1-(2-Hydroxycyclohexyl)-*N*-(*p*-bromophenyl)methanesulfonimidmorpholide (10). To a solution of **1b** (1.28 g, 4 mmol) in ether (50 mL) was added a solution of *n*-BuLi (5.1 mL, 10% w/v, 8 mmol) at room temperature. After being stirred for 30 min, the reaction mixture was refluxed and a solution of cyclohexene oxide (0.78 g, 8 mmol) in ether (50 mL) was added. After being refluxed for 20 h, the reaction mixture was washed with water (3 × 50 mL), dried over $MgSO_4$, and filtered. The filtrate was evaporated to give a brown oil, which was chromatographed on silica gel by elution with dichloromethane–ethyl acetate (9:1) to give desired **10** (0.65 g, 1.56 mmol, 38.9%, pale brown oil): ^1H NMR ($CDCl_3$) δ 1.10–2.23 (m, 9 H, cyclohexyl), 3.13–3.37 (m, NCH_2), 3.50–3.73 (m, 4 H, OCH_2), 6.85–7.35 (4 H, Ar); ^{13}C NMR ($CDCl_3$) δ 24.60, 25.62, 31.69, 35.48, 42.15, 72.81 (cyclohexyl), 53.80 (SCH_2), 46.54 (NCH_2), 66.42 (OCH_2), 124.81, 131.86, 142.80, 167.45 (Ar). Anal. Calcd for $C_{17}H_{25}BrN_2O_3S$: C, 48.57; H, 5.56. Found: C, 48.94; H, 5.99.

Preparation of 1,1-Diphenylethylene Oxide (12b). To a solution of dimsyl sodium (prepared from 0.16 g of NaH; 4.0 mmol) in DMSO (100 mL) was added **2** (1.25 g, 3.9 mmol) portionwise at 50 °C for 30 min. After the mixture was stirred for 2 h at room temperature, a solution of benzophenone (0.35 g, 1.95 mmol) in DMSO (20 mL) was added dropwise at room temperature. After being stirred for 3 days, the reaction mixture was poured into water (100 mL) and extracted with hexane (3 × 30 mL). The combined extract was dried over $MgSO_4$ and evaporated to give **12b** (0.30 g, 1.53 mmol, 78.9%). Other epoxides were prepared in a similar manner. **12a**: bp 56–60 °C (2 mmHg) [lit.[12] bp 67–68 °C (8 mmHg)]. **12b**: bp 92–93 °C (0.011 mmHg). **12c**; bp 30.2 °C (0.009 mmHg) [lit. bp 70 °C/ (8 mmHg)].

Preparation of 2,2-Diphenyloxetane (13a). To a solution of dimsyl sodium (prepared from 0.44 g of NaH, 18.4 mmol) in DMSO (100 mL) was added **2** (5.86 g, 18.4 mmol) in DMSO (100 mmol) at 50 °C for 30 min. After the mixture was stirred for 2 h at 50 °C, a solution of benzophenone (0.78 g, 4.28 mmol) in DMSO (20 mL) was added dropwise at 50 °C. After being stirred for 3 days, the reaction mixture was poured into water (100 mL) and extracted with hexane (3 × 30 mL). The combined extract was dried over $MgSO_4$ and evaporated to give 2,2-diphenyloxetane **13a** (0.7 g, 3.3 mmol, 77.7%). The yield was estimated by GLC. **13b** was prepared in a similar manner. **13a**: bp 111–115 °C (0.013 mmHg) [lit.[13] bp 109–112 °C (0.013 mmHg)], **13b**: bp 31–35 °C (0.009 mmHg) [lit. bp 30–35 °C (0.008 mmHg)].

Registry No. **1a**, 76867-83-9; **1b**, 115204-35-8; **1c**, 115204-36-9; **1d**, 115204-37-0; **1e**, 115204-38-1; **2**, 93938-04-6; **5a**, 115204-39-2; **5b**, 115204-40-5; **5c**, 115204-41-6; **7a**, 115204-42-7; **7b**, 115204-43-8; **8**, 115204-44-9; **9a**, 115204-45-0; **9b**, 115204-46-1; **10**, 115204-47-2; **12a**, 96-09-3; **12b**, 882-59-7; **12c**, 2085-88-3; **13a**, 884-73-1; **13b**, 19352-10-4; *p*-$MeC_6H_4NHS(=O)Me$, 19977-37-8; *p*-$BrC_6H_4NHS(=O)Me$, 115204-48-3; *p*-$ClC_6H_4NHS(=O)Me$, 69726-88-1; Me_2NH, 124-40-3; MeNHPh, 100-61-8; MeS(=O)(Cl)=NTs, 28614-56-4; PhCHO, 100-52-7; PhCOPh, 119-61-9; PhCOOCOPh, 93-97-0; Me_3SiCl, 75-77-4; MeCOPh, 98-86-2; morpholine, 110-91-8; cyclohexene oxide, 286-20-4.

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Photochemistry of Cyclopropene Derivatives. Intramolecular Hydrogen Transfer Reaction of Some 1-(Alkyl-substituted)cyclopropenes

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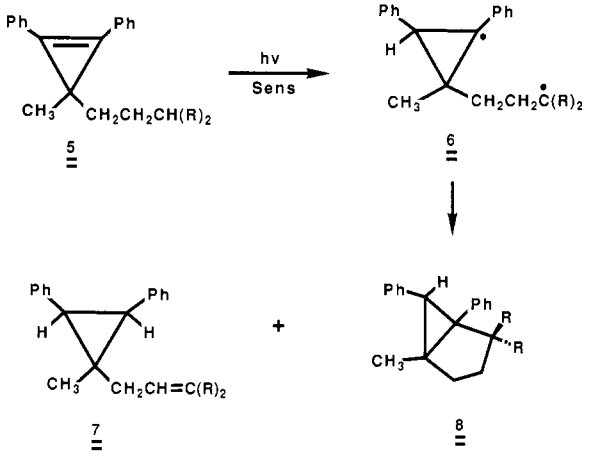
Received February 24, 1988

The photochemical behavior of a number of 1-(alkyl-substituted)cyclopropenes that contain a hydrogen atom in the γ or δ position of the side chain has been studied in mechanistic detail. The triplet state, generated by sensitization techniques, undergoes hydrogen atom abstraction by a mechanism analogous to the Norrish type II process of carbonyl compounds. The quantum yield for the triplet-state hydrogen transfer reaction decreased substantially with deuterium substitution. The value of the isotope effect ($k_H/k_D \sim 3.0$) correlated well with related results in the literature indicating an early transition state for hydrogen transfer. The high regioselectivity of hydrogen transfer can be attributed to the stereoelectronic requirements for abstraction as well as the fact that the resulting diradical produced allows for maximum delocalization of the radical centers.

Intramolecular hydrogen transfer reactions of excited states have been the subject of intense research activity since their first discovery by Norrish in 1937.[1] Most studies have centered on the photochemistry of ketones possessing γ-hydrogens.[2-7] In contrast to carbonyl compounds, examples of hydrogen abstraction in the direct and sensitized photolysis of olefins are less common.[8-27]

Scheme I



Considering the wealth of photochemistry exhibited by alkenes,[28] a systematic study of the hydrogen transfer

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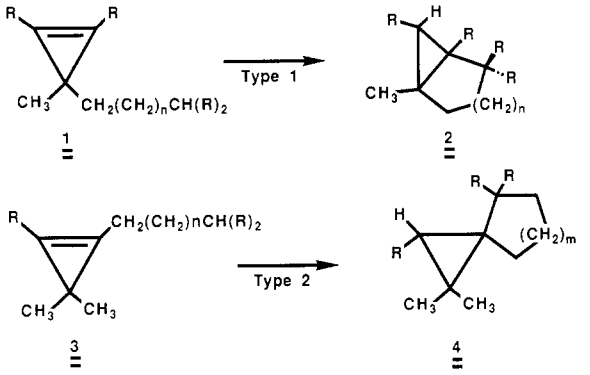
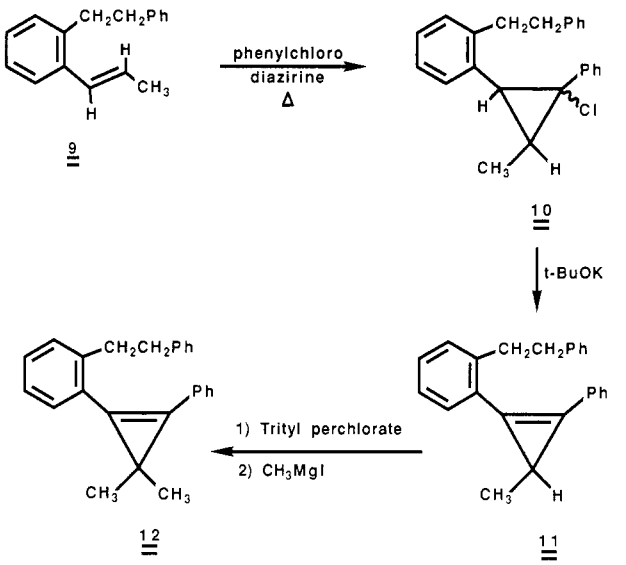
reaction to the $\pi-\pi^*$ excited state of an alkene should be of considerable interest.

