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Triplet Energy Dissipation in Methylenecyclopropane Rearrangement

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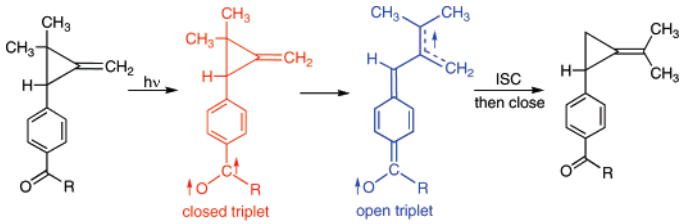
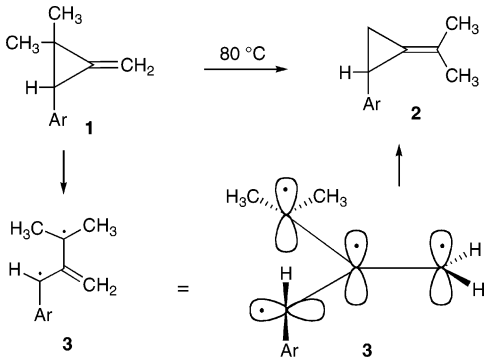


Certain 1,1-dimethyl-2-aryl-3-methylenecyclopropanes containing carbonyl substituents undergo rearrangement when irradiated with 350 nm light. These rearrangements occur via the (n,π^*) triplet state, which fragments the strained cyclopropane bond. Intersystem crossing followed by ring closure gives the observed products. No photoreduction is seen in *i*-PrOH. Potential Norrish type II processes are also bypassed. It is suggested that the cyclopropane bond fragmentation dissipates the triplet energy and that the new intermediates are not energetic enough to abstract hydrogen atoms in an intramolecular fashion or from solvent. Nitro substituted systems undergo analogous photoinitiated rearrangements. Benzophenone sensitization of naphthyl, biphenyl, styrene, and phenylacetylene analogues also leads to rearrangement, presumably via the sensitized generation of triplet states. When triplet states cannot be accessed by direct irradiation or by sensitized processes, methylenecyclopropane rearrangements do not occur. An exception is the ferrocenyl analogue, which does not photorearrange, presumably due to the very short lifetime of the triplet intermediate.

Introduction

We have been interested in the methylenecyclopropane rearrangement as a probe for free radical stabilizing effects. Toward this end, we have examined the thermal rearrangement of numerous methylenecyclopropanes of a general structure **1**.[1] These rearrangements proceed thermally to give **2** via the intermediacy of biradicals **3**, where radical stabilizing groups on the aromatic ring enhance the rearrangement rate.



While the thermal methylenecyclopropane rearrangement is a much studied reaction,[2] there are only isolated examples of photochemical variants.[3,4] Thus, direct irradiation of **4** under

(1) Creary, X. *Acc. Chem. Res.* **2006**, *39*, 761.

(2) (a) Kon, G. A. R.; Nanji, H. R. *J. Chem. Soc.* **1932**, 2557. (b) Ettlinger, M. G. *J. Am. Chem. Soc.* **1952**, *74*, 5805. (c) Ullman, C. F. *J. Am. Chem. Soc.* **1960**, *82*, 505. (d) Chesick, J. P. *J. Am. Chem. Soc.* **1963**, *85*, 2720. (e) Gilbert, J. C.; Butler, J. R. *J. Am. Chem. Soc.* **1970**, *92*, 2168. (f) Gajewski, J. J. *J. Am. Chem. Soc.* **1968**, *90*, 7178. (g) Gajewski, J. J. *J. Am. Chem. Soc.* **1971**, *93*, 4450. (h) Doering, W. v. E.; Birladeanu, L. *Tetrahedron* **1973**, *29*, 499. (i) Gajewski, J. J.; Chou, S. K. *J. Am. Chem. Soc.* **1977**, *99*, 5696. (j) Gajewski, J.; Benner, C. W.; Stahly, B. N.; Hall, R. F.; Sato, R. I. *Tetrahedron* **1982**, *38*, 853.

(3) (a) Gilbert, J. C.; Butler, J. R. *J. Am. Chem. Soc.* **1970**, *92*, 7493. (b) Gros, W. A.; Luo, T.; Gilbert, J. C. *J. Am. Chem. Soc.* **1976**, *98*, 2019.

(4) (a) Kende, A. S.; Goldschmidt, Z.; Smith, R. F. *J. Am. Chem. Soc.* **1970**, *92*, 7606. (b) Kagan, J. *Helv. Chim. Acta* **1972**, *55*, 1219. (c) Goldschmidt, Z.; Mauda, S. *Tetrahedron Lett.* **1976**, 4183. (d) Baum, T.; Rossi, A.; Srinivasan, R. *J. Am. Chem. Soc.* **1985**, *107*, 4411. (e) Leigh, W. *J. Chem. Rev.* **1993**, *93*, 487. (f) Takahashi, Y.; Mori, Y.; Nakamura, A.; Tomioka, H. *Tetrahedron Lett.* **2005**, *46*, 8415. (g) Takahashi, Y.; Sakakibara, T.; Tominaga, T.; Inaba, M.; Tomioka, H. *J. Photochem. Photobiol., A* **2007**, *185*, 253. For related photochemical processes, see (h) Gilbert, J. C.; Luo, T. *J. Org. Chem.* **1981**, *46*, 5237. (i) Maier, G.; Jürgen, D.; Tross, R.; Reisenauer, H. P.; Hess, B. A., Jr.; Schaad, L. J. *Chem. Phys.* **1994**, *189*, 383.

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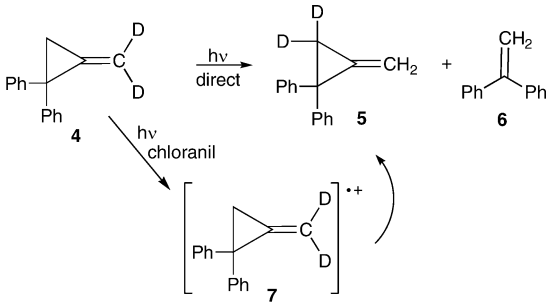
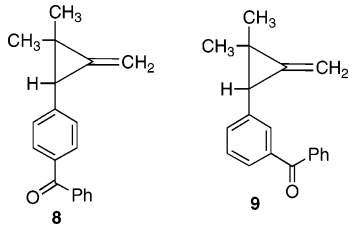
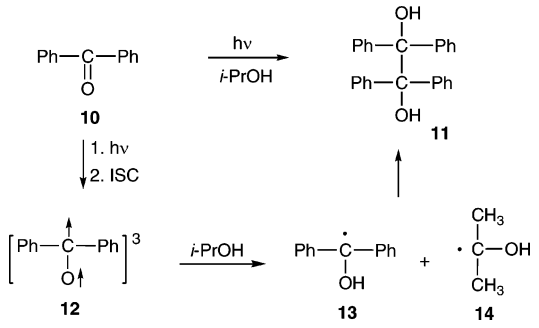
rather harsh conditions gave a competing methylenecyclopropane rearrangement and photofragmentation to 1,1-diphenylethylene and vinylidene.[3] These reactions are believed to occur on the singlet energy surface. In another interesting variation, a photosensitized reaction of **4** using chloranil or anthraquinone as sensitizers also led to the rearranged product **5**.[5] This reaction is proposed to occur via radical cation intermediates generated by one electron oxidation of **4** by the photoexcited oxidant.



With these precedents in mind, we have now sought to carry out analogous rearrangements under photochemical conditions where excited state triplets are involved. The carbonyl containing systems **8** and **9** were chosen for initial investigation since the photochemistry of carbonyl compounds is well- understood.



