclopentene: bicyclopentane, 3:7).[17] They have the same zfs parameters and can therefore be expected to have similar exchange energies. The E_a values are extremely close, but **4-d_4** was observed to experience the largest matrix-site effects.[17] An argument was made that the CD_2 group was a poorer through-bond coupling unit than CH_2, and therefore spin-orbit coupling was reduced in **4-d_4**, which might have caused the decrease in decay rate.[17] This line of reasoning suffers from a contradiction: Reduced through-bond coupling will begin to destroy the balance of through-bond and through-space effects that give rise to the nearly degenerate NBMOs. This will begin to lift the near degeneracy and cause a favoring of the singlet state; the singlet-triplet gap narrows and the triplet would be expected to decay more quickly at a given temperature, not more slowly.

Attributing the decrease in decay rates to a decrease in intersystem-crossing rates due to reduced hyperfine coupling would be consistent with the observed data. The calculated total hyperfine coupling decreases as the rates do. Had an E_a value of 4.0 kcal/mol been assigned to the decay at 77 K of **4-d_4**, a log A value of 7.3 would have resulted, quantifying therein the reduced efficiency of intersystem crossing.

Buchwalter and Closs observed a similar retardation of decay rate when they studied **1** and perdeutero-**1**, **1-d_8**.[12] **1** decayed fairly rapidly at 5.5 K, but **1-d_8** decayed too slowly to study at that same temperature. Again, total hyperfine coupling will decrease

(the hyperfine coupling constants of hydrogen are generally six times greater than that of deuteria).[17] Thus the conclusion that hyperfine coupling is the mechanism of intersystem crossing in the 1,3-cyclopentadiyl system could explain the absence of normal heavy-atom effects and the retardation of decay rates upon the substitution of deuteria for hydrogens.



1-d_8

Additionally, if hyperfine coupling were an important mechanism for intersystem crossing, and because the hyperfine couplings exhibited in these 1,3-diaryl-1,3-cyclopentadiyls do seem to remain relatively constant (*vide supra*), it would support the validity of the correlation of decay rates with |*D*/hc| values. This is because yet another potentially varying property of these compounds (intersystem-crossing rates; the pre-exponential factor *A* in the Arrhenius treatment) does not change appreciably. This would leave the reduction in exchange energy, which arises because the electrons are, on average, farther apart (as is evidenced by the decrease in |*D*/hc| values), as the only changing parameter which correlates with the observed decay rates.

Interestingly, the analysis which leads to Table 1-5 gives a |*D*/hc| value for **7-BrBr** which, in the absence of spin-orbit coupling effects on |*D*/hc| (*i.e.*, $|D/hc|_{calculated}$ in Table 1-5, 0.0429 cm^{-1}), is between that of **7-MeOPhSO$_2$** (0.0430 cm^{-1}) and **7-MePhSO$_2$** (0.0428 cm^{-1}), both of which exhibit significant decay at 77 K. To the extent that the |*D*/hc| values are useful indicators of kinetic stability in this system, **7-BrBr** could be said to owe its stability at 77 K to the presence spin-orbit coupling -- a "reverse" heavy-atom effect.

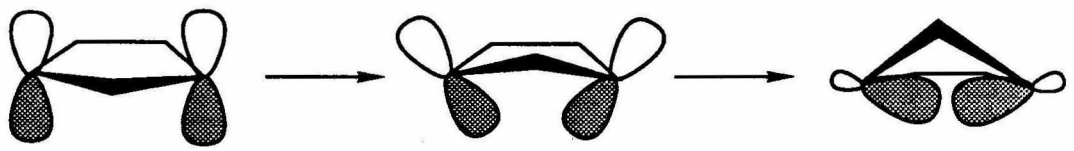
Unfortunately, no value for |*D*/hc| was reported for 6-Br-**10**,[57a] so no comparison of spin-orbit effects on |*D*/hc| values with spin-orbit effects on intersystem-crossing rates in biradicals can be made. In contrast to that system, no kinetic instability of bromo-substituted TMM derivatives **9-HBr** and **9-BrBr** (Table 1-4) was reported.[62] Comparisons with these systems may not be justified, however, because they are delocalized biradicals with large preferences for the triplet state (about 14 kcal/mol in the case of TMMs[2m]), and the 1,3-diaryl-1,3-cyclopentadiyls are localized biradicals with roughly a 900 cal/mol preference for the triplet state.[7,17]

Without careful and detailed kinetic studies over a range of temperatures of the heavy atom-containing 1,3-diaryl-1,3-cyclopentadiyls, the above discussions concerning the heavy-atom effect on kinetic stability and the actual mechanism of intersystem crossing are, at best, tentative conjectures, regardless of the results they may rationalize. Spin-orbit coupling is generally regarded as being the dominant mechanism of intersystem crossing in biradicals, not hyperfine coupling.[65,66] This conclusion is based primarily on results from experiments performed on flexible acyclic biradicals. Studies at cryogenic temperatures on triplet-ground state systems more akin to the 1,3-diaryl-1,3-cyclopentadiyls are lacking.

In their discussion of trimethylene biradicals, Carlacci and Doubleday, *et al.*, examine the 1,3-cyclopentadiyl system and observe that, "in order to undergo intersystem crossing, the molecule must distort in an 'envelope flapping' motion."[65] The motion they describe is essentially that of the bridge-flip reaction (only from planar biradical toward the ring-closed bicyclopentane form), which requires a disrotatory motion of the radical centers. This movement causes one lobe of each *p* orbital to point toward the other radical center (and approach the position of the bridgehead carbon-bridgehead carbon bond) and causes the other lobe of each *p* orbital to point away from the other radical center.

When the long axes of the two *p* orbitals are approximately perpendicular, the spin-orbit coupling is large ($\approx$0.6 cm^{-1}).[65,67] The magnitude of this number is much greater than the total hyperfine coupling in this system and is much greater than the effect of

0.0003 cm^{-1} per bromine on the |*D*/hc| values in the 1,3-diaryl-1,3-cyclopentadiyls. Therefore, a more plausible explanation for not observing a heavy-atom effect in the bromine-containing 1,3-diaryl-1,3-cyclo-pentadiyls is that the spin-orbit contributions of bromines in this system are negligible as compared to the spin-orbit coupling which already exists. This conclusion does not address the decrease in decay rates seen upon the substitution of deuteria on the five-membered ring, but it is more in keeping with the conventional wisdom on the mechanism of intersystem crossing.



If, for some reason, spin-orbit coupling were smaller than 0.6 cm^{-1} in 1,3-cyclo-pentadiyl systems, *e.g.*, more on the order of the hyperfine coupling (0.01 cm^{-1}), hyperfine coupling would contribute significantly to intersystem-crossing rates, and the hyperfine-coupling explanation of the decreased decay rates for the deuterated compounds would remain plausible. This could still be consistent with the absence of heavy-atom *effects if 0.0003* cm^{-1} (much less than 0.01 cm^{-1}) is a fair indicator of their magnitude.

Another possible explanation for the absence of an observable heavy-atom effect in the bromine-containing 1,3-diaryl-1,3-cyclopentadiyls is related to the shapes of the singlet and triplet surfaces, on which we have little information. As shown in Figure 1-46, if the geometry at which the singlet and triplet surfaces intersect is little or no higher above the lowest energy triplet geometry than the singlet-triplet gap energy (≈900 cal/mol), a barrier to closure to the bicyclopentane of up to 3 kcal/mol might exist on the singlet surface (recall that E_a = 4.0 kcal/mol for the decay of **4**[17]). This would reflect the need for the then near-planar singlet biradical to undergo a part of the bridge-flip reaction which still requires

additional movements of the molecule in the solid matrix.. At 77 K, $RT \approx 153$ cal/mol, a 3 kcal/mol barrier is significant, and an increase in the intersystem-crossing rate might not be discernable.

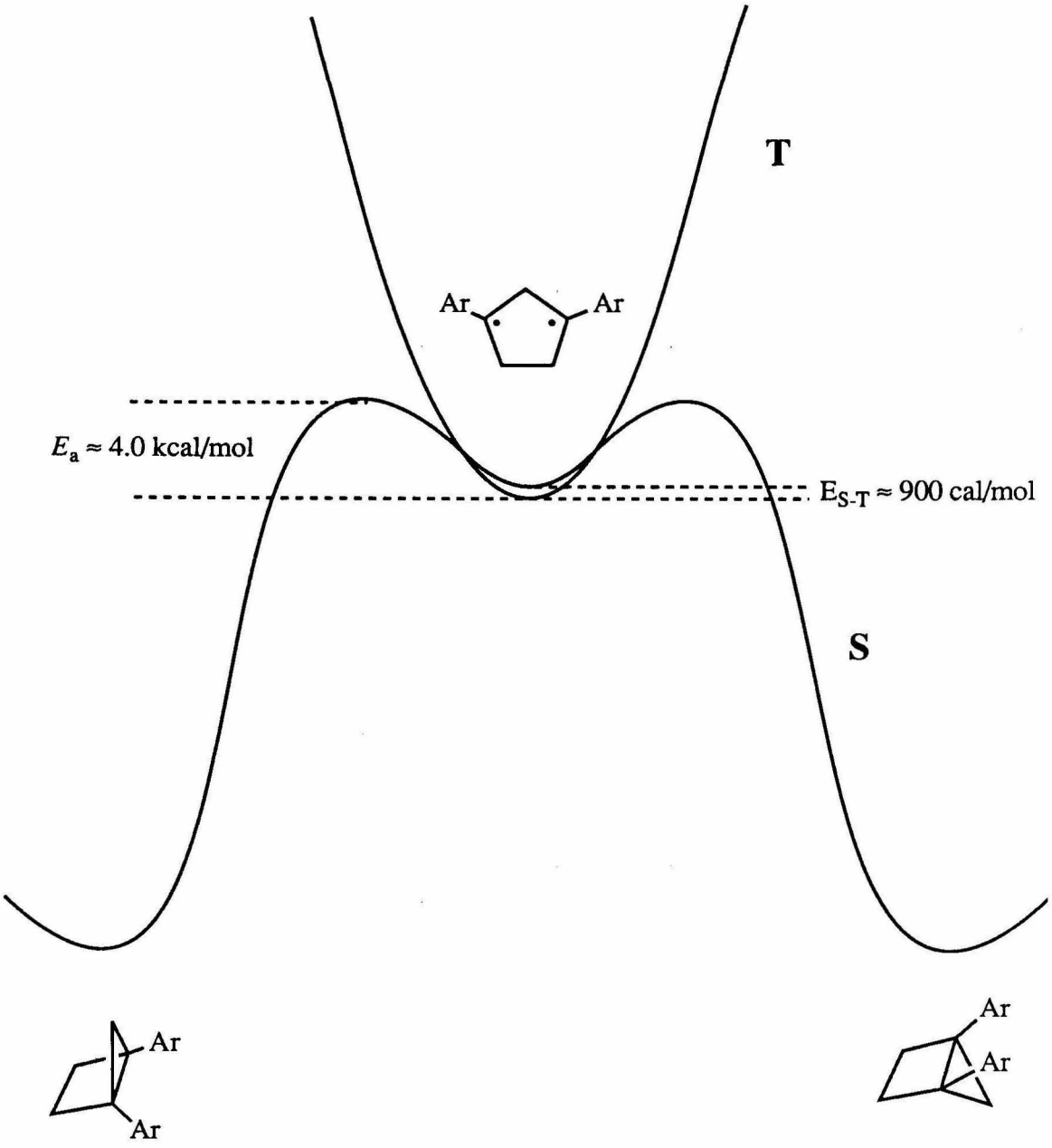


Figure 1-46

Also note that this scenario could be a way for the contribution of hyperfine coupling to the intersystem-crossing rate to increase. If the singlet and triplet states intersect at a geometry not much different from the planar triplet geometry, the overlap and perpendicularity of the *p* orbitals might not be sufficient to produce large amounts of spin-orbit coupling.[65,67] The scenario discussed above for the case when spin-orbit coupling and hyperfine coupling are of similar magnitudes would then apply. In that way, the notion of a significant barrier to closure remaining after intersystem crossing could also be consistent with the decreased decay rates for deuterated cyclopentadiyls.

Summary

A series of diazene precursors to both 1,4-diarylbicyclo[2.1.0]pentanes **6-XY** and 1,3-diaryl-1,3-cyclopentadiyls **7-XY** has been synthesized. Much established methodology was utilized, but significant modifications were made to overcome the difficulties encountered in the Diels-Alder-hydrogenation sequence of reactions with 1,4-diaryl-1,3-cyclopentadienes **8-XY** and triazolinediones and in the subsequent hydrazinolyses of the urazoles obtained.

Linear free-energy relationships for these biradicals were found to be dependent on both substituents present. A sum of the two individual substituent constants was therefore used as an overall constant to represent the fact that each radical unit contributes equally to the observed properties of these systems. This is the first attempted and observed correlation of biradical properties with *para*-substituent effects determined in other systems.

The 1,4-diarylbicyclo[2.1.0]pentanes **6-XY** were prepared from the diazenes by thermolysis. In analogy to the studies made on **5**, variable temperature NMR studies were performed to obtain free energies of activation at coalescence to determine the effects of *para* substituents on the bridge-flip reaction. It was found that the substituents had only small effects, but these gave a reasonable correlation to the Hammett substituent constants derived from the thermolysis of *para*-substituted dibenzyl mercurials, $\sigma_J^{\bullet}$. The reduced

degree of the effects relative to the reaction from which the $\sigma_J^{\bullet}$ constants were derived was attributed to the incomplete formation of benzylic radical character at the transition state for the bridge-flip reaction and to the fact that the radical centers are actually cumyl centers, which are known to experience reduced substiutuent effects *vis à vis* benzyl radicals.

The 1,3-diaryl-1,3-cyclopentadiyls **7-XY** were prepared by photolysis of the diazenes at cryogenic temperatures. They have triplet grounds states. The zero-field splitting parameter |*E*/hc| is found to be constant for the series and indicates that *para* substituents cause no substantial change in the molecular symmetry. The zero-field splitting parameter |*D*/hc| was found to correlate extremely well with the general Hammett substituent constant for *para* groups, σ_p.

This correlation allowed the separation of the observed values of |*D*/hc| for the bromine-containing members of the series into contributions from spin-orbit coupling effects and from the inductive and resonance effects of the substituents. The spin-orbit coupling effects of the bromines on |*D*/hc| values were observed to be quite small relative to hyperfine couplings and estimated spin-orbit effects based on orbital interactions in the absence of heavy atoms. This was cited as the reason for no observation of standard heavy-atom effects on intersystem-crossing rates in the bromine-containing molecules. The possible roles of hyperfine coupling, spin-orbit coupling, and barriers to closure on the singlet surface in the observed decay kinetics of related biradicals were also discussed.

The phenylsulfonyl-containing members of this series were found to undergo significant unimolecular decay at 77 K. The relative ordering of the decay rates correlated well with |*D*/hc| -- the lower the value of |*D*/hc|, the faster the rate of decay. Because, on average, the electrons are farther apart in a triplet with a lower value of |*D*/hc| than in one with a higher value, and because the farther apart the electrons are, the smaller the exchange energy is, this was interpreted as the decay being caused by a decrease in the exchange energy, which decreases the singlet-triplet gap. Other possible causes of the observed decay behavior were discussed and found to be improbable.

This work has added to the knowledge available for those endeavoring to design and synthesize organic molecules with novel properties. If one plans to include a localized biradical subunit in a larger macromolecular structure as a means of achieving high-spin coupling,[2m] one should then also seek to avoid the inclusion of strongly electron-withdrawing groups which can act upon the radical centers of the biradical subunit. Strongly electron-withdrawing substituents can lessen the spin density at radical centers, reduce exchange interactions, and thereby decrease the singlet-triplet gap and kinetic stability of high-spin (triplet ground state) localized biradicals.

Appendix A

Additional Efforts Toward the Synthesis of 1,3-Diaryl-1,3-cyclopentadiyls and 1,4-Diarylbicyclo[2.1.0]pentanes

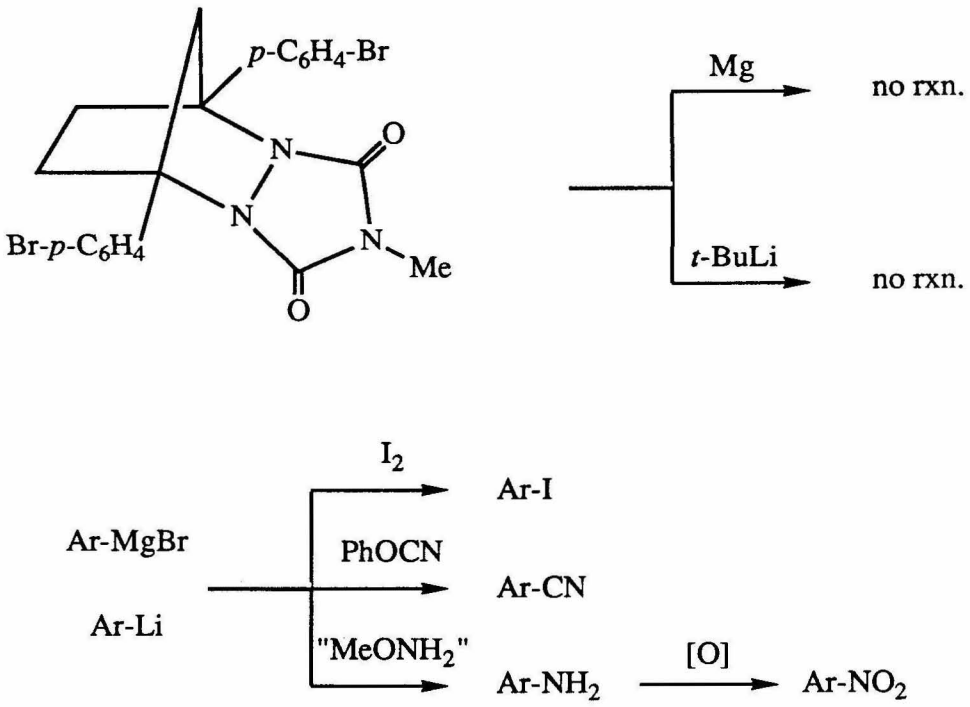
The *para*-substituted 1,3-diaryl-1,3-cyclopentadiyls **7-XY** and 1,4-diarylbicyclo-[2.1.0]pentanes **6-XY** described in Chapter 1 were not the only ones whose preparations were attempted. In addition to the methoxy, methyl, bromo, and phenylsulfonyl substituents, determined efforts were made to introduce a more strongly electron-donating group, dimethylamino, and two more "classical" electron-withdrawing groups, cyano and nitro. Additionally, some attempts were made to introduce the iodo group so as to further investigate the heavy-atom effect (or its absence).

Initial work involved trying to functionalize the N-methyl urazole formed by the reaction of 1,4-di(4-bromophenyl)-1,3-cyclopentadiene **8-BrBr** and MTAD and subsequent reduction (Scheme A-1). Attempts to form the Grignard reagent failed, even when activated magnesium[68] was used. Formation of the aryllithium compounds with *t*-butyllithium resulted in little or no formation of even the mono-aryllithium, let alone any of the doubly reacted material. Appropriate quenching of the organometallic reagents that would have been formed could have provided a convenient route to desired substituents: iodine for the iodo group,[69] phenyl cyanate for the cyano group,[70] and a methoxyamine derivative followed by oxidation to provide the amino, then nitro, groups.[71]

Though success was deemed highly unlikely, attempts to form the aryllithium reagent from **8-BrBr** were made. No characterizable products were obtained. That was also the result of the aryl version of the Gabriel synthesis[72] (substitution of arylbromides with phthalimide ion) applied to **8-BrBr** and of attempts to directly nitrate 1,4-diphenyl-1,3-cyclopentadiene **8-HH** (Scheme A-2).

Endeavors to introduce the cyano functionality by reacting the di(4-bromophenyl) N-methyl urazole with potassium cyanide and a palladium catalyst were fruitless.[73] This methodology, and the use of sodium cyanide with a nickel catalyst,[74] also failed when applied to **8-BrBr**. Rosenmund-von Braun conditions[75] did not to convert this diene to the di(4-cyanophenyl) derivative (Scheme A-3).

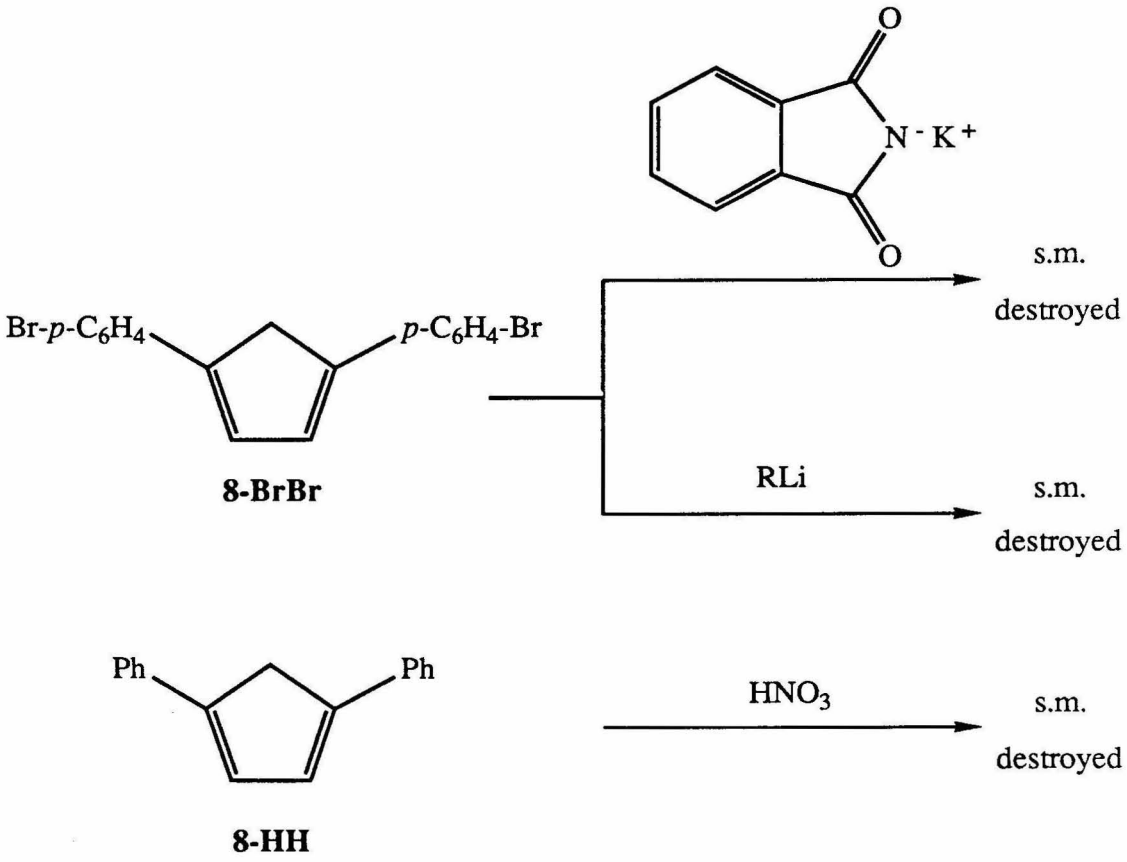
Scheme A-1



The failure of the di(4-bromophenyl) N-methyl urazole to react might be due to complexation of the various metal reagents by the abundance of heteroatoms in the urazole moiety. This could poison the metal catalysts and hinder the reactivity of the organo-metallic compounds. The high temperatures required for the substitution reactions cause decomposition of the diarylcyclopentadienes, as do the strong bases and acids used in aryllithium formation and nitration.

These experiences convinced us that it was necessary to have the desired functionalities (or suitable precursors) present in the acetophenones and β–benzoylpropionate esters. Functional and protecting group choices were severely limited by the harsh conditions of the cyclopentadiene-forming reaction. Our efforts were turned to the introduction of amino functionality because subsequent diazotization and substitution or methylation offerred a convenient route to the other functional groups.

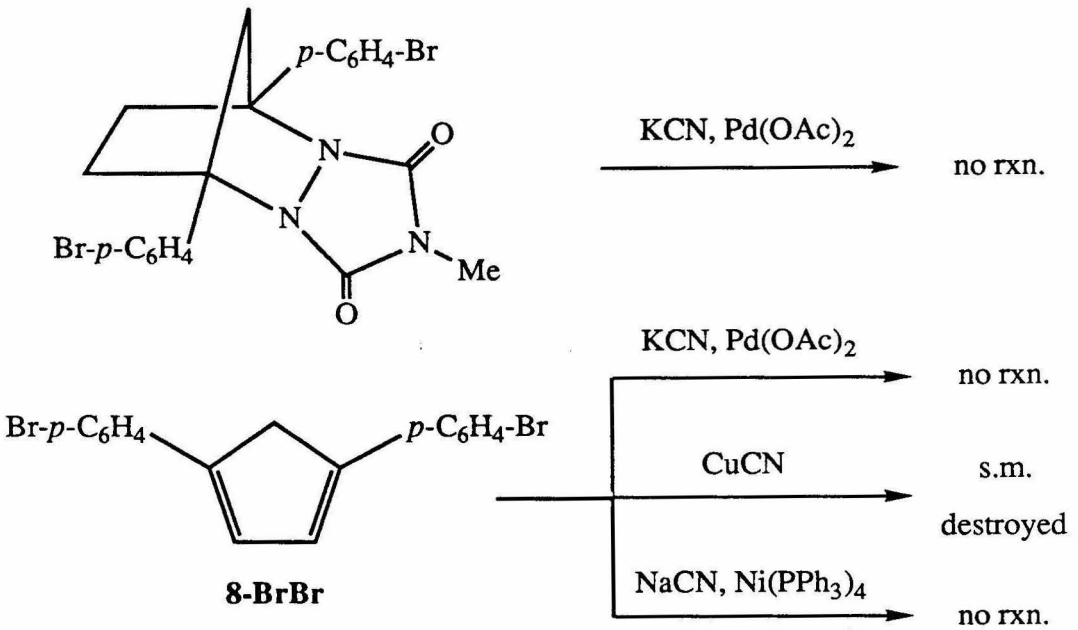
Scheme A-2



p-Aminoacetophenone,[22] which itself did not successfully react to give the diarylcyclopentadiene, was protected as both the phthalimide and dimethylpyrrole[76] derivatives (Scheme A-4). The phthalimide derivative was not expected to survive the hydrolysis with refluxing aqueous hydroxide in the last step of the cyclopentadiene-forming reaction. It was hoped that it would prevent the amino group from interfering with the carbonyl chemistry in the previous steps. However, no diarylcyclopentadiene was produced in its reaction. The dimethylpyrrole derivative did give cyclopentadiene (with a solvent change from refluxing benzene to refluxing toluene necessary for successful reaction), but the amino funtionality could not be regenerated. The stability of the

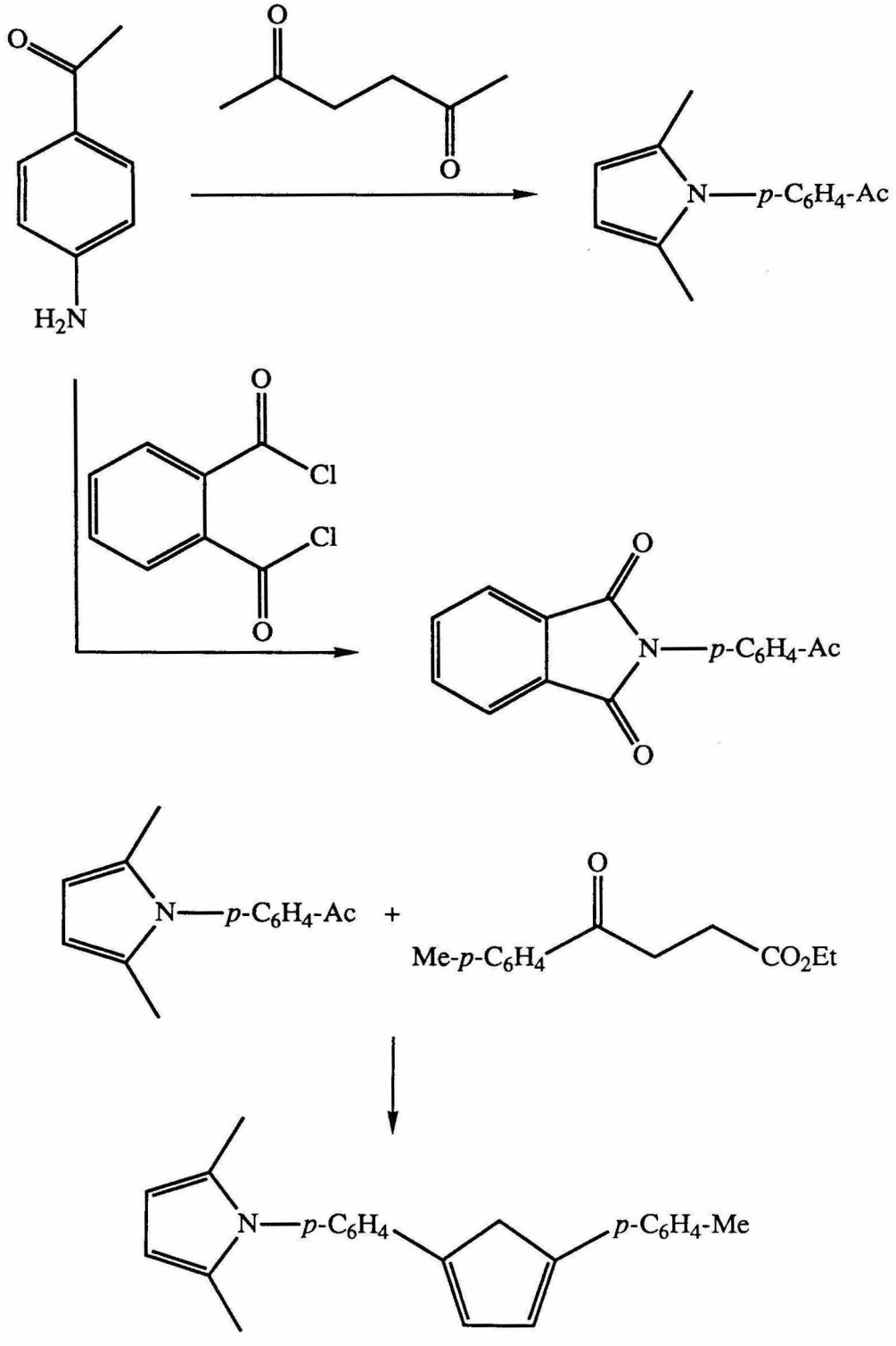
dimethylpyrrole was sufficient to necessitate the use of conditions which destroyed the rest of the molecule. The dimethylpyrrole-substituted cyclopentadiene did not undergo the two-step Diels-Alder cycloaddtiion-diimide reduction sequence successfully.

