

since authentic radicals like **34** add oxygen in competition with ring-opening and oxygen addition products derived from **34** are not observed.⁴⁴

Other important problems in lipid peroxidation involve the transition of model studies like those reported in this account to in vivo systems. The early reports

(44) Porter, N.; Zuraw, P. *J. Chem. Soc., Chem. Commun.* 1985, 1472.

by Corongiu²⁸ are encouraging, but the analytical problems of studying in vivo lipid peroxidation are formidable. Natural targets of lipid peroxidation are fatty esters such as phospholipids present in membranes and these compounds are complex mixtures of different phospholipid classes and molecular species. We have directed some attention to this challenging problem,²⁵ but much remains to be done.

Photoexcited States of Allyl Anions

LAREN M. TOLBERT

School of Chemistry, Georgia Institute of Technology, Atlanta, Georgia 30332

Received June 10, 1985 (Revised Manuscript Received February 20, 1986)

One of the triumphs of Hückel molecular orbital (HMO) theory has been its utility in representing the charge distribution and other ground-state properties of resonance-stabilized carbanions. Thus for odd-alternant hydrocarbon anions, the charge is localized on the odd-numbered ("starred" atoms in the Dewar formalism) and is zero on the even-numbered ("unstarred") atoms. Hückel theory predicts a considerably different charge distribution in the excited state, and we wondered if such a simple model could have any predictive power for carbanions.

One of the impediments to the development of carbanion photochemistry was recognition that it is usually

characterized by electron ejection rather than adiabatic photochemistry.¹ This propensity was certainly taken advantage of when Bunnett and others recognized that the $S_{RN}1$ reaction could be photostimulated.² However, in the absence of suitable electron acceptors, redox chemistry was the common result.

For instance, irradiation of cyclopentadienyl anion produced a reductive dimer,^{3a} irradiation of phenyllithium produced the oxidative dimer biphenyl,^{3b} and irradiation of the 3-pentanone enolate produced oxidative and reductive dimers as the major reaction products (see Figure 1),^{3c} along with a small amount of 2-pentene oxide **2**, the apparent product of cyclization/protonation. This latter product suggested that

(1) For reviews, see: (a) Tolbert, L. M. *Org. Photochem.* 1983, 6, 177. (b) Fox, M. A. *Chem. Rev.* 1979, 79, 253.

(2) For a review, see: Rossi, R. A.; de Rossi, Rita H. *Aromatic Substitution by the $S_{RN}1$ Mechanism*; ACS Monograph Series No. 178; American Chemical Society: Washington, DC, 1983.

(3) (a) van Tamelen, E.; Brauman, J. I.; Ellis, L. E. *J. Am. Chem. Soc.* 1971, 93, 6145. (b) van Tamelen, E.; Brauman, J. I.; Ellis, L. E. *Ibid.* 1967, 89, 5073. (c) van Tamelen, E.; Schwartz, J.; Brauman, J. I. *Ibid.* 1970, 92, 5798.

Laren Malcolm Tolbert was born in New Orleans, LA, in 1949, and spent his childhood in Louisiana and Brazil. After completing his undergraduate degree in Chemistry and Mathematics at Tulane University in New Orleans in 1970, he was an NSF fellow at the University of Wisconsin, obtaining his Ph. D. with Professor Howard Zimmerman in 1975. Following postdoctoral work with R. B. Woodward at Harvard University, he joined the faculty of the University of Kentucky in 1976. He received an Alfred P. Sloan fellowship in 1983 and in 1985 became Professor of Chemistry at the Georgia Institute of Technology.

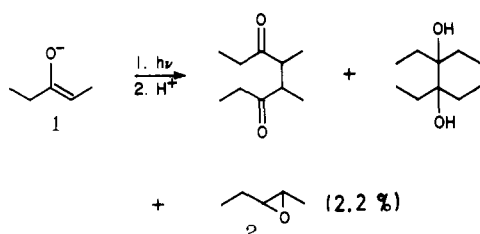


Figure 1. Pentanone enolate photolysis.

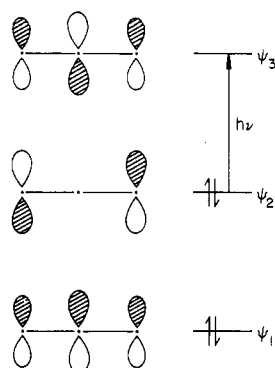


Figure 2. Allyl MO's.

we could circumvent the oxidative, radical pathway and observe adiabatic carbanion photochemistry with which we hoped to test the predictions of the Hückel and other molecular orbital theories.