It should be recognized that **8** and **9** are also substituted benzophenones and that benzophenones are subject to photoreduction when irradiated in certain solvents.[6] For example, irradiation of benzophenone in isopropyl alcohol leads to the formation of benzopinacol (**11**).



This classic photochemical reaction proceeds by excitation of the benzophenone followed by rapid intersystem crossing (ISC) to give the triplet state of benzophenone (**12**). This triplet readily abstracts a hydrogen atom from isopropyl alcohol to generate the radical **13**. Subsequent coupling of **13** gives the observed product **11**. With this photoreduction mechanism in mind, we now report on the photochemistry of **8** and **9** and related substrates.

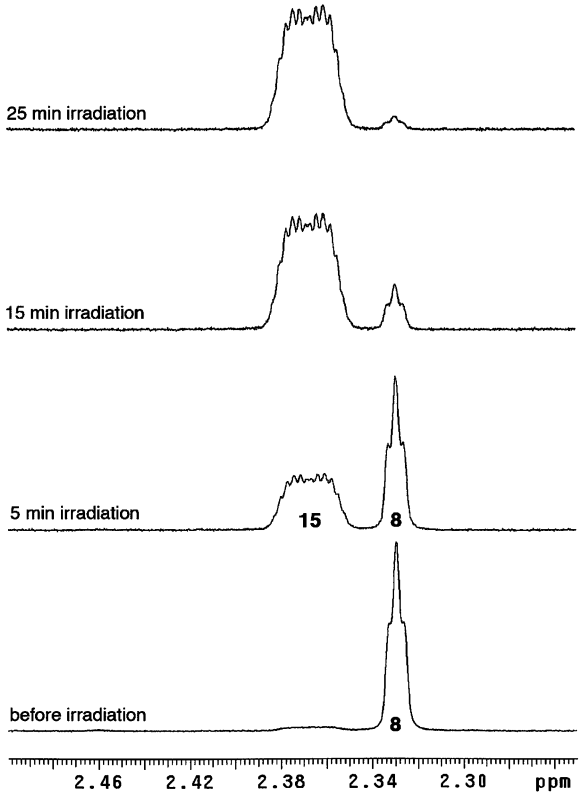


FIGURE 1. Evolving ^{1}H NMR spectra (benzylic region) during irradiation of **8** in C_6D_6 at 350 nm.

Results and Discussion

The first experiment carried out was room-temperature irradiation of **8** in C_6D_6 using light centered at 350 nm.[7] A smooth reaction occurred to give exclusively the rearranged product **15**, as illustrated by the evolving NMR spectra in Figure 1. When the photolysis was carried out in isopropyl alcohol as the solvent, the same product was formed (Figure 2). No photoreduction of **8** to the corresponding pinacol occurred under conditions where benzophenone was readily reduced to benzopinacol. This rearrangement of **8** to **15** was quite efficient photochemically and proceeded with comparable efficiency to that of the photoreduction of benzophenone to benzopinacol. The rearranged product **15** also resisted photoreduction when irradiated in *i*-PrOH.

The mechanism in Scheme 1 is suggested to account for the facile photoinduced rearrangement of **8** as well as the lack of photoreduction in *i*-PrOH. Photoexcitation of **8** followed by intersystem crossing would give the closed (n,π^*) triplet **17**. This closed triplet is suggested to fragment the strained cyclopropane bond very rapidly to give the ring opened triplet

(5) (a) Takahashi, Y.; Miyashi, T.; Mukai, T. *J. Am. Chem. Soc.* **1983**, *105*, 6511. (b) Miyashi, T.; Takahashi, Y.; Mukai, T.; Roth, H. D.; Schilling, M. L. M. *J. Am. Chem. Soc.* **1985**, *107*, 1079. (c) Miyashi, T.; Takahashi, Y.; Ohaku, H.; Ikeda, H.; Morishima, S. *Pure Appl. Chem.* **1991**, *63*, 223.

(6) (a) Ciamician, G.; Silber, P. *Chem. Ber.* **1900**, *33*, 2911. (b) Ciamician, G.; Silber, P. *Chem. Ber.* **1901**, *34*, 1641. (c) Pitts, J. N., Jr.; Letsinger, R. L.; Taylor, R. P.; Patterson, J. M.; Recktenwald, G.; Martin, R. B. *J. Am. Chem. Soc.* **1959**, *81*, 1068. (d) Moore, W. M.; Hammond, G. S.; Foss, R. P. *J. Am. Chem. Soc.* **1961**, *83*, 2789. (e) Hammond, G. S.; Baker, W. P.; Moore, W. M. *J. Am. Chem. Soc.* **1961**, *83*, 2795.

(7) All photolyses in this paper were carried out in a Rayonet Photochemical Reactor (Southern New England Ultraviolet Company) using lamps that emit over a narrow range centered at 350 nm. For details of lamp output, see www.rayonet.org.

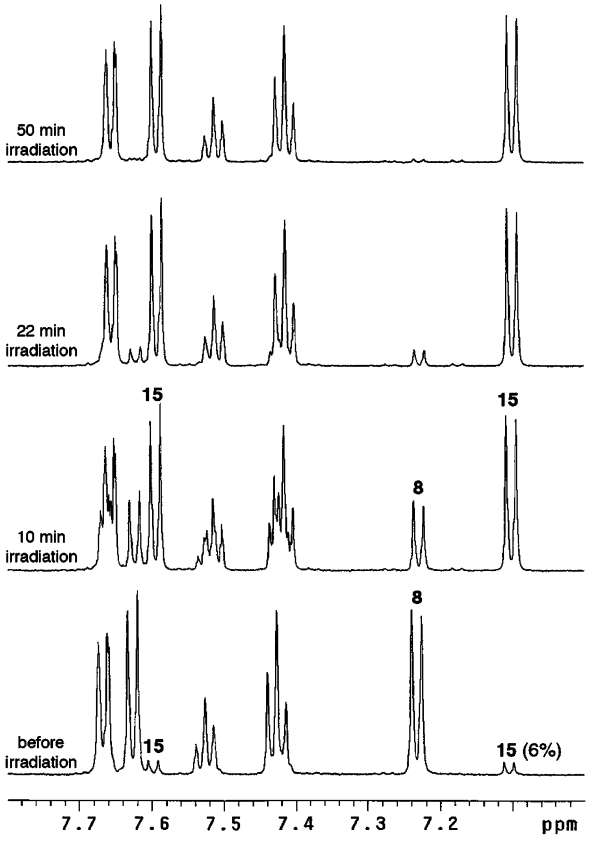
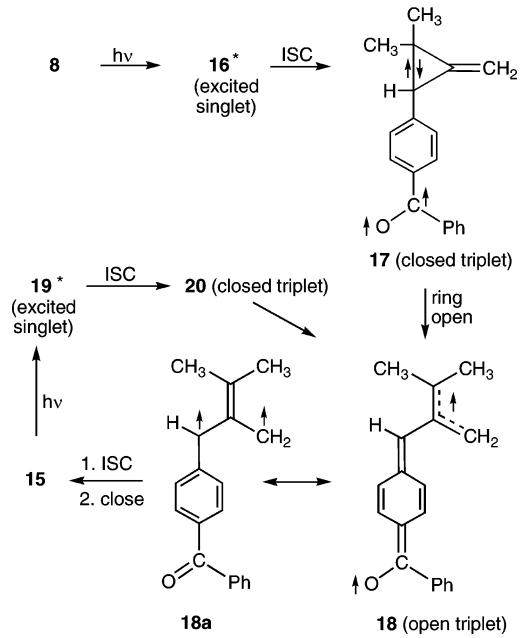
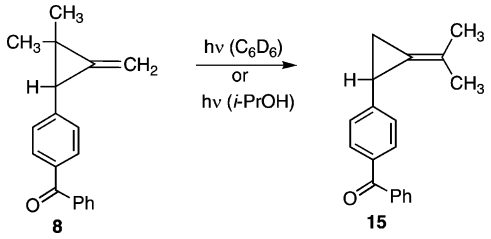


FIGURE 2. Evolving ^{1}H NMR spectra (aromatic region) during irradiation of **8** in *i*-PrOH at 350 nm.