Scheme A-3



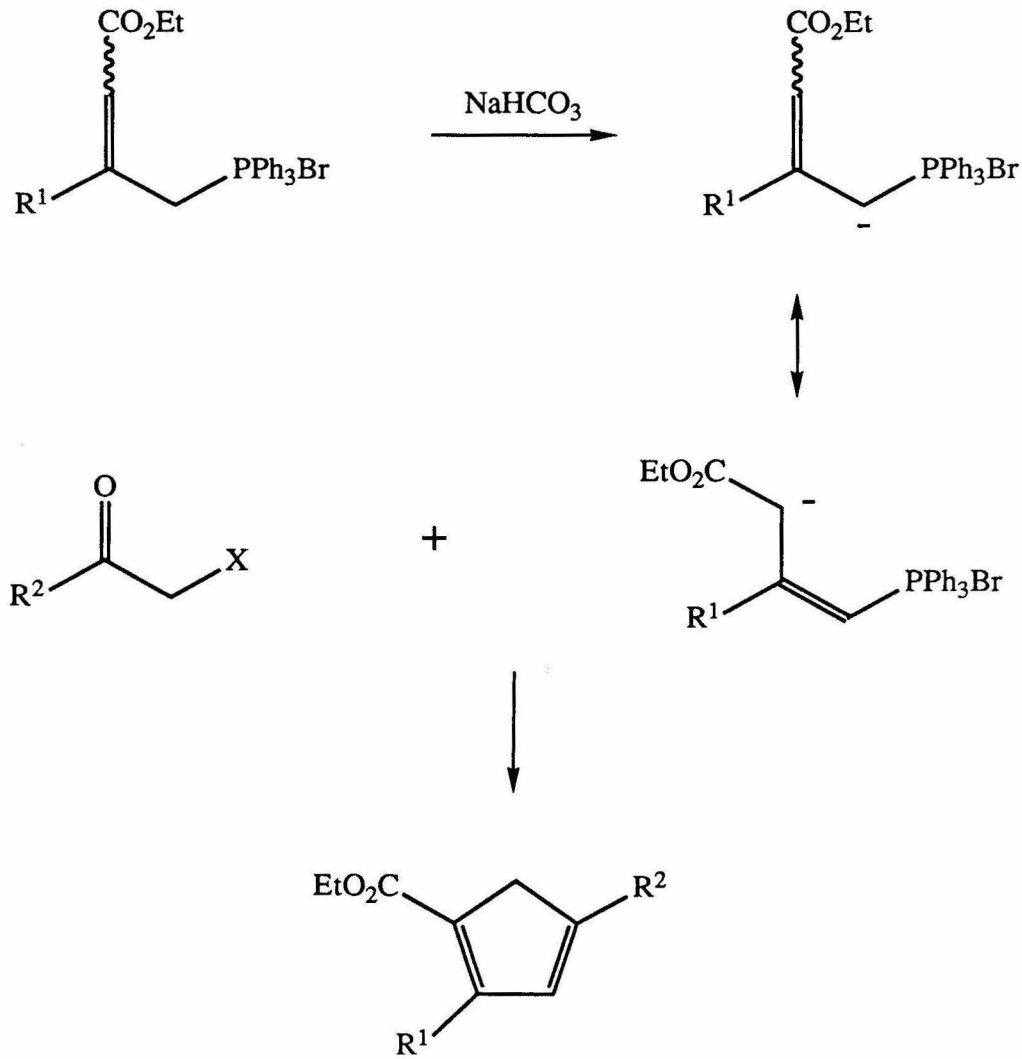
Stymied in our efforts to prepare amino-substituted diarylcyclopentadienes, we then essayed to individually synthesize the nitro, cyano, and dimethlyamino compounds, rather than proceed through a common intermediate. Because strongly electron-withdrawing groups are not tolerated in the reaction to form the diarylcyclopentadienes,[27cd] and because attempts at protecting nitrogen functionality had been unsuccessful, a version of a recently published alternative route was attempted as a means of producing the 1,4-di(4-nitro-phenyl)-1,3-cyclopentadiene.

Scheme A-4


O
O
O
H2N
N—p-C6H4-Ac
O
Cl
Cl
O
O
N—p-C6H4-Ac
O
N—p-C6H4-Ac
+
O
Me-p-C6H4
CO2Et
N—p-C6H4
p-C6H4-Me

Scheme A-5 outlines the reaction of allylidene triphenylphosphoranes with α-halo-ketones.[77] The published work found that a phenyl group was acceptable as either R group when the other was methyl. No report of using phenyl as both R groups in the same reaction was made. The product of this reaction would be the cross-conjugated ester intermediate which is treated with refluxing aqueous hydroxide in the mechanism outlined in Chapter 1 for the "standard" cyclopentadiene-forming reaction (Scheme 1-5).[27]

Scheme A-5

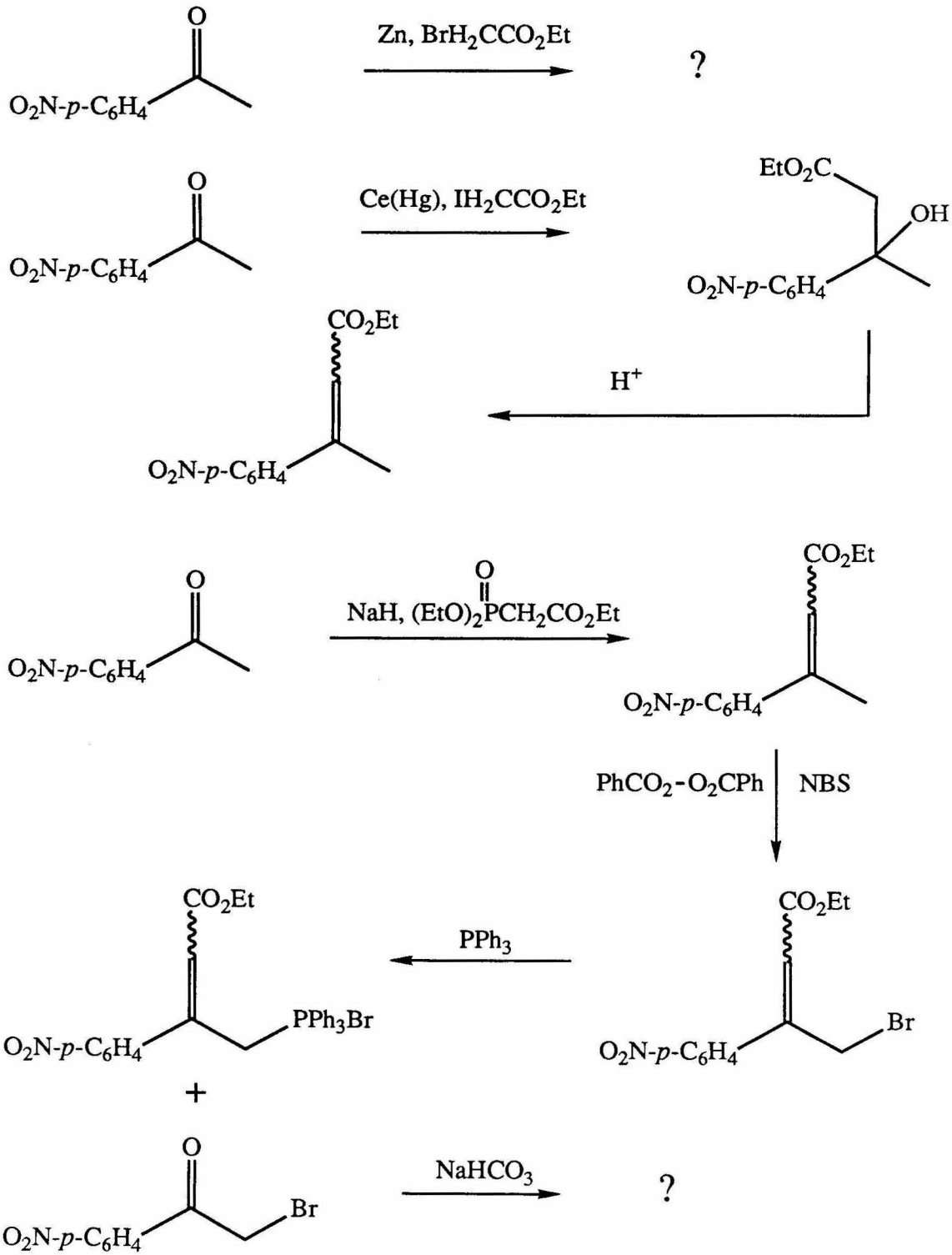


α-Bromo-*p*-nitroacetophenone was obtained commercially.[22] Scheme A-6 outlines the preparation of the unsaturated ester needed. One published route, the reaction of *p*-nitroacetopheneone with the Reformatskii reagent formed from zinc and ethyl bromoacetate, followed by dehydration during distillation, proved irreproducable.[78] A similar reaction[79] in which ethyl iodoacetate, cerium amalgam, and *p*-nitroacetopheneone were reacted provided hydroxy ester which was dehydrated by heating with an acid catalyst to form the unsaturated ester. The most convenient route to the unsaturated ester was Horner-Emmons-Wadsworth reaction of triethylphosphonoacetate, sodium hydride, and *p*-nitroacetophenone.[80] Allylic bromination with N-bromosuccinimide and benzoyl peroxide gave the bromide,[81] which was in turn reacted with triphenylphosphine to give the Wittig salt.

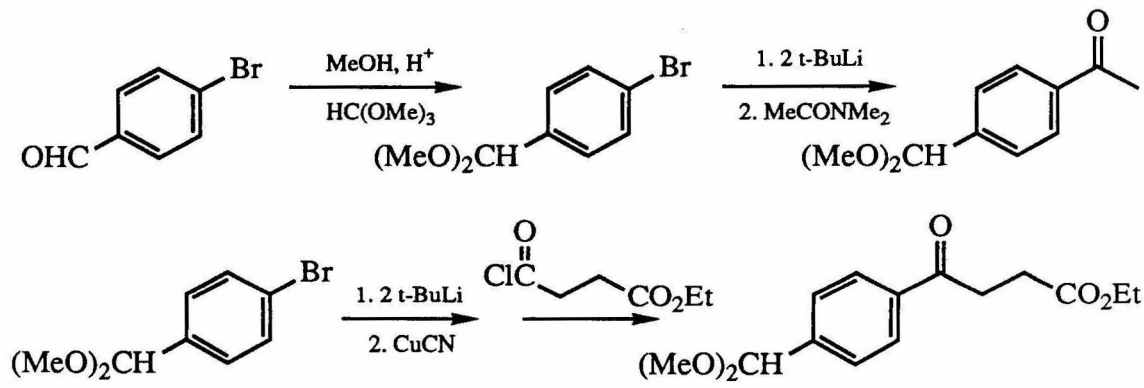
When the reaction depicted in Scheme A-5 was attempted, addition of the base (sodium bicarbonate) and mixing led to immediate formation of a deep purple color. No cyclopentadiene products could be isolated. It is possible that the ylide formed undergoes electron transfer with the highly electron-deficient α-bromo-*p*-nitroacetophenone, or that it is unreactive due to the strong electron-withdrawing nature of the nitro group. Repetition of the reaction at slightly elevated temperature produced the same results.

Scheme A-7 outlines the route intended to yield cyano-substituted diarylcyclopentadienes. *p*-Bromobenzaldehyde was protected as the dimethyl acetal, converted to the aryllithium reagent, and added to N,N-dimethylacetamide to give the *p*-(dimethoxymethyl)acetophenone. The dimethyl acetal of *p*-bromobenzaldehyde could also be converted to the aryllithium and then the lithium cuprate, which reacted with ethyl succinyl chloride to give ethyl β-*p*-(dimethoxymethyl)benzoylpropionate. This acetophenone and ester underwent condensation with each other and with the *p*-methyl-, methoxy-, and bromo-substituted acetophenones and ethyl β-benzoylpropionates discussed in Chapter 1 to give the correspondingly substituted diarylcyclopentadienes shown. Condensation with *p*-dimethylaminoacetophenone (*vide infra*) was also successful.

Scheme A-6

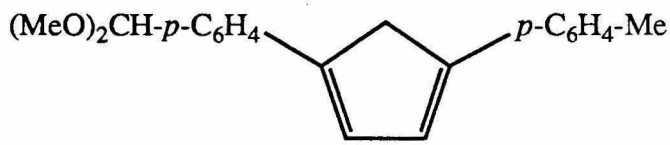

O
Zn, BrH2CCO2Et
?
O2N-p-C6H4
O
Ce(Hg), IH2CCO2Et
EtO2C
OH
O2N-p-C6H4
CO2Et
H+
O2N-p-C6H4
O
NaH, (EtO)2PCH2CO2Et
O
CO2Et
O2N-p-C6H4
O2N-p-C6H4
PhCO2-O2CPh
NBS
CO2Et
CO2Et
PPh3
PPh3Br
Br
O2N-p-C6H4
O2N-p-C6H4
+
O
NaHCO3
?
Br
O2N-p-C6H4

Scheme A-7

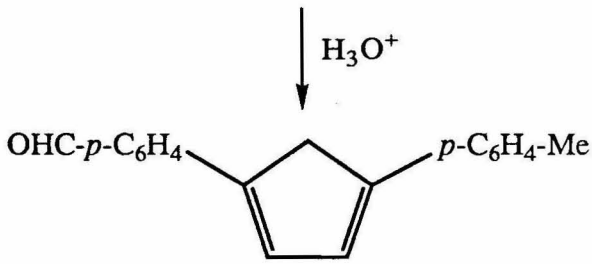


8-XY

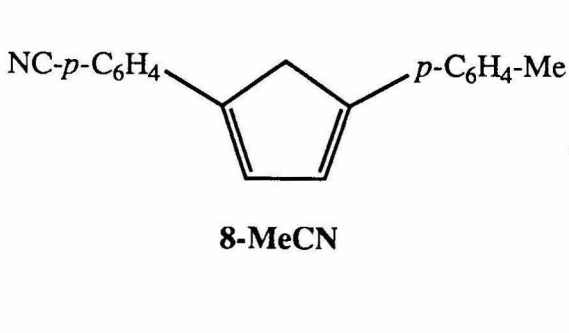
X	Y
Me	$(MeO)_2CH$
MeO	$(MeO)_2CH$
Br	$(MeO)_2CH$
Me_2N	$(MeO)_2CH$
$(MeO)_2CH$	$(MeO)_2CH$



8-Me$(MeO)_2$CH



8-MeCHO



8-MeCN

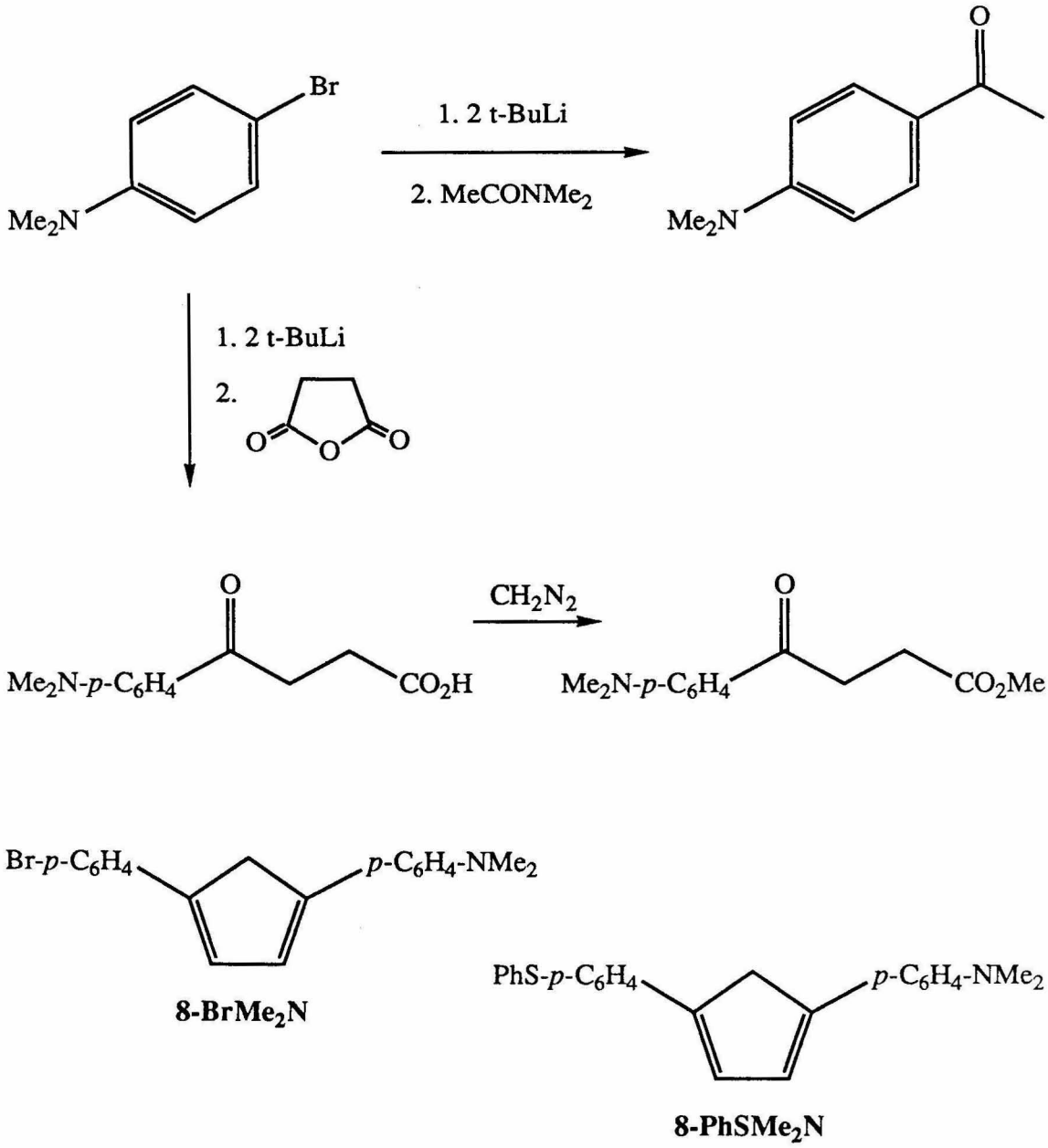
Mild acidic hydrolysis of **8-Me(MeO)$_2$CH** cleanly afforded **8-MeCHO**. It should be noted that the (dimethoxymethyl)phenyl-substituted cyclopentadienes did not have a long shelf life. Attempted deprotection of any which had been stored for extended periods gave intractable mixtures of ill-defined compounds.

Several attempts to convert the aldehyde to the nitrile were made. Formation of the oxime followed by acid-catalyzed dehydration with anhydrous magnesium sulfate failed to convert the oxime.[82] Formation of the oxime followed by attempted dehydration in hot formic acid destroyed the starting material.[83] Formation of the oxime followed by treatment with selenium dioxide failed to convert the oxime.[84] The O-sulfonic acid oxime failed to dehydrate.[85] Heating the oxime under vacuum did not accomplish dehydration, but did destroy the starting material. 1,1'-Carbonyldiimidazole did not dehydrate the oxime.[86] Formation of the hydrazone followed by treatment with mercuric oxide did not produce nitrile.[87] Dehydration of the oxime with cyanuric chloride did afford the nitrile in low yields ($\leq$ 25%).[88]

8-MeCN appeared to undergo the two-step Diels-Alder cycloaddtiion-diimide reduction sequence successfully. Unfortunately, the low yields obtained in the conversion of the aldehyde to the nitrile made this route impractical. (**8-MeCHO** failed to give the desired reduced adduct urazole because, in part, diimide reduces arylcarbonyl moieties to alcohols,[34a] which was observed.)

Scheme A-8 illustrates the preparation of *p*-dimethylaminoacetophenone and methyl β-*p*-dimethylaminobenzoylpropionate. *p*-Dimethylaminoacetophenone was readily produced by converting *p*-bromo-N,N-dimethylaniline to the aryllithium and reacting that with N,N-dimethylacetamide. The β-*p*-dimethylaminobenzoylpropionate could not be obtained by Friedel-Crafts acylation[26] or *via* the cuprate chemistry described previously. However, reaction of the aryllithium formed from *p*-bromo-N,N-dimethylaniline with succinic anhydride followed by esterification with diazomethane yielded the desired β-*p*-dimethyl-aminobenzoylpropionate.

Scheme A-8



8-BrMe$_2$N

8-PhSMe$_2$N

Attempts to synthesize **8-Me_2NMe_2N** by condensing methyl β-*p*-dimethylamino-benzoylpropionate and *p*-dimethylaminoacetophenone failed. *p*-Dimethylaminoaceto-phenone did react successfully with ethyl β-*p*-bromobenzoylpropionate and ethyl β-*p*-thiophenoxybenzoylpropionate to give **8-$BrMe_2N$** and **8-$PhSMe_2N$**. These dienes would not undergo Diels-Alder reaction with MTAD or with PTAD under a variety of conditions. Unlike any of the other reactions of this type, when either triazolinedione was added a dark brown color instantly appeared. The only identifiable compound isolable from these reactions was some recovered diarylcyclopentadiene. Presumably, electron transfer from the electron-rich cyclopentadiene system to the electron-poor triazolinedione occurred and charge-transfer complexes formed.

Experimental

General:

90-MHz NMR was performed on a Varian EM-390 continuous-wave spectrometer, 300-MHz NMR was performed on a General Electrics QE-300 FT-NMR spectrometer, 400-MHz NMR was performed on a JEOL JNM-GX400 FT-NMR spectrometer, and 500-MHz NMR was performed on a Bruker AM500 FT-NMR spectrometer. Deutero-chloroform was usually the NMR solvent and was purified by distillation from CaH_2. Tetramethylsilane or the proton signal from residual chloroform in deuterochloroform was used as an internal standard.

Exact mass determinations were obtained from the Analytical Facility at the University of California, Riverside. GCMS was performed on a Hewlett-Packard 5890 GC/5970 MS instrument equipped with a twelve-meter OV-101 capillary column.

A Varian E-line Century Series X-band spectrometer was used for EPR experiments. An ESR-900 liquid helium continuous-flow cryostat (Oxford) was used to obtain EPR spectra at 6 K. A liquid nitrogen-filled quartz finger dewar (Oxford) was used for 77 K experiments. Either a 500-W or 1000-W mercury-xenon arc lamp (Oriel) was focused into the microwave cavity for photolysis. Optical filters (Schott; UG-11/KG-5/WG-305) were used to obtain light in the desired wavelength range ($305\ nm \leq \lambda \leq 386\ nm$).

Water refers to distilled water. Petroleum ether used was the commercial 35-60 °C fraction. Diethyl ether (ether), tetrahydrofuran (THF), and 2-methyltetrahydrofuran (MTHF) were purified by distillation from sodium-benzophenone ketyl. Dry methylene chloride, chloroform, acetonitrile, triethylamine and pyridine were prepared by standing over 4A molecular sieves or by distillation from CaH_2. Toluene was dried by distillation from sodium sand. Dry N,N-dimethylacetamide (DMA) was Aldrich HPLC grade. All other solvents were reagent grade or better and used as purchased unless otherwise noted. Reagents were used as received from the commercial vendors (primarily Aldrich) except where noted.

Inert atmosphere was provided by the use of argon passed through a Drierite-filled gas drying tower. Reactions performed with exclusion of moisture were run either under argon or with a Drierite-filled drying tube. Experiments in which the apparatus was oven-dried and then assembled under a flow of argon were conducted under an argon atmosphere at all stages prior to work-up. Removal of solvent refers to rotary evaporation to apparent dryness followed by further evaporation at the low pressure provided by a vacuum pump (0.1 - 0.5 torr) to remove any residual solvent.

Silica gel for flash column chromatography was 40-63 μm mesh; column sizes are listed as length x diameter. TLC was visualized with UV-light and/or with vanillin stain followed by heating. -78 °C temperatures were attained using dry ice-acetone baths, 0 °C temperatures were attained using ice-water baths, and -40 °C temperatures were attained with dry ice-acetonitrile baths.

***p*-Thiophenoxyacetophenone** - 50 ml dry DMA, 21.67 gm thiophenol (0.20 mole), and 13.0 gm 85% KOH (11.05 gm KOH, 0.20 mole) were mixed in a 250-ml round-bottom flask. The stirred mixture was distilled under argon to remove water (T ≈ 155 °C, ≈20 ml distillate collected). The mixture was cooled and 40 ml more dry DMA was added. A solid white precipitate was present; the stirred mixture was warmed until a suspension was achieved. 39.15 gm *p*-bromoacetophenone (0.20 mole) was added and the mixture was refluxed for 23 hrs., during which time the solution turned brown (from the original orange after *p*-bromo-acetophenone addition). The mixture was cooled to room temperature and then poured into a mixture of 250 ml water and 250 ml $CHCl_3$. After vigorous mixing, the phases were separated. The organic phase was dried with anhydrous $MgSO_4$, treated with activated charcoal, and gravity filtered. Solvents were removed *in vacuo* to leave ≈44 gm brown solid. The solid was recrystallized form 1:1 ethanol : water to give 36.1 gm light tan crystals (80%), which displayed properties identical to the literature values.[26c] Mass spectrum, *m/e* 107, 184, 213, 228.

The ethyl *para*-substituted β-benzoylpropionates were synthesized in similar ways; the following is representative:

Ethyl *p*-thiophenoxybenzoylpropionate - A 2-l three-neck round-bottom flask was equipped wtih a reflux condenser, mechanical stirrer, and gas outlet to a $NaOH_{(aq)}$-filled trap. The flask was charged with 40 ml (44.72 gm, 0.24 mole) diphenylsulfide, 450 ml CS_2, and 38.40 gm (0.29 mole) $AlCl_3$. The mixture was stirred and 24.02 gm succinic anhydride was added (0.24 mole), after which the solids dissolved and the solution became red. The mixture was stirred at room temperature for 20 hrs. 350 ml water and 160 ml conc. $HCl_{(aq)}$ were then added with stirring. A white precipitate formed and was isolated by suction filtration. The filtrate was extracted with 100 ml $CHCl_3$, and the isolated white solid was dissolved in $CHCl_3$. The combined $CHCl_3$ solutions were dried with anhydrous $MgSO_4$ and gravity filtered. The solvents were removed *in vacuo* to leave a slightly yellow white solid. This solid was mixed with 500 ml absolute EtOH, 40 ml triethylortho-formate (35.6 gm, 0.,24 mole), and 2 ml conc. $HCl_{(aq)}$. This mixture was refluxed for 48 hrs. The reaction was cooled to room temperature, and 100 ml saturated $NaHCO_{3(aq)}$, 500 ml water, and 500 ml $CHCl_3$ were then added. The mixture was stirred vigorously, then the phases were separated. The organic phase was dried with anhydrous $MgSO_4$ and gravity filtered. Removal of solvent *in vacuo* left 62.15 gm viscous amber liquid (82%). 90-MHz ^1H NMR ($CDCl_3$) δ 1.2 (t, 3H), 2.7 (t, 2H), 3.2 (t, 2H), 4.1 (q, 2H), 7.1-7.9 (m, 9H). Mass spectrum, *m/e* 106, 152, 184, 213, 269, 314.

Ethyl *p*-methylbenzoylpropionate - 90-MHz ^1H NMR ($CDCl_3$) δ 1.25 (t, 3H), 2.4 (s, 3H), 2.75 (t, 2H), 3.25 (t, 2H), 4.15 (q, 2H), 7.2-7.95 (m, 4H). Mass spectrum, *m/e* 91, 119, 147, 175, 220.

Ethyl *p*-methoxybenzoylpropionate - 90-MHz ^1H NMR ($CDCl_3$) δ 1.25 (t, 3H), 2.75 (t, 2H), 3.25 (t, 2H), 3.85 (s, 3H), 4.15 (q, 2H), 6.85-8.05 (m, 4H).

Ethyl *p*-bromobenzoylpropionate - 90-MHz ^{1}H NMR ($CDCl_3$) δ 1.25 (t, 3H), 2.75 (t, 2H), 3.25 (t, 2H), 4.15 (q, 2H), 7.5-7.9 (m, 4H). Mass spectrum, *m/e* 76, 104, 155, 157, 183, 185, 239, 241, 284, 286.

***p*-Dimethylaminoacetophenone** - A dry, argon-flushed 500-ml three-neck round-bottom flask was charged with 50 ml dry THF and a dry magnetic stirring bar. The flask and contents were cooled to -78 °C and then 125 ml 1.7 M *t*-BuLi (0.213 mole) in pentane was added *via* syringe. A yellow solid complex formed and was allowed to cool at -78 °C for 20 min. A solution of 20.0 gm *p*-bromo-N,N-dimethylaniline (0.100 mole) in 125 ml dry THF was cooled to -78 C under argon for 20 min. and then cannulated into the cold *t*-BuLi solution. A white precipitate formed, replacing the yellow solid complex. This mixture was stirred for 1 hr. past addition. 14 ml dry DMA (13.12 gm, 0.151 mole) was then added *via* syringe, and all solids disappeared to leave a clear pale solution. Stirring was continued at -78 °C for 0.5 hr., then the mixture was warmed to room temperature. Stirring at room temperature was continued for 14 hrs., then 100 ml of half-saturated $NaCl_{(aq)}$ and 100 ml $CHCl_3$ were added. The mixture was stirred vigorously, then the phases were separated. The organic phase was washed with 100 ml of half-saturated $NaCl_{(aq)}$ then 100 ml of saturated $NaCl_{(aq)}$. The organic phase was then dried with anhydrous $MgSO_4$ and gravity filtered. Solvent was removed *in vacuo* to leave 15.9 gm pure white solid (97%). 90-MHz ^{1}H NMR ($CDCl_3$) δ 2.5 (s, 3H), 3.1 (s, 6H), 6.65-7.9 (m, 4H). Mass spectrum, *m/e* 77, 91, 105, 118, 148, 163.

Methyl *p*-dimethylaminobenzoylpropionate - 500 ml dry THF was cooled to -78 °C in a dry, argon-flushed 1-l three-neck round-bottom flask for 30 min. 124 ml 1.7 M *t*-BuLi (0.211 mole) in pentane was added *via* syringe. A yellow suspension formed and was stirred at -78 °C for 30 min. 20.0 gm *p*-bromo-N,N-dimethylaniline (0.100 mole) was then added gradually, a white suspension formed, and this mixture was stirred for 1 hr. at -78 °C. Meanwhile, a dry, argon-flushed 2-l three-neck round-bottom flask was charged with 1300 ml dry THF and 40.1 gm succinic anhydride (0.401 mole). This mixture was

cooled to -78 °C and gave a cloudy white suspension. The cold aryl lithium solution was cannulated into the cold succinic anhydride suspension over 20 min. This mixture was stirred at -78 °C for 1 hr., then allowed to warm to room temperature. Stirring at room temperature continued for 20 hrs. 200 ml water was then added, followed by enough 2 M $HCl_{(aq)}$ to give pH ≈6. This mixture was stirred for 24 hrs., then poured into 2 l half-saturated $NaHCO_{3(aq)}$ and stirred for 8 hrs. The phases were separated and volatile organics were removed from the aqueous phase *in vacuo*. The remaining aqueous phase was acidified to pH 5 with conc. $HCl_{(aq)}$, which caused a white solid to precipitate. This solid was isolated by suction filtration and dried overnight in a vacuum desiccator to leave 11.9 gm white powder, the propionic acid (47%).

