Diradical Pathways in Vinylcyclopropene Triplet Rearrangements: Mechanistic and Exploratory Organic Photochemistry[1,2]

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Received October 10, 1984

The triplet photochemistry of 1-phenyl-2-methyl-3-*p*-tolyl-3-isobutenylcyclopropene (1), 1-*p*-tolyl-2-methyl-3-phenyl-3-isobutenylcyclopropene (2), and 1-*p*-tolyl-2-phenyl-3-methyl-3-isobutenylcyclopropene (3) was investigated. In contrast to the singlet photochemistry, the triplet reactions were straightforward. Of the several mechanisms considered previously in connection with cyclopropene photochemistry, one (the type C mechanism) was shown to account for the various rearrangements. This mechanism proceeds via a cyclobutenylcarbinyl diradical resulting from an effective ring expansion of the vinylcyclopropene reactant. Marked regioselectivity in forming this diradical was defined and rationalized. Further, it was shown that the type C mechanism is operating solely. Finally it was found that this mechanism accounts for the photochemistry of all known triplet vinylcyclopropene rearrangements. In our study, quantum efficiencies were determined. For the isomers having one aryl group on the cyclopropene double bond, the efficiencies totaled 0.29, while for the isomer having two aryl groups on the double bond, the efficiency was 0.030. The differences are related to the localization energy for bonding between excited and unexcited vinyl groups. An independent approach to the cyclobutenylcarbinyl diradical was devised, making use of the corresponding azo compound wherein the nitrogen linked the diradical centers. This approach to the diradical afforded the same distribution of products as the cyclopropene photochemistry.

Following the initial discovery of the rearrangement of vinylcyclopropenes,[3a,4a] we, and the Padwa group, have reported[3,4] a number of additional examples that demonstrate the broad generality of rearrangement of vinylcyclopropenes to afford cyclopentadienes. Despite the versatility of the rearrangement, the reaction mechanism has remained uncertain. With this situation in mind, we designed a system that promised to differentiate among a number of plausible mechanistic alternatives. Also, we noted a greater simplicity in the rearrangement of the triplet cyclopropenes and focused our attention on the sensitized rearrangement.

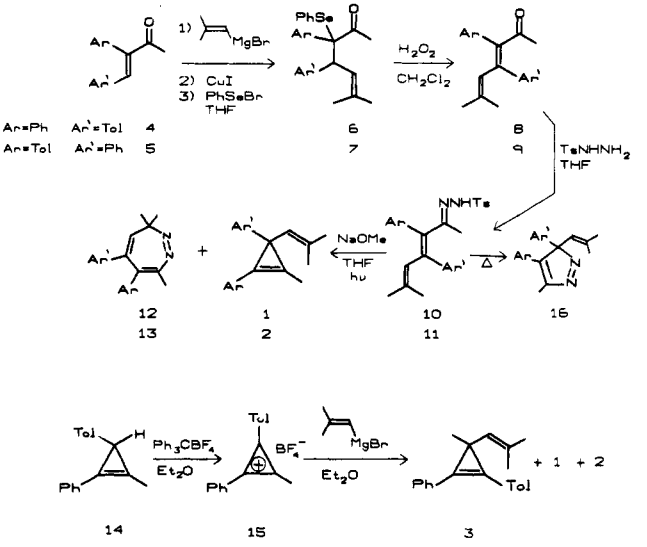
For our study we selected three vinylcyclopropenes: 1-phenyl-2-methyl-3-*p*-tolyl-3-isobutenylcyclopropene (1), 1-*p*-tolyl-2-methyl-3-phenyl-3-isobutenylcyclopropene (2), and 1-*p*-tolyl-2-phenyl-3-methyl-3-isobutenylcyclopropene (3).

Results

Synthesis of the Photochemical Reactants. The syntheses of the three cyclopropenes 1, 2, and 3 are outlined in Scheme I. One interesting point is that the role of light in the step converting tosylhydrazones 10 and 11 to diazepines 12 and 13, respectively, seems to be the conversion of trans to cis stereoisomer, which permits diazepine formation.

Also, it was noted that thermolysis of the tosylhydrazone 10, instead of affording the desired diazepine 12, led primarily to the pyrazole 16.

Scheme I. Synthesis of Vinylcyclopropene Reactants



Scheme II outlines the preparation of potential photoproducts.

Exploratory Photochemistry of the Cyclopropenes. The direct irradiation of vinylcyclopropenes (e.g., 1) afforded a complex mixture of products. In contrast, the *p*-(dimethylamino)benzophenone-sensitized irradiation proved quite straightforward. In fact, the simplicity of sensitized cyclopropene photochemistry compared with direct photolyses has proven relatively general in our experience.

Thus, the sensitized photochemistry of cyclopropene 1 led to cyclopentadienes 25 and 34, both of which had been synthesized as outlined in Scheme II. Similarly, sensitized irradiation of cyclopropene 2 gave rise to cyclopentadienes 26 and 35. These, too, had been synthesized (note Scheme II).

Finally, sensitized photolysis of cyclopropene 3 gave all four of these photoproducts (i.e., 25, 26, 34, and 35). All three rearrangements are depicted in eq 1–3.

Efficiencies for the Cyclopropene Rearrangements. The quantum yields were determined by using *p*-(dimethylamino)benzophenone (E_T ca. 67 kcal/mol[5]). These

(1) (a) This is paper 143 of our photochemical series and 201 of our general papers. (b) For a preliminary communication describing some of this work, note: Zimmerman, H. E.; Fleming, S. A. *J. Am. Chem. Soc.* **1983**, *105*, 622–624.

(2) (a) For paper 200 of our general series, see: Zimmerman, H. E.; Linder, L. W. *J. Org. Chem.*, in press. (b) For paper 142 of our photochemical papers, see: Zimmerman, H. E.; Carpenter, C. W., Weber, A. M. *J. Am. Chem. Soc.* **1985**, *107*, 1073–1074.

(3) (a) Zimmerman, H. E.; Aasen, S. *J. Am. Chem. Soc.* **1977**, *99*, 2342–2344. (b) Zimmerman, H. E.; Aasen, S. M. *J. Org. Chem.* **1978**, *43*, 1493–1506. (c) Zimmerman, H. E.; Hovey, M. C. *J. Org. Chem.* **1979**, *44*, 2331–2345. (d) Zimmerman, H. E.; Kreil, D. J. *J. Org. Chem.* **1982**, *47*, 2060–2075.

(4) Note also: (a) Padwa, A.; Blacklock, T. J.; Getman, D.; Hatanake, N.; Loza, R. *J. Org. Chem.* **1978**, *43*, 1481–1492. (b) For a recent publication giving further references, note: Padwa, A.; Blacklock, T. J.; Loza, R. *J. Org. Chem.* **1982**, *47*, 3712–3721.

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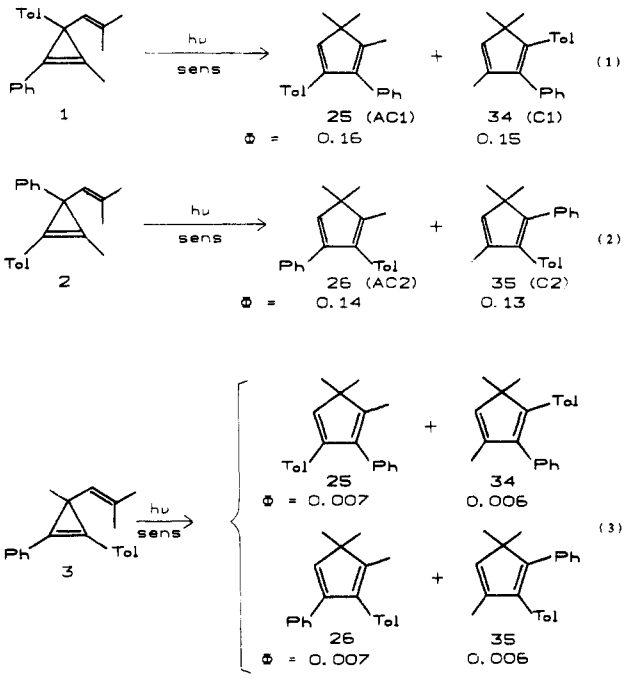


values are included in eq 1–3. Interestingly, the efficiencies for the cyclopropenes bearing one aryl group on the three-ring double bond (i.e., **1** and **2**) were an order of magnitude greater than the quantum yield for cyclopropene **3** having a *cis*-stilbenyl chromophore. This point is considered below.

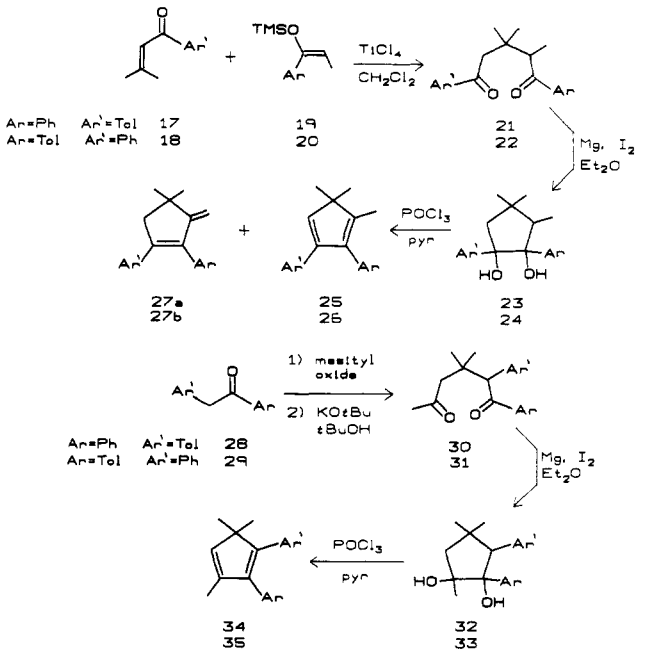
Independent Generation of the Cyclobutenylcarbinyl Diradical. One mechanism of particular interest (vide infra) proceeds via the cyclobutenylcarbinyl diradical **36**.

Our approach to this problem began with diazepine **12**. Photoreaction of **12** required extended reaction times but did lead to the cyclopentadienes **25** and **34**, although in low (20%) yield. As is seen below, an independent photochemical route of this type leading to these cyclopentadienes was desired for mechanistic reasons. An approach with better yields was desired.

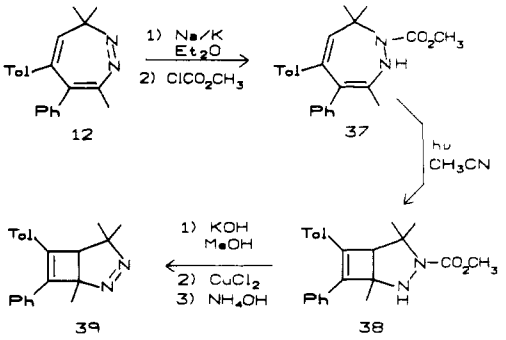
Treatment of diazepine **12** with sodium–potassium alloy in ether, followed by quenching with methyl chloroformate, led to monocarbomethoxylated diazepine **37**. This transformation is included in Scheme III. One view of the reaction is the preferential acylation of the diazepine dianion, resulting from introduction of two electrons, at one nitrogen such that maximum delocalization of the resulting monoanion results. Irradiation of carbomethoxylated diazepine **37** led smoothly to the bicyclic product **38**. This, in turn, was decarbomethoxylated with potassium hydroxide in methanol. The resulting bicyclic hydrazo compound was oxidized, without isolation, by using cupric chloride to afford the Cu(II) complex of the desired bicyclic azo compound **39**. These transformations are summarized in Scheme III.

(5) (a) The estimated triplet energy is taken as that of *p*-aminobenzophenone as in ref 22b,c. (b) Porter, G.; Suppan, P. *Trans. Faraday Soc.* **1965**, *61*, 1664–1673. (c) O'Connell, E. J., Jr. *J. Chem. Soc., Chem. Commun.* **1969**, 571–572.

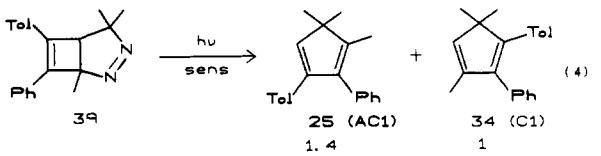
Scheme II. Synthesis of Photoproducts



Scheme III. Synthesis for the Bicyclic Azo Compound 39



Triplet Photochemistry of the Bicyclic Azo Compound. The bicyclo azo compound **39** was photolyzed with *p*-(dimethylamino)benzophenone (E_T ca. 67 kcal/mol[5]) and observed to afford cyclopentadienes **25** and **34** in a (1.4 ± 0.15):1 ratio. Refer to eq 4. We note that these are the

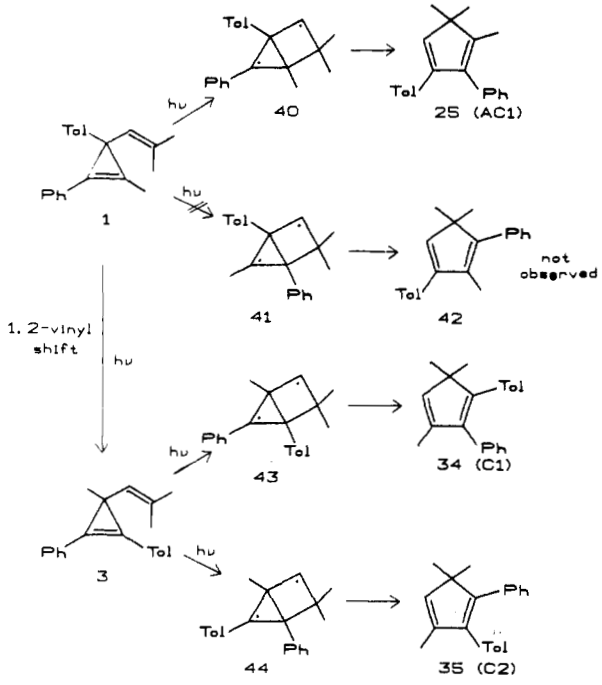


same products obtained (note eq 1) in the triplet photochemistry of cyclopropene **1** and also that the product distribution is the same within experiment error (i.e., (1.4 ± 0.15):1).

Photoproduct Stability. Not only the quantum yields but also our mechanistic conclusions would be in error if the cyclopentadiene photoproducts **25**, **26**, **34**, and **35** were not stable under photolysis conditions. This was of some special concern since cyclopentadiene scrambling seemed plausible.[3d,6] However, the four cyclopentadienes of present interest proved to be stable under reaction conditions utilized in this study.

(6) (a) Note the rearrangement of 2-ethyl-3-methylindene.[6b] (b) Giacherio, D.; Morrison, H. A. *J. Am. Chem. Soc.* **1978**, *100*, 7109–7110. (c) Baldwin, J. E.; Andrews, C. D. *J. Am. Chem. Soc.* **1977**, *99*, 4851–4853. (d) Further investigation has revealed that the photochemical conversion of 1,5,5-trimethyl-2,3-diphenylcyclopentadiene to 1,2-diphenyl-3,5,5-trimethylcyclopentadiene reported in our earlier work[3c] is incorrect.

