Cyclopropanols. X. Oxidation of Cyclopropanols by Photoexcited Aryl Ketones

C. H. DePuy,* H. L. Jones,[1] and W. M. Moore

Contribution from the Departments of Chemistry, University of Colorado, Boulder, Colorado 80302, The Colorado College, Colorado Springs, Colorado 80903, and Utah State University, Logan, Utah 84321.
Received March 20, 1972

Abstract: Cyclopropanols undergo facile reactions with photoexcited aryl ketones such as benzophenone. These are oxidation–reduction processes involving the transfer of the hydroxyl hydrogen atom from the cyclopropanol to the ketone. From studies of the quantum yields it is concluded cyclopropanols react with high efficiency and are equivalent to such reactive substrates as benzhydrol in these photochemical oxidation–reductions. Several ketones, such as fluorenone, which are normally unreactive toward hydrogen atom abstraction do react readily with cyclopropanols.

It is clear from earlier studies that the O–X bond of cyclopropanols (X = H) and cyclopropanol derivatives (X = NO) may undergo homolytic fission much more readily than the analogous bonds of a typical aliphatic alcohol.[2] As has been previously argued,[3] the observed rate enhancements are best explained by synchronous O–X bond fission and ring opening rather than by any special stability of an intermediate cyclopropoxy radical. In a concerted process the developing orbital of the oxygen radical could be stabilized by overlap with an orbital of the neighboring carbon atom. This, coupled with the strain energy released as the ring opens, seems to account for the remarkable increases in the reactivity of these compounds in homolytic processes.

It seemed possible that hydrogen abstraction reactions of the O–H bond of a cyclopropanol might be observed, despite the fact that the O–H bond dissociation energy of alcohols is ordinarily significantly higher than that for C–H bonds.

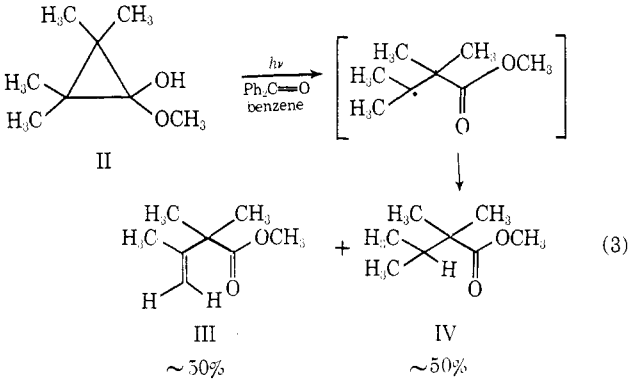
An attractive reagent for the study of such a hydrogen abstraction process would be the photoexcited state of benzophenone (eq 1). Aryl ketones such as benzophenone are reduced when irradiated in solutions containing alcohols, amines, hydrocarbons, or ethers which are capable of acting as hydrogen atom donors.[4] For alcohols the reaction mechanism is thought to involve hydrogen atom abstraction by the triplet excited state of ketone, followed by a second hydrogen atom transfer, this time to a molecule of the ketone in the ground state. The benzophenone triplet (with an energy of about 69 kcal/mol above the ground state) is a highly selective hydrogen abstraction agent and is generally capable of abstracting only at activated positions (*i.e.*, adjacent to a hydroxyl group). Substrates which lack hydrogen in such activated positions are generally unreactive.

The only substantiated example of the photochemical abstraction of a hydrogen atom from the O–H bond of an alcohol occurs in a flavin analog, 9-(2′-hydroxy-2′-methylpropyl)isoalloxazine (I), investigated by Moore and coworkers,[5] in which intramolecular transfer occurs from the tertiary hydroxyl group in the side chain to the photoexcited isoalloxazine nucleus (eq 2). When the reaction is carried out in deuterium oxide, the rate is slowed by a factor of 4.9, which is compatible with hydroxyl–deuterium transfer. Other isoalloxazines when photolyzed in D_2O under identical conditions do not show a kinetic isotope effect. Kendall and Leermakers[6] have reported the photochemical reduction of pyruvic acid upon irradiation in *tert*-butyl alcohol. This process is only one-tenth as efficient as the reduction in isopropyl alcohol, despite the fact that the excited state of pyruvic acid is of higher energy than that of benzophenone. Prolonged irradiation of benzophenone or of 2-mercaptomesitylene in *tert*-butyl alcohol-*d* has shown that deuterium is introduced into the methyl groups of the alcohol.[7] Apparently abstraction from the methyl C–H bonds occurs in these systems.