SCHEME 1

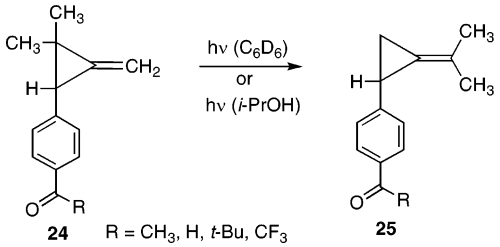


18. Hence, triplet **17** does not live long enough to abstract a hydrogen atom from the solvent. The triplet **18**, formed after the release of approximately 40 kcal/mol of strain energy associated with the methylenecyclopropane ring,[8] is not energetic enough to abstract a hydrogen atom. Therefore, no photoreduction in *i*-PrOH was observed. Triplet **18**, also represented by **18a**, needs only to spin invert and close the ring to give the observed product **15**. The rearranged product **15** is also resistant to photoreduction since the excited triplet state **20** derived from the irradiation of **15** should also dissipate its energy by cyclopropane bond fragmentation. The resultant open triplet is identical to **18**, and it should simply reconvert (after ISC) back to **15**. These suggestions are summarized in Figure 3.



In view of the proposed ability of the unpaired electron in **17** to facilitate fragmentation of the cyclopropane bond, the *m*-benzoyl derivative **9** was next investigated. This substrate also underwent facile photochemical rearrangement to give **21** in C_6D_6 as well as in *i*-PrOH. Again, no photoreduction was observed. This observation leads to the suggestion that the *m* substituted (n,π^*) triplet **22** can also facilitate cyclopropane bond fragmentation. A valence bond rationalization of this observation is given in Scheme 2. It is suggested that ring opening of triplet **22** leads to the open triplet **23**. Spins from the *m* situated radical centers of **23** can be delocalized to the same three positions (indicated by the asterisk) of the phenyl ring. Hence, these radical centers interact, and **23a** is a viable resonance contributor. Spin inversion and ring closure again give the rearrangement product **21** with no photoreduction in *i*-PrOH.

The (n,π^*) triplet state of acetophenone lies 74 kcal/mol above the ground state and is accessible by irradiation of the weak absorption band with a maximum centered at 319 nm.[9] With this in mind, the *p*-acetyl derivative **24** (R = CH_3) was irradiated in C_6D_6 and in *i*-PrOH using 350 nm light. Facile rearrangement to **25** (R = CH_3) occurs, presumably due to energy absorption at the tail end of the $n \rightarrow \pi^*$ band of **24** (R = CH_3). The other carbonyl derivatives **24** (R = H, *t*-Bu, or CF_3) also rearrange photochemically in C_6D_6 and in *i*-PrOH with no photoreduction in this latter solvent. These rearrangements undoubtedly proceed via the (n,π^*) triplet states derived from **24**.



The Norrish type II photoreaction of ketones is another well-understood photochemical process.[10] Thus, irradiation of vale-

(8) Johnson, W. T. G.; Borden, W. T. *J. Am. Chem. Soc.* **1997**, *119*, 5930.

(9) Pitts, J. N., Jr.; Wan, J. K. S. *The Chemistry of the Carbonyl Group*, Patai, S., Ed.; Wiley-Interscience: New York, 1966; Ch. 16.

(10) (a) Wagner, P. J. *Acc. Chem. Res.* **1971**, *4*, 168−177. (b) Turro, N. J. *Modern Molecular Photochemistry*; The Benjamin/Cummings Publishing Company, Inc.: Menlo Park, CA, 1978; Ch. 10.

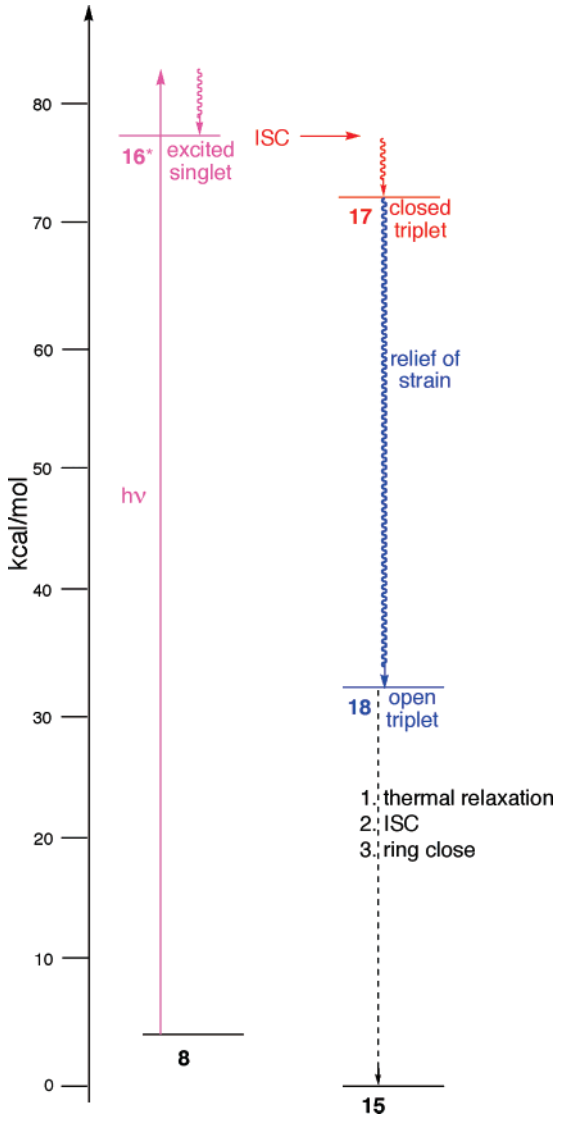
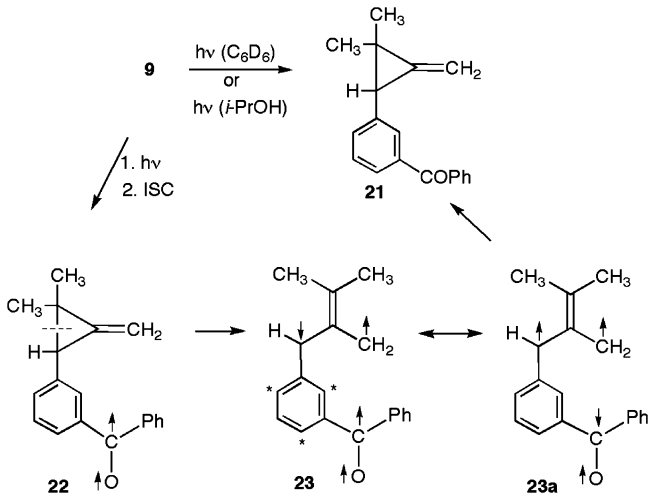


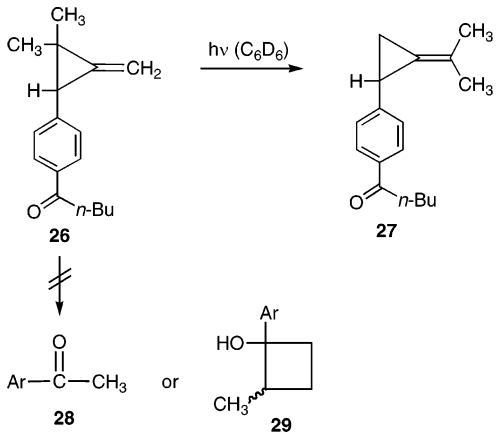
FIGURE 3. Photochemical pathway for the rearrangement of **8** to **15**.