Scheme IV. Application of Mechanism A to the Rearrangement of Cyclopropene 1



Interpretative Discussion

Molecular Reaction Mechanism. At the outset four possible mechanisms seemed to be a priori possibilities: A, B, C, and D. These alternatives have precedent in mechanisms considered in the singlet photochemistry of vinylcyclopropenes as well as being advanced as possibilities for the triplet rearrangements.[3] For convenience of discussion we label the four photoproducts with designations intended to indicate which mechanism leads from which reactant to which product. Thus product C1 derives from cyclopropene reactant 1 via mechanism C. Similarly product AC1 derives from reactant 1 by both mechanisms A and C.

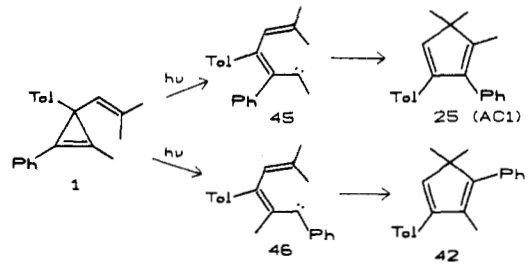
Mechanism A involves an intermediate housane diradical and is depicted in Scheme IV as applied to the rearrangement of vinylcyclopropene 1. This example is representative and suffices.

This mechanism is seen to lead to the observed photoproduct **25** (i.e., AC1). The nonformation of cyclopentadiene **42** experimentally would be reasonable on the basis of this mechanism, since the housane diradical **41** leading to this product is less delocalized than diradical **40** leading to the observed product.

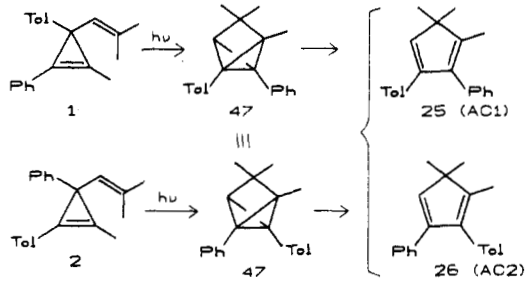
However, a major weakness in the mechanism is its inability to account for the second photoproduct, cyclopentadiene **34** (i.e., C1). An extension of mechanism A would be required as shown in Scheme IV; this extension requires a 1,2-vinyl shift to afford cyclopropene **3**, which then would have to undergo mechanism A. Further, the regioselectivity needed to account for formation of only cyclopentadiene **34** and not **35** would be difficult to rationalize.

A fatal inadequacy of mechanism A results from the experimental observation that cyclopropene **3** affords four cyclopentadienes in roughly equal amounts and thus cannot be an intermediate in the triplet photochemistry of cyclopropene 1, which affords only two products. Nevertheless, with the evidence in hand at this point, we could properly invoke mechanism A as accounting for one of the two photoproducts, namely cyclopentadiene **25** (AC1).

Scheme V. The Carbene Mechanism B



Scheme VI. Electrocyclic Mechanism D



A parallel consideration of the photochemistry of cyclopropene **2** uncovers the same inability of mechanism A to account for more than one product, namely **26** (AC2).

Mechanism B involves fission of a σ bond to afford a vinylcarbene as shown in Scheme V. However, evidence is available to indicate that triplet cyclopropenes do not open to afford carbenes.[7,8] Even more cogently, despite the total differences in mechanism B compared to mechanism A, the two are precisely structurally equivalent. This has been noted before.[3c] Hence mechanism B can account for formation of only cyclopentadiene **25** (AC1) from cyclopropene **1**.

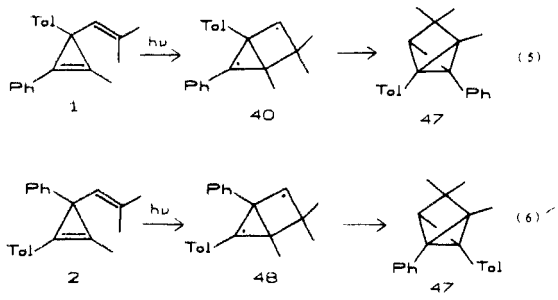
Similar reasoning, applied to cyclopropene **2**, reveals a parallel deficiency of mechanism B.

A third mechanism, which we have termed D, is outlined in Scheme VI. This proceeds by a $2\pi + 2\pi$ cycloaddition of the vinyl group to the three-membered-ring π bond. Here reactants **1** and **2** are used to illustrate the consequences of the mechanism. Also, only the regioselectivity of cycloaddition needed to lead to observed products is considered. We find that mechanism D is capable of generating only one of the two photoproducts from each of cyclopropenes **1** and **2**, that is, **25** (AC1) from **1** and **26** (AC2) from **2**.

However, this is a minor deficiency compared with a fatal one. Accordingly, it is noted that the cycloaddition steps starting from cyclopropenes **1** and **2** lead to the same tricyclic intermediate **47** and thus mechanism D cannot account for the experimental observation of obtaining different products from cyclopropenes **1** and **2** as outlined in eq 1 and 2 of the Results.

There is an additional, intriguing conclusion possible. To the extent that the housane diradical mechanism A operates to generate just photoproducts **25** (AC1) and **26** (AC2), one might consider "touching" (i.e., reversible bonding) of the diradical centers as depicted in eq 5 and 6. Such reversible bonding between the diradical centers leads to the same tricyclic pentane **47** and thus would lead to common product distributions starting with cyclopropenes **1** and **2**. Hence, if the housane triplet diradicals

(7) Zimmerman, H. E.; Bunce, R. A. *J. Org. Chem.* **1982**, *37*, 3377–3396.
(8) Pincock, J. A.; Moutsokapas, A. A. *Can. J. Chem.* **1977**, *55*, 979–985.



40 and 48 are formed, they do not close.

In contrast to the preceding three pathways, mechanism C leads from each of the three cyclopropene reactants, 1–3, to the observed products. The course of mechanism C, as applied to the reaction of cyclopropenes 1 and 2, is detailed in Scheme VII. The more complex case of the reaction of cyclopropene 3 is outlined in Scheme VIII. In all cases the experimentally observed products are predicted without including any products not encountered.

Thus far we have discussed evidence regarding deficiencies in mechanisms A, B, and D as well as noting the capabilities of mechanism C in accounting for the observed reaction course. An additional conclusion is possible; this derives from comparison of the product ratios obtained in the irradiations of cyclopropenes 1 and 2 with the ratios encountered in the irradiation of cyclopropene 3.

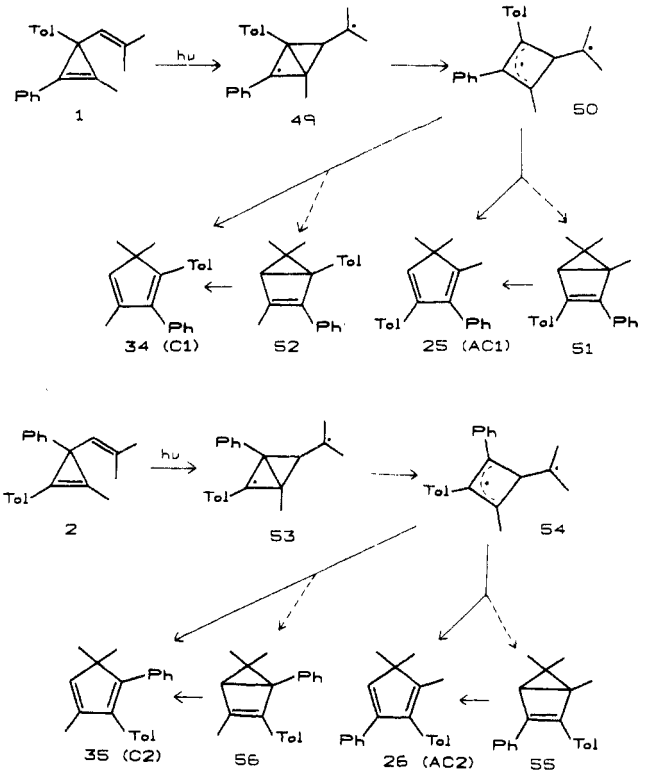
Inspection of eq 1 and 2 shows the ratio of products from cyclopropene 1, C1 to AC1, to be 0.89 (±0.05) and the ratio of products from cyclopropene 2, C2 to AC2, to be 0.90 (±0.05). Equation 3, depicting the photochemistry of cyclopropene 3, gives the ratio of C1 to AC1 as 0.90 and the ratio of C2 to AC2 as 0.90.

Hence the ratio of C1 to AC1 is the same in photochemistry starting with cyclopropene 1 as that starting with 3. Similarly, the ratio of C2 to AC2 is the same starting with 2 as starting with 3. This has significance as can be understood by reference to Scheme IX. We note a competition wherein the excited triplet of cyclopropene 1 (i.e., ^{3}1*) may react via mechanism C to afford cyclobutenylcarbinyl diradical **50** with a rate constant of k_1 and then onward to the observed photoproducts C1 and AC1. Alternatively, ^{3}1* may lead with a rate constant of k_{o1} to product AC1 by other mechanisms (e.g., A, B, and/or D); here we assume the preferential formation of AC1 by these other mechanisms based on the predictions of these mechanisms as described above.

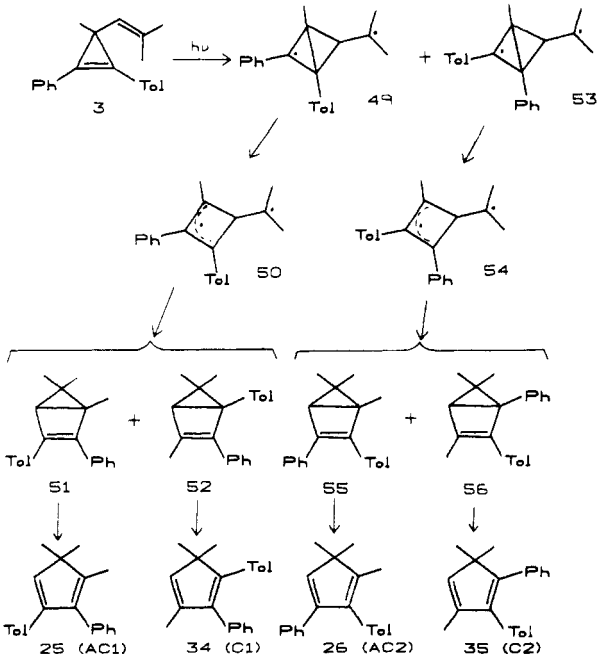
Similarly triplet ^{3}3* may react to afford the same cyclobutenyl diradical **50** with a rate constant k_3 or react by the alternative mechanisms to afford C1 with a rate constant of k_{o3}.

To the extent that the cyclobutenylcarbinyl diradical **50** is accepted as intervening at least to some extent, it may be seen that the two alternative modes of closure afford the two cyclopentadiene products C1 and AC1. Further, this diradical is arrived at from both starting vinylcyclopropenes 1 and 3. Thus, the identity of the product ratio corresponds to the diradical closing with regioselectivity independent of the source of the diradical. Any of the alternative mechanisms considered leads the two cyclopropene reactants to different products. Any occurrence of other mechanisms starting with ^{3}1* would afford additional cyclopentadiene AC1, while occurrence of other mechanisms starting with ^{3}3* would increase the amount of cyclopentadiene C1 resulting. That is, intrusion of other mechanisms of the type considered (i.e., A, B, or D) would change the product ratios deriving from triplets ^{3}1* and ^{3}3* in different directions from the common value actually

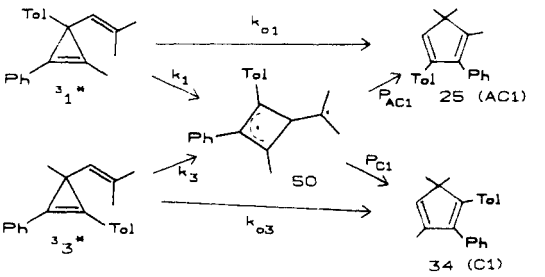
Scheme VII. Cyclobutenylcarbinyl Diradical Mechanism C



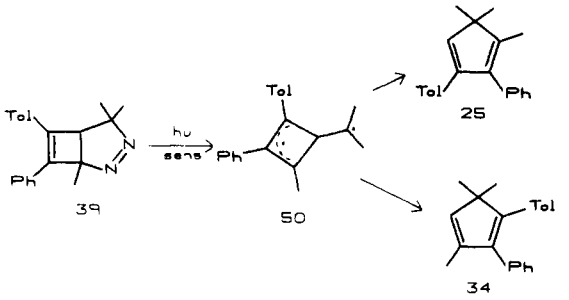
Scheme VIII. Mechanism C Applied to the Photochemistry of Cyclopropene 3



Scheme IX. Product Distributions as a Function of Mechanism



Scheme X. Triplet Diradical Generation



observed and would predict a nonidentity of product ratios.

Similar reasoning can be applied to the observed product ratios arising from the photolysis of vinylcyclopropenes **2** and **3**. Experimentally, the same ratio of AC2 to C2 is observed as predicted on the basis of the common cyclobutenylcarbinyl diradical **54**. Operation of mechanism A, B, or D is inconsistent with this observation for reasons parallel to those given above for the reactions of **1** and **3**.

Details of the Ring-Expansion Processes. One facet that has not been considered is the nature of the two ring-expansion processes of mechanism C as outlined in Scheme VII. Thus the formation of the cyclobutenylcarbinyl diradical (e.g.) **50** from cyclopropene **1** is formally a 1,2-shift. Similarly, the conversion of the cyclobutenylcarbinyl diradical **50** to product cyclopentadiene (e.g.) **25** is, again, formally a 1,2-shift.

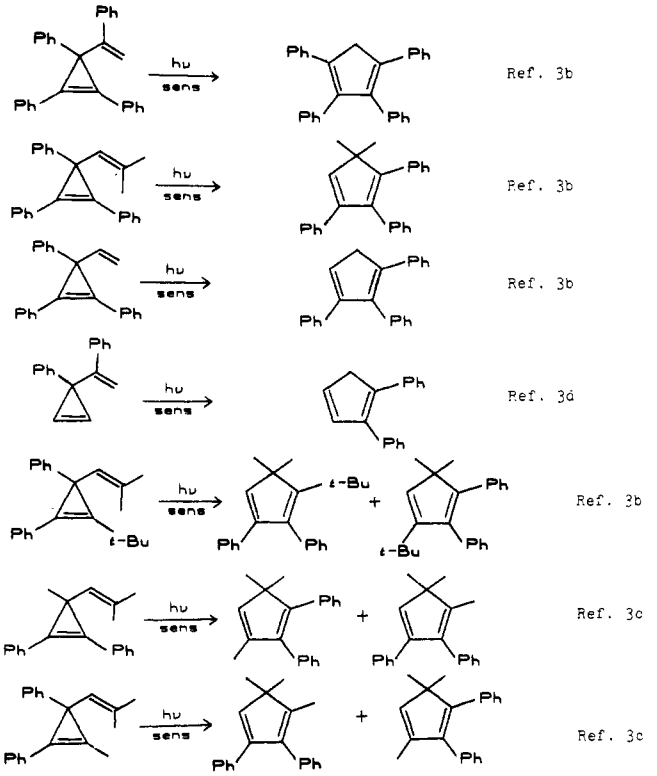
Almost all 1,2-shifts of vinyl and aryl groups proceed by initial π–π bonding followed by fission of the original σ bond holding the migrating group.[9] Following this reasoning, the bicyclobutanylcarbinyl diradical (e.g.) **49** should be formed first by such π–π bonding.