In a new, unblemished 500-ml Erlenmeyer flask were placed 40 ml water, 16 gm KOH (285 mmole), and 300 ml ether. This mixture was stirred until the KOH dissolved and was then cooled to 0 °C. 13.6 gm N-methyl-N'-nitro-N-nitrosoguanidine (MNNG, 92.5 mmole; Aldrich) was added portionwise over 15 min. to the stirred cold solution. Stirring at 0 °C continued for 5 min. past the end of addition, then it was halted and the phases were allowed to separate. The ethereal diazomethane solution was decanted into a new, unblemished 400-ml beaker. This ethereal diazomethane solution was added portionwise to a suspension of 10.0 gm of the above-prepared acid (45.2 mmole) in 175 ml 1,4-dioxane and 125 ml EtOAc in a new, unblemished 500-ml Erlenmeyer flask. Gas evolved and solids dissolved as the CH_2N_2 was added. The reaction was stirred for 20 min. past the end of addition. Excess CH_2N_2 was quenched with acetic acid. The mixture was then washed with 3 x 100 ml saturated $NaHCO_{3(aq)}$ and 50 ml saturated $NaCl_{(aq)}$. The organic solution was dried with anhydrous Na_2SO_4 and gravity filtered. Removal of solvents *in vacuo* left 10.5 gm white crystals (99%). 90-MHz ^1H NMR ($CDCl_3$) δ 2.7 (t, 2H), 3.0 (s, 6H), 3.2 (t, 2H), 3.65 (s, 3H), 6.55-7.95 (m, 4H).

***p*-Bromo(dimethoxymethyl)benzene** - A 1-l round-bottom flask was charged with 10.0 gm *p*-bromobenzaldehyde (54.0 mmole), 20 ml trimethylorthoformate

(19.35 gm, 182 mmole), 200 ml MeOH, and 1 ml conc. $HCl_{(aq)}$. The solution was stirred at room temperature for 11 hrs., then refluxed for 7 hrs. protected from moisture. The reaction was cooled to room temperature, then 100 ml saturated $NaHCO_{3(aq)}$, 100 ml CH_2Cl_2, and 50 ml saturated $NaCl_{(aq)}$ were added. The mixture was stirred vigorously, then the phases were separated. The aqueous phase was extracted with 50 ml CH_2Cl_2. The combined organic phases were dried with anhydrous $MgSO_4$ and gravity filtered. Removal of solvent *in vacuo* left 12.2 gm pure clear, colorless liquid (98%). 90-MHz ^1H NMR ($CDCl_3$) δ 3.3 (s, 6H), 5.3 (s, 1H), 7.2-7.5 (m, 4H). Mass spectrum, *m/e* 91, 120, 131, 155, 199, 201, 230, 232.

***p*-(Dimethoxymethyl)acetophenone** - A dry 1-l round-bottom flask was charged with 20.0 gm *p*-bromo(dimethoxymethyl)benzene (86.5 mmole) and 200 ml dry THF. This solution was cooled to -78 °C under argon. 107 ml 1.7 M *t*-BuLi (182 mmole) in pentane was added *via* syringe. The solution was stirred at -78 °C for 1 hr., then 12 ml dry DMA was *via* syringe (11.24 gm, 130 mmole). This mixture was stirred for 1 hr. at -78 °C, then it was allowed to warm to room temperature and stirred for 17 hrs. Upon warming, the solution became clear and golden yellow. 10 ml saturated $NaHCO_{3(aq)}$, 100 ml half-saturated $NaCl_{(aq)}$, and 100 ml $CHCl_3$ were added after the 17 hrs. at room temperature. The mixture was stirred vigorously, then the phases were separated. The organic phase was washed with 100 ml half-saturated $NaCl_{(aq)}$ basified with 5 ml saturated $NaHCO_{3(aq)}$, then with 100 ml saturated $NaCl_{(aq)}$ basified with 5 ml saturated $NaHCO_{3(aq)}$. The organic phase was then dried with anhydrous $MgSO_4$ and gravity filtered. Removal of solvent *in vacuo* left 22 gm viscous yellow liquid. Vacuum fractional distillation (≈1 torr, 78 °C) gave 10.53 gm clear, colorless liquid (63%). 90-MHz ^1H NMR ($CDCl_3$) δ 2.6 (s, 3H), 3.35 (s, 6H), 5.4 (s, 1H), 7.4-8.0 (m, 4H). Mass spectrum, *m/e* 77, 105, 120, 133, 163, 164.

Ethyl *p*-(dimethoxymethyl)benzoylpropionate - 500 ml dry THF in a dry 1-l round-bottom flask was cooled to -78 °C. 100 ml of 1.7 M *t*-BuLi (170 mmole) in pentane

was added *via* syringe and a yellow complex formed. This mixture was stirred at -78 °C for 30 min. 18.75 gm *p*-bromo-(dimethoxymethyl)benzene (81.1 mmole) in 10 ml dry THF was added dropwise *via* pressure-equalizing addition funnel over 20 min. This solution was stirred for 1 hr. at -78 °C, then 8.20 gm CuCN was added. This mixture was stirred at -78 °C for 30 min., then 13 ml ethyl succinyl chloride was added *via* syringe (15 gm, 91 mmole). The dark green solution was warmed to room temperature and stirred for 21 hrs. 100 ml saturated $NaHCO_{3(aq)}$ was added and the mixture was stirred for 75 min. 200 ml CCl_4 was added and the phases were separated. The organic phase was washed with 2 x 100 ml saturated $NaCl_{(aq)}$, dried with anhydrous Na_2SO_4, and gravity filtered. Solvent was removed *in vacuo* to leave 24.45 gm viscous green liquid. Kugelrohr distillation (50 millitorr, 200 °C) gave 19.5 gm clear liquid (85%). 90-MHz ^1H NMR ($CDCl_3$) δ 1.2 (t, 3H), 2.7 (t, 2H), 3.2 (t, 2H), 3.3 (s, 6H), 4.15 (q, 2H), 5.4 (s, 1H), 7.3-8.0 (m, 4H). Mass spectrum, *m/e* 75, 105, 120, 179, 189, 235, 249, 280.

***p*-(2,5-Dimethylpyrrolo)acetophenone** - 9.00 gm 2,5-dioxohexane (79 mmole), 200 ml benzene, 10.0 gm *p*-aminoacetophenone (74 mmole), and 1 ml glacial acetic acid were refluxed under argon in a 500-ml flask for 75 hrs. A Dean-Stark trap was used to remove water. The reaction was then cooled to room temperature and washed with 100 ml saturated $NaHCO_{3(aq)}$. Removal of solvent *in vacuo* left 15.0 gm pure yellow-orange solid (95%). 90-MHz ^1H NMR ($CDCl_3$) δ 2.0 (s, 6H), 2.65 (s, 3H), 5.9 (s, 2H), 7.2-8.1 (m, 4H). Mass spectrum, *m/e* 77, 99, 128, 154, 170, 212, 213.

***p*-Phthalimidoacetophenone** - 200 ml dry THF, 21 ml dry triethylamine (15.3 gm, 151 mmole), 0.45 gm N,N-dimethylaminopyridine (3.7 mmole), and 11 ml phthaloyl dichloride (15.5 gm, 76 mmole) were mixed in a dry 1-l round-bottom flask under argon. 10.0 gm *p*-amino-acetophenone (74 mmole) dissolved in 200 ml dry THF was added over 10 min. to the above solution. The mixture was stirred for 68 hrs. at room temperature. 300 ml CH_2Cl_2 and 500 ml water were then added. The mixture was stirred vigorously, then the phases were separated. The organic phase was washed with 500 ml water,

3 x 250 ml 2 M $HCl_{(aq)}$, 3 x 250 ml saturated $Na_2CO_{3(aq)}$, and 500 ml saturated $NaCl_{(aq)}$. The organic phase was then dried with anhydrous $MgSO_4$ and gravity filtered. Removal of solvent *in vacuo* left a solid which was recrystallized from absolute EtOH to give 14.0 gm white solid (71%). 90-MHz ^1H NMR ($CDCl_3$) δ 2.6 (s, 3H), 7.3-8.2 (m, 8H).

Ethyl 3-(4-nitrophenyl)-2-butenoate (Method 1) - An oven-dried argon-flushed 1-l three-neck round-bottom flask was equipped with a 250-ml pressure-equalizing addition funnel, mechanical stirrer, and a septum. 14.9 gm cerium chips (106 mmole) were rinsed with dry hexane, dried, and placed in the flask. 200 ml dry THF, 14.2 gm *p*-nitro-acetophenone (86 mmole), and 0.90 gm mercuric chloride (3.3 mmole) were also added. This mixture was stirred and quickly became cloudy. It was then cooled to -40°C. The addition funnel was charged with 100 ml dry THF and 22 gm freshly distilled ethyl iodoacetate (103 mmole). The ethyl iodoacetate solution was added over 10 min. to the -40 °C mixture in the flask, taking care that the temperature did not exceed -30 °C. The mixture was stirred for 80 min. at -40 °C, during which time it darkened to an opaque brown. The mixture was then warmed to room temperature and stirred for 14 hrs. 200 ml half-saturated $NH_4Cl_{(aq)}$ and 200 ml CH_2Cl_2 were added. The mixture was stirred vigorously, then the phases were separated. The organic phase was dried wtih anhydrous $MgSO_4$ and gravity filtered. Removal of solvent *in vacuo* left 16 gm crude hydroxy ester as a viscous brown liquid.

The crude hydroxy ester was dissolved in 200 ml benzene in a 1-l round-bottom flask, 1 ml conc. $H_2SO_{4(aq)}$ was added, and the solution was refluxed for 14 hrs. protected from moisture wtih a Dean-Stark trap to remove water. The reaction was cooled, 100 ml saturated $NasHCO_{3(aq)}$ was added, and the mixture was stirred vigorously. The phases were then separated, and the organic layer was dried with anhydrous $MgSO_4$ and gravity filtered. Removal of solvent *in vacuo* left a residue that was Kugelrohr distilled to give 8.4 gm (42% overall) orange solid and liquid which were a mixture of isomers. 90-MHz ^1H NMR ($CDCl_3$) δ 1.1-1.4 (overlapping triplets, 6 H), 2.6 (s, 2H), 3.5 (s, 2H), 5.3-5.7

(three singlets, 2H), 6.2 (m, 1H), 7.5-8.4 (m, 4 H). Mass spectrum, *m/e* 63, 89, 115, 133, 163, 179, 207, 235.

Ethyl 3-(4-nitrophenyl)-2-butenoate (Method 2) - A dry, argon-flushed 1-l three-neck round-bottom flask equipped with a reflux condenser, argon inlet valve, and stoppers was charged with 17.41 gm triethylphosphonoacetate (77.7 mmole) and 250 ml dry THF. 3.2 gm sodium hydride as a dispersion in mineral oil (60% by weight; 1.9 gm NaH, 80 mmole) was added portionwise. Mixture was stirred for 30 min., by which time the gas evolution and exotherm had ceased. 13.22 gm *p*-nitroacetophenone (80.0 mmole) was then added, after which the solution turned from yellow, to orange, to red, to brown, to opaque dark purple-brown. The mixture was stirred at room temperature for 30 min. past addition, then it was gently refluxed for 19 hrs. The mixture was then cooled to room temperature, 300 ml water and 300 ml CH_2Cl_2 were added, and the mixture was stirred vigorously. The phases were separated and the organic layer was dried with anhydrous $MgSO_4$ and gravity filtered. Solvent was removed *in vacuo* to leave a residue which was dissolved in ether-pentane. An insoluble brown material was removed by gravity filtration and the solvents were removed from the filtrate *in vacuo* to leave 16.53 gm (90%) yellow solid product which was a mixture of the *E*- and *Z*-isomers. Spectral data as above.

Ethyl 4-bromo-3-(4-nitrophenyl)-2-butenoate - 6.08 gm ethyl 3-(4-nitrophenyl)-2-butenoate (25.8 mmole), 50 ml CCl_4, 4.70 gm N-bromosuccinimide (26.4 mmole), and 0.34 gm azoisobutyronitrile (AIBN; 2.1 mmole) were refluxed in a 100 ml flask under argon for 8 hrs. The reaction was cooled to room temperature and suction filtered to remove solids. The collected solids were washed with CCl_4. Solvent was removed *in vacuo* from the combined filtrates to leave 9 gm golden brown solid which was used directly in the next reaction. Mass spectrum, *m/e* 115, 160, 189, 206, 268, 270, 296, 298, 313, 315.

Ethyl 3-(4-nitrophenyl)-4-triphenylphosphonium-2-butenoate bromide - 9 gm of crude ethyl 4-bromo-3-(4-nitrophenyl)-2-butenoate from above was dissolved in

50 ml dry benzene in a 300-ml round bottom flask. 7.50 gm Ph_3P (28.6 mmole) was added and the mixture was stirred at room temperature for 25 hrs. Suction filtration allowed isolation of a golden solid, which was washed with CCl_4, benzene, and pentane. The solid was then dried in a vacuum desiccator overnight to leave 6.0 gm product Wittig salt as a tan solid. 90-MHz ^1H NMR ($CDCl_3$) δ 1.15 (t, 3H), 3.9 (q, 2H), 6.1-8.15 (m, 22H).

The 1,4-diaryl-1,3-cyclopentadienes were prepared in the same way; the following is representative (the choice of which component, *p*-substituted acetophenone or ethyl *p*-substituted benzoylpropionate, bears which substituent is arbitrary; changes in procedure, if any, are noted for specific compounds):

1,4-Di(4-methoxyphenyl)-1,3-cyclopentadiene (8-MeOMeO) - 9.55 gm ethyl *p*-methoxy-benzoylpropionate (40.4 mmole) and 6.07 gm *p*-methoxyaceotphenone (40.4 mmole) were added to a suspension of 1.95 gm NaH (81.3 mmole; 3.25 gm of a dispersion of sodium hydride in mineral oil, 60% by weight) in 240 ml dry benzene. The solution was heated at 70 °C. for 12 hrs. The reaction mixture was then cooled and poured into 300 ml ice and water in a 1-l separatory funnel. After extraction, the aqueous phase was collected and set aside. The benzene phase was concentrated to ≈30 ml by rotary evaporation. 18 ml of 10% (w/w) $NaOH_{(aq)}$ was added to the concentrated benzene phase and the mixture was refluxed for 10 min. The mixture was cooled and the phases were separated. The aqueous phase was added to the previously saved aqueous phase. The combined aqueous portions were refluxed for 30 min. Gas was evolved, a solid formed, and it was isolated by suction filtration. The solid was then washed with water and dried on the fritted-glass funnel. Recrystallization of the solid from benzene gave 3.49 gm yellow crystals (31%). 90-MHz ^1H NMR ($CDCl_3$) δ 3.7 (s, 2H), 3.8 (s, 6H), 6.6-7.6 (m, 10H).

1,4-Di(4-bromophenyl)-1,3-cyclopentadiene (8-BrBr) - 23%. 90-MHz ^{1}H NMR ($CDCl_3$) δ 3.7 (s, 2H), 6.9 (s, 2H), 7.45 (s, 8H). Mass spectrum, *m/e* 95, 108, 189, 215, 295, 297, 374, 376, 378.

1-(4-Bromophenyl)-4-(4-methoxyphenyl)-1,3-cyclopentadiene (8-BrMeO) - 22%. 90-MHz ^{1}H NMR ($CDCl_3$) δ 3.75 (s, 2H), 3.8 (s, 3H), 6.8-7.5 (s, 10H), . Mass spectrum, *m/e* 101, 163, 203, 232, 326, 328.

1-(4-bromophenyl)-4-(4-methylphenyl)-1,3-cyclopentadiene (8-BrMe) - 24%. 90-MHz ^{1}H NMR ($CDCl_3$) δ 2.35 (s, 3H), 3.8 (m, 2H), 6.9 (m, 2H), 7.1-7.55 (m, 8H). Mass spectrum, *m/e* 101, 115, 189, 215, 310, 312.

1,4-Di(4-methylphenyl)-1,3-cyclopentadiene (8-MeMe) - 24%. 90-MHz ^{1}H NMR ($CDCl_3$) δ 2.35 (s, 6H), 3.7 (s, 2H), 6.85 (s, 2H), 7.0-7.6 (m, 8H). Mass spectrum, *m/e* 101, 115, 152, 202, 215, 246.

1-(4-Methoxyphenyl)-4-(4-thiophenoxyphenyl)-1,3-cyclopentadiene (8-MeOPhS) - Stirred at 80 °C for 16 hrs. 14%. (See procedure for **8-PhSPhS** for improved procedure for better yields. The thiophenoxy group increases the solubility of intermediates in polar organic solvents; they do not come out of the benzene phase as well when refluxed with $NaOH_{(aq)}$ so yields of material from the concentrated base are reduced.) 90-MHz ^{1}H NMR ($CDCl_3$) δ 3.7 (s, 2H), 3.8 (s, 3H), 6.7-7.5 (m, 15H). Mass spectrum, *m/e* 77, 115, 139, 203, 232, 247, 356.

1-(4-Methylphenyl)-4-(4-thiophenoxyphenyl)-1,3-cyclopentadiene (8-MePhS) - Stirred at 80 °C for 16 hrs. 5%. (See procedure for **8-PhSPhS** for improved procedure for better yields. The thiophenoxy group increases the solubility of intermediates in polar organic solvents; they do not come out of the benzene phase as well when refluxed with $NaOH_{(aq)}$ so yields of material from the concentrated base are reduced.) 90-MHz ^{1}H NMR ($CDCl_3$) δ 2.35 (s, 3H), 3.7 (s, 2H), 6.8-7.6 (m, 15H). Mass spectrum, *m/e* 77, 115, 155, 170, 215, 231, 249, 340.

1,4-Di(4-thiophenoxyphenyl)-1,3-cyclopentadiene (8-PhSPhS) - Stirred at 80 °C for 16 hrs. The concentrated benzene layer left after reflux with $NaOH_{(aq)}$ was diluted wiht hexanes and a solid precipitated. This solid was collected and refluxed with $NaOH_{(aq)}$ as usual. It was then treated in the usual way (collected by suction filtration, washed with water, dried) to give 24% product. 90-MHz ^1H NMR ($CDCl_3$) δ 3.7 (s, 2H), 6.9 (s, 2H), 7.15-7.55 (m, 18H).

1-(4-Bromophenyl)-4-(4-dimethylaminophenyl)-1,3-cyclopentadiene (8-BrMe$_2$N) - Stirred at 80 °C for 16 hrs. 47%. 90-MHz ^1H NMR ($CDCl_3$) δ 3.0 (s, 6H), 3.75 (s, 2H), 6.8-7.5 (m, 10H), . Mass spectrum, *m/e* 130, 170, 215, 260, 295, 297, 339, 341.

1-(4-Dimethylaminophenyl)-4-(4-thiophenoxyphenyl)-1,3-cyclopentadiene (8-Me$_2$NPhS) - Stirred at 80 °C for 16 hrs. 16%. 90-MHz ^1H NMR ($CDCl_3$) δ 2.95 (s, 6H), 3.7 (s, 2H), 6.6-7.5 (m, 15H).

1-(4-Methylphenyl)-4-(4-(dimethoxymethyl)phenyl)-1,3-cyclopentadiene (8-Me(MeO)$_2$CH) - Stirred at 80 °C for 16 hrs. 29%. 90-MHz ^1H NMR ($CDCl_3$) δ 2.35 (s, 3H), 3.3 (s, 6H), 3.75 (s, 2H), 5.4 (s, 1H), 6.8-7.6 (m, 10 H). Mass spectrum, *m/e* 115, 138, 189, 215, 260, 275, 306.

1-(4-Methoxyphenyl)-4-(4-(dimethoxymethyl)phenyl)-1,3-cyclopentadiene (8-MeO(MeO)$_2$CH) - Stirred at 80 °C for 16 hrs. 39%. 90-MHz ^1H NMR ($CDCl_3$) δ 3.3 (s, 6H), 3.7 (s, 2H), 3.75 (s, 3H), 5.35 (s, 1H), 6.7-7.55 (m, 10H). Mass spectrum, *m/e* 101, 115, 165, 189, 202, 261, 276, 292.

1-(4-Bromophenyl)-4-(4-(dimethoxymethyl)phenyl)-1,3-cyclopentadiene (8-Br(MeO)$_2$CH) - Stirred at 80 °C for 16 hrs. 20%. 90-MHz ^1H NMR ($CDCl_3$) δ 3.3 (s, 6H), 3.75 (s, 2H), 5.4 (s, 1H), 6.9 (s, 2H),7.4-7.6 (m, 8H). Mass spectrum, *m/e* 75, 115, 130, 202, 215, 260, 324, 326, 339, 341, 370, 372.

1-(4-Dimethylaminophenyl)-4-(4-(dimethoxymethyl)phenyl)-1,3-cyclopentadiene (8-$Me_2N(MeO)_2CH$) - Stirred at 80 °C for 16 hrs. 39%. 90-MHz ^1H NMR ($CDCl_3$) δ 2.95 (s, 6H), 3.35 (s, 6H), 3.7 (s, 2H), 5.4 (s 1H), 6.6-7.7 (m, 10 H).

1,4-Di(4-(dimethoxymethyl)phenyl)-1,3-cyclopentadiene (8-$(MeO)_2CH(MeO)_2CH$) - Stirred at 80 °C for 16 hrs. 26%. 90-MHz ^1H NMR ($CDCl_3$) δ 3.35 (s, 12H), 3.7 (s, 2H), 5.35 (s, 2H), 6.9 (s, 2H), 7.3-7.6 (m, 8H). Mass spectrum, *m/e* 75, 115, 152, 202, 215, 289, 335, 366.

1-(4-Methylphenyl)-4-(4-(2,5-dimethylpyrrolo)phenyl)-1,3-cyclopentadiene - Stirred at 100 °C in toluene for 16 hrs. Recrystallized from MeOH/water, 9%. 90-MHz ^1H NMR ($CDCl_3$) δ 2.05 (s, 6H), 2.35 (s, 3H), 3.8 (s, 2H), 5.9 (s, 2H), 6.85-7.7 (m, 10H). Mass spectrum, *m/e* 77, 115, 128, 162, 215, 253, 267, 325.

1-(4-Formylphenyl)-4-(4-methylphenyl)-1,3-cyclopentadiene (8-MeCHO) - A 250-ml round-bottom flask was charged with 2.25 gm **8-$Me(MeO)_2CH$** (7.34 mmole), 100 ml THF, 25 ml water, and 10 drops conc. $HCl_{(aq)}$. The mixture was stirred at room temperature for 4.5 hrs. A yellow precipitate formed after 10 min. 25 ml saturated $NaHCO_{3(aq)}$ was added to quench the acid, then the yellow solid was isolated by suction filtration and washed with water. The solid was dried in a vacuum desiccator to give 1.60 gm bright yellow solid (84%). 90-MHz ^1H NMR ($CDCl_3$) δ 2.35 (s, 3H), 3.75 (s, 2H), 6.9 (m, 2H), 7.0-7.9 (m, 8H), 9.95 (s, 1H). Mass spectrum, *m/e* 101, 115, 152, 202, 215, 260.

1-(4-Cyanophenyl)-4-(4-methylphenyl)-1,3-cyclopentadiene (8-MeCN) - 250 mg (0.960 mmole) **8-MeCHO**, 70 mg hydroxylamine hydrochloride (1.01 mmole), 180 μl dry pyridine (176 mg, 2.23 mmole), and 25 ml 7:3 $CHCl_3$ were mixed in a 300-ml round-bottom flask and refluxed for 4.5 hrs. under argon. The aldoxime solution was cooled to room temperature and the solvents were removed *in vacuo*. 90 mg cyanuric chloride (0.50 mmole) and 10 ml dry pyridine were added to the residual solid (aldoxime) and the solution was refluxed for 60 min., then cooled to room temperature. 300 ml water

was added and the solid which precipitated was collected by suction filtration. After being air-dried on the fritted-glass funnel, the solid was triturated with $CH_3CN/CH_2Cl_2/CHCl_3$ and suction filtered to remove an almost-black solid. Solvent was removed from the filtrate *in vacuo* to leave 170 mg solid. Column chromatography of this solid (19 cm x 3.5 cm; 3:1 petroleum ether : ethyl acetate) gave 62 mg product nitrile as a dark yellow solid (25%). R_f = 0.58 (1:1 petroleum ether : ethyl acetate). Mass spectrum, *m/e* 101, 128, 152, 190, 215, 227, 242, 257.

The procedures for preparation of the two N-methyl urazoles are similar; the following is representative:

1,7-Di(4-bromophenyl)-4-methyl-2,4,6-triazatricyclo[5.2.1.$0^{2,6}$]-decane-3,5-dione - 500 mg **8-BrBr** (1.33 mmole) was suspended in 250 ml dry hexanes under argon in a 500-ml round-bottom flask. 160 mg MTAD (1.41 mmole) dissolved in 150 ml dry ether was cannulated into the suspension. After a few minutes, all solids had dissolved and the pink color had diminished. Solvent was removed *in vacuo* to leave a pink-white solid. This solid was dissolved in 35 ml ethyl acetate at 0 °C and 10 drops glacial acetic acid were added. This solution was introduced into a Griffin-Worden tube charged with 500 mg 5% Rh/Al_2O_3. The reaction mixture was stirred at 0 °C under 45 psi $H_{2(g)}$ for 1 hr. The reaction mixture was then suction filtered through Celite and the collected solids were washed with 20 ml EtOAc. 20 ml CH_2Cl_2 was added to the combined filtrates, and this solution was washed with 10 ml saturated $NaHCO_{3(aq)}$. The organic phase was separated, dried with anhydrous $MgSO_4$, and gravity filtered. Solvent was removed *in vacuo* to leave ≈650 mg solid. Column chromatography of this solid (20 cm x 5 cm; solvent gradient proceeding from 100% petroleum ether to 2:1 to 1:1 petroleum ether : ethyl acetate) allowed isolation of 250 mg white solid (38%). R_f = 0.38 (1:1 petroleum ether : ethyl acetate). 500-MHz ^1H NMR ($CDCl_3$) δ 2.32 (d, 1H), 2.35 (m, 2H), 2.59 (m, 2H), 2.83 (dt, 1H), 3.00 (s, 3H), 7.44-7.53 (m, 8H). Exact mass: calculated for $C_{20}H_{17}N_3O_2Br_2$ 488.9688, found 488.9682 (M^+).

1,7-Di(4-methoxyphenyl)-4-methyl-2,4,6-triazatricyclo[5.2.1.0^{2,6}]-decane-3,5-dione - 37%. R_f = 0.33 (1:1 petroleum ether : ethyl acetate). 400-MHz ^{1}H NMR ($CDCl_3$) δ 2.26 (d, 1H), 2.37 (m, 2H), 2.57 (m, 2H), 2.91 (dt, 1H), 2.99 (s, 3H), 3.81 (s, 6H), 6.92 -7.51 (m, 8H). Exact mass: calculated for $C_{22}H_{23}N_3O_4$ 393.1688, found 393.1681 (M^+).

The procedures for preparation of the N-phenyl urazoles are similar; the following is representative:

1,7-Di(4-methylphenyl)-4-phenyl-2,4,6-triazatricyclo[5.2.1.0^{2,6}]-decane-3,5-dione - 164 mg **8-MeMe** (0.666 mmole) was dissolved in 5 ml glyme in a 25-ml round-bottom flask. The suspension was stirred for 5 min., then ≈150 mg PTAD was added. All solids dissolved, fluorescence was no longer observed, and a reddish-orange color persisted. The solution was then cooled to 0 °C and 1.30 gm potassium azodicarboxylate[34a] was added (6.69 mmole). A solution of 0.80 gm AcOH (13.3 mmole) in 5 ml glyme was then added dropwise *via* syringe/syringe pump over 5 hrs. to the stirred mixture at 0 °C under argon. Stirring at 0 °C continued for 3 hrs. past the completion of addition, then the mixture was allowed to warm to room temperature and was stirred overnight. 5 ml CH_2Cl_2 was then added, followed by the slow, careful addition of 5 ml water. The mixture was transferred to a separatory funnel and 10 ml water was added. The phases were mixed vigorously, then they were separated. The aqueous layer was extracted with 10 ml CH_2Cl_2. The organic phases were combined, then dried with anhydrous $MgSO_4$ and gravity filtered. Removal of solvent *in vacuo* left 210 mg orange-white solid. Column chromatography of this solid (11 cm x 4 cm; solvent gradient proceeding from 1:1 to 2:1 to 5:1 to 19:1 CH_2Cl_2 : petroleum ether) allowed isolation of 168 mg white solid (60%). R_f = 0.16 (4:1 petroleum ether : ethyl acetate). 500-MHz ^{1}H NMR ($CDCl_3$) δ 2.36 (s, 6H), 2.36 (d, 1H), 2.54 (m, 2H), 2.67 (m, 2H), 3.03 (dt, 1H), 7.22-7.57 (m, 13H). Exact mass: calculated for $C_{27}H_{25}N_3O_2$ 423.1947 (M^+), $C_{27}H_{26}N_3O_2$ 424.2025 (MH^+), found 424.2007 (MH^+).

1-(4-Bromophenyl)-7-(4-methylphenyl)-4-phenyl-2,4,6-triazatricyclo-[5.2.1.0^{2,6}]decane-3,5-dione - 54% from **8-BrMe**. R_f = 0.12 (4:1 petroleum ether : ethyl acetate). 500-MHz ^{1}H NMR ($CDCl_3$) δ 2.36 (s, 3H), 2.37 (d, 1H), 2.54 (m, 2H), 2.67 (m, 2H), 2.99 (dt, 1H), 7.22-7.55 (m, 13H). Exact mass: calculated for $C_{26}H_{22}N_3O_2Br$ 487.0896, found 487.0886 (M^+).

1-(4-Bromophenyl)-7-(4-methoxyphenyl)-4-phenyl-2,4,6-triazatricyclo-[5.2.1.0^{2,6}]decane-3,5-dione - 50% from **8-BrMeO**. R_f = 0.18 (CH_2Cl_2). 500-MHz ^{1}H NMR ($CDCl_3$) δ 2.36 (d, 1H), 2.55 (m, 2H), 2.66 (m, 2H), 2.99 (dt, 1H), 3.81 (s,3H), 6.93-7.55 (m, 13H). Exact mass: calculated for $C_{26}H_{22}N_3O_3Br$ 503.0845, found 503.0825 (M^+).

1,7-Di(4-thiophenoxyphenyl)-4-phenyl-2,4,6-triazatricyclo[5.2.1.0^{2,6}]-decane-3,5-dione - 51% from **8-PhSPhS**. R_f = 0.13 (4:1 petroleum ether : ethyl acetate). 500-MHz ^{1}H NMR ($CDCl_3$) δ 2.38 (d, 1H), 2.55 (m, 2H), 2.66 (m, 2H), 2.97 (dt, 1H), 7.26-7.57 (m, 23H). Exact mass: calculated for $C_{37}H_{29}N_3O_2S_2$ 611.1701 (M^+), $C_{37}H_{28}N_3O_2S_2$ 610.1623 ([M - H]$^+$), found 610.1595 ([M - H]$^+$).

1-(4-Methylphenyl)-7-(4-thiophenoxyphenyl)-4-phenyl-2,4,6-triazatricyclo[5.2.1.0^{2,6}]decane-3,5-dione - 50% from **8-MePhS**. R_f = 0.21 (4:1 petroleum ether : ethyl acetate). 500-MHz ^{1}H NMR ($CDCl_3$) δ 2.37 (d, 1H), 2.37 (s, 3H), 2.55 (m, 2H), 2.67 (m, 2H), 3.01 (dt, 1H), 7.23-7.58 (m, 18H). Exact mass: calculated for $C_{32}H_{27}N_3O_2S$ 517.1824 (M^+), $C_{32}H_{26}N_3O_2S$ 516.1746 ([M - H]$^+$), found 516.1747 ([M - H]$^+$).