Theory

The simplest resonance-stabilized carbanion, the allyl anion, has an occupied NBMO (ψ_2 , see Figure 2) in the ground state. As a consequence of the antisymmetry of this MO, the negative charge density in the ground state is localized on carbon atoms 1 and 3, in accord with qualitative resonance concepts. In the one electron description of the excited state, an electron is removed from ψ_2 and placed in ψ_3 , with a corresponding increase in charge density at atom 2 from 0.0 to -0.5 and a decrease at atoms 1 and 3 from -0.50 to -0.25 . Could such a charge distribution have photochemical consequences?

For the allyl anion, the statement that negative charge is greatest at atom 2 in the excited state requires that basicity be greater at that atom. Equivalently, the free energy of trimethylene diradical (the C-2 conjugate acid) should be lower than that of propene (the C-1 conjugate acid) in the excited state. An MC-SCF calculation confirmed this prediction,⁴ although the significance of the differing heats of formation to the basicities of the underlying conjugate base was not recognized. Thus one photochemical consequence of charge redistribution might be a photoprotonation at C-2 to yield a trimethylene diradical and thence a cyclopropane. Although experimental evidence for this pathway is sparse, the formation of the epoxide from 3-pentanone enolate photolysis^{3c} is a possible example of this phenomenon.

Primary Photochemical Processes in Carbanions. Using the allyl anion as the prototypical resonance-stabilized carbanion, we can consider what other photochemical consequences we might expect if the charge distribution is governed by occupation of the

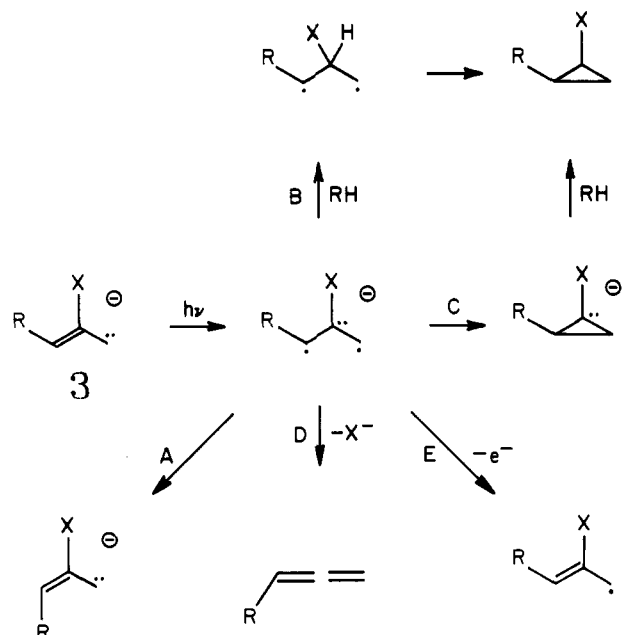


Figure 3. Reaction pathways for photoexcited allyl anions.

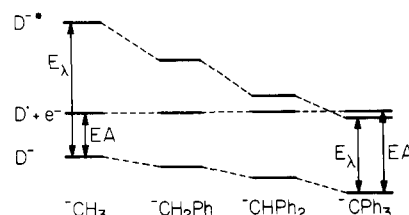


Figure 4. Effect of phenyl substitution.

symmetric antibonding MO ψ_3 . Besides increased charge density at the central carbon atom, we expect a decreased 1,2-bond order and an increased conrotatory 1,3-bond order. Thus, if we consider a prototypical allyl anion 3 tagged with a stereochemical label R and an electronic label X , we can predict several results of such charge redistribution; they will be expressed as primary photochemical processes, as illustrated in Figure 3. These are (A) $E-Z$ isomerization, (B) protonation, (C) cyclization to a cyclopropyl anion, and (D) α -bond cleavage, particularly if X is a suitable leaving group. Additionally we must contend with (E) electron ejection, (F) fluorescence, (G) radiationless decay, and (H) intersystem crossing to the triplet. It has been our continuing goal to establish examples of pathways A-D not involving photooxidation and to explore the validity of the simple Hückel model in predicting reactivity.

The formation of epoxide 3 in Brauman, Ellis, and van Tamelen's study of 3-pentanone enolate (1) (Figure 1)^{3c} occurs either by an initial protonation at C-3 (Path B) or by cyclization to the epoxide anion (Path C). However, the major products in this case are the oxidative and reductive dimers, which are apparently the products of electron transfer from enolate to parent ketone. Thus nonoxidative processes will compete only if electron transfer is minimized. An approach to this problem, which we and others have used, is to recognize that the effect of phenyl substitution on carbanionic centers is to shift absorption maxima to longer wavelengths and to increase the electron affinity of the corresponding radicals (See Figure 4). Thus inclusion of phenyl substituents into the carbanion stabilizes the excited state at the expense of the photoejected neutral

(4) (a) Bernardi, F.; Robb, M. A.; Schlegel, H. B.; Tonachini, G. *J. Am. Chem. Soc.* 1984, 106, 1198.