Our attention during the past few years has been concentrated on the photochemistry of systems containing the cyclopropene ring. These investigations have uncovered interesting cycloaddition,[29] fragmentation,[30] and internal hydrogen transfer processes.[31] Two basic structural variants of the internal hydrogen transfer reaction can be achieved by altering the point of attachment of the side chain to the cyclopropene ring. We refer to these two modes as type 1 and type 2 intramolecular hydrogen transfer routes. In our previous studies with type 1



molecules, we observed that the triplet-sensitized irradiation of cyclopropenes that possess γ-hydrogens lead to products involving transfer of hydrogen from the side chain to the $\pi-\pi^*$ excited state of the alkene. The products obtained result from disproportionation and/or collapse of a biradical intermediate.[31] An example leading to both types of products is shown in Scheme I. In this paper we have explored the triplet-sensitized photochemistry of type 2 cyclopropenes with the hope of gaining additional information concerning the nature of the hydrogen abstraction reaction. The results reported below summarize various aspects of this effort.[32]

Scheme II



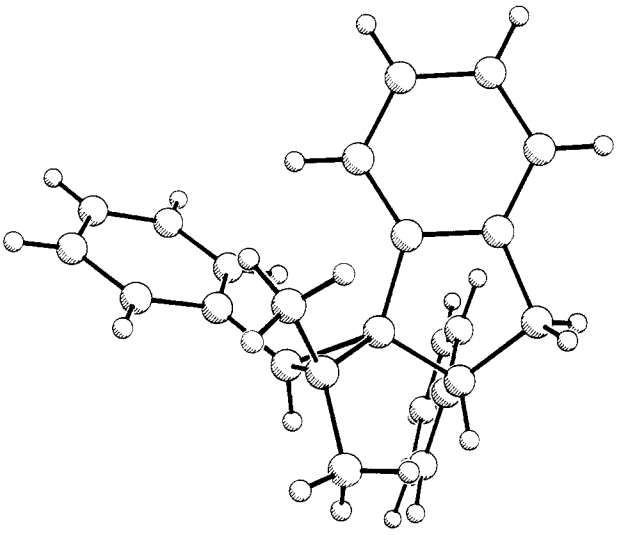


Figure 1. X-ray crystal structure of spiro benzocyclopentane **13**.

Results and Discussion

As our first model we chose to investigate the triplet-sensitized photochemistry of 1-phenyl-2-[*o*-(2-phenylethyl)phenyl]-3,3-dimethylcyclopropene (**12**). The requisite cyclopropene was prepared by the method outlined in Scheme II. Heating alkene **9** with phenylchlorodiazirine in benzene afforded a mixture of isomeric (phenylchlorodisubstituted)cyclopropanes **10**. The mixture of isomers was not separated but was stirred with potassium *tert*-butoxide to give cyclopropene **11**. Treatment of **11** with trityl perchlorate followed by reaction with methylmagnesium iodide according to the general procedure of Breslow[33] gave **12** in good yield. The sensitized irradiation of **12** in benzene thioxanthone produced spirobenzocyclopropane **13** as the exclusive photoproduct in 80% isolated yield (Φ = 0.26), mp 105–106 °C. The structure of **13** was unequivocally established by an X-ray single-

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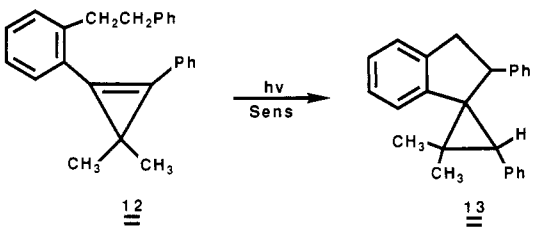
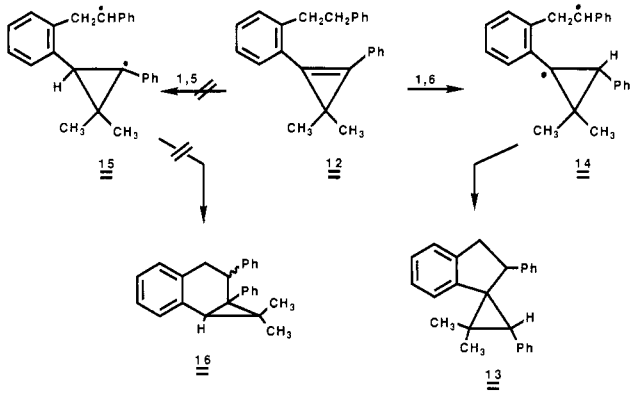


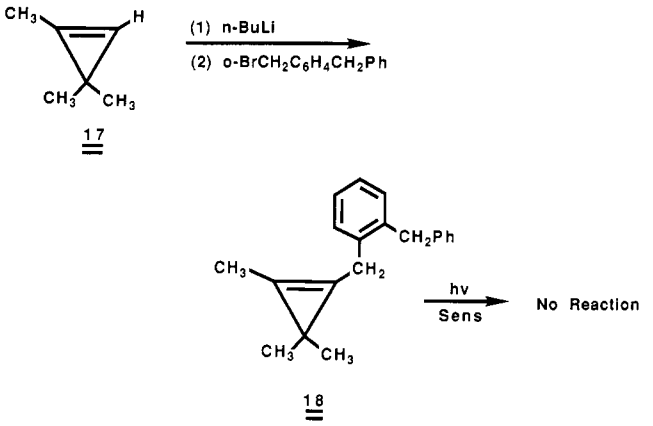
12 13

crystal structure analysis. The intensity data were measured on a Nicolet R_3 four-circle diffractometer by using Cu K_α radiation. Compound **13** crystallizes in the monoclinic space group $P2_{1/n}$ with 8 molecules per unit cell. The cell constants are a = 14.558 Å, b = 8.689 Å, c = 29.709 Å, and β = 90.86°. The structure was derived by using direct methods and refined by least squares to give a R value of 0.0588 for all the data. The overall geometry of the molecule is shown in Figure 1.

Intramolecular hydrogen atom transfer in acyclic molecules is very specific in that 1,5-transfer generally predominates over 1,6-transfer and other possible modes.[34-36] With carbonyl compounds, efficient intramolecular abstraction of hydrogen requires that the C–H bond axis be directed toward the half vacant n orbital of the carbonyl oxygen atom.[37] In these reactions the 1,5-hydrogen transfer proceeds via a six-membered cyclic transition state. The resulting 1,4-diradical intermediate either undergoes elimination or cyclization to produce a cyclobutanol.[2] It is well known that 1,6-hydrogen transfer is sterically less favorable than 1,5-hydrogen transfer.[38-40] With alkenes, 1,6-hydrogen shifts generally take place only when γ-hydrogen atoms are absent.[41] In the above case, however, photocyclization proceeds via a seven-membered transition state even though a 1,5-hydrogen transfer is possible. Thus, the formation of **13** is quite reasonably explained in terms of a 1,6-hydrogen transfer followed by cyclization of the resulting 1,5-diradical **14**.

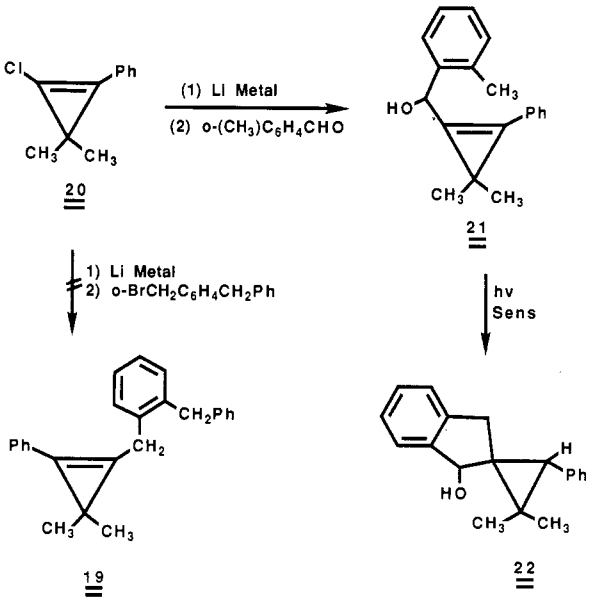


In view of the stringent spatial requirements associated with the internal hydrogen transfer reaction, we thought it worthwhile to study a number of related systems. This led us to examine the triplet-sensitized irradiation of a 1-(*o*-benzyl-substituted)cyclopropene so as to compare its photochemical behavior with cyclopropene **12**. Treatment of 1,3,3-trimethylcyclopropene (**17**) with *n*-butyllithium followed by reaction of the resulting lithiate[42] with *o*-benzylbenzyl bromide gave cyclopropene **18** in good yield.



