Photoreduction of Benzophenone in Methyl 2-Octyl Ether. Effects of Mercaptan, Disulfide, and Oxygen[1]

Saul G. Cohen and Stelios Aktipis

Contribution from the Department of Chemistry, Brandeis University, Waltham, Massachusetts 02154. Received March 2, 1966

Abstract: Ultraviolet photoreduction of benzophenone in methyl 2-octyl ether proceeds 0.17 times as fast as in 2-propanol and leads to benzpinacol (44%) and other products. From the effect of concentration of the ether in benzene on the rate, k_{de}/k_8, the ratio of rate constants for deactivation of the triplet and abstraction of hydrogen by the triplet is 0.16 M. From the effect of naphthalene, k_8 is estimated to be $\sim 2 \times 10^6$ M^{-1} sec^{-1}. The reaction is strongly retarded by 0.04 M 2-mercaptomesityl group, present initially either as mercaptan or disulfide, initial equilibration of the two valence states resulting from the inhibition reactions. The sulfur compound is slowly consumed during the inhibition (eq 7a) and photoreduction proceeds after each molecule of sulfur compound has negated the chemical consequences of about 20 quanta. The sulfur compound is not consumed during prolonged inhibition of the photoreduction of benzophenone in 2-octanol (eq 7). The sulfur compound is destroyed rapidly and is not an inhibitor during photoreduction in ether in the presence of air. It shows diminished effectiveness in retarding photoreduction in alcohol under air. Oxygen accelerates the photoreduction of benzophenone in the ether, retards it in the alcohol. In photoreduction in optically active ether some racemization of recovered ether is observed, indicating that about half of the initially formed radicals revert to starting material (eq 9). Extensive racemization of the ether occurs during inhibition of the photoreduction (eq 12). Inhibition of photoreduction in the presence of *t*-butyl alcohol-OD leads to incorporation of carbon-bound deuterium in the recovered ether, largely at the secondary ether carbon (eq 12) and in the recovered *t*-butyl alcohol. Inhibition results from repeated hydrogen transfer reactions of mercaptan and disulfide (eq 4 and 12).

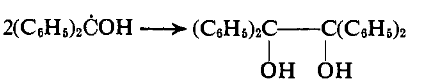
The light-induced reduction of benzophenone by 2-propanol[2] proceeds *via* the first excited triplet of the ketone[3,4] and the free radicals I and II. The quantum yield for reduction of benzophenone has been

$$(C_6H_5)_2C{=}O^* + (CH_3)_2CHOH \longrightarrow \underset{\text{I}}{(C_6H_5)_2\dot{C}OH} + \underset{\text{II}}{(CH_3)_2\dot{C}OH} \qquad (1)$$

reported to be approximately 1,[4] approximately 2,[5] and dependent upon the concentration of benzophenone,[6] rising toward 2 at high concentrations as the reaction[5] of eq 2 becomes important. The reaction of eq 1

$$(C_6H_5)_2C{=}O + \text{II} \longrightarrow \text{I} + (CH_3)_2C{=}O \qquad (2)$$

proceeds in the indicated direction because of the excitation energy; reconversion of the radicals I and II to the starting materials, benzophenone and 2-propanol, would be a thermodynamically favorable disproportionation reaction. This does not occur normally, as indicated by high quantum yields and the absence of racemization when the reaction is studied in an optically active alcohol.[5,7c] The reaction of eq 2 dominates kinetically, and the radicals I form benzpinacol.



$$2(C_6H_5)_2\dot{C}OH \longrightarrow (C_6H_5)_2\underset{OH}{\underset{|}{C}}-\underset{OH}{\underset{|}{C}}(C_6H_5)_2 \qquad (3)$$

The photoreduction is, however, retarded and inhibited by low concentrations of mercaptans and disulfide[7a-c] as new rapid reactions (eq 4 and 5) are introduced which convert the radicals I and II to the starting materials. The thermodynamically favorable disproportionation of radicals I and II is, in effect, catalyzed by the sulfur compounds. In these reactions

$$(C_6H_5)_2\dot{C}OH + AS\cdot\ (ASSA) \longrightarrow (C_6H_5)_2C{=}O + ASH\ (ASH + AS\cdot) \qquad (4)$$

$$(CH_3)_2\dot{C}OH + ASH \longrightarrow (CH_3)_2CHOH + AS\cdot \qquad (5)$$

the mercaptan and disulfide are regenerated in the steps which restore the system to its initial state, and they may function repeatedly in this way, a few molecules negating the chemical consequences of many quanta. They also offer such protection in systems in which only one intermediate radical may be formed,[8] the benzophenone–benzhydrol and acetophenone–α-phenylmethylcarbinol systems, in which the one intermediate is both oxidized by thiyl radical or disulfide and reduced by mercaptan (eq 6). These reactions also lead to

$$AS\cdot + RR'CHOH \xrightarrow{ASH} RR'\dot{C}OH \xrightarrow{AS\cdot} RR'C{=}O + ASH \qquad (6)$$

protection of benzophenone from damage by ^{60}Co γ radiation in 2-propanol.[7c,9] Evidence for this mechanism of protection has been found in racemization and deuterium exchange studies,[7,8] in the equivalent effects of mercaptan and disulfide,[7,8] in the mercaptan-catalyzed, benzophenone-sensitized decarbonylation of aldehydes,[10] and in flash photolysis experiments.[11]

The ketone–alcohol system leads only to α-hydroxyalkyl radicals, RR'$\dot{C}$OH, and provides no reaction by which thiyl radicals may be removed irreversibly.