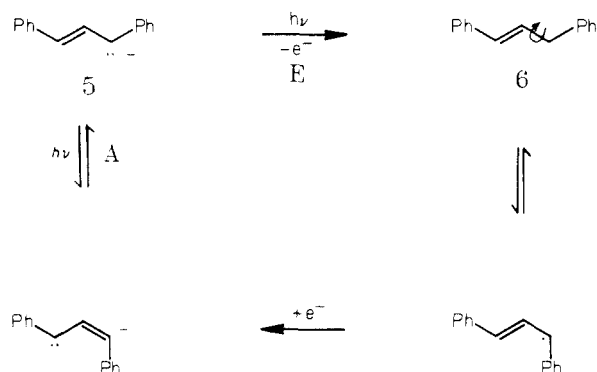


Figure 5. Pathways for diphenylallyl anion isomerizations.

(Path E) and enables the nonradical pathways to intervene.

Even with these safeguards, electron transfer remains the default primary photochemical process. For instance, irradiation of triphenylmethyl anion in dimethyl sulfoxide results in the electron-transfer-induced decomposition of solvent and formation of the products of methyl radical addition.⁵

However, for most resonance-stabilized carbanions electron transfer does not compete effectively, and we are able to examine other pathways. Moreover, although we have appealed to a model based upon the allyl anion, even with extensive substitution the symmetries of the NBMO's are maintained and the basis for predicting the reactivity in such systems remains intact. Using Figure 3 as our reaction scheme, now we consider the various decay pathways.

***E-Z* Isomerization.** 1,3-Diphenylallyl anion undergoes rapid thermal isomerization between *E,E* and *E,Z* forms at room temperature. At low temperature in tetrahydrofuran, the ground-state interconversion can be frozen out and photochemical conversion of the more stable *E,E* form to the *E,Z* conformer observed.^{6a} The mechanism of this reaction can involve two distinct pathways. One pathway involves prior photoejection (Path E) followed by rapid bond rotation in the resulting radical, a precedented and low activation energy process (see Figure 5).^{6b} A second pathway involves bond rotation during the lifetime of the excited state (Path A) and provides a decay mechanism similar to that for stilbene.

In order to distinguish between these two possibilities for a model allyl anion, we required systems for which the two pathways would result in contrasting chemistry. Our approach was based upon the premise that substituents at C-2 would have no effect on the ground-state chemistry of either the anion or the radical, since the NBMO containing the pair of electrons for the anion or single electron for the radical possesses a node at C-2. Thus photochemistry which proceeded via prior photoejection would be independent of C-2 substituent. Conversely, a bound excited state would have an electron in a symmetric antibonding orbital which would be strongly dependent upon the identity of the C-2 substituent. The parameter we chose to vary in probing the *E-Z* isomerization was the reduction potential of

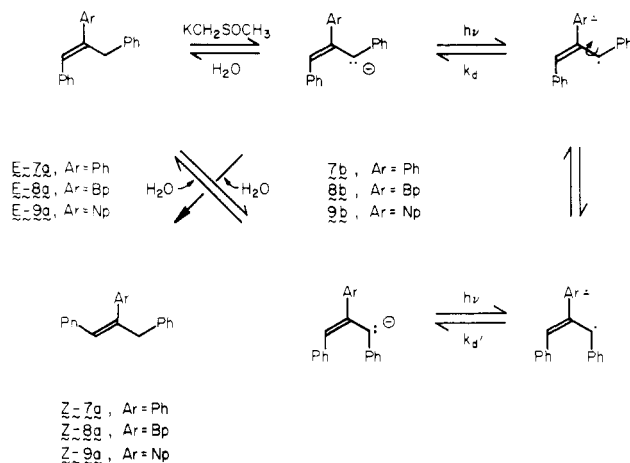


Figure 6. 2-Aryl-1,3-diphenylpropenyl isomerizations.