In similar fashion the ring expansion of the cyclobutenylcarbinyl diradical **50** might be anticipated to proceed via housenes **51** and **52** initially, rather than undergoing a simple 1,2-σ-bond shift as a one-step ring expansion. However, as noted in the Experimental Section, all attempts to detect housenes at temperatures sufficient to permit reaction revealed no such intermediates. It may well be then that the ring expansion is indeed direct.

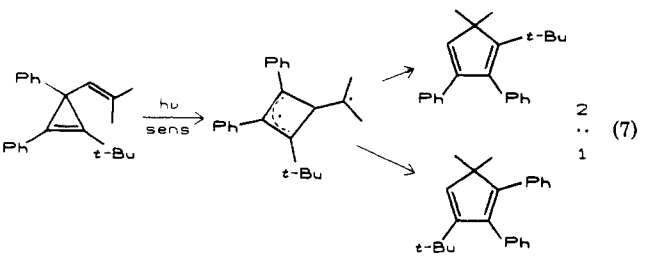
Independent Generation of the Cyclobutenylcarbinyl Diradical. Since the mechanism outlined in Scheme VII invokes the triplet cyclobutenylcarbinyl diradical **50**, the generation of this species from bicyclic azo precursor **39** with subsequent formation of the same product cyclopentadienes **25** and **34** and with the same (1:1.4) regioselectivity within experimental error as encountered in the cyclopropene photochemistry provides confirming evidence for intervention of the cyclobutenylcarbinyl diradical **50**.[12] Note Scheme X.

In our earlier studies,[10] for example, thermal decomposition, direct irradiation, and sensitized reaction of barrelene-derived azo compounds all afforded different reactivities, each reflecting the electronic state of the diradical generated. Hence it appears that reaction of azo precursors via different electronic states provides an approach to the corresponding electronic states of the derived diradicals. In the present case sensitization should afford the cyclobutenylcarbinyl diradical as the triplet.

Table I. Predicted and Observed Triplet Cyclopropene Photoproducts



Regioselectivity Encountered in the Rearrangement Mechanism. Not only in the present photochemical study but also in all of the examples in Table I in which the cyclopropene π bond is unsymmetrically substituted, dramatic regioselectivity is observed in the vinyl-to-cyclopropene π-bond bridging. In each case the exclusively preferred bridging process is the one leading to the more delocalized bicyclobutanylcarbinyl diradical. One especially interesting case proceeds in this fashion despite the bridging occurring at a *tert*-butyl-bearing center.[3a,b] Note eq 7. Again, mechanism C predicts and accounts for all of the triplet products.



Present evidence bearing on the closure of the cyclobutenylcarbinyl diradicals suggests little selectivity, and we are investigating this process further.

General Validity of Mechanism C. Thus far we have derived mechanism C from the experimental results of the present study. Equally convincing is an application of this mechanism, with its known regioselectivity incorporated, to the various literature examples of the triplet vinylcyclopropene-to-cyclopentadiene rearrangement.[3] Table I lists the previously reported triplet vinylcyclopropene-

(9) Zimmerman, H. E. In "Rearrangements in Ground and Excited States"; DeMayo, P., Ed.; Academic Press: New York, 1980; Vol. 3, Chapter 6.

(10) Zimmerman, H. E.; Boettcher, R. J.; Buehler, N. E.; Keck, G. E.; Steinmetz, M. G. *J. Am. Chem. Soc.* **1976**, *98*, 7680–7689. For more recent applications of this approach note ref 11.

(11) Adam, W.; DeLucchi, O.; Peters, K.; Peters, E. M.; von Schering, H. G. *J. Am. Chem. Soc.* **1982**, *104*, 5747–5753.

(12) (a) In an interesting publication[12b] a similar bicyclic azo compound, however with different substituents, has been reported. In contrast to the triplet behavior of our study the thermolysis led primarily to one of two possible cyclopentadienes. The differing behavior may derive from the different substitution or, more likely, from the reaction being ground state. (b) Huisgen, R.; Reissig, H.-U. *J. Chem. Soc., Chem. Commun.* **1979**, 568–570.

to-cyclopentadiene rearrangements. Remarkably, each of these examples has the reaction products predicted by mechanism C.

Lack of Reversibility in Mechanism C. An interesting further conclusion may be derived regarding mechanism C. In contrast to the direct irradiations involving singlet photochemistry where 1,2-vinyl shifts, to give isomeric vinylcyclopropenes, are commonplace,[3] in the present triplet photochemistry no 1,2-vinyl-shifted products were encountered. Since the first step of mechanism C (note Scheme VII) is the first step of a 1,2-vinyl shift, any reversibility in mechanism C would readily be detected in the form of the vinyl-shift process. For example, the half-migrated (i.e., bicyclobutanylcarbinyl) diradical **49** is formed from both cyclopropene 1 and also **3**. Reversibility would lead to interconversion of 1 and **3**.

Higher Efficiencies in Less Delocalized Cyclopropenes. The quantum yield for the 1,2-diarylcyclopropene **3** is 10-fold lower than that for the 1-arylcyclopropenes 1 and **2**. It does appear that bridging to chromophores with more diffuse excitation is less efficient. The reason for this is that, as bridging develops and engenders a diradical, more vertical excited-state delocalization is lost in bridging to the more extended π system.

Geometry of the Cyclobutenylcarbinyl Diradical. Reference to structures **36h** and **36m** shows that two alternative geometries are possible for this diradical. The former constitutes a Hückel orbital array and the latter a Möbius array.[13] For S_0 of the cyclobutenylcarbinyl diradical one might anticipate the Möbius geometry to be favored, since systems with $4N$ electrons are favored by Möbius systems in the ground state. However, in the triplet reaction, the Hückel geometry affords an approach toward HOMO–LUMO degeneracy and thus maximizes intersystem crossing to ground-state product.[13e] In this conformation, a pivoting motion approaching Möbius geometry is needed either to form the σ bond required to generate a housene or to directly ring expand. Such a twist could enhance intersystem crossing by spin–orbit coupling.

Factors Leading to the Triplet Mechanism C. In earlier studies, we have noted that triplet excited states tend to react via mechanisms which lead to species with large S_1–T_1 separations (i.e., large exchange integrals, K) while singlet excited states tend to utilize "small-K pathways". We categorized a number of types of reactions as belonging to the "small-K" or the "large-K" variety.[14] Mechanism C in the present study involves formation of a diradical species by bridging of two vinyl groups. Such an extended π system tends to have a large K. The operation of mechanisms A and B in singlet vinylcyclopropene photochemistry suggests that these processes are inherently concerted and cyclic in nature. Thus as the three-ring σ bond is broken as exemplified by the carbene extreme (i.e., mechanism B) a new σ bond is most likely being formed (as in mechanism A).

Hence it appears that operation of the mechanism C triplet vinylcyclopropene rearrangements, in contrast to the singlet mechanism A and B rearrangements, provides us with still another example of exchange integral control in organic photochemistry.

Conclusion

The major consequence of the present study has been in providing a single mechanism for all of the triplet vinylcyclopropene rearrangements and in demonstrating the simplicity and universality of this photochemistry.

Experimental Section[15]

3-Phenyl-3-(phenylseleno)-4-*p*-tolyl-6-methyl-5-hepten-2-one. In a typical run[3c] 13.4 mL (0.130 mol) of isobutenyl bromide in 20 mL of tetrahydrofuran was added to 3.28 g (0.130 mol) of magnesium in 100 mL of tetrahydrofuran. This mixture was refluxed for 16 h and cooled to 0 °C, and 2.96 g (0.0155 mol) of cuprous iodide[16] was added in portions over 5 min. The solution went from yellow to dark gray. A 50-mL solution of 24.5 g (0.10 mol) of 3-phenyl-4-*p*-tolylbuten-2-one[17] in tetrahydrofuran at 0 °C was added in 30 min. The gray solution was stirred at 0 °C for ca. 1 h and then was quenched with phenylselenyl bromide[18] (from 24.3 g (77.8 mmol) of diphenyl diselenide and 3.74 mL (72.5 mmol) of bromine) in 50 mL of tetrahydrofuran at 0 °C. The slurry was stirred for 1.5 h and then quenched with 50 mL of saturated aqueous ammonium chloride. Ether extraction, six water washes, and concentration gave 35.0 g of a brown oil. The crude material was chromatographed on a 7 × 20 cm silica gel column, packed and eluted with 5% ether–hexane. Concentration of the first 2.0 L gave 27.5 g of a mixture of diphenyl diselenide, 3-phenyl-3-(phenylseleno)-4-*p*-tolyl-6-methyl-5-hepten-2-one, and 3-phenyl-4-*p*-tolyl-6-methyl-5-hepten-2-one. The desired 3-phenyl selenide was separated by a second silica gel chromatography on a 7 × 200 cm column. Packing and eluting with 3% ether–hexane and collecting 40-mL fractions gave the following: fractions 22–27, diphenyl diselenide; 28–41, 15.7 g of a mixture of diphenyl diselenide and the 3-phenyl selenide; 42–70, 10.5 g (30%) of the 3-phenyl selenide as an oil identified by NMR. Rechromatography of the overlapping fractions brought the yield to 22.6 g (58%) of the 3-phenyl selenide, initially as an oil, nearly pure by NMR. Recrystallization from pentane gave 13.56 g (35%) of 3-phenyl-3-(phenylseleno)-4-*p*-tolyl-6-methyl-5-hepten-2-one as white crystals, mp 127–129 °C.

The spectral data were as follows: 270-MHz ($CDCl_3$) δ 7.6–6.4 (m, 14 H, arom), 5.802 (d sept, 1 H, J = 4.7, 1 Hz, =CH), 4.294 (d, 1 H, J = 4.7 Hz, CH), 2.150 (s, 3 H, CH_3), 2.122 (s, 3 H, CH_3),

(13) (a) Zimmerman, H. E. *J. Am. Chem. Soc.* **1966**, *88*, 1564–1565. (b) Zimmerman, H. E. Acc. *Chem. Res.* **1971**, *4*, 272–280. (c) Zimmerman, H. E. "Quantum Mechanics for Organic Chemists", Academic Press: New York, 1975. (d) Zimmerman, H. E. In "Pericyclic Reactions"; Marchand, A., Lehr, R., Eds.; Academic Press: New York, 1977; Vol. 1. Zimmerman, H. E. *Tetrahedron* **1982**, *38*, 753–758. (e) Zimmerman, H. E. *J. Am. Chem. Soc.* **1966**, *88*, 1566–1567.

(14) (a) Zimmerman, H. E.; Armesto, D.; Amezua, M. G.; Gannett, T. P.; Johnson, R. P. *J. Am. Chem. Soc.* **1979**, *101*, 6367–6383. (b) Zimmerman, H. E.; Factor, R. E. *J. Am. Chem. Soc.* **1980**, *102*, 3538–3548. (c) Zimmerman, H. E.; Penn, J. H.; Johnson, M. R. *Proc. Natl. Acad. Sci. U.S.A.* **1981**, *78*, 2021–2025.

(15) Melting points were determined with a calibrated hot-stage apparatus. Elemental analyses were performed by Galbraith Laboratories, Inc., Knoxville, TN 36921.

All reactions were run under a dry nitrogen atmosphere unless otherwise stated. Anhydrous magnesium sulfate was used as a drying agent. Column chromatography was performed on silica gel (Matheson Coleman and Bell, grade 62, 60–200 mesh) mixed with Sylvania 2282 phosphor and slurry packed into quartz columns, permitting monitoring by a hand-held UV lamp. High-pressure liquid chromatography (HPLC) was performed on a liquid chromatograph employing an LDC 254-nm detector and an LDC 6000-psi minipump. Analyses were performed with a 1 × 30 cm polished stainless steel column packed with 7–10-μm porous silica beads. Purified hexane was used as eluant.

Acetonitrile used for irradiation experiments was distilled from calcium hydride before use. Photograde benzene was prepared by washing with the following: saturated aqueous potassium permanganate and concentrated sulfuric acid; water; sulfuric acid until no discoloration; saturated aqueous sodium bicarbonate; brine. The benzene was then dried over magnesium sulfate, refluxed over calcium hydride for 10 h, and distilled under nitrogen.

Hexane employed in HPLC was washed with nitric acid and sulfuric acid (1:1), water, aqueous saturated sodium bicarbonate, and brine. The hexane was dried over anhydrous calcium chloride and passed through alumina. Finally, the hexane was distilled from calcium hydride.

Tetrahydrofuran (THF) was purified by storage over potassium hydroxide, followed by successive distillation under nitrogen from calcium hydride, lithium aluminum hydride, and sodium benzophenone ketyl. Dichloromethane was purified by distillation from phosphorus pentoxide.

(16) Kauffman, G. B.; Pinnell, R. P. *Inorg. Synth.* **1960**, *6*, 3–6.

(17) Appriou, P.; Breliuet, J.; Teste, J. *Bull. Soc. Chim. Fr.* **1970**, 1497–1502.

1.747 (d, 3 H, J = 1.0 Hz, =CCH_3), 1.185 (d, 3 H, J = 1.0 Hz, =CCH_3); IR (neat) 3050, 3010, 2960, 2920, 2860, 1690, 1600, 1580, 1510, 1445, 1360, 1195, 1030, 710, 695 cm^{-1}; mass spectrometry for $C_{27}H_{28}OSe$, m/e (calcd) 368.2140, (found) 368.2140.

Anal. Calcd for $C_{27}H_{28}OSe$: C, 72.48; H, 6.26. Found: C, 72.16; H, 6.12.

3-*p*-Tolyl-4-phenylbuten-2-one. A mixture of 37.6 mL (0.254 mol) of *p*-tolylacetone, 25.9 mL (0.254 mol) of benzaldehyde, 2.50 mL of piperidine, and 150 mL of benzene was refluxed in a Dean–Stark trap apparatus for 18 h. The benzene was distilled off, the pot was cooled, and 50 mL of hexane–ether (2:1) was added. The solution was cooled to −78 °C and filtered and the filtrate was washed with hexane–ether (−78 °C), giving 35.5 g (60%) of crude material, mp 50–51 °C. Recrystallizing from the same solvent gave 32.9 g (54%) of 3-*p*-tolyl-4-phenylbuten-2-one, mp 51.5–53 °C.

The spectral data were as follows: 270-MHz NMR ($CDCl_3$) δ 7.611 (s, 1 H, =CH), 7.26–7.01 (m, 9 H, arom), 2.391 (s, 3 H, CH_3), 2.298 (s, 3 H, CH_3); IR ($CHCl_3$) 3020, 3005, 2920, 1685 (s), 1600, 1520, 1495, 1455, 1365, 1240, 1160, 700 cm^{-1}; mass spectrometry for $C_{17}H_{16}O$, m/e (calcd) 236.1201, (found) 236.1202.

Anal. Calcd for $C_{17}H_{16}O$: C, 86.44; H, 6.78. Found: C, 86.55; H, 6.93.