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[1] We are pleased to acknowledge generous support of this work by the U. S. Atomic Energy Commission, AT(30-1)-2499.

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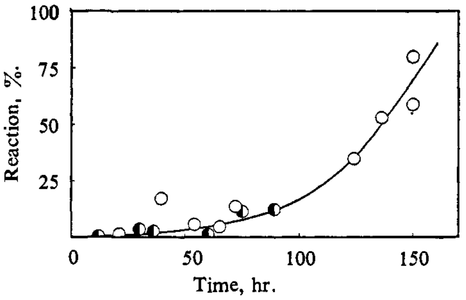
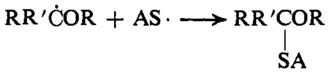


Figure 1. Photoreduction of 0.50 M benzophenone in methyl 2-octyl ether in the presence of 0.040 M sulfur moiety: ○, 0.020 M 2-mercaptomesitylene + 0.010 M 2-mesityl disulfide; ◐, 0.020 M 2-mesityl disulfide.

Combination of the hydroxyalkyl radical with a thiyl radical, in place of the disproportionation of eq 4, would lead to a thiohemiketal which may decompose to ketone and mercaptan (eq 7), the products of the disproportionation, and this might be responsible for the extended usefulness of the mercaptan against the action of many quanta. However, photoexcited ketones may abstract hydrogen from other donors than alcohols, from hydrocarbons,[12-14] from ethers,[15,16] and from other compounds.[17] In these systems the donor-derived radicals may persist, and they do appear to lead[13,15,16] to the three products of the possible radical combination reactions. In the presence of mercaptans, these radicals might lead to irreversible consumption of thiyl radicals (eq 7a). We have previously made a preliminary report on the photoreduction of benzophenone in methyl 2-octyl ether, on its retardation and inhibition by 2-mercaptomesitylene and 2-mesityl disulfide, and on consumption of these sulfur compounds during the inhibition.[18] A detailed report on these and other aspects of this system follows.

$$\mathrm{RR'\dot{C}OH + AS\cdot \longrightarrow RR'\underset{\overset{|}{SA}}{C}OH \longrightarrow RR'C{=}O + ASH} \qquad (7)$$



$$\mathrm{RR'\dot{C}OR + AS\cdot \longrightarrow RR'\underset{\overset{|}{SA}}{C}OR} \qquad (7a)$$

Results

Ultraviolet irradiations were carried out on 1-ml aliquots in evacuated, ground-glass closed Pyrex tubes or in sealed tubes, and in the closed tubes under argon. In exploratory experiments 0.5 M solutions of benzophenone in methyl 2-octyl ether were irradiated alone and in the presence of 0.04 M 2-mercaptomesitylene. A sample without additive showed very low carbonyl absorption at 6.0 μ after irradiation for 40 hr, and work-up after 60 hr of irradiation led to recovered methyl 2-octyl ether, 44% yield of benzpinacol, and a residue which appeared to be a mixture of the other two products of radical combination. A sample containing 0.04 M mercaptan showed no decrease in absorption due to the carbonyl group after irradiation for 40 hr, and work-up led to recovery of the ether and 98% recovery of benzophenone. Inhibition appeared complete.

In rate studies aliquots of 0.05 M benzophenone in the ether, containing none and three concentrations of 2-mercaptomesitylene and/or 2-mesityl disulfide, were irradiated for varying periods and analyzed spectrophotometrically for remaining benzophenone. Concentrations of remaining benzophenone in the presence of the sulfur compounds were determined from the absorption at 6.0 μ; in the absence of additive, from the absorption at 335 mμ or at 6.0 μ. Benzophenone was reduced in methyl 2-octyl ether in the absence of additive with approximate zero-order kinetics at a rate of 1.1×10^{-2} mmole ml^{-1} hr^{-1}, ~50% complete in 22 hr, with lamp No. 1, and at a rate of 1.6×10^{-2} mmole ml^{-1} hr^{-1}, with lamp No. 2. Benzophenone was reduced by 2-propanol under the same conditions, lamp No. 2, at a rate of 9.6×10^{-2} mmole ml^{-1} hr^{-1}. The presence of 0.010 M 2-mercaptomesitylene showed very little if any retardation. In the presence of 0.020 M 2-mercaptomesitylene considerable scatter was observed in the rates of photoreduction. This was reduced when the reactions were carried out in sealed tubes. An inhibition period was observed which was followed by fairly rapid photoreduction.