Table I
Properties of 2-Aryl-1,3-diphenylpropenyl Anions

property	substituent		
	phenyl	4-biphenyl	2-naphthyl
pK_a	28.9	28.8	29.2
λ_{max}	540 nm	578 nm	528 nm
δ_{C-2} (para carbon)	112 ppm	112 ppm	112 ppm
$-E_{1/2}$ (substituent)	~ 3.5 V	2.7 V	2.5 V
<i>Z/E</i> ratio			
before irradiation	0.37	0.30	0.86
after irradiation	0.40	0.82	0.36
isomerization of added <i>cis</i> -stilbene	86%	11%	8%

the substituent, using as electronic probes phenyl, 4-biphenyl, and 2-naphthyl as sterically equivalent aryl substituents in 2-aryl-1,3-diphenylpropenyl anions **7b-9b** (Figure 6).⁷ In fact, both ¹H NMR and ¹³C NMR spectra of all three anions in a variety of solvents were indistinguishable save for the resonances associated with the C-2 substituent.⁷ Moreover, the chemical shifts of atoms in the substituents were unperturbed by anion formation, indicating that the simple Hückel model placing no charge at the central atom was correct.

In contrast to the ground-state properties, excited-state properties were quite different for the three anions. Substituents that stabilized the LUMO's, 2-naphthyl and 4-biphenyl, were also effective in inducing *cis-trans* isomerization. When *cis*-stilbene was added as a probe for electron transfer [*cis*-Stilbene is known to undergo efficient isomerization in the presence of a high (negative) potential electron donor.⁸], the 2-naphthyl anion **9b** was the least effective (see Table I). These results are consistent with the description of a bound excited state stabilized by a central substituent.

Excited-State Protonation. Although changes in basicities upon photoexcitation might lead to protonation at sites of higher charge density in the excited state, evidence for protonation at such alternative sites is sparse. One example of protonation by an acid too weak to protonate in the dark is provided by irradiation of cyclononatetraene, which yields cyclization products of the intermediate cyclononatetraene.⁹ As a preliminary model, we examined the prototropic behavior of 1,3-diphenylindenyl anion **10** (Figure 7). In

(5) (a) Tolbert, L. M. *J. Am. Chem. Soc.* **1978**, *100*, 3952. (b) Tolbert, L. M. *Ibid.* **1980**, *102*, 6808.

(6) (a) Parkes, H. M.; Young, R. N. *J. Chem. Soc. Perkin Trans 2* **1978**, 249. (b) Boche, G.; Buckl, K.; Martens, D.; Schneider, D. R. *Liebigs Ann. Chem.* **1980**, 1135.

(7) Tolbert, L. M.; Ali, M. Z. *J. Org. Chem.* **1985**, *50*, 3288.

(8) Fox, M. A.; Singletary, N. J. *J. Org. Chem.* **1982**, *47*, 3412.

(9) Schwartz, J. *Chem. Commun.* **1969**, 833.

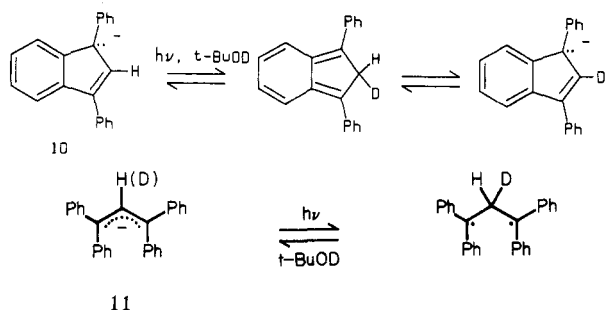


Figure 7. H/D exchange in allyl anions.

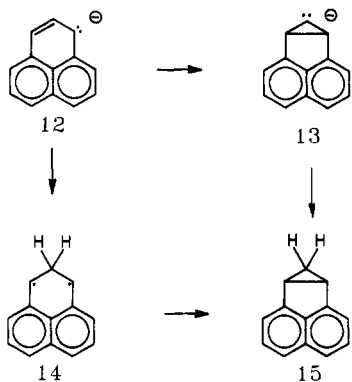


Figure 8. Photocyclization of phenalenyl anion.

deuterated *tert*-butyl alcohol, this anion does in fact undergo a facile deuterium exchange.^{10a} Similarly, 1,1,3,3-tetraphenylpropenyl anion (11) undergoes photo-promoted H/D exchange at C-2 in the presence of *t*-BuOD (Figure 7).^{10b}

