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Photochemistry of Some Allenic Counterparts of Cyclohexenones and 2,5-Cyclohexadienones[1]

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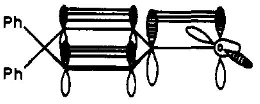
Abstract: Allenic analogs of 4,4-diphenylcyclohexenone and a similar counterpart of 4,4-diphenyl-2,5-cyclohexadienone were synthesized. These molecules have a 2-electron π-MO perpendicular to the six-ring π-system. This perpendicular π-orbital is analogous to the oxygen p_y orbital which is orthogonal to the carbonyl π-bond. The photochemistry of the allenic systems was explored with the finding that the triplets were unreactive and the singlets underwent a phenyl migration to form bicyclic photoproducts whose structures were established by spectral means, degradation, and independent synthesis. Excited states involving appreciable out-of-plane to π or π to out-of-plane excitations are defined as π–$\perp^*$ and $\perp$-π^*, respectively. MNDO-CI level and CASSCF ab initio computations with geometry optimization were carried out with the objective of determining the role of $\perp$-π^* and π-$\perp^*$ transitions and for comparison with the experimental results.

Introduction

In our previous investigations we have reported the rearrangement of a variety of 4,4-disubstituted cyclohexenones[2] and 2,5-cyclohexadienones.[3] The former were shown to proceed by a γ- to β-carbon aryl migration while the latter were shown to react with β–β-bonding in what we termed a type A rearrangement. The majority of these rearrangements have been shown to proceed by n–π^* excited states.[2,3] One intriguing idea was the construction of all-carbon analogs in which the p_y (i.e., "n") orbital of the oxygen was replaced by the orthogonal π-orbital (i.e., $\perp$ orbital) of an allenic bond. For this study we selected ketone analogs having a simple dimethylallenyl moiety. The similarity in electronic configuration is seen in structure **1**, which is pseudoisoconjugate with **2**.



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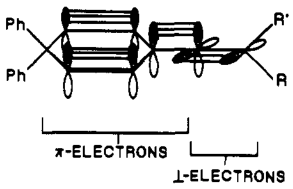

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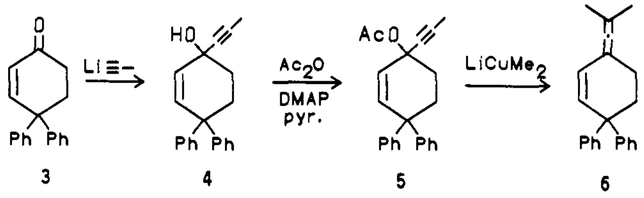
Results

Synthesis of Allenic Photochemical Reactants and Potential Photoproducts. The initial problem posed was the synthesis of the desired photochemical reactants. We began with the preparation of dimethyl ene allene **6**. Equation 1 outlines the approach



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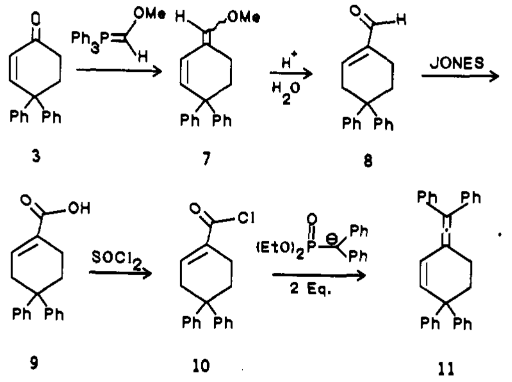
employed. The dimethyl cuprate conversion of propargyl acetates to allenes[4] provided a particularly convenient final step in the synthesis of this photoreactant.

Scheme I. Synthesis of Diphenyl Ene Allene **11**



Another allenic system of interest was the diphenyl ene allene **11**, which is closely related to the 4,4-diphenylcyclohexenone **3** whose photochemistry we have previous studied exhaustively.[2] The synthesis employed for the dimethyl counterpart **6** proved unsatisfactory for this allene, since the similar diphenylcuprate reaction with the appropriate propargyl acetate proceeded only in low yield. A more satisfactory approach is outlined in Scheme I. One interesting facet of the synthesis was the reaction of the unsaturated enol ether **7** to give the conjugated aldehyde **8**. Although kinetic protonation of dienols is known[5] to afford kinetically the β,γ-unsaturated carbonyl product over a wide pH

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(1) (a) This is publication 228 of our general series and 165 of our photochemical publications. (b) For photochemical publication 164 see: Zimmerman, H. E.; Wright, C. W. *J. Am. Chem. Soc.* **1992**, *114*, 6603-6613.

(2) (a) Zimmerman, H. E.; Wilson, J. W. *J. Am. Chem. Soc.* **1964**, *86*, 4036-4042. (b) Zimmerman, H. E.; Hancock, K. G. *J. Am. Chem. Soc.* **1968**, *90*, 3749-3760. (c) Zimmerman, H. E.; Samuelson, G. *J. Am. Chem. Soc.* **1969**, *91*, 5307-5318. (d) Zimmerman, H. E.; King, R. K.; Xu, J.-H.; Caufield, C. E. *J. Am. Chem. Soc.* **1985**, *107*, 7724-7732. (e) Zimmerman, H. E.; King, R. K.; Xu, J.-H.; Caufield, C. E. *J. Am. Chem. Soc.* **1985**, *107*, 7732-7744. (f) Zimmerman, H. E.; Solomon, R. D. *J. Am. Chem. Soc.* **1986**, *108*, 6279-6289. (g) Zimmerman, H. E.; Weber, A. M. *J. Am. Chem. Soc.* **1989**, *111*, 995-1007. (h) Zimmerman, H. E.; St.Clair, J. D. *J. Org. Chem.* **1989**, *54*, 2125-2137.

(3) (a) Zimmerman, H. E.; Schuster, D. I. *J. Am. Chem. Soc.* **1962**, *84*, 4527-4540. (b) Zimmerman, H. E.; Hackett, P.; Juers, D. F.; McCall, J. M.; Schröder, B. *J. Am. Chem. Soc.* **1971**, *93*, 3653-3662. (c) Zimmerman, H. E.; Jones, G., II. *J. Am. Chem. Soc.* **1970**, *92*, 2753-2761. (d) Zimmerman, H. E.; Keck, G. E.; Pflederer, J. L. *J. Am. Chem. Soc.* **1976**, *98*, 5574-5581. (e) Zimmerman, H. E.; Pasteris, R. J. *J. Org. Chem.* **1980**, *45*, 4864-4875. (f) Zimmerman, H. E.; Lynch, D. C. *J. Am. Chem. Soc.* **1985**, *107*, 7745-7756. (g) Zimmerman, H. E.; Lamers, P. H. *J. Org. Chem.* **1989**, *54*, 5788-5804.

(4) Rona, P.; Crabbe, P. *J. Am. Chem. Soc.* **1968**, *91*, 3289-3292.

(5) (a) Zimmerman, H. E. In *Molecular Rearrangements*; DeMayo, P., Ed.; Interscience: New York, 1963; Chapter 6, pp 345-406. (b) Paufler, R. M. Ph.D. Thesis, Northwestern University, 1960. (c) Malhatra, S. K.; Ringold, H. J. *J. Am. Chem. Soc.* **1965**, *87*, 3228-3236.

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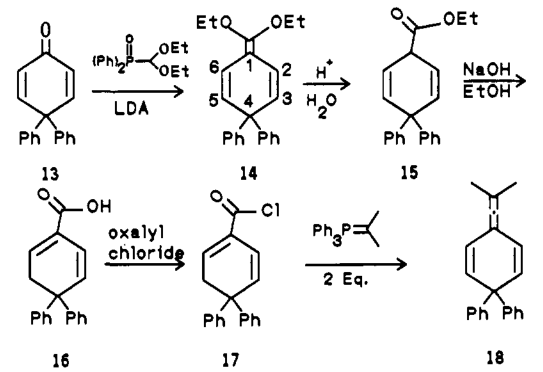
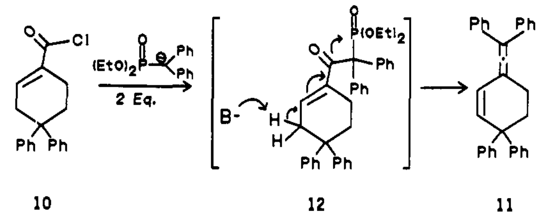
Scheme II. Synthesis of Dimethyl Diene Allene **18**



range via the enolate, dienyl enol ethers protonate kinetically at the diene terminus.[5b] Thus, although **8** is the thermodynamic product, it must result from kinetic control.

One novel synthetic step is the conversion of the unsaturated acid chloride **10** to tetraphenylallene **11**. The closest precedent is the work of Bestmann[6] in which saturated acid chlorides were converted to allenes using the more traditional Wittig reagents. In the present instance, the reaction of diethyl (diphenylmethyl)phosphonate with the unsaturated acid chloride **10** proceeded by a mechanism in which the vinylogous proton is abstracted from the acylated phosphonate **12**, as in eq 2.[7]

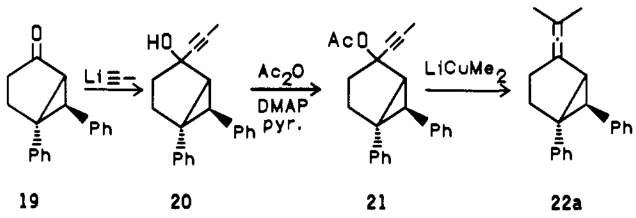


(2)

For preparation of the dimethyl diene allene **18** an alternative approach was required due to facile aromatization of the corresponding diene aldehyde (i.e., dehydro-**8**). This approach is outlined in Scheme II.