In the presence of 0.04 M 2-mesityl thiyl group, present initially either as the mercaptan or the disulfide or as a mixture of the two, strong retardation was observed over a long period. The reduction proceeded at a rate of about 5×10^{-4} mmole ml^{-1} hr^{-1}, as compared with the uninhibited rate of 1.1×10^{-2} mmole ml^{-1} hr^{-1}, and was about 5% complete in 60 hr. The retardation broke down after about 100 hr and photoreduction then proceeded at a somewhat reduced rate, as compared with the normal rate in the absence of mercaptan. Some data are summarized in Figure 1.

Analyses for remaining thiol and disulfide as a function of time of irradiation were carried out by vapor phase chromatography. In a solution of 0.50 M benzophenone and 0.020 M 2-mesityl disulfide in methyl 2-octyl ether, concentration of disulfide gradually decreased and that of thiol increased, reaching about 30% disulfide, 70% thiol after about 35 hr. When the solution contained initially 0.040 M 2-mercaptomesitylene, equilibration to about 70% thiol and 30% disulfide occurred more rapidly. On prolonged irradiation concentration of both disulfide and mercaptan decreased, about 15% of the original being present after 96 hr, and a substantial extent of photoreduction of the benzophenone had occurred. When the solution contained initially 0.020 M 2-mercaptomesitylene, decrease in total mercaptan and disulfide was observed more quickly and substantial depletion of the sulfur compounds, accompanied by photoreduction of benzophenone, was observed after 40 hr. All irradiations were with lamp No. 1. Some results are summarized in Figures 2 and 3.

On the other hand similar analyses for thiol and disulfide as a function of time of irradiation, carried out on solutions of 0.5 M benzophenone and 0.04 M 2-mercaptomesitylene in 2-octanol, showed that a mixture of mercaptan and disulfide was formed and

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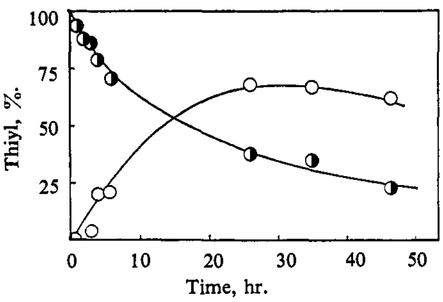

Figure 2. Irradiation of 0.50 *M* benzophenone and 0.020 *M* 2-mesityl disulfide in methyl 2-octyl ether. Analyses for mercaptan and disulfide: ○, 2-mercaptomesitylene; ◑, 2-mesityl disulfide.

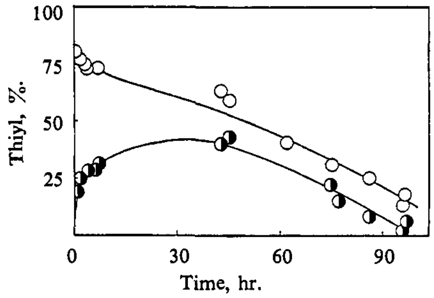

Figure 3. Irradiation of 0.50 *M* benzophenone and 0.040 *M* 2-mercaptomesitylene in methyl 2-octyl ether. Analyses for mercaptan and disulfide: ○, 2-mercaptomesitylene; ◑, 2-mesityl disulfide.

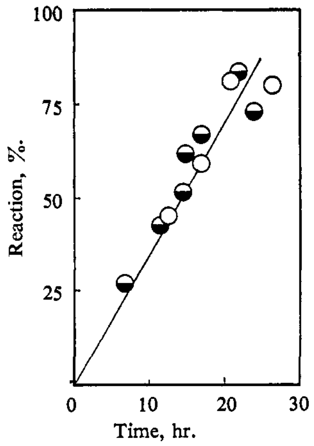

Figure 4. Photoreduction of 0.50 *M* benzophenone in methyl 2-octyl ether under air: ○, 0.040 *M* 2-mercaptomesitylene; ◒, no additive.

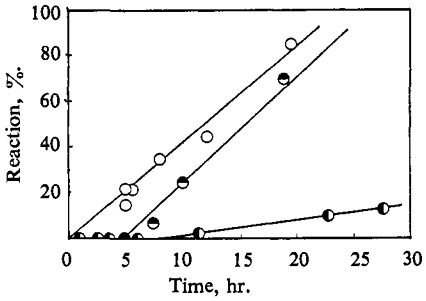

Figure 5. Photoreduction of 0.50 *M* benzophenone in 2-octanol under air: ○, no additive; ◓, 0.010 *M* 2-mercaptomesitylene; ◐, 0.040 *M* 2-mercaptomesitylene.

that only a small part of the sulfur compound was consumed on long radiation. After irradiation periods of 40, 84, 120, and 138 hr, the percentages of remaining sulfur compound as mercaptan and disulfide were, respectively, 72 and 32%, 71 and 27%, 65 and 22%, and 65 and 18%. Effective inhibition of the photoreduction persisted.