1-(4-Methoxyphenyl)-7-(4-thiophenoxyphenyl)-4-phenyl-2,4,6-triazatricyclo[5.2.1.0^{2,6}]decane-3,5-dione - 54% from **8-MeOPhS**. R_f = 0.11 (4:1 petroleum ether : ethyl acetate). 500-MHz ^{1}H NMR ($CDCl_3$) δ 2.36 (d, 1H), 2.55 (m, 2H), 2.65 (m, 2H), 3.01 (dt, 1H), 3.82 (s, 3H), 6.93-7.57 (m, 18H). Exact mass: calculated for $C_{32}H_{27}N_3O_2S$ 533.1773 (M^+), $C_{32}H_{28}N_3O_2S$ 534.1851 (MH^+), found 534.1858 (MH^+).

The procedures for preparation of the phenylsulfonyls are similar; the following is representative:

1,7-Di(4-phenylsulfonylphenyl)-4-phenyl-2,4,6-triazatricyclo-[5.2.1.0^{2,6}]decane-3,5-dione - 300 mg of 1,7-di(4-thiophenoxyphenyl)-4-phenyl-2,4,6-triazatricyclo[5.2.1.0^{2,6}]decane-3,5-dione (0.490 mmole), 30 ml acetone, 10 ml water, and 3.65 gm Oxone[22] (5.94 mmole) were stirred at room temperature for 40 hours. The reaction was poured into 150 ml water and then extracted with 3 x 100 ml CH_2Cl_2. The organic portions were combined, dried with anhydrous $MgSO_4$, and gravity filtered. Removal of solvent *in vacuo* left 331 mg slightly yellow powder (100%). R_f = 0.26 (1:1 petroleum ether : ethyl acetate). 500-MHz ^{1}H NMR ($CDCl_3$) δ 2.47 (d, 1H), 2.54 (m, 2H), 2.74 (m, 2H), 2.90 (dt, 1H), 7.32-7.99 (m, 23H). Exact mass: calculated for $C_{37}H_{29}N_3O_6S_2$ 675.1498 (M^+), $C_{37}H_{28}N_3O_2S_2$ 674.1419 ([M - H]$^+$), found 674.1393 ([M - H]$^+$).

1-(4-Methylphenyl)-7-(4-phenylsulfonylphenyl)-4-phenyl-2,4,6-triazatricyclo[5.2.1.0^{2,6}]-decane-3,5-dione - 100% from 1-(4-methylphenyl)-7-(4-thiophenoxyphenyl)-4-phenyl-2,4,6-triazatricyclo[5.2.1.0^{2,6}]decane-3,5-dione. R_f = 0.30 (1:1 petroleum ether : ethyl acetate). 500-MHz ^{1}H NMR ($CDCl_3$) δ 2.37 (s, 3H), 2.41 (d, 1H), 2.55 (m, 2H), 2.72 (m, 2H), 2.97 (dt, 1H), 7.23-8.00 (m, 18H). Exact mass: calculated for $C_{32}H_{27}N_3O_4S$ 549.1722 (M^+), $C_{32}H_{26}N_3O_4S$ 548.1644 ([M - H]$^+$), found 548.1642 ([M - H]$^+$).

1-(4-Methoxyphenyl)-7-(phenylsulfonylphenyl)-4-phenyl-2,4,6-triazatricyclo[5.2.1.0^{2,6}]-decane-3,5-dione - 100% from 1-(4-methoxyphenyl)-7-(4-thiophenoxyphenyl)-4-phenyl-2,4,6-triazatricyclo[5.2.1.0^{2,6}]decane-3,5-dione. R_f = 0.26 (1:1 petroleum ether : ethyl acetate). 500-MHz ^{1}H NMR ($CDCl_3$) δ 2.40 (d, 1H), 2.56 (m, 2H), 2.70 (m, 2H), 2.98 (dt, 1H), 3.82 (s, 3H), 6.93-8.00 (m, 18H). Exact mass: calculated for $C_{32}H_{27}N_3O_4S$ 565.1671 (M^+), $C_{32}H_{26}N_3O_4S$ 564.1583 ([M - H]$^+$), found 564.1588 ([M - H]$^+$).

Semicarbazides from N-methyl urazoles: With careful exclusion of oxygen, 30 mg N-methyl urazole, 1.3 ml argon-sparged 2-PrOH, and 30 mg crushed KOH are refluxed under argon for 70 min. The reaction is subsequently cooled to room temperature, acidified with 300 µl argon-sparged 3 M $HCl_{(aq)}$, basified with 500 µl argon-sparged 1 M $NH_{3(aq)}$, and diluted with 3 ml argon-sparged water. The mixture is then extracted with 2 x 5 ml CH_2Cl_2 (freshly distilled). The combined organic portions are dried with anhydrous $MgSO_4$ and gravity filtered. Solvents are removed *in vacuo* to leave the semicarbazide.

Hydrazines from N-phenyl urazoles:

For N-phenyl urazoles without phenylsulfonyl groups: With careful exclusion of oxygen, 20 mg urazole, 1 ml hydrzine hydrate, and 1 ml argon-sparged 2-PrOH are refluxed in a 25-ml round-bottom flask under argon for 6 hrs. The reaction is then cooled to room temperature and 5 ml argon-sparged CCl_4 is added. The mixture is stirred vigorously, then the phases are separated. The aqueous phase is extracted with 5 ml more CCl_4. The combined organic portions are dried with anhydrous $MgSO_4$ and gravity filtered through a plug of glass wool in a disposable pipette. Removal of solvent *in vacuo* leaves the hydrazine as a white powder.

For N-phenyl urazoles with phenylsulfonyl groups: With careful exclusion of oxygen, 20 mg urazole, 1 ml freshly distilled THF, 1 ml hydrzine hydrate, and 1 ml argon-sparged 2-PrOH are refluxed in a 25-ml round-bottom flask under argon for 10 hrs. The reaction is then cooled to room temperature and 5 ml argon-sparged CH_2Cl_2 is added. The mixture is stirred vigorously, then the phases are separated. The aqueous phase is extracted with 5 ml more CH_2Cl_2. The combined organic portions are dried with anhydrous $MgSO_4$ and gravity filtered through a plug of glass wool in a disposable pipette. Removal of solvent *in vacuo* leaves the hydrazine as a white powder.

Diazenes from semicarbazides and hydrazines: Under argon, the solid hydrazine or semicarbazide is dissolved in 1 ml freshly distilled CH_2Cl_2 in a 25-ml round-bottom flask.

The solution is cooled to 0 °C and 100 mg nickel peroxide[39] is added. The suspension is stirred under argon at 0 °C for 35 min. It is then cannulated through teflon tubing onto a pad of CH_2Cl_2-rinsed Celite in a jacketed fritted-glass filter funnel cooled to -78 °C. The reaction mixture is forced through the Celite and fritted glass with argon and collected in a dry, argon-flushed 25-ml round-bottom flask also cooled to -78 °C. The reaction flask is rinsed with 2 ml freshly distilled CH_2Cl_2, which is also cannulated onto the Celite, where it rinses the collected solids as it is forced into the collection flask. The combined filtrates are warmed to 0 °C and subjected to vacuum (20 μ) at that temperature until all solvent is removed to leave solid diazene.

1,4-Diarylbicyclo[2.1.0]pentanes (6-XY) - The cold solid diazene is dissolved in 0.5 ml freshly distilled CH_2Cl_2 at 0 °C. This solution is cannulated through teflon tubing into a clean, dry 5 mm o.d., 3.5 mm i.d., medium-walled quartz NMR tube (equipped with a graded seal joining the quartz tube to a pyrex ground-glass joint) under argon. (The tubes are washed with dilute $NaOH_{(aq)}$, water, and MeOH, then dried under vacuum, prior to use.) The tube is then fitted with a vacuum stopcock and the solvent is removed *in vacuo* at 0 °C to leave a white solid coating the inner surface of the tube. ≈0.3 ml $CDCl_3$ is vacuum-transferred from CaH_2 into the tube, then the solution is degassed by three freeze-pump-thaw cycles. The tube is then sealed under vacuum with an oxygen-natural gas torch. The tube is placed in a 60 °C water bath for 1 hr., which thermally deazotizes the sample to give the 1,4-diarylbicyclo[2.1.0]pentane in $CDCl_3$ solution.

The bridge-flip reaction of the 1,4-diarylbicyclo[2.1.0]pentanes was monitored on a 300-MHz NMR spectrometer equipped with a variable temperature probe. The temperature controller was calibrated with an ethylene glycol standard. The samples were heated until the signals for the 5_x and 5_n protons merged; the coalescence temperature was determined as the one higher than which no further narrowing of the merged signals occurred.

1,4-Di(4-methoxyphenyl)bicyclo[2.1.0]pentane (6-MeOMeO) - 300-MHz ^{1}H NMR ($CDCl_3$) δ 1.55 (d, 1H), 1.74 (dt, 1H), 1.91 (m, 2H), 2.54 (m, 2H), 3.77 (s, 6H), 6.76-7.48 (m, 8H).

1,4-Di(4-methylphenyl)bicyclo[2.1.0]pentane (6-MeMe) - 300-MHz ^{1}H NMR ($CDCl_3$) δ 1.58 (d, 1H), 1.81 (dt, 1H), 1.90 (m, 2H), 2.38 (s, 6H), 2.55 (m, 2H), 6.97-7.14 (m, 8H).

1,4-Di(4-bromophenyl)bicyclo[2.1.0]pentane (6-BrBr) - 300-MHz ^{1}H NMR ($CDCl_3$) δ 1.68 (d, 1H), 1.81 (dt, 1H), 1.95 (m, 2H), 2.56 (m, 2H), 6.91-7.39 (m, 8H).

1-(4-methoxyphenyl)-4-(4-phenylsulfonylphenyl)bicyclo[2.1.0]pentane (6-MeOPhSO$_2$) - 300-MHz ^{1}H NMR ($CDCl_3$) δ 1.72 (d, 1H), 1.86 (dt, 1H), 1.94 (m, 2H), 2.56 (m, 2H), 3.79 (s, 3H), 6.98-7.98 (m, 13H).

1-(4-methylphenyl)-4-(4-phenylsulfonylphenyl)bicyclo[2.1.0]pentane (6-MePhSO$_2$) - 300-MHz ^{1}H NMR ($CDCl_3$) δ 1.73 (d, 1H), 1.92 (dt, 1H), 1.95 (m, 2H), 2.31 (s, 3H), 2.58 (m, 2H), 7.02-7.92 (m, 13H).

1,4-Di(4-phenylsulfonylphenyl)bicyclo[2.1.0]pentane (6-PhSO$_2$PhSO$_2$) - 300-MHz ^{1}H NMR ($CDCl_3$) δ 1.83 (d, 1H), 1.96 (dt, 1H), 1.98 (m, 2H), 2.59 (m, 2H), 7.12-7.99 (m, 18H).

1,3-Diaryl-1,3-cyclopentadiyls (7-XY) - The cold solid diazene is dissolved in 0.5 ml freshly distilled CH_2Cl_2 at 0 °C. This solution is cannulated through teflon tubing into a clean, dry 4 mm o.d. thin-walled quartz EPR tube under argon. (The tubes are washed with dilute $NaOH_{(aq)}$, water, and MeOH, then oven-dried, prior to use.) The tube is then fitted with a vacuum stopcock and the solvent is removed *in vacuo* at 0 °C to leave a white solid coating the inner surface of the tube. ≈1 ml MTHF is vacuum-transferred from sodium-benzophenone ketyl into the tube. The solution is degassed by three freeze-pump-thaw cycles. The diazenes are photochemically deazotized at either 77 K or 6 K in the cavity of an EPR spectrometer with either a 500- or 1000-W Hg(Xe) arc lamp with filters

to restrict the incident light to 305 nm $\leq \lambda \leq$ 386 nm. 77 K was achieved by using a liquid nitrogen-filled quartz finger dewar, 6 K was achieved by using a continuous-flow liquid helium cryostat; both pieces of equipment were mounted in the cavity of the EPR spectrometer prior to photolysis. At these temperatures, the diazene sample is in an MTHF glass. The data for **7- XY** are listed in Table 1-3.

The decay traces of **7-MeOPhSO$_2$**, **7-MePhSO$_2$**, and **7-PhSO$_2$PhSO$_2$** were obtained by photolyzing in the above wavelength range for 10 min. at 77 K. The rise of the signals at 3040 G, 3040 G, and 3055 G, respectively (at 9.27 GHz), were monitored at a microwave power of 0.2 mW for the 10-min. photolysis, then the decrease of the signals was monitored under the same conditions for 50 min.

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Chapter 2

Progress Toward the Synthesis of Non-Kekulé Naphthalene, a Series of Tetramethyleneethanes, and Bi(cyclobutadienyl)

Overview

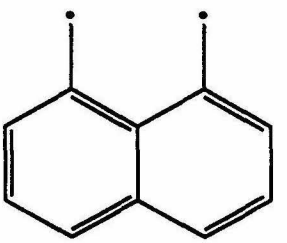
As chemists' understanding of molecules and the forces which shape them has grown, and as the computational facilities available to researchers have increased in power and lessened in cost, the complexity of the molecules subjected to theoretical and computational study has increased. It has long been recognized as desirable to viably treat complicated chemical systems computationally, as many of them do not lend themselves to ready experimental study and yet contain interesting and useful information. However, theory has not yet attained the stature which allows its results to be accepted without question. Nor, for that matter, given the difficulty in examining systems of current interest, has experiment.

A synergism between theory and experiment has evolved. Theorists predict unmeasured properties for known molecules and propose entirely new molecules for study. Experimentalists endeavor to make these compounds and determine their properties, thereby validating theoretical predictions or calling them into question. Theory demands newer and more exacting experiments. Experiment requires theory to agree with observed fact and accurately predict future results.

The relationship between theory and experiment is particularly evident in the field of biradical research. Biradicals are molecular species which have been defined as "neutral structures with one fewer than the number of bonds allowed by valence theory"[1] and, alternatively, as "molecules in which two electrons occupy two degenerate or nearly degenerate molecular orbitals."[2] Initially born through research into reactive intermediates and mechanisms in photochemistry, thermochemistry, and cycloadditions,[3] the field now also includes the study of biradicals as unique compounds in their own right and the design and preparation of novel organic materials with unique optical and magnetic properties.[4] It has therefore become a proving ground for theories concerned with the elucidation and explanation of electron interactions.

Obviously, synthesis and study of each and every molecule of interest is not possible due to constraints on resources. This shortfall can be mitigated by the availability of reliable, high-quality theoretical studies. Successful and reliable application of theory to biradicals is of added importance due to the inability of current experimental methods to always readily and unambiguously determine facts of central importance to the field. This includes the ground state spin preference (singlet or triplet) of a biradical and the magnitude of this preference.

Theory has succeeded on several occasions. *Ab initio* calculations correctly predicted the rectangular shape of cyclobutadiene in advance of experimental proof. In fact, early experiments actually suggested that cyclobutadiene was square.[5] Also, qualitative theory predicted that 1,8-naphthoquinodimethane **1** would have a triplet ground state, which was eventually confirmed by experiment. Initial experiments wrongly assigned a singlet ground state.[6] These achievements notwithstanding, the literature still contains calculations of extremely dubious quality. An example is the prediction of a 60 kcal/mole singlet-triplet energy gap in **1**.[4]

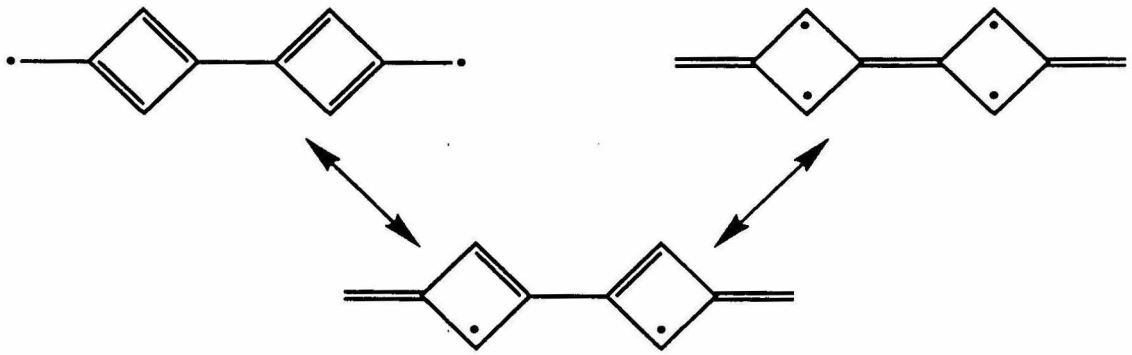


1

Now, as research efforts turn toward larger and more intricate arrays of unpaired electrons in organic systems in attempts to achieve organic-based ferromagnetism, it is vital to possess sound methods for the prediction of how these electrons will interact. The size of these systems limits the applicability of high quality *ab initio* methods. The

curious researcher must then turn to semi-empirical and qualitative treatments. These are far more accessible in terms of time, effort, and simplicity, but the question of ease of use *vs.* accuracy arises. Yet even the results of the best current *ab initio* calculations must be examined critically due to the complexities of the problems being addressed. It is incumbent upon experiment to prove theory's abilities.

Non-Kekulé naphthalene **2**, bi(cyclobutadienyl) **3**, and the tetramethyleneethane derivatives **4** are biradicals. Each has been the subject of theoretical study, is intellectually appealing in its own right, and presents a considerable synthetic challenge. **2** and **3** are each the second in a family of compounds with intriguing properties. The parent tetramethyleneethane is one of the simplest non-Kekulé hydrocarbons and has received a great deal of attention as a test of various theoretical methods. The tetramethyleneethane family of compounds is of special interest due to the current conflict between theory and experiment concerning ground state multiplicity. These considerations prompted us to attempt to prepare these molecules.



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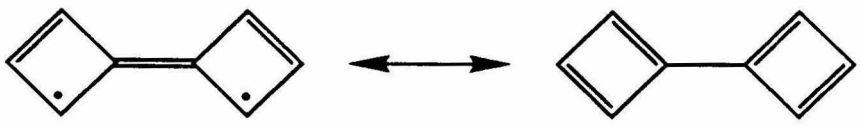

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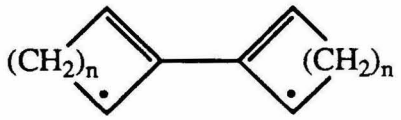
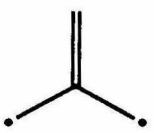


n = 1, 2, 3

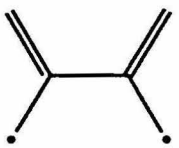
4

Background

Non-Kekulé[7] molecules are those for which no classical Kekulé structures can be written; they contain enough atoms but not enough bonds to satisfy the standard rules of valence. Biradicals in which the two unpaired electrons are in classical π-conjugation with each other ("delocalized" biradicals) are non-Kekulé molecules in which the unpaired electrons are topologically prevented from forming a π bond.[8] The simplest and most thoroughly examined member of this class of compounds is trimethylenemethane (TMM). Theoretical treatments predict a triplet ground state for TMM,[9] and this has been confirmed by experiment.[10] Tetramethyleneethane (TME) is also a simple member of this class and formally consists of two allyl radicals with a bond between the two central carbons. As noted above, the ground state of TME is a matter of dispute: *ab initio*[11] and qualitative theories predict a singlet (*vide infra*), experiments by Dowd, *et al.*,[12] are currently consistent with a triplet (or nearly degenerate singlet and triplet states). Taken together, TMM and TME nominally form a paradigm for the prediction and understanding of many properties of non-Kekulé hydrocarbons, as one or the other is found as a structural subunit in a large number of other members of this group.

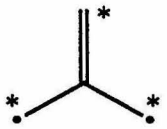


TMM

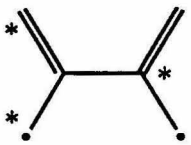


TME

TMM and TME are also both alternant hydrocarbons. This class of compounds is comprised of molecules whose carbon framework can be divided into two sets such that no two atoms of the same set are nearest neighbors.[13] These sets are referred to as "starred" and "non-starred;" the number of starred atoms is n*, the number of non-starred atoms is n°. The formula for assignment of "starred" and "non-starred" atoms should be clear from the examples of TMM and TME below. If $n^* \neq n^\circ$, the set with the greater number of atoms is arbitrarily designated the "starred" set (*i.e.*, $n^* \geq n^\circ$ by convention).



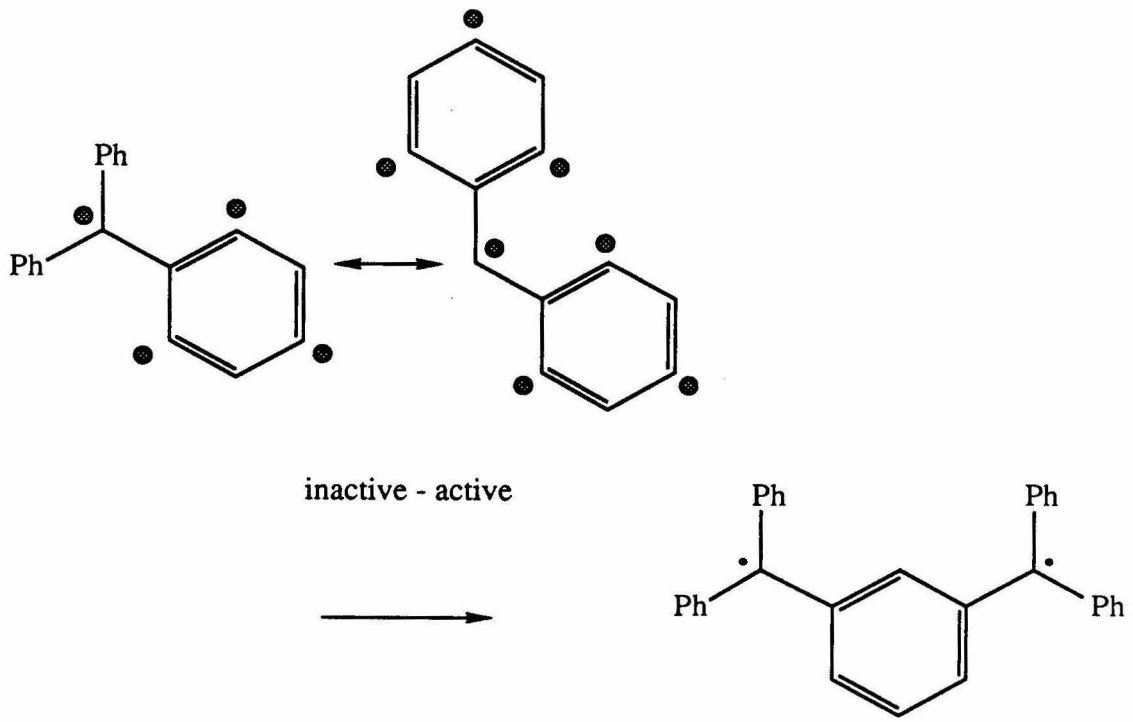
TMM



TME

A non-Kekulé molecule is anticipated when simple theoretical treatment (the Hückel level) of the π-electron system gives two (or a natural number multiple of two) incompletely occupied non-bonding molecular orbitals (NBMOs).[14] For two electrons in two NBMOs, three different orbital occupancies are possible: both electrons in one orbital (spins antiparallel, a singlet), an electron in each orbital with spins antiparallel (a singlet), an electron in each orbital with spins parallel (a triplet).[15] Invocation of Hund's rule predicts the high-spin species will be lowest in energy.[16] This arises because the spin portion of the wavefunction which describes the triplet is symmetric, so the spatial portion will be antisymmetric (the Pauli principle). The two electrons in the triplet will consequently not be found in the same region of space simultaneously (the probability of this vanishes),[17] and the exchange energy (an electrostatic term)[15] is lowered relative to the singlet state. The singlet has no such intrinsic prevention of electrons being in the same region of space and suffers greater electrostatic repulsions between the electrons, which makes it energetically less favorable *vis-à-vis* the triplet.

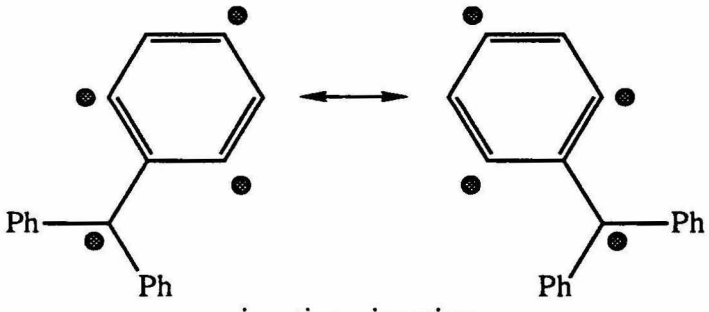
By the reasoning of Hund's rule, all π-conjugated non-Kekulé biradicals would be expected to be triplets. However, it has been recognized that Hund's rule may not be applicable to these molecules, and this realization has produced several qualitative theories for the prediction of ground states. Hückel first perceived this problem and based his assessment of ground state on connectivity patterns.[18] If two fragments of a π-conjugated non-Kekulé molecule are joined at inactive sites, it is a singlet. If the fragments are joined at an active site and an inactive site, it is a triplet. The classification of a site as active or inactive is based on the Hückel molecular orbital (HMO) coefficients of the NBMOs. If the value of the HMO coefficient is zero at a carbon, the carbon is an inactive site; if non-zero, the carbon is an active site.



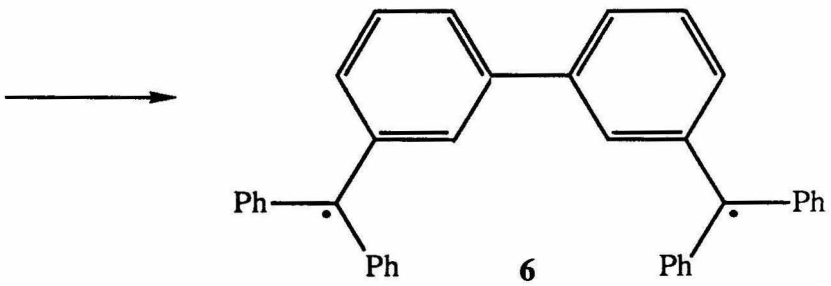
5

The rationale behind these predictions derives from the elimination of exchange at this level of approximation (Hückel theory), the two π-electron systems are

isolated from each other when the fragments are joined at inactive sites. Consequently, the exchange energy vanishes, and Hund's rule is no longer relevant.[15] This reasoning was first applied to the non-Kekulé hydrocarbons of Schlenk and Brauns[19] to explain why **5** is a triplet and **6** is a singlet.

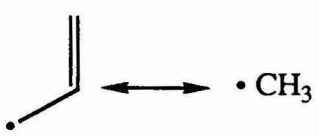


inactive - inactive



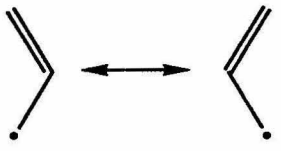
6

It can also be applied to TMM and TME. TMM is formed by the union of the active carbon of methyl radical with the inactive central carbon of an allyl radical. This correctly predicts a triplet ground state for TMM. TME is formed by the union of two allyl radicals at their inactive central carbons. Thus a singlet ground state is indicated, in contradiction of experimental findings.



TMM

inactive - active



TME

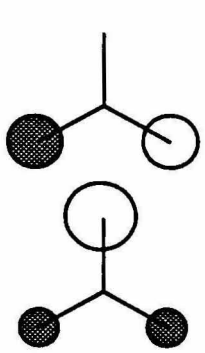
inactive - inactive

A different approach was taken by Longuet-Higgins,[20] who developed a model which, when combined with Hund's rule, predicts the spin multiplicity of the ground state. For a planar, alternant hydrocarbon with N π centers and T double bonds in the resonance structure with the most double bonds, the spin multiplicity, M, is given by eq. 2-1.

$$M = N - 2T + 1 \qquad (2\text{-}1)$$

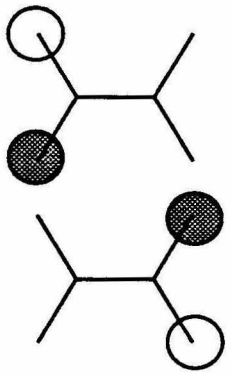
For TMM, with four π centers and one double bond, the spin multiplicity is predicted to be three, that is, a triplet ground state. For TME, with six π centers and two double bonds, a triplet is again predicted.

In a return to the evaluation of the problem by consideration of the nature of the NBMOs of a non-Kekulé molecule, Borden and Davidson[11a] developed the concept of disjoint and non-disjoint NBMOs to predict ground state preference. If the NBMOs or their linear combinations can be restricted to separate, non-overlapping regions of space, they are considered to be disjoint. If the NBMOs span common atoms in the molecule, they are non-disjoint. TMM can be seen to have non-disjoint NBMOs; TME has disjoint NBMOs.



TMM

non-disjoint



TME

disjoint

In a biradical with non-disjoint NBMOs, the electrons in those orbitals are free to occupy the same regions of space in the absence of other effects. However, in order to minimize the Coulombic repulsions such potential juxtaposition causes, the triplet state is

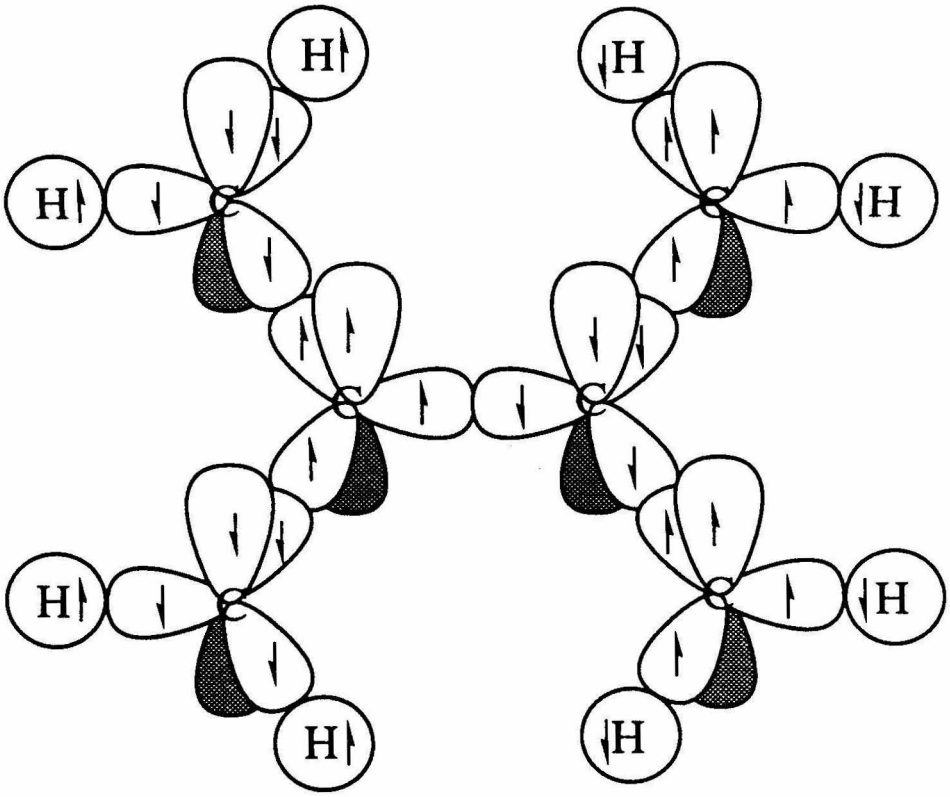
preferred relative to the singlet (the Pauli principle correlates the electrons of like spin and keeps them apart, *vide supra*). This is the case for TMM, which has a triplet ground state.