An apparent example of excited-state protonation at the central atom of a "1,3-diarylallyl anion" is represented by Hunter's report of the high-yield photochemical generation of cyclopropacenaphthene **15** from the phenalenyl anion **12** in the presence of *tert*-butyl alcohol (Figure 8).^{11a} Protonation at C-2 yields the known 2H-phenalene diradical, which can rapidly cyclize to the cyclopropane. An alternative mechanism involves direct cyclization to the cyclopropyl anion **13**. However, examination of the relative energies of the phenalenyl anion and the presumed cyclopropyl anion intermediate **13** reveals that the excited state does not possess enough energy for its formation. For propenyl anion itself, calculations indicate a gas phase activation barrier of >50 kcal for the direct cyclization.^{11b} However, for a delocalized anion such as the phenalenyl anion, these numbers must be corrected for the relative pK_a 's. On the reactant side, the anion must be adjusted for the relative pK_a 's of propene (ca. 42) and phenalene (18); i.e., $1.4(42-18) = 34$ kcal. On the product side, since the sp^3 hybridized carbanionic site is not stabilized in either case, the estimated difference in pK_a 's will be approximately zero. Thus phenalenyl anion is stabilized by an additional 34 kcal, and the transition-state energy would reflect an additional fraction of that 34 kcal required for charge localization. Since the S_1 energy of phenalenyl anion is approximately 500 nm (54 kcal), there is not enough excitation energy to overcome the already high ground-state barrier of Path A.

- (10) (a) Siddiqui, S. Ph. D. Thesis, University of Kentucky, 1982. (b) Ali, M. Z. University of Kentucky, Ph.D. Thesis 1982, to be published.
 (11) (a) Hunter, D. H.; Perry, R. A. *J. Chem. Soc., Chem. Commun.* 1980, 877. (b) Dewar, M. J. S.; Nelson, D. J. *J. Org. Chem.* 1982, 47, 2614.
 (12) Baum, G.; Schechter, H. *J. Org. Chem.* 1976, 41, 2120.

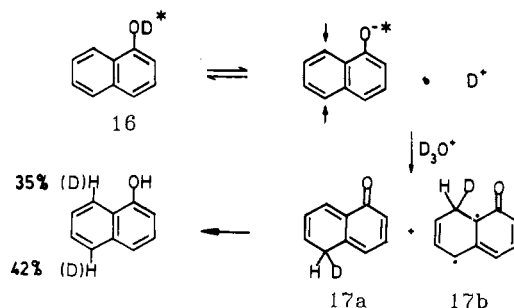


Figure 9. 1-Naphthol decay pathways.

A more startling example of protonation to give a carbon acid not readily available in the ground state is provided by the aqueous photochemistry of 1-naphthol (**16**). We were prompted by recent results of Shizuka¹³ and of J. H. Clark^{14a} to examine this process in more detail.^{14b} The presence of a radiationless proton quenching process suggested the possibility of protonation at an alternative carbon site. Since Hückel calculations, as well as Pariser-Parr-Pople calculations,¹³ predict increased electron density at C-5 and C-8 in the excited state, we examined the photoinduced deuterium exchange of 1-naphthol in aqueous acidic acetonitrile and discovered that both C-5 and C-8 undergo deuterium exchange at a nearly statistical rate, a reaction which is not observed in the ground state (Figure 9). Such H/D exchange requires the intermediacy of the novel tautomers **17a** and **17b** and suggests that photo-protonation of anions may provide an entry to new reactive intermediates.

Cyclization. Irradiation of 2-aryl-1,3-diphenylpropenyl anions conceivably could result in the formation of a cyclopropyl anion, since the substituent could stabilize an anionic center at C-2. Besides 2-phenyl-, 2-(4-biphenyl)-, and 2-(2-naphthyl)-,⁷ we irradiated 2-(4-chlorophenyl)- and 2-(4-cyanophenyl)-1,3-diphenylpropenyl anions, as well as the antiaromatic 7-phenyl-2:3,4:5-dibenzocycloheptatrienyl anion.¹⁵ In none of the photochemical mixtures were cyclopropane products observed, even when proton sources for fast protonation of intermediate cyclopropyl anions were employed. Cyclopropane formation was also not observed in a number of systems investigated by Fox.¹⁶ Thus the energetic cost of "charge localization" makes cyclization for resonance-stabilized allyl anions non-competitive.

To the extent than an ion-pairing solvent can stabilize a localized charge better than a delocalized one, the effect of charge localization can be minimized. In the limit, when the anion-counterion bond becomes covalent, one can expect such reactions to occur. In fact, an allyl "anion", cinnamylmagnesium bromide, is known to undergo exactly this cyclization.¹⁷

Bond Cleavage. When a photoexcited carbanion contains, next to the site of increased negative charge, a nucleofuge such as a halogen, bond heterolysis can

(13) Tsutsumi, K.; Shizuka, H. *Z. Phys. Chem. (Wiesbaden)* 1980, 122, 129.