In irradiations of benzophenone in methyl 2-octyl ether in the presence of the sulfur compounds, occasional samples were found in which photoreduction appeared to be proceeding more rapidly than would be expected from the over-all rate. It seemed that irregularities might arise from leakage of air into the tubes during the irradiation. The effect of air was examined by irradiation of 1-ml aliquots, without additive and with 0.040 *M* 2-mercaptomesitylene, with the free volume (16.5 ml) of the tubes filled with air. This corresponds to 0.13 mmole of oxygen as compared with 0.04 mmole of the sulfur compound. It is remarkable that the reductions, both in the absence and in the presence of the sulfur compound, proceeded more rapidly than in the absence of air, with zero-order kinetics, at a rate of 1.6×10^{-2} mmole ml^{-1} hr^{-1} as compared with 1.1×10^{-2} mmole ml^{-1} hr^{-1}. Some data are summarized in Figure 4.

On the other hand, in the corresponding alcohol, 2-octanol, presence of air diminished the rate of photoreduction to 3.0×10^{-2} mmole ml^{-1} hr^{-1}, from 3.5×10^{-2} mmole ml^{-1} hr^{-1} under vacuum. In the presence of 0.010 *M* 2-mercaptomesitylene, which in vacuum leads to extended inhibition, air led to a short inhibition period of 5 hr, after which photoreduction proceeded at the normal rate. When 0.040 *M* 2-mercaptomesitylene was present, air resulted in an inhibition period of about 10 hr which was followed by a strongly retarded rate of photoreduction. Some results are summarized in Figure 5.

Analyses were carried out for remaining mercaptan and disulfide in irradiations under air of benzophenone and 0.04 *M* 2-mesityl mercaptan in methyl 2-octyl ether and in 2-octanol. In both solvents the concentration of thiol falls to zero in about 3 hr, being converted largely to the disulfide. Concentration of the latter passes through a maximum in this period and then decreases to zero in the ether and to a low value in the alcohol. Some data are summarized in Table I and Figure 6.

Information about the photoreduction of benzophenone by the ether and its retardation by the sulfur compounds was sought by study of the reactions in optically active methyl 2-octyl ether. Irradiation of 0.20 *M* benzophenone in the optically active ether for 226 hr led to photoreduction and to recovered ether, $[\alpha]^{22}\text{D}$ 8.95°, down from 9.35°, indicating racemization of about 0.24 *M* ether. Irradiation of 0.22 *M* benzophenone, 0.011 *M* 2-mesityl disulfide, and 0.022 *M* 2-mercaptomesitylene in optically active ether led to steady decrease in rotation over most of the irradiation period of 187 hr. The recovered ether had $[\alpha]^{23}\text{D}$ 6.75°, down from 8.95°, indicating racemization of about 1.4 *M* ether. Other experiments were carried out in a mixture of optically active and inactive methyl 2-octyl ether of $\alpha^{22}_{\text{obsd}}$ 4.52°, 1 dm. Irradiation of 0.50 *M* benzophenone, 0.02 *M* 2-mercaptomesitylene, and 0.010 *M* 2-mesityl disulfide in the ether led to steady decrease in rotation over the irradiation period

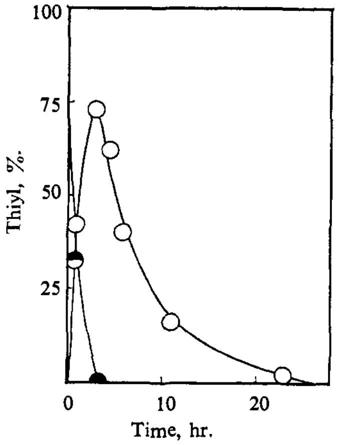

Figure 6. Irradiation of 0.50 *M* benzophenone and 0.040 *M* 2-mercaptomesitylene in methyl 2-octyl ether under air. Analyses for mercaptan and disulfide: ○, 2-mesityl disulfide; ◓, 2-mercaptomesitylene.

of 148 hr and to recovery of ether of $\alpha^{22}{}_{\text{obsd}}$ 3.71°, corresponding to racemization of about 1.0 *M* ether, corrected for the initial content of racemic material. Irradiation of 0.50 *M* benzophenone in the ether in the absence of sulfur additive led to precipitation of benzpinacol, and, after 254 hr of irradiation, to recovery of ether of $\alpha^{22}{}_{\text{obsd}}$ 4.04°, corresponding to racemization of about 0.58 *M* ether. Comparable irradiation of 0.020 *M* mercaptan and 0.010 *M* disulfide in the ether led to little or no racemization; irradiation of the ether itself led to no racemization.