Disjoint NBMOs effectively keep the electrons confined to different regions of space and this negates the Coulombic repulsions of the singlet state. Thus the singlet state is no longer destabilized relative to the triplet state. In fact, at the self-consistent field (SCF) level of theory, the singlet and triplet states are degenerate in a molecule with disjoint NBMOs (in neither state are the electrons of the NBMOs found in the same region of space).[15] When higher order effects are considered (configuration interaction, CI), the singlet state can be stabilized by dynamic spin polarization.[21] This leads to the prediction of a singlet ground state for TME.

Dynamic spin polarization is a phenomenon whereby electrons of opposite spin can correlate to reduce electrostatic repulsions.[22] If, on any given atom, the electrons involved in bonding to other atoms are all of like spin, they are kept from simultaneously occupying the same region of the space around that atom by the Pauli principle. This reduces the unfavorable Coulombic interactions between the electrons and forms the basis for the original, atomic, version of Hund's rule (and helps explain the triplet ground state[23] of methylene carbene, H_2C:). If two atoms are connected by a bond, the electrons in the bond are necessarily of opposite spin. A prescription for an energetically favorable alternation of electron spins (...α–β–α–β...) on nearest-neighbor atoms in the molecular framework evolves. The alternation gives rises to the term "spin polarization." Because the scheme ...α–β–α... is not static and can just as readily be ...β–α–β..., the term "dynamic" is included.[22]

This is illustrated for singlet TME. The triplet state interrupts the pattern and therefore does not benefit to the degree the singlet does. The electrons in bonds are still of opposite spin, but all the bonding electrons on the same atom are no longer of like spin. A π electron on one carbon must have spin opposite that of the other bonding electrons on that

carbon to form the triplet. Nevertheless, the experimentally observed ground state for TME is the triplet.



Ovchinnikov[24] has used a semi-empirical valence bond approach to derive a simple relationship between the total spin, S, of an alternant hydrocarbon and the number of "starred" and "non-starred" atoms, eq. 2-2.

$$S = (n^* - n^\circ) \div 2 \qquad (2\text{-}2)$$

This allows a direct calculation of the spin multiplicity, M (= $2S$ + 1), according to eq. 2-3.

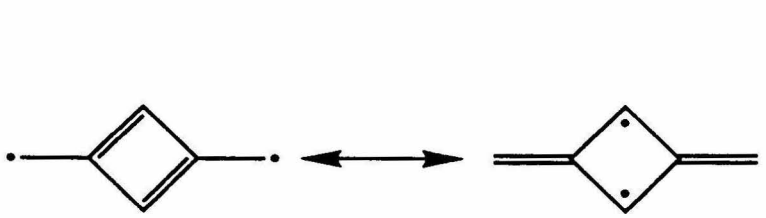
$$M = (n^* - n^\circ) + 1 \qquad (2\text{-}3)$$

Again, TMM is correctly predicted to be a triplet (M = (3 - 1) + 1 = 3), but TME is incorrectly predicted to be a singlet (M = (3 - 3) + 1 = 1).

It has been shown that when $n^* = n^\circ$, a biradical system is disjoint.[11a] The converse is not necessarily true; disjoint alternant systems with $n^* \neq n^\circ$ exist (*e.g.*, pentamethylene-

propane, PMP).[14] Such systems are not predicted to have singlet ground states by the Ovchinnikov formalism, which contradicts the predictions of the Borden and Davidson approach.

The foregoing chronicles a significant amount of agreement in the case of TMM amongst the qualitative predictive theories discussed. Hund's rule, Hückel's approach (active/inactive sites), Longuet-Higgins' formula (eq. 2-1), the work of Borden and Davidson (disjoint/non-disjoint NBMOs), and Ovchinnikov's formalism (eq. 2-2 and 2-3) all agree on the triplet ground state. This is in accord with experiment and high-level *ab initio* calculations.[9,10] All these methods are also in agreement for a variety of other non-Kekulé hydrocarbons, such as 2,4-dimethylene-1,3-cyclobutadiyl (non-Kekulé benzene) **7**,[8] 1,3-benzoquinodimethane **8**,[6] and 1,8-naphthoquinodimethane **1**,[6] each of which possesses non-disjoint NBMOs.



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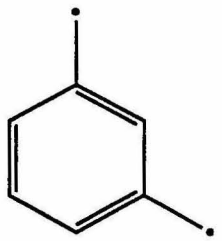
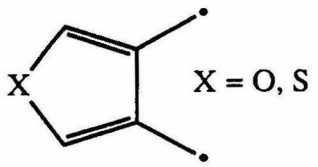


8

For TME and derivatives, there is no such harmony. Hund's rule, Longuet-Higgins' formula, and experiment[12] suggest a triplet ground state for TME itself. Hückel's approach, the work of Borden and Davidson, Ovchinnikov's formalism, and high-level *ab initio* calculations[11] predict a singlet ground state. *Ab initio*,[25] semi-empirical,[26] and qualitative[27] levels of theory are in agreement concerning the singlet ground states of a series of heteroatom-bridged TME derivatives **9**. These results have been confirmed by the experimental work of Berson, *et al.*[28] For these compounds, however, Hund's rule and Longuet-Higgins' formula are contradicted.



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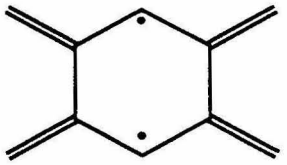

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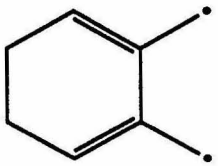

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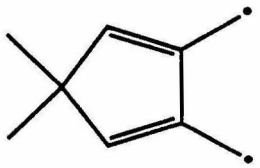
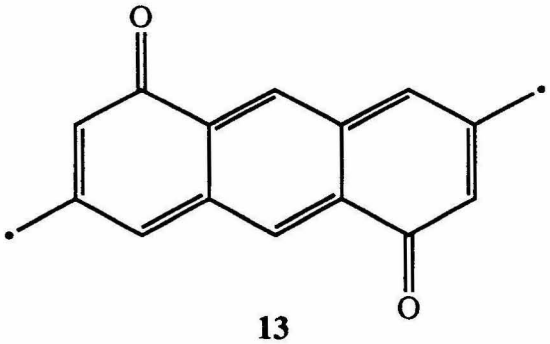


12

TME derivatives 2,3,5,6-tetramethylene-1,4-cyclohexanediyl **10**,[28] 2,3-dimethylene-cyclohexa-1,3-diene **11**,[29] and 5,5-dimethyl-2,3-dimethylenecyclopentadiene **12**[30] have been found by experiment to have triplet ground states. These findings contradict *ab initio* calculations,[11b,31] though semi-empirical methods agree with some experiments.[26] In these instances, the predictions of the above-described qualitative theories break down along the same lines as for TME itself. For **10**, the ultraviolet-visible (UV-vis) spectrum of the triplet predicted by the *ab initio* calculations of Borden, *et al.*,[32] is in good agreement with that observed experimentally by Roth, *et al.*,[29] who used the calculated spectrum to help identify the triplet ground state. The irony is that the very same *ab initio* work predicts a singlet ground state.

The common feature in TME and its derivatives, aside from the lack of consistency between theories and between theories and experiments, is that they have disjoint NBMOs. Clearly, at this time, no reliable method for the prediction of ground states for disjoint non-Kekulé biradicals exists. At best, if the molecule in question has disjoint NBMOs, it can be said that the singlet and triplet states will be close in energy.[27] A final example of the

quandary presented by molecules with disjoint NBMOs is 2,6-dimethyleneanthracenediyl-4,8-dioxy **13**, which has been found by the Berson group to have a triplet ground state.[32] This alternant non-Kekulé hydrocarbon biradical is disjoint, has n* = n°, and has no NBMO degeneracy at the Hückel level.



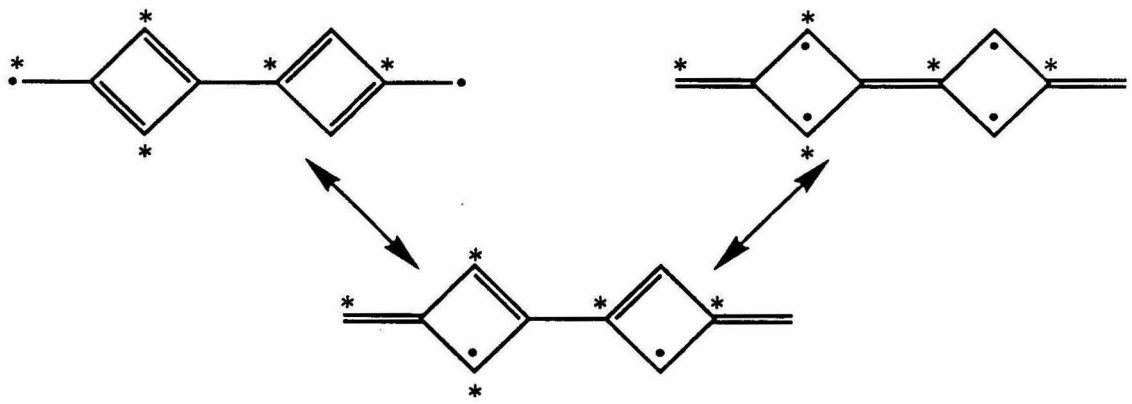
13

One approach to sorting out the conflicting predictions for the TME family would be to synthesize a variety of compounds with rationally varying structural features and to attempt to correlate these aspects with the experimentally observed physical properties. With enough information, it may eventually be possible to modify the theoretical treatments of these compounds so as to enable the accurate prediction of the spin state preference and the magnitude of that preference.

Our target series of TME derivatives (the TMEs **4**) would explore the effects of changing the sizes of the rings in which are imbedded the two allyl fragments which constitute a TME without restricting the species to planar geometries. As the ring size shrinks from six to five to four, the active sites of each separate allyl fragment are pulled farther away from those of the other fragment and are, within each fragment, pushed closer together. Nominally, the angle formed by the three π centers of each fragment is compressed from 120° to 108° to 90° as the ring size lessens. The through-space interactions of the electrons between the two allyl fragments would be expected to decrease, while those within each fragment should increase. Through-bond interactions would be expected to

remain constant; the connectivity and bonding patterns are not changed. In this manner, the effects of through-space coupling in TMEs could be selectively probed.

Another benefit from the syntheses of **4** is the understanding and development of the synthetic methodology needed to synthesize small-ring polyenes. Of immediate concern to us, and of similar structure to **4**, are compounds **2** and **3**. One of the resonance structures for **2** is clearly a TME derivative and differs from the four-membered ring version of **4** by only the presence of two exocyclic methylene groups. Another resonance structure of **2** is similar to a resonance structure of **3**.



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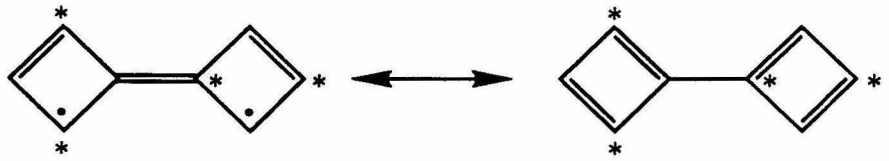


3

For **2**, both Hund's rule and Longuet-Higgins' formula predict a triplet ground state (eq. 2-1, ten π centers, four double bonds, $M = 10 - 2(4) + 1 = 3$). Pranata and Dougherty performed analyses of **2** at various levels of theory.[33] Examination at the Hückel level shows it to be disjoint, and it is a π-conjugated alternant non-Kekulé hydrocarbon with n* = n°. These facts suggest it will be a singlet (Borden and Davidson, Ovchinnikov). Pople-

Parr-Pariser theory applied to **2** confirms the disjointedness of the NBMOs and predicts a singlet ground state. The adequacy of this method was verified by comparison with experimentally determined properties of non-Kekulé benzene **7**;[8] it performed well.

Our interest in **2** originally stemmed from the synthesis and study of **7** (non-disjoint, $n^* = 4$, $n^\circ = 2$, triplet ground state) by Dougherty and Snyder.[8,34] **2** is the second in the series of the so-called "non-Kekulé acenes."[34] The next higher member of the series would have three four-membered rings (non-Kekulé anthracene), the next four, and so on. The theoretical work of Dougherty and Pranata forecast several interesting properties for the non-Kekulé acenes, including the existence of a parity rule for the prediction of the ground state multiplicities of the members of this class of compounds. For those non-Kekulé acenes with an odd number of four-membered rings, a triplet ground state is expected; those with an even number should possess a singlet ground state. If these predictions were substantiated experimentally, it would signify tremendous progress in our understanding of non-Kekulé molecules.

Cyclobutadiene is an anti-aromatic annulene and a biradical (it has two NBMOs occupied by two electrons).[5] **3** is to cyclobutadiene as biphenyl is to benzene, is an alternant hydrocarbon with $n^* = n^\circ$, and is not a non-Kekulé molecule. Extension of the motif which leads to **3** gives polycyclobutadiene, which is forecast to be an organic polymer with a very small (perhaps zero) band gap.[35]

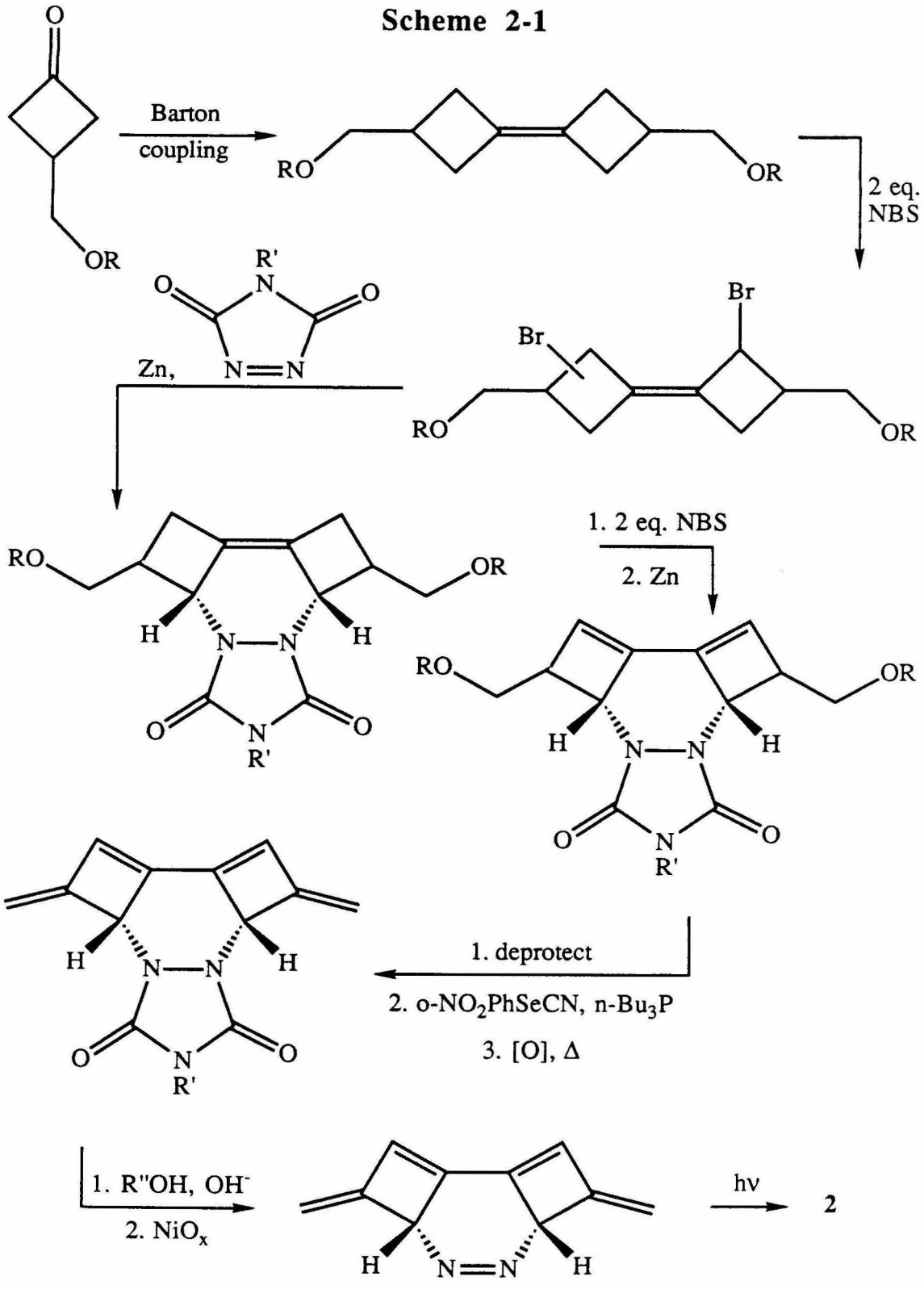
3 has two disjoint NMBOs;[36] the approaches of Ovchinnikov, Borden and Davidson, and Longuet-Higgins ($M = 8 - 2(4) + 1 = 1$) predict a singlet ground state. It also has been predicted by *ab initio* molecular orbital theory to be a singlet ground state biradical with substantial double-bond character in the bond joining the two four-membered rings.[36] This can be rationalized as two anti-aromatic π-electron systems being less energetically favorable than two unpaired electrons. Again, experimental evaluation of these predictions should allow improvement of our understanding of biradicals with disjoint NMBOs.

Synthesis and Discussion

Our efforts toward the syntheses of **2**, **3**, and **4** began with the attempt to prepare **2**. Our group had recently synthesized[36] and studied[37] non-Kekulé benzene **7**; **2** was the next in the series of non-Kekulé acenes.[34] The syntheses proposed for our target compounds aim to prepare diazenes, thermal or photochemical treatment of which causes nitrogen to be extruded and leaves the desired biradical. The use of such "azo precursors" to biradicals is an established method in the field and receives widespread use.[38]

The general outline proposed for the synthesis of diazene **14**, the azo precursor to **2**, is shown in Scheme 2-1; a summary follows. The starting material, a protected 3-(hydroxymethyl)cyclobutanone, is itself a synthesized intermediate. This ketone is converted to the symmetrical olefin *via* the Barton coupling[39] reaction. This is accomplished in a manner analogous to the known coupling of cyclobutanone.[40] Allylic bromination with two equivalents of N-bromosuccinimide (NBS) is followed by 1,4-elimination to form the conjugated diene which reacts *in situ* with an N-substituted 1,2,4-triazoline-3,5-dione (or other dienophile). A second allylic bromination-1,4-elimination sequence would follow to give diene. Deprotection to give the alcohols and subsequent diselenide formation is to be followed by oxidation and elimination to form the exocyclic double bonds.[41] This would yield the conjugated tetraene. Decomposition of the urazole moiety with alcoholic hydroxide would provide the semicarbazide,[8,37,42] nickel peroxide oxidation of which[8,37,43] culminates the synthesis of **14**.

Scheme 2-1

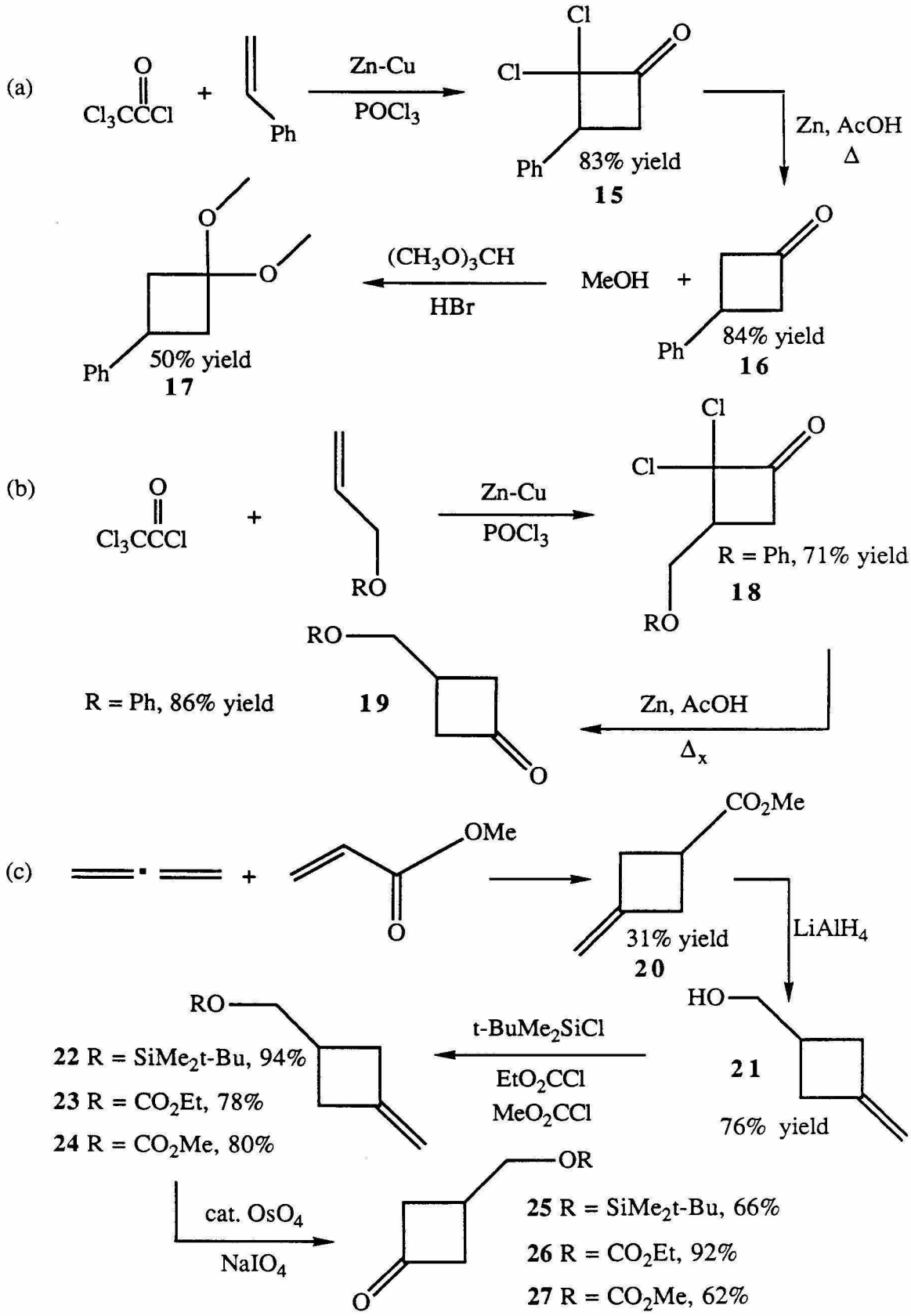

Barton coupling
2 eq. NBS
Zn,
1. 2 eq. NBS
2. Zn
1. deprotect
2. o-NO2PhSeCN, n-Bu3P
3. [O], Δ
1. R"OH, OH-
2. NiOx
hν
2

14

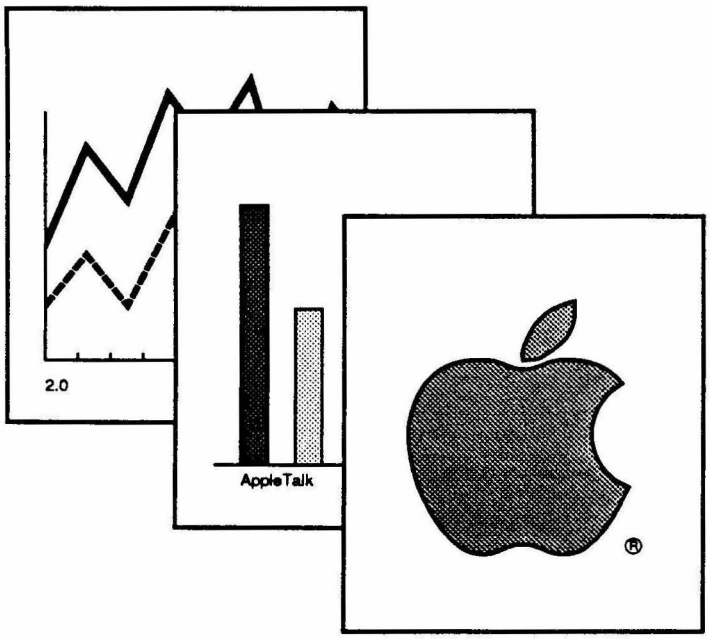
Versatile methods for the syntheses of protected 3-(hydroxymethyl)cyclobutanones have been devised. These allow the introduction of a variety of protecting groups for the alcohol, which provides flexibility in the synthesis. Scheme 2-2 summarizes the paths taken to form the protected 3-(hydroxymethyl)cyclobutanones. The sequence shown in part (a) was followed to the point of the dimethyl ketal **17** with the yields shown. It was based upon the facility of substituted cyclobutanone formation provided by the reaction of a ketene with an olefin.[43] Dichloroketene, generated *in situ* from trichloroacetyl chloride and zinc-copper couple in the presence of phosphorus oxychloride, is known to be a reactive and readily available ketene.[44] It reacted with styrene to give 2,2-dichloro-3-phenylcyclobutanone **15**. Dehalogenation of α,α-dihalogenated ketones, in particular 2,2-dichlorocyclobutanones, with zinc and refluxing acetic acid is well precedented[45b,45] and proved to conveniently give 3-phenylcyclobutanone **16**. After formation of **17** by acid-catatlyzed ketalization of **16** with methanol (and trimethylorthoformate as a dehydrating agent), ruthenium tetroxide oxidation of the phenyl ring to the acid[46] and subsequent borane reduction to the alcohol were planned. This path was abandoned after routes (b) and (c) were explored.

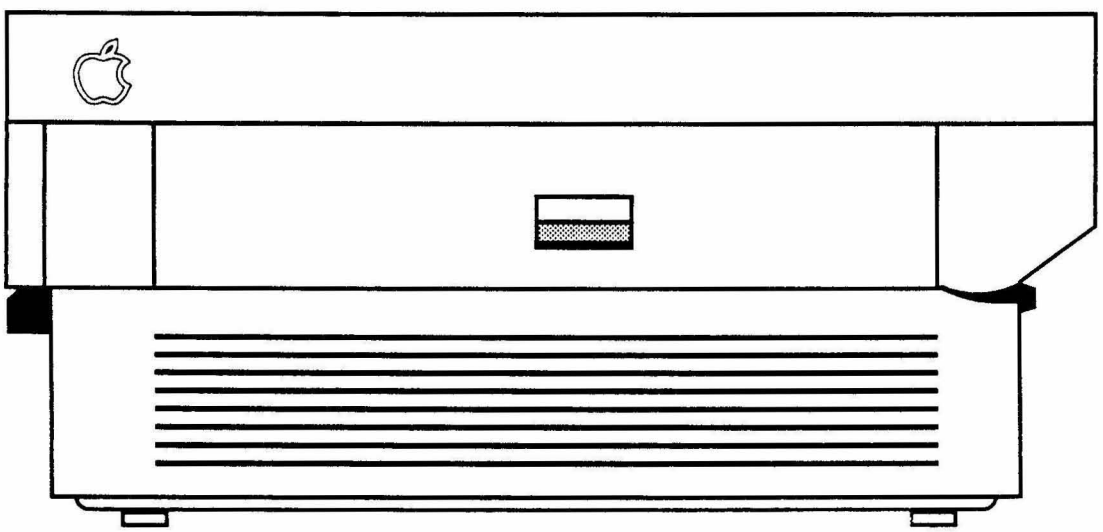
The sequence in path (b) includes the initial efforts made to synthesize the desired cyclobutanones. Those efforts involved the attempted cycloaddition of allyl acetate and allyl *t*-butyl ether with dichloroketene (R = Ac and R = *t*-Bu in Scheme 2-2(b)). These attempts tended to end with the production of an intractable brown-black sludgy oil. The work of Malherbe, Rist, and Bellus clarified the situation.[47] They found that, with but few exceptions, the allylic ethers, sulfides, and selenides they attempted to cycloadd with ketenes gave instead products from the nucleophilic attack of the heteroatom of the allylic portion on the carbonyl carbon of the ketene, which was followed by a Claisen rearrangement. A mixture of products was almost always obtained. One of the exceptions they found was allyl phenyl ether, which gave the expected cycloaddition product, **18**, presumably because of the reduced nucleophilicity of the oxygen atom. This ether is

Scheme 2-2


(a)
Cl3CCCl
Ph
Zn-Cu
POCl3
Cl
Ph
83% yield
15
Zn, AcOH
Δ
(CH3O)3CH
HBr
MeOH +
84% yield
16
50% yield
17
(b)
Cl3CCCl
RO
Zn-Cu
POCl3
R = Ph, 71% yield
18
R = Ph, 86% yield
19
Zn, AcOH
Δx
(c)
OMe
CO2Me
31% yield
20
LiAlH4
HO
21
76% yield
t-BuMe2SiCl
EtO2CCl
MeO2CCl
22 R = SiMe2t-Bu, 94%
23 R = CO2Et, 78%
24 R = CO2Me, 80%
cat. OsO4
NaIO4
OR
25 R = SiMe2t-Bu, 66%
26 R = CO2Et, 92%
27 R = CO2Me, 62%

LaserWriter Plus





65132

commercially available[48] and thus provides a two-step sequence for the preparation of 3-(phenoxymethyl)cyclobutanone **19**. However, phenyl ethers are not versatile protecting groups for alcohols; their removal often necessitates the use of a reagent such as boron tribromide (which in this case would return the alkyl bromide rather than the alcohol).[49]

The method in part (c) is the method of choice. The cycloaddition of allene and methyl acrylate to give methyl 3-methylenecyclobutanecarboxylate **20** is carried out in a bomb and routinely gives thirty grams of product per reaction.[50] The lithium aluminum hydride (LAH) reduction of the ester to the alcohol **21** is known,[51] but a modification of the work-up procedure increased the yield to 93% from the reported 58%. This change involved quenching the reaction mixture by sequential addition of x ml water, x ml 15% aqueous sodium hydroxide, and $3x$ ml water (x = grams of LAH used),[52] instead of quenching by pouring into aqueous acid, as reported. **21** is a C6 alcohol and is quite hygroscopic. The modified method produces a granular precipitate which is easily removed by filtration and minimizes exposure to excess water. Protection of the hydroxyl group is easily accomplished and almost any protecting group desired can be introduced. Those we found useful include the *t*-butyldimethylsilyl **22**, ethoxycarbonyl **23**, and methoxycarbonyl **24** derivatives.

The oxidation of the exocyclic double bond to the ketone was originally attempted with ozone. This gave a complex mixture of products which apparently included some desired product. A far more satisfactory procedure was the osmium tetroxide-catalyzed sodium periodate oxidation conducted in a solution of dioxane and water.[53] The yield of the *t*-butyldimethylsilyl-protected ketone **25** obtained in this manner was 66%, the yield of ethoxycarbonyl-protected ketone **27** was 92%. This difference can be rationalized on the basis of the difference in solubilities of the two olefins in the dioxane-water solution. The carbonate functionality imparts a greater solubility than the greasy silyl ether. This allows for quicker reaction, which reduces the possibility of decomposition of the starting material (the carbonate is a sturdier protecting group than the silyl ether). The yield of methoxycar-

bonyl derivative **27** suffered from the problems often encountered in attempts at a massive increase in the scale of a reaction.