(1) National Science Foundation Traineeship, 1965–1967; Conoco Fellowship, 1967–1968.
(2) (a) S. E. Schaafsma, H. Steinberg, and T. J. DeBoer, *Recl. Trav. Chim. Pays-Bas*, **85**, 70 (1966); (b) D. H. Gibson and C. H. DePuy, *Tetrahedron Lett.*, 2203 (1969).
(3) C. H. DePuy, H. L. Jones, and D. H. Gibson, *J. Amer. Chem. Soc.*, **94**, 3924 (1972).
(4) (a) G. Ciamician and P. Silber, *Chem. Ber.*, **33**, 2911 (1900); (b) S. G. Cohen and S. Artipis, *J. Amer. Chem. Soc.*, **88**, 3587 (1966); (c) C. Walling and M. J. Gibian, *ibid.*, **87**, 3361 (1965); (d) S. G. Cohen and R. J. Baumgarten, *ibid.*, **89**, 3471 (1967).
(5) W. M. Moore and C. Baylor, *ibid.*, **88**, 5677 (1966).
(6) P. S. Kendall and P. A. Leermakers, *ibid.*, **88**, 2766 (1966).
(7) S. G. Cohen and S. Aktipis, *Tetrahedron Lett.*, 579 (1965).

Results and Discussion

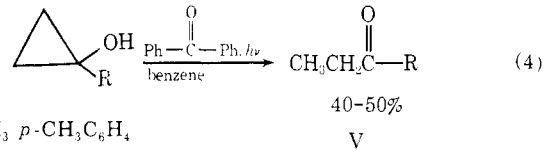
When a solution of a cyclopropanol and benzophenone in degassed benzene is irradiated in a Pyrex flask with the light from a mercury arc lamp, rapid reduction occurs and benzpinacol is obtained in high yield. An especially favorable example is the irradiation of 1-methoxy-2,2,3,3-tetramethylcyclopropanol (II) and benzophenone in benzene (eq 3). Irradiation



(3)

of a 1.75:1.0 ketone–alcohol mixture for 60 min gives an approximately equimolar mixture of methyl 2,2,3-trimethylbutenoate (III) and methyl 2,2,3-trimethylbutanoate (IV), plus a high yield of benzpinacol.

In general, the products from highly substituted cyclopropanols like II result from the disproportionation of the intermediate alkyl radicals and are identified by comparison with authentic samples. Cyclopropanols which, upon hydrogen abstraction and ring opening, give tertiary radicals react most readily and afford the cleanest reaction products. Cyclopropanols which open to give primary radicals, for instance, 1-methyl- or 1-*p*-tolylcyclopropanol, react more slowly and give rise to complex product mixtures including dimers, mixed dimers with benzhydryl radical (*vide infra*) and disproportionation products. Usually the abstraction product (V) predominates (eq 4).



(4)

R = CH_3 *p*-$CH_3C_6H_4$

To verify that the alcohol function is necessary for the reaction, several cyclopropanes were examined under identical conditions. Samples of 2,2-dimethylphenylcyclopropane, 1,2,2-trimethylcyclopropyl methyl ether, and 1,2,2-trimethylcyclopropyl acetate were found unchanged after 48 hr of irradiation in degassed solutions of benzene containing approximately equimolar amounts of benzophenone. This represents about 50 times the half-lives of corresponding cyclopropanols. In addition, irradiation of the alcohols without added ketone or with catalytic amounts (15:1 alcohol:benzophenone) showed that the cyclopropanols themselves are stable under the conditions and that no significant free-radical chain reaction occurs.

Quantum Yield Studies. Using Moore's[8] method of actinometry, the limiting quantum yield for the benzophenone–benzhydrol system at 0.075 *M* concentration in each reagent was determined (Table I). Simultaneous irradiation of an actinometer solution and of a sample containing benzophenone and a cyclopropanol (all reagents at 0.075 *M*) allowed the calculation of the quantum yield (Φ), for the cyclopropanol reaction. From these experiments it is apparent that at this concentration, cyclopropanols, particularly those in which the ring carbons are alkylated, react as efficiently with benzophenone as does benzhydrol (Table I). Thus cyclopropanols must be among the more reactive organic substrates in photoreductions, since benzhydrol is about twice as reactive as the classic hydrogen atom donor, isopropyl alcohol.[9]

Table I. Quantum Yields for 0.075 *M* Benzophenone

Alcohol	Quantum yield
Benzhydrol	0.52 ± 0.02
Pentamethylcyclopropanol	0.60 ± 0.03
1-*n*-Propylcyclopropanol	0.26 ± 0.02

Kinetic Isotope Effects. An important feature of photochemical oxidation–reduction is the abstraction of the hydrogen atom for which significant isotope effects are usually observed.[5,9] Isotope effects in the benzophenone–cyclopropanol system were examined by equilibrating solutions of the reactants (benzophenone and 1,2,2-trimethylcyclopropanol) in benzene with either H_2O or D_2O. The solutions were then irradiated in pairs, after which the relative conversion of benzophenone in the deuterated and undeuterated samples was determined. The system exhibited significant isotope effects with k_H/k_D ranging from 3.6 to 6.6 over several runs (Table II). The large spread in the values is due to the low conversion of benzophenone in the deuterated samples. Despite the uncertainty in the exact value of the deuterium isotope effect for cyclopropanols, it does approximate Moore's result for the isoalloxazine[5] and further substantiates that it is the hydroxyl-hydrogen atom that is being abstracted from the alcohols.