3-*p*-Tolyl-3-(phenylseleno)-4-phenyl-6-methyl-5-hepten-2-one. A mixture of 2.50 g (0.103 mol) of magnesium and 10.2 mL (0.103 mL) of isobutenyl bromide in 100 mL of tetrahydrofuran was refluxed for 20 h. The brown solution was cooled to 0 °C, and 2.42 g (12.7 mmol) of cuprous iodide[16] was added. A solution of 20.0 g (84.7 mmol) of 3-*p*-tolyl-4-phenylbuten-2-one in 30 mL of tetrahydrofuran at 0 °C was added. The solution was stirred at 0 °C for 30 min and then was quenched with phenylselenyl bromide prepared from 16.7 g (53.5 mmol) of diphenyl diselenide and 2.60 mL (50.4 mmol of bromine in 30 mL of tetrahydrofuran. The same workup as used for the previous 3-phenyl selenide was employed with a crude yield of 18.2 g. Recrystallization from pentane gave 12.7 g (35%) of 3-*p*-tolyl-3-(phenylseleno)-4-phenyl-6-methyl-5-hepten-2-one, mp 137–139 °C.

The spectral data were as follows: 270-MHz NMR ($CDCl_3$) δ 7.80–6.85 (m, 14 H, arom), 5.809 (br d, 1 H, J = 8.9 Hz, =CH), 4.241 (d, 1 H, J = 9.1 Hz, CH), 2.353 (s, 3 H, $ArCH_3$), 2.170 (s, 3 H, CH_3C=O), 1.738 (br s, 3 H, =CH_3) 1.164 (br s, 3 H, =CCH_3); IR ($CHCl_3$) 3060, 3000, 2920, 1685 (s), 1600, 1510, 1450, 1440, 1360, 1200, 1025, 810, 700 cm^{-1}; mass spectrometry for $C_{27}H_{28}OSe$, m/e (calcd) 368.2140, (found) 368.2140.

Anal. Calcd for $C_{27}H_{28}OSe$: C, 72.48; H, 6.26. Found: C, 72.43; H, 6.45.

3-Phenyl-4-*p*-tolyl-6-methyl-3,5-heptadien-2-one. To a solution of 1.30 g (2.90 mmol) of 3-phenyl-3-(phenylseleno)-4-*p*-tolyl-6-methyl-5-hepten-2-one in 10 mL of methylene chloride and 0.410 mL of pyridine was added 1.01 mL (8.90 mmol) of 30% hydrogen peroxide in 0.60 mL of water as in the Reich procedure.[18] The reaction was stirred for 1 h and then poured into sodium bicarbonate and ether. The organic layer was washed with 10% hydrochloric acid, water, and brine and then dried over magnesium sulfate. Concentration left 0.82 g (98%) of the dienone, mp 102–104 °C. Recrystallization in methanol left 0.606 g (72%) of 3-phenyl-4-*p*-tolyl-6-methyl-3,5-heptadien-2-one as needle-like crystals, mp 104–105 °C.

The spectral data were as follows: 270-MHz NMR ($CDCl_3$) δ 7.20–7.00 (m, 9 H, arom), 5.850 (sept, 1 H, J = 1.1 Hz, =CH), 2.364 (s, 3 H, $ArCH_3$), 1.952 (s, 3 H, CH_3C=O), 1.681 (d, 3 H, J = 1.1 Hz, =CCH_3), 1.201 (d, 3 H, J = 1.1 Hz, =CCH_3); IR ($CHCl_3$) 3020, 2995, 1700, 1520, 1510, 1420, 1200 (s), 920, 790, 660 cm^{-1}; mass spectrometry for $C_{21}H_{22}O$, m/e (calcd) 290.1671, (found) 290.1671.

Anal. Calcd for $C_{21}H_{22}O$: C, 86.91; H, 7.58. Found: C, 86.83; H, 7.56.

3-*p*-Tolyl-4-phenyl-6-methyl-3,5-heptadien-2-one. The oxidation procedure reported above was carried out on 18.2 g (41.9 mmol) of 3-*p*-tolyl-3-(phenylseleno)-4-phenyl-6-methyl-5-hepten-2-one, with 14.3 mL (126 mmol) of 30% aqueous hydrogen peroxide, 6.75 mL (83.8 mmol) of pyridine, and 8.0 mL of water in 200 mL of methylene chloride. Isolation of 12.1 g (99%) of crude material, mp 101–103 °C, was followed by recrystallization from ethanol to give 11.1 g (91%) of 3-*p*-tolyl-4-phenyl-6-methyl-3,5-heptadien-2-one, mp 103.5–105 °C.

The spectral data were as follows: 270-MHz NMR ($CDCl_3$) δ 7.40–7.00 (m, 9 H, arom), 5.890 (sept, 1 H, J = 1.5 Hz, =CH), 2.348 (s, 3 H, $ArCH_3$), 1.934 (s, 3 H, CH_3C=O), 1.695 (d, 3 H, J = 1.5 Hz, =CCH_3), 1.186 (d, 3 H, J = 1.5 Hz, =CCH_3); IR ($CHCl_3$) 3010, 2920, 2840, 1680 (s), 1600, 1450, 1220, 1180, 760, 700 cm^{-1}; mass spectrometry for $C_{21}H_{22}O$, m/e (calcd) 290.1671, (found) 290.1671.

Anal. Calcd for $C_{21}H_{22}O$: C, 86.91; H, 7.58. Found: C, 86.49; H, 7.75.

3-Phenyl-4-*p*-tolyl-6-methyl-3,5-heptadien-2-one Tosylhydrazone. In a typical run 4.26 g (14.7 mmol) of 3-phenyl-4-*p*-tolyl-6-methyl-3,5-heptadien-2-one and 2.73 g (14.7 mmol) of tosylhydrazine were dissolved in 150 mL of tetrahydrofuran[19] ($LiAlH_4$ dried). The solution was filtered after slight warming and then concentrated to ca. 50 mL. After storing at ambient temperature under nitrogen for 10 h, the solution was concentrated, 50% ether–hexane was added, and the precipitate was filtered to give 3.73 g (55%) of tosylhydrazone, mp 150–152 °C. Recrystallization from methanol gave 2.17 g (32%) of 3-phenyl-4-*p*-tolyl-6-methyl-3,5-heptadien-2-one tosylhydrazone, mp 160–161 °C.

The spectral data were as follows: 270-MHz NMR ($CDCl_3$) δ 7.56–6.92 (m, 13 H, arom), 5.785 (sept., 1 H, J = 1.1 Hz, =CH), 2.426 (s, 3 H, $ArCH_3$), 2.298 (s, 3 H, $ArCH_3$), 1.632 (d, 3 H, J = 1.1 Hz, =CCH_3), 1.539 (s, 3 H, CH_3), 1.140 (d, 3 H, J = 1.1 Hz, =CCH_3); IR ($CHCl_3$) 3300, 3220, 3000, 2920, 1600, 1510, 1500, 1440, 1380, 1340, 1200, 1155 (s), 1050, 920, 900, 810 cm^{-1}; UV (ethanol) λ_{max} 266 (ϵ 8000), 310 sh (5000) nm; mass spectrometry for $C_{28}H_{30}N_2O_2S$, m/e (calcd) 457.9680, (found) 457.9680.

Anal. Calcd for $C_{21}H_{22}N_2O_2S$: C, 73.36; H, 6.55. Found: C, 73.37; H, 6.85.

3-*p*-Tolyl-4-phenyl-6-methyl-3,5-heptadien-2-one Tosylhydrazone. In 100 mL of methanol, 2.42 g (13.0 mmol) of tosylhydrazine and 3.70 g (12.7 mmol) of 3-*p*-tolyl-4-phenyl-6-methyl-3,5-heptadien-2-one were heated to reflux and filtered, and 0.15 mL (0.14 equiv) of concentrated hydrochloric acid was added. Refluxing was continued for 9.5 h, and then the solution was cooled to −15 °C. The mixture was filtered and the solid washed with cold ethanol. Crystallization from methanol gave 4.80 g (82%) of 3-*p*-tolyl-4-phenyl-6-methyl-3,5-heptadien-2-one tosylhydrazone, mp 164–166 °C.

The spectral data were as follows: 270-MHz NMR ($CDCl_3$) δ 7.7–6.9 (m, 13 H, arom), 5.824 (sept, 1 H, J = 1.5 Hz, =CH), 2.434 (s, 3 H, $ArCH_3$), 2.372 (s, 3 H, $ArCH_3$), 1.653 (d, 3 H, J = 1.5 Hz, =CCH_3), 1.547 (s, 3 H, CH_3C=N), 1.123 (d, 3 H, J = 1.5 Hz, =CCH_3); IR ($CHCl_3$) 3010, 2980, 2880, 1700, 1610, 1425, 1100, 780, 710 cm^{-1}.

Anal. Calcd for $C_{21}H_{22}N_2O_2S$: C, 73.36; H, 6.55. Found: C, 73.13; H, 6.43.

1-Phenyl-2-methyl-3-*p*-tolyl-3-isobutenylcyclopropene. Following the procedure described by Zimmerman and Hovey,[3c] a 1-L solution of 1.07 g (2.34 mmol) of 3-phenyl-4-*p*-tolyl-6-methyl-3,5-heptadien-2-one tosylhydrazone in tetrahydrofuran was stirred with 0.338 g (6.25 mmol) of sodium methoxide in the dark under nitrogen for 10 h. The solution was then photolyzed through a sodium vanadate filter (0% T < 320 nm) for 1.25 h on a 450-W Hanovia immersion lamp. Concentration, dilution with 20 mL of pentane, and aqueous washing gave a yellow oil on concentration. Chromatography on a hexane-slurried silica gel column (1.2 × 30 cm), eluting with hexane, gave 0.454 g (71%) of cyclopropene as an oil. Recrystallization from methylene chloride and pentane gave 0.390 g (61%) of 1-phenyl-2-methyl-3-*p*-tolyl-3-isobutenylcyclopropene, mp 56–58 °C.

Elution with 50% ether–hexane gave 0.090 g (10%) of 3,3,7-trimethyl-5-*p*-tolyl-6-phenyl-3*H*-1,2-diazepine as an oil, pure by NMR.

The spectral data for the cyclopropene were as follows: 270-MHz NMR ($CDCl_3$) δ 7.48–6.91 (m, 6 H, arom), 5.674 (sept, 1 H, J = 1.1 Hz, =CH), 2.322 (s, 3 H, $ArCH_3$), 2.283 (s, 3 H, =CCH_3),

(18) Reich, H. J.; Renga, J. M.; Reich, I. L. *J. Am. Chem. Soc.* **1975**, *97*, 5434–5447.

(19) Bertz, S. H.; Dabbagh, G. *J. Org. Chem.* **1983**, *48*, 116–119.

1.760 (d, 3 H, J = 1.1 Hz, =CCH_3), 1.642 (d, 3 H, J = 1.1 Hz, =CCH_3); IR ($CHCl_3$) 3005, 2940, 2830, 2700 (w), 1845, 1595, 1510, 1490, 1375, 1185, 1070, 910, 850, 835, 820, 760, 690 cm^{-1}; UV (cyclohexane) λ_{max} 266 (s 14 000), 257 sh (13 000), 284 sh (8000) nm; mass spectrometry for $C_{21}H_{22}$, m/e (calcd) 274.1722, (found) 274.1722.

Anal. Calcd for $C_{21}H_{22}$: C, 91.97; H, 8.03. Found: C, 92.13; H, 7.80.

The spectral data for the diazepine were as follows: 270-MHz NMR ($CDCl_3$) δ 7.35–7.00 (m, 9 H, arom), 6.172 (s, 1 H, =CH), 2.289 (s, 3 H, =CCH_3), 2.248 (s, 3 H, $ArCH_3$), 1.455 (s, 3 H, CH_3), 1.282 (s, 3 H, CH_3); IR ($CHCl_3$) 3000, 2980, 2925, 2860, 1700 (w), 1520, 1460, 1380, 1260, 920 (s), 830, 700 cm^{-1}; mass spectrometry for $C_{21}H_{22}N_2$, m/e (calcd) 302.1783, (found) 302.1783.

Anal. Calcd for $C_{21}H_{22}N_2$: C, 83.44; H, 7.28. Found: C, 83.80; H, 7.66.

1-*p*-Tolyl-2-methyl-3-phenyl-3-isobutenylcyclopropene. With the same procedure as for the previous cyclopropene, 0.503 g (1.10 mmol) of 3-*p*-tolyl-4-phenyl-6-methyl-3,5-heptadien-2-one tosylhydrazone and 0.160 g (2.96 mmol) of sodium methoxide in 1 L of tetrahydrofuran (dried over $LiAlH_4$) was photolyzed for 0.5 h, followed by concentration, dilution with water, pentane extraction, and concentration of the organic layer to give 0.281 g of a yellow oil. Chromatography on a 1.2 × 40 cm 5% ether–hexane-slurried silica gel column gave 0.217 g (72%) of cyclopropene. Recrystallization from methylene chloride and pentane gave pure 1-*p*-tolyl-2-methyl-3-phenyl-3-isobutenylcyclopropene (0.138 g, 46%), mp 63–65 °C.

Elution with 50% ether–hexane yielded 56.0 mg (17%) of 3,3,7-trimethyl-5-phenyl-6-*p*-tolyl-3*H*-1,2-diazepine as an oil which was pure by NMR.

The spectral data for the cyclopropene were as follows: 270-MHz NMR ($CDCl_3$) δ 7.48–6.84 (m, 9 H, arom), 5.674 (sept, 1 H, J = 1,2 Hz, =CH), 2.299 (s, 6 H, $ArCH_3$ and =CCH_3), 1.768 (d, J = 1.2 Hz, =CCH_3), 1.639 (d, 3 H, J = 1.2 Hz, =CCH_3); IR ($CHCl_3$) 3005, 2920, 2840, 1845, 1620, 1590, 1490, 1440, 1375, 1275, 870, 850, 820, 700 cm^{-1}; UV (cyclohexane) λ_{max} 266 (ϵ 207 700), 282 sh (13 400), 256 sh (17 500) nm; mass spectrometry for $C_{21}H_{22}$, m/e (calcd) 274.1722, (found) 274.1722.

Anal. Calcd for $C_{21}H_{22}$: C, 91.97; H, 8.03. Found: C, 91.72; H, 7.94.

3-Phenyl-4-*p*-tolylbuten-2-one Tosylhydrazone. In 300 mL of methanol were dissolved 50.0 g (0.212 mol) of 4-*p*-tolyl-3-phenylbuten-2-one and 39.9 g (0.214 mol) of tosylhydrazine. The mixture was heated to reflux and 2.41 mL (0.14 equiv) of concentrated hydrochloric acid was added. The solution was refluxed 1 h and then was cooled and filtered to give 77.1 g (90%) of white powder, mp 134–136 °C. Recrystallization from pentane after filtration of insoluble material gave 59.1 g (69%) of 3-phenyl-4-*p*-tolylbuten-2-one tosylhydrazone, mp 144–146 °C.

The spectral data were as follows: 270-MHz NMR ($CDCl_3$) δ 7.59–6.72 (m, 14 H, arom and vinyl), 2.404 (s, 3 H, $ArCH_3$), 2.235 (s, 3 H, $ArCH_3$), 1.960 (s, 3 H, CH_3C=N); IR ($CHCl_3$) 3290, 3010, 1600, 1510, 1380, 1345, 1160 (s), 1015, 820, 700 cm^{-1}; mass spectrometry for $C_{24}H_{24}N_2O_2S$, m/e (calcd) 404.1480, (found) 404.1461.