SCHEME 2



rophenone, PhCO-*n*-Bu, gives 1-phenyl-2-methylcyclobutanols as well as acetophenone. This reaction occurs via the triplet state, which readily abstracts a hydrogen atom from the γ-carbon of the butyl group. The resultant 1,4-biradical can either cyclize

SCHEME 3



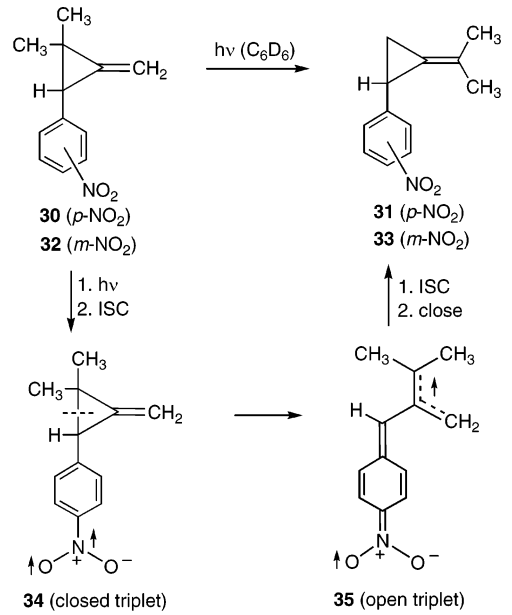
to give cyclobutanols or fragment to give an enol, the precursor of acetophenone. With the possibility of the Norrish type II reaction in mind, the substrate **26** was next irradiated. Rearrangement readily occurred to give **27** only (Scheme 3). There were no traces of Norrish type II photoproducts **28** or **29** under conditions where the model ketone PhCO-*n*-Bu readily gave acetophenone and 1-phenyl-2-methylcyclobutanols. As in the case of the benzophenone analogue **8**, it is suggested that the initial triplet derived from **26** readily ring opens and thereby dissipates its energy. The resultant ring opened triplet lacks the energy necessary for intramolecular hydrogen atom abstraction.

The photochemistry of nitro compounds is very analogous to that of carbonyl compounds.[11] Thus, irradiation of nitrobenzenes leads to an (n,π^*) singlet state, which undergoes ISC to produce the (n,π^*) triplet state. This triplet state, which has biradical properties, can lead to both intra- and intermolecular hydrogen atom abstraction.[12] With this in mind, the *p*- and *m*-nitro derivatives **30** and **32**[13] were irradiated at 350 nm. The result was the facile rearrangement to **31** and **33**, respectively. As in the case of the carbonyl derivatives, the suggested mechanism in Scheme 4 involves the photoexcitation of **30** followed by conversion to the triplet **34**. Facile fragmentation of the cyclopropane bond of **34** leads to the open triplet **35**, which can undergo intersystem crossing and subsequent closure of the singlet biradical to give the observed product **31**.

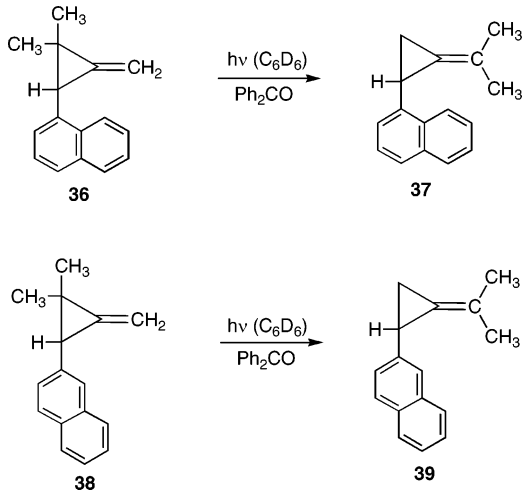
To further verify the ability of triplet intermediates to lead to the methylenecyclopropane rearrangement, the naphthyl substrates **36** and **37**[14] were next investigated under photochemical conditions. Under irradiation in C_6D_6 with 350 nm light, rearrangement was a relatively slow process (Figure 4) since **36** and **37** do not absorb strongly at this wavelength. However, it is known that the triplet state of naphthalene, which lies 61 kcal/mol above the ground state, can be efficiently accessed by a photosensitized reaction with triplet benzophenone (69 kcal/mol above the ground state).[15] With this in mind, benzophenone was added to solutions of **36** and **37** in C_6D_6.

(11) Morrison, H. A. *The Chemistry of the Nitro and Nitroso Groups*; Feuer, H., Ed.; Wiley-Interscience: New York, 1969; pp 165−213.
(12) (a) Morrison, H.; Migdalof, B. *J. Org. Chem.* **1965**, *30*, 3996. (b) Kaneko, C.; Yamada, S.; Yokoe, I. *Tetrahedron Lett.* **1966**, 4729. (c) Hurley, R.; Testa, A. *J. Am. Chem. Soc.* **1966**, *88*, 4330.
(13) Creary, X.; Mehrsheikh-Mohammadi, M. E.; McDonald, S. *J. Org. Chem.* **1987**, *52*, 3254.
(14) Creary, X.; Mehrsheikh-Mohammadi, M. E.; McDonald, S. *J. Org. Chem.* **1989**, *54*, 2904.

SCHEME 4

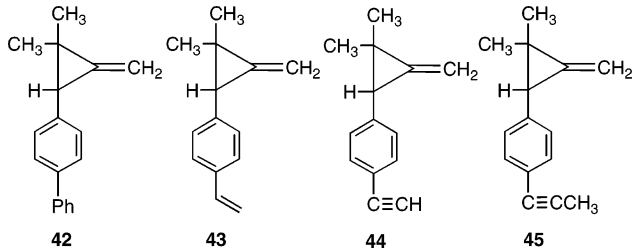


Irradiation led to the facile rearrangement to **37** and **39**, respectively. A comparison of this benzophenone sensitized reaction of **36** with the reaction in the absence of benzophenone is shown in Figure 4.

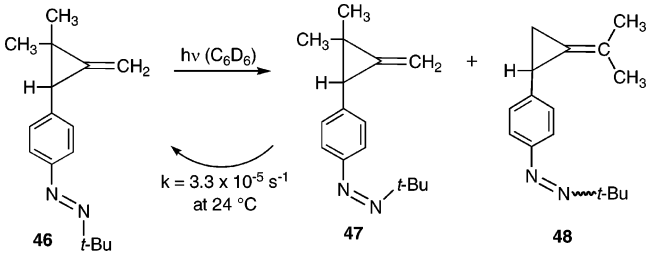


To account for the facile rearrangement in the presence of benzophenone, it is suggested (Scheme 5) that the triplet energy transfer from benzophenone to **36** leads to a closed (π,π^*) triplet represented by **40**. Triplet **40** readily fragments the strained cyclopropane bond to give the open triplet **41**, which lies approximately 40 kcal/mol lower in energy. Subsequent ISC and ring closure leads to **37**. Analogous processes occur in the photosensitized rearrangement of the 3-naphthyl derivative **38**.