Unfortunately, cyclopropene **18** proved to be stable, even on extended photolysis in the presence of a variety of triplet sensitizers. We suspect that the triplet state of this bis(alkyl-substituted)cyclopropene lies significantly higher than the sensitizer and therefore energy transfer does not occur.

In order to lower the triplet-state energy of the strained π bond, we attempted to prepare the analogous 1-(phenyl-substituted)cyclopropene **19**. Treatment of 1-phenyl-2-chloro-3,3-dimethylcyclopropene (**20**)[43] with lithium metal followed by reaction with *o*-benzylbenzyl bromide (or iodide) only produced the coupled bibenzyl as a consequence of an electron-transfer reaction. We



found, however, that the lithiate derived from **20** reacted smoothly with *o*-methylbenzaldehyde to give cyclopropene **21** in high yield. When the sensitized irradiation of **21** was carried out in benzene (thioxanthone), spirobenzocyclopentane **22** was obtained as the exclusive photoproduct in 85% isolated yield (Φ = 0.24) [NMR ($CDCl_3$, 360 MHz) δ 0.82 (s, 3 H), 0.87 (s, 3 H), 1.57 (s, 1 H), 1.90 (br s, 1 H), 3.19 (d, 1 H, J = 15.0 Hz), 3.25 (d, 1 H, J = 15.0 Hz), 4.95 (s, 1 H), and 6.95–7.35 (m, 9 H). As was the case with

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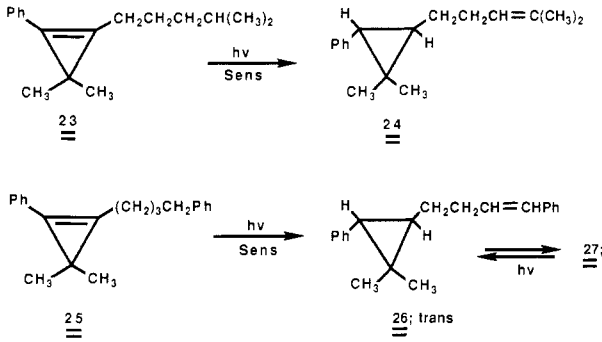
cyclopropene **12**, the hydrogen transfer reaction proceeds via a seven-membered transition state.

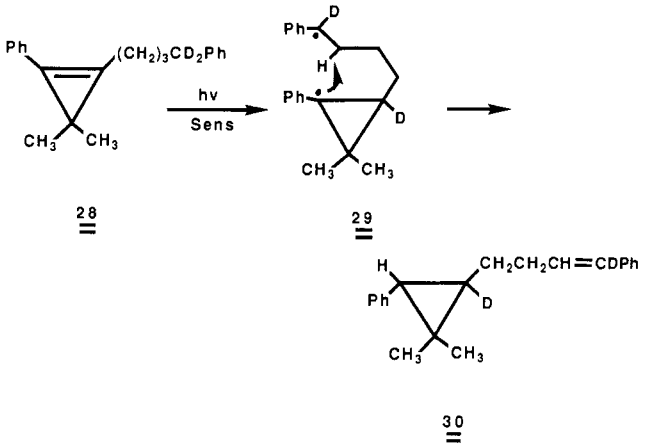
We have also studied the triplet-induced photobehavior of cyclopropenes **23** and **25**. These compounds were prepared by treating 1-phenyl-2-chlorocyclopropene **20** with lithium metal followed by reaction with the appropriate alkyl halide. The sensitized irradiation of **23** produced the 2-(methylpentenyl-substituted)cyclopropane **24** in high yield (85%, $\Phi = 0.21$). Similar behavior was observed with



cyclopropene **25**. Consideration of the product distribution as a function of time showed that the trans isomer **26** was initially formed. Isomerization about the π bond to the cis isomer **27** occurred only when the photolysis was carried out for longer periods of time. The exclusive formation of **26** probably reflects the most stable conformation of the initially generated diradical intermediate and parallels the thermodynamic difference in olefin stability.[44]

Substitution of hydrogen with deuterium in organic compounds may exert a marked effect on certain properties of their excited states.[45-48] Theory predicts that deuterium should decrease the rate of $T^* \rightarrow S_0$ and $S^* \rightarrow S_0$ radiationless transitions.[49] The extent of the primary deuterium isotope effect will depend on how extensively the C–D bond interacts with the excited state. Deuterium labeling has been widely used in mechanistic studies of the type II photoelimination of ketones.[50-55] Primary kinetic isotope effects have been reported for several ketones with values of k_H/k_D ranging from 0.9 to 5.5.[56,57] In order to provide more detailed information concerning the hydrogen transfer reaction, we have examined the effect of incorporating a deuterium onto the δ position of the side chain. Synthesis of the desired substrate **28** involved treating 1-phenyl-2-chloro-3,3-dimethylcyclopropene (**20**) with lithium metal followed by reaction with 1-bromo-4,4-dideuterio-4-phenylbutane. The NMR spectrum of the resulting sensitized photoproduct **30** is perfectly consistent

Path A



with the deuterium distribution observed (see Experimental Section). Thus the reaction is completely stereospecific and involves transfer of the deuterium atom via a six-membered transition state in marked contrast to the results encountered with cyclopropenes **12** and **21**. It is also worth noting that diradical **29** prefers to undergo exclusive disproportionation rather than coupling as was encountered with cyclopropenes **12** and **21**. The transition state for disproportionation requires that the C–H bond in the γ-position of the side chain be in close proximity to the radical center on the cyclopropane ring. This geometry is most easily attained with diradical **29**.

The quantum yield for the triplet-state hydrogen transfer reaction of **25** → **26** decreased substantially with deuterium substitution ($\Phi_{25} = 0.25$ vs $\Phi_{28} = 0.085$). The value of the isotope effect (k_H/k_D = ca. 3.0) for this system[58] correlates well with related results in the literature,[59] indicating an early transition state according to Hammond's postulate.[60]

In a previous paper[31] we had shown that the quantum yield of reaction of 1,2-bis(phenyl-substituted)cyclopropenes in the presence of quenchers can be used to calculate the rate constant for hydrogen abstraction. Since the intersystem-crossing quantum yield for these systems is close to zero,[61,62] it is necessary to use a sensitizer to populate the triplet state. With unsymmetrically substituted 1-(phenyl-substituted)-2-(alkyl-substituted)-cyclopropenes, however, the quantum yield for reaction was found to depend on the concentration of starting material. As a consequence of this dependence, it was not possible to determine the rate of hydrogen transfer by Cristol's method.[63] This unusual concentration effect is only observed with unsymmetrically substituted cyclopropenes and probably is related to a bimolecular electron-transfer reaction that occurs at higher concentrations.