Table II. Kinetic Isotope Effects for Benzophenone–1,2,3-Trimethylcyclopropanol

% convn with H_2O	% convn with D_2O	k_H/k_D
6.9	1.5	4.6
14.5	4.0	3.6
14.7	3.2	4.6
14.6	2.2	6.6

The ability of a photoexcited ketone to abstract hydrogen is dependent on its having both a reasonably long-lived excited state and on its excited state having a localized unpaired electron on the oxygen atom. Some aryl ketones, such as 2-acetonaphthone and fluorenone, do not ordinarily abstract hydrogen, probably because the excited states result from $\pi \rightarrow \pi^*$ excitation and have little alkoxy radical character.[10] Others, such as *p*-aminobenzophenone and Michler's ketone, are believed to have inactive charge transfer excited states.[11] However, in the presence of a good hydrogen atom

(8) W. M. Moore and M. Ketchum, *J. Amer. Chem. Soc.*, **84**, 1368 (1962).

(9) W. M. Moore and M. D. Ketchum, *J. Phys. Chem.*, **68**, 214 (1964).

(10) (a) G. S. Hammond and P. A. Leermakers, *ibid.*, **66**, 1148 (1962); (b) G. S. Hammond and P. A. Leermakers, *J. Amer. Chem. Soc.*, **84**, 207 (1962).

(11) S. G. Cohen and J. I. Cohen, *ibid.*, **89**, 164 (1967).

donor, such as tri-*n*-butylstannane[10] or certain amines,[11] many of these inactive ketones are reduced.

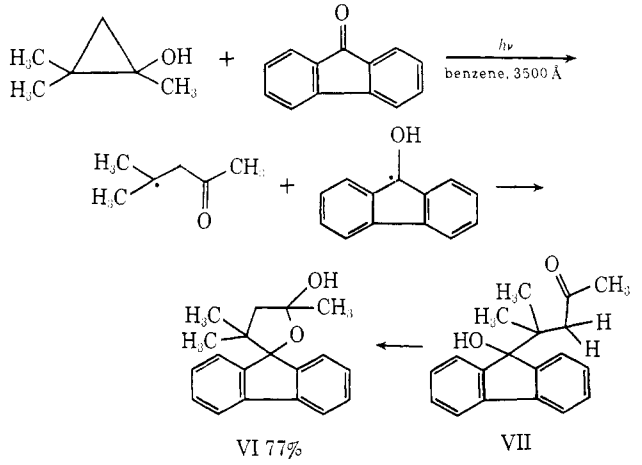
Several ketones were irradiated in the presence of cyclopropanols in order to examine the reactivity of the alcohols in greater detail. The samples were prepared in benzene-d_6 in nmr sample tubes and the effect on the cyclopropanols was determined by successive recordings of the spectrum. Acetophenone, benzophenone, Michler's ketone, and fluorenone all caused rapid conversion of the cyclopropanols. Although the products were not isolated in all cases, it is easily observed in the nmr spectrometer that they involve ring-opening isomerizations. In the presence of 2-acetonaphthone or benzalacetophenone the cyclopropanols appeared to be stable during prolonged irradiation.

Of those ketones tested, only benzophenone and acetophenone are reduced in 2-propanol. Acetonaphthone reacts in the presence of alkyl tin hydrides, but not in the presence of amines.[11] Fluorenone has been shown to be reduced by irradiation in the presence of some amines,[12] and by tri-*n*-butylstannane.[13]

Photooxidation of Cyclopropanols by Fluorenone. The reaction of solutions containing fluorenone and various cyclopropanols is particularly interesting. The configurations of the lowest excited states of fluorenone are not yet clearly defined, and the reactive triplet may be derived either from π,π^* or from n,π^* excitation. In some cases even a singlet excited state has been shown to account for a part of the total reactivity of the molecule.[13]

Irradiation of fluorenone and 1,2,2-trimethylcyclopropanol solutions gives high yields of the mixed dimer 2-hydroxy-2,4,4-trimethylspiro(oxolane-5,9′-fluorene) (VI, Scheme I). About 16% of the fluorenone is recovered and another 7% is isolated as fluorenone pinacol. The reaction presumably proceeds as in Scheme I, the γ-hydroxy ketone (VII) serving as the precursor of the spiro compound, although this intermediate has not been detected.