(14) (a) Webb, S. P.; Yeh, S. W.; Philips, L. A.; Tolbert, M. A.; Clark, J. H. *J. Am. Chem. Soc.* 1984, 106, 7286. (b) Webb, S. P.; Phillips, L. A.; Yeh, S. W.; Tolbert, L. M.; Clark, J. H. *J. Phys. Chem.*, submitted for publication.

(15) Tolbert, L. M.; Ali, M. Z. *J. Org. Chem.* 1982, 47, 4793.

(16) Fox, M. A.; Chen, C.-C.; Campbell, K. A. *J. Org. Chem.* 1983, 48, 321.

(17) Cohen, S.; Yogev, A. *J. Am. Chem. Soc.* 1976, 98, 2013.

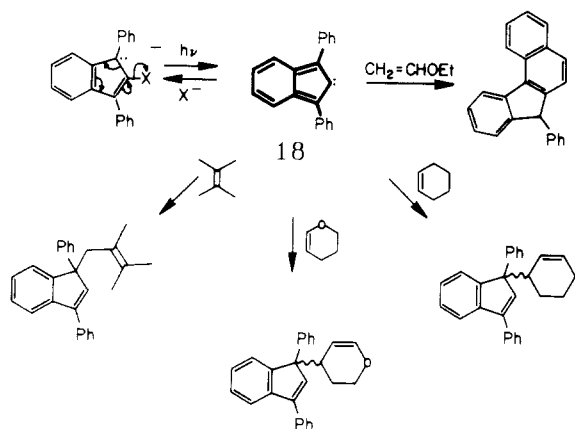


Figure 10. Photolysis of 2-chloro-1,3-diphenylindenyl anion.

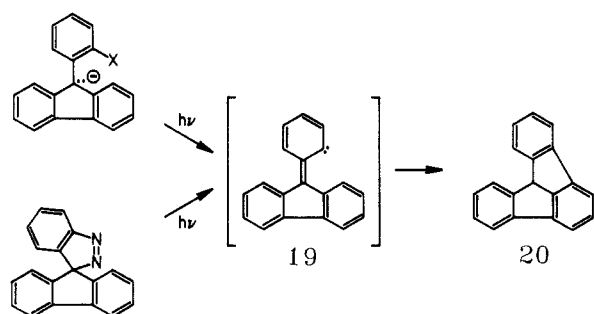
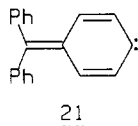


Figure 11. Photolysis of 9-(2-chlorophenyl)fluorenyl anion.

result in a process similar to α -cleavage of α -halocarbanions. For instance, the thermally stable 2-chloro-1,3-diphenylindenyl anion undergoes facile dehalogenation to yield 1,3-diphenylisoindenylidene 18, which undergoes a variety of addition reactions in the presence of olefins (Figure 10).¹⁸ Irradiation of 9-(2-chlorophenyl)fluorenyl anion¹⁹ produces 6-fluorenylidene-cyclohexadienylidene 19 in much higher yields than the more conventional low-yield approach involving pyrolysis of spiro[fluorene-9,3'-indazole]¹² (Figure 11). Similarly, (4-chlorophenyl)diphenylmethyl anion produces 4-diphenylmethylenecyclohexadienylidene (21).¹⁰



Although our primary concern here is the study of anionic excited states, we emphasize that this photochemical approach provides a facile entry into a number of reactive intermediates and products. This process presents an especially appealing alternative to irradiation of the corresponding azoalkanes, which are not always available by synthesis, and provides higher yields in many cases. An example is provided by the work of Guyon, Boule, and Lemaire, who observed the formation of a carbene 23 from irradiation of 2-chlorophenolate anion (22) (Figure 12).²⁰

Other reactive intermediates can also be generated. For the excited state of 2-(4-chlorophenyl)-1,3-di-

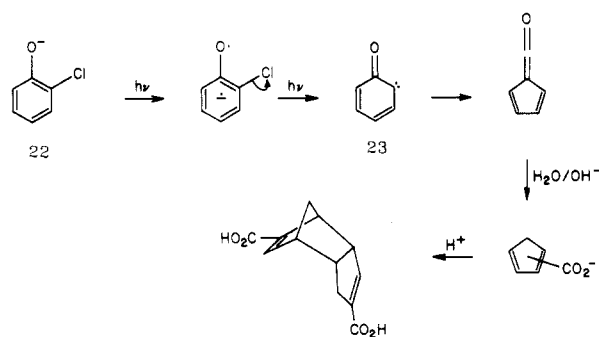


Figure 12. Photolysis of *o*-chlorophenolate anion.