This approach began with the reaction of diphenyl(diethoxymethyl)phosphine oxide with 4,4-diphenylcyclohexadienone (**13**) to afford ketene acetal **14**; this reaction is patterned after the general method of van Der Gen.[8] Interestingly, mild acidic hydrolysis of the acetal led to the unconjugated ester **15**. That this was a kinetic phenomenon was indicated by the observation of conjugation under mildly acidic conditions when monitored by NMR. It seems likely that the steric repulsions due to coplanarity of the ethoxyl oxygens of the ketene acetal with the proximate vinyl C-2 and C-6 hydrogens[9] are not relieved in the cation resulting from protonation at the terminus of the conjugated system (i.e., at C-3 or C-5). In contrast, protonation at C-1 pyramidalizes this carbon permitting it to move out of the six-ring plane and also permits twisting of the diethoxy carbon, thus further relieving the steric strain. Commonly, conjugated enol ethers protonate at the end of the conjugated system to afford maximum resonance delocalization,[5b] but in this case the steric effect must dominate. The final step of the synthesis in Scheme II utilized the general method of Bestmann[6] cited above.

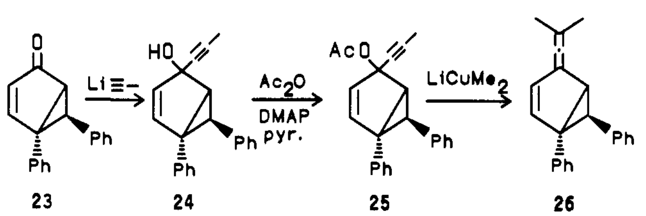
In the case of the dimethyl ene allene **6** one potential photoproduct (i.e., **22**) was synthesized as described in eq 3. The philosophy of this synthesis was akin to that employed for the



(3)

allenic photochemical reactant **6**. In this synthesis the reactant trans bicyclic ketone **19** was readily available from the known photochemistry of 4,4-diphenylcyclohexenone.[2a,b] One concern in this synthesis was potential three-membered ring opening resulting from electron transfer to the propargyl allylic tertiary acetates (e.g., **21** in eq 3). This was not encountered, and the ethynyl acetates reacted to afford allenic product in high yields (70–80%). Similarly, possible methyl introduction at alternative, allylic positions was not a problem.[10a] Despite the likelihood of an electron-transfer mechanism[10b] giving a delocalized radical intermediate, no cyclopropyl ring opening is observed.

A related synthesis derived from the known 5,6-diphenylbicyclo[3.1.0]hex-3-ene-2-one (**23**)[11] is outlined in eq 4. This, too, proceeded without the potential complications cited above.



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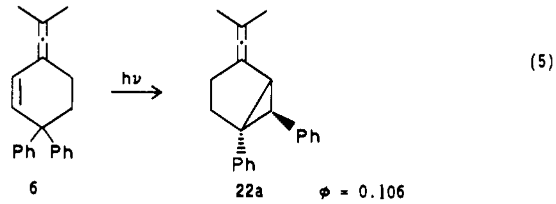
Photochemistry of an Allenic Analog of an Enone: The Dimethyl Ene Allene 6. The photochemistry began with irradiation of the dimethyl ene allene **6**. Preparative photolysis of this allene afforded a single, isomeric photoproduct which proved identical to the independently synthesized (vide supra) bicyclic allene **22a**. The reaction proceeded in a 61% yield (94% based on unrecovered reactant). The rearrangement is shown in eq 5. The reaction



(5)

was completely diastereoselective. Absence of the cis stereoisomer **22b** was demonstrated by comparison of the NMR spectrum after photolysis with the spectrum of independently synthesized[12] *cis*-dimethylallene **22b**. A quantum yield was determined for the reaction using the Black Box apparatus[13] and a nickel–copper–bismuth filter solution designed to give a maximum at 285 nm and a range of 250–325 nm. This was used along with an electronic actinometer.[14] The quantum yield is given in eq 5.

Photochemistry of a Second Allenic Analog of an Enone, Tetraphenylallene 11. It was of interest to determine the photochemical course of an allene in which the lower energy chromophore resided in the perpendicular (i.e., ⊥) π system rather

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[6] Bestmann, H. J.; Hartung, H. *Chem. Ber.* **1965**, *98*, 1198–1207.

[7] An alternative mechanism involving initial proton loss to afford the corresponding unsaturated ketene and subsequent reaction of the ketene with the phosphonate cannot totally be excluded.

[8] Schaik, T. A. M.; Henzen, A. V. van der Gen, A. *Tetrahedron Lett.* **1983**, *24*, 1303–1306.

[9] (a) Technically, this is an example of $A^{(1,3)}$ strain.[9b,c] (b) Johnson, F. *J. Am. Chem. Soc.* **1965**, *87*, 5492–5493. (c) Johnson, F. *J. Am. Chem. Soc.* **1965**, *76*, 5513–5514.

[10] (a) Brinkmeyer, R. S.; Macdonald, T. L.; Reagan, D. R. *J. Org. Chem.* **1980**, *45*, 4740–4747. (b) Cope, A. C.; Holmes, H. L.; House, H. O. *Org. Reactions* **1957**, *9*, 107–331.

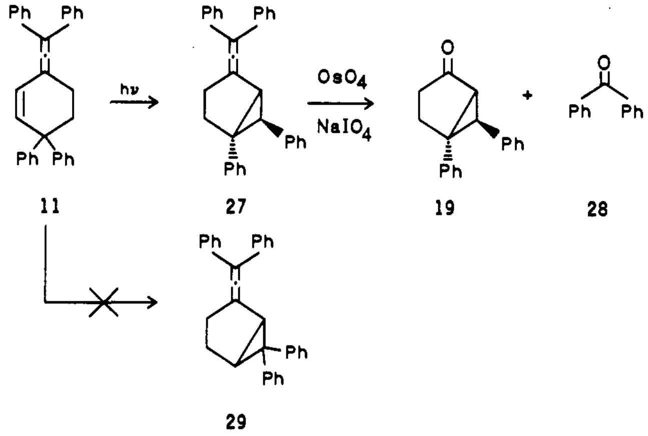
[11] Zimmerman, H. E.; Diehl, D. R. *J. Am. Chem. Soc.* **1979**, *101*, 1841–1857.

[12] Morrisey, M. Senior Honors Thesis, University of Wisconsin—Madison, 1982.

[13] Zimmerman, H. E. *Mol. Photochem.* **1971**, *3*, 281–292.

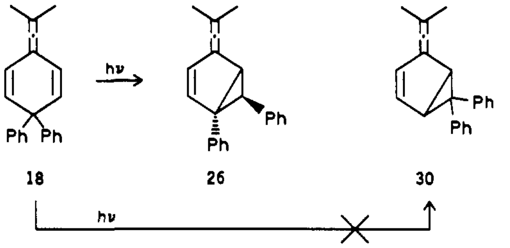
[14] Zimmerman, H. E.; Cutler, T. P.; Fitzgerald, V. R.; Weight, T. J. *Mol. Photochem.* **1977**, *8*, 379–385. (b) Carroll, F. A.; Quina, F. H. *J. Am. Chem. Soc.* **1972**, *94*, 6246–6247.

than the six-ring π-moiety. It was for this purpose that the tetraphenylallene **11** was selected. Irradiation of this compound led to exclusive formation of an isomeric tetraphenylallene. A priori, two structures were considered for the photoproduct—one arising from a C-4 to C-3 phenyl migration to afford bicyclic allene **27**, and the other deriving from a type A rearrangement to afford the isomeric allene **29**. The possibility for a type A rearrangement was suggested by our earlier study of 1-(diphenylmethylene)-4,4-diphenylcyclohexa-2,5-diene.[11] However, oxidative degradation as in eq 6 led to the known *trans*-5,6-diphenylbicyclo[3.1.0]hexan-2-one (**19**) confirming that the reaction had proceeded by the phenyl migration mechanism.



(6)

Photochemistry of an Allenic Analog of a 2,5-Cyclohexadienone. Irradiation of dimethyl diene allene **18** led to a single photoproduct. Again, two a priori photoproducts were possibilities, that arising from phenyl migration to afford the 5,6-diphenylbicyclic allene **26** or the 6,6-diphenylbicyclic allene **30** which would arise from a type A rearrangement. The reaction course was found to arise from phenyl migration by comparison of the photoproduct with the previously synthesized (vide supra) 5,6-diphenylbicyclic allene **26**. The photochemistry is depicted in eq 7.



(7)

Theoretical Considerations: Computations. The excited-state behavior of the allenes under discussion was studied from two directions. The experimental approach has been delineated above. It seemed appropriate to determine what excited-state behavior might be predicted theoretically. To this end, MNDO-CI[15] and ab initio computations were carried out for S_1. In the case of the MNDO-CI calculations, three bonding MO's and two antibonding MO's were included (i.e., in the "active space"). For the ab initio calculations GAUSSIAN90[16] was employed with CASSCF[17] with two bonding and two antibonding MO's and an STO-3G basis set. In both the MNDO and the ab initio computations, geometry optimization was carried out. Interestingly, the MNDO-CI calculations led to an energy minimum at nearly linear allenic geometry while the GAUSSIAN90-CASSCF computations led to a bent geometry. The energies are given in Table I. Further computational details are in the Experimental Section.

Table I. Calculated Energies of Allene S_1

molecule[a]	calcn type	C=C=C angle	S_1 energy[b]
dimethyl ene allene **6**	MNDO-CI[c]	179.4434	73.2305[d]
diphenyl ene allene **11**	MNDO-CI[c]	162.3274	94.4439[d]
dimethyl diene allene **18**	MNDO-CI[c]	179.9720	155.3789[d]
dimethyl diene allene **18**	MNDO-CI	118.4220	170.7888[d]
dimethyl diene allene **18**	G-90 CASSCF	115.0987	−380.8313[e]
dimethyl diene allene **18**	G-90 CASSCF	176.9760	−380.7457[e]

[a] The phenyls on C-4 were removed to conserve calculation time. [b] MNDO energies are heats of formation while GAUSSIAN90 energies are total electronic energies and so are not comparable. [c] Geometry optimization was begun with linear allenic bonds, and second minima were not encountered. [d] Energy is given in kcal/mol. [e] Energy is given in hartrees.