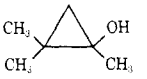
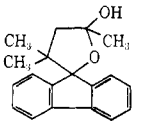
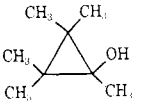
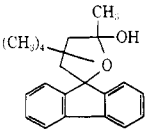
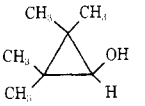
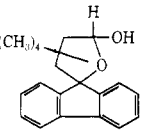
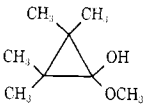
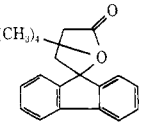
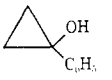
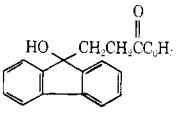
Scheme I



VI 77% VII

Other cyclopropanols also formed mixed dimers in high yield (Table III), and in several cases cyclization also occurs. Other products included fluorenone pinacol (10–20%) and disproportion and abstraction products of the ring-opened alkyl radicals. In a typical photolysis experiment, a degassed benzene solution 0.04 *M* in fluorenone and in a cyclopropanol was irradiated for 1–2 hr under argon, with eight 8-W 3500-Å lamps in a Rayonet photochemical reactor. This treatment resulted in complete conversion of the cyclopropanols, although some fluorenone was always isolated from chromatography of the products.

Table III

Cyclopropanol	Main product	Yield[a]
		77%
		68%
		79%
		58%
		78%

[a] Based on pure material from column chromatography of reaction mixtures.

Using the same system of matched sample tubes and benzophenone–benzhydrol actinometry as employed for benzophenone, some quantum yield data were obtained. These are compared to the published values for the only other known fluorenone photoreduction, that with an amine (Table IV). Although the quantum yields for fluorenone are lower than those for benzophenone, the reaction is still fairly efficient, indicating that the hydroxyl hydrogen atoms of cyclopropanols are readily abstracted even by aryl ketones which are normally unreactive in such processes.

Table IV. Quantum Yields for Fluorenone Photoreduction

Compound	Fluorenone
1-*n*-Propylcyclopropanol[a]	0.10
Pentamethylcyclopropanol[a]	0.33
Triethylamine[b]	0.76

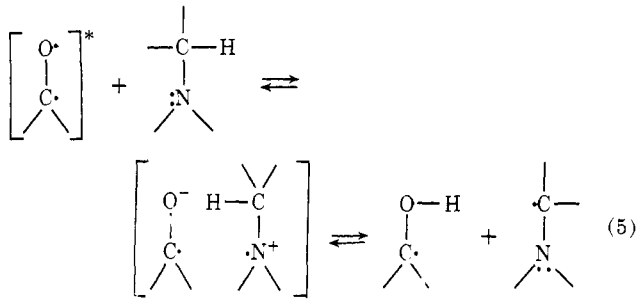
[a] 0.075 *M* ketone and 0.075 *M* cyclopropanol in benzene. [b] Cohen,[12a] 0.03 *M* fluorenone and 0.04 *M* amine in cyclohexane.

That cyclopropanols will promote reasonably efficient photoreductions of fluorenone is a surprising re-

(12) (a) S. G. Cohen and J. B. Guttenplan, *Tetrahedron Lett.*, 5353 (1968); (b) R. S. Davidson and P. F. Lambeth, *Chem. Commun.*, 1265 (1967).

(13) G. A. Davis, P. A. Carapellucci, K. Szoc, and J. D. Gresser, *J. Amer. Chem. Soc.*, **91**, 2264 (1969).

sult. Amines, the only other class of compounds active in such a process, are generally agreed to interact through an electron and not a hydrogen transfer[12,13] (eq 5). In fact, this may be a general characteristic of



(5)

reactions of diaryl ketones having low energy $\pi \rightarrow \pi^*$ transitions. An analogous "electron abstraction" mechanism for cyclopropanols could be imagined, but this is contradicted by our observation that cyclopropyl methyl ethers are unreactive toward fluorenone even though electron transfer should be possible. The kinetic isotope effects observed for benzophenone reductions also argue against such a mechanism.

Yang[14] has postulated that aromatic ketones with low-lying π,π^* states may be able to abstract hydrogen through vibronic coupling with slightly more energetic n,π^* states. Although we have not examined solvent effects in the reactions, the use of nonpolar solvents (benzene, hexane) should lower the energy of the n,π^* state of fluorenone more than the π,π^* state and would thereby increase the mixing of the two states. Many ketones are known to be more reactive in nonpolar solvents;[11,12a,13] therefore, the combination of a slightly reactive ketone with the very labile cyclopropanols must account for the reactions.