Scheme 2-3

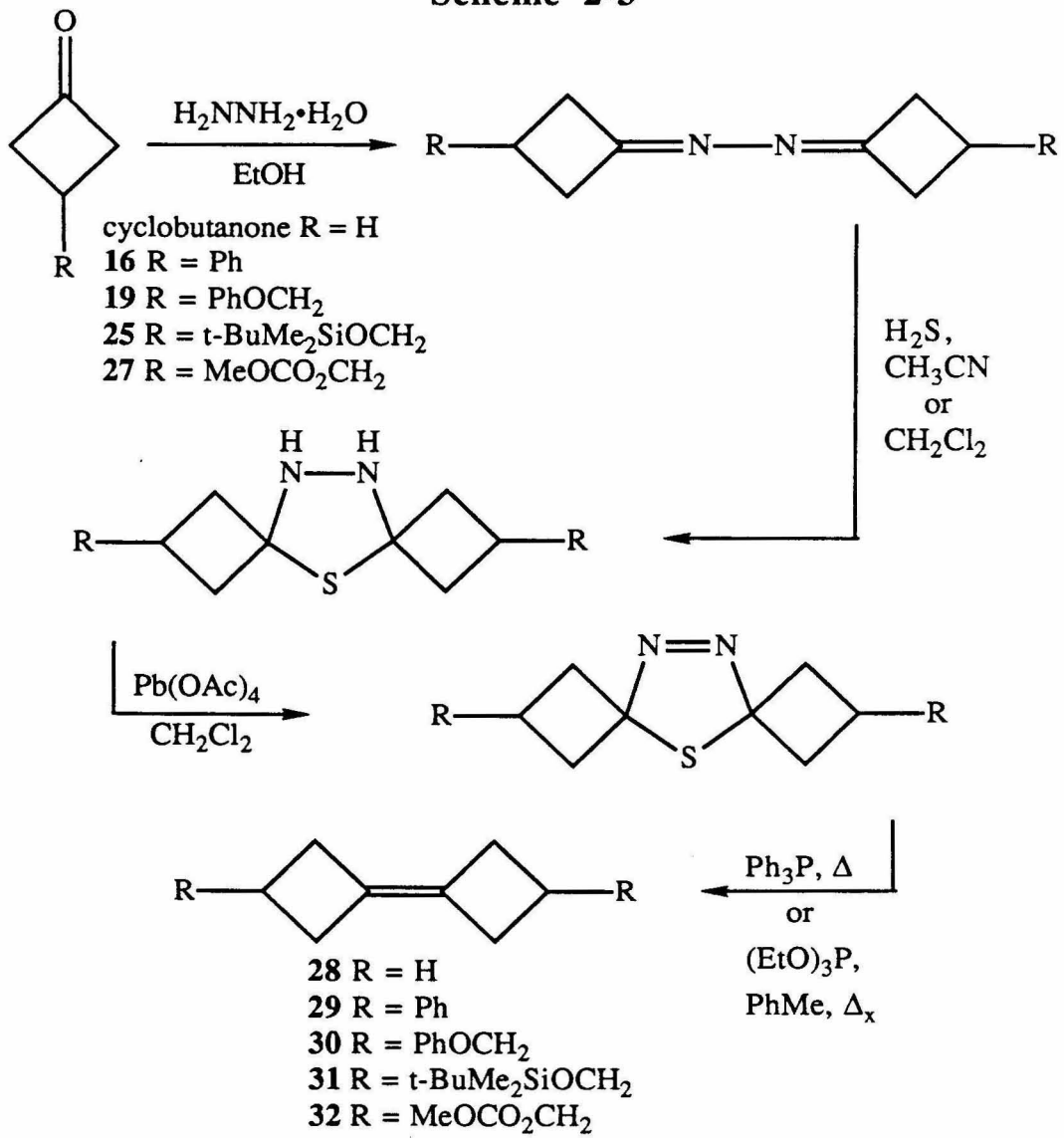


Table 2-1: Yields of symmetrical olefins and intermediates in Barton coupling reaction.

cyclobutanone, R =	azine[a]	hydrazine[a]	azo[a]	olefin[b]	overall[c]
cyclobutanone, H	95%	95%	94%	56%, **28**	48%
16, Ph	-	91%	100%	62%, **29**	56%
19, $PhOCH_2$	80%	100%	100%	100%, **30**	80%
25, t-$BuMe_2SiOCH_2$	100%	100%	100%	79%, **31**	79%
27, $MeOCO_2CH_2$	90%	100%	90%	47%, **32**	39%

a -- yield of crude, isolated material based on previous step
b -- yield of purified olefin based on previous step
c -- overall yield of purified olefin from starting cyclobutanone

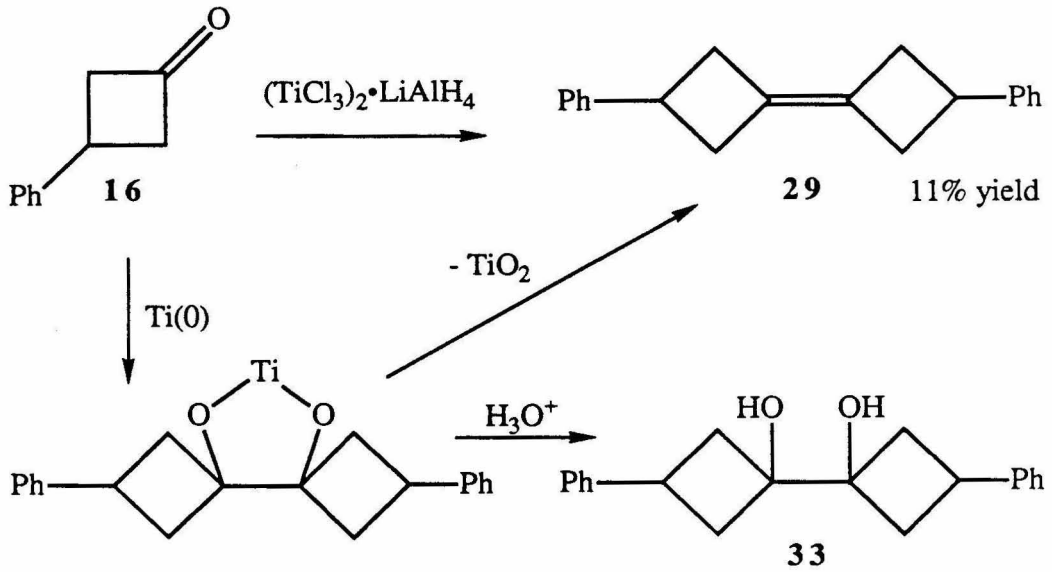
The Barton coupling sequence is outlined in Scheme 2-3. Representative results are given in Table 2-1. This is the first time the coupling of 3-substituted cyclobutanones has been reported. It is actually a four-step sequence which requires isolation, though not purification, of the intermediates. The first step is formation of the symmetrical azine by condensation with hydrazine. Hydrogen sulfide addition gives the dispiro hydrazine derivative. Due to the fact that amounts much smaller than those used in Garratt's synthesis of bi(cyclobutylidene) **28** (coupling of cyclobutanone)[41] were employed (tenths of grams rather than twenty grams), his procedure was modified. Azine formation and hydrogen sulfide addition are done in two steps and in solution, rather than simultaneously in neat cyclobutanone.

Lead tetraacetate oxidation of the hydrazine moiety to the azo compound is followed by thermolysis and sulfur extrusion with a phosphorus compound as shown. A further modification of Garratt's original procedure involved the use of triethylphosphite instead of triphenylphosphine for the sulfur extrusion step for the higher molecular weight olefins. Garratt's procedure calls for distillation of the volatile bi(cyclobutylidene) from the triphenylphosphine and triphenylphosphine sulfide as it is formed. The involatility of the higher weight olefins precluded this treatment. Triethylphosphite was used so it and its sulfide could be evaporated from the product olefins. This variation was based upon a similar one made by McMurry.[54]

The obvious alternative to the Barton coupling procedure is the well known McMurry coupling accomplished with a titanium(0) species.[55] This reaction was attempted on **16** (Scheme 2-4). The reaction resulted in a complex mixture of products separable by flash chromatography. One isolated product was the desired 3,3'-diphenylbi(cyclobutylidene) **29** in 11% yield. This assignment is based on a comparison of NMR spectra with those of an authentic sample made *via* the Barton coupling route. The product isolated in the largest amount had an NMR spectrum suggestive of the corresponding pinacol **33**, formed in approximately 50% yield. Pinacols are known intermediates in the McMurry coupling and

result from incomplete deoxygenation.[56] This would not be a surprising observation: reation to change an sp^2 center into an sp^3 center will generally release strain in a cyclobutane ring system; transformation back into an sp^2 center would be less energetically favorable.

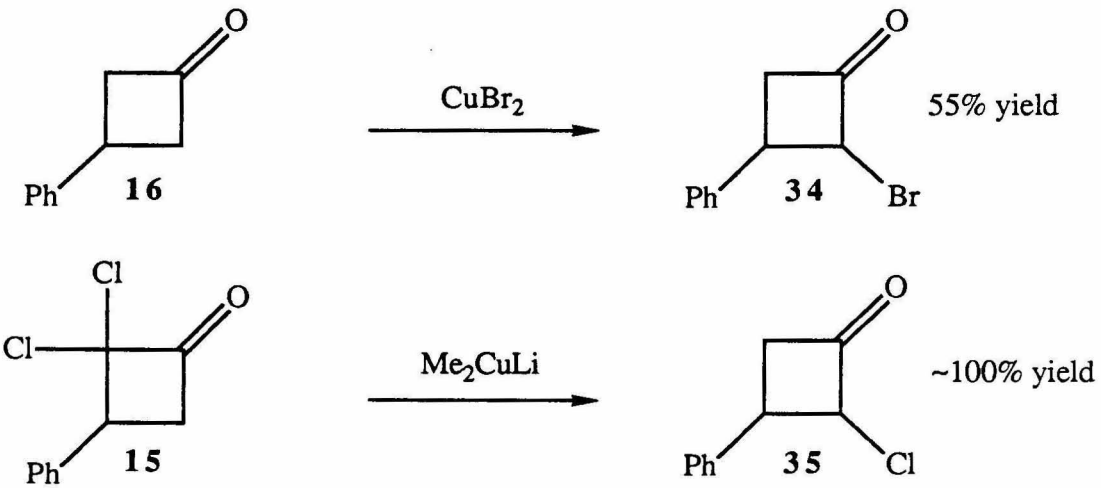
Scheme 2-4



Though no literature precedents exist for the McMurry coupling of cyclobutanones, McMurry feels there is no fundamental reason they should not react successfully.[57] The reason for the absence of attempts on such substrates in initial experiments to determine the scope of the McMurry reaction was their lack of commercial availability.[58] The extreme oxygen sensitivity of the coupling reagent and the need for many attempts and practice runs in order to obtain satisfactory reaction has been indicated.[58] Additionally, the McMurry reaction will not tolerate the presence of other easily reducible groups, such as halogens α to the carbonyl to be coupled.[57] Efforts to couple chloroacetone which resulted in decomposition of the starting material confirmed this.

With the goal of introducing the bromines prior to the olefin stage so as to offer an alternative to the allylic bromination step, Barton coupling of the α-halo cyclobutanones shown in Scheme 2-5 was attempted. **16** was brominated with cupric bromide[59] to give 2-bromo-3-phenylcyclobutanone **34** in moderate yield. **15** was mono-dehalogenated with lithium dimethylcuprate[60] to give 2-chloro-3-phenylcyclobutanone **35** in essentially quantitative yield. The reaction of these haloketones with hydrazine and hydrogen sulfide gave unidentifiable products. Given Conia's work with α-halo cyclobutanones,[61] these results were not unexpected. Amines were found to react with α-halo cyclobutanones to give substitution, elimination, and Favorskii reaction products. α-Halo ketones are also known to be dehalogenated during Wolff-Kishner reduction.[62]

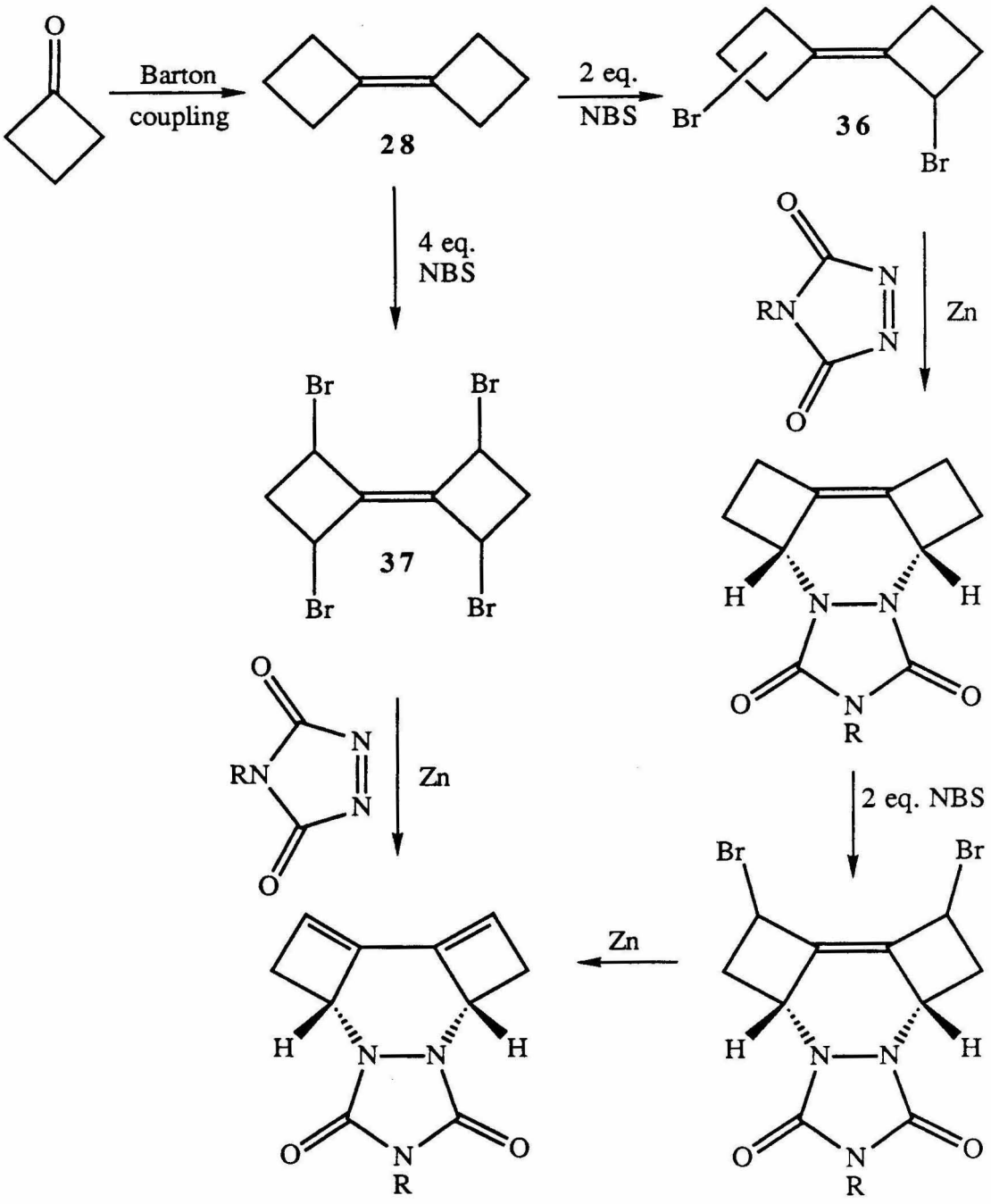
Scheme 2-5



In order to investigate the allylic bromination-1,4-elimination-Diels-Alder-allylic bromination-1,4-elimination sequence, unsubstituted bi(cyclobutylidene) **28** was chosen as a model (Scheme 2-6). This choice derived from the facts that the twofold allylic bromination of **28** has been performed,[63] and cyclobutanone is more readily available[49] than the protected 3-(hydroxymethyl)cyclobutanones. 1,4-Eliminations of dibromides with zinc are common,[64] as are the Diels-Alder reactions between dienes and N-substituted 1,2,4-triazoline-3,5-diones[65] (N-phenyl-1,2,4-triazoline-3,5-dione, PTAD, has been called

a "super-dienophile").[66] There is also some precedent for the one-pot elimination and cycloaddition procedure.[67]

Scheme 2-6



Dibromination of **28** with two equivalents of NBS in refluxing carbon tetrachloride with azoisobutyronitrile (AIBN) as radical initiator (the method of Garratt, *et al.*)[64] yields a mixture of the monobromide and several dibromides **36**. Slight variation of the number of

equivalents of NBS used did not substantially affect the distribution of products. When greater than four equivalents were used, a mixture of tetrabromides **37** was obtained. Though **36** was reasonably stable when stored in a freezer at -10 °C, **37** decomposed to a mixture of tribromides within a day (as revealed by gas chromatography-mass spectrometry, GCMS, analysis). Dibromides with both bromines on the same ring (or carbon) will not give 1,4-elimination.

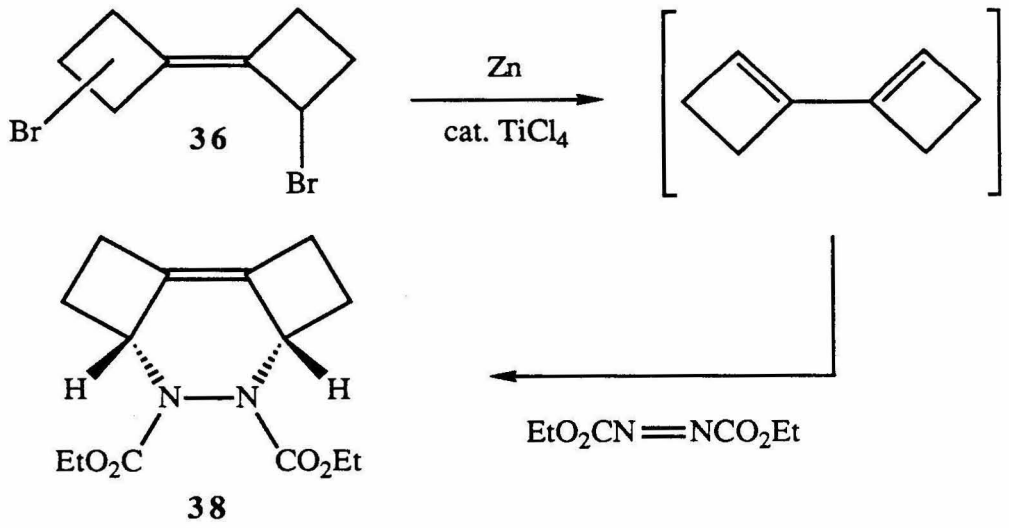
Results from initial attempts to effect 1,4-elimination and Diels-Alder reaction of the bromides were disappointing. 1,4-Elimination-Diels-Alder reactions with **37** yielded no products resembling any desired product. **36** was stirred in tetrahydrofuran with zinc-copper couple[45d] and one of three dienophiles: PTAD, N-methyl-1,2,4-triazoline-3,5-dione (MTAD), and diethyl azodicarboxylate (DEAD). DEAD, the weakest dienophile of the three, was the only one to give any reaction. A complex mixture of products was obtained from which a solid compound could be isolated. GCMS data of this material were not consistent with the desired adduct (a molecular weight high by two atomic mass units was indicated), nor did nuclear magnetic resonance (NMR) data indicate desired product.

GCMS and NMR did, however, suggest that features expected in the desired adduct, such as the carboethoxy groups, were present. A double bond was present in this compound -- osmium tetroxide reacted with a solution of the compound in dioxane-water to give a dark brown color that disappeared upon the addition of sodium periodate (the brown color corresponds to formation of an osmate ester, its disappearance implies cleavage to carbonyl fragments).[54] Various attempts to reduce this double bond (with diimide, borane, and catalytic hydrogenation) and to characterize the reduced products were unsuccessful.

It was found that dehalogenation of **36** at 0 °C with zinc powder and catalytic titanium tetrachloride produced the diene,[68] bi(cyclobutenyl), which reacted with DEAD (though not MTAD or PTAD) to form the desired Diels-Alder adduct **38** in 24% yield after purification by flash chromatography (Scheme 2-7). GCMS and NMR data were consistent with this product and different from the unidentifiable material discussed previously. GCMS and

NMR data of the reduced material obtained by diimide reduction of the double bond in **38** corresponded to that expected. This methodology applied to **37** yielded no identifiable products.

Scheme 2-7



The step in the preparation of **14** which proved to be the downfall of the proposed plan was the allylic bromination following the 1,4-elimination-Diels-Alder sequence. Attempts to perform twofold allylic bromination on **38** with NBS and AIBN in refluxing carbon tetrachloride failed. The results were either uncharacterizable materials or unreacted **38**. Molecular modelling calculations (MM2) on this ring system reveal a pronounced convexity; it is cup-shaped. Presumably, the convex shape of the adduct bends the rings sufficiently that allylic resonance (and therefore the reactivity of the allylic positions) is reduced; the allylic positions are bent out of the position necessary for the orbital overlap with the double bond which would provide the allylic reactivity.

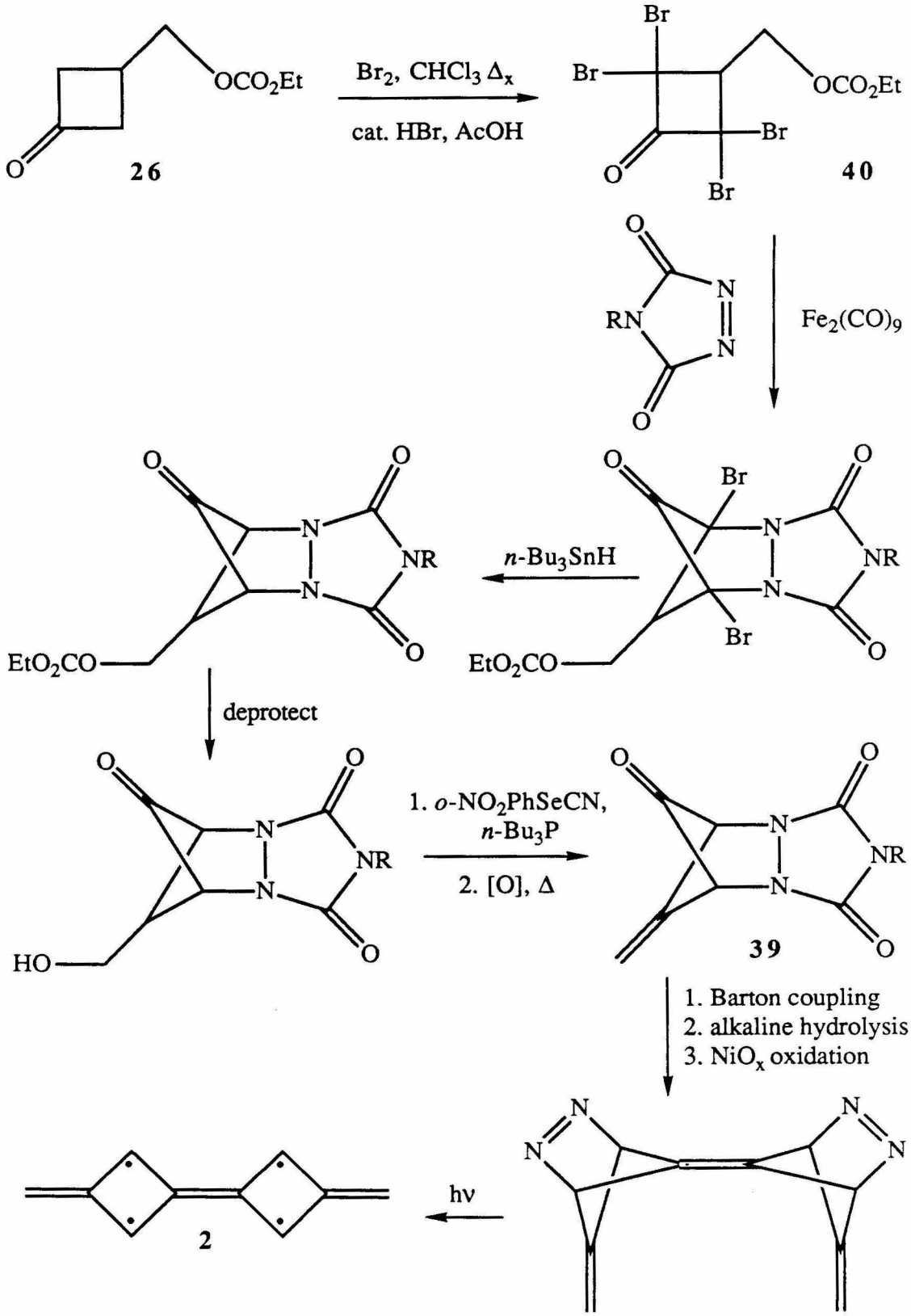
The first variation on our original plan for the synthesis of **2** maintained the idea of coupling ketones to form the carbon framework. The compound such a notion requires is **39**, the urazole precursor to the oxo-analog of **7**. The proposed synthesis of **39** is shown

in Scheme 2-8, along with the intended route for its transformation to the tetraradical resonance form of **2**. The majority of the sequence consists of previously described reactions. Two new steps involve the use of diiron nonacarbonyl to form the dibromo oxyallyl cation species which would react with an N-substituted 1,2,4-triazoline-3,5-dione and the use of tri-*n*-butyltin hydride to debrominate the adduct which is formed. The use of the iron reagent in such a manner is well precedented[69] and has been reviewed by Noyori,[46] one of the developers of this reaction. It has not, however, ever been used on cyclobutanone derivatives. The use of tin hydride should present no unforeseen problems; it is the application of a known procedure.[70] The conditions of azine formation in the Barton coupling were thought mild enough to avoid hydrazinolysis of the urazole.

The choice of preparing the tetrabromoketone was based on the observation by Noyori and others that the presence of radical- and cation-stabilizing groups at those sites was conducive to a successful reaction.[46,70] It is also synthetically easier to perbrominate the α–positions rather than attempt to mono-brominate them (particularly in the case of cyclobutanones).[62] Various attempts to brominate **25** failed. The variations included reaction with NBS and with pyrrolidine hydrotribromide,[71] acid-, base-, and auto-catalyzed bromination, and the use of excess and stoichiometric bromine. 2,2,4,4-tetrabromocyclobutanone has been prepared by Conia, *et al.*, by treating cyclobutanone with excess bromine in refluxing carbon tetrachloride for three days.[62] This method was tried but yielded no desired product.

It appears, however, that a 3-substituted 2,2,4,4-tetrabromocyclobutanone can be obtained. Because the silyl ether was not surviving bromination conditions particularly well and the phenyl ether was not even considered (facile bromination of the phenolic benzene ring would certainly occur), ethyl (3-oxocyclobutyl)methyl carbonate **26** was

Scheme 2-8


OCO2Et
O
26
Br2, CHCl3 Δx
cat. HBr, AcOH
Br
Br
Br
Br
OCO2Et
O
40
RN
N
N
O
Fe2(CO)9
Br
Br
NR
EtO2CO
n-Bu3SnH
deprotect
HO
1. o-NO2PhSeCN,
n-Bu3P
2. [O], Δ
39
1. Barton coupling
2. alkaline hydrolysis
3. NiOx oxidation
hν
2

made (*vide supra*). **26** was subjected to fifteen equivalents of bromine in refluxing chloroform with catalysis by hydrobromic acid in acetic acid under anhydrous conditions for six days.

Analysis of the 400-MHz NMR of the crude material indicates no protons α to the cyclobutanone carbonyl and shows the expected ethyl pattern and doublet and triplet peaks. Further evidence for the presence of the tetrabromoketone **40** comes from infrared (IR) spectral data. The ketone carbonyl absorption of the starting cyclobutanone is 1785 cm^{-1}, that of the isolated product is 1820 cm^{-1}. A similar shift is seen in the carbonyl absorptions of cyclobutanone (1775 cm^{-1}) and 2,2,4,4-tetrabromocyclobutanone (1815 cm^{-1}).[62] GCMS of the crude material provided information as to the mixture's thermal stability: it seems to decompose at temperatures near 150 °C to 175 °C The presence of **40** could neither be verified nor repudiated from GCMS data. Peaks in the neighborhood of the expected molecular ion peak for **40** were observed. A molecular ion peak which corresponds to the tribromoketone was also observed.

The crude product is unstable on silica gel at room temperature, but may survive at temperatures of -10 °C and lower. Mass recovery and integration of the 90-MHz NMR of the crude material imply a yield of roughly 55% of **40**. No satisfactory method for the purification of the crude material was determined. Unfortunately, reactions of unpurified **40** with diiron nonacarbonyl and MTAD, with zinc-copper couple[45d] and DEAD, or with sodium iodide and DEAD yielded no characterizable products.

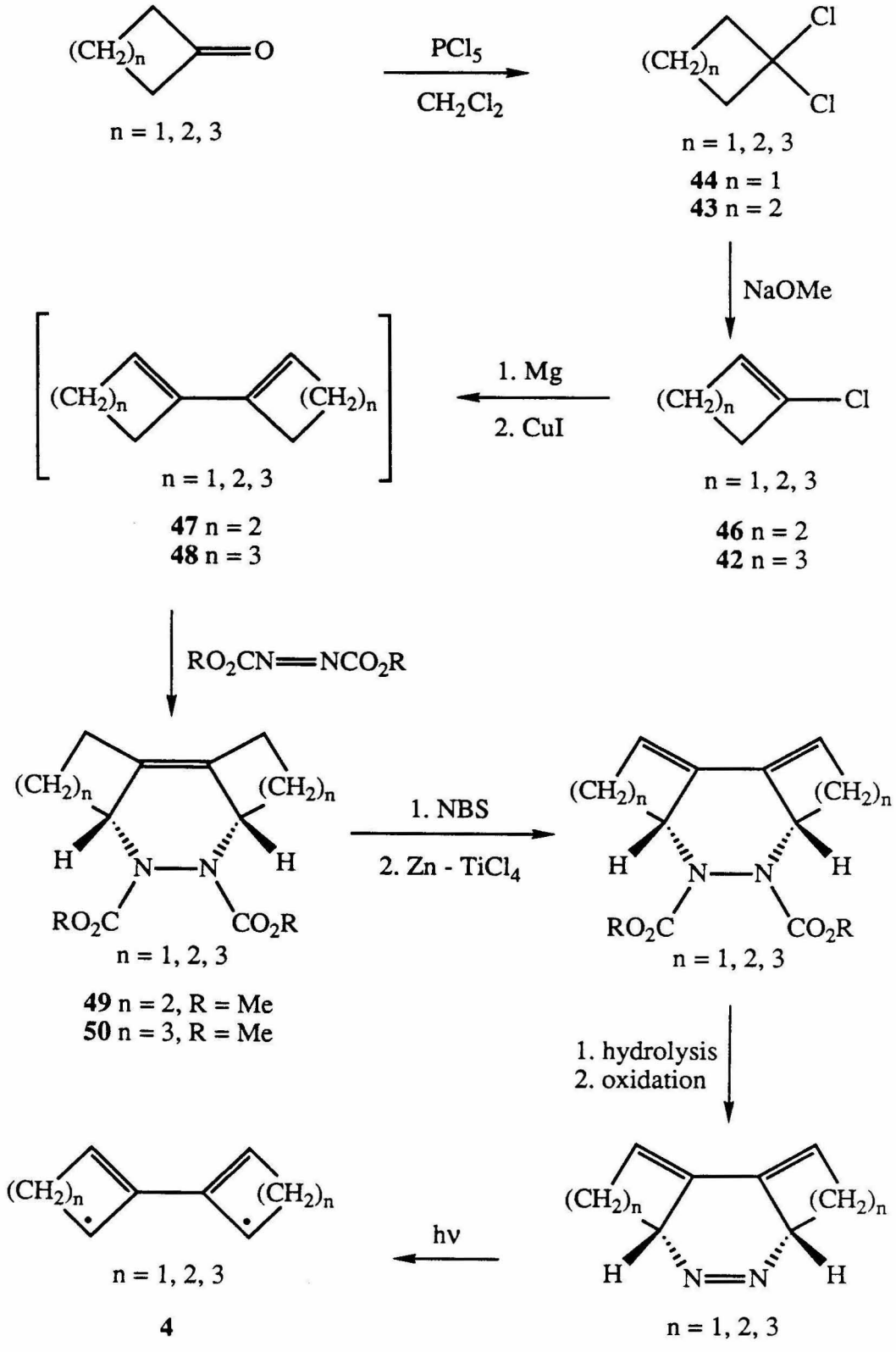
By this time, the debate over TME had taken on validity with the reliable determination of the ground states of several TME derivatives and TME itself (*vide supra*). We also determined that a new approach to the synthesis of the diene intermediate was needed; allylic bromination-1,4-elimination was not a clean or high-yield procedure. These factors, coupled with our recognition of the utility of higher ring homologues as model compounds for our efforts on four-membered rings, prompted us to embark on the syntheses of TME derivatives **4**.