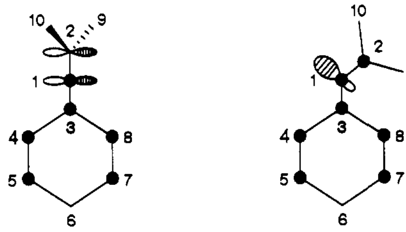
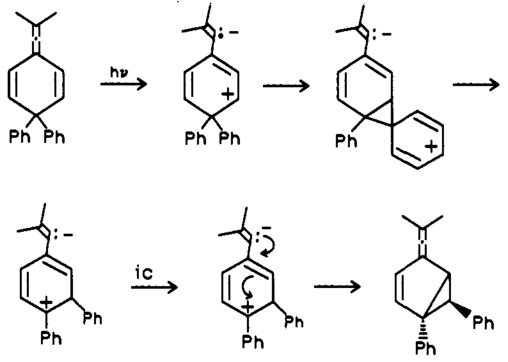


Figure 1. Linear and bent excited states of dimethyl diene allene **18**.

Scheme III. Mechanism of Rearrangement of the Dimethyl Diene Allene **18**



Interpretative Discussion

The rearrangements observed for the three allenic systems studied all involve a C-4 to C-3 phenyl migration. Particularly in the case of the dimethyl diene allene **18**, an a priori possibility existed for a type A rearrangement, so characteristic of 2,5-cyclohexadienones. This, however, did not occur as indicated in eq 7. Furthermore, the phenyl migration mechanism applies equally well to the noncross-conjugated allenic systems **6** and **11**.

The mechanism followed is formally similar to that encountered in our earlier studies with the 1-methylene-4,4-diphenylcyclohexa-2,5-diene **34** which is cross-conjugated in a fashion similar to that of the presently studied dimethyl diene allene **18**.[3b] This rearrangement is structurally and electronically different from the type A rearrangement encountered for 1-(2,2-diphenylmethylene)-4,4-diphenylcyclohexa-2,5-diene (**35**).[11] The two alternative rearrangements in eqs 6 and 7 are seen to proceed via the reaction mechanism shown in Scheme III. In this context, we note that the polarization depicted in Scheme III is the inverse of that of typical n–π^* reactions but in accord with our calculations and those of the literature (vide infra).

Theoretical Aspects of the Photochemistry. With the experimentally observed rearrangements in hand, it is of interest to look at the theoretical results deriving from the MNDO-CI[15] calcu-

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(15) (a) QCPE Program No. 455, Quantum Chemistry Program Exchange, Indiana University. Stewart, J. J.; Seiler, F. J. *QCPE Bull.* **1985**, *5*, 133–144. (b) Dewar, M. J. S.; Thiel, W. *J. Am. Chem. Soc.* **1977**, *99*, 4899–4912.

(16) *Gaussian 90*; Frisch, M. J.; Head-Gordon, M.; Trucks, G. W.; Foresman, J. B.; Schlegel, H. B.; Raghavachari, K.; Robb, M. A.; Binkley, J. S.; Gonzales, C.; Defrees, D. J.; Fox, D. J.; Whiteside, R. A.; Seeger, R.; Melins, C. F.; Baker, J.; Martin, R. L.; Kahn, L. R.; Stewart, J. J. P.; Topial, S.; Pople, J. A., Gaussian, Inc., Pittsburgh, PA, 1990.

(17) (a) Hegerty, D.; Robb, M. A. *Mol. Phys.* **1979**, *38*, 1795–1812. (b) Eade, R. E.; Robb, M. A. *Chem. Phys. Lett.* **1981**, *83*, 362–368.

lations and the GAUSSIAN90[16] SCF and CASSCF[16,17] calculations. The most reliable results are likely to result from GAUSSIAN90 CASSCF which shows S_1 of the allene to be bent as shown in Figure 1. In contrast, MNDO-CI computations led to an energy minimum for S_1 with a linear geometry. This result, too, is included in Figure 1.

Interestingly, both the MNDO-CI and the CASSCF computations located two minima, corresponding to the linear and the bent geometries. However, in the MNDO-CI case, the linear geometry was lower in energy while the CASSCF found the bent geometry to be lower.

These results are reminiscent of and consistent with those of Johnson[18] dealing with allene itself, where a 102° valence angle was found along with planarity of the remaining system. Additionally, Johnson found a local minimum with a linear geometry. Thus, S_1 of the parent allene has minima corresponding to the more complex molecule presently studied.

The Weinhold NBO analysis[19] proved most useful in interpreting the nature of the S_1 excited state. This analysis gave reasonable p-orbital weighted bond orders C-4–C-5 and C-7–C-8 and thus π-bonds between atoms 4 and 5 as well as between atoms 7 and 8. The lone-pair hybrid on atom 1 was close to s^3p^2 hybridized and is populated by somewhat less than two electrons. Three parallel p-orbitals were found at C-1, C-2, and C-3, forming an allylic system. The p-orbital at C-1 was especially electron deficient with a density of 0.4822. Thus, the three atoms—C-1, C-2, C-3—have a structure reminiscent of an allylic system with a carbenoid carbon at C-1.

The conclusion from this analysis is that in S_1 an electron has been promoted from a π molecular orbital to a nearly in-plane, heavily s-weighted hybrid at the center (i.e., at C-1) of the original allenic moiety. In the process, molecular relaxation leads to bending of the allenic system. Additionally, the p-orbital at C-1 is left particularly electron deficient. The remaining portion of the π-system is slightly electron deficient. For example, the π-electron densities at C-5 and C-7, analogous to the β-atoms of a cyclohexadienone, are 0.9488 and 0.9353, respectively. In this, we note that the nonequivalence of the two β-electron densities derives from the bent nature of the allenic moiety and the resulting lack of molecular symmetry.

Another facet of the excited state is the bond order between carbons 5 and 7. This corresponds to the β,β-bond order of cyclohexadienone photochemistry. In the cyclohexadienone n–π^* triplet, this bond order was positive and accounted for the occurrence of the type A rearrangement. However, in the π–$\perp^*$ allene photochemistry presently under study, the NBO analysis revealed this bond order to be slightly negative (i.e., antibonding). Hence, it is understandable that the rearrangement occurred by phenyl migration rather than the type A process.

Throughout, the triplet excited states were completely unreactive. This can be understood on the basis of the "free rotor effect" we have discussed in connection with the energy dissipation process available to systems with nonconstrained π-systems and the twisting known for allenic triplets.

In Figure 1 we have included the geometry of the dimethyl diene allene **18**, as calculated by GAUSSIAN90-CASSCF STO-3G for the excited singlet. The vertical excited state obtained initially on excitation will have the same geometry as ground state and will bend as a result of molecular relaxation. The interesting point is that excitation may be intepreted as involving a π to $\perp^*$ transition, since a π-system electron is promoted to an incipient s^3p^2-hybrid. The molecular relaxation involves bending of the allenic moiety and twisting as well to bring the methyl groups into planarity.

Conclusion. Photochemical rearrangements of allenic systems analogs of cyclohexenones and cyclohexadienones exhibit phenyl migration rather than the type A rearrangement. The excited state involves π–$\perp^*$ excitation in a process which is reminiscent but the inverse of the well-known n–π^* transition.

Experimental Section

General Procedures. Melting points were determined on a calibrated hot-stage apparatus. Elemental analyses were performed by Galbraith Laboratories Inc., Knoxville, TN 37650. All reactions were performed under an atmosphere of dry nitrogen. Column chromatography was performed on silica gel (Matheson, Coleman and Bell, grade 62, 60–200 mesh), basic alumina (Fisher Scientific, 80–200 mesh), or neutral alumina (Fisher Scientific, 80–200 mesh, deactivated by treatment of 500 g of alumina with 1 L of ethyl acetate, followed by washing with methanol and drying 4 h in a 110 °C oven) mixed with Sylvania 2282 phosphor and slurry-packed into quartz columns to allow monitoring with a hand-held UV lamp. Preparative thick-layer chromatography was carried out with MN-Kieselgel G/UV 254 silica gel. High-pressure liquid chromatography (HPLC) was performed on a liquid chromatograph employing an LDC 254-nm detector and an LDC 6000-psi minipump, using a 0.95- × 25-cm polished stainless steel column packed with 3-5-μm octadecyl-coated porous silica beads.[21] Neutral workup refers to quenching the reaction with water, extracting with ether, unless otherwise specified, washing the organic layer with water and brine, drying, filtering, and concentrating in vacuo. Acidic workup included a 10% aqueous hydrochloric acid wash after ether extraction. Basic workup included a saturated aqueous sodium bicarbonate wash after ether extraction. Digestion refers to stirring the residue solid in the appropriate solvent for 1 h, filtering any residual solids from the solvent, and removing the solvent in vacuo. Exploratory photolyses were carried out with a Hanovia 450-W medium-pressure mercury lamp equipped with the appropriate 2-mm filter or with the appropriate filter solution recirculating. All photolysis solutions were purged with purified nitrogen[22] both prior to and during photolysis. Acetonitrile, pentane, methanol, and methylene chloride were distilled from calcium hydride. Tetrahydrofuran (THF) and dimethoxyethane (DME) were purified by storage over potassium hydroxide, followed by successive distillation, under a nitrogen atmosphere, from calcium hydride, lithium aluminum hydride, and sodium benzophenone ketyl. Diethyl ether was dried by distillation from sodium benzophenone ketyl. HPLC hexane was prepared by washing with nitric acid and sulfuric acid (1:1), water, saturated aqueous sodium bicarbonate, and brine, drying over calcium chloride, passing through alumina, and distilling from calcium hydride.