What about the possibility of other triplet photosynthesized methylenecyclopropane rearrangements of substrates of a general structure **1**? To achieve benzophenone sensitization, it will be necessary to have substrates with triplet energies lower than 69 kcal/mol. Substrates **42**−**45** were next examined since they are expected to meet this criterion.[16] Indeed, these substrates all underwent facile rearrangement when irradiated in a C_6D_6 solution containing benzophenone. In the absence of benzophenone, these substrates gave no photoreaction. In addition, fluorenone, which has a triplet energy of only 53 kcal/mol, was an ineffective sensitizer. Hence, rearrangements of the naphthyl derivative **36** and the biphenyl analogue **42** were not sensitized by added fluorenone.



The azo derivative **46** is another substrate of interest[17] whose photochemical behavior on irradiation using 350 nm light is illustrated in Figure 5. Direct irradiation led to a relatively inefficient methylenecyclopropane rearrangement (only about 15% in 2 h). However, there was a much more efficient photochemical process involving *E*- to *Z*-isomerization. Ultimately, a photostationary state consisting of 47% **46** and 53% **47** was produced. Fluorescent laboratory light also promoted this isomerization, although a different photostationary state was attained. The *Z*-isomer **47** was a labile substance, and as shown in Figure 5, it reverted back to **46** on standing in the dark (half-life of 5.9 h at 24 °C). This *E*- to *Z*-photoisomerization of azo compounds is a well-established process[18] and has been studied for many compounds, including the related substrate (*t*-butylazo)benzene, Ph—N═N—*t*-Bu.[19] The photochemistry of **46** appears to be very analogous to that of Ph—N═N—*t*-Bu except for the superimposition of a slow methylenecyclopropane rearrangement. It is suggested that a triplet state of **46** is responsible for this inefficient methylenecyclopropane rearrangement.



Lest the impression be created that all of our methylenecyclopropanes undergo photoinitiated methylenecyclopropane

(15) (a) Terenin, A.; Ermolaev, V. *J. Chem. Soc., Faraday Trans. 2* **1956**, *52*, 1042. For related intramolecular processes, see: (b) Engel, P. A.; Horsey, D. W.; Scholz, J. N.; Karatsu, T.; Kitamura, A. *J. Phys. Chem.* **1992**, *96*, 7524.

(16) Triplet energies of biphenyl, styrene, and phenylacetylene are 66, 62, and 72 kcal/mol, respectively. See: Murov, S. L.; Carmichael, I.; Hug, G. L. *Handbook of Photochemistry*, 2nd ed.; Marcel Dekker: New York, 1993. The cyclopropyl groups in **42**−**45** should further lower the triplet energies of **42**−**45**, making the triplet states of these substrates accessible from triplet benzophenone.

(17) Creary, X.; Engel, P. S.; Kavaluskas, N.; Pan, L.; Wolf, A. *J. Org. Chem.* **1999**, *64*, 5634.

(18) (a) Engel, P. A.; Bodager, G. A. *J. Org. Chem.* **1988**, *53*, 4748. (b) Engel, P. A.; Melaugh, R. A.; Page, M. A.; Szilagyi, S.; Timberlake, J. W. *J. Am. Chem. Soc.* **1976**, *98*, 1971. (c) Drewer, R. J. *The Chemistry of Hydrazo, Azo, and Azoxy Groups*; Patai, S., Ed.; Wiley-Interscience: New York, 1975; pp 935−1015.

(19) Porter, N. A.; Funk, M. O. *Chem. Commun.* **1973**, 263.

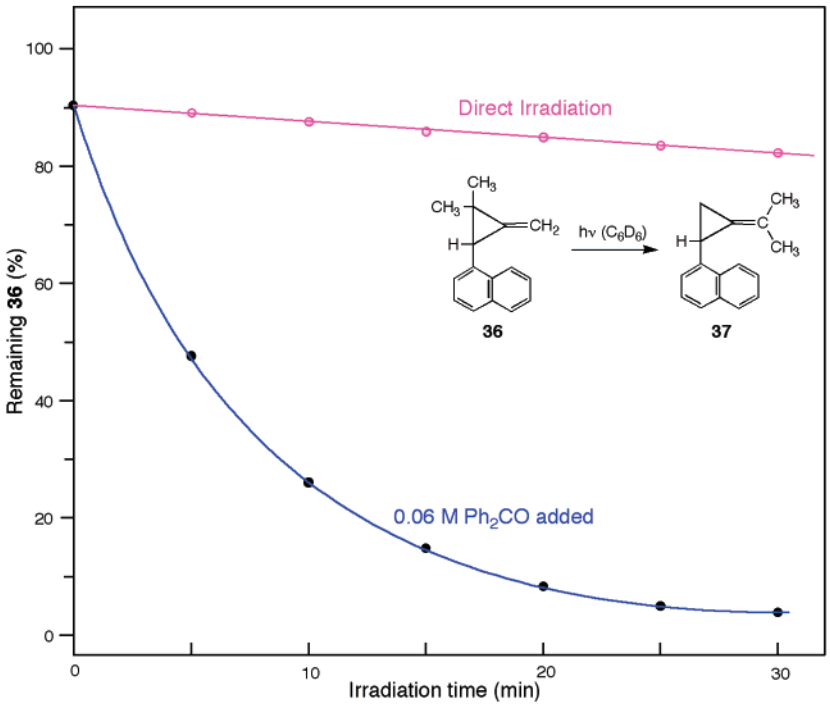
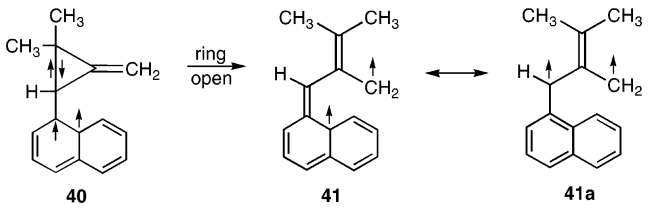
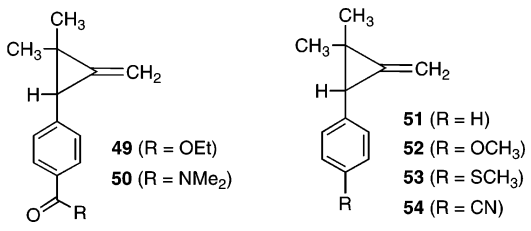


FIGURE 4. Plot of the amount of **36** remaining after irradiation in C_6D_6 vs irradiation time. About 10% of **37** was present at the beginning of irradiation.

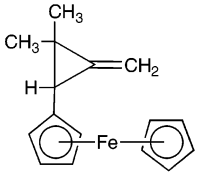
SCHEME 5



rearrangement, unsuccessful reactions must be addressed. The ester **49** and the amide **50** resisted photochemical rearrangement. This behavior of **49** and **50** contrasts with that of other carbonyl derivatives and is undoubtedly due to the inability to access the (n,π*) triplet states of **49** and **50** using 350 nm light. The simple unsubstituted system **51** (R = *p*-H), with an expected triplet energy in excess of 80 kcal/mol,[16] did not undergo rearrangement under direct irradiation with 350 nm light or with attempted benzophenone photosensitization. Neither the *p*-OCH_3 and *p*-SCH_3 derivatives **52** and **53** nor the *p*-cyano derivative **54** photorearranged. The key to successful photorearrangement undoubtedly lies with the accessibility of the triplet excited state.