Anal. Calcd for $C_{24}H_{24}N_2O_2S$: C, 71.28; H, 5.94. Found: C, 70.94; H, 6.08.

1-Phenyl-2-methyl-3-*p*-tolylcyclopropene. The Dürr reaction[20] was employed. A suspension of 20.0 g (49.5 mmol) of 3-phenyl-4-*p*-tolylbuten-2-one tosylhydrazone and 4.43 g (105 mmol) of oil-free sodium hydride in a mixture of 2.4 L of hexane, 300 mL of diglyme, and 0.30 mL of *tert*-butyl alcohol was photolyzed through a Pyrex filter with a 450-W Hanovia immersion lamp for 4 h. The suspension was filtered, the filtrate was concentrated, and pentane was added. The organic layer was washed with water, dried, and stored overnight at −20 °C. Filtration and concentration of the filtrate gave 5.34 g (49%) of 1-phenyl-2-methyl-3-*p*-tolylcyclopropene as an oil. Chromatography led to rearrangement.

The spectral data were as follows: 100-MHz NMR ($CDCl_3$) δ 7.4–6.8 (m, 9 H, arom), 2.77 (s, 1 H, CH), 2.22 (s, 6 H, $ArCH_3$ and =CCH_3); IR ($CHCl_3$) 3020, 2920, 2875, 1600, 1515, 1495, 1180, 1150, 820, 700 cm^{-1}.

(20) Durr, H. *Angew Chem.* **1967**, *79*, 1104–1105.

Anal. Calcd for $C_{17}H_{16}$: C, 92.72; H, 7.27. Found: C, 93.11; H, 7.01.

1-*p*-Tolyl-2-phenyl-3-methylcyclopropenium Tetrafluoroborate. The following procedure is based on the general method of Breslow.[21] In 50 mL of anhydrous ether was dissolved 5.34 g (19.4 mmol) of 1-phenyl-2-methyl-3-*p*-tolylcyclopropene to which was rapidly added a solution of 6.41 g (19.4 mmol) of trityl tetrafluoroborate in 30 mL of acetonitrile. The mixture was diluted with 20 mL of ether and filtered. The solid was dried to give 1.61 g (27%) of 1-*p*-tolyl-2-phenyl-3-methylcyclopropenium tetrafluoroborate.

The spectral data were as follows: 270-MHz NMR (CD_3CN) δ 7.47–7.19 (m, 9 H, arom), 2.368 (s, 3 H, CH_3), 2.347 (s, 3 H, CH_3); IR (KBr) 3190, 3030, 2940, 2880, 1610, 1500, 1430, 1240, 1080, 1050, 850, 710 cm^{-1}.

1-*p*-Tolyl-2-phenyl-3-methyl-3-isobutenylcyclopropene. A solution of 1.61 g (5.2 mmol) of 1-*p*-tolyl-2-phenyl-3-methylcyclopropenium tetrafluoroborate in 15 mL of tetrahydrofuran was cooled to −78 °C. Two equiv of isobutenylmagnesium bromide (prepared from 1.33 mL (13.7 mmol) of isobutenyl bromide and 0.380 g (15.7 mol) of magnesium) in 16 mL of tetrahydrofuran was added dropwise. The reaction was allowed to warm to 25 °C, stirred 4 h, poured over ice water, and ether extracted. Washing with brine, drying with magnesium sulfate, concentrating, and chromatographing on a 1.5 × 20 cm hexane-slurried silica gel column gave the following 10-mL fractions with hexane elution: fractions 4–6, 0.550 g (38%) of 1-*p*-tolyl-2-phenyl-3-methyl-3-isobutenylcyclopropene; 7–10, 0.210 g of a mixture of 1-*p*-tolyl-2-phenyl-3-methyl-3-isobutenylcyclopropene and 1,3-diaryl-2-methyl-3-isobutenylcyclopropene. Recrystallization of the 3-methylcyclopropene from methanol gave 0.504 g (35%) of 1-*p*-tolyl-2-phenyl-3-methyl-3-isobutenylcyclopropene, mp 55–57 °C.

The spectral data for 1-*p*-tolyl-2-phenyl-3-methyl-3-isobutenylcyclopropene were as follows: 270-MHz NMR ($CDCl_3$) δ 7.66–6.98 (m, 9 H, arom), 5.520 (br s, 1 H, =CH), 2.367 (s, 3 H, $ArCH_3$), 1.666 (s, 3 H, CH_3), 1.659 (s, 3 H, CH_3), 1.588 (s, 3 H, CH_3); IR ($CHCl_3$) 3005, 2950, 2900, 2840, 2700 (w), 1810, 1590, 1500, 1440, 1370, 1110, 1055, 1020, 910, 820, 760 (s), 690 cm^{-1}; UV (cyclohexane) λ_{max} 322 (ϵ 24 000), 340 (18 700), 310 sh (20 300) nm; mass spectrometry for $C_{21}H_{22}$, m/e (calcd) 274.1722, (found) 274.1722.

Anal. Calcd for $C_{21}H_{22}$: C, 91.97; H, 8.03. Found: C, 92.20; H, 7.76.

1-*p*-Tolyl-2,3,3-trimethyl-5-phenyl-1,5-pentanedione. A modification of the Mukaiyama[22] procedure was used. A solution of 10.0 g (43.5 mmol) of 1-*p*-tolyl-1-(trimethylsiloxy)propene[23] in 20 mL of methylene chloride was added to 6.70 g (41.8 mmol) of 3,3-dimethylacrylophenone and 4.80 mL (44.7 mmol) of titanium tetrachloride in 100 mL of methylene chloride at −78 °C. The solution was stirred 2 h, quenched with aqueous sodium carbonate, water washed, and dried over magnesium sulfate. Concentration and chromatography on a 2.5 × 60 cm 5% ether–hexane-slurried silica gel column eluting with 5% ether–hexane gave the following: fraction 1, 150 mL, 7.47 g (58%) of colorless 1-*p*-tolyl-2,3,3-trimethyl-5-phenyl-1,5-pentanedione as an oil.

The spectral data were as follows: 100-MHz NMR ($CDCl_3$) δ 8.2–7.2 (m, 9 H, arom), 4.08 (q, 1 H, J = 7.0 Hz, CH), 3.08 (AB q, 2 H, J = 12.0 Hz, CH_2), 2.36 (s, 6 H, $C(CH_3)_2$); IR (neat) 3080, 3040, 2980, 2880, 1710, 1680, 1600, 1410, 1400, 1300, 1250, 980, 770, 750 cm^{-1}; mass spectrometry for $C_{21}H_{24}O_2$, m/e (calcd) 308.1776, (found) 308.1782.

Anal. Calcd for $C_{21}H_{24}O_2$: C, 81.81; H, 7.79. Found: C, 81.55; H, 8.05.

1-Phenyl-2,3,3-trimethyl-5-*p*-tolyl-1,5-pentanedione. The same procedure as used for 1-*p*-tolyl-2,3,3-trimethyl-5-phenyl-1,5-pentanedione was followed starting with 8.11 g (46.6 mmol) of 3,3-dimethyl-*p*-methylacrylophenone,[24] 10.0 g (48.5 mmol) of 1-phenyl-1-(trimethylsiloxy)propene,[23] and 5.46 mL (50.8 mmol)

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of titanium tetrachloride in 125 mL of methylene chloride. Chromatography on a 2.5 × 150 cm silica gel column, packed and eluted with 5% ether–hexane, gave the following 40-mL fractions: fractions 9–20, 1.75 g of acrylophenone; fractions 21–24, 1.05 g of a mixture of acrylophenone and pentanedione; fractions 25–31, 7.90 g (55%) of pure 1-phenyl-2,3,3-trimethyl-5-*p*-tolyl-1,5-pentanedione as a colorless oil.

The spectral data were as follows: 100-MHz NMR ($CDCl_3$) δ 8.0–7.0 (m, 9 H, arom), 4.15 (q, 1 H, J = 5.0 Hz, CH), 3.09 (AB q, 2 H, J = 12.0 Hz, CH_2), 2.38 (s, 3 H, $ArCH_3$), 1.19 (d, 3 H, J = 5.0 Hz, CH_3), 1.15 and 1.12 (2 s, 6 H, $C(CH_3)_2$); IR (neat) 3060, 2980, 2920, 2880, 1680, 1670, 1600, 1450, 1220, 980, 710 cm^{-1}; mass spectrometry for $C_{21}H_{24}O_2$, m/e (calcd) 308.1776, (found) 308.1762.

Anal. Calcd for $C_{21}H_{24}O_2$: C, 81.81; H, 7.79. Found: C, 81.56; H, 7.79.

1-Phenyl-2-*p*-tolyl-3,3-dimethyl-1,5-hexanedione. A modification of the Zimmerman and Aasen[3b] procedure was followed using 1.86 g (9.49 mmol) of 1-phenyl-2-*p*-tolylethanone,[25] 1.14 mL (9.97 mmol) of mesityl oxide, and 0.340 g (3.03 mmol) of potassium *tert*-butoxide, stirred as 2.0 mL distilled *tert*-butyl alcohol was added. The suspension was heated until the material dissolved, and then the heat was removed. The solution was stirred for ca. 20 min, poured over 5% hydrochloric acid, and ether extracted. The ethereal layer was washed with water and brine and dried to give 2.78 g of crude material. Chromatography on a 2.5 × 100 cm 12.5% ether–hexane-slurried silica gel column, eluting with 12.5% ether–hexane, gave the following 100-mL fractions: fractions 7–9, 0.20 g of 1-phenyl-2-*p*-tolylethanone; fractions 10–13, 1.22 g (40%) of pure 1-phenyl-2-*p*-tolyl-3,3-dimethyl-1,5-hexanedione; fractions 14–17, 1.10 g of 3-phenyl-4-*p*-tolyl-5,5-dimethyl-2-cyclohexen-1-one, mp 119–121 °C.

The spectral data for 1-phenyl-2-*p*-tolyl-3,3-dimethyl-1,5-hexanedione were as follows: 100-MHz NMR ($CDCl_3$) δ 7.9–6.9 (m, 9 H, arom), 5.13 (s, 1 H, CH), 2.55 (AB q, 2 H, J = 16.0 Hz, CH_2), 2.25 (s, 3 H, $ArCH_3$), 2.00 (s, 3 H, $CH_3C{=}O$), 1.17 and 1.15 (s, 6 H, $C(CH_3)_2$); IR (neat) 2985, 2920, 2880, 1700, 1680, 1600, 1500, 1440, 1110, 910, 730, 690 cm^{-1}; mass spectrometry for $C_{21}H_{24}O_2$, m/e (calcd) 308.1776, (found) 308.1776.

Anal. Calcd for $C_{21}H_{24}O_2$: C, 81.81; H, 7.79. Found: C, 81.54; H, 7.69.

The spectral data for 3-phenyl-4-*p*-tolyl-5,5-dimethyl-2-cyclohexen-1-one were as follows: 270-MHz NMR ($CDCl_3$) δ 7.47–7.04 (m, 9 H, arom), 6.631 (s, 1 H, =CH), 3.799 (s, 1 H, CH), 2.294 (AB q, 2 H, J = 14.0 Hz, CH_2), 2.287 (s, 3 H, $ArCH_3$), 1.259 and 0.825 (2 s, 6 H, $C(CH_3)_2$); IR ($CHCl_3$) 3000, 2975, 1660 (s), 1600, 1510, 1450, 1355, 1305, 1260, 900, 830, 700 cm^{-1}; mass spectrometry for $C_{21}H_{22}O$, m/e (calcd) 290.1671, (found) 290.1671.

1-*p*-Tolyl-2-phenyl-3,3-dimethyl-1,5-hexanedione. The procedure used in the synthesis of the previous dione was carried out on 4.00 g (19.0 mmol) of 1-*p*-tolyl-2-phenylethanone,[26] 2.24 mL (19.8 mmol) of mesityl oxide, and 0.682 g (6.09 mmol) of potassium *tert*-butoxide in 4.0 mL of *tert*-butyl alcohol. The chromatography was performed on a 2.5 × 90 cm silica gel column, packed and eluted with 12.5% ether–hexane. The following 100-mL fractions were collected: fractions 3–6, 2.50 g of ethanone; fractions 7–10, 0.770 g (37% based on unrecovered starting material) of pure 1-*p*-tolyl-2-phenyl-3,3-dimethyl-1,5-hexanedione as a colorless oil; fractions 11–15, 1.24 g (60%) of 3-*p*-tolyl-4-phenyl-5,5-dimethyl-2-cyclohexen-1-one, mp 130–132 °C.

The spectral data for 1-*p*-tolyl-2-phenyl-3,3-dimethyl-1,5-hexanedione were as follows: 100-MHz NMR ($CDCl_3$) δ 7.9–7.0 (m, 9 H, arom), 5.23 (s, 1 H, CH), 2.47 (AB q, 2 H, J = 14.0 Hz, CH_2), 2.24 (s, 3 H, $ArCH_3$), 2.05 (s, 3 H, $CH_3C{=}O$), 1.18 and 1.14 (2 s, 6 H, $C(CH_3)_2$); IR (neat) 3010, 2980, 2870, 1710, 1675, 1600, 1365, 1175, 740, 710 cm^{-1}.

Anal. Calcd for $C_{21}H_{24}O_2$: C, 81.81; H, 7.79. Found: C, 81.63; H, 7.80.

The spectral data for 3-*p*-tolyl-4-phenyl-5,5-dimethyl-2-cyclohexen-1-one were as follows: 270-MHz NMR ($CDCl_3$) δ 7.40–7.02 (m, 9 H, arom), 6.653 (s, 1 H, =CH), 3.836 (s, 1 H, CH), 2.292 (AB q, 2 H, J = 17.4 Hz, CH_2), 1.264 (s, 3 H, CH_3), 0.825 (s, 3 H, CH_3); IR ($CHCl_3$) 3000, 2980, 1660 (s), 1600, 1515, 1495, 1450, 1350, 1305, 1265, 900, 810, 705 cm^{-1}.

Anal. Calcd for $C_{21}H_{22}O$: C, 86.87; H, 7.58. Found: C, 86.78; H, 7.21.

1,5,5-Trimethyl-2-*p*-tolyl-3-phenyl-2,3-cyclopentanediol. To a stirred suspension of 4.93 g (0.203 mol) of magnesium powder in 300 mL of anhydrous ether was added 25.77 g (0.10 mol) of iodine[27] in small portions over 1 h. This solution was refluxed until clear and then 10.43 g (0.034 mol) of 1-*p*-tolyl-2,3,3-trimethyl-5-phenyl-1,5-pentanedione in 10 mL of anhydrous ether was added over 1 h. The solution was refluxed 24 h, cooled to 0 °C, and quenched with aqueous ammonium chloride. The organic layer was washed with aqueous sodium thiosulfate, water, and brine, dried over magnesium sulfate, and concentrated. The crude yield was 10.4 g (99%) of a mixture of diastereomeric cyclopentanediols, mp 88–95 °C. Recrystallization from pentane gave 0.768 g (23%) of one isomer of 1,5,5-trimethyl-2-*p*-tolyl-3-phenyl-2,3-cyclopentanediol, mp 129–130 °C. For further transformation the mixture of stereoisomers was successfully used.