4,4-Diphenyl-1-(1′-propynyl)cyclohex-2-en-1-ol (4). To a −78 °C solution of 7.40 mL (0.13 mol) of propyne in 130 mL of ether was added dropwise 84 mL of a 1.5 M hexane solution (0.13 mol) of *n*-butyllithium. After the solution was stirred for 10 min at −78 °C, a solution of 10.0 g (40 mmol) of 4,4-diphenylcyclohex-2-en-1-one[23] in 200 mL of ether was added dropwise and the mixture stirred an additional 15 min at −78 °C. The mixture was then allowed to warm to ambient temperature and then quenched with saturated aqueous ammonium chloride solution. Neutral workup[20] and concentration in vacuo afforded 11.1 g of a brown oil, which was chromatographed on a 5.5- × 40-cm silica gel column: fraction 1, 3.5 L of 10% ether in hexane, nil; 2, 1 L of 20% ether in hexane, 10.1 g of a clear oil, which was recrystallized from ether in hexane to yield 9.92 g (86%) of 4,4-diphenyl-1-(1′-propynyl)cyclohex-2-en-1-ol as a white solid, mp 65-67 °C.

The spectral data were the following: ^{1}H NMR (CDCl$_3$, 200 MHz) δ 7.40–7.10 (m, 10 H, arom), 6.15 (d, $J = 9.9$ Hz, 1 H, vinyl), 5.93 (d, $J = 9.9$ Hz, 1 H, vinyl), 2.47 (m, 2 H, CH$_2$), 2.02 (s, 1 H, OH), 1.95 (m, 2 H, CH$_2$), 1.85 (s, 3 H, CH$_3$); IR (CHCl$_3$) 3580 (br), 3060, 3020, 2980, 2920, 2230, 1130, 1110 cm^{-1}; MS *m/e* 288.1514 (calcd for $C_{21}H_{20}O$, *m/e* 288.1514).

Anal. Calcd for $C_{21}H_{20}O$: C, 87.46; H, 6.99. Found: C, 87.60; H, 6.97.

4,4-Diphenyl-1-(1′-propynyl)cyclohex-2-en-1-ol Acetate (5).[24] A mixture of 2.50 g (8.76 mmol) of 4,4-diphenyl-(1-(1′-propynyl)cyclohex-2-en-1-ol, 100 mg (0.82 mmol) of (*N*,*N*-dimethylamino)pyridine, 2.40 mL (17 mmol) of triethylamine, and 2.2 mL (24 mmol) of acetic anhydride was stirred at ambient temperature for 14 h. The mixture was diluted with 50 mL of ether and subjected to neutral workup,[20] yielding 1.81 g of a brown solid after removal of solvent in vacuo. Recrystallization in 9:1 hexane–chloroform yielded 1.52 g (51%) of 4,4-diphenyl-

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1-(1′-propynyl)cyclohex-2-en-1-ol acetate as tan crystals, mp 107.5–108.5 °C.

The spectral data were the following: ^{1}H NMR (CDCl$_3$, 200 MHz) δ 7.40–7.20 (m, 10 H, arom), 6.25 (d, J = 10.0 Hz, 1 H, vinyl), 6.15 (d, J = 10.0 Hz, 1 H, vinyl), 2.50 (m, 2 H, CH$_2$), 2.20 (m, 2 H, CH$_2$), 2.03 (s, 3 H, CH$_3$), 1.86 (s, 3 H, CH$_3$); IR (CHCl$_3$) 3010, 2920, 2240, 1740, 1600, 1495, 1450, 1370, 1270, 1250, 1180, 1050, 1020, 1010, 960, 920, 840 cm^{-1}; MS m/e 330.1619 (calcd for $C_{23}H_{22}O_2$, m/e 330.1619).

Anal. Calcd for $C_{23}H_{22}O_2$: C, 83.60; H, 6.71. Found: C, 83.46; H, 6.62.

2-Methyl-3-(4′,4′-diphenylcyclohex-2′-en-1′-ylidene)prop-2-ene (6).[4] To a slurry of 8.10 g (0.042 mol) of copper(I) iodide in 80 mL of tetrahydrofuran cooled to 0 °C was added 48 mL (0.084 mol) of 1.75 M methyllithium as a solution in ether dropwise. After 5 min, 7.00 g (21.2 mmol) of 4,4-diphenyl-1-(1′-propynyl)cyclohex-2-en-1-ol acetate in 50 mL of tetrahydrofuran was added dropwise and the mixture allowed to stir at 0 °C for 4 h. After being warmed to ambient temperature, the solution was quenched with saturated aqueous ammonium chloride and subjected to neutral workup.[20] Removal of solvent in vacuo yielded 5.32 g of a clear oil. This oil eluted with 1% ether in hexane on a 3.5- × 25-cm neutral alumina column: fraction 1, 700 mL, nil; 2, 1 L, 5.1 g of a clear oil. This oil was recrystallized from pentane to give 4.70 g (78%) of 2-methyl-3-(4′,4′-diphenylcyclohex-2′-en-1′-ylidene)prop-2-ene as a white solid, mp 92–95 °C.

The spectral data were the following: ^{1}H NMR (CDCl$_3$, 200 MHz) δ 7.30–7.10 (m, 10 H, arom), 6.20 (d, J = 9.9 Hz, 1 H, vinyl), 6.02 (d, J = 9.9 Hz, 1 H, vinyl), 2.45–2.35 (m, 2 H, CH$_2$), 2.30–2.20 (m, 2 H, CH$_2$), 1.70 (s, 6 H, CH$_3$); IR (CHCl$_3$) 3060, 3030, 2985, 2940, 2910, 2865, 1940, 1600, 1490, 1445, 1410, 1360, 1215, 1185, 1130, 1110, 1100, 1080, 1050, 1035, 1025, 1005, 995, 980, 975 cm^{-1}; UV (95% EtOH) λ_{max} 242 nm (ϵ 21 960), λ_{sh} 270 nm (ϵ 1980); MS m/e 286.1722 (calcd for $C_{22}H_{22}$, m/e 286.1722).

Anal. Calcd for $C_{22}H_{22}$: C, 92.26; H, 7.74. Found: C, 92.49; H, 7.90.

Exploratory Direct Photolysis of 2-Methyl-3-(4′,4′-diphenylcyclohex-2′-en-1′-ylidene)prop-2-ene (6). A solution of 75 mg (0.262 mmol) of 2-methyl-3-(4′,4′-diphenylcyclohex-2′-en-1′-ylidene)prop-2-ene in 150 mL of 2-methyl-2-propanol was photolyzed[20] through a Corex filter for 4 h. Removal of solvent in vacuo yielded 76 mg of yellow oil. This was subjected to HPLC.[20] Elution with 5% ether in hexane gave the following: fraction 1, 26 mg of 2-methyl-3-(4′,4′-diphenylcyclohex-2′-en-1′-ylidene)prop-2-ene; fraction 2, 46 mg of a clear oil. Low-temperature recrystallization of this oil gave 43 mg (61%) of 2-methyl-3-(5′,6′-*trans*-diphenylbicyclo[3.1.0]hexylidene)prop-2-ene as a white solid, mp 21–22 °C.

The spectral data were the following: ^{1}H NMR (CDCl$_3$, 200 MHz) δ 7.40–7.11 (m, 10 H, arom), 2.60 (m, 2 H, cyclopropyl), 2.33–2.20 (m, 3 H, CH$_2$), 1.77 (s, 3 H, CH$_3$), 1.74 (s, 3 H, CH$_3$), 1.22 (m, 1 H, CH$_2$); IR (CHCl$_3$) 3045, 3020, 2910, 2850, 1950, 1600, 1495, 1445, 1075, 1040, 800 cm^{-1}; MS m/e 286.1722 (calcd for $C_{22}H_{22}$, m/e 286.1722).

Anal. Calcd for $C_{22}H_{22}$: C, 92.26; H, 7.74. Found: C, 92.05; H, 7.81.

Exploratory Sensitized Photolysis of 2-Methyl-3-(4′,4′-diphenylcyclohex-2′-en-1′-ylidene)prop-2-ene (6). A solution of 50 mg (0.175 mmol) of 2-methyl-3-(4′,4′-diphenylcyclohex-2′-en-1′-ylidene)prop-2-ene and 25 mg (0.137 mmol) of benzophenone in 220 mL of 2-methyl-2-propanol was photolyzed[20] through a Pyrex filter for 15 h. Removal of solvent in vacuo yielded 72 mg of white solid. This was placed on a methanol-deactivated 20- × 20-cm silica gel plate and eluted with pentane, giving two bands: band 1 (R_f 0.9), 44 mg of starting 2-methyl-3-(4,4′-diphenylcyclohex-2′-en-1′-ylidene)prop-2-ene; band 2 (R_f 0.3), 25 mg of benzophenone.

5,6-*trans*-Diphenyl-2-(1′-propynyl)bicyclo[3.1.0]hexan-2-ol (20). To a −78 °C solution of 2.2 mL (39 mmol) of propyne in 40 mL of ether was added dropwise 25 mL of a 1.5 M hexane solution (38 mmol) of *n*-butyllithium. After being stirred for 10 min at −78 °C, a solution of 2.30 g (12.1 mmol) of 5,6-*trans*-diphenylbicyclo[3.1.0]hexanone[25] in 30 mL of ether was added dropwise and the mixture stirred an additional 15 min at −78 °C. The mixture was then allowed to warm to ambient temperature and then quenched with saturated aqueous ammonium chloride solution. Neutral workup[20] and concentration in vacuo afforded 1.62 g of a clear oil, which was recrystallized from ether in hexane to afford 1.48 g (48%) of 5,6-*trans*-diphenyl-2-(1′-propynyl)bicyclo-[3.1.0]hexan-2-ol as a white solid, mp 89–90 °C.

The spectral data were the following: ^{1}H NMR (CDCl$_3$, 200 MHz) δ 7.57–7.23 (m, 10 H, arom), 3.01 (s, 1 H, OH), 2.60 (d, J = 8.1 Hz, 1 H, cyclopropyl), 2.32 (d, J = 8.1 Hz, 1 H, cyclopropyl), 2.25 (m, 2 H, CH$_2$), 1.90 (s, 3 H, CH$_3$), 1.80 (m, 1 H, CH$_2$), 0.88 (m, 1 H, CH$_2$); IR (CHCl$_3$) 3580 (br), 3040, 3000, 2940, 2860, 1600, 1495, 1445, 1065, 1025 cm^{-1}; MS m/e 288.1514 (calcd for $C_{21}H_{20}O$, m/e 288.1514).