We believe that the first step involved in the production of the diradical intermediate is rate controlling and is therefore sensitive to isotopic substitution at the benzylic carbon. It should be noted, however, that another pathway

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(58) The value of the isotope effect remained constant (ca. 3.0) from −20 °C to +65 °C. Correlating quantum yields with isotope effects is normally a dangerous occupation because of excited-state lifetime assumptions. In this case, however, the lifetimes are very similar.
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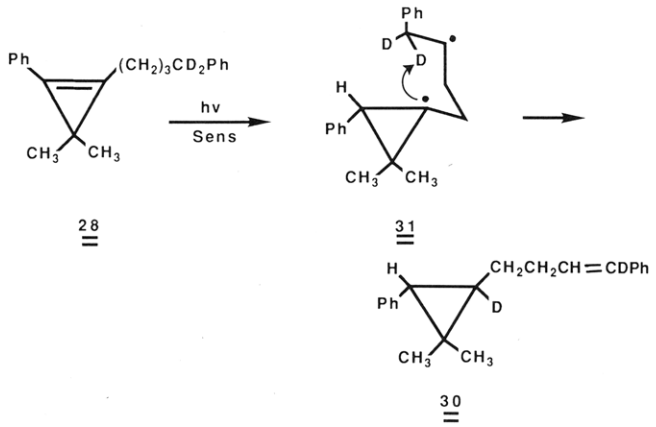
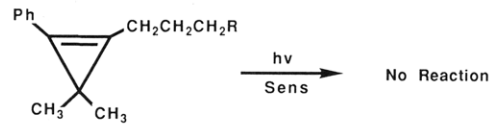
is conceivable and involves transfer of the γ-hydrogen as the initial step. This will result in the formation of diradical **31**, which can then undergo internal disproportionation to give **30**. The isotope effect if route B were

Path B



28 31 30

the exclusive pathway would be close to unity. The experimentally observed isotope effect (k_H/k_D = 3.0), however, could actually be the weighted average of the two pathways. In order to probe the feasibility of γ-hydrogen transfer (i.e., path B), we examined the sensitized irradiation of the lower homologue **32**. We found, however, that



32; R=Ph
33; R=CH3

1-(3,3-dimethyl-2-phenylcyclopropen-1-yl)-3-phenylpropane (**32**) could be completely recovered even under extended irradiation in the presence of thioxanthone. This observation clearly demonstrates the necessity of having a hydrogen atom in the δ-position of the side chain and eliminates path B from further consideration. We also examined the triplet-sensitized irradiation of cyclopropene **33** and found it to be perfectly stable. The reluctance of **33** to undergo reaction is probably due to the difficulty of transferring a primary hydrogen atom to the π–π* triplet state.

In our previous hydrogen transfer studies with type 1 cyclopropenes,[31] we observed that the triplet lifetimes of bis(aryl-substituted)cyclopropenes are 100 times greater than those for related phenyl alkyl ketones.[2] The longer lifetimes were suggested to reflect the weaker C–H bond being formed in the abstraction reaction. In addition, the rate constant for abstraction was found to be much more sensitive to the strength of the γ C–H bond than that observed with the corresponding phenyl alkyl ketone system. This is to be expected since a benzylic type radical (π–π* model)[64] should be much more selective than an alkoxy radical (n–π* model) toward hydrogen abstraction as a consequence of the greater endothermicity of the reaction. In order to determine whether a δ-allylic hydrogen atom could be transferred with type 2 cyclopropenes, we examined the sensitized behavior of 1-(3,3-dimethyl-2-phenylcyclopropen-1-yl)-5-hexene (**34**). In this case the δ C–H bond is activated as a consequence of allylic

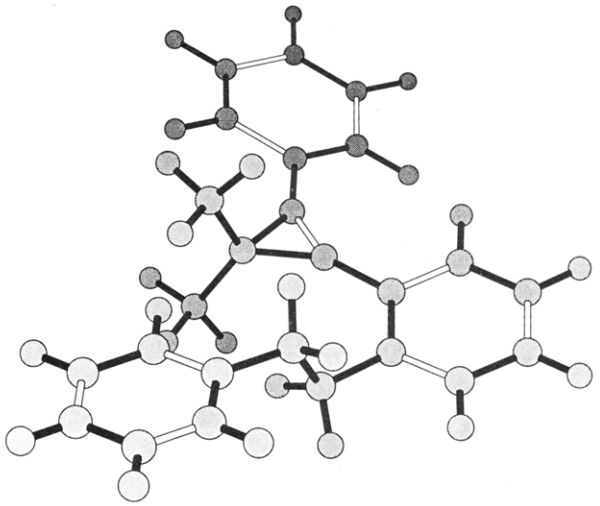
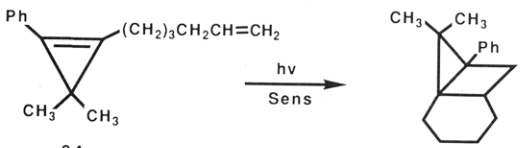


Figure 2. Lowest energy conformer of cyclopropene **12**.

delocalization of the resulting radical center. Interestingly, the sensitized irradiation of **34** gave rise to a single photoproduct whose structure was assigned as the intramolecular [2 + 2]-cycloadduct **35**. With this system the



34 35

triplet excited state prefers to undergo an intramolecular [2 + 2]-cycloaddition rather than the hydrogen transfer reaction. More than likely the weak C–H bond that is being formed in the hydrogen abstraction reaction plays an important role in the competition between the two possible processes.

At this point it is worthwhile to consider the geometrical details of the transition state involving transfer of the side-chain hydrogen atom to the triplet π–π* state. The well-known order 1,5 > 1,6 ≫ 1,4 in rates of intramolecular hydrogen atom transfers in acyclic systems was originally thought to reflect a cyclic six-ring transition-state geometry which is strain free.[65-68] A perfect analogy to cyclohexane, however, requires a severely nonlinear geometry for hydrogen transfer. Linearity is usually considered to be the most favorable arrangement for the hydrogen transfer reaction.[69] Recent MO calculations by Houk and Dorigo indicate that the six-ring transfer is actually disfavored enthalpically with respect to seven-ring transfer.[70] The experimental preference for a six-membered transition state was suggested to be the result of a more favorable entropy of activation.[70]

We have carried out force field modeling calculations[71] so as to determine the lowest energy conformation of the

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(71) We thank Professor Kosta Steliou of the University of Montreal for providing a copy of the extensively rewritten Still Model program (version 2.92).

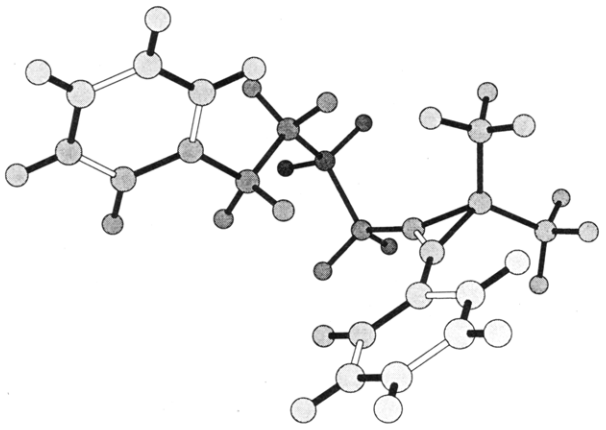

Figure 3. Reactive conformer of cyclopropene **25**.

starting cyclopropene. These molecular mechanics calculations indicate a total energy of 59.70 kcal for the lowest energy state of **12** and implicate the ground-state geometry shown in Figure 2. Such a geometry is ideal for a 1,6-hydrogen transfer since the benzylic hydrogen at C_7 is within bonding distance (2.85 Å) of the π–π^* excited state. Thus, the high regioselectivity of hydrogen transfer observed with **12** is a consequence of the stereoelectronic requirements for abstraction as well as the fact that the resulting diradical (i.e. **16**) allows for maximum delocalization of the radical centers. A similar situation also prevails with cyclopropene **21**.

Molecular mechanics calculations indicate that the lowest energy state (E_T = 51.80 kcal) of the (4-(phenylbutyl)-substituted)cyclopropene **25** corresponds to the expected extended conformer. In order for a remote hydrogen to be within bonding distance of the excited π–π^* state, the alkyl group must rotate about both the α,β- and β,γ-bonds. The conformation that brings the δ-hydrogen within bonding distance to the excited state is only 2.1 kcal higher than the extended conformer and its geometry is shown in Figure 3. We assume that excitation does not destroy the planarity of the system and consequently the excited state-geometry should be very similar to that of the ground state. The arrangement of atoms shown in Figure 3 is easily attained within the lifetime of the π–π^* triplet state. The distance between the δ CH hydrogen and the cyclopropene carbon is calculated as 2.87 Å. Moreover, the δ-CHC angle shown in the figure is close to 180°, which is considered to be most favorable for hydrogen transfer. Thus, with these alkyl substituted type 2 cyclopropenes, hydrogen transfer proceeds via a six-membered transition state as a consequence of both stereoelectronic factors and bonding distances.

We are continuing to examine the hydrogen transfer reaction of related systems and will report additional findings at a later date.

Experimental Section

Melting points were determined on a Thomas-Hoover capillary melting point apparatus and are uncorrected. Infrared spectra were run on a Perkin-Elmer Model 283 infrared spectrometer. Proton NMR spectra were obtained on Varian EM-390 and Nicolet NMC-360 MHz spectrometers. ^{13}C NMR spectra were recorded on an IBM NB 200 SY FT spectrometer. Microanalyses were performed at Atlantic Microlabs, Atlanta, GA. Mass spectra were determined with a VG MM-7070S mass spectrometer at an ionizing voltage of 70 eV.