Experimental Section

Spectral Data. All infrared (ir) spectra were recorded on a Beckman IR-10 spectrophotometer using matched sodium chloride cells of 0.05-, 0.10-, or 0.25-mm path length. Mass spectra were obtained using a Varian CH-7 spectrometer. Nuclear magnetic resonance (nmr) spectra were obtained using a Varian A-60-A spectrometer. Ultraviolet studies were carried out using a Coleman Model 124 spectrophotometer with matched quartz cells of 1.0-cm path length.

Gas Phase Chromatography (gpc). All gpc analyses were performed on an F & M Scientific Model 700 gas chromatograph.

The cyclopropanols were synthesized by methods previously described.[3,15]

Benzophenone. A. 1-Methylcyclopropanol. A solution of 0.074 g (0.001 mol) of the alcohol and 0.181 g (0.001 mol) of benzophenone in 0.5 ml of benzene-d_6 in an nmr sample tube was degassed with an argon stream and an nmr spectrum was recorded; nmr (C_6D_6) τ 2.3 and 2.7 (benzophenone multiplets), 6.23, 8.65, 9.25, 9.70 (cyclopropanol). Ater irradiation with a 450-W lamp, in a Pyrex probe at 0° for 6 hr, the alcohol had been consumed, the benzophenone was largely converted to benzpinacol, and the following nmr spectrum was recorded: τ 2.5, 2.9, and 6.32 (benzpinacol); 8.05 (quartet), 8.30 (s), 9.18 (t), all from 2-butanone which was 45% of the product; and a broad, complex region from τ 7.2 to 8.0 and peaks at 8.2–8.3 which were not assigned but which comprised 50% of the product spectrum. A solution of 0.10 g (0.00056 mol) of benzophenone in 0.582 g (0.008 mol) of the alcohol was degassed and was irradiated for 48 hr. Gpc analysis of the alcohol–benzophenone mixture after irradiation showed only 7–10% conversion to 2-butanone. Likewise, analysis by nmr spectroscopy indicated about 7% of the alcohol had been converted to methyl ketone products while all the benzophenone was converted to benzpinacol.

B. Pentamethylcyclopropanol. A solution of 0.064 g (0.0005 mol) of the cyclopropanol and 0.092 g (0.0005 mol) of benzophenone in 0.5 ml of benzene-d_6 was degassed with argon. The nmr spectrum before irradiation was recorded, the sample was irradiated for 2.5 hr, and a second spectrum was recorded. The benzophenone had been converted to benzpinacol. The products from the alcohol were a 50:40 mixture of 2,3,3-trimethyl-1-penten-4-one (identified by comparison to a known sample) and 2,3,3-trimethyl-4-pentanone: nmr (C_6D_6) τ 8.20 (septet, J = 7 Hz), 8.28 (s, $COCH_3$), 9.20 (s, 6), 9.40 (d, 6, J = Hz), which was identified by comparison to the product of base-catalyzed ring opening of the cyclopropanol.

C. 1-Methoxy-2,2,3,3-tetramethylcyclopropanol. A solution of 0.78 g (0.542 mmol) of the cyclopropanol and 0.006 g (0.033 mmol) of benzophenone in 0.5 ml of benzene-d_6 was degassed and irradiated for 3 hr, but no significant conversion of the alcohol was observed. Enough benzophenone was added to bring the ratio to 1:1 and complete conversion of the alcohol to methyl 2,2,3-trimethyl-3-butenoate (45%) [nmr (CCl_4) τ 5.20 (m, 2), 6.40 (s, 3, OCH_3), 8.31 (m, 3), 8.72 (s, 6)] and methyl 2,2,3-trimethylbutyrate [nmr (CCl_4) τ 6.40 (s, 3, OCH_3), 8.17 (septet, 1, J = 7 Hz), 8.95 (s, 6), 9.20 (d, 6, J = 7 Hz)] identified by comparison with the spectrum of the material obtained from treatment of the alcohol with sodium methoxide.

D. Benzophenone and Other Cyclopropanes. Four nmr sample tubes were prepared. Tube 1 contained 0.061 g (0.335 mmol) of benzophenone and 0.050 g (0.340 mmol) of 1-phenyl-2,2-dimethylcyclopropane in 0.5 ml of benzene-d_6. Tube 2 contained 0.061 g (0.335 mmol) of benzophenone and 0.034 g (0.300 mmol) of 1,2,2-trimethylcyclopropyl methyl ether in 0.5 ml of benzene-d_6. Tube 3 contained 0.016 g (0.335 mmol) of benzophenone and 0.058 g (0.400 mmol) of 1,2,2-trimethylcyclopropyl acetate in 0.5 ml of benzene-d_6. Tube 4 contained 0.061 g (0.335 mmol) of benzophenone in 0.5 ml of benzene-d_6. Each sample was carefully degassed with argon and an nmr spectrum of each was recorded, along with an integral trace. After irradiation with six 3500-Å lamps, for 48 hr, all the samples were noticeably yellow in color, but no reaction could be detected in the nmr spectrum. The samples were also analyzed by gpc on a 5 ft × 0.25 in. Carbowax 20M column at 80 and 150° for volatile materials. In all cases only the solvent and the starting materials were evident, although benzophenone and other high molecular weight materials were not detectable under the conditions employed.