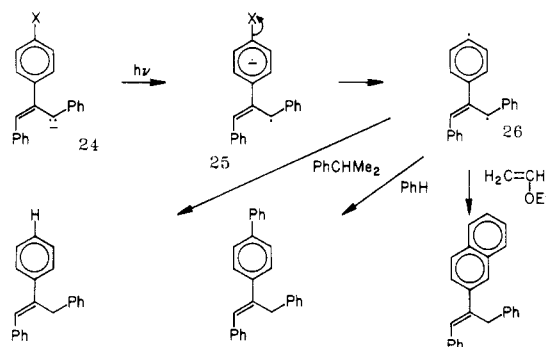


Figure 13. Photolysis of 2-(4-chlorophenyl)-1,3-diphenylpropenyl anion.

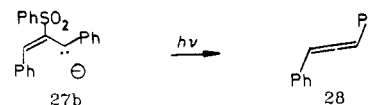


Figure 14. Allene formation by photocleavage.

phenylpropenyl anion 24, charge is redistributed into the C-2 substituent. The resulting bond cleavage yields a hypovalent intermediate 26 which forms unusual addition products to olefins (Figure 13).^{10b}

Finally, 1,3-diphenyl-2-phenylsulfenylpropenyl anion 27a or the phenylsulfonylethyl anion 27b undergoes facile photopromoted elimination to yield 1,3-diphenylallene (28, Figure 14).¹³ Use of this technique to produce strained allenes is currently under investigation.

Photophysical Properties. Our main thesis has been that the photoreactivity of carbanions can be rationalized by an appeal to the way in which charge is distributed in the excited state. In part, the behavior of carbanions under irradiation is revealed by processes that lead to no permanent photochemistry but rather show up in absorptive and emissive properties. For carbanions, particularly important are the effects of counterions. To the extent that charge is redistributed in the excited state, there should be an appreciable decrease in ion pairing upon photoexcitation. For instance, the charge in triphenylmethyl anion is localized predominantly at the central carbon in the ground state but it is delocalized into the phenyl rings in the excited state. There should be, therefore, a weaker electrostatic attraction between the counterion and the central carbon in the excited state. This is exactly what is observed spectroscopically for this and similar anions in ion pairing solvents.^{21,22}

(18) (a) Tolbert, L. M.; Siddiqui, S. *J. Am. Chem. Soc.* **1982**, *104*, 4273. (b) Tolbert, L. M.; Siddiqui, S. *Ibid.* **1984**, *106*, 5538.

(19) Tolbert, L. M.; Ali, M. *Z. Abstracts of Papers*, 184th National Meeting of the American Chemical Society, Kansas City; American Chemical Society Washington, DC, 1982; ORGN 42.

(20) Guyon, C.; Boule, P.; Lemaire, J. *Tetrahedron Lett.* **1982**, 1581.

(21) (a) Hogen-Esch, T. E.; Plodinec, J. *J. Am. Chem. Soc.* **1978**, *100*, 7633.

(22) Fox, M. A.; Voynick, T. *Tetrahedron Lett.* **1980**, 3943.

Table II
Excited-state Lifetimes of 9-Arylfluorenyl Anions in Me₂SO

aryl substituent	Hammett σ constant	τ (ns)
<i>p</i> -MeO	-0.27	26.4
<i>p</i> - <i>t</i> -Bu	-0.20	38.8
<i>p</i> -Me	-0.17	38.8
<i>m</i> -Me	-0.07	42.0
H	0.00	44.0
<i>m</i> -MeO	0.12	45.4
<i>p</i> -Cl	0.23	42.7
<i>m</i> -Cl	0.37	39.3

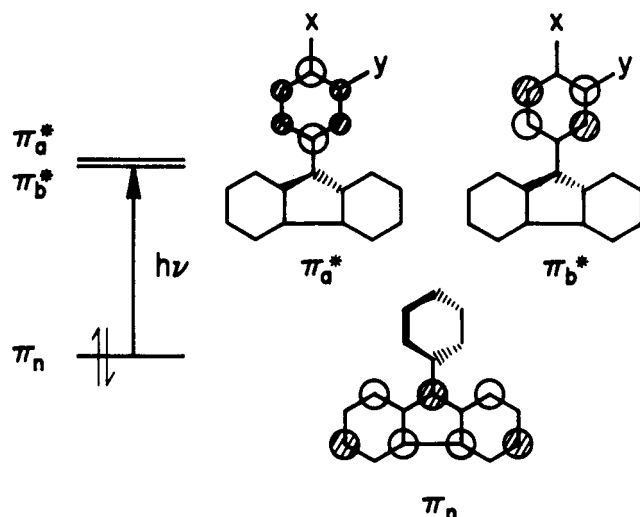


Figure 15. MO's for 9-arylfluorenyl anions.