Preparation of 1-Phenyl-2-[*o*-(2-phenylethyl)phenyl]-3,3-dimethylcyclopropene (12). A solution containing 2.5 g of [*o*-(2-phenylethyl)phenyl]magnesium bromide in 50 mL of ether was prepared according to the procedure of Riecke.[72] The solution was cooled to 0 °C, 3.0 g of propionaldehyde was added, and the mixture was allowed to warm to room temperature over a 2-h period. A saturated ammonium chloride solution was added to the mixture and the solution was stirred until both phases became clear. The organic phase was taken up in ether, washed with water, and dried over magnesium sulfate. The solvent was removed under reduced pressure and the resulting yellow oil was taken up in 25 mL of benzene. To this solution was added 30 mg of *p*-toluenesulfonic acid, and the mixture was heated at reflux for 4 h. The solvent was removed under reduced pressure and the residue was subjected to silica gel chromatography using hexane as the eluent. The major component isolated from the column contained 2.0 g of a mixture of *cis*- and *trans*-1-[*o*-(2-phenylethyl)phenyl]-1-propene as a clear oil: NMR ($CDCl_3$, 60 MHz) δ (cis) 1.87 (d, 3 H, J = 6.0 Hz), (trans) 1.90 (d, 3 H, J = 6.0 Hz), 2.92 (br s, 4 H), (cis) 6.02 (q, 1 H, J = 6.0 Hz), (trans) 6.23 (q, 1 H, J = 6.0 Hz) and 6.80–7.70 (m, 10 H); IR (neat) 3048, 1605, 1510, 1460, 960, 750 and 700 cm^{-1}.

A solution containing 2.0 g of the above mixture and 1.8 g of phenylchlorodiazirine in 100 mL of benzene was heated at reflux for 6 h and was then cooled to room temperature.[73] The solvent was removed under reduced pressure and the residue was taken up in 50 mL of tetrahydrofuran. To this solution was added 1.6 g of potassium *tert*-butoxide at −78 °C, and the mixture was allowed to warm to 0 °C and was stirred at this temperature for 3 h. The solution was then stirred at 25 °C for 10 h and was diluted with 30 mL of water. The organic layer was extracted with ether, which was then washed with water and dried over magnesium sulfate. The solvent was removed under reduced pressure and the residue was subjected to silica gel chromatography using hexane as the eluent. The major component isolated contained 1.72 g (60%) of a white solid, mp 45–46 °C, whose structure is assigned as 1-phenyl-2-[*o*-(2-phenylethyl)phenyl]-3-methylcyclopropene on the basis of its spectral properties: NMR ($CDCl_3$, 60 MHz) δ 1.40 (d, 3 H, J = 5.0 Hz), 2.36 (q, 1 H, J = 5.0 Hz), 2.70–3.62 (m, 4 H) and 6.98–8.10 (m, 10 H); IR (KBr) 3045, 1800, 1610, 1480, 1440, 1340, 1075, 1065, 1025, 980, 760 and 695 cm^{-1}; MS, m/e 310 (M^+, base).

To a 500-mg sample of the above cyclopropene in 30 mL of acetonitrile was added 1.0 g of trityl perchlorate at 0 °C. After being stirred at 25 °C for 1 h, the mixture was diluted with 350 mL of anhydrous ether and the solid was filtered and washed with ether to give 1-phenyl-2-[*o*-(2-phenylethyl)phenyl]-3-methylcyclopropenyl perchlorate as a white solid, mp 187–188 °C. To a suspension containing 560 mg of this material in 30 mL of tetrahydrofuran at −78 °C was added 4 mL of a 3.0 M solution of methylmagnesium iodide in ether. The mixture was stirred at −78 °C for 3 h and was then allowed to warm to room temperature. The excess Grignard reagent was destroyed with a saturated ammonium chloride solution and the organic layer was taken up in ether, washed with water, and dried over magnesium sulfate. Removal of the solvent left a yellow oil, which was subjected to silica gel chromatography using hexane as the eluent. The major component was a clear oil whose structure was assigned as 1-phenyl-2-[*o*-(2-phenylethyl)phenyl]-3,3-dimethylcyclopropene (**12**) on the basis of its spectra data: NMR ($CDCl_3$, 60 MHz) δ 1.25 (s, 6 H), 2.71–3.36 (m, 4 H) and 6.9–7.78 (m, 14 H); IR (neat) 3065, 1800, 1660, 1585, 1480, 1445, 1350, 1250, 1165, 1060, 740 and 690 cm^{-1}; UV (95% ethanol) 342 nm (ϵ 10900), 323 (18700) and 229 (13300). Anal. Calcd for $C_{25}H_{24}$: C, 92.54; H, 7.46. Found: C, 92.46; H, 7.38.

Triplet-Sensitized Irradiation of 1-Phenyl-2-[*o*-(2-phenylethyl)phenyl]-3,3-dimethylcyclopropene (12). A solution containing 280 mg of **12** and 30 mg of thioxanthone in 250 mL of benzene was irradiated with a 450-W Hanovia lamp equipped with a Uranium filter sleeve for 2 h under an argon atmosphere. Removal of the solvent under reduced pressure left a yellow oil, which was subjected to silica gel chromatography using hexane as the eluent. The major component isolated contained 225 mg (80%) of a white solid, mp 105–106 °C, whose structure was assigned as spirobenzocyclopentane **13** on the basis of its spectral properties: NMR ($CDCl_3$, 360 MHz) δ 1.15 (s, 3 H), 1.57

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(73) Padwa, A.; Pulwer, M. J.; Blacklock, T. *J. Org. Synth.* **1981**, *60*, 53.

(s, 3 H), 2.05 (s, 1 H), 3.17 (d, 1 H, J = 14.0 Hz), 3.52 (d, 1 H, J = 8.0 Hz), 3.61 (dd, 1 H, J = 14.0 and 8.0 Hz), 5.85 (d, 1 H, J = 8.0 Hz) and 6.80–7.30 (m, 14 H); IR (KBr) 3075, 1595, 1490, 1445, 1375, 1065, 1020, 745 and 715 cm^{-1}; UV (95% ethanol) 283 nm (ϵ 2000), 270 (1900) and 234 (7600); ms, m/e 324 (M^+, base). Anal. Calcd for $C_{25}H_{24}$: C, 92.54; H, 7.46. Found: C, 92.48; H, 7.47.

The molecular structure of **13** was unequivocally determined by an X-ray crystal structure analysis. The compound crystallizes in the monoclinic space group $P2_{1/n}$ with 8 molecules per unit cell. The cell constants are a = 14.558 (3) Å, b = 8.689 (2) Å, c = 29.709 (7) Å, and β = 90.86 (2)°. The structure was solved by direct methods using the random starting point tangent refinement routines of the SHELXTL software package and was refined to an R value of 0.0588 for 2195 independent observed reflections.

Preparation of 1-(*o*-Benzylbenzyl)-2,3,3-trimethylcyclopropene (18). To 4.58 mL of a 2.5 M methyllithium solution was added 10 mL of ether. The solution was cooled to 0 °C and 0.60 g of 1,3,3-trimethylcyclopropene[74] (**17**) was added.[77] The flask was allowed to warm to room temperature and was stirred for 40 h. To this solution was added 1.91 g of *o*-benzylbenzyl bromide in 5 mL of anhydrous ether at −78 °C. The mixture was allowed to warm to room temperature and was stirred for an additional 48 h. The reaction was quenched with a saturated ammonium chloride solution, washed with water, and dried over anhydrous sodium sulfate. The mixture was filtered and the solvent was removed under reduced pressure. Chromatography of the crude residue on a 4-mm silica gel chromatotron plate with heptane as the eluent gave 0.90 g (48%) of 1-(*o*-benzylbenzyl)-2,3,3-trimethylcyclopropene (**18**): NMR ($CDCl_3$, 360 MHz) δ 1.00 (s, 6 H), 1.85 (t, 3 H, J = 1.4 Hz), 3.79 (q, 2 H, J = 1.4 Hz), 4.05 (s, 2 H) and 7.10–7.30 (m, 9 H); IR (neat) 3105, 3000, 2900, 2835, 1595, 1485, 1425, 1415, 1360, 730 and 700 cm^{-1}; UV (95% ethanol) 254 nm (ϵ 6170); MS, m/e 262 (M^+), 247 (base), 219, 192, 171, 105 and 91. Anal. Calcd for $C_{20}H_{22}$: C, 91.55; H, 8.45. Found: C, 91.48; H, 8.49.

Extended irradiation of **18** in the presence of thioxanthone gave recovered starting material.