E. 1-*p*-Methylphenylcyclopropanol. A solution was prepared from 0.183 g (1.0 mmol) of benzophenone, 0.152 g (1.02 mmol) of the cyclopropanol, and 25 ml of benzene and was degassed by two freeze–thaw cycles before being irradiated for 24 hr with two 8-W 3500-Å lamps. The nmr spectrum of the crude product was obtained: nmr (CCl_4) τ 2.24 and 2.83 (m), 7.12 (quartet), 7.64 (s), 8.84 (t). The main product is 1-*p*-methylphenyl-1-propanone, identified from a comparison of the nmr spectrum of propiophenone.

F. Quantum Yield Studies. The quantum yield of a 0.075 M benzophenone–benzhydrol actinometer was first determined by the method of Moore and Ketchum[8] to be 0.52. The quantum yield studies were carried out in a Rayonet photochemical reactor using two to four 8-W 3500-Å phosphor lamps. An aluminum rack was constructed which had a central shaft fitted to a 0–1500 rpm variable speed motor. For the actinometer quantum yield determinations and for all subsequent determinations, two matched tubes were employed. These were constructed from a single length of 18-mm Pyrex tubing and were fitted with 19/38 joints and stopcocks; the rates of photoreduction of identical benzophenone–benzhydrol solutions in these tubes were determined to agree within experimental error. All samples were degassed *in vacuo* by three freeze–thaw cycles and sealed prior to irradiation. The percentage of benzophenone consumed was determined by first diluting 2.0 ml of the photolysis sample to 10.0 ml; the absorbance was then measured *vs.* benzene in 10-mm cells at 345 mμ. The samples were prepared from stock solutions of 0.2500 M benzophenone, 0.2500 M benzhydrol, and 0.2500 M cyclopropanols in benzene. Pipets were used to transfer 3.0 ml of each appropriate stock solution and the mixtures were diluted to 10.0 ml in volumetric flasks. After degassing, the sample of benzophenone–cyclopropanol and the benzophenone–benzhydrol actinometer sample were placed in the Rayonet reactor and irradiated to 15% benzophenone conversion. Exactly equal irradiation of both samples was assured by the merry-go-round

(14) N. C. Yang and R. L. Dusenbery, *J. Amer. Chem. Soc.*, **90**, 5899 (1968).

(15) (a) C. H. DePuy, *Accounts Chem. Res.*, **1**, 33 (1968); (b) C. H. DePuy, H. L. Jones, and D. H. Gibson, *J. Amer. Chem. Soc.*, **90**, 5306 (1968).

apparatus. The average experimental error under these conditions was on the order of 5–10%.

G. Kinetic Isotope Effect. A stock solution of 0.2500 *M* 1,2,2-trimethylcyclopropanol in benzene was prepared. A 25-ml solution containing 6.0 ml of the cyclopropanol stock solution and 6.0 ml of the benzophenone stock solution was prepared, giving a concentration of 0.060 *M* in both reagents. This solution was divided into the matched sample tubes, and 5.0 ml of water was added to tube A and 5.0 ml of deuterium oxide to tube B. Aliquots of 2.0 ml from each solution were then withdrawn and diluted to 10.0 ml with benzene, and the absorbance at 345 mμ was determined. The samples were equilibrated and partially deoxygenated by bubbling argon through the tubes, at 0°, for 15 min. The tube caps were fitted and, using the attached stopcocks, each sample was taken through two freeze–thaw degassing cycles.

After irradiation on the merry-go-round apparatus in the Rayonet reactor, the samples were opened and two samples were taken. The 2.0-ml aliquots were diluted, as before, and the absorbance was determined. The ratio of the percentage of benzophenone conversion in the water equilibrated sample to that in the deuterium oxide equilibrated sample was used to calculate the isotope effect, k_H/k_D.

Other Ketones. A. Michler's Ketone. A solution of 0.067 g (0.250 mmol) of Michler's ketone and 0.033 g (0.255 mmol) of pentamethylcyclopropanol in 0.75 ml of benzene-d_6 was prepared and degassed. The sample was irradiated, through Pyrex with a 450-W Hanovia lamp for 1.8 hr. Analysis by nmr indicated that all of the cylopropanol had reacted and peaks due to radical disproportionation products were observed. The aromatic region of the spectrum was altered from the pattern of the ketone and a clear yellow material, which could be removed only by ethanolic potassium hydroxide, was coated on the sides of the sample tube. A detailed analysis of the products was not attempted.