Table I. Irradiation of 0.50 *M* Benzophenone and 0.04 *M* 2-Mercaptomesitylene in Methyl 2-Octyl Ether and in 2-Octanol under Air. Analyses for 2-Mercaptomesitylene and 2-Mesityl Disulfide

Irradiation, hr	2-Mercaptomesitylene, %	2-Mesityl disulfide, %
1.0[a]	32	42
3.1[a]	0	73
4.5[a]	0	62
6.5[a]	0	41
11.0[a]	0	16
23.0[a]	0	2
47.0[a]	0	0
0.9[b]	35	49
1.4[b]	30	52
2.8[b]	6	81
3.6[b]	0	87
6.0[b]	0	49
11.0[b]	0	20
23.0[b]	0	18

[a] In methyl 2-octyl ether. [b] In 2-octanol.

Further evidence about the course of this photoreduction and its inhibition was sought in experiments in 1:1 methyl 2-octyl ether–*t*-butyl alcohol-OD. Methyl 2-octyl ether-2-D, the reference standard for infrared analyses for extent of incorporation of deuterium, was prepared by reduction of 2-octanone with lithium aluminum deuteride and conversion of the 2-octanol-2-D to the ether. *t*-Butyl alcohol-OD, the intended pool of deuterium for transfer to the ether in the photoreactions, was prepared by treatment of *t*-butyl alcohol with sodium hydride followed by deuterium oxide. A solution of 0.25 *M* benzophenone and 0.01 *M* 2-mesityl disulfide in 1:1 methyl 2-octyl ether–*t*-butyl alcohol-OD was irradiated for 355 hr with lamp No. 1 and the "unreacted" ether was recovered. The ether appeared to show, by infrared analysis, presence of 6.4%, 0.32 *M*, deuterated ether. Other irradiations were carried out with lamp No. 3 which was about four times as effective in leading to photoreduction. Irradiation of 0.25 *M* benzophenone and 0.02 *M* 2-mercaptomesitylene in the ether–*t*-butyl alcohol-OD for 50 hr led to recovery of ether and *t*-butyl alcohol, both of which contained carbon-bound deuterium, the ether showing 7.1%, 0.40 *M*, deuterated compound. Irradiation of 0.25 *M* benzophenone alone in the ether–*t*-butyl alcohol-OD also led to recovery of ether which contained deuterated compound, 1.6%, 0.09 *M*. Irradiation of the solvent pair with 0.02 *M* 2-mercaptomesitylene and 0.010 *M* mesityl disulfide in the absence of benzophenone led to incorporation of less than 1% deuterium, while irradiation of the solvent pair itself led to no incorporation of deuterium in the ether.

The recovered methyl 2-octyl ether, containing 7.1% deuterated compound, was examined further. It was cleaved by hydrogen iodide, leading to 2-octyl iodide which contained deuterium. This was treated with trimethylamine oxide,[19] leading to 2-octanone which, by infrared examination, appeared to contain little if any deuterium.

Information about the rate of the initial step in the photoreduction, abstraction of hydrogen from the ether by excited benzophenone, was sought in experiments in which (a) the reaction was carried out in benzene with varying concentration of the ether and (b) the effect of a physical quencher, naphthalene, was examined. In experiment a, the extent of photoreduction of benzophenone in the solutions was determined at each concentration of ether after 9 hr of irradiation and from these data rates were estimated. They are summarized in Table II. A plot of the reciprocal of the rate against the reciprocal of the concentration was linear, leading below to a calculation of k_{de}/k_{8}, the ratio of the rate constant for deactivation of the triplet in the ether to the rate constant for abstraction of hydrogen from the ether by the triplet.

Table II. Photoreduction of 0.5 *M* Benzophenone by Methyl 2-Octyl Ether in Benzene[a]

[Ether], *M*	[Benzophenone], *M*	Rate, $10^2 \times$ *M* hr^{-1}
0.13	0.43	0.78
0.19	0.41	0.97
0.28	0.40	1.05
0.42	0.39	1.17
0.74	0.37	1.42
5.19[b]	0.35	1.67

[a] Samples were irradiated for 9 hr, lamp no. 2. [b] Neat methyl 2-octyl ether.

Quenching was examined in 0.50 *M* benzophenone and varying concentrations of naphthalene[20] in methyl 2-octyl ether, irradiated for 17.5 hr. Rates were esti-

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mated from the extents of photoreduction and are summarized in Table III. The reciprocal of the rate was proportional to the concentration of naphthalene, leading below to a calculation of k_q/k_8, the ratio of the rate constant for quenching of the triplet by naphthalene to the rate constant for hydrogen abstraction.