Scheme 2-9 outlines our intended route. The syntheses are straightforward to the point of converting the Diels-Alder adduct to the diene. This was the major synthetic hurdle we needed to clear to prepare these compounds; we felt with a ready supply of precursor adduct, a useful method for the transformation to diene could be discovered. This has not proven to be the case.

Conversion of the cyclic ketones to the *gem*-dichlorides with phosphorus pentachloride in methylene chloride (noted as the best solvent for this reaction)[72] proceeded as expected for cyclohexanone, cyclopentanone, cyclobutanone, and 3-ethoxycyclobutanone **41**. 1,1-Dichlorocyclohexane was prepared in a manner which caused direct elimination of hydrogen chloride to give 1-chlorocyclohexene **42**; the other ketones reacted to give 1,1-dichlorocyclopentane **43**, 1,1-dichlorocyclobutane **44**, and 1,1-dichloro-3-ethoxycyclobutane **45**, respectively. Elimination of hydrogen chloride to form 1-chlorocyclopentene **46** was accomplished by treating **43** with sodium methoxide. Elimination in the four-membered ring systems required stronger bases such as potassium *t*-butoxide and lithium diisopropylamide. In the case of **41**, these also caused elimination of ethanol and created an intractable mixture of products.

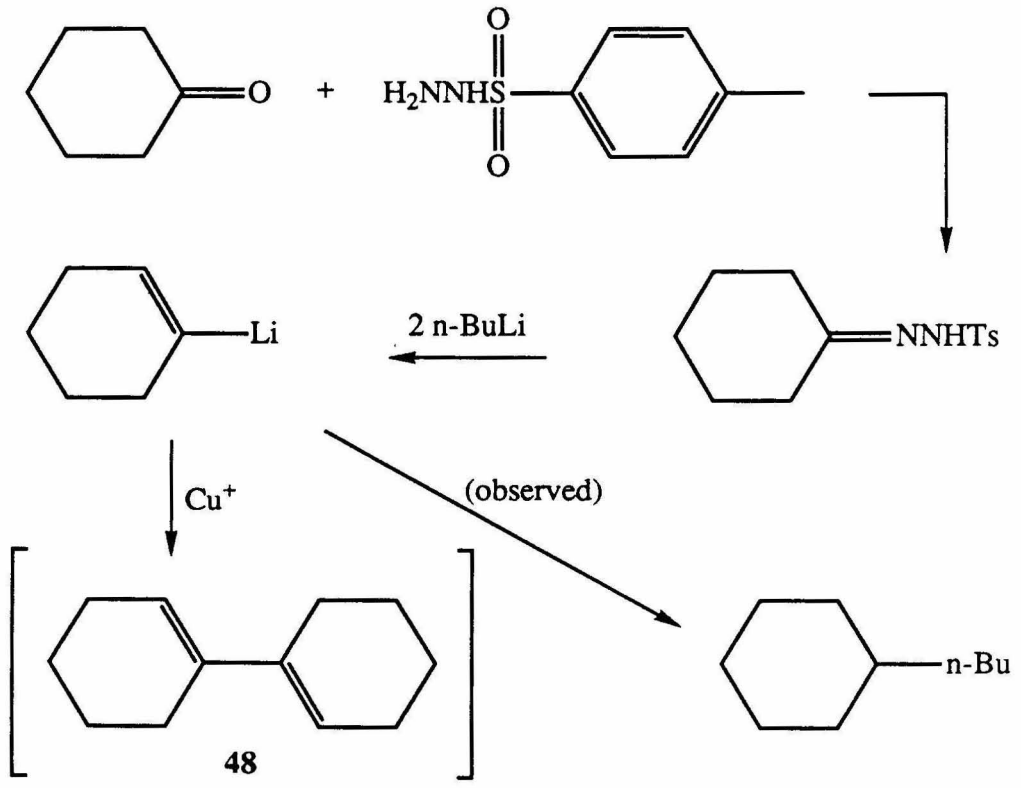
42 and **46** were both converted to the corresponding Grignard reagents and coupled to the conjugated dienes by the use of copper iodide. This reaction had been previously performed on 1-bromocyclobutene.[73] (Due to the inapplicability of current methods for the preparation of bromocyclobutenes to the substituted bromocyclobutene derivatives we required for the syntheses of our target compounds, and due to the general lack of alternative halocyclobutene syntheses, this potential synthetic route had not been our initial effort toward **2**.) Conversion of the vinyl chlorides to Grignards was not facile with magnesium in refluxing THF, though it sufficed to provide dienes in usable quantity after coupling. The use of activated (Rieke) magnesium[74] in refluxing 1,2-dimethoxyethane (glyme) could be expected to improve the reactions.

Scheme 2-9


(CH2)n
O
n = 1, 2, 3
PCl5
CH2Cl2
Cl
Cl
n = 1, 2, 3
44 n = 1
43 n = 2
NaOMe
Cl
n = 1, 2, 3
46 n = 2
42 n = 3
1. Mg
2. CuI
n = 1, 2, 3
47 n = 2
48 n = 3
RO2CN=NCO2R
H
N
N
RO2C
CO2R
n = 1, 2, 3
49 n = 2, R = Me
50 n = 3, R = Me
1. NBS
2. Zn - TiCl4
n = 1, 2, 3
1. hydrolysis
2. oxidation
n = 1, 2, 3
hν
n = 1, 2, 3
4

Preferably, vinyl bromides or vinyl iodides would be used instead of vinyl chlorides. Methods to prepare the other vinyl halides can be envisioned, but they are bereft of the convenience of the vinyl chloride route. For example, bromination of the cycloalkenyl chloride should provide the 1,2-dibromo-1-chlorocycloalkane. Because bromination gives a *trans* orientation of the bromines,[75] one bromine and the chlorine will have a *cis* orientation. Application of a 1,2-elimination method (such as dehalogenation with zinc)[76] could return the vinyl bromide. Alternatively, appropriate quenching of a cycloalkenyl lithium could provide a different vinyl halide.[77]

Scheme 2-10



Efforts to directly couple cyclohexenyl lithium (from the treatment of the tosylhydrazone of cyclohexane with *n*-butyl lithium, Scheme 2-10)[78] and trap the diene **48** with MTAD were unsuccessful. GCMS analysis of the reaction mixtures revealed almost

exclusive formation of butylcyclohexane. Even if this sequence had succeeded, the applicability of this vinyl lithium preparation method to the other members of this target group was questionable; cyclobutenyl lithium compounds have not been prepared by this method.

The conjugated dienes bi(cyclopentenyl) **47** and bi(cyclohexenyl) **48** underwent Diels-Alder cycloaddition with dimethyl azodicarboxylate (DMAD), but not with MTAD. The adducts so made, **49** and **50**, are strained tricyclo compounds with a molecular conformation which exhibits pronounced convexity, just as **38** does. The failure of MTAD and PTAD to react in all three bi(cycloalkenyl) systems could be due to added strain in the tetracylo adducts they would form or to the instability of MTAD and PTAD in the polar solvents used in the reactions.

Various procedures were used to attempt to change **49** into the diene. Allylic bromination (to be followed by 1,4-elimination) with NBS and AIBN returned unreacted starting material. This was probably for the same reason cited for the failure of this methodology with **38**.

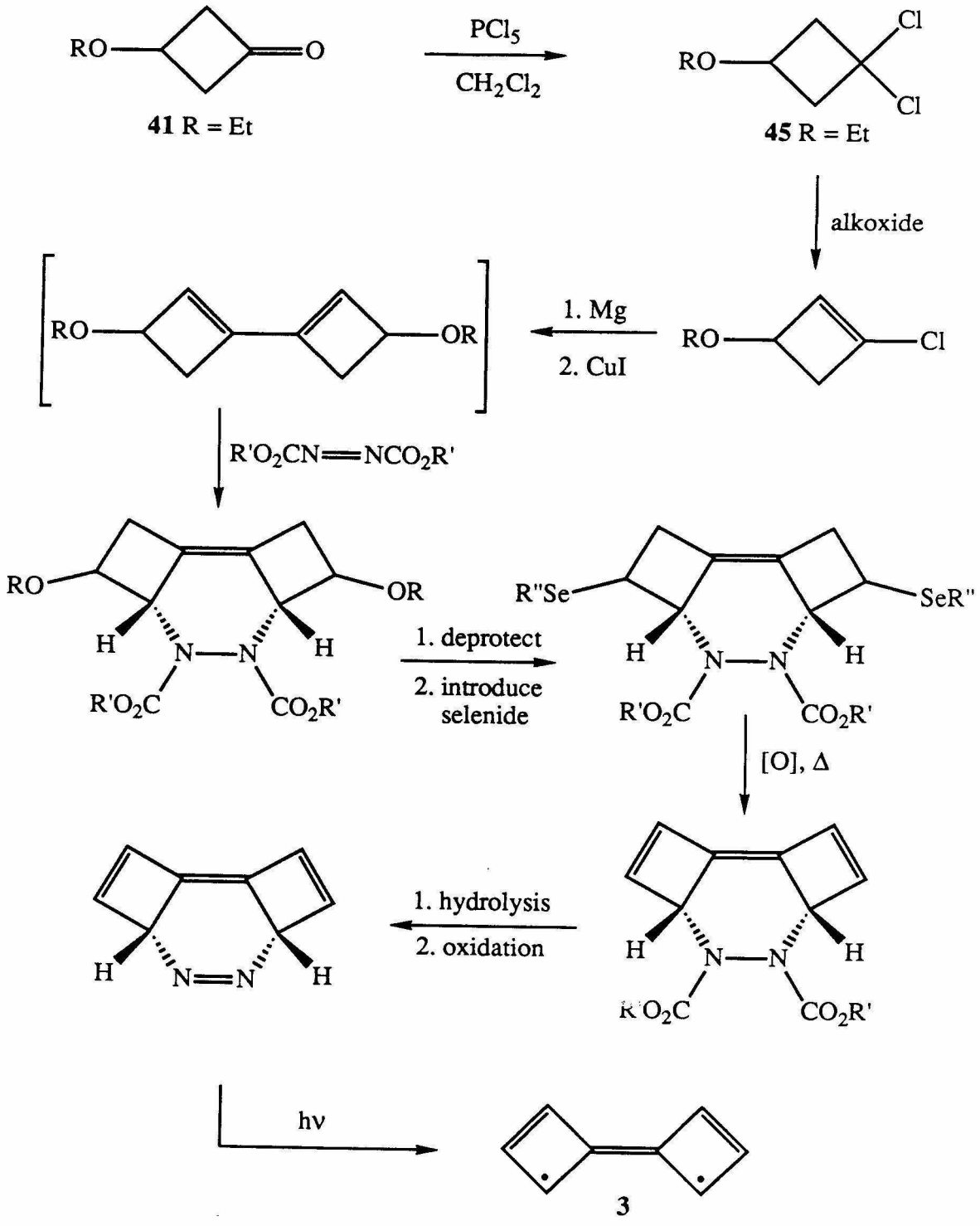
Attempted brominations in carbon tetrachloride gave an uptake of any initially added bromine, quickly followed by evolution of white vapor and the uptake of any subsequently added bromine (bromine was added slowly, dropwise, until the yellow-orange color of bromine persisted). Overall uptake of bromine was on the order of two equivalents. Addition of less bromine yielded a mixture of compounds which included unreacted starting material. Addition of base to the products of bromination afforded a mixture of elimination products, some with the desired molecular weight (GCMS).

An interpretation of these observations is that bromine added to the double bond, but because bromination is *trans* and the "underside" of the substrate is concave and crowded, hydrogen bromide (the white vapor) quickly eliminated to form another double bond which reacted with more bromine. This prompted us to try procedures for *cis* addition to double bonds. There was no reaction with molybdenum pentachloride (a reagent reported to give

cis chlorination of double bonds).[79] Reaction with osmium tetroxide gave a brown color (indicative of osmate ester formation),[54] but work-up with hydrogen sulfide to afford the *cis* hydroxylated product[80] gave no indication of success.

Further efforts to synthesize **2** and **4** were halted, effectively stymied by our current inability to convert the olefin into a diene. The proposed preparation of **3** (Scheme 2-11) was forsaken as well, due to the problems encountered with the elimination reaction of **45** to form the cyclobutenyl chloride (*vide supra*).

Scheme 2-11


RO
O
41 R = Et
PCl5
CH2Cl2
Cl
Cl
45 R = Et
alkoxide
1. Mg
2. CuI
OR
R'O2CN=NCO2R'
R"Se
SeR"
1. deprotect
2. introduce selenide
[O], Δ
1. hydrolysis
2. oxidation
hν
3

Conclusion and Future Options

Significant progress has been made toward the syntheses of **2**, **3**, and **4**. Two different routes to bi(cycloalkenyl) compounds in these systems have been established: Barton coupling of a cycloalkanone followed by twofold allylic bromination and 1,4-elimination, and direct coupling of cycloalkenyl halides. Conditions for Diels-Alder cycloaddition to the dienes have been determined; azodicarboxylates and not triazolinediones undergo successful reaction. The reactivity of adducts **38**, **49**, and **50** has been explored. Due to their convexity, both sides of the double bond are not accessible for reaction. Also, the conformation of the cycloalkylidene rings is such that the reactivity of the allylic positions is sharply reduced. Additionally, the scope of reactions applicable to four-membered rings has been broadened.

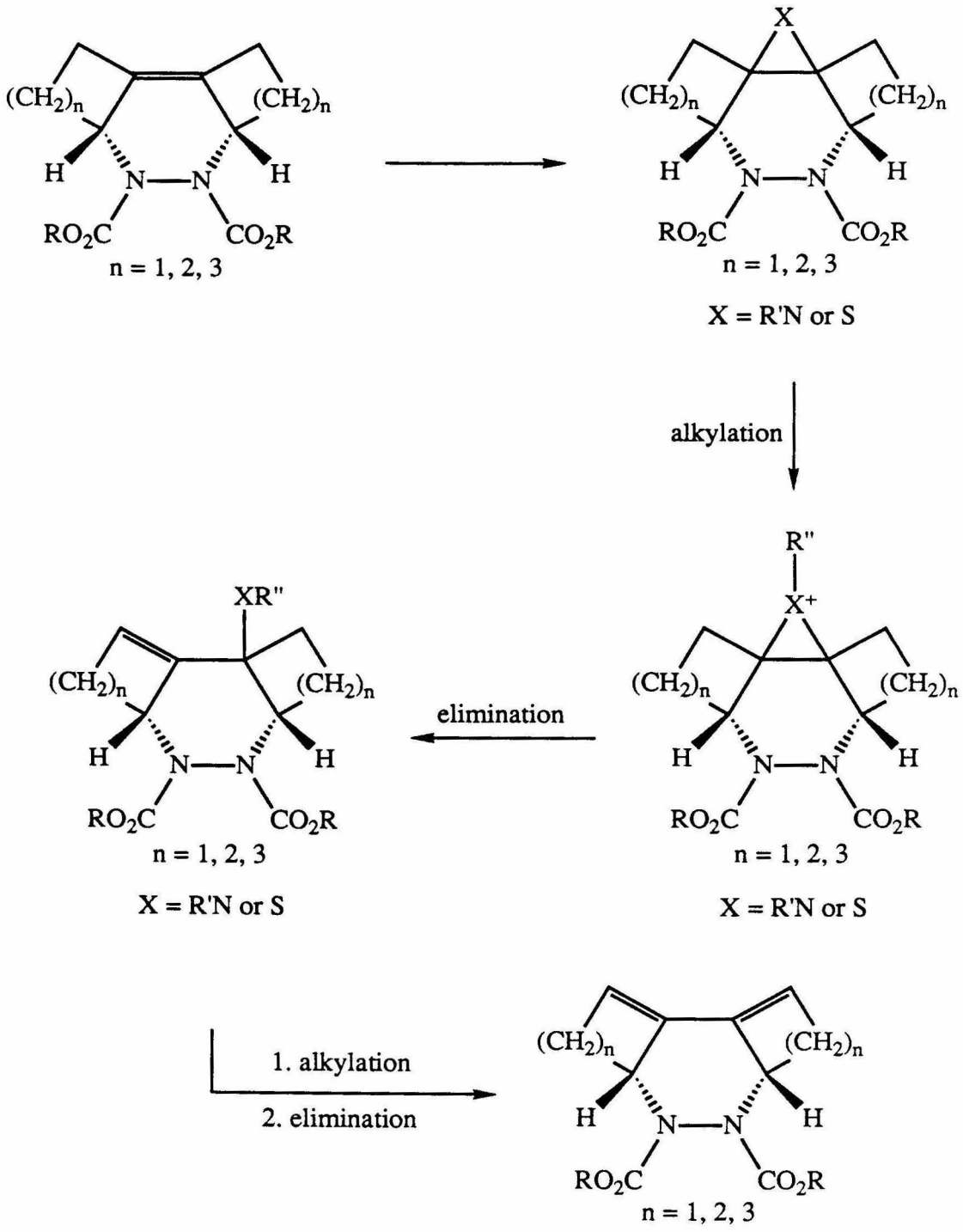
The problems encountered to this point are unlikely to be without solutions. The foregoing section includes possible improvements and alternatives to the reactions already performed. Scheme 2-12 outlines an option for creating dienes from olefins such as **38**, **49**, and **50**. Addition of a nitrene to the double bond,[81] alkylation of the aziridine product, and elimination of the quaternary ammonium moiety,[82] followed by another alkylation-elimination sequence should provide the desired diene. The same alkylation-elimination motif would be valid if the thiirane derivative could be prepared. A possibility for thiirane formation is conversion of the olefin to an epoxide, followed by formation of the episulfide by treatment with triphenylphosphine sulfide.[83]

Perhaps the most promising variation would involve coupling of cycloalkenyl halides substituted in a fashion to allow functional group transformations to be used to facilitate diene preparation, rather than adding the required functionality at the olefin stage. However, given the rigors of the coupling reaction, the conformation required for the Diels-Alder reaction, the conformation and functionality of the olefin product, and the challenge of making the appropriately substituted cycloalkenyl halide itself (particularly in

the four-membered ring systems), no one scheme of substituent functionality, protecting group(s), and starting material preparation presents itself as being particularly outstanding.

Alternatives which will allow the successful preparation of **3** are similarly difficult to develop. They most likely need to include the syntheses of differently substituted cyclobutane rings and cyclobutenyl halides, which represent considerable synthetic challenges. Of course, none of these discussions address the as yet unencountered problems sure to arise with the introduction of the tri- and tetraenes, or with the hydrolyses of the carbamates and subsequent oxidations to diazenes.

Scheme 2-12


(CH2)n
(CH2)n
H
N—N
H
RO2C
CO2R
n = 1, 2, 3
X
X = R'N or S
alkylation
R"
X+
elimination
XR"
1. alkylation
2. elimination

Experimental

General:

90-MHz NMR was performed on a Varian EM-390 continuous-wave spectrometer, 400-MHz NMR was performed on a JEOL JNM-GX400 FT-NMR spectrometer, and 500-MHz NMR was performed on a Bruker AM500 FT-NMR spectrometer. Deutero-chloroform was used as the NMR solvent. Tetramethylsilane or the proton signal from the residual chloroform in the deuterochloroform was used as an internal standard.

Mass spectra and exact mass determinations were obtained from the Analytical Facility at the University of California, Riverside. GCMS was performed on a Hewlett-Packard 5890 GC/5970 MS instrument equipped with a twelve-meter OV-101 capillary column or was obtained from the Analytical Facility at the University of California, Riverside.

Melting points are uncorrected. IR was performed on a Perkin-Elmer 1600 series FTIR spectrometer. Silica gel for flash column chromatography was 40-63 μm mesh; column sizes are listed as length x diameter. TLC was visualized with UV-light and/or with vanillin stain followed by heating.

Water refers to distilled water. Petroleum ether used was the commercial 35-60 °C fraction. Diethyl ether (ether) and tetrahydrofuran (THF) were purified by distillation from sodium-benzophenone ketyl. Dry methylene chloride, chloroform, acetonitrile, triethylamine and pyridine were prepared by standing over 4A molecular sieves. Toluene was dried by distillation from sodium sand. All other solvents were reagent grade or better and used as purchased unless otherwise noted. Reagents were used as received from the commercial vendors (primarily Aldrich) except where noted. Zn-Cu couple was prepared by the methods of Krepski and Hassner[45a] and LeGoff.[45d]

Inert atmosphere was provided by the use of argon passed through a Drierite-filled gas drying tower. Reactions performed with exclusion of moisture were run either under argon or with a Drierite-filled drying tube as the moisture excluder. Experiments in which the apparatus was oven-dried and then assembled under a flow of argon were conducted under

an argon atmosphere at all stages prior to work-up. Removal of solvent refers to rotary evaporation to apparent dryness followed by further evaporation at the low pressure provided by a vacuum pump (0.1 - 0.5 torr) to remove any residual solvent.

2,2-Dichloro-3-phenylcyclobutanone (15) - prepared by the method of Krepski and Hassner.[45a]

3-Phenylcyclobutanone (16) - 1.00 gm **15** (4.65 mmoles), 1.22 gm zinc powder (18.7 mmoles), and 25 ml glacial acetic acid were mixed in a 50-ml flask. The mixture was refluxed for 24 hrs. with stirring. Dissolution of all solids was observed with heating. The reaction mixture was cooled to room temperature and poured onto 200 ml ice/water mixture. To this was added 25 ml CCl_4. 100 ml saturated $NaHCO_3$(aq) was added slowly to the stirred two-phase mixture. Stirring was continued until the bubbling ceased. The phases were separated and the aqueous phase was extracted with 2 x 25 ml CCl_4 The combined organic phases were washed with 3 x 50 ml saturated Na_2CO_3(aq), dried with anhydrous $MgSO_4$, and gravity filtered. Removal of solvent left 0.76 gm yellow oil and white solid. Kugelrohr distillation of this mixture (0.5 torr, 110 °C) gave 0.57 gm (84%) of product ketone as a clear, colorless, fragrant liquid. R_f (9:1 petroleum ether : ethyl acetate) 0.31. 90-MHz ^1H NMR ($CDCl_3$) δ 3.0-3.8 (m, 5H), 7.3 (s, 5H). Mass spectrum, *m/e* 146 (parent).

1,1-Dimethoxy-3-phenylcyclobutane (17) - 0.20 gm **16** (1.37 mmoles), 5 ml MeOH (3.96 gm, 124 mmoles), 10 ml trimethylorthoformate (9.68 gm, 91.2 mmoles), and 3 drops 48% hydrobromic acid were mixed in a 50-ml flask. The solution was stirred under argon for 22 hrs. 15 ml CCl_4 and 10 ml saturated Na_2CO_3(aq) were added and the mixture was stirred for 4 hrs. 10 ml water was added and the phases were separated. The aqueous phase was extracted with 3 x 15 ml CCl_4. The combined organic phases were dried with anhydrous $MgSO_4$ and gravity filtered. Removal of solvent left 0.13 gm (50%) clear, colorless liquid ketal. R_f (9:1 petroleum ether : ethyl acetate) 0.36. 90-MHz ^1H

NMR ($CDCl_3$) δ 2.0-2.35 (m, 2H), 2.5-2.85 (m, 2H), 3.15 (s, 3H), 3.25 (s, 3H), 3.3-3.5 (m, 1H).

2,2-Dichloro-3-(phenoxymethyl)cyclobutanone (18) - prepared by the method of Malherbe, Rist, and Bellus.[45b]

3-(Phenoxymethyl)cyclobutanone (19) - dechlorination was accomplished in the same manner as for the preparation of **16**. Kugelrohr distillation (0.5 torr, 160 °C) gave 1.26 gm (88%) clear, colorless oil which solidified to a clean, white solid when stored at -10 °C (from 2.00 gm **18**, 8.16 mmoles). 90-MHz ^1H NMR ($CDCl_3$) δ 2.5-3.4 (m, 5H), 4.1 (d, 2H), 6.8-7.4 (m, 5H). Mass spectrum, *m/e* 176 (parent).

Methyl 3-methylenecyclobutanecarboxylate (20) - prepared by the method of Cripps, Williams, and Sharkey.[51a]

(3-Methylenecyclobutyl)methanol (21) - A three-neck 250-ml flask, pressure-equalizing addition funnel, and reflux condenser were oven-dried and then assembled while hot under a flow of argon. A solution of 5.00 gm **20** (39.6 mmoles) in 50 ml dry ether was syringed into the addition funnel. 50 ml of 1.0 M $LiAlH_4$ in ether (50.0 mmoles, 1.90 gm) was syringed into the flask. The solution in the addition funnel was added over a 35-min. period to the stirred solution in the flask. A water/ice bath was used to cool the reaction flask during the addition and was removed after the addition was completed. Stirring was continued for an additional 11 hrs. past the end of the addition. At that time, 2 ml water, 2 ml 15% (w/w) NaOH(aq), and 6 ml water were added dropwise in that order.[53] The ether solution was suction filtered and the collected solids were washed with ether. The combined ether portions were stirred with anhydrous $MgSO_4$ overnight to effect drying. Gravity filtration and removal of solvent left 3.77 gm faintly yellow liquid. Kugelrohr distillation (water-aspirator pressure, ≈ 130 °C) gave 3.60 gm (93%) clear, colorless liquid alcohol. R_f (9:1 petroleum ether : ethyl acetate) 0.21. 90-MHz ^1H NMR ($CDCl_3$) δ 2.0-3.0 (m, 6H), 3.6 (d, 2H), 4.75 (m, 2H).

(3-Methylenecyclobutyl)methyl *t*-butyldimethylsilyl ether (22) - 0.65 gm **21** (6.62 mmoles), 1.10 gm *t*-butyldimethylsilyl chloride (7.30 mmoles), 1.1 ml dry triethylamine (0.80 gm, 7.9 mmoles), 0.04 gm 4-dimethylaminopyridine (0.33 mmole), and 50 ml dry CH_2Cl_2 were mixed in a 100-ml flask.[85] The solution was stirred for 23 hrs. under argon. The CH_2Cl_2 solution was then washed successively with 2 x 25 ml water and 2 x 25 ml saturated NH_4Cl (aq). The solution was dried with anhydrous Na_2SO_4 and gravity filtered. Removal of solvent left a brown liquid which was filtered through silica gel, which was then washed with copious amounts of CH_2Cl_2. The combined CH_2Cl_2 portions were rotary evaporated to leave 1.32 gm (94%) clear, colorless, volatile liquid ether. R_f (9:1 petroleum ether : ethyl acetate) 0.74. 90-MHz ^1H NMR ($CDCl_3$) δ 0.1 (s, 6H), 1.0 (s, 9H), 2.1-2.9 (m, 5H), 3.6 (d, 2H), 4.75 (m, 2H).

Ethyl (3-methylenecyclobutyl)methyl carbonate (23) - 0.99 gm **21** (10.1 mmoles) was dissolved in 75 ml dry CH_2Cl_2 in a 250-ml flask. 1.1 ml dry pyridine (1.08 gm, 13.7 mmoles) was added followed by 1.2 ml ethylchloroformate (1.36 gm, 12.6 mmoles). The solution was stirred while protected from moisture for 1.5 hrs. The pink reaction solution was washed with 2 x 200 ml water and 250 ml 0.63 M aqueous acetic acid, dried with anhydrous $MgSO_4$, and gravity filtered. Removal of solvent left 1.62 gm yellow liquid and white solid. Filtration of this mixture through silica gel, which was subsequently washed with 9:1 petroleum ether : ethyl acetate, left 1.35 gm (78%) clear, colorless liquid carbonate after combination of the organic portions and removal of solvent. R_f (9:1 petroleum ether : ethyl acetate) 0.48. 90-MHz ^1H NMR ($CDCl_3$) δ 1.3 (t, 3H), 2.1-3.0 (m, 5H), 4.0-4.4 (overlapping quartet and doublet, 4H), 4.8 (m, 2H).

Methyl (3-methylenecyclobutyl)methyl carbonate (24) - 3.60 gm **21** (36.7 mmoles) was dissolved in 250 ml dry CH_2Cl_2 in a 500-ml flask. 3.7 ml dry pyridine (3.63 gm, 45.9 mmoles) and 3.2 ml methyl chloroformate (3.91 gm, 41.4 mmoles) were added, a slight exotherm was observed, and the solution became pink. After 5 min., the solution turned a straw yellow color. By 23 hours of stirring, the solution was colorless.

The solution was stirred while protected from moisture for a total of 68 hrs. The reaction solution was washed with 2 x 250 ml water, then 1 x 200 ml 0.2 M HCl (aq). The CH_2Cl_2 solution was then dried with anhydrous $MgSO_4$ and gravity filtered. Removal of solvent left 4.59 gm (80%) of clear, colorless, fragrant liquid carbonate. R_f (9:1 petroleum ether : ethyl acetate) 0.43. 90-MHz ^1H NMR ($CDCl_3$) δ 2.2-3.1 (m, 5H), 3.8 (s, 3H), 4.2 (d, 2H), 4.7-4.9 (m, 2H).

3-(*t*-Butyldimethylsiloxymethyl)cyclobutanone (25) - 1.68 gm **22** (7.91 mmoles), 21 mg OsO_4 (83 μmoles), 30 ml dioxane, and 10 ml water were mixed in a 100-ml flask.[54] The flask was stoppered and the mixture was stirred for 15 min., by which time the solution was brown (osmate ester formation). 3.55 gm $NaIO_4$ (16.6 mmoles) was added portionwise to the stirred solution over 25 min. The mixture was then stirred for 88.5 hrs. The yellow reaction mixture was suction filtered and the collected white solid was washed with CCl_4. 50 ml water was added to the filtrate. This solution was then extracted with 3 x 30 ml CCl_4. The combined CCl_4 portions were dried with anhydrous $MgSO_4$ and gravity filtered. Rotary evaporation left a liquid, the flash chromatography (9:1 petroleum ether : ethyl acetate, 11 cm x 6 cm) of which gave 1.13 gm (66%) clear, colorless liquid ketone. R_f (9:1 petroleum ether : ethyl acetate) 0.43. 90-MHz ^1H NMR ($CDCl_3$) δ 0.1 (s, 6H), 0.95 (s, 9H), 2.4-2.85 (m, 1H), 2.85-3.1 (m, 4H), 3.75 (d, 2H). Mass spectrum, *m/e* 214 (parent).