It was also determined that, under identical conditions, 1-phenylcyclopropanol was consumed, although the reaction was much slower.

B. Benzalacetophenone (Chalcone). Irradiation of a degassed solution of 1.03 g (0.008 mol) of pentamethylcyclopropanol and 1.60 g (0.008 mol) of chalcone for 30 hr did not produce any detectable reaction.

C. 2-Acetonaphthone. A solution of 0.065 g (0.65 mmol) of 1,2,2-trimethylcyclopropanol and 0.109 g (0.64 mmol) of 2-acetonaphthone in 0.5 ml of benzene-d_6 was degassed and irradiated. After 24 hr the aromatic proton region of the nmr spectrum was unchanged. A small amount of decomposition of the cyclopropanol had occurred. As evidence of this, some new signals in the region of τ 8.3 were observed and were thought to be due to acid- or base-catalyzed ring opening of the alcohol.

D. Acetophenone. A solution of 0.085 g (0.85 mmol) of 1,2,2-trimethylcyclopropanol and 0.101 g (0.90 mmol) of acetophenone in 0.5 ml of benzene-d_6 was degassed with argon and irradiated. After 5 hr, about 30% of the cyclopropanol had reacted, as determined from the nmr spectrum. After 20 hr the cyclopropanol had been consumed, and in the nmr spectrum a large number of new signals were apparent between τ 7.8 and 9.2. The pattern of the aromatic protons was also considerably altered, but none of the products were identifiable.

Fluorenone. A. 1,2,2-Trimethylcyclopropanol. A benzene solution (225 ml) of 1.80 g (0.01 mol) of fluorenone and 1.00 g (0.01 mol) of the cyclopropanol was degassed and irradiated under argon with eight 3500-Å lamps in the Rayonet reactor. The reduction was monitored by examining the carbonyl region of the ir spectrum. The residue (2.8 g) was chromatographed on 75 g of silica gel with initial elution by hexane, gradually changed to hexane–benzene and benzene–ether. Three products were isolated, 0.43 g (16%) of fluorenone, 0.19 g (7%) of fluorenone pinacol (mp 196–199°) (lit.[12a] 195–197°), and 2.07 g (77%) of 2-hydroxy-2,4,4-trimethylspiro(oxolane-5,9′-fluorene): mp 122–124°; ir (CCl_4) 3608 (O–H), 3050 (several, aromatic C–H), 2980 cm^{-1} (aliphatic C–H); nmr ($CDCl_3$) τ 2.60 (m, 8), 7.28 (s, OH), 7.50 (s, 1), 7.59 (s, 1), 8.22 (s, 3), 9.00 (s, 3), 9.08 (s, 3); nmr (C_6D_6) τ 2.67 (m, 8), 6.90 (s, OH), 7.56 (s, 1), 7.87 (s, 1), 8.35 (s, 3), 9.10 (s, 6); mass spectrum *m/e* (relative intensity) 280(13), 262(17), 219(52), 181(100), 165(26), 152(42).

B. 2,2,3,3-Tetramethylcyclopropanol. As in part A, 0.92 g (0.008 mol) of the cyclopropanol and 1.45 g (0.008 mol) of fluorenone were photolyzed in 200 ml of benzene. Chromatography of the residue, 2.10 g (89%), gave 0.326 g (15%) of fluorenone, 0.08 g (4%) of fluorenone pinacol, 0.03 g (1.5%) of tetramethylspiro(cyclopropane-1,9′-fluorene), and 1.65 g (79%) of 2-hydroxy-3,3,4,4-tetramethylspiro(oxolane-5,9′-fluorene): ir (CCl_4) 3610 (O–H), 3060 (aromatic C–H), 2980 cm^{-1} (aliphatic C–H); nmr ($CDCl_3$) τ 2.67 (m, 8), 4.62 (d, 1) 6.95 (s, 1, OH), 8.70 (s, 3), 8.88 (s, 3), 9.12 (s, 3), 9.39 (s, 3).