Anal. Calcd for $C_{21}H_{20}O$: C, 87.46; H, 6.99. Found: C, 87.55; H, 7.03.

5,6-*trans*-Diphenyl-2-(1′-propynyl)bicyclo[3.1.0]hexan-2-ol Acetate (21).[24] A mixture of 1.50 g (5.21 mmol) of 5,6-*trans*-diphenyl-2-(1′-propynyl)bicyclo[3.1.0]hexan-1-ol, 50 mg (0.4 mmol) of (*N*,*N*-dimethylamino)pyridine, 1.3 mL (9 mmol) of triethylamine, and 1.2 mL (13 mmol) of acetic anhydride was stirred at ambient temperature for 16.5 h. The mixture was diluted with 50 mL of ether and subjected to neutral workup,[20] yielding 1.54 g of a brown solid after removal of solvent in vacuo. Recrystallization from ethanol yielded 1.33 g (75.0%) of 5,6-*trans*-diphenyl-2-(1′-propynyl)bicyclo[3.1.0]hexan-2-ol acetate as white needles, mp 118–122 °C.

The spectral data were the following: ^{1}H NMR (CDCl$_3$, 200 MHz) δ 7.48–7.41 (m, 10 H, arom), 2.73 (d, J = 8.6 Hz, 1 H, cyclopropyl), 2.62 (d, J = 8.6 Hz, 1 H, cyclopropyl), 2.36–2.14 (m, 2 H, CH$_2$), 2.08, (s, 3 H, CH$_3$), 1.90 (s, 3 H, CH$_3$), 0.82 (m, 1 H, CH$_2$); IR (CHCl$_2$) 3000, 2920, 2220, 1725, 1595, 1490, 1440, 1365, 1245, 1045, 1015, 900 cm^{-1}; MS m/e 330.1619 (calcd for $C_{23}H_{22}O_2$, m/e 330.1619).

Anal. Calcd for $C_{23}H_{22}O_2$: C, 83.60; H, 6.71. Found: C, 82.32; H, 6.57.

2-Methyl-3-(5′,6′-*trans*-diphenylbicyclo[3.1.0]hexylidene)prop-2-ene (22a).[4] To a slurry of 1.00 g (5.25 mmol) of copper(I) iodide in 10 mL of tetrahydrofuran cooled to 0 °C was added 6.2 mL of 1.75 M methyllithium as a solution in ether (10.9 mmol) dropwise. After 5 min, 900 mg (2.73 mmol) of 5,6-*trans*-diphenyl-2-(1′-propynyl)bicyclo-[3.1.0]hexan-2-ol acetate in 6.0 mL of tetrahydrofuran was added dropwise and the mixture allowed to stir at 0 °C for 4 h. After being warmed to ambient temperature, the solution was quenched with saturated aqueous ammonium chloride and subjected to neutral workup.[20] Removal of solvent in vacuo yielded 540 mg (70%) of 2-methyl-3-(5′,6′-*trans*-diphenylbicyclo[3.1.0]hexylidene)prop-2-ene as a clear oil. The spectral data were identical with those found for the material produced from the direct irradiation of 2-methyl-3-(4′,4′-diphenylcyclohex-2′-en-1′-ylidene)prop-2-ene.

4,4-Diphenylcyclohex-1-eneformaldehyde (8).[26] To a slurry of 18.0 g (0.055 mmol) of (methoxymethyl)triphenylphosphonium chloride in 160 mL of tetrahydrofuran at 0 °C was added 6.10 g (54.4 mmol) of potassium *tert*-butoxide in 200 mL of tetrahydrofuran slowly. After the mixture was stirred for 1 h at ambient temperature, 6.70 g (27.0 mmol) of 4,4-diphenylcyclohex-2-en-1-one[23] in 50 mL of tetrahydrofuran was added dropwise. After being stirred for an additional 2 h, the mixture was diluted with 200 mL of ether. Neutral workup[20] yielded 20.6 g of a tan oil, which was chromatographed on a 5.5- × 30-cm silica gel column: fraction 1, 600 mL of 25% ether in hexane, nil; 2, 1 L 25% of ether in hexane, 7.44 g of a clear oil. This oil was dissolved in 400 mL of tetrahydrofuran with 100 mL of 10% hydrochloric acid and refluxed for 20 h. The mixture was cooled to ambient temperature, diluted with 600 mL of water, and subjected to neutral workup.[20] Removal of solvent in vacuo yielded 9.03 g of a golden oil which was chromatographed on a 5.5- × 15-cm silica gel column: fraction 1, 600 mL of 10% ether in hexane, nil; 2, 1.5 L of 10% ether in hexane, 7.12 g of a white solid. This solid was recrystallized from pentane to yield 6.80 g (96%) of 4,4-diphenylcyclohex-1-eneformaldehyde as white crystals, mp 97–100 °C.

The spectral data were the following: ^{1}H NMR (CDCl$_3$, 200 MHz) δ 9.44 (s, 1 H, ald), 7.25–7.00 (m, 10 H, arom), 6.92 (t, J = 6.2 Hz, 1 H, vinyl), 2.95 (m, 2 H, CH$_2$), 2.41 (d, J = 6.2 Hz, 2 H, CH$_2$), 1.98 (m, 2 H, CH$_2$): IR (CHCl$_3$) 3060, 3030, 3025, 3010, 2980, 2935, 2890, 2870, 1680 (s), 1650, 1645, 1495, 1455, 1395, 1225, 1220, 1195, 1190, 1165, 1125, 1030, 965, 950, cm^{-1}; MS m/e 262.3503 (calcd for $C_{19}H_{18}O$, m/e 262.3501).

Anal. Calcd for $C_{19}H_{18}O$: C, 86.96; H, 6.92. Found: C, 87.09; H, 7.01.

4,4-Diphenylcyclohex-1-enecarboxylic Acid (9). To a solution of 6.80 g (25.9 mmol) of 4,4-diphenylcyclohex-1-eneformaldehyde in 180 mL of acetone was added 31.4 mL (84.0 mmol) of Jones reagent[27] dropwise. The mixture was stirred for 1 h at ambient temperature and quenched with 2-propanol. The resultant green precipitate was removed by filtration and the solvent removed in vacuo. This residue was dissolved in 500 mL of ether and subjected to neutral workup.[20] Removal of solvent in vacuo yielded 4.92 g of a white solid which was recrystallized from chloroform in hexane to give 4.80 g (96%) of 4,4-diphenylcyclohex-1-enecarboxylic acid as a white solid, mp 230–232 °C.

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The spectral data were the following: ^{1}H NMR (CDCl$_3$, 200 MHz) δ 7.25–7.00 (m 11 H, arom and vinyl), 2.80 (m, 2 H, CH$_2$), 2.41 (t, J = 6.0 Hz, 2 H, CH$_2$), 2.0 (m, 2 H, CH$_2$); IR (CHCl$_3$) 3600–2400 (br), 3090, 3060, 3030, 3010, 2985, 2970, 2940, 1690, 1655, 1650, 1600, 1495, 1445, 1440, 1425, 1320, 1275, 1230, 1220, 1215, 1210, 1170 cm^{-1}; MS *m/e* 278.1306 (calcd for $C_{19}H_{18}O_2$, *m/e* 278.1305).

Anal. Calcd for $C_{19}H_{18}O_2$: C, 81.99; H, 6.52. Found: C, 81.63; H, 6.67.

4,4-Diphenylcyclohex-1-enecarboxylic Acid Chloride (10). A mixture of 4.80 g (17.3 mmol) of 4,4-diphenylcyclohex-1-enecarboxylic acid, 19 mL of thionyl chloride, and 65 mL of benzene was refluxed for 20 h, and after the mixture was cooled to ambient temperature, the solvent was removed in vacuo to yield 5.02 g (99%) of 4,4-diphenylcyclohex-1-enecarboxylic acid chloride as a yellow oil.

The spectral data were the following: ^{1}H NMR (CDCl$_3$, 200 MHz) δ 7.56 (m, 1 H, vinyl), 7.25–7.03 (m, 10 H, arom), 3.00 (m, 2 H, CH$_2$), 2.40 (t, J = 6.0 Hz, 2 H, CH$_2$), 2.11 (m, 2 H, CH$_2$); IR (CHCl$_3$) 3090, 3060, 3030, 3010, 2990, 2940, 1765, 1750, 1750, 1685, 1680, 1645, 1595, 1495, 1445, 1440, 1390, 1375, 1230, 1190, 1175, 1150, 1125, 1075, 1035, 1020 cm^{-1}.

1,1-Diphenyl-2-(4′,4′-diphenylcyclohex-2′-en-1′-ylidene)ethene (11). To a solution of 13.7 g (48.9 mmol) of diethyl diphenylmethylphosphonate[28] in 40 mL of tetrahydrofuran cooled to 0 °C was added 28.7 mL (43.1 mmol) of 1.5 M *n*-butyllithium in hexane dropwise, and the solution was stirred for 30 min at ambient temperature. A solution of 5.02 (16.6 mmol) of 4,4-diphenylcyclohex-1-enecarboxylic acid chloride in 40 mL of tetrahydrofuran was added dropwise, and the resulting solution was stirred for 2 h at ambient temperature. The solution was then diluted with 500 mL of ether and subjected to neutral workup[20] to yield 12.9 g of a golden oil. This was chromatographed on a 5.5- × 30-cm silica gel column and eluted with 5% ether in hexane to give the following: fraction 1, 500 mL, nil; 2, 1 L, 1.6 g of a white solid. This was recrystallized from ether in hexane to afford 1.43 g (20%) of 1,1-diphenyl-2-(4′,4′-diphenylcyclohex-2′-en-1′-ylidene)ethene as white crystals, mp 141–143 °C.