Preparation of 1-(3,3-Dimethyl-2-phenylcyclopropen-1-yl)-*o*-methylbenzyl Alcohol (21). To a suspension containing 1.0 g of a 30% lithium dispersion in 10 mL of anhydrous ether was added 1.55 g of 1-chloro-3,3-dimethyl-2-phenylcyclopropene (**20**) in 25 mL of anhydrous ether. The mixture was stirred at room temperature for 16 h and was then cooled to −100 °C and 3 mL of freshly distilled HMPA was added. The resulting mixture was stirred for 30 min and was then quenched by the addition of 1.04 g of *o*-methylbenzaldehyde in 5 mL of anhydrous ether. The mixture was allowed to stir for 15 h at room temperature followed by quenching with a saturated ammonium chloride solution. The organic layer was separated and the aqueous layer was extracted with ether. The combined ether extracts were dried over magnesium sulfate and the solvent was removed under reduced pressure. The residue was chromatographed on a 2 × 15 cm silica gel column using 5% ether–hexane as the eluent to give 1.62 g (68%) of a clear oil whose structure was assigned as 1-(3,3-dimethyl-2-phenylcyclopropen-1-yl)-*o*-methylbenzyl alcohol (**21**) on the basis of its spectral properties: NMR ($CDCl_3$, 90 MHz) δ 1.21 (s, 3 H), 1.34 (s, 3 H), 1.42 (s, 1 H), 2.35 (s, 3 H), 5.95 (s, 1 H) and 7.00–7.56 (m, 9 H); IR (neat) 3560–3220, 3070–2860, 1840, 1605, 1490, 1450, 1370, 1170, 1030, 770, 700 and 640 cm^{-1}; UV (95% ethanol) 272 nm (ϵ 14 900); MS, m/e 264 (M^+), 249 (base), 143, 105 and 77. Anal. Calcd for $C_{19}H_{20}$: C, 91.88; H, 8.12. Found: C, 91.84; H, 8.06.

Triplet-Sensitized Irradiation of 1-(3,3-Dimethyl-2-phenylcyclopropen-1-yl)-*o*-methylbenzyl Alcohol (21). A solution containing 200 mg of **21** and 20 mg of thioxanthone in 200 mL of benzene was irradiated with a 450-W Hanovia lamp equipped with a uranium glass filter sleeve for 20 min. The solvent was removed under reduced pressure and the residue was subjected to silica gel chromatography using a 5% methanol–hexane mixture as the eluent. The major fraction contained 180 mg (90%) of a clear oil whose structure was assigned as spirobenzocyclopentane **22** on the basis of its spectral properties: NMR ($CDCl_3$, 360 MHz) δ 0.82 (s, 3 H), 0.87 (s, 3 H), 1.57 (s, 1 H), 1.90 (br s, 1 H), 3.19 (d, 1 H, J = 15.0 Hz), 3.25 (d, 1 H, J = 15.0 Hz), 4.95 (s, 1 H) and 6.95–7.35 (m, 9 H); IR (neat) 3650–3150, 3060–2860, 1730, 1600, 1490, 1440, 1390, 1120, 1010, 750 and 700 cm^{-1}; UV (95%, ethanol) 268 nm (ϵ 11 500) and 215 (sh, 17 000). Anal. Calcd for $C_{19}H_{20}$: C, 91.88; H, 8.12. Found: C, 91.76; H, 7.98.

Preparation of 1-(3,3-Dimethyl-2-phenylcyclopropen-1-yl)-4-methylpentane (23). To a suspension containing 1.0 g of a 30% lithium dispersion in 10 mL of anhydrous ether was added 1.55 g of 1-chloro-3,3-dimethyl-2-phenylcyclopropene (**20**) in 25 mL of anhydrous ether. The mixture was stirred at room temperature for 16 h and was then cooled to −100 °C and 3 mL of freshly distilled HMPA was added. The resulting mixture was stirred for 30 min and was quenched by the addition of 1.26 g of 5-bromo-2-methylpentane in 5 mL of anhydrous ether. The mixture was allowed to stir for 15 h at room temperature and this was quenched with a saturated ammonium chloride solution. The organic layer was separated and the aqueous layer was extracted with ether. The combined ether extracts were dried over magnesium sulfate and the solvent was removed under reduced pressure. The residue was chromatographed on a 2 × 15 cm silica gel column using hexane as the eluent to give 1.91 g (96%) of a clear oil whose structure was assigned as 1-(3,3-dimethyl-2-phenylcyclopropen-1-yl)-4-methylpentane (**23**) on the basis of its spectral properties: NMR (CCl_4, 90 MHz) δ 0.88 (d, 6 H, J = 7.2 Hz), 1.26 (s, 6 H), 1.40–1.86 (m, 5 H), 2.55 (t, 2 H, J = 7.2 Hz) and 7.03–7.33 (m, 5 H); IR (neat) 3080–2850, 1840, 1605, 1590, 1500, 1460, 1400, 1380, 1270, 1190, 1140, 1090, 930, 780 and 710; UV (95% ethanol) 268 nm (ϵ 14 930); MS, m/e 228 (M^+), 213, 185, 143 (base), 91 and 77. Anal. Calcd for $C_{17}H_{24}$: C, 89.41; H, 10.59. Found: C, 89.28; H, 10.31.

Triplet-Sensitized Irradiation of 1-(3,3-Dimethyl-2-phenylcyclopropen-1-yl)-4-methylpentane (23). A solution containing 188 mg of **23** and 19 mg of thioxanthone in 200 mL of benzene was irradiated with a 450-W Hanovia lamp equipped with a Pyrex glass filter sleeve for 15 min. The solvent was removed under reduced pressure and the residue was subjected to silica gel chromatography using hexane as the eluent. The major fraction contained 117 mg (63%) of a clear oil whose structure was assigned as [2,2-dimethyl-3-(4-methyl-3-pentenyl)cyclopropyl]benzene (**24**) on the basis of its spectral properties: NMR ($CDCl_3$, 360 MHz) δ 0.90 (s, 3 H), 1.11 (q, 1 H, J = 6.5 Hz), 1.30 (s, 3 H), 1.53–1.69 (m, 2 H), 1.62 (d, 1 H, J = 6.5 Hz), 1.70 (s, 3 H), 1.80 (s, 3 H), 2.24 (q, 2 H, J = 7.3 Hz), 5.30 (t, 1 H, J = 7.3 Hz) and 7.20–7.38 (m, 5 H); IR (neat) 3060–2860, 1600, 1490, 1450, 1375, 1120, 1030, 730, 700 and 620 cm^{-1}; UV (95% ethanol) 222 mm (ϵ 6770). Anal. Calcd for $C_{17}H_{24}$: C, 89.41; H, 10.59. Found: C, 89.36; H, 10.42.

Preparation of 1-(3,3-Dimethyl-2-phenylcyclopropen-1-yl)-4-phenylbutane (25). To a suspension containing 1.0 g of a 30% lithium dispersion in 10 mL of anhydrous ether was added 1.55 g of 1-chloro-3,3-dimethyl-2-phenylcyclopropene (**20**) in 25 mL of anhydrous ether. The mixture was stirred at room temperature for 16 h and was then cooled to −100 °C and 3 mL of freshly distilled HMPA was added. The resulting mixture was stirred for 30 min and was quenched by the addition of 1.85 g of 4-bromo-1-phenylbutane in 5 mL of anhydrous ether. The mixture was allowed to stir for 15 h at room temperature and this was quenched with a saturated ammonium chloride solution. The organic layer was separated and the aqueous layer was extracted with ether. The combined ether extracts were dried over magnesium sulfate and the solvent was removed under reduced pressure. The residue was chromatographed on a 2 × 15 cm silica gel column using hexane as the eluent to give 1.63 g (79%) of a clear oil whose structure was assigned as 1-(3,3-dimethyl-2-phenylcyclopropen-1-yl)-4-phenylbutane (**25**) on the basis of its spectral properties: NMR ($CDCl_3$, 360 MHz) δ 1.15 (s, 6 H), 1.58–1.63 (m, 4 H), 2.50–2.58 (m, 4 H) and 7.05–7.30 (m, 10 H); IR (neat) 3070–2860, 1845, 1605, 1500, 1485, 1370, 1260, 1080, 1035, 915, 750 and 700 cm^{-1}; UV (95% ethanol) 270 nm (ϵ 9300); MS, m/e 276 (M^+), 261, 185, 143, and 91 (base). Anal. Calcd for $C_{21}H_{24}$: C, 91.25; H, 8.75. Found: C, 91.13, H 8.77.