C. Pentamethylcyclopropanol. A solution of 1.28 g (0.01 mol) of the cyclopropanol and 1.63 g (0.009 mol) of fluorenone in 150 ml of benzene was irradiated. After stripping the solvent 2.56 g (80%) of residue remained which after chromatography gave 0.15 g (6%) of fluorenone, 0.07 g (2.7%) of tetramethylspiro(cyclopropane-1,9′-fluorene), 0.35 g (13–14%) of impure pinacol, and 1.74 g (68%) of 2-hydroxy-2,3,3,4,4-pentamethylspiro(oxolane-5,9′-fluorene): mp 120–124°; ir (CCl_4) 3610 (OH), 3060 (aromatic C–H), 2980 cm^{-1} (aliphatic C–H); nmr ($CDCl_3$) τ 2.3–3.0 (m, 8), 7.84 (s, 1, OH), 8.49 (s, 3), 8.73 (s, 3), 8.95 (s, 3), 9.02 (s, 3), 9.45 (s, 3); mass spectrum *m/e* (relative intensity) 308(8), 290(8), 233(13), 209(27), 181(100), 165(14), 152(18).

D. Tetramethylcyclopropanone Methyl Hemiketal. Fluorenone (1.80 g, 0.01 mol) and the cyclopropanol (1.44 g, 0.01 mol) were photolyzed in 200 ml of benzene. After evaporation of the solvent, 2.83 g (88%) of a residue remained. In parts B, C, and D, nmr analysis of small scale reactions demonstrated that the volatile materials were the radical disproportionation products observed in the benzophenone photoreduction (benzophenone, parts B, C). Chromatography of the residue gave 0.48 g (17%) of fluorenone, 0.53 g (19%) of pinacol (impure), 0.04 g (1.5%) of tetramethylspiro(cyclopropane-1,9′-fluorene), and 1.61 g (58%) of 2,2,3,3-tetramethylspiro(δ-lactone-5,9′-fluorene): mp 198–200° (sublimes); ir (CCl_4) 3070 (aromatic C–H), 2980 (aliphatic C–H), 1780 cm^{-1} (δ-lactone); nmr ($CDCl_3$) τ 2.62 (m, 8), 8.57 (s, 6), 9.18 (s, 6); mass spectrum *m/e* (relative intensity) 292 (26), 264 (8), 181 (65), 180 (100), 165 (21), 152 (44), 84 (100).

E. 1-Phenylcyclopropanol. A solution of 0.18 g (0.98 mmol) of fluorenone and 0.14 g (1.03 mmol) of the alcohol in 20 ml of benzene was photolyzed for 6 hr. After removing the solvent, the residue was examined in the ir spectrometer: ir (CCl_4) 3600 (O—H), 3630, 2950 (aromatic and aliphatic C—H), 1685 cm^{-1} (C=O). In the nmr spectrometer the following signals were recorded: nmr (CCl_4) τ 2.75 (m), 5.30 (s, OH), 6.95 and 7.60 (broad, featureless multiplets). Similarly, 0.30 g (2.0 mmol) of 1-*p*-tolylcyclopropanol and 0.39 g (2.0 mmol) of fluorenone were photolyzed in 25 ml of benzene, giving 0.68 g of residues. On column chromatography, 0.53 g (78%) of a polar material was eluted with 90:10 methylene chloride–methanol. The material gave only one spot on tlc and was believed to be 3-(9′-hydroxy-9′-fluorenyl)-1-phenyl-1-propanone: ir (CCl_4) 3610 (O—H), 3050, 2930 and 2860 (aromatic and aliphatic C—H), 1685 cm^{-1} (C=O); nmr (CCl_4) τ 2.2–3.2 (m), 6.83 (m), 7.70 (m), 7.87 (s).

F. Quantum Yields. Quantum yields for the photoreduction of fluorenone by 1-*n*-propylcyclopropanol and by pentamethylcyclopropanol were determined as in part F of the benzophenone reactions. Two matched sample tubes were again employed and the benzophenone–benzhydrol actinometer was used. The percentage of conversion of fluorenone was determined from the measured absorbance in the uv spectrometer at 380 mμ.

G. 1,2,2-Trimethylcyclopropyl Methyl Ether. A solution of 1,2,2-trimethylcyclopropyl methyl ether and fluorenone in the ratio of 1.0:0.75 in 0.5 ml of benzene-d_6 was degassed with argon. The nmr spectrum was recorded and the sample was irradiated in the Rayonet reactor with four 3500-Å lamps for 13 hr. A second nmr spectrum was recorded and was found to be unchanged from the initial spectrum, exhibiting signals due to fluorenone [nmr (C_6D_6) τ 2.34 (m, 2), 2.87 (m, 6)] and the cyclopropyl methyl ether [nmr (C_6D_6) τ 6.87 (s, 3), 8.75 (s, 6), 9.04 (s, 3), 9.75 (quartet, 2, AB)]. The conditions of the photolysis would have caused reaction of a like amount of 1,2,2-trimethylcyclopropanol and fluorenone in less than 2 hr.

Acknowledgment. We wish to thank the National Science Foundation for a grant (No. GP-13783X) in support of this work.