The spectral data were as follows: 100-MHz NMR ($CDCl_3$) δ 7.2–6.5 (m, 9 H, arom), 3.44 (br s, 1 H, OH), 2.47 (AB q, 2 H, J = 15.0 Hz, CH_2), 2.40 (q, 1 H, J = 6.0 Hz, CH), 2.35 (s, 3 H, $ArCH_3$), 1.59 (br s, 1 H, OH), 1.36 and 1.34 (2 s, 6 H, $C(CH_3)_2$), 0.80 (d, 3 H, J = 6.0 Hz, CH_3); IR ($CHCl_3$) 3600 (sh), 3500 (br), 3005, 2960, 2880, 1520, 1500, 1450, 1370, 820, 700 (s) cm^{-1}; mass spectrometry for $C_{21}H_{26}O_2$, m/e (calcd) 310.1933, (found) 310.1933.

Anal. Calcd for $C_{21}H_{26}O_2$: C, 81.29; H, 8.39. Found: C, 81.39; H, 8.40.

1,5,5-Trimethyl-2-phenyl-3-*p*-tolyl-2,3-cyclopentanediol. With the same procedure as in the previous example, a 1.06-g (3.44 mmol) sample of 1-phenyl-5-*p*-tolyl-2,3,3-trimethyl-1,5-pentanedione in 5 mL of anhydrous ether was added to a 30-mL anhydrous ether solution of 0.520 g (21.4 mol) of magnesium powder and 2.74 g (10.8 mmol) of iodine prepared as before. By use of the same workup as described above, the crude yield was 1.03 g (97%) of a mixture of cyclopentanediols, mp 85–90 °C. Recrystallization from pentane gave 0.246 g (23%) of 1,5,5-trimethyl-3-*p*-tolyl-2-phenyl-2,3-cyclopentanediol, mp 139–141 °C.

The spectral data were as follows: 100-MHz NMR ($CDCl_3$) δ 7.6–7.1 (m, 9 H, arom), 2.41 (br s, 1 H, OH), 2.75 (q, 1 H, J = 6.0 Hz, CH), 2.63 (br s, 1 H, OH), 2.42 (AB q, 2 H, J = 15.0 Hz, CH_2), 2.36 (s, 3 H, $ArCH_3$), 1.21 and 1.15 (2 s, 6 H, $C(CH_3)_2$), 0.68 (d, 3 H, J = 6.0 Hz, CH_3); IR ($CHCl_3$) 3600 (sh), 3500 (br), 3005, 2960, 2880, 1600, 1520, 1500, 1450, 1380, 820, 710 cm^{-1}; mass spectrometry for $C_{21}H_{26}O_2$, m/e (calcd) 310.1933, (found) 310.1936.

Anal. Calcd for $C_{21}H_{26}O_2$: C, 81.29; H, 8.39. Found: C, 81.02; H, 8.29

1-*p*-Tolyl-2-phenyl-3,5,5-trimethyl-2,3-cyclopentanediol. The reductive coupling procedure[27] was carried out on 1.24 g (3.96 mmol) of 1-phenyl-2-*p*-tolyl-3,3-dimethyl-1,5-hexanedione, 0.610 g (25.1 mol) of magnesium powder, and 3.17 g (12.5 mmol) of iodine in 75 mL of anhydrous ether as before. After workup a quantitative yield was obtained (1.26 g) of a mixture of isomeric diols. One of the diols was obtained by several recrystallizations from pentane. The yield was 0.408 g (33%) of 1-*p*-tolyl-2-phenyl-3,5,5-trimethyl-2,3-cyclopentanediol, mp 118–120 °C.

The spectral data were as follows: 100-MHz NMR ($CDCl_3$) δ 7.6–6.8 (m, 9 H, arom), 4.06 (br s, 1 H, OH), 3.52 (AB q, 2 H, CH_2), 2.80 (br m, 1 H, OH), 2.20 (s, 3 H, $ArCH_3$), 1.22 (s, 3 H, CH_3), 1.10 (br s, 6 H, 2 × CH_3); IR ($CHCl_3$) 3400 (br), 3020, 2950, 2920, 2860, 1520, 1450, 1385, 1370, 1120, 1050, 915, 740, 700 cm^{-1}; mass spectrometry for $C_{21}H_{26}O_2$, m/e (calcd) 310.1933, (found) 310.1933.

Anal. Calcd for $C_{21}H_{26}O_2$: C, 81.29; H, 8.39. Found: C, 81.42; H, 8.65.

1-Phenyl-2-*p*-tolyl-3,5,5-trimethyl-2,3-cyclopentanediol. The reductive coupling procedure was used starting with 1.90 g (6.16 mmol) of 1-*p*-tolyl-2-phenyl-3,3-dimethyl-1,5-hexanedione in 20 mL of anhydrous ether which was added to 0.860 g (35.4 mol) of magnesium powder complexed with 4.49 g (17.7 mmol) of iodine in 80 mL of anhydrous ether. After workup as before, a quantitative crude yield (1.89 g) was obtained as a foam. Recrystallization from pentane gave 0.576 g (30%) of 1-phenyl-2-

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p-tolyl-3,5,5-trimethyl-2,3-cyclopentanediol, mp 127–129 °C. As with each previous cyclopentanediol, the next transformation was successful starting with a mixture of the stereoisomers.

The spectral data were as follows: 100-MHz NMR ($CDCl_3$) δ 7.8–6.8 (m, 9 H, arom), 3.77 (AB q, 2 H, J = 14.0 Hz, CH_2), 3.50 (s, 1 H, CH), 2.62 (br s, 2 H, 2 × OH), 2.18 (s, 3 H, $ArCH_3$), 1.12 (s, 3 H, CH_3), 1.05 (s, 3 H, CH_3), 1.01 (s, 3 H, CH_3); IR ($CHCl_3$) 3580 (sh), 3460 (br), 3005, 2975, 2920, 1600, 1515, 1490, 1450, 1365, 810, 700 cm^{-1}.

Anal. Calcd for $C_{21}H_{26}O_2$: C, 81.29; H, 8.39. Found: C, 81.34; H, 8.33.

1,5,5-Trimethyl-2-phenyl-3-*p*-tolylcyclopentadiene. To a solution of 1,5,5-trimethyl-2-phenyl-3-*p*-tolyl-2,3-cyclopentanediol (9.42 g, 30.4 mmol) in 150 mL of dry pyridine was added 8.34 mL (90.9 mmol) of phosphorus oxychloride.[28] The reaction refluxed for 2 h and then was quenched by pouring over ice and pentane. Washing the organic layer with 10% hydrochloric acid, water, and brine, drying over magnesium sulfate, and concentrating gave 7.05 g of a mixture of 1,5,5-trimethyl-2-phenyl-3-*p*-tolylcyclopentadiene and 1-methylene-2-phenyl-3-*p*-tolyl-5,5-dimethyl-2-cyclopentene. Chromatography on a silver nitrate impregnated alumina column[29] allowed separation of 1-methylene-2-phenyl-3-*p*-tolyl-5,5-dimethylcyclopent-2-ene by eluting with 15% benzene–hexane. The crude yield of cyclopentadiene was 4.23 g (46%), mp 58–60 °C. Recrystallization in ethanol gave 3.05 g (33%) of 1,5,5-trimethyl-2-phenyl-3-*p*-tolylcyclopentadiene, mp 64–66 °C.

The spectral data were as follows: 270-MHz NMR ($CDCl_3$) δ 7.30–6.80 (m, 9 H, arom), 6.278 (s, 1 H, =CH), 2.254 (s, 3 H, $ArCH_3$), 1.824 (s, 3 H, $=CCH_3$), 1.195 (s, 6 H, $C(CH_3)_2$); IR ($CHCl_3$) 3000, 2950, 2910, 1850, 1600, 1500, 1460, 1440, 1000, 820, 700 cm^{-1}; mass spectrometry for $C_{21}H_{22}$, m/e (calcd) 274.1722, (found) 274.1722.

Anal. Calcd for $C_{21}H_{22}$: C, 91.97; H, 8.03. Found: C, 91.72; H, 8.19.

1,5,5-Trimethyl-2-*p*-tolyl-3-phenylcyclopentadiene. A solution of 10.4 g (33.5 mmol) of 1,5,5-trimethyl-2-*p*-tolyl-3-phenyl-2,3-cyclopentanediol in 200 mL of pyridine was stirred as 10.8 mL (0.118 mol) of phosphorus oxychloride was added. Reflux for 2 h and workup as in the previous dehydration[28] experiment gave 7.88 g of a mixture of 1,5,5-trimethyl-2-*p*-tolyl-3-phenylcyclopentadiene and 1-methylene-2-*p*-tolyl-3-phenyl-5,5-dimethylcyclopent-2-ene (2:1). Separation of the double-bond isomers on 10% silver nitrate impregnated alumina,[29] eluting with 15% benzene–hexane, gave 4.70 g (52%) of cyclopentadiene, mp 42–48 °C, as the first band. Recrystallization from methanol gave 3.81 g (41%) of 1,5,5-trimethyl-2-*p*-tolyl-3-phenylcyclopentadiene, mp 57–58 °C.

The spectral data were as follows: 270-MHz NMR ($CDCl_3$) δ 7.28–6.80 (m, 9 H, arom), 6.310 (s, 1 H, =CH), 2.314 (s, 3 H, $ArCH_3$), 1.826 (s, 3 H, $=CCH_3$), 1.192 (s, 6 H, $C(CH_3)_2$); IR ($CHCl_3$) 3010, 2980, 2960, 1700, 1600, 1500, 1460, 1440, 820, 700 cm^{-1}; mass spectrometry for $C_{21}H_{22}$, m/e (calcd) 274.1722, (found) 274.1722.

Anal. Calcd for $C_{21}H_{22}$: C, 91.97; H, 8.03. Found: C, 91.50; H, 7.91.

1-Phenyl-2-*p*-tolyl-3,5,5-trimethylcyclopentadiene. Dehydration of 1-phenyl-2-*p*-tolyl-3,5,5-trimethyl-2,3-cyclopentanediol (1.75 g, 5.64 mmol) with 1.60 mL (17.4 mmol) of phosphorus oxychloride in 50 mL of dry pyridine and workup as before gave a 1.01-g (65%) yield of crude cyclopentadiene, mp 50–52 °C. Recrystallization from methanol and methylene chloride gave 0.912 g (59%) of 1-phenyl-2-*p*-tolyl-3,5,5-trimethylcyclopentadiene, mp 55–57 °C.

The spectral data were as follows: 270-MHz NMR ($CDCl_3$) δ 7.24–6.90 (m, 9 H, arom), 6.009 (q, 1 H, J = 1.0 Hz, =CH), 2.234 (s, 3 H, $ArCH_3$), 1.884 (d, 3 H, J = 1.0 Hz, $=CCH_3$), 1.215 (s, 6 H, $C(CH_3)_2$); IR ($CHCl_3$) 3020, 2950, 2920, 2860, 1600, 1510, 1490, 1460, 1440, 1110, 835, 800, 745, 700 cm^{-1}; mass spectrometry for $C_{21}H_{22}$, m/e (calcd) 274.1722, (found) 274.1722.

Anal. Calcd for $C_{21}H_{22}$: C, 91.97; H, 8.03. Found: C, 92.05; H, 8.10.

1-*p*-Tolyl-2-phenyl-3,5,5-trimethylcyclopentadiene. Dehydration of 1-*p*-tolyl-2-phenyl-3,5,5-trimethyl-2,3-cyclopentanediol (1.26 g, 4.06 mmol) was carried out as with the previous diols using 1.17 mL (12.6 mmol) of phosphorus oxychloride in 50 mL of pyridine to give, after workup and recrystallization in methanol, 0.650 g (53%) of pure 1-*p*-tolyl-2-phenyl-3,5,5-trimethylcyclopentadiene, mp 56–58 °C.

The spectral data were as follows: 270-MHz NMR ($CDCl_3$) δ 7.33–6.83 (m, 9 H, arom), 6.002 (q, 1 H, J = 1.49 Hz, =CH), 2.227 (s, 3 H, $ArCH_3$), 1.870 (d, 3 H, J = 1.4 Hz, $=CH_3$), 1.221 (s, 6 H, $C(CH_3)_2$); IR ($CHCl_3$) 3020, 2950, 2920, 2860, 1510, 1460, 1445, 1380, 1360, 835, 800, 760, 705 cm^{-1}; mass spectrometry for $C_{21}H_{22}$, m/e (calcd) 274.1722, (found) 274.1722.

Anal. Calcd for $C_{21}H_{22}$: C, 91.97; H, 8.03. Found: C, 91.78; H, 8.13.

Reduction of 3,3,7-Trimethyl-5-*p*-tolyl-6-phenyl-3*H*-1,2-diazepine. A solution of 90.0 mg (0.298 mmol) of diazepine in 10 mL of ether at −20 °C was stirred as sodium/potassium (1:1) alloy was added (0.045 mL, 0.66 mmol). The reaction was allowed to warm to 23 °C and stirred for 30 min. Quenching with 0.051 mL (0.66 mmol) of methyl chloroformate and decanting the solution into water gave, after water and brine washing, a yellow oil. Chromatography on a 1.2 × 20 cm column gave the following 25-mL fractions: fraction 1, ca. 0.01 g of chloroformate; fraction 2, 0.017 g of a mixture of the monocarbomethoxylated diazepine and methyl 3,3-dimethyl-5-*p*-tolyl-6-phenyl-7-methylene-1,2-diazepine-2-carboxylate; fraction 3, 0.006 g of monocarbomethoxylated diazepine; fraction 4, 0.065 g of unreacted diazepine. Recycling the unreacted diazepine gave 20.3 mg (19%) of methyl 3,3-dimethyl-5-*p*-tolyl-6-phenyl-7-methyl-1,2-diazepine-2-carboxylate, mp 126–128 °C.

The spectral data for methyl 3,3-dimethyl-5-*p*-tolyl-6-phenyl-7-methyl-1,2-diazepine-2-carboxylate were as follows: 270-MHz NMR ($CDCl_3$) δ 7.20–6.75 (m, 9 H, arom), 5.982 (s, 1 H, =CH), 3.790 (s, 3 H, OCH_3), 2.175 (s, 3 H, $ArCH_3$), 2.027 (s, 3 H, $=CCH_3$), 1.410 (s, 6 H, $C(CH_3)_2$); IR ($CHCl_3$) 3000, 2980, 2960, 2875, 1710 (s), 1520, 1450, 1350, 1110, 1100, 820, 730, 700 cm^{-1}; mass spectrometry for $C_{23}H_{26}N_2O_2$, m/e (calcd) 362.1994, (found) 362.1994.

Anal. Calcd for $C_{23}H_{26}N_2O_2$: C, 76.20; H, 7.18. Found: C, 76.50; H, 7.53.

Methyl 1,4,4-Trimethyl-6-*p*-tolyl-7-phenyl-2,3-diazabicyclo[3.2.0]heptene-3-carboxylate. A solution of 40 mL of acetonitrile and 20.0 mg of diazepine was irradiated[30] 1 h through a Pyrex filter with a 450-W Hanovia lamp. Concentration and chromatography on a 1.2 × 20 cm column packed with 50% ether–hexane-slurried silica gel, eluting with 50% ether–hexane and taking 15-mL fractions, gave in fractions 9–11 17.5 mg of methyl 1,4,4-trimethyl-6-*p*-tolyl-7-phenyl-2,3-diazabicyclo-[3.2.0]heptene-3-carboxylate. This material was carried forward without further purification.