Triplet-Sensitized Irradiation of 1-(3,3-Dimethyl-2-phenylcyclopropen-1-yl)-4-phenylbutane (25). A solution containing 200 mg of **25** and 20 mg of thioxanthone in 200 mL of benzene was irradiated with a 450-W Hanovia lamp equipped

(74) Closs, G. C.; Closs, L. E.; Bell, W. A. *J. Am. Chem. Soc.* **1963**, *85*, 3796.

with a Pyrex glass filter sleeve for 10 min. The solvent was removed under reduced pressure and the residue was subjected to silica gel chromatography using hexane as the eluent to give a 3:2 mixture of two compounds that were separated by reversed-phase HPLC. The minor fraction contained 50 mg (25%) of a clear oil whose structure was assigned as [2,2-dimethyl-3-(*Z*)-(4-phenyl-3-butenyl)cyclopropyl]benzene (**27**) on the basis of its spectral properties: NMR ($CDCl_3$, 360 MHz) δ 0.75 (s, 3 H), 1.03 (q, 1 H, J = 6.8 Hz), 1.20 (s, 3 H), 1.55–1.74 (m, 3 H), 2.47–2.55 (m, 2 H), 5.75 (dt, 1 H, J = 11.6 and 7.4 Hz), 6.45 (d, 1 H, J = 11.6 Hz) and 7.10–7.35 (m, 10 H); IR (neat) 2980–2860, 1600, 1440, 1380, 1020 and 700 cm^{-1}; UV (95% ethanol) 228 nm (ϵ 12 260); MS, m/e 276 (M^+), 233, 185, 145, 117 (base), 91 and 77. Anal. Calcd for $C_{21}H_{24}$: C, 91.25; H, 8.75. Found: C, 91.18, H, 8.80.

The second fraction contained 128 mg (64%) of a clear oil whose structure was assigned as [2,2-dimethyl-3(*E*)-(4-phenyl-3-butenyl)cyclopropyl]benzene (**26**) on the basis of its spectral properties: NMR ($CDCl_3$, 360 MHz) δ 0.80 (s, 3 H), 1.08 (q, 1 H, J = 6.8 Hz), 1.22 (s, 3 H), 1.52–1.76 (m, 3 H), 2.34–2.42 (m, 2 H), 6.29 (dt, 1 H, J = 15.8 and 6.8 Hz), 6.42 (d, 1 H, J= 15.8 Hz) and 7.15–7.35 (m, 10 H); IR (neat) 2970–2840, 1600, 1440, 1370, 1020 and 700 cm^{-1}; UV (95% ethanol) 252 nm (ϵ 27 800); MS, m/e 276 (M^+, base), 233, 145, 117, 91 and 77. Anal. Calcd for $C_{21}H_{24}$: C, 91.25; H, 8.75. Found: C, 91.23, H, 8.79.

Preparation of 1-(3,3-Dimethyl-2-phenylcyclopropen-1-yl)-4,4-dideuterio-4-phenylbutane (28). To a suspension containing 1.0 g of a 30% lithium dispersion in 10 mL of anhydrous ether was added 1.55 g of 1-chloro-3,3-dimethyl-2-phenylcyclopropene (**20**) in 25 mL of anhydrous ether. The mixture was stirred at room temperature for 16 h and was then cooled to −100 °C and 3 mL of freshly distilled HMPA was added. The resulting mixture was stirred for 30 min at this temperature and was quenched by the addition of 1.87 g of 4-bromo-1,1-dideuterio-1-phenylbutane in 5 mL of anhydrous ether. The mixture was allowed to stir for 15 h at room temperature and was then quenched with a saturated ammonium chloride solution. The organic layer was separated and the aqueous layer was extracted with ether. The combined ether extracts were dried over magnesium sulfate and the solvent was removed under reduced pressure. The residue was chromatographed on a 2 × 15 cm silica gel column using hexane as the eluent to give 1.72 g (71%) of a clear oil whose structure was assigned as 1-(3,3-dimethyl-2-phenylcyclopropen-1-yl)-4,4-dideuterio-4-phenylbutane (**28**) on the basis of its spectral properties: NMR ($CDCl_3$, 360 MHz) δ 1.15 (s, 6 H), 1.58–1.63 (m, 2 H), 2.52 (t, 2 H, J = 7.2 Hz) and 7.05–7.30 (m, 10 H); IR (CCl_4) 2980–2850, 1840, 1440, 1370 and 690; UV (95% ethanol) 272 nm (ϵ 10 600); MS, m/e 278 (M^+), 263, 185, 143 (base), 93 and 77.

Triplet-Sensitized Irradiation of 1-(3,3-Dimethyl-2-phenylcyclopropen-1-yl)-4,4-dideuterio-4-phenylbutane (28). A solution containing 50 mg of **28** and 4 mg of thioxanthone in 200 mL of benzene was irradiated with a 450-W Hanovia lamp equipped with a Pyrex glass filter sleeve for 10 min. The solvent was removed under reduced pressure and the residue was subjected to silica gel chromatography using hexane as the eluent to give a 1:1 mixture of two compounds that was separated by reversed-phase HPLC. The first fraction contained 18 mg (39%) of a clear oil, which was identified as [1-deuterio-2,2-dimethyl-3(*Z*)-(4-deuterio-4-phenyl-3-butenyl)cyclopropyl]benzene (*cis*-**30**) on the basis of its spectral properties: NMR ($CDCl_3$, 360 MHz) δ 0.78 (s, 3 H), 1.18 (s, 3 H), 1.55–1.70 (m, 3 H), 2.41–2.49 (m, 2 H), 5.69 (t, 1 H, J = 7.1 Hz) and 7.05–7.30 (m, 10 H); IR (CCl_4) 3080–2870, 1720, 1600, 1500, 1450, 1260, 1100 and 1010 cm^{-1}; UV (95% ethanol) 230 nm (ϵ 11 640); MS, m/e 278 (M^+, base), 234, 146, 118, 92 and 91.

The second fraction isolated contained 18 mg (39%) of a clear oil whose structure was assigned as [1-deuterio-2,2-dimethyl-3-(*E*)-(4-deuterio-4-phenyl-3-butenylcyclopropyl]benzene (*trans*-**30**) on the basis of its spectral properties: NMR ($CDCl_3$, 360 MHz) δ 0.78 (s, 3 H), 1.20 (s, 3 H), 1.52–1.76 (m, 3 H), 2.34–2.42 (m, 2 H), 6.29 (t, 1 H, J = 7.1 Hz) and 7.15–7.35 (m, 10 H); IR (CCl_4) 3090–2860, 1550, 1450, 1260, 1100 and 1000 cm^{-1}; UV (95% ethanol) 250 nm (ϵ 25 900); MS, m/e 278 (M^+), 234, 146, 118 (base), 92 and 91.

Preparation of 1-(3,3-Dimethyl-2-phenylcyclopropen-1-yl)-3-phenylpropane (32). To a suspension containing 1.0 g of a 30% lithium dispersion in 10 mL of anhydrous ether was added 1.55 g of 1-chloro-3,3-dimethyl-2-phenylcyclopropene (**20**) in 25 mL of anhydrous ether. The mixture was stirred at room temperature for 16 h and was then cooled to −100 °C, and 3 mL of freshly distilled HMPA was added. The resulting mixture was stirred for 30 min and was quenched by the addition of 1.73 g of 3-bromo-1-phenylpropane in 5 mL of anhydrous ether. The mixture was allowed to stir for 15 h at room temperature, followed by quenching with a saturated ammonium chloride solution. The organic layer was separated and the aqueous layer was extracted with ether. The combined ether extracts were dried over magnesium sulfate, and the solvent was removed under reduced pressure. The residue was chromatographed on a 2 × 15 cm silica gel column using hexane as the eluent to give 1.80 g (78%) of a clear oil whose structure was assigned as 1-(3,3-dimethyl-2-phenylcyclopropen-1-yl)-3-phenylpropane (**32**) on the basis of its spectral properties: NMR (CCl_4, 90 MHz) δ 1.28 (s, 6 H), 1.95 (p, 2 H, J = 7.2 Hz), 2.60 (t, 2 H, J = 7.2 Hz), 2.70 (t, 2 H, J = 7.2 Hz) and 7.00–7.36 (m, 10 H); IR (neat) 3070–2850, 1840, 1600, 1590, 1500, 1460, 1380, 1050, 930, 780, and 710 cm^{-1}; UV (95% ethanol) 264 mm (ϵ 13 100); MS, m/e 262 (M^+), 247, 219, 143 (base), 91 and 77. Anal. Calcd for $C_{20}H_{22}$: C, 91.55; H, 8.45. Found: C, 91.47; H, 8.32.

Extended irradiation of **32** in the presence of thioxanthone afforded recovered starting material.