The spectral data were the following: ^{1}H NMR (CDCl$_3$, 200 MHz) δ 7.35–7.15 (m, 20 H, arom), 6.42 (d, J = 9.0 Hz, 1 H, vinyl), 6.22 (d, J = 9.0 Hz, 1 H, vinyl), 2.50 (s, 4 H, CH$_2$); IR (CHCl$_3$) 3085, 3060, 3030, 2950, 2930, 2870, 2850, 1950, 1600, 1580, 1490, 1470, 1460, 1445, 1310, 1285, 1250, 1190, 1075, 1030, 1000 cm^{-1}; UV (MeOH) λ_{max} 248 nm (ϵ 80580), λ 300 nm (ϵ 48800); MS *m/e* 410.2033 (calcd for $C_{32}H_{26}$, *m/e* 410.2034).

Anal. Calcd for $C_{32}H_{26}$: C, 93.62; H, 6.38. Found: C, 93.93; H, 6.60.

Exploratory Direct Photolysis of 1,1-Diphenyl-2-(4′,4′-diphenylcyclohex-2′-en-1′-ylidene)ethene (11). A solution of 50.0 g (0.122 mmol) of 1,1-diphenyl-2-(4′,4′-diphenylcyclohex-2′-en-1′-ylidene)ethene in 220 mL of *tert*-butyl alcohol was photolyzed[20] for 3 h and solvent removed in vacuo to yield 45 mg of a white solid. Recrystallization from chloroform in hexane yielded 39 mg (78%) of **27** as a white solid, mp 105–108 °C.

The spectral data were the following: ^{1}H NMR (CDCl$_3$, 200 MHz) δ 7.18–6.99 (m, 20 H, arom), 4.17 (m, 2 H, cyclopropyl), 2.33–2.10 (m, 4 H, CH$_2$); IR (CHCl$_3$) 3090, 3065, 3020, 2905, 2850, 1950(w), 1600, 1495, 1450, 1075, 1035, 910 cm^{-1}; MS *m/e* 410.2037 (calcd for $C_{32}H_{26}$, *m/e* 410.2034).

Anal. Calcd for $C_{32}H_{26}$: C, 93.62; 6.38 H. Found: C, 93.84; H, 6.53.

Exploratory Direct Photolysis of 1,1-Diphenyl-2-(4′,4′-diphenylcyclohex-2′-en-1′-ylidene)ethene and Oxidative Degradation of the Photoproduct. A solution of 75.0 mg (0.183 mmol) of 1,1-diphenyl-2-(4′,4′-diphenylcyclohex-2′-en-1′-ylidene)ethene in 220 mL of *tert*-butyl alcohol was photolyzed[1] for 5 h and solvent removed in vacuo to yield 62 mg of a white solid. Recrystallization from chloroform in hexane yielded 56 mg (75%) of a white solid, mp 106–108 °C. The procedure of Lemieux and Johnson[29] was employed. To a solution of 56 mg (0.137 mmol) of the photoproduct in 1.0 mL of ether and 1.0 mL of water was added 17.0 mg (0.07 mmol) of osmium tetraoxide. To this solution was added 70 mg (0.33 mmol) of finely powdered sodium metaperiodate, and the solution was stirred an additional 1.5 h. The solution was then filtered and the supernatant diluted with 50 mL of ether and subjected to neutral[1] workup. Removal of solvent in vacuo yielded 61 mg of a yellow solid, which was chromatographed on a 20- × 20-cm silica gel thick layer plate eluting with 5% ether in hexane to give the following: band 3 (R_f 0.51), 2 mg of uncharacterized material; band 2 (R_f 0.31), 21 mg of benzophenone as a white solid; band 1 (R_f 0.05), 28 mg of 5,6-*trans*-diphenylbicyclo[3.1.0]hexanone as a white solid. The benzophenone was recrystallized from ethanol to give 17 mg of a white solid, mp 49–51 °C. Spectral data confirmed this identity. Band 1 was recrystallized from ethanol to give 22 mg of the known[25] 5,6-*trans*-diphenylbicyclo[3.1.0]hexan-2-one as a white solid, mp 73–74 °C (lit.[25] mp 73–74 °C).

Exploratory Sensitized Photolysis of 1,1-Diphenyl-2-(4′,4′-diphenylcyclohex-2′-en-1′-ylidine)ethene (11). A solution of 50 mg (0.12 mmol) of 1,1-diphenyl-2-(4′,4′-diphenylcyclohex-2′-en-1′-ylidene)ethene and 50 mg of thioxanthone in 200 mL of anhydrous benzene was photolyzed[20] through a 0.02 M sodium metavanadate solution in 5% sodium hydroxide (transmission maximum, 384 nm, no transmission below 310 nm) for 3.75 h. Removal of solvent in vacuo yielded 100 mg of a white solid. NMR analysis showed only thioxanthone and 1,1-diphenyl-2-(4′,4′-diphenylcyclohex-2′-en-1′-ylidene)ethene.

1-(Diethoxymethylene)-4,4-diphenyl-2,5-cyclohexadiene (14).[8] To a solution of 4.60 g (15.0 mmol) of diethoxymethyldiphenylphosphine oxide[30] in 300 mL of 3:1 tetrahydrofuran–ether cooled to −98 °C was added lithium diisopropylamide (16.5 mmol) in 50 mL of tetrahydrofuran dropwise, keeping the temperature below −98 °C. After the solution was stirred for 1 min, 3.70 g (15.0 mmol) of 4,4-diphenylcyclohexa-2,5-dien-1-one[3a] in 30 mL of tetrahydrofuran was added dropwise, keeping the temperature below −90 °C. After being stirred for an additional 5 min, the reaction was quenched with 60 mL of water and allowed to warm to ambient temperature. Solid potassium carbonate was added to the mixture, the layers were separated, and the organic phase was dried over magnesium sulfate and filtered. Solvent was removed in vacuo to give 6.14 g of a yellow oil.

This oil was placed in 75 mL of tetrahydrofuran with 1.84 (16.5 mmol) of potassium *tert*-butoxide and stirred for 1 h at ambient temperature. Solvent was removed in vacuo and the residue digested[20] twice with 250 mL of hexane. Filtration and removal of solvent in vacuo afforded 4.65 g of a yellow oil, which was chromatographed on a 2.7- × 15-cm neutral alumina column. Elution with hexane gave the following: fraction 1, 100 mL, nil; 2, 300 mL, 3.05 (61%) of 1-(diethoxymethylene)-4,4-diphenyl-2,5-cyclohexadiene as a clear oil.

The spectral data were the following: ^{1}H NMR (CDCl$_3$, 200 MHz) δ 7.30–7.15 (m, 10 H, arom), 6.50 (d, J = 10.2 Hz, 2 H, vinyl), 5.80 (d, J = 10.2 Hz, 2 H, vinyl), 3.92 (q, J = 7.1 Hz, 4 H, CH$_2$), 1.29 (t, J = 7.1 Hz, 6 H, CH$_3$); IR (CHCl$_3$) 3025, 3010, 3000, 2990, 2985, 1660, 1570, 1490, 1440, 1405, 1380, 1360, 1300, 1200, 1095 cm^{-1}; MS *m/e* 332.1770 (calcd for $C_{23}H_{24}O_2$, *m/e* 332.1770).

Ethyl 4,4-Diphenylcyclohexa-2,5-diene-1-carboxylate (15). A solution of 5.52 g (16.6 mmol) of 1-(diethoxymethylene)-4,4-diphenyl-2,5-cyclohexadiene in 110 mL of tetrahydrofuran, 110 mL of water, and 18 mL of 10% hydrochloric acid was refluxed for 16 h. After being cooled to ambient temperature, the mixture was diluted with 200 mL of water and subjected to neutral workup.[20] Removal of solvent in vacuo yielded 4.82 g of a yellow oil. Recrystallization from methanol afforded 4.69 g (94%) of ethyl 4,4-diphenylcyclohexa-2,5-diene-1-carboxylate as white crystals, mp 86.0–88.5 °C.

The spectral data were the following: ^{1}H NMR (CDCl$_3$, 200 MHz) δ 7.35–7.20 (m, 10 H, arom), 6.16 (dd, J = 2.1, 10.4 Hz, 2 H, vinyl), 6.02 (dd, J = 3.1, 10.4 Hz, 2 H, vinyl), 4.17 (q, J = 7.1 Hz, 2 H, CH$_2$), 3.75 (m, 1 H, CH), 1.28 (t, J = 7.1 Hz, 3 H, CH$_3$); IR (CHCl$_3$) 3100, 3000, 2990, 2850, 1725(s), 1605, 1500, 1440, 1350, 1250, 1170 cm^{-1}; MS *m/e* 304.1464 (calcd for $C_{21}H_{20}O_2$, *m/e* 304.1470).

Anal. Calcd for $C_{21}H_{20}O_2$: C, 82.85; H, 6.63. Found: C, 82.66; H, 6.50.

4,4-Diphenylcyclohexa-1,5-diene-1-carboxylic Acid (16). A solution of 4.69 g (15.6 mmol) of ethyl 4,4-diphenylcyclohexa-2,5-diene-1-carboxylate in 400 mL of ethanol and 300 mL of 2 M sodium hydroxide was stirred for 4 h at ambient temperature, and the solvent was removed in vacuo to one-quarter volume. After dilution with 500 mL of water, the soluiton was acidified to pH 3 with 10% hydrochloric acid and extracted twice with methylene chloride. The combined organics were subjected to neutral workup,[20] and the solvent was removed in vacuo to give 3.88 g of a yellow solid. Recrystallization of this solid from methylene chloride in hexane yielded 3.70 g (88%) of 4,4-diphenylcyclohexa-1,5-diene-1-carboxylic acid as white crystals, mp 198–201 °C.

The spectral data were the following: ^{1}H NMR (CDCl$_3$, 200 MHz) δ 7.32–7.16 (m, 11 H, aromatic and vinyl), 6.54 (dd, J = 1.5, 9.9 Hz, 1 H, vinyl), 6.39 (d, J = 9.9 Hz, 1 H, vinyl), 3.07 (d, J = 4.7 Hz, 2 H, CH$_2$); IR (CHCl$_3$) 3400–2400 (br), 3050, 3025, 2975, 2940, 1695, 1660, 1590, 1500, 1450, 1275, 1250 cm^{-1}; MS *m/e* 276.1152 (calcd for $C_{19}H_{16}O_2$, *m/e* 276.1151).