The spectral data were as follows: 270-MHz NMR ($CDCl_3$) δ 7.50–6.95 (m, 9 H, arom), 3.802 (s, 3 H, OCH_3), 3.255 (s, 1 H, CH), 2.350 (s, 3 H, $ArCH_3$), 1.948 (br s, 3 H, CH_3), 1.267 (s, 3 H, CH_3), 1.220 (s, 3 H, CH_3); IR ($CHCl_3$) 3020, 2960, 2925, 2875, 1700 (s), 1440, 1330, 1260, 1090, 900, 810 cm^{-1}; mass spectrometry for $C_{23}H_{26}N_2O_2$, m/e (calcd) 362.1994, (found) 362.1994.

Anal. Calcd for $C_{23}H_{26}N_2O_2$: C, 76.20; H, 7.18. Found: C, 76.33; H, 7.47.

1,4,4-Trimethyl-6-*p*-tolyl-7-phenyl-2,3-diazabicyclo-[3.2.0]heptadiene. Run 1. A 10.0-mg (0.028 mmol) sample of methyl 1,4,4-trimethyl-6-*p*-tolyl-7-phenyl-2,3-diazabicyclo-[3.2.0]heptene-3-carboxylate was placed in 1.0 mL of deoxygenated ethylene glycol, and 3.0 mg (0.053 mmol) of pulverized potassium hydroxide was added. The mixture was stirred at 125 °C for 1 h (under nitrogen) and cooled to 23 °C with ca. 0.1 g of ice, and then 0.1 mL of 50% hydrochloric acid was added. The solution was warmed to 40 °C and stirred for 1 h, and then 2 M cupric sulfate was added dropwise. No red precipitate was observed, so the reaction was ether extracted and washed with water and brine. The oil was chromatographed on a 1.5 × 20 cm hexane-slurried silica gel column. Elution with hexane gave, as the only

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(29) Silver nitrate impregnated alumina made per procedure of: Goering, H. L.; Closson, W. D.; Olson, A. C. *J. Am. Chem. Soc.* **1961**, *83*, 3507–3511.

(30) (a) Kan, G.; Thomas, M. T.; Snieckus, V. *J. Chem. Soc., Chem. Commun.* **1971**, 1022–1023. (b) See also: Anderson, C. D.; Sharp, J. T. *J. Chem. Soc., Perkin Trans. 1* **1980**, 1230–1232.

fraction, 4.5 mg of 1,5,5-trimethyl-2-*p*-tolyl-3-phenylcyclopentadiene and 1-*p*-tolyl-2-phenyl-3,5,5-trimethylcyclopentadiene in approximately a 30:1 ratio as shown by 270-MHz NMR.

Run 2. A solution of 5.0 mL of methanol and 20.0 mg (0.055 mmol) of methyl 1,4,4-trimethyl-6-*p*-tolyl-7-phenyl-2,3-diazabicyclo[3.2.0]heptene-3-carboxylate was stirred as 10.3 mg (0.18 mmol) of powdered potassium hydroxide was added. The reaction was refluxed for 18 h and then concentrated. Water was added and the slurry neutralized with ca. 1 mL of 10% hydrochloric acid. Extraction with methylene chloride and concentration left a yellow oil which was dissolved in 3 mL of methanol and 2 mL of water. The solution was stirred for 10 min, and then 40.0 mg (0.23 mmol) of cupric chloride was added. A red sticky substance formed after 1 h. This material and the aqueous layer were extracted with ether, and the organic layer was washed with water and brine. Concentration gave, as a yellow oil, 8.0 mg (60%) of 1,4,4-trimethyl-6-*p*-tolyl-7-phenyl-2,3-diazabicyclo[3.2.0]heptadiene. Crystallization from pentane and methylene chloride gave microcrystals with mp 68–70 °C.

The spectral data were as follows: 270-MHz NMR ($CDCl_3$) δ 7.60–7.00 (m, 9 H, arom), 3.056 (s, 1 H, CH), 2.289 (s, 3 H, $ArCH_3$), 1.951 (s, 3 H, CH_3), 1.688 (s, 3 H, CH_3), 1.175 (s, 3 H, CH_3); IR ($CHCl_3$) 3010, 2960, 2920, 2850, 1600, 1510, 1495, 1445, 1320, 1230, 1180, 700 cm^{-1}; mass spectrometry for $C_{21}H_{22}N_2$, *m/e* (calcd) 302.1783, (found) 302.1760.

Anal. Calcd for $C_{21}H_{22}N_2$: C, 83.44; H, 7.28. Found: C, 83.27; H, 7.06.

Photolysis of 1,4,4-Trimethyl-6-*p*-tolyl-7-phenyl-2,3-diazabicyclo[3.2.0]heptadiene. A solution of 9.0 mL of photograde benzene,[31] 10.0 mg (0.033 mmol) of diazabicyclo[3.2.0]heptadiene, and 20.0 mg (0.089 mmol) of *p*-(dimethylamino)benzophenone was photolyzed[32] for 10 h at 366 nm. The solution was concentrated and chromatographed on a 1.2 × 20 cm hexane-slurried silica gel column. Hexane elution yielded 8.0 mg of a mixture of 1,5,5-trimethyl-2-phenyl-3-*p*-tolylcyclopentadiene and 1-*p*-tolyl-2-phenyl-3,5,5-trimethylcyclopentadiene (1.3:1) as shown by spectral data and HPLC.[33] These isomers were separable by the procedure described below. In a second run using 15.0 mg (0.050 mmol) of azo reactant and 42.5 mg (0.188 mmol) of sensitizer, there was isolated 13.2 mg of the cyclopentadienes assayed as 1.6:1.

General Procedure for Exploratory Photolysis. Irradiations were performed with one of three filter solutions in addition to a Pyrex sleeve (except where noted) and with a Hanovia 450-W medium-pressure mercury lamp. The filter solutions are as follows: (1) 0.02 M sodium metavanadate in a 5% aqueous sodium hydroxide solution (0% $T < 340$ nm); (2) 0.04 M sodium metavanadate in 5% aqueous sodium hydroxide solution (0% $T < 350$ nm); (3) 0.07 M sodium metavanadate solution in 5% aqueous sodium hydroxide (0% $T < 360$ nm). The photograde solvent[31] for each run is indicated, and sensitized runs were made with *p*-(dimethylamino)benzophenone.[5] All runs were purged with nitrogen[34] before and during the photolysis.

Exploratory Sensitized Photolysis of 1-Phenyl-2-methyl-3-*p*-tolyl-3-isobutenylcyclopropene. In 150 mL of benzene were dissolved 34.5 mg (0.126 mmol) of cyclopropene and 0.23 g (1.02 mmol) of sensitizer. Irradiation through filter no. 2 for 35 min followed by concentration and chromatographic separation of the sensitizer gave a mixture of two cyclopentadienes. Separation by HPLC[35] yielded 11.8 mg of 1,5,5-trimethyl-2-phenyl-3-*p*-tolylcyclopentadiene and 7.8 mg of 1-*p*-tolyl-2-phenyl-3,5,5-trimethylcyclopentadiene. The spectral data for the two cyclopentadienes were identical with those of independently synthesized materials (vide supra).

Exploratory Sensitized Photolysis of 1-*p*-Tolyl-2-methyl-3-phenyl-3-isobutenylcyclopropene. In 250 mL of benzene were dissolved 0.201 g (0.733 mmol) of 1-*p*-tolyl-2-methyl-3-phenyl-3-isobutenylcyclopropene and 1.31 g (5.82 mmol) of *p*-(dimethylamino)benzophenone. Irradiation (filter no. 2) for 30 min, concentration, and chromatography on a 1.2 × 20 cm hexane-slurried silica gel column eluted with hexane gave (100% mass balance) a 1.00:1.16 mixture of 1,5,5-trimethyl-2-*p*-tolyl-3-phenylcyclopentadiene and 1-phenyl-2-*p*-tolyl-3,5,5-trimethylcyclopentadiene. Separation of the cyclopentadienes by HPLC[35] gave 0.090 g (45%) of 1,5,5-trimethyl-2-*p*-tolyl-3-phenylcyclopentadiene and 0.085 g (42%) of 1-phenyl-2-*p*-tolyl-3,5,5-trimethylcyclopentadiene. The spectral data for the mixture are identical with those of independently synthesized materials.

Exploratory Sensitized Photolysis of 1-Phenyl-2-*p*-tolyl-3-methyl-3-isobutenylcyclopropene. In 200 mL of benzene were dissolved 28.0 mg (0.102 mmol) of 1-phenyl-2-*p*-tolyl-3-methyl-3-isobutenylcyclopropene and 0.150 g (0.667 mmol) of *p*-(dimethylamino)benzophenone. The solution was degassed for 1.5 h and photolyzed for 0.75 h through filter solution no. 3. Concentration and chromatography on a 8% ether–hexane slurry packed silica gel column (1.5 × 20 cm) gave, in the second 50-mL fraction, the following: 1,5,5-trimethyl-2-phenyl-3-*p*-tolylcyclopentadiene, 1,5,5-trimethyl-2-*p*-tolyl-3-phenylcyclopentadiene, 1-*p*-tolyl-2-phenyl-3,5,5-trimethylcyclopentadiene, and 1-phenyl-2-*p*-tolyl-3,5,5-trimethylcyclopentadiene. The mixture (25.0 mg, 88%) was in a ratio of 1.00:1.2:0.75:0.75 as determined by NMR and HPLC.[33] Separation by HPLC[35] with several reinjections and recycling gave poor yields of the pure compounds because of overlapping. The spectral data were identical with those of independently synthesized material (vide supra).

Photolysis of 3,3,7-Trimethyl-5-*p*-tolyl-6-phenyl-3*H*-1,2-diazepine. Run 1. In 150 mL of dry acetonitrile was dissolved 0.065 g (0.20 mmol) of diazepine. Irradiation for 7 h through a Corex filter gave a yellow oil on concentration (98% recovery of material). Chromatography on a 1.2 × 20 cm hexane-slurried silica gel column, eluting with hexane, gave several products. The first 50-mL fraction contained 23.0 mg (35%) of a mixture of 1,5,5-trimethyl-2-phenyl-3-*p*-tolylcyclopentadiene and 1-*p*-tolyl-2-phenyl-3,5,5-trimethylcyclopentadiene. Separation and identification of these isomers were performed as before (vide supra).

Run 2. In 150 mL of dry acetonitrile was dissolved 70.5 mg (0.233 mmol) of diazepine. The compound was irradiated through a Corex filter for 4 h. Concentration and chromatography of the resulting oil on a 1.2 × 20 cm hexane slurried silica gel column, eluting with hexane, gave the following 25-mL fractions: fraction 1, hexane eluant, 36.5 mg of a 1:1 mixture of 1,5,5-trimethyl-2-phenyl-3-*p*-tolylcyclopentadiene and 1-*p*-tolyl-2-phenyl-3,5,5-trimethylcyclopentadiene; fraction 2, 20% ether–hexane, nil; fraction 3, 50% ether–hexane, 10.2 mg of a mixture of compounds lacking vinyl signals by NMR; fraction 4, ether, nil.

Minimum Detection of Cyclopentadienes. By use of a series of dilutions from an original volumetric solution of pure cyclopentadiene in chloroform-*d*, it was determined that the cyclopentadienes are detectable by 270-MHz NMR as low as 2.1×10^{-4} mmol in 0.5 mL of solution.

Low-Temperature Sensitized Photolysis of Cyclopropene 1. Run 1. A solution of 0.7 mg (0.25 mmol) of cyclopropene, 0.36 mg (1.4 mmol) of sensitizer, and 5 mL of acetone was made. This solution was degassed, and then a 1.5-mL aliquot was photolyzed through filter no. 2 for 0.5 h in an NMR tube. Analysis of the sample indicated that the room-temperature photolysis of the cyclopropane in acetone behaves as does the benzene runs (vide supra).

Run 2. The same experiment as run 1 was performed in acetone-d_6. Degassing for 0.5 h beforehand was carried out. The results correspond with those for run 1 as shown by 270-MHz NMR.

Run 3. In 10 mL of acetone-d_6 were dissolved 43.0 mg (0.16 mmol) of cyclopropene 1 and 0.36 g (1.60 mmol) of *p*-(dimethylamino)benzophenone, and the solution was degassed for 0.5 h. A 1.5-mL portion was transferred to a dry, nitrogen-purged NMR tube, and the sample was photolyzed for 20 min in a stream of nitrogen maintained at −25 °C and monitored by a calibrated thermocouple next to the tube. The transfer to the precooled

(31) Zimmerman, H. E.; Little, R. D. *J. Am. Chem. Soc.* **1974**, *96*, 4623–4630.

(32) The 200-W Osram lamp described for quantum yield determination was used in this photolysis.

(33) Expanded peaks were digitized and integrated by using a Summagraphics Bitpad interfaced to a DEC PDP 11/T55 minicomputer. The internal standard for HPLC ratios was naphthalene and 1-isobutenyl-2-phenyl-3-methylindene for NMR.

(34) Meites, L.; Meites, T. *Anal. Chem.* **1948**, *20*, 984–985.

(35) (a) Preparative high-pressure liquid chromatography (HPLC) was performed with two 2 ft × $^3/_8$ in. stainless steel columns packed with 7–12-μm silica gel beads[36b] and eluting with purified hexane. (b) Zimmerman, H. E.; Welter, T. R.; Tartler, D.; Bunce, R. A.; Ramsden, W. D.; King, R., unpublished results.

VT NMR was via a dry ice–carbon tetrachloride bath. This procedure gave no indication of intermediate housene species upon analysis by NMR.

Photolysis Apparatus for Quantum Yield Determinations. All quantum yield determinations were run on the microoptical bench.[36a] Light output was measured for each run by a digital electronic actinometer[36b] calibrated by ferrioxalate actinometry.[36c] The light source was an Osram HBO 20-W high-pressure lamp with a Bausch and Lomb Model 33-86-79 monochromator with a 5.2-mm entrance slit and 3.0-mm exit slit giving a band-pass of 22 nm at half-peak height. Each photolysis was purged with nitrogen[34] for 0.75 h before and during the run. *p*-(Dimethylamino)benzophenone was the sensitizer[5] and the cell volume was 46 mL.

Summary of Quantum Yield Results for 1-Phenyl-2-methyl-3-*p*-tolyl-3-isobutenylcyclopropene. The data are listed as follows: mass (mmol) of starting material; mass (mmol) of 4-(dimethylamino)benzophenone; light absorbed; mmol of photoproduct 1, quantum yield; mmol of photoproduct 2, quantum yield; percent conversion. Analysis was by 270-MHz NMR integration.[33]

Run 1A: 36.4 mg (0.13 mmol) of cyclopropene; 0.308 g (1.36 mmol) of sensitizer; 0.034 mEinstein; 0.0036 mmol of 1,5,5-trimethyl-2-phenyl-3-*p*-tolylcyclopentadiene, $\Phi = 0.106$; 0.0033 mmol of 1-*p*-tolyl-2-phenyl-3,5,5-trimethylcyclopentadiene, $\Phi = 0.097$; 5.6%.