The triplet energy of ferrocene is approximately 40 kcal/mol above the ground state and is readily accessible from a variety of sensitizers.[20] For example, ferrocene quenches the triplet derived from fluorenone (53 kcal/mol) at a diffusion controlled rate. With this in mind, the ferrocenyl derivative **55**[14] was investigated. We were initially surprised when direct irradiation of **55** resulted in no rearrangement. Substrate **55** also resisted photosensitized rearrangement when fluorenone or benzophenone were added as sensitizers. The lifetime of the triplet state of ferrocene, which is only 0.6 ns,[21] offers a clue as to why the triplet state of **55** fails to lead to rearrangement. Benzophenone has a triplet lifetime[22] of 10 μs ($\sim 10^5$ longer than that of ferrocene), and if triplet lifetimes of methylenecyclopropanes such as **8** and **9** are comparable, then this is apparently long enough to permit fragmentation of the cyclopropane bond. It is suggested that the triplet state of **55** does not live long enough to fragment the cyclopropane bond. Instead, as in the case of ferrocene itself, rapid return to the ground state occurs via radiationless decay, and **55** remains photochemically inert.



55

Finally, the *O*-methyl oxime derivative **56**[17] gave no reaction on direct irradiation. Benzophenone sensitization also gave no methylenecyclopropane rearrangement. However, **56** was not inert under photosensitized conditions. Benzophenone sensitized irradiation led to isomerization of the *E*-oxime **56** to the *Z*-isomer **57**, and ultimately a mixture consisting of 42% **56** and 58% **57** was produced. Fluorenone, with a triplet energy

(20) Herkstroeter, W. G. *J. Am. Chem. Soc.* **1975**, *97*, 4161.

(21) Maciejewski, A.; Jaworska-Augustyniak, A.; Szeluga, Z.; Wojtczak, J.; Karolczak, J. *Chem. Phys. Lett.* **1988**, *153*, 227.

(22) Bell, J. A.; Linschitz, H. *J. Am. Chem. Soc.* **1963**, *85*, 528.

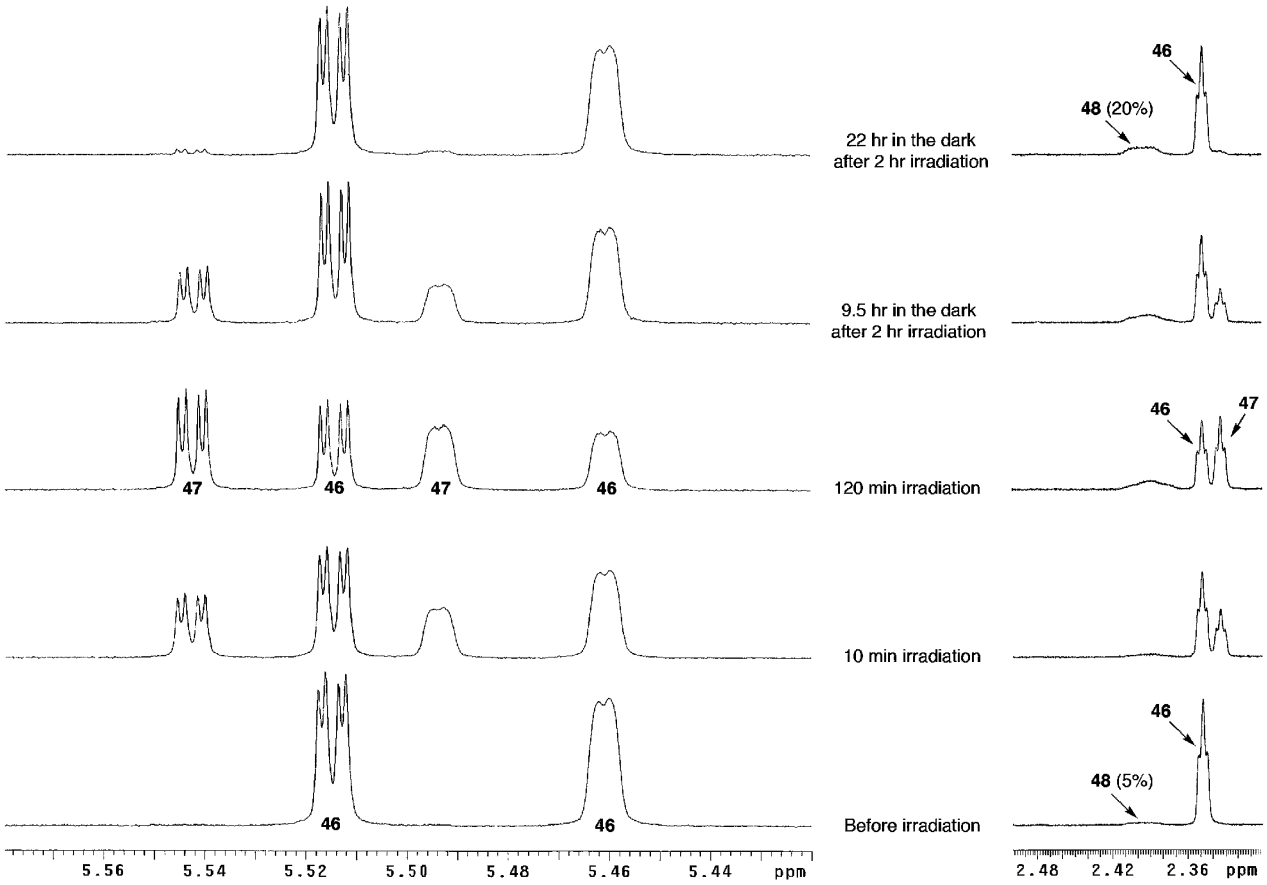
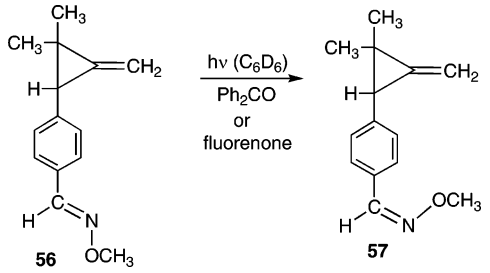


FIGURE 5. Evolving ^{1}H NMR spectra (olefinic and benzylic regions) during and after irradiation of **46** in C_6D_6.

of only 53 kcal/mol, was also an effective photosensitizer, and use of this sensitizer led to almost complete conversion of **56** to the *Z*-isomer **57**. The fact that direct irradiation with 350 nm light gave no isomerization, while benzophenone or fluorenone sensitization led to **57**, suggests that a triplet state of **56** is involved in this transformation. Yet, there is no methylenecyclopropane rearrangement from this triplet state. The reason for the lack of cyclopropane bond fragmentation in this triplet state is not understood. Theoretical studies are in progress to determine the precise nature of the lowest triplet state of *O*-methyl oximes.

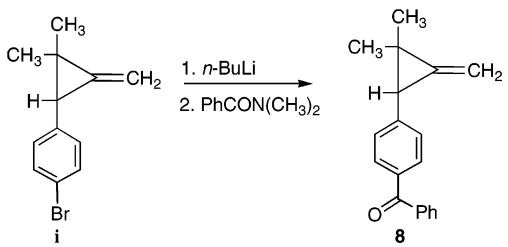


Conclusion

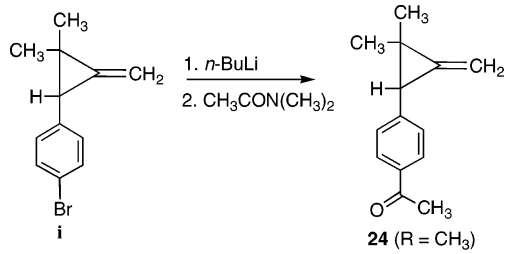
Photolyses of carbonyl substituted 1,1-dimethyl-2-aryl-3-methylenecyclopropanes leads to (n,π^*) triplets and subsequent methylenecyclopropane rearrangement. Under conditions where benzophenone in *i*-PrOH is readily photoreduced, the methylenecyclopropane analogues **8** and **9** are not reduced. Neither is the Norrish type II photoreaction observed in **26**. These well-established photochemical processes are bypassed due to fragmentation of the cyclopropane bond and subsequent dissipation of the triplet energy. The new intermediates are no longer energetic enough to abstract hydrogen atoms. Triplets derived from benzophenone sensitization of naphthyl derivatives **36** and **38**, as well as hydrocarbons **42**−**45**, also undergo the methylenecyclopropane rearrangement. When the triplet states cannot be accessed photochemically, rearrangements do not occur. An exception is the ferrocenyl analogue **55**, which does not photorearrange due to the short triplet lifetime.