Anal. Calcd for $C_{19}H_{16}O_2$: C, 82.58; H, 5.84. Found: C, 82.62; H, 5.78.

4,4-Diphenylcyclohexa-1,5-diene-1-carboxylic Acid Chloride (17). A solution of 50 mg (1.81 mmol) of 4,4-diphenylcyclohexa-1,5-diene-1-carboxylic acid in 7.0 mL of anhydrous benzene and 1.0 mL of oxalyl

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chloride was refluxed for 10 h. After the solution was cooled to ambient temperature the solvent was removed in vacuo to give 52 mg (95%) of 4,4-diphenylcyclohexa-1,5-diene-1-carboxylic acid chloride as a yellow solid.

The spectral data were the following: ^{1}H NMR (CDCl$_3$, 200 MHz) δ 7.40–7.10 (m, 11 H, aromatic and vinyl), 6.52 (dd, J = 10.0, 1.6 Hz, 1 H, vinyl), 6.45 (dd, J = 10.0, 1.0 Hz, 1 H, vinyl), 3.17 (d, J = 4.8 Hz, 2 H, CH$_2$); IR (CHCl$_3$) 3020, 3005, 2995, 1780 (s), 1595, 1495, 1445, 1330, 1180, 1150, 1075, 935, 815 cm^{-1}; MS m/e 278.0801 (calcd for $C_{19}H_{15}OCl$, m/e 278.0864).

2-Methyl-3-(4′,4′-diphenylcyclohexa-2′,5′-dien-1′-ylidene)prop-2-ene (18). To a slurry of 140 mg (3.49 mmol) of potassium hydride in 10 mL of tetrahydrofuran was added 1.60 g (3.49 mmol) of isopropyltriphenylphosphonium iodide, and the resulting suspension was stirred 1 h until a dark red color was achieved. A solution of 52 mg (1.72 mmol) of 4,4-diphenylcyclohexa-1,5-diene-1-carboxylic acid chloride in 5.0 mL of tetrahydrofuran was added dropwise, and the resulting mixture was refluxed for 20 h. Solvent was removed in vacuo and the residue digested in 1% ether–pentane to afford 44 mg of a white solid. This was chromatographed on a 20- × 20-cm neutral alumina plate and eluted twice with pentane to afford the following: band 1 (R_f 0.84), 105 mg (21%) of 2-methyl-3-(4′,4′-diphenylcyclohexa-2′,5′-dien-1′-ylidene)prop-2-ene as a clear oil.

The spectral data were the following: ^{1}H NMR (CDCl$_3$, 200 MHz) δ 7.45–7.21 (m, 10 H, arom), 6.23 (d, J = 10.1 Hz, 2 H, vinyl), 6.08 (d, J = 10.1 Hz, 2 H, vinyl), 1.73 (s, 6 H, CH$_3$); IR (CHCl$_3$) 3080, 3030, 2985, 2960, 2915, 1940, 1600, 1490, 1450, 1410, 1360, 1210, 1180, 1075, 1050, 1035, 1000, 980, 975 cm^{-1}; MS m/e 284.1564 (calcd for $C_{22}H_{20}$, m/e 284.1565); UV (cyclohexane) λ_{max} 250 nm (ϵ 13 200), λ_{sh} 272 nm (ϵ 4200).

Anal. Calcd for $C_{22}H_{20}$: C, 92.91; H, 7.09. Found: C, 92.60; H, 6.95.

Exploratory Direct Photolysis of 2-Methyl-3-(4′,4′-diphenylcyclohexa-2′,5′-dien-1′-ylidene)prop-2-ene (18). A solution of 75 mg (0.264 mmol) of 2-methyl-3-(4′,4′-diphenylcyclohexa-2′,5′-dien-1′-ylidene)prop-2-ene in 220 mL of 2-methyl-2-propanol was photolyzed[20] for 4 h through a Pyrex filter and solvent removed in vacuo to yield 76 mg of a yellow oil. This was chromatographed on a 20- × 20-cm methanol-deactived silica gel plate and eluted twice with pentane to yield the following: band 1 (R_f 0.92), 47 mg (63%) of 2-methyl-3-(5′,6′-*trans*-diphenylbicyclo[3.1.0]hex-2′-en-1′-ylidene)prop-2-ene as a clear oil; band 2, 14 mg of 2-methyl-3-(4′,4′-diphenylcyclohexa-2′,5′-dien-1′-ylidene)prop-2-ene as a clear oil.

The spectral data for 2-methyl-3-(5′,6′-*trans*-diphenylbicyclo[3.1.0]hex-2′-en-1′-ylidene)prop-2-ene were the following: ^{1}H NMR (CDCl$_3$, 200 MHz) δ 7.37–7.05 (m, 10 H, arom), 6.24 (d, J = 5.5 Hz, 1 H, vinyl), 5.67 (d, J = 5.5 Hz, 1 H, vinyl), 3.17 (d, J = 8.8 Hz, 1 H, cyclopropyl), 2.86 (d, J = 8.8 Hz, 1 H, cyclopropyl), 1.74 (s, 3 H, CH$_3$), 1.70 (s, 3 H, CH$_3$); IR (CDCl$_3$) 3090, 3060, 3030, 2980, 2930, 1940, 1600, 1560, 1540, 1505, 1495, 1470, 1455, 1435, 1245, 1215, 1095, 1030, 985 cm^{-1}; MS m/e 284.1564 (calcd for $C_{22}H_{20}$, m/e 284.1565).

Anal. Calcd for $C_{22}H_{20}$: C, 92.91; H, 7.09. Found: C, 92.65; H, 7.17.

Exploratory Sensitized Photolysis of 2-Methyl-3-(4′,4′-diphenylcyclohexa-2′,5′-dien-1′-ylidene)prop-2-ene (18). A solution of 50 mg (0.176 mmol) of 2-methyl-3-(4′,4′-diphenylcyclohexa-2′,5′-dien-1′-ylidene)prop-2-ene in 150 mL of 2-methyl-2-propanol with 50 mg (0.274 mmol) of benzophenone was photolyzed[20] for 5 h through a Pyrex filter. Removal of solvent in vacuo yielded 96 mg of a white solid. NMR analysis showed only starting 2-methyl-3-(4′,4′-diphenylcyclohexa-2′,5′-dien-1′-ylidene)prop-2-ene and benzophenone.

5,6-*trans*-Diphenyl-2-(1′-propynyl)bicyclo[3.1.0]hex-2-en-2-ol (24). To a −78 °C solution of 1.4 mL (25 mmol) of propyne in 25 mL of ether was added dropwise 16 mL of a 1.5 M hexane solution (25 mmol) of *n*-butyllithium. After the solution was stirred for 10 min at −78 °C, a solution of 1.90 g (7.71 mmol) of 5,6-*trans*-diphenylbicyclo[3.1.0]hex-3-en-2-one[11] in 35 mL of ether was added dropwise and the mixture stirred an additional 15 min at −78 °C. The mixture was then allowed to warm to ambient temperature and then quenched with saturated aqueous ammonium chloride solution. Neutral workup[20] and concentration in vacuo afforded 2.02 g of a clear oil, which was chromatographed on a 1.8- × 40-cm silica gel column: fraction 1, 600 mL of 25% ether in hexane, nil; 2, 600 mL of 25% ether in hexane, 1.24 g of a yellow oil. This was recrystallized from ether in hexane to afford 1.12 g (50%) of 5,6-*trans*-diphenyl-2-(1′-propynyl)bicyclo[3.1.0]hex-3-en-2-ol as a white solid, mp 89–90 °C.

The spectral data were the following: ^{1}H NMR (CDCl$_3$, 200 MHz) δ 7.50–7.21 (m, 10 H, arom), 6.05 (d, J = 5.3 Hz, 1 H, vinyl), 5.42 (d, J = 5.3 Hz, 1 H, vinyl), 3.13 (d, J = 8.8 Hz, 1 H, cyclopropyl), 2.48 (d, J = 8.8 Hz, 1 H, cyclopropyl), 1.89 (br s, 4 H, CH$_3$ + OH); IR (CHCl$_3$) 3600 (br), 3060, 3030, 2980, 2930, 2230, 1600, 1560, 1540, 1495, 1470, 1455, 1445, 1380, 1245, 1030, 985 cm^{-1}; MS m/e 286.1358 (calcd for $C_{21}H_{18}O$, m/e 286.1357).

Table II. Summary of Direct Quantum Yield Results for 2-Methyl-3-(4′,4′-diphenylcyclohex-2′-en-1′-ylidene)prop-2-dene

run	reactant (mmol)	mEinstein absorbed	bicyclic product ϕ	% convn
1	0.70	0.026	0.506	7.44
2	0.70	0.021	0.466	6.42
3	0.69	0.011	0.345	4.55
4	0.70	0.0074	0.305	3.61
5	0.60	0.0026	0.205	1.80

Anal. Calcd for $C_{21}H_{18}O$: C, 88.08; H, 6.34. Found: C, 87.62; H, 6.15.

5,6-*trans*-Diphenyl-2-(1′-propynyl)bicyclo[3.1.0]hex-3-en-2-ol Acetate (25).[24] A mixture of 90 mg (3.14 mmol) of 5,6-*trans*-diphenyl-2-(1′-propynyl)bicyclo[3.1.0]hex-3-en-2-ol, 3.0 mg (0.020 mmol) of (*N,N*-dimethylamino)pyridine, 0.65 mL (4.5 mmol) of triethylamine, and 0.65 (7.5 mmol) of acetic anhydride was stirred at ambient temperature for 37 h. The mixture was diluted with 50 mL of ether and subjected to neutral workup,[20] yielding 72 mg of a brown solid after removal of solvent in vacuo. Recrystallization from dichloromethane in hexane yielded 69 mg (70%) of 5,6-*trans*-diphenyl-2-(1′-propynyl)bicyclo[3.1.0]hex-3-en-2-ol acetate as white crystals, mp 94–95 °C.