Ethyl (3-oxocyclobutyl)methyl carbonate (26) - 0.12 gm **23** (0.705 mmole) was dissolved in 9 ml dioxane and 3 ml water in a 50-ml flask. 2 mg OsO_4 (7.87 μmoles) was added, the flask stoppered, and the mixture stirred for 15 min. The solution turned dark brown (osmate ester formation). 0.32 gm $NaIO_4$ was added (1.50 mmoles).[54] Stirring was continued for 25 hrs. The reaction mixture was suction filtered, the collected solids were washed with $CHCl_3$, and 50 ml water was added to the filtrate. The diluted filtrate was extracted with 3 x 25 ml $CHCl_3$. The combined organic portions were dried with $MgSO_4$ and gravity filtered. Removal of solvent left 0.16 gm yellow liquid with

suspended brown particles. Flash chromatography (9:1 petroleum ether : ethyl acetate, 11 cm x 2.5 cm) gave 0.11 gm (92%) clear, colorless oil. R_f (9:1 petroleum ether : ethyl acetate) 0.16. IR, 1750 cm^{-1} (carbonate carbonyl), 1785 cm^{-1} (ketone carbonyl). 90-MHz ^1H NMR ($CDCl_3$) δ 1.3 (t, 3H), 2.6-3.4 (m, 5H), 4.0-4.4 (overlapping quartet and doublet, 4H).

Methyl (3-oxocyclobutyl)methyl carbonate (27) - 4.50 gm **24** (28.8 mmoles), 73 mg OsO_4 (287 μmoles), 345 ml 1,4-dioxane, and 115 ml water were stirred at room temperature for 30 min.; the solution quickly turned brown and darkened to become almost black in color due to osmate ester formation. 13.0 gm $NaIO_4$ (60.8 mmoles) was added portionwise over 60 min.; this caused the solution to turn golden yellow, and a flocculent white precipitate formed. Stirring was continued for an additional 69 hr. The reaction mixture was then suction filtered and the collected solids were washed with 200 ml $CHCl_3$. 1 l of water was added to the filtrate which was then extracted with 3 x 100 ml $CHCl_3$. The $CHCl_3$ portions were dried with anhydrous $MgSO_4$, gravity filtered, and rotary evaporated to leave a black liquid. Kugelrohr distillation (0.9 torr, 140 °C) gave 3.64 gm clear, yellow liquid, which was dissolved in CH_2Cl_2 and treated with activated charcoal. Gravity filtration and removal of solvent left 2.82 gm (62%) clear, viscous liquid. R_f (9:1 petroleum ether : ethyl acetate) 0.10. 90-MHz ^1H NMR ($CDCl_3$) δ 2.8-3.4 (m, 5H), 3.8 (s, 3H), 4.3 (d, 2H). Mass spectrum, *m/e* 59, 71, 82, 130, 158.

Barton coupling procedure - the procedures for the first three steps in the syntheses of bi(cyclobutylidene) **28**, 3,3'-diphenylbi(cyclobutylidene) **29**, 3,3'-di(phenoxymethyl)bi(cyclobutylidene) **30**, 3,3'-di(*t*-butyldimethylsiloxymethyl)-bi(cyclobutylidene) **31**, and 3,3'-di(methoxycarboxymethyl)bi(cyclobutylidene) **32** are the same. The procedures for **30** are illustrative. The fourth and final step in the synthesis of **28** is that used by Bee, Beeby, Everett, and Garratt.[41] The fourth step is the same for the syntheses of the four other olefins and is illustrated by that for **30**.

Symmetrical azine of 19 - 0.50 gm **19** (2.84 mmoles), 5 ml absolute EtOH, and 69 μl hydrazine hydrate (71 mg, 1.42 mmoles) were mixed in a 25-ml flask. The flask was stoppered and the contents stirred for 67.5 hrs. Removal of solvent left 0.39 gm (80%) white solid azine.

3,8-Di(phenoxymethyl)-5-thia-10,11-diazadispiro[3.1.3.2]undecane - 0.39 gm of the above azine (1.12 mmoles) was dissolved in 5 ml dry CH_3CN and 4 ml dry CH_2Cl_2. Dissolution was not complete. H_2S was bubbled through the stirred mixture for 7 hrs. All solids dissolved within the first 45 min. of H_2S bubbling. Removal of solvent left 0.43 gm (100%) clean, white solid undecane.

3,8-Di(phenoxymethyl)-5-thia-10,11-diazadispiro[3.1.3.2]undec-10-ene- 30 ml dry CH_2Cl_2 and 0.65 gm $Pb(OAc)_4$ (1.47 mmoles) were combined in a 100-ml flask. A pressure-equalizing addition funnel which contained a solution of 0.43 gm of the above undecane (1.12 mmoles) in 15 ml dry CH_2Cl_2 was affixed to the flask. The stirred $Pb(OAc)_4$ suspension was cooled to 0 °C under a flow of argon. The solution in the addition funnel was then added dropwise over 20 min. Stirring of the reaction mixture was continued for 3 hrs. at 0 °C. The reaction mixture was filtered through Celite; the collected solids were washed with CH_2Cl_2. The combined organic portions were washed with 85 ml saturated $NaHCO_3$(aq), dried with $MgSO_4$, and gravity filtered. Removal of solvent left 0.43 gm (100%) slightly yellowed white solid undecene.

3,3'-Di(phenoxymethyl)bicyclobutylidene (30) - 0.43 gm of the above undecene (1.12 mmoles), 4 ml dry toluene, and 5.8 ml triethylphosphite (5.62 gm, 33.8 mmoles) were combined in a 25-ml flask. A reflux condenser was attached and the reaction was protected from moisture. The stirred solution was then refluxed for 18 hrs. The reaction mixture was allowed to cool to room temperature and the solvent was removed. Flash chromatography (9:1 petroleum ether : ethyl acetate, 11 cm x 4 cm) of the solid so obtained gave 0.36 gm (100%) clean, white solid product. R_f (9:1 petroleum ether

: ethyl acetate) 0.66. 90-MHz ^{1}H NMR ($CDCl_3$) δ 2.1-2.9 (m, 10H), 3.95 (d, 4H), 6.8-7.4 (m, 10H). Mass spectrum, *m/e* 320 (parent).

Bi(cyclobutylidene) (28) - 90-MHz ^{1}H NMR ($CDCl_3$) δ 1.7-2.2 (m, 4H), 2.3-2.8 (m, 8H). Mass spectrum, *m/e* 27, 39, 52, 65, 80, 93, 108.

3,3'-Diphenylbi(cyclobutylidene) (29) - R_f (9:1 petroleum ether : ethyl acetate) 0.66, m.p. 57-61 °C. 90-MHz ^{1}H NMR ($CDCl_3$) δ 2.5-3.8 (m, 10H), 7.2-7.5 (m, 10H). Mass spectrum, *m/e* 260 (parent).

3,3'-Di(*t*-butyldimethylsiloxymethyl)bi(cyclobutylidene) (31) - 90-MHz ^{1}H NMR ($CDCl_3$) δ 0.1 (s, 12H), 0.9 (s, 18H), 2.0-2.8 (m, 10H), 3.6 (d, 4H),. Mass spectrum, *m/e* 75, 91, 133, 171, 207, 340.

3,3'-Di((carbomethoxy)oxymethyl)bi(cyclobutylidene) (32) - 90-MHz ^{1}H NMR ($CDCl_3$) δ 2.0-2.9 (m, 10H), 3.8 (s, 6H), 4.15 (d, 4H). Mass spectrum, *m/e* 59, 91, 117, 133, 284.

3,3'-Diphenylbi(cyclobutylidene) (29) (*via* McMurry coupling) - A 100-ml three-neck flask, pressure-equalizing addition funnel, and reflux condenser were oven-dried and then assembled while hot under a flow of argon. 0.50 gm [$(TiCl_3)_2$•$LiAlH_4$] (1.44 mmoles) and 30 ml dry THF were introduced into the flask. This mixture turned black upon stirring. 0.20 gm **16** (1.37 mmoles) was dissolved in 10 ml dry THF. This solution was added dropwise *via* the addition funnel over 5 min. The reaction mixture was then refluxed with stirring for 48 hrs.[56(a),(c)] The reaction was allowed to cool to room temperature and 50 ml saturated Na_2CO_3(aq) was added. The mixture was suction filtered and the collected solids were washed with CH_2Cl_2 and ether. The combined organic portions were dried with $MgSO_4$ and gravity filtered. Removal of solvent left 0.16 gm yellow oil and solid film. Flash chromatography (9:1 petroleum ether : ethyl acetate, 10 cm x 4 cm) of this mixture allowed collection of 0.02 gm (11%) yellow oil which slowly crystallized (R_f, 9:1 petroleum ether : ethyl acetate, 0.66). It was identical in all respects to an authentic sample of **29** prepared *via* the Barton coupling procedure, m.p. 57-61 °C. 90-

MHz ^{1}H NMR ($CDCl_3$) δ 2.5-3.8 (m, 10H), 7.2-7.5 (m, 10H). Mass spectrum, *m/e* 260 (parent). Five other fractions were collected, combined weight 0.14 gm (100% mass recovery from the column). The lowest R_f compound was eluted from the column with 1:4 petroleum ether : ethyl acetate and consisted of 0.11 gm light yellow viscous oil. 90-MHz ^{1}H NMR ($CDCl_3$) δ 1.7-3.3 (m, 10H), 3.3-4.5 (broad multiplet, 2H), 7.1-7.4 (m, 10H). This compound may be the corresponding pinacol, **1,1'-dihydroxy-3,3'-diphenylbi(cyclobutyl) 33**, in 50% yield.

2-Bromo-3-phenylcyclobutanone (34) - 0.61 gm finely ground $CuBr_2$ (2.72 mmoles) and 10 ml ethyl acetate were added to a 50-ml three-neck flask. The flask was equipped with a reflux condenser and pressure-equalizing addition funnel. A solution of 0.20 gm **16** (1.37 mmoles) in 10 ml $CHCl_3$ was placed in the addition funnel. Reflux of the stirred $CuBr_2$ suspension was commenced. The solution in the addition funnel was added to the refluxing ethyl acetate solution, a white precipitate formed and HBr was evolved, and the solution turned green. Reflux was continued for 7.5 hrs.[60] The reaction mixture was cooled, treated with activated charcoal, and gravity filtered. Removal of solvent left 0.33 gm yellow-green liquid. Flash chromatography (9:1 petroleum ether : ethyl acetate, 32 cm x 2 cm) gave 0.17 gm (55%) yellow liquid bromoketone. 90-MHz ^{1}H NMR ($CDCl_3$) δ 3.1-3.9 (m, 3H), 5.0 (d, 1H), 7.1-7.5 (m, 5H).

2-Chloro-3-phenylcyclobutanone (35) - A 500-ml flask and a pressure-equalizing addition funnel were oven-dried and then assembled while hot under a flow of argon. A solution of 1.00 gm **15** (4.65 mmoles) in 50 ml dry ether was placed in the funnel. 200 ml dry ether and 1.65 gm $CuBr{\bullet}Me_2S$ (8.03 mmoles) were placed in the flask. The stirred suspension in the flask was cooled to -78 °C with a dry ice/acetone bath for 30 min. 10 ml of 1.5 M MeLi in ether (15 mmoles) was added while the temperature was maintained at -78 °C. The solution was stirred for 30 min. and then the solution in the funnel was added over 30 min. This solution was stirred for an additional 30 min. at -78 °C, after which 100 ml saturated aqueous NH_4Cl was added. This mixture was poured

into 200 ml water. The phases were separated and the blue aqueous phase was washed with 50 ml ether. The combined ether portions were dried with $MgSO_4$ and gravity filtered. Removal of the solvent left 0.84 gm (100%) clear viscous oil. 90-MHz ^1H NMR ($CDCl_3$) δ 2.8-4.2 (m, 3H), 5.1 (d, 1H), 7.1-7.4 (m, 5H).

Dibromobi(cyclobutylidene) (36) - 1.00 gm **28** (9.24 mmoles), 20 ml CCl_4, 3.30 gm NBS (18.5 mmoles, recrystallized from water), and 50 mg AIBN (300 μmoles) were added, in that order, to a 50-ml flask equipped with a magnetic stir bar. The sides of the flask were rinsed down with an extra 5 ml CCl_4. The NBS was at the bottom of the flask. The reaction was refluxed and stirred for 1.5 hrs. under argon. It was then cooled for 1 hr. in a -20 °C freezer. This resulted in a dark brown solid (succinimide) floating atop the yellow CCl_4 solution. The solid was removed by suction filtration through Celite; the collected solids were washed with CCl_4. Solvent was removed from the combined CCl_4 portions to leave 2.61 gm brown-orange oil. Kugelrohr distillation of this oil (130 °C, 0.125 torr) allowed collection of 1.58 gm (64%) of a mixture of dibromides as a yellow liquid. 90-MHz ^1H NMR ($CDCl_3$) δ 1.5-3.7 (m). Mass spectrum, *m/e* 27, 51, 105, 158, 160, 185, 187, 266.

2,2',4,4'-Tetrabromobi(cyclobutylidene) (37) - 0.10 gm **28** (.92 mmole), 10 ml CCl_4, 0.69 gm NBS (3.9 mmoles, recrystallized from water), and 14 mg AIBN (85 μmoles) were added, in that order, to a 50-ml flask equipped with a magnetic stir bar. The NBS was at the bottom of the flask. The reaction was refluxed and stirred for 2.5 hrs. under argon. It was then cooled for 1 hr. in a -20 °C freezer. This resulted in a dark brown solid (succinimide) floating atop the yellow CCl_4 solution. The solid was removed by suction filtration through Celite; the collected solids were washed with CCl_4. Solvent was removed from the combined CCl_4 portions to leave 0.39 gm (≈100%) of a mixture of tetrabromides as a yellow-orange oil. Mass spectrum, *m/e* 51, 77, 104, 158, 185, 237, 264, 310.

6,7-Diaza-6,7-dicarbethoxytricyclo[6.2.0.0^{2,5}]dec-1-ene (38) - 0.17 gm **36** (640 μmoles), and a dry magnetic stirring bar were placed in a dry 25-ml flask. The flask was capped with a septum and evacuated and flushed with argon five times. 10 ml dry, anoxic THF was added *via* syringe. The yellow solution was cooled to 0 °C with an ice/water bath. 6 μl $TiCl_4$ (10 mg, 55 μmoles) was syringed in, followed by the introduction of 0.13 gm Zn dust (2.0 mmole). The mixture was stirred at 0 °C under argon for 4.5 hrs. At this time, GCMS indicated disappearance of starting dibromide and presence of bi(cyclobutenyl). The reaction mixture was cooled to -78 °C with a dry ice/acetone bath, then cannulated with argon pressure through a plug of glass wool (to remove solids) into a stirred, 0 °C solution of 0.2 ml DEAD (0.22 gm, 1.3 mmoles) in 2 ml dry, anoxic THF in a dry 25-ml flask. This solution was stirred for 1.5 hrs. at 0 °C, then stirred for 26 hrs. at room temperature. GCMS indicated absence of bi(cyclobutenyl) and the presence of a compound with a parent ion of *m/e* 280. 10 ml ether and 10 ml water were added to the reaction mixture, and the two phases were mixed thoroughly. The phases were then separated, and the aqueous phase was washed with 2 x 10 ml ether. The three ethereal portions were combined, dried with anhydrous $MgSO_4$, and gravity filtered. Removal of solvent left 0.31 gm orange oil. A flash column (9:1 petroleum ether : ethyl acetate, 13 cm x 2 cm) allowed isolation of 44 mg (24%) of the Diels-Alder adduct. R_f (9:1 petroleum ether : ethyl acetate) 0.07. 90-MHz ^1H NMR ($CDCl_3$) δ 1.25 (t, 6H), 1.5-2.7 (m, 10H), 4.15 (quartet, 4H). Mass spectrum, *m/e* 29, 80, 107, 135, 163, 207, 235, 252.

To further characterize the Diels-Alder adduct (by diimide reduction of the double bond), 22 mg **38** (78 μmoles) was dissolved in 4 ml dry glyme in a dry 25-ml flask. 100 mg potassium azodicarboxylate ($KO_2CN{=}NCO_2K$, PADC)[86] and a dry magnetic stirring bar were added. 60 mg acetic acid in 2 ml dry glyme was added over 1 hr. *via* syringe and syringe pump. After 3 hr. of stirring at room temperature, 10 ml CH_2Cl_2 and 5 ml water were added. The phases were separated, and the organic phase was dried with anhydrous

$MgSO_4$ and gravity filtered. Removal of solvent left 16 mg oily solid. 400-MHz ^1H NMR ($CDCl_3$) δ 1.25 (t, 6H), 1.5-2.6 (m, 12H), 4.15 (quartet, 4H). Mass spectrum, *m/e* 29, 81, 115, 165, 209, 237, 282.

Ethyl (2,2,4,4-tetrabromo-3-oxocyclobutyl)methyl carbonate (40) - 0.40 gm **26** (2.32 mmoles), 60 ml dry $CHCl_3$, 1.80 ml bromine (5.58 gm, 34.9 mmoles), and 1 drop 30% HBr in AcOH were mixed in a 100-ml flask and refluxed for 6 days under argon. The reaction mixture was allowed to cool to room temperature. Removal of solvent left 1.29 gm viscous yellow-orange liquid. IR, 1750 cm^{-1} (carbonate carbonyl), 1820 cm^{-1} (ketone carbonyl). 400-MHz and 90-MHz ^1H NMR ($CDCl_3$) δ 1.3 (t, 3H), 3.9 (t, 1H), 4.2 (quartet, 2H), 4.6 (d, 2H). See text for discussion of chromatography, IR, and GCMS results. **Methyl (2,2,4,4-tetrabromo-3-oxocyclobutyl)methyl carbonate** was prepared from **27** in a similar fashion. 90-MHz ^1H NMR ($CDCl_3$) δ 3.85 (s, 3H) overlapped with 3.9 (t, 1H), 4.6 (d, 2H). Mass spectrum, *m/e* 59, 199, 274, 393, 416.

3-Ethoxycyclobutanone (41)[87] - 200 ml liquid ketene (gaseous ketene produced by a ketene generator and condensed) was collected in two 100-ml flasks at -78 °C. The flasks were capped with septa and placed in a stainless steel bomb which contained 500 ml ethyl vinyl ether cooled to -20 °C. The bomb was sealed and heated, with shaking, to ≈105 °C for 6.5 hrs. It was then cooled to room temperature, and the contents were removed. The two flasks were recovered unbroken; the two swollen septa were recovered separate from the flasks. Unreacted ethyl vinyl ether was removed by atmospheric distillation. Distillation at water-aspirator pressure (80 °C) allowed collection of 90 ml clear, colorless liquid. Careful vacuum distillation (water-aspirator pressure, 80-88 °C) of this distillate gave 82.6 gm (15%) clear, colorless liquid. 90-MHz ^1H NMR ($CDCl_3$) δ 1.2 (t, 3H), 2.6-3.5 (m, 4H), 3.5 (q, 2H), 4.3 (quintet, 1H).

3-*t*-Butyldimethylsiloxycyclobutanone can be prepared from **2,2-dichloro-3-*t*-butyldimethylsiloxycyclobutanone**, which can be prepared from dichloroketene and ***t*-butyldimethylsiloxyethene.**[88] The procedures:

250 ml dry THF was stirred at room temperature under argon with 100 ml 2.5 M n-BuLi in hexanes (0.25 mole) for 40 hrs. 37.68 gm *t*-butyldimethylsilyl chloride (0.25 mole) was added in ≈10 gm portions over 15 min. A slight exotherm was noted and a white precipitate formed. The reaction was stirred for 2 hrs. past *t*-butyldimethylsilyl chloride addition. The mixture was then suction filtered through a glass frit. The filtrate was rotary evaporated and the residue was distilled at water-aspirator pressure to leave 25.53 gm (65%) ***t*-butyldimethylsiloxyethene**. 90-MHz ^{1}H NMR ($CDCl_3$) δ 0.1 (s, 6H), 0.9 (s, 9H), 4.05 (d, 1H), 4.4 (d, 1H), 6.35 (dd, 1H). Mass spectrum, *m/e* 45, 59, 75, 101, 158.

Under argon, 2.00 gm *t*-butyldimethylsiloxyethene (12.6 mmoles), 100 ml dry pentane, and 4.0 ml dry triethylamine (2.9 gm, 29 mmoles) were placed in an oven-dried 250-ml three-neck flask. The flask and contents were cooled to 0 °C and 2.5 ml dichloroacetyl chloride (3.8 gm, 26 mmoles) in 35 ml dry pentane was added over 3 hrs. *via* syringe and syringe pump.[89] A white precipitate formed immediately upon addition of the triethylamine solution. 15 min. after the end of the addition, the cooling bath was removed and the reaction was allowed to warm to room temperature. The reaction was stirred at room temperature for 45 min. It was then suction filtered through Celite and sufficient CH_2Cl_2 was added to keep the compounds in the filtrate in solution. Removal of solvent left 4.42 gm dark brown viscous liquid and solid, which contained **2,2-dichloro-3-*t*-butyldimethylsiloxycyclobutanone** and was used without further purification in the next step. Mass spectrum, *m/e* 45, 57, 59, 73, 75, 93, 95, 113, 115, 168, 170, 211, 213, 226, 228.

The crude 2,2-dichloro-3-t-butyldimethylsiloxycyclobutanone was dissolved in 120 ml methanol saturated with NH_4Cl. Zn powder was added and the mixture was stirred for

3.25 hrs.[90] Addition of zinc caused an exotherm and the brown solution turned yellow with a touch of green. The reaction mixture was then suction filtered and the collected solids were washed with CH_2Cl_2. The combined filtrates were rotary evaporated to leave an oily brown residue. 100 ml ether was added and the mixture was stirred vigorously. The phases were then separated and the organic phase was washed with 2 x 50 ml water. It was then dried with anhydrous $MgSO_4$, treated with activated charcoal, and gravity filtered. Removal of solvent left 1.55 gm golden brown liquid. Kugelrohr distillation gave 1.17 gm (46% for the two steps) clear liquid **3-*t*-butyldimethylsiloxycyclobutanone**. 90-MHz ^1H NMR ($CDCl_3$) δ 0.1 (s, 6H), 0.9 (s, 9H), 3.0-3.5 (m, 4H), 4.3-4.6 (m, 1H).

1-Chlorocyclohexene (42) - 120 gm PCl_5 (0.58 mole) and 750 ml dry CH_2Cl_2 were introduced into a 2-l flask. The flask and contents were then cooled to 0 °C and 54 ml cyclohexanone (51.14 gm, 0.52 mole) were added *via* syringe. All solids dissolved, gas evolved, and an exotherm occurred. The mixture was stirred at 0 °C for 1.25 hrs., then was warmed to room temperature and stirred for 1.5 hrs. With cooling, 600 ml water containing 120 gm NaOH (3 moles) was added slowly and gave rise to a strong exotherm. This mixture was stirred for 40 min. at 0 °C, then for 2 hrs. at room temperature. The phases were separated, and the burgundy-colored organic layer was dried with anhydrous $MgSO_4$ and gravity filtered. 100 ml methanol was added to the filtrate, followed by 57.00 gm NaOMe (1.1 moles). The addition of NaOMe caused the burgundy-colored solution to be replaced by a white precipitate and a yellow solution. This mixture was refluxed, with stirring, for 1 hr. 600 ml more MeOH and 100 gm more NaOMe were added. The mixture was refluxed for an additional hour, then stirred at room temperature for 24 hrs. 1.5 l water and 400 ml pentane were then added with vigorous mixing. The phases were then separated, and the organic layer was dried with anhydrous $MgSO_4$ and gravity filtered. Distillation at atmospheric pressure removed solvent then allowed collection of 22.42 gm (37%) vinyl chloride as a clear, colorless liquid, b.p. 144 °C. 90-MHz ^1H NMR ($CDCl_3$) δ 1.2-2.5 (m, 8H), 5.65-5.9 (m, 1H). Mass spectrum, *m/e* 39, 53, 65, 81, 88, 101, 116.

1,1-Dichlorocyclopentane (43) - 50.0 gm PCl5 (0.24 mole) and 500 ml dry CH2Cl2 were introduced into a 1-l flask. The stirred suspension was cooled to 0 °C with an ice/water bath. 20 ml cyclopentanone (19.0 gm, 0.23 mole) was added. The reaction was stirred, protected from moisture, for 2 hrs. at 0 °C. 101 gm $NaHCO_3$ (1.2 mole) was then added slowly and carefully to the 0 °C solution. Vigorous gas evolution and an exotherm occurred. After the addition of $NaHCO_3$ was completed, 300 ml water was added and the mixture stirred overnight. The phases were then separated. The organic phase was dried with anhydrous $MgSO_4$ and gravity filtered. Careful fractional atmospheric distillation removed solvent and allowed collection of 18.0 gm (57%) clear, faintly yellow liquid, collected at 108-120 °C. 90-MHz ^1H NMR ($CDCl_3$) δ 1.5-2.8 (m). Identical to commercial product.[49]

1,1-Dichlorocyclobutane (44) - 11 gm PCl_5 (53 mmoles) was suspended in 100 ml CH_2Cl_2 and then 3.40 gm cyclobutanone (48.5 mmoles) was added. The reaction was stirred for 20 hrs. at room temperature, then 200 ml saturated Na_2CO_3(aq) was added, followed by 24 hrs. of stirring at room temperature. 200 ml water was added and the phases were separated. The organic phase was dried with anhydrous $MgSO_4$ and gravity filtered. Atmospheric distillation to remove solvent left a yellow liquid. 90-MHz ^1H NMR ($CDCl_3$) δ 1.9-2.5 (m, 2H), 2.8-3.2 (m, 4H).

1,1-Dichloro-3-ethoxycyclobutane (45) - Under argon, 20.05 gm **41** (0.18 mole), 300 ml dry CH_2Cl_2, and 37 gm PCl_5 (0.18 mole) were stirred for 11 hrs. at room temperature. 400 ml saturated Na_2CO_3(aq) was added slowly and carefully; an exotherm and gas evolution resulted. The mixture was stirred for 3 hrs. (pH aq. phase ≈9). The phases were then separated and the organic phase was dried with anhydrous $MgSO_4$ and gravity filtered. Solvent was removed by atmospheric distillation. Vacuum fractional distillation at water-aspirator pressure gave 2.75 gm (9%) clear, pale yellow liquid at 85 °C. 90-MHz ^1H NMR ($CDCl_3$) δ 1.1 (t, 3H), 2.6-3.3 (m, 4H) overlapped with 3.3 (q, 2H), 4.1 (quintet, 1H). Mass spectrum, *m/e* 29, 41, 51, 77, 87, 105, 107, 133, 135.

1-Chlorocyclopentene (46) - 17.8 gm **43** (0.13 mole) and 200 ml MeOH were mixed in a 1-l flask. 8.00 gm NaOMe (0.15 mole) was added, followed by 50 ml MeOH to wash down the sides of the flask. An exothermic reaction ensued, and the solution was stirred for 1 hr. at room temperature. 300 ml water and 250 ml pentane were added with vigorous mixing. The phases were then separated and the organic phase was dried with anhydrous $MgSO_4$ and gravity filtered. Solvent was removed by careful distillation at atmospheric pressure; further distillation gave 10.1 gm clear, colorless liquid (77%). Identical to commercial product.[49]

Bi(cyclopentenyl) (47) - 25.3 gm **46** (0.25 mole), 300 ml dry, anoxic THF, and 10 gm Mg turnings (0.41 mole) were mixed in a dry, argon-flushed 500-ml three-neck flask. The mixture was stirred at room temperature for 20 min., followed by reflux for 80 min. (0.10 ml ethyl iodide was added as an initiator). Heating was halted and 64 gm (0.34 mole) CuI was added in two portions. A self-sustaining reaction and reflux ensued for 20 min.; the solution turned green and Mg was consumed. Reflux subsided and the solution became brownish ($Cu^{(0)}$). Heat was applied and the reaction was refluxed for an hour. The mixture was then stirred at room temperature overnight. Suction filtration of the reaction mixture through Celite gave a filtrate which contained ≈54 mmoles diene (≈44%; determined by comparison of integration signal of vinylic protons *vs.* that of added benzene). 90-MHz ^1H NMR ($CDCl_3$) δ 1.3-1.7 (m, 4H), 3.2-3.6 (m, 8H), 5.3-5.6 (m, 2H).

Bi(cyclohexenyl) (48) - 22.2 gm **42** (0.19 mole), 300 ml dry, anoxic THF, 50.0 gm CuI (0.26 mole), and 8.0 gm Mg turnings (0.33 mole) were mixed in a dry, argon-flushed 1-l three-neck flask. The mixture was stirred mechanically for 20 min. at room temperature and then for 40 min. at reflux. 0.10 ml ethyl iodide was then added to initate reaction, followed by 2 hrs. reflux. The solution turned green to darker green to black. The reaction was then stirred for 44 hrs. at room temperature, getting progressively darker as time went on. 250 ml ether was added to the black mixture, followed by suction

filtration through Celite. The collected solids were washed with 50 ml ether. The filtrates were combined to give a pale yellow solution. GCMS showed two peaks: unreacted **42** and product diene in a 3.5:1 ratio. This implies a yield of 35 mmoles, 5.7 gm, of diene (37%). Mass spectrum, *m/e* 53, 79, 91, 105, 119, 133, 162.

7,8-Diaza-7,8-dicarbomethoxytricyclo[7.3.0.0^{2,6}]dodec-1-ene (49) - 9.34 gm DMAD (64 mmoles) was added to the filtrate containing **47** and the solution was stirred for 2.25 hrs. 250 ml ether was added, which caused a solid to precipitate. The solid was removed by suction filtration and was washed with ether. The combined filtrates were washed with 3 x 200 ml water and 100 ml saturated NaCl(aq). This gave a clear, bright yellow organic solution which was dried with anhydrous $MgSO_4$ and gravity filtered. Removal of solvent left 5.5 gm dark, orange-brown, viscous oil. Flash chromatography (9:1 petroleum ether : ethyl acetate, 12 cm x 10 cm) allowed isolation of 1.97 gm white solid (13%, based on 54 mmoles diene). R_f (9:1 petroleum ether : ethyl acetate) 0.08. 500-MHz ^{1}H NMR ($CDCl_3$) δ 1.2-2.5 (m, 14H), 3.65 (s)/3.75 (s) (6H, coalesces with warming). Mass spectrum, *m/e* 59, 91, 93, 134, 161, 205, 221, 280.

8,9-Diaza-8,9-dicarbomethoxytricyclo[8.4.0.0^{2,7}]tetradec-1-ene (50) - 10.25 gm DMAD (70 mmoles) was added to the filtrate containing **48** and the solution was stirred at room temperature for 5.5 hrs. 500 ml water was added, and the mixture was stirred vigorously. The phases were separated, and the organic phase was washed with 2 x 300 ml water and 100 ml saturated NaCl(aq). This left a clear, golden-yellow solution which was dried with anhydrous $MgSO_4$ and gravity filtered. Removal of volatile components left 7 gm viscous brown oil. Flash chromatography (9:1 petroleum ether : ethyl acetate, 10 cm x 10 cm) allowed isolation of 2.67 gm white solid (25%, based on 35 mmoles diene). R_f (9:1 petroleum ether : ethyl acetate) 0.08. 500-MHz ^{1}H NMR ($CDCl_3$) δ 1.1-2.0 (m, 16H), 2.65 (m, 2H), 3.7 (s, 6H). Mass spectrum, *m/e* 59, 91, 133, 161, 174, 205, 233, 249, 308.

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