Experimental Procedures

General. Most of the methylenecyclopropanes used in this study were prepared as previously described. See the text for appropriate references. The procedures given next are for those not previously described. ^{1}H NMR spectra were recorded at 600 MHz, and ^{13}C NMR spectra were recorded at 151 MHz.

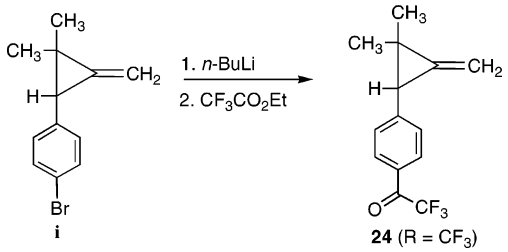


Preparation of Methylenecyclopropane 8. A solution of 751 mg of bromide **i**[23] in 8 mL of THF was cooled to −78 °C, and 2.5 mL of 1.6 M *n*-BuLi in hexanes was added dropwise. After 30 min at −78 °C, a solution of 566 mg of *N*,*N*-dimethylbenzamide in 5 mL of THF was added dropwise. The mixture was allowed to warm to room temperature, and water was then added. The mixture was transferred to a separatory funnel with ether, and the ether extract was washed with water and a saturated NaCl solution and dried over a mixture of Na_2SO_4 and $MgSO_4$. After filtration, the solvents were removed using a rotary evaporator, and the residue was chromatographed on 10 g of silica gel. The column was eluted with 5−10% ether in hexanes. A total of 705 mg of product (85% yield) was obtained in two fractions. The first fraction (440 mg) was rechromatographed on 9 g of silica gel and eluted with 0−4% ether in hexanes. A 241 mg sample that contained 94% **8** along with 6% **15** eluted with 2% ether in hexanes and was used for photochemical studies. ^{1}H NMR of **8** (600 MHz, $CDCl_3$) δ 7.79 (d, J = 8.1 Hz, 2 H), 7.73 (d, J = 8.1 Hz, 2 H), 7.57 (t, J = 7.4 Hz, 1 H), 7.47 (t, J = 7.8 Hz, 2 H), 7.28 (d, J = 8.0 Hz, 2 H), 5.62 (d of d, J = 2.4, 0.8 Hz, 1 H), 5.57 (d, J = 1.2 Hz, 1 H), 2.54 (t, J = 1.8 Hz, 1 H), 1.38 (s, 3 H), 0.90 (s, 3 H). ^{13}C NMR of **8** (151 MHz, $CDCl_3$) δ 196.5, 145.0, 144.0, 137.9, 135.1, 132.2, 130.01, 129.97, 128.7, 128.2, 103.9, 32.4, 26.2, 25.0, 18.4. Exact mass (FAB) calcd for $C_{19}H_{18}O$ 262.1358, found 262.1342.

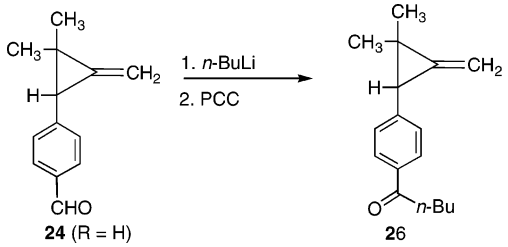


Preparation of Methylenecyclopropane 24 (R = CH_3). A solution of 537 mg of bromide **i** in 5 mL of THF was cooled to −78 °C, and 1.5 mL of 1.6 M *n*-BuLi in hexanes was added dropwise. After 40 min at −78 °C, this solution was transferred via cannula to a solution of 347 mg of *N*,*N*-dimethylacetamide in 10 mL of ether at −78 °C. The mixture was allowed to warm to room temperature, and water was then added. The mixture was transferred to a separatory funnel with ether, and the ether extract was washed with water and saturated NaCl solution and dried over a mixture of Na_2SO_4 and $MgSO_4$. After filtration, the solvents were removed using a rotary evaporator, and the residue was chromatographed on 15 g of silica gel. The column was eluted with 5−15% ether in hexanes. A total of 230 mg of product (51% yield; **24**/**25** ratio = 4.9:1) was obtained. This mixture was used for photochemical studies. ^{1}H NMR of **24** (R = CH_3) (600 MHz, $CDCl_3$) δ 7.86 (d, J = 8.4 Hz, 2 H), 7.26 (d, J = 8.4 Hz, 2 H), 5.61 (d of d, J = 2.4, 0.8 Hz, 1 H), 5.56 (d, J = 1.4 Hz, 1 H), 2.575 (s, 3 H), 2.51 (t, J = 2.0 Hz, 1 H), 1.37 (s, 3 H), 0.86 (s, 3 H). ^{13}C NMR of **24** (R = CH_3) (151 MHz, $CDCl_3$) δ 197.8, 144.9, 144.6, 134.9, 129.0, 128.1, 103.9, 32.3, 26.5, 26.2, 24.9, 18.3. Exact mass (FAB) calcd for $C_{14}H_{16}O$ 200.1201, found 200.1194.

Preparation of Methylenecyclopropane 24 (R = CF_3). A solution of 568 mg of bromide **i** in 5 mL of THF was cooled to −78 °C, and 1.6 mL of 1.6 M *n*-BuLi in hexanes was added dropwise. After 20 min at −78 °C, this solution was transferred via cannula to a solution of 520 mg of ethyl trifluoroacetate in 9 mL of ether at −78 °C. The mixture was allowed to warm to room temperature, and water was then added. The mixture was transferred to a separatory funnel with ether, and the ether extract was washed with water and saturated NaCl solution and dried over a mixture of Na_2SO_4 and $MgSO_4$. After filtration, the solvents were removed



using a rotary evaporator, and the residue was chromatographed on 15 g of silica gel. A total of 460 mg of product (76% yield; **24**/**25** ratio = 3.1:1) was obtained. This mixture was used for photochemical studies. ^{1}H NMR of **24** (R = CF_3) (600 MHz, $CDCl_3$) δ 7.97 (d, J = 8.2 Hz, 2 H), 7.33 (d, J = 8.3 Hz, 2 H), 5.63 (d of d, J = 2.4, 0.8 Hz, 1 H), 5.56 (d, J = 1.6 Hz, 1 H), 2.54 (t, J = 2.0 Hz, 1 H), 1.39 (s, 3 H), 0.89 (s, 3 H). ^{13}C NMR of **24** (R = CF_3) (151 MHz, $CDCl_3$) δ 180.1 (q, J = 35 Hz), 148.0, 144.4, 129.9 (q, J = 2 Hz), 129.5, 127.6, 116.8 (q, J = 292 Hz), 104.3, 32.7, 26.3, 26.0, 18.3. Exact mass (FAB) calcd for $C_{14}H_{13}F_3O$ 254.0918, found 254.0921.



Preparation of Methylenecyclopropane 26. A solution of 60 mg of aldehyde **24** (R = H)[17] in 2 mL of ether was added dropwise to 0.5 mL of 1.6 M *n*-BuLi dissolved in 2 mL of ether at −78 °C. The mixture was warmed to 0 °C, and water was then added. The ether phase was separated, washed with water and saturated NaCl solution and dried over a mixture of Na_2SO_4 and $MgSO_4$. After filtration, the solvents were removed using a rotary evaporator, and the crude alcohol product was used in the next step without further purification.