The spectral data were the following: ^{1}H NMR (CDCl$_3$, 200 MHz) δ 7.45–7.10 (m, 10 H, arom), 6.19 (d, J = 5.4 Hz, 1 H, vinyl), 5.60 (d, J = 5.4 Hz, 1 H, vinyl), 3.10 (d, J = 8.8 Hz, 1 H, cyclopropyl), 2.87 (d, J = 8.8 Hz, 1 H, cyclopropyl), 2.10 (s, 3 H, CH$_3$), 1.86, (s, 3 H, CH$_3$); IR (CHCl$_3$) 3050, 2975, 2220, 1720, 1600, 1490, 1435, 1365, 1240, 1030 cm^{-1}; MS m/e 328.1459 (calcd for $C_{23}H_{20}O_2$, m/e 328.1464).

Anal. Calcd for $C_{23}H_{20}O_2$: C, 84.18; H, 6.14. Found: C, 83.79; H, 6.54.

2-Methyl-3-(5′,6′-*trans*-diphenylbicyclo[3.1.0]hex-2′-en-1′-ylidene)prop-2-ene (26).[4] A slurry of 860 mg (4.4 mmol) of copper(I) iodide in 10 mL of ether cooled to 0 °C was added 8.9 mL of 1.0 M methyllithium as a solution in ether (8.8 mmol) dropwise. After 5 min, 820 mg (2.5 mmol) of 5,6-*trans*-diphenyl-2-(1′-propynyl)bicyclo[3.1.0]hex-3-en-2-ol acetate in 6.0 mL of ether was added dropwise and the mixture allowed to stir at −5 °C for 5 h. After being warmed to ambient temperature, the solution was quenched with saturated aqueous ammonium chloride and subjected to neutral workup.[20] Removal of solvent in vacuo yielded 720 mg of a brown oil. To a 20- × 20-cm neutral alumina plate was chromatographed 250 mg of this material. Elution with 2% ether in hexane gave the following: band 1 (R_f 0.87), 120 mg (49%) of 2-methyl-3-(5′,6′-*trans*-diphenylbicyclo[3.1.0]hex-2′-en-1′-ylidene)prop-2-ene as a clear oil. The spectral data were identical with those found for the material produced from the direct irradiation of 2-methyl-3-(4′,4′-diphenylcyclohexa-2′,5′-dien-1′-ylidene)prop-2-ene.

Photolysis Equipment for Quantum Yield Determinations. Quantum yields were performed on the "Wisconsin black box".[13] Light output was measured with a digital actinometer[14] calibrated with ferrioxalate actinometry. The following filter solution combination was used: (a) 2 M nickel sulfate in 5% sulfuric acid, (b) 0.8 M copper sulfate in 5% sulfuric acid, (c) 2.46 × 10^{-3} M bismuth trichloride in 40% hydrochloric acid. This combination gave a transmission maximum at 285 nm (35%) and was opaque above 325 nm and below 250 nm. All runs were performed in 260 mL of solvent and were analyzed by NMR with triphenylmethane as the internal standard.

Summary of Direct Quantum Yields for 2-Methyl-3-(4′,4′-diphenylcyclohex-2′-en-1′-ylidene)prop-2-ene (6). The quantum yield for the appearance of 2-methyl-3-(5′,6′-*trans*-diphenylbicyclo[3.1.0]hexylidene)prop-2-ene in 2-methyl-2-propanol was determined to be 0.106.

Quantum Mechanics Calculations. The quantum mechanics calculations were done using the MOPAC[31] package using the MNDO[32] approximation. The two phenyls at the C-4 position were removed to save computation time and should have no effect on the relative ordering of reacting molecular orbitals. Initial geometries were obtained using the MM87[33] program. These initial geometries were then geometry optimized using the MOPAC package with configuration interaction equal to five. The ground state, first excited singlet, and first excited triplet were geometry optimized with configuration interaction. The reported bond

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orders are obtained employing the appropriate linear combination of Slater determinants for each C.I. eigenstate. The S_1 and S_0 of dimethyl diene allene **18** were also optimized using GAUSSIAN90 with an STO-3G basis set, and CASSCF with an active space of 4 was used for geometry optimization of S_1.

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Solvent Effects on the Competitive β-Scission and Hydrogen Atom Abstraction Reactions of the Cumyloxyl Radical. Resolution of a Long-Standing Problem[1]

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Abstract: Laser flash photolysis (LFP) techniques with detection in the infrared and in UV-visible regions of the spectrum have been used in combination with detailed product studies to assess solvent effects on the hydrogen abstraction and β-scission reactions of cumyloxyl radicals. The variation in the ratio of the products of these two competing processes in solvents with different polarities is due to the solvent's influence on β-scission. The rate constants for β-scission at 30 °C, k_β^{CumO}, were $(2.6_3 \pm 0.2_4) \times 10^5$, $(3.7_5 \pm 0.5_3) \times 10^5$, $(5.5_4 \pm 2.0_0) \times 10^5$, $(5.8_4 \pm 1.0_6) \times 10^5$, $(6.3_3 \pm 0.4_3) \times 10^5$, and $(19._6 \pm 3._4) \times 10^5$ $\mathrm{s^{-1}}$ in CCl_4, C_6H_6, C_6H_5Cl, $(CH_3)_3COH$, CH_3CN, and CH_3COOH, respectively. The rate constants for hydrogen abstraction from cyclohexane were essentially identical in these six solvents, viz., $k_a^{\mathrm{CumO}} = (1.2_4 \pm 0.1_2) \times 10^6$ $\mathrm{M^{-1}\,s^{-1}}$. There is a reasonably good linear correlation between log $(k_\beta^{\mathrm{CumO}}/\mathrm{s^{-1}})$ and certain cybotactic solvent parameters indicating that solvent effects on k_β^{CumO} are due to a localized interaction between the transition state for β-scission and adjacent solvent.

During the 1960's Cheves Walling and co-workers published an extensive series of pioneering papers on the photochemically initiated free-radical chain halogenations of a wide variety of organic compounds by *tert*-butyl hypochlorite and related hypohalites.[4-17] Provided a "contaminating" simultaneous chain reaction which is carried by chlorine atoms has been suppressed by the addition of "chlorine atom traps" (generally alkenes)[17-19] the overall process may be represented by the following:

$$(CH_3)_3COCl \xrightarrow{h\nu} (CH_3)_3CO^\bullet + Cl^\bullet \tag{1}$$

$$(CH_3)_3CO^\bullet \xrightarrow{k_\beta^{t\text{-BuO}}} (CH_3)_2C{=}O + CH_3^\bullet \tag{2}$$

$$(CH_3)_3CO^\bullet + RH \xrightarrow{k_a^{t\text{-BuO}}} (CH_3)_3COH + R^\bullet \tag{3}$$

$$R^\bullet(CH_3^\bullet) + (CH_3)_3COCl \rightarrow RCl(CH_3Cl) + (CH_3)_3CO^\bullet \tag{4}$$

Chlorination of a single substrate RH in an "inert" solvent (i.e., a solvent which does not act as a hydrogen atom donor, or is a poor donor, to *tert*-butoxyl) and measurement of the product ratio $[(CH_3)_3COH]/[(CH_3)_2CO]$ or, alternatively, of the ratio $[RCl]/[(CH_3)_2CO]$ over a range of known substrate concentrations yields the ratio of the rate constants for hydrogen abstraction from RH to β-scission, $k_a^{t\text{-BuO}}/k_\beta^{t\text{-BuO}}$. During the course of such routine measurements the most unexpected and exciting discovery was made: viz., solvents could have a dramatic effect on the magnitude of $k_a^{t\text{-BuO}}/k_\beta^{t\text{-BuO}}$.[12,13] For example,[13] with 0.1 M cyclohexane as RH at 40 °C the $[(CH_3)_3COH]/[(CH_3)_2CO]$ ratios obtained with *tert*-butyl hypochlorite varied from 5.50 in $CFCl_2CF_2Cl$ to 2.62 in benzene and 1.78 in CH_3CN to 0.70 in acetic acid. This solvent effect cannot be attributed to interference from a "contaminating" chlorine atom chain because *tert*-butoxyl radicals generated by thermal decomposition of di-*tert*-butylperoxyloxalate, reaction 5, gave essentially the same results, viz.,

$$(CH_3)_3COC(O)OOC(O)OC(CH_3)_3 \xrightarrow{\Delta} 2(CH_3)_3CO^\bullet + 2CO_2 \tag{5}$$

with 0.1 M cyclohexane at 40 °C the $[(CH_3)_3CO]/[(CH_3)_2CO]$ ratios were 7.5, 3.5, 1.6, and 1.1 in $CFCl_2CF_2Cl$, C_6H_6, CH_3CN, and CH_3COOH, respectively.[13]

The decrease in $k_a^{t\text{-BuO}}/k_\beta^{t\text{-BuO}}$ with increasing solvent polarity could, a priori, be due to the following: (i) a decrease in $k_a^{t\text{-BuO}}$, (ii) an increase in $k_\beta^{t\text{-BuO}}$, or (iii) both a decrease in $k_a^{t\text{-BuO}}$ and an increase in $k_\beta^{t\text{-BuO}}$. As Walling and co-workers were the first to point out,[10,12] "solvent effects on competitive radical reactions must reflect different degrees of solvent interaction with the *transition states* rather than with the *radicals* (assuming (radical-solvent) complexing to be a rapid process)." It was also pointed out that "Solvent interaction with the transition state for β-scission presents no difficulties, but in the transition state involving an alkoxy(l) radical and a substrate such as cyclohexene, solvent molecules should be sterically excluded from close vicinity to the alkoxy(l) radical".[10] Accordingly, Walling and Wagner[13] ascribed "the large solvent effects on $k_a^{t\text{-BuO}}/(k_\beta^{t\text{-BuO}})$ ratios chiefly to solvation of the transition state for the β-scission process". In the preceding quote the word "chiefly" would appear to be present

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