For solvents in which ions are solvent-separated, counterion effects will be minimal. In fact, we have failed to detect any counterion effects in Me₂SO, which is known to accommodate solvent-separated carbanions. For instance, the excited state decay rate or fluorescence quantum yield of 9-arylfluorenyl anions is unaffected by addition of 10-fold excesses of lithium, potassium, or sodium chloride. Rather, the excited-state lifetime is a function of the substituents on the 9-aryl group (see Table II).²³ Substituents that are para-donating or meta-withdrawing decrease the excited state lifetime. MNDO calculations confirm that the nature of the excited state is charge transfer from C-9 to the perpendicular aryl ring, which contains two degenerate lowest unoccupied molecular orbitals (LUMOs), π_a^* and π_b^* (see Figure 15). A para-donating or meta-withdrawing group lowers the energy of π_b^* relative to π_a^* . Since the symmetry of π_b^* matches that of one of the subjacent orbitals, we postulate that the resulting coupling leads to a more efficient excited state decay.

Applications to Neutral Molecule Photochemistry

For the reasons we have previously stated, cyclization of an allyl anion as a primary process apparently only occurs when the counterion (i.e., magnesium) forms a highly covalent bond. This reaction is, in fact, an example of a photochemical 1,2-migration on an allyl

(23) Tolbert, L. M.; Raya, Narciso, unpublished results.

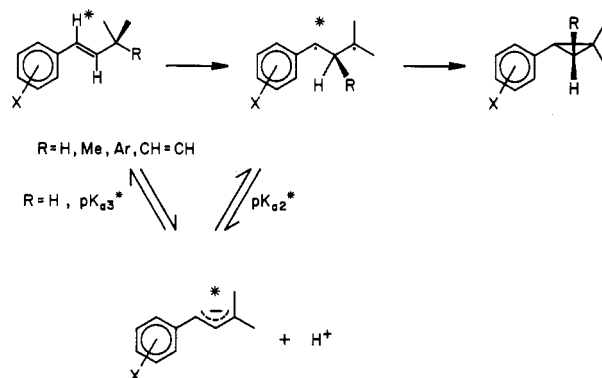


Figure 16. 1,2-Sigmatropic migration on allyl system.

system, one of the most ubiquitous of photochemical reactions (see Figure 16). One might ask if there is a relationship between formation of a trimethylene diradical by a 1,2-sigmatropic shift and by protonation of an allyl anion. We believe there is.

For the prototypical hydrogen atom migration for 1-phenylpropene (Figure 16, R = H) in the excited state,²⁴ we consider the anion produced by deprotonation. Again, because of charge redistribution in the anion, an increased basicity at C-2 with a decreased basicity at C-1 results. Thus proton shift from C-3 to C-2 in the excited state is an exothermic process. The relevance of the anion MO's to hydrogen migration in an allyl system, for which formal negative charge never develops, is as follows: We have created a cycle using equilibrium pK_a^* 's which, since it is a thermodynamic cycle, is independent of mechanism. Thus a knowledge of the way charge distributes in a conjugate base provides a predictive tool for evaluating reactivity in neutral systems.

Concluding Remarks

Provided that certain precautions are taken to avoid electron ejection as a mechanistic pathway, the photochemistry of carbanions can be rationalized by an appeal to the Hückel molecular orbitals. That such an appeal succeeds is gratifying, given the lack of suitable advanced molecular orbital techniques; it implies that charge distribution in odd-alternant hydrocarbon anions is a less subtle function of the calculational technique. Of course, for more complex systems more sophisticated calculational techniques are in order, and we are now investigating those. Ironically, understanding the way in which charge is distributed in carbanion excited states helps in the understanding of neutral photochemistry in a straightforward fashion, and the calculated⁴ exothermicity of photopromoted 1,2-proton shifts becomes less startling than it seems.

Support of this research by the National Science Foundation, by the U. S. Department of Energy Office of Basic Energy Sciences, and by the Alfred P. Sloan Foundation is gratefully acknowledged.

(24) (a) Griffin, G. W.; Marcantonio, A. F.; Kristinsson, H.; Petterson, R. C.; Irving, C. S. *Tetrahedron Lett.* **1965**, 2952. (b) Hixson, S. S.; Ruede, P., unpublished results. (c) Ruede, P. Ph. D. Thesis, University of Massachusetts, 1982.