Table III. Effect of Naphthalene on the Photoreduction of 0.50 M Benzophenone in Methyl 2-Octyl Ether[a]

[Naphthalene], $10^3 \times M$	[Benzophenone], M	Rate, 10^2 M hr^{-1}
0.0		1.67
0.85	0.235	1.53
1.70	0.245	1.45
2.5	0.270	1.32
3.4	0.280	1.26
4.2	0.295	1.17
5.1	0.310	1.09
6.0	0.310	1.09
6.8	0.320	1.03

[a] Samples were irradiated for 17.5 hr, lamp No. 2.

Discussion

The photoreduction of benzophenone in methyl 2-octyl ether proceeds about 0.17 as fast as in 2-propanol. If a limiting quantum yield of 2 is accepted[5,6] for the latter, a corresponding quantum yield (ϕ) of 0.34 is indicated for the reaction in the ether, less if the quantum yield in 2-propanol is lower. A reaction corresponding to that of eq 2 is not possible in the ether and photoreduction at best could proceed only half as fast as in the alcohol, leading to a maximum value of $\phi = 1$. The photoreduction of benzophenone in alcohols is an efficient process. The initially formed radicals I and II do not disproportionate, as indicated by studies in optically active alcohols[5,7c] and in 2-propanol-OD;[8] reaction 2 intervenes; the ketone-derived radicals I also do not disproportionate, and they lead to benzpinacol (eq 3), not to benzhydrol. However photoreduction of benzophenone in optically active methyl 2-octyl ether leads to racemization of ~1.2 moles of ether in the recovered ether per mole of ketone reduced, in addition to racemized moieties that may be incorporated in products of radical combination. Although other interpretations may be adduced, it seems reasonable to propose that reaction of excited benzophenone with the ether results, directly or indirectly, in removal of hydrogen from the asymmetric carbon atom (eq 8), and that the two radicals enter into

$$(C_6H_5)_2C{=}\overset{*}{O} + RR'CHOR \longrightarrow (C_6H_5)_2\dot{C}OH + RR'\dot{C}OR \quad (8)$$

both combination and disproportionation reactions, leading to 44% yield of benzpinacol (eq 3), the other two products of radical combination, and to racemic ether (eq 9). Reaction 9 regenerates the starting materials;

$$(C_6H_5)_2\dot{C}OH + RR'\dot{C}OR \longrightarrow (C_6H_5)_2\,C{=}O + RR'CHOR \quad (9)$$

the extent of racemization indicates that the hydrogen abstraction may be considerably more rapid than the observed rate of photoreduction and may have a quantum yield of about 0.75, based on 2 for the reduction in 2-propanol. Photoreduction of the benzophenone in a mixture of the ether and t-butyl alcohol-OD led to recovered ether containing carbon-bound deuterium, consistent with reaction 9, but less than would be indicated by the extent of racemization. However the t-butyl alcohol was not inert; part of the photoreduction proceeded by abstraction of unactivated hydrogen from the alcohol, less deuterium would be transferred to the ether, and quantitative interpretation of this experiment may not be made.

On the basis that the rate of 1.67×10^{-2} M hr^{-1} corresponds to $\phi = 0.75$ for abstraction of hydrogen, the rate data in Table II may be converted to quantum yields and a linear plot of $1/\phi$ against the reciprocal of the concentration of ether may be constructed. This fits an equation of the type

$$\frac{1}{\phi} = \frac{1}{a}\left(1 + \frac{k_{de}}{k_8[\text{ether}]}\right) \quad (10)$$

in which a is the yield of the chemically active excited state.[21] The slope of this line (0.21 M) is $(1/a)(k_{de}/k_8)$, where $1/a$ is equal to the intercept 1.32 and k_{de}/k_8 is 0.16 M, the ratio of the rate constant for solvent and self-quenching to the rate constant for hydrogen abstraction in the system benzophenone–methyl 2-octyl ether in benzene. The corresponding value for benzophenone–benzhydrol in benzene is 0.05 M, the higher value in the ether probably resulting from a lower value of k_8.

The rate data of Table III may be converted similarly to approximate quantum yields. A linear plot of $1/\phi$ against concentration of naphthalene may be constructed, fitting an equation of the type[21] of eq 11, in

$$\frac{1}{\phi} = \frac{1}{a}\left(1 + \frac{k_{de} + k_q[Q]}{k_8\,[\text{ether}]}\right) \quad (11)$$

which k_q is the rate constant for quenching of excited benzophenone by naphthalene and the other constants are as before. From the slope the value of $(1/a)(k_q/k_8 \cdot [\text{ether}])$ may be estimated (128 M^{-1}) and this leads to 500 for k_q/k_8. If k_q has a value for a diffusion-controlled reaction, ~10^9 M^{-1} sec^{-1}, k_8, the rate constant for abstraction of hydrogen from methyl 2-octyl ether by excited benzophenone, is ~2×10^6 M^{-1} sec^{-1}, and k_{de}, the constant for decay of triplet benzophenone in this system, is ~3×10^5 sec^{-1}, consistent with reported values.[22] The results are not changed if a lower standard value for the quantum yield in the benzophenone–2-propanol reference system is chosen.