Run 1B: 46.6 mg (0.17 mmol) of cyclopropene; 0.309 g (1.38 mmol) of sensitizer; 0.045 mEinstein; 0.0046 mmol of 1,5,5-trimethyl-2-phenyl-3-*p*-tolylcyclopentadiene, $\Phi = 0.103$; 0.0038 mmol of 1-*p*-tolyl-2-phenyl-3,5,5-trimethylcyclopentadiene, $\Phi = 0.086$; 6.2%.

Run 1C: 40.0 mg (0.14 mmol) of cyclopropene; 0.309 g (1.38 mmol) of sensitizer; 0.084 mEinstein; 0.0057 mmol of 1,5,5-trimethyl-2-phenyl-3-*p*-tolylcyclopentadiene, $\Phi = 0.068$; 0.0053 mmol of 1-*p*-tolyl-2-phenyl-3,5,5-trimethylcyclopentadiene, $\Phi = 0.063$; 9.4%.

Run 1D: 46.1 mg (0.17 mmol) of cyclopropene; 0.308 g (1.36 mmol) of sensitizer; 0.400 mEinstein; 0.0207 mmol of 1,5,5-trimethyl-2-phenyl-3-*p*-tolylcyclopentadiene, $\Phi = 0.051$; 0.0178 mmol of 1-*p*-tolyl-2-phenyl-3,5,5-trimethylcyclopropentadiene, $\Phi = 0.045$; 24.1%.

In all runs the two cyclopentadienes were the only photoproducts detected by 270-MHz NMR or HPLC.

Summary of Quantum Yield Results for 1-*p*-Tolyl-2-methyl-3-phenyl-3-isobutenylcyclopropene. The data are listed as before: mass (mmol) of starting material; mass (mmol) of 4-(dimethylamino)benzophenone; light absorbed; mmol of photoproduct 1, quantum yield; mmol of photoproduct 2, quantum yield; percent conversion. Analysis was performed by 270-MHz NMR integration.

Run 2A: 46.3 mg (0.17 mmol) of cyclopropene; 0.308 g (1.36 mmol) of sensitizer; 0.031 mEinstein; 0.0029 mmol of 1,5,5-trimethyl-2-*p*-tolyl-3-phenylcyclopentadiene, $\Phi = 0.094$; 0.0026 mmol of 1-phenyl-2-*p*-tolyl-3,5,5-trimethylcyclopentadiene, $\Phi = 0.086$; 4.0%.

Run 2B: 46.1 mg (0.17 mmol) of cyclopropene; 0.308 g (1.36 mmol) of sensitizer; 0.055 mEinstein; 0.0039 mmol of 1,5,5-trimethyl-2-*p*-tolyl-3-phenylcyclopentadiene, $\Phi = 0.071$; 0.0038 mmol of 1-phenyl-2-*p*-tolyl-3,5,5-trimethylcyclopentadiene, $\Phi = 0.069$; 5.0%.

Run 2C: 46.0 mg (0.17 mmol) of cyclopropene; 0.308 g (1.36 mmol) of sensitizer; 0.093 mEinstein; 0.0059 mmol of 1,5,k-trimethyl-2-*p*-tolyl-3-phenylcyclopentadiene, $\Phi = 0.063$; 0.0054 mmol of 1-phenyl-2-*p*-tolyl-3,5,5-trimethylcyclopentadiene, $\Phi = 0.058$; 7.5%.

Run 2D: 46.3 mg (0.17 mmol) of cyclopropene; 0.308 g (1.36 mmol) of sensitizer; 0.45 mEinstein; 0.0185 mmol of 1,5,5-trimethyl-2-*p*-tolyl-3-phenylcyclopentadiene, $\Phi = 0.041$; 0.0149 mmol of 1-phenyl-2-*p*-tolyl-3,5,5-trimethylcyclopentadiene, $\Phi = 0.033$; 24.8%.

Summary of Quantum Yield Results for 1-*p*-Tolyl-2-phenyl-3-methyl-3-isobutenylcyclopropene. The data are listed as before: mass (mmol) of starting material; mass (mmol) of *p*-(dimethylamino)benzophenone; light absorbed; mmol of photoproduct 1, quantum yield; mmol of photoproduct 2, quantum yield; mmol of photoproduct 3, quantum yield; mmol of photoproduct 4, quantum yield; percent conversion. Analysis was by NMR integration and HPLC.[33]

Run 3A: 44.0 mg (0.160 mmol) of cyclopropene; 0.408 g (1.81 mmol) of sensitizer; 0.055 mEinstein; 0.0005 mmol of 2-phenyl-3-*p*-tolyl-1,5,5-trimethylcyclopentadiene, $\Phi = 0.0091$; 0.0005 mmol of 2-*p*-tolyl-3-phenyl-1,5,5-trimethylcyclopentadiene, $\Phi = 0.009$; 0.0004 mmol of 1-*p*-tolyl-2-phenyl-3,5,5-trimethylcyclopentadiene, $\Phi = 0.0067$; 0.0004 mmol of 1-phenyl-2-*p*-tolyl-3,5,5-trimethylcyclopentadiene, $\Phi = 0.0067$; 1.1%.

Run 3B: 46.3 mg (0.169 mmol) of cyclopropene; 0.308 g (1.36 mmol) of sensitizer; 0.10 mEinstein; 0.0011 mmol of 2-phenyl-3-*p*-tolyl-1,5,5-trimethylcyclopentadiene, $\Phi = 0.0114$; 0.0011 mmol of 2-*p*-tolyl-3-phenyl-1,5,5-trimethylcyclopentadiene, $\Phi = 0.0114$; 0.0013 mmol of 1-*p*-tolyl-2-phenyl-3,5,5-trimethylcyclopentadiene, $\Phi = 0.0136$; 0.0013 mmol of 1-phenyl-2-*p*-tolyl-3,5,5-trimethylcyclopentadiene, $\Phi = 0.0136$; 3.0%.

Run 3C: 44.5 mg (0.162 mmol) of cyclopropene; 0.402 g (1.78 mmol) of sensitizer; 0.18 mEinstein; 0.0027 mmol of 2-phenyl-3-*p*-tolyl-1,5,5-trimethylcyclopentadiene, $\Phi = 0.015$; 0.0027 mmol of 2-*p*-tolyl-3-phenyl-1,5,5-trimethylcyclopentadiene, $\Phi = 0.015$; 0.0025 mmol of 1-*p*-tolyl-2-phenyl-3,5,5-trimethylcyclopentadiene, $\Phi = 0.0139$; 0.0025 mmol of 1-phenyl-2-*p*-tolyl-3,5,5-trimethylcyclopentadiene, $\Phi = 0.0139$; 6.5%.

Run 3D: 44.7 mg (0.163 mmol) of cyclopropene; 0.408 g (1.81 mmol) of sensitizer; 0.17 mEinstein; 0.0025 mmol of 2-phenyl-3-*p*-tolyl-1,5,5-trimethylcyclopentadiene, $\Phi = 0.0148$; 0.0024 mmol of 2-*p*-tolyl-3-phenyl-1,5,5-trimethylcyclopentadiene, $\Phi = 0.0148$; 0.0022 mmol of 1-*p*-tolyl-2-phenyl-3,5,5-trimethylcyclopentadiene, $\Phi = 0.0130$; 0.0021 mmol of 1-phenyl-2-*p*-tolyl-3,5,5-trimethylcyclopentadiene, $\Phi = 0.0130$; 6.2%.

Photolysis of 1,2-Diphenyl-3-methyl-3-isobutenylcyclopropene.[3c] Several runs were made on the microoptical bench and are reported as follows: mmol of cyclopropene; mmol of *p*-(dimethylamino)benzophenone; solvent treatment; ratio of 1,2-diphenyl-3,5,5-trimethylcyclopentadiene to 1,5,5-trimethyl-2,3-diphenylcyclopentadiene; percent conversion.

Run 4A: 0.21 mmol of cyclopropene; 2.72 mmol of sensitizer; bubbled air through benzene before photolysis for 2 h; 10:1; 30% conversion.

Run 4B: 0.20 mmol of cyclopropene; 2.70 mmol of sensitizer; air-saturated benzene for ca. 1.5 h; 5:1; 20% conversion.

Run 4C: 0.20 mmol of cyclopropene; 2.72 mmol of sensitizer; degassed with purified nitrogen for 48 min; 1:1; 6% conversion.

Run 4D: 0.17 mmol of cyclopropene; 1.70 mmol of sensitizer; not degassed but freshly distilled benzene (under nitrogen) was used; 1:1; 3.3% conversion.

Photostability of Cyclopentadienes. A 200-mL benzene solution of 70.2 mg (0.256 mmol) of 1,5,5-trimethyl-2-*p*-tolyl-3-phenylcyclopentadiene and 49.9 mg (2.22 mmol) of *p*-(dimethylamino)benzophenone was nitrogen purged and irradiated for 2 h with the Hanovia apparatus (filter no. 3). Concentration and chromatographic separation of the sensitizer gave only original cyclopentadiene (54.0 mg, 80% mass balance) identified by spectral data.

In 150 mL of benzene were dissolved 1,5,5-trimethyl-2-phenyl-3-*p*-tolylcyclopentadiene (20.0 mg) and *p*-(dimethylamino)benzophenone (0.202 g). The solution was photolyzed for 0.5 h with the Hanovia apparatus through filter no. 3, concentrated, and chromatographed. Only starting material was recovered, with a 90% mass balance.

A benzene solution (150 mL) of 1-phenyl-2-*p*-tolyl-3,5,-trimethylcyclopentadiene (47.0 mg, 0.172 mmol) and *p*-(dimethylamino)benzophenone (0.310 g, 1.38 mmol) was photolyzed for 0.5 h with the Hanovia apparatus through filter no. 3. Concentration and chromatography left 40.0 mg of nonrearranged cyclopentadiene.

The same procedure was carried out on 61.0 mg (0.223 mmol) of 1-*p*-tolyl-2-phenyl-3,5,5-trimethylcyclopentadiene and 0.401 g (1.78 mmol) of *p*-(dimethylamino)benzophenone. Upon concentration of the photolysate, no isomeric cyclopentadiene, indene, or vinylcyclopropene was detected by NMR.

(36) (a) Zimmerman, H. E. *Mol. Photochem.* **1971**, *3*, 281–292. (b) Zimmerman, H. E.; Cutler, T. P.; Fitzgerald, V. R.; Weight, T. J. *Mol. Photochem.* **1977**, *8*, 379–385. (c) Hatchard, C. G.; Parker, C. A. *Proc. R. Soc. London, Ser. A.* **1956**, *235*, 518–536.

Acknowledgment. Support of this research by NIH Grant GM07487 and the National Science Foundation is gratefully acknowledged. Mechanistic aspects were supported by NSF, while exploration of the synthetic aspects were supported by NIH.

Registry No. 1, 84131-33-9; 2, 84131-34-0; 3, 84131-35-1; 4, 16736-13-3; 5, 96633-25-9; 6, 96633-23-7; 7, 96633-26-0; 8, 96633-27-1; 9, 96633-28-2; 10, 96633-29-3; 11, 96633-30-6; 12, 96633-31-7; 13, 96633-32-8; 14, 96633-34-0; 15, 96633-52-2; 17, 14618-89-4; 18, 5650-07-7; 19, 37471-46-8; 20, 96633-36-2; 21, 96633-37-3; 22, 96633-35-1; 23, 96633-42-0; 24, 96633-41-9; 25, 84131-36-2; 26, 84131-38-4; 27a, 96633-45-5; 27b, 96633-46-4; 28, 2430-99-1; 29, 2001-28-7; 30, 96633-38-4; 31, 96633-40-8; 32, 96633-43-1; 33, 96633-44-2; 34, 84131-37-3; 35, 84131-39-5; 37, 96633-48-6; 37 (1-carbomethoxy analogue), 96633-47-5; 38, 96633-49-7; 39, 96633-50-0; $(PhSe)_2$, 1666-13-3; Br_2, 7726-95-6; PhSeBr, 34837-55-3; $CH_3COCHPhCH(Tol)CH{=}C(CH_3)_2$, 96633-24-8; $TolCH_2COCH_3$, 2096-86-8; PhCHO, 100-52-7; $TsNHNH_2$, 1576-35-8; $TolCH{=}C(Ph)C(CH_3){=}NNHTs$, 96633-33-9; $(CH_3)_2C{=}CHMgBr$, 38614-36-7; $ClCO_2CH_3$, 79-22-1; mesityl oxide, 141-79-7; 3-phenyl-4-*p*-tolyl-5,5-dimethyl-2-cyclohexen-1-one, 96633-39-5; 3-*p*-tolyl-4-phenyl-5,5-dimethyl-2-cyclohexen-1-one, 96648-86-1.

Transmission of Electronic Substituent Effects in 4-Substituted Bicyclo[2.2.2]octyl Systems

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Received August 22, 1984

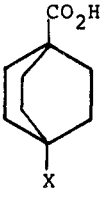
Carbon-13 substituent chemical shifts are reported for a series of 4-substituted bicyclo[2.2.2]octyl acetylenes, benzenes, cyanides, ethylenes, aldehydes, and esters. These shifts, for atoms contained in unsaturated probe linkages, are proportional to substituent field effects (σ_F). Unlike fluorine-19 chemical shifts in corresponding bicyclo[2.2.2]octyl fluorides, no definitive evidence is found for significant substituent electronegativity effects. This result is confirmed by ab initio molecular orbital calculations on bicyclo[2.2.2]octyl acetylenes and cyanides and some corresponding model systems. Unlike the corresponding aromatic side-chain derivatives, infrared intensity data for stretching absorptions of the unsaturated probes in the bicyclo[2.2.2]octyl compounds do not follow polar substituent effects.

The three principal electronic interactions between a probe group and a relatively remote substituent are[1-4] the electronegativity (χ), field (F), and resonance (R) effects. The electronegativity effect[2,5] (also earlier referred to as a σ-inductive effect) originates in an electronegativity difference between a substituent (X) and the atom to which it is attached and is transmitted by successive, but diminishing, relay along chains of atoms as shown schematically.

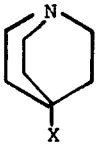
$$\overset{\delta\delta\delta+}{-}CH_2\text{-}\overset{\delta\delta+}{C}H_2\text{-}\overset{\delta+}{C}H_2\text{-}\overset{\delta-}{X}$$

The field effect involves the direct through-space transmission to the probe of the electrostatic dipole at the substituent. The weight of recent evidence suggests[1-3] that, compared to field effects, electronegativity effects are not significant after the first atom of attachment. Nevertheless, there are some results[6,7] suggesting that electronegativity, or related effects, are important in certain systems.

Suitable model compounds to study the relative importance of these two effects should be structurally rigid, to avoid problems arising from uncertain conformation, and capable of being synthesized with a reasonable range of substituents. Many earlier studies of electronic substituent effects involved meta- and para-substituted benzenes, which meet these criteria, but the concomitant presence of resonance and π-inductive[4] effects make analysis difficult. The "classic systems[1]" for such studies therefore have been 4-substituted bicyclo[2.2.2]octane-1-carboxylic acids[8,9] (1) and 4-substituted quinuclidines[9,10] (2), although it has been suggested[11] that results in the latter case may not be completely insulated from through-bond and substituent-induced structural effects.



(1)



(2)

Such systems have been used[9] to define σ_F values.[12]

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