A mixture of 145 mg of pyridinium chlorochromate in 3 mL of methylene chloride was stirred at room temperature as a solution of the crude alcohol prepared as stated previously in 0.5 mL of CH_2Cl_2 was added in one portion. The mixture was stirred for 10 h at room temperature, and then 5 mL of pentane was added. The pentane/CH_2Cl_2 mixture was filtered through a small amount of silica gel in a pipet, and the solvents were then removed using a rotary evaporator. The residue was taken up into 5% ether in pentane and filtered through 0.3 g of silica gel. Solvent removal gave 61 mg (78% yield) of ketone **26**. ^{1}H NMR of **26** (600 MHz, $CDCl_3$) δ 7.86 (d, J = 8.4 Hz, 2 H), 7.25 (d, J = 8.4 Hz, 2 H), 5.61 (d of d, J = 2.4, 0.8 Hz, 1 H), 5.55 (d, J = 1.4 Hz, 1 H), 2.93 (t, J = 7.5 Hz, 2 H), 2.50 (t, J = 2.0 Hz, 1 H), 1.71 (quintet, J = 7.5 Hz, 2 H), 1.41 (sextet, J = 7.5 Hz, 2 H), 1.37 (s, 3 H), 0.95 (t, J = 7.5 Hz, 3 H), 0.86 (s, 3 H). ^{13}C NMR of **26** (151 MHz, $CDCl_3$) δ 200.3, 145.0, 144.3, 134.9, 129.0, 127.9, 103.8, 38.3, 32.4, 26.6, 26.2, 24.9, 22.6, 18.3, 14.0. Exact mass (FAB) calcd for $C_{17}H_{22}O$ 242.1671, found 242.1658.

Photolyses in C_6D_6. General Procedures. The following procedure is representative. Benzene-d_6 was deoxygenated by briefly bubbling N_2 through the stock sample. A solution of 5.6 mg of **8** in 330 mg of C_6D_6 was placed in an NMR tube under N_2. The NMR tube was sealed under N_2 and placed in a Rayonet Photochemical Reactor fitted with 350 nm lamps.[7] The tube was irradiated for various time periods at ambient temperature (22 °C) using the air-cooling provided by the reactor fan. The tube was periodically analyzed by 600 MHz ^{1}H NMR spectroscopy, and

(23) Creary, X. *J. Org. Chem.* **1978**, *43*, 1777.

typical data are given in Figure 1. In a separate experiment, a sample under N_2 in an NMR tube was cooled to −78 °C, evacuated at 0.1 mm, and sealed under vacuum before irradiation. There was no difference in reactivity between the sample sealed under vacuum and the sample sealed under N_2. Most experiments were therefore carried out in sealed tubes under N_2 rather than under vacuum.

Photolyses in *i*-PrOH. General Procedures. The following procedure is representative. A solution of 5.9 mg of **8** in 270 mg of nitrogen purged *i*-PrOH was sealed in a 3 mm NMR tube under nitrogen. The NMR tube was irradiated using 350 nm lamps for various time periods at ambient temperature (22 °C) using the air-cooling provided by the reactor fan. The tube was periodically analyzed by 600 MHz ^{1}H NMR spectroscopy, and typical spectral data are given in Figure 2. On completion of the irradiation, *i*-PrOH was removed using a rotary evaporator with the last traces of solvent being removed at 0.1 mm pressure. The product **15** was identified by ^{1}H NMR spectral comparison with an authentic sample.

Product Analyses. In a separate experiment, a solution of 32 mg of **8** in 1.40 g of C_6D_6 was irradiated for 100 min using 350 nm lamps. The solvent was removed using a rotary evaporator, and the residue was placed on a column made from 0.50 g of silica gel and eluted with 8% ether in hexanes. The solvent was removed using a rotary evaporator, and the product **15** (30 mg, 94% yield) was characterized by NMR spectroscopy. ^{1}H NMR of **15** (600 MHz, $CDCl_3$) δ 7.78 (d, J = 8 Hz, 2 H), 7.71 (d, J = 8 Hz, 2 H), 7.57 (t, J = 8 Hz, 1 H), 7.47 (t, J = 8 Hz, 2 H), 7.16 (d, J = 8 Hz, 2 H), 2.63 (m, 1 H), 1.93 (m, 3 H), 1.79 (m, 3 H), 1.78 (m, 3 H), 1.19 (m, 1 H). ^{13}C NMR of **15** (151 MHz, $CDCl_3$) δ 196.4, 148.8, 138.0, 134.8, 132.1, 130.5, 129.9, 128.2, 125.9, 123.5, 119.7, 22.3, 22.2, 20.6. 16.1. Exact mass (FAB) calcd for $C_{19}H_{18}O$ 262.1358, found 262.1367.

All of the other products formed in photochemical studies in this paper (**21**, **25**, **27**, **31**, **33**, **37**, **39**, and **48**) were characterized by NMR spectral comparison with samples previously prepared by thermal rearrangement of the corresponding 1,1-dimethyl-2-aryl-3-methylenecyclopropanes.[13,14,17,23]

Photolysis of 8 in *i*-PrOH. Quantum Yield Estimation. A solution of 15.1 mg of benzophenone in 1.0 mL of nitrogen purged *i*-PrOH (0.082 M) was prepared, and a portion of this solution was sealed in an NMR tube under nitrogen. The tube was irradiated using 350 nm lamps for 3.0 min at ambient temperature (22 °C). Analysis by 600 MHz ^{1}H NMR showed that 30.9% of the benzophenone had been converted to benzopinacol.

In a similar fashion, a solution of 21.9 mg of **8** in 1.0 mL of *i*-PrOH (0.082 M) was prepared and sealed in an NMR tube. The sample was irradiated for 3.0 min, and this was followed by analysis by ^{1}H NMR, which showed that 20.5% **8** had converted to **15**. The quantum yield for the disappearance of benzophenone is therefore 1.5 times greater than for conversion of **8** to **15**.[24]

Benzophenone Sensitized Reactions. The following procedure is representative. A solution of 8.6 mg of **36** in 625 mg of deoxygenated C_6D_6 was prepared, and 273 mg of this solution was placed in a 3 mm NMR tube. The first tube was then sealed under nitrogen. Benzophenone (4.2 mg) was then added to the remaining solution, and a second 3 mm NMR tube was prepared from this solution and sealed under nitrogen. These two samples were irradiated for various time periods using 360 nm light at ambient temperature (22 °C). The samples were periodically analyzed by 600 MHz ^{1}H NMR spectroscopy. Typical spectra are given in the Supporting Information, and quantitative results are shown graphically in Figure 4.

Supporting Information Available: ^{1}H and ^{13}C NMR of **8**, **15**, **24** (R = CH_3), **24** (R = CF_3), and **26**, as well as evolving ^{1}H NMR spectra during irradiation of **24** (R = CH_3), **26**, **30**, **36**, and **56**. This material is available free of charge via the Internet at http://pubs.acs.org.

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(24) Previously determined quantum yields for the disappearance of benzophenone at 335 nm in nitrogen flushed *i*-PrOH ranged from 0.66 to 1.37.[6c] In completely degassed *i*-PrOH, the quantum yield was 1.8−1.9. Since the theoretical quantum yield for benzophenone disappearance in *i*-PrOH is 2.0, the efficiency of conversion of **8** to **15** actually exceeds the quantum efficiency of benzophenone photoreduction in nitrogen flushed *i*-PrOH.