Preparation of 1-(3,3-Dimethyl-2-phenylcyclopropen-1-yl)-1-butane (33). To a suspension containing 1.0 g of a 30% lithium dispersion in 10 mL of anhydrous ether was added 1.55 g of 1-chloro-3,3-dimethyl-2-phenylcyclopropene (**20**) in 25 mL of anhydrous ether. The mixture was stirred at room temperature for 16 h and was then cooled to −100 °C, and 3 mL of freshly distilled HMPA was added. The resulting mixture was stirred for 30 min and was quenched by the addition of 1.19 g of *n*-butyl bromide in 5 mL of anhydrous ether. The mixture was allowed to stir for 15 h at room temperature. This was followed by quenching with a saturated ammonium chloride solution. The organic layer was separated and the aqueous layer was extracted with ether. The combined ether extracts were dried over magnesium sulfate and the solvent was removed under reduced pressure. The residue was chromatographed on a 2 × 15 cm silica gel column using hexane as the eluent to give 1.50 g (86%) of a clear oil whose structure was assigned as 1-(3,3-dimethyl-2-phenylcyclopropen-1-yl)-1-butane (**33**) on the basis of its spectral properties: NMR ($CDCl_3$, 360 MHz) δ 0.98 (t, 3 H, J = 7.3 Hz), 1.25 (s, 6 H), 1.45 (m, 2 H), 1.66 (m, 2 H), 2.60 (t, 2 H, J = 7.3 Hz) and 7.10–7.30 (m, 5 H); IR (neat) 3020–2920, 1840, 1600, 1450, 770 and 650 cm^{-1}; UV (95% ethanol) 270 nm (ϵ 14 000); MS, m/e 200 (M^+), 185, 143 (base), 105 and 91. Anal. Calcd for $C_{15}H_{20}$: C, 89.94; H, 10.06. Found: C, 89.76; H, 9.85.

Extended irradiation of **33** in the presence of thioxanthone afforded recovered starting material.

Preparation of 1-(3,3-Dimethyl-2-phenylcyclopropen-1-yl)-5-hexene (34). To a suspension containing 1.0 g of a 30% lithium dispersion in 10 mL of anhydrous ether was added 1.55 g of 1-chloro-3,3-dimethyl-2-phenylcyclopropene (**20**) in 25 mL of anhydrous ether. The mixture was stirred at room temperature for 16 h and was then cooled to −100 °C, and 3 mL of freshly distilled HMPA was added. The resulting mixture was stirred for 30 min and was quenched by the addition of 1.41 g of 6-bromo-1-hexene in 5 mL of anhydrous ether. The mixture was allowed to stir for 15 h at room temperature, and this was followed by quenching with a saturated ammonium chloride solution. The organic layer was separated and the aqueous layer was extracted with ether. The combined ether extracts were dried over magnesium sulfate and the solvent was removed under reduced pressure. The residue was chromatographed on a 2 × 15 cm silica gel column using hexane as the eluent to give 1.51 g (77%) of a clear oil whose structure was assigned as 1-(3,3-dimethyl-2-phenylcyclopropen-1-yl)-5-hexene (**34**) on the basis of its spectral properties: NMR ($CDCl_3$, 360 MHz) δ 1.28 (s, 6 H), 1.54 (p, 2 H, J = 7.2 Hz), 1.70 (p, 2 H, J = 7.2 Hz), 2.11 (q, 2 H, J = 7.2 Hz), 2.62 (t, 2 H, J = 7.2 Hz), 4.92 (dd, 1 H, J = 10.2 and 2.0 Hz), 4.98 (dd, 1 H, J = 17.1 and 2.0 Hz), 5.75 (ddt, 1 H, J = 17.1, 10.2 and 7.2 Hz) and 7.15–7.35 (m, 5 H); IR (neat) 3080–2830, 1835, 1640, 1600, 1480, 1445, 1360, 990, 910, 790, 760 and 690 cm^{-1}; UV (95% ethanol) 268 nm (ϵ 13 840), 222 (8440) and 217 (10 000); MS,

m/e 226 (M^+), 211, 185, 143, (base), 115 and 91. Anal. Calcd for $C_{17}H_{22}$: C, 90.21; H, 9.79. Found: C, 90.14; H, 9.64.

Triplet-Sensitized Irradiation of 1-(3,3-Dimethyl-2-phenylcyclopropen-1-yl)-5-hexene (34). A solution containing 200 mg of **34** and 20 mg of thioxanthenone in 200 mL of benzene was irradiated with a 450-W Hanovia lamp equipped with a Uranium glass filter sleeve for 2 h. The solvent was removed under reduced pressure and the residue was subjected to silica gel chromatography using hexane as the eluent. The major fraction contained 135 mg (69%) of a clear oil whose structure was assigned as 2,2-dimethyl-3-phenyltricyclo[4.3.0.$0^{1,3}$]nonane (**35**) on the basis of its spectral properties: NMR ($CDCl_3$, 360 MHz) δ 0.78 (s, 3 H), 1.06 (dt, 1 H, J = 12.5 and 2.7 Hz), 1.22 (s, 3 H), 1.32 (dt, 1 H, J = 13.2 and 2.7 Hz), 1.44 (dd, 1 H, J = 11.1 and 2.5 Hz), 1.45–1.78 (m, 5 H), 1.85–1.93 (m, 1 H), 2.15 (dd, 1 H, J = 11.1 and 4.8 Hz), 2.27 (m, 1 H) and 7.13–7.32 (m, 5 H); IR (neat) 3060–2860, 1750, 1605, 1500, 1445, 1390, 1375, 925, 810, 760 and 700 cm^{-1}; UV (95% ethanol) 222 nm (ϵ 7050); MS, m/e 226 (M^+), 211 (base), 183, 91 and 77; HRMS calcd for $C_{17}H_{22}$ 226.1722, found 226.1718.

Quantum Yield Determinations. Quantum yields were determined by using a "merry-go-round" apparatus[75] equipped with a 450-W Hanovia lamp housed in a quartz well at the center of the carriage. Samples in 13-mm Pyrex test tubes were degassed to 5×10^{-3} mm in 5 freeze–thaw cycles and then sealed. Benzophenone–benzhydrol actinometry was used for quantum yield determinations. An actinometer yield of 0.69 was used when the concentration of benzophenone and benzhydrol in benzene was 0.1 M.[76] For the sensitized runs a filter solution of potassium dichromate in aqueous potassium carbonate was circulated through the well and the entire unit allowed to run for 1 h prior to use.[77] A Uranium glass filter sleeve and Corning 7-54 filters were also used in conjunction with the filter solution. The concentrations were adjusted so that the sensitizer absorbed more than 98% of the light. The conversions were run to 25% or less. The mass balance in these runs was generally better than 98%.

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Supplementary Material Available: Experimental details for the preparation of 4-bromo-1,1-dideuterio-1-phenylbutane (3 pages). Ordering information is given on any current masthead page.

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Stereochemical Equilibrium in Benzoctalones[1]

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Stereochemical equilibrations have been carried out at 25 °C on a series of benzoctalones having the ketone function adjacent to the epimerizable ring-juncture positions and either hydrogen or methyl at the ring-juncture position β to the ketone; trans/cis ratios are presented and discussed. The introduction of the angular methyl group invariably shifted equilibria in the direction of the cis epimer, by ca. 1.2–2.1 kcal/mol in the anthracenoid compounds and by 0.6–1.4 kcal/mol in the phenanthrenoids. Anthracenoid systems always had trans/cis ratios greater than unity, whether methylated or not, and produced consistently higher proportions of trans epimer than corresponding phenanthrenoid systems. The latter, when angularly methylated, invariably favored the cis epimers at equilibrium. The only system favoring the cis epimer in both the angularly methylated and unmethylated forms was the phenanthrenoid having the ketone within the bay region, probably due to steric interactions there that destabilize the trans epimers.

In seeking experimental data on stereochemical equilibrium in unsymmetrical octahydrophenanthrenes,[2] we became aware that what was then available in the literature was quite fragmentary. We therefore undertook a systematic study to generate accurate experimental data on trans–cis equilibrium for several entire families of benzoctalins—both octahydrophenanthrenes and octahydroanthracenes, both unsubstituted and angularly methylated. Beyond our own specific data requirements, we felt that this stereochemical aspect of benzoctalins must reflect very closely the situation in the octalins[3] and represented an incompletely studied simple perturbation of the decalin system.

Steric and conformational effects in the decalins have long been of basic interest, and the interactions governing the trans–cis equilibrium in decalin are well studied and understood.[4] An abundance of data has also accumulated

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