Retardation and inhibition of the photoreduction of benzophenone in methyl 2-octyl ether by the sulfur compounds, 2-mercaptomesitylene and 2-mesityl disulfide, while basically similar in character to the inhibition of photoreduction in alcohols,[7,8] showed substantial difference in detail, some predictable, some not. Quantitatively, the sulfur compounds were less effective in inhibiting the reaction in the ether than in alcohols: 0.01 M sulfur moiety, which had completely inhibited photoreduction by 2-propanol had practically no effect in the ether, while 0.02 M sulfur moiety showed a distinct but short inhibition period. The absence of effect of 0.01 M mercaptan may be due in part to destruction of the sulfur compound by oxidation, since peroxides may be present in the ether in our procedures, and the system is exceedingly sensitive to oxygen. The lesser effectiveness of the sulfur compound may also

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(21) W. H. Moore, G. S. Hammond, and R. P. Foss, *J. Am. Chem. Soc.*, **83**, 2789 (1961).

(22) J. A. Bell and H. Linschitz, *ibid.*, **85**, 528 (1963).

be due in part to the persistence of the ether-derived radical, the reaction of eq 2 not being available, and possibly higher reactivity of this radical in combination processes which may consume the benzophenone-derived radical, and with which the reactions of the sulfur compounds may compete less favorably.

Strong retardation and a substantial inhibition period were observed in the presence of 0.04 *M* sulfur moiety (Figure 1); as in the alcohols the same effectiveness was observed whether the sulfur compound was present initially as mercaptan or disulfide since each was converted to a mixture of the two during irradiation (Figures 2 and 3). Extrapolation of the reaction curve (Figure 1) after extended irradiation, back to zero reaction, indicated an inhibition period of about 100 hr, a time sufficient to lead to photoreduction of ~1.1 *M* benzophenone by the ether in the absence of sulfur compound. Analyses for remaining thiol and disulfide during irradiation showed equilibration of initial mercaptan or disulfide at about 70% mercaptan, 30% disulfide, followed by depletion of the sulfur compounds; at the extrapolated end of the inhibition period, little mercaptan or disulfide remained (Figure 3). A sample of ether which had been subjected in advance to catalytic hydrogenation showed no decrease in consumption of the sulfur compounds, indicating that adventitious olefin was not responsible. Irradiation of mercaptan and disulfide in the ether for 100 hr in the absence of benzophenone led to no consumption of the sulfur compounds. Irradiation of the mercaptan and benzophenone in 2-octanol for 138 hr led to equilibration of the sulfur compounds and to very little loss of mercaptan and disulfide. While the photoreduction in the ether was retarded, the mercaptan and disulfide were being consumed, and this consumption required the presence of the benzophenone and presumably depended upon the occurrence of the initial photochemical reactions characteristic of the ether system.

Protection of the large amount of benzophenone by the small quantity of sulfur compound, which is not a physical quencher,[7-10] indicates, as in the alcohols, hydrogen atom transfer reactions in which the sulfur compounds are regenerated in their alternate valence states and are used repeatedly, each molecule negating the chemical consequences of many quanta (eq 4 and 12). In the alcohol system this may go on practically

$$RR'\dot{C}OR + ASH\ (ASD) \longrightarrow RR'CHOR\ (RR'CDOR) + AS\cdot \qquad (12)$$

indefinitely since a mechanism for consumption of the sulfur compound is not available (eq 7). However in the ether system the thiyl radical may be consumed by a product of the initial photochemical reaction and it appears to be so consumed, but relatively slowly. Each sulfur species participates about 20 times in reactions 4 and 12, regenerating benzophenone, before the thiyl radical apparently reacts with the ether-derived radical and disappears from the system, reaction 7a.

Reaction 4 has been demonstrated in flash photolysis experiments in the 2-propanol system,[11] and presumably occurs in the ether system also. That reaction 12 is involved in the retardation by the sulfur compounds is shown by extensive racemization of optically active ether during retardation, and in the results of experiments in *t*-butyl alcohol-OD. Racemization of ~1.4 *M* ether during irradiation for 187 hr in the presence of 0.044 *M* thiyl moiety compares satisfactorily with a hypothetical photoreduction of ~2.0 *M* benzophenone in this period, estimated from the uninhibited rate of photoreduction. The presence of the sulfur compound could lead to sufficient masking to account for the difference. Irradiation of benzophenone in a 1:1 mixture of methyl 2-octyl ether and *t*-butyl alcohol-OD in the presence of 2-mercaptomesitylene or 2-mesityl disulfide led to introduction of carbon-bound deuterium in both the ether and the alcohol, to a much greater extent than in the absence of the sulfur compound. This indicates that triplet benzophenone abstracted hydrogen both from the ether and from the unactivated methyl groups of *t*-butyl alcohol, and that, in reactions related to eq 12, deuterated mercaptan transferred deuterium to the radicals derived from the ether and from the alcohol. The hydrogen was largely abstracted from the 2 position in the ether, and the deuterium was placed there by the mercaptan, as indicated by cleavage to 2-octyl iodide which retained deuterium, and oxidation to 2-octanone which retained little. The conclusion with respect to *t*-butyl alcohol was supported by the observation that benzophenone undergoes reduction when irradiated in *t*-butyl alcohol alone[23] and that carbon-bound deuterium is introduced into the *t*-butyl alcohol when a solution of 0.5 *M* benzophenone and 0.04 *M* 2-mercaptomesitylene in *t*-butyl alcohol-OD is irradiated, the photoreduction being inhibited.

Effects of Oxygen. Our work on inhibition by mercaptan and disulfide of the photoreduction and of the ^{60}Co γ-ray-induced reduction of benzophenone by alcohols has been carried out under vacuum or in an inert atmosphere.[7-9] Studies in the presence of oxygen are important because radiation damage of organisms, and protection against it by sulfur compounds, to which these chemical studies are related, may take place under aerobic conditions. In the photoreduction of benzophenone by the ether, air actually increased the rate of photoreduction by almost 50%, and completely negated the effects of the sulfur compounds (Figure 4). This is quite remarkable since air had been reported to decrease the rate of photoreduction of benzophenone by alcohols, whether by oxidizing the benzophenone ketyl radicals back to benzophenone[5] or by quenching excited triplet benzophenone.[21] Ethers are peroxidized[24] very readily in free radical processes, and alcohols are not. In the photoreduction of benzophenone by the ether, the ether-derived radical may react rapidly with oxygen, leading to a peroxy radical which may not reconvert the benzophenone-derived radical to benzophenone as effectively as does the ether radical itself. The racemization studies indicate that about half the ether-derived radicals normally oxidize the ketyl radical in this way, and if the oxygen prevented half of this reversal the observed increase in rate of photoreduction would be accounted for. This reaction of the ether radical would remove the triplet oxygen and decrease quenching; we have shown that radical-molecule reactions may under these circumstances compete favorably with physical quenching.[25] Furthermore, the ether-peroxides and/or ether-peroxy radicals might rapidly oxidize the mercaptan and di-

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(23) Experiments carried out in part by J. Nicholson.

(24) A. Rieche and R. Meister, *Angew. Chem.*, **49**, 101 (1936).

(25) S. G. Cohen and W. V. Sherman, *J. Am. Chem. Soc.*, **85**, 1642 (1963).

sulfide to products which would not be inhibitors for the photoreduction. Indeed analysis for mercaptan and disulfide indicated that, in irradiations of benzophenone and mercaptan in the ether under air, mercaptan disappears very rapidly, disulfide builds up rapidly and then disappears (Table I and Figure 6). In photoreduction of benzophenone in the related alcohol (2-octanol) oxygen of air led not to an increase, but to a modest decrease in rate, consistent with results in other alcohol systems.[5,20] The sulfur compounds continued to show inhibiting and retarding activity in the presence of air, but to a diminished extent (Figure 5), since they were in due course oxidized (Table I). The greater effectiveness of the sulfur compounds under air in the alcohol system as compared with the ether system probably arises from two factors: (1) the ketone–alcohol system is more sensitive than the ketone–ether system to inhibition by the sulfur compounds, and the effect is observed at lower residual concentrations of sulfur compound; (2) the alcohol–air system may be a less effective oxidant for the sulfur compounds than the ether–air system. It will be of interest to examine the effects of sulfur compounds, in the presence and absence of oxygen, on photochemical and radiation induced reactions in aqueous systems,[26] as also in the presence of amino compounds.[27]

Experimental Section

Benzophenone (Fisher reagent) was recrystallized from petroleum ether (bp 30–60°), mp 48.6–49°. **2-Octanol** (Eastman Organic Chemicals, White Label) was used as received. **2-Mercaptomesitylene** and **2-mesityl disulfide** were prepared as described previously.[28]

Methyl 2-Octyl Ether. Sodium hydride (54% dispersion in mineral oil, 52 g, 1.16 moles, Metal Hydrides) was suspended in 500 ml of ether and 151 g (1.16 moles) of 2-octanol was added. The mixture was refluxed for 3 hr in a flask fitted with a drying tube, and methyl iodide (165 g, 1.16 moles, Fisher reagent) was added; boiling was continued overnight. The mixture was filtered and the filtrate was boiled with potassium metal for several hours and distilled, leading to 120 g (0.83 mole), 72% yield of methyl 2-octyl ether, bp 60–61° (10 mm) (lit.[29] bp 76–77° (40 mm)) **Optically active methyl 2-octyl ether** was prepared from previously prepared[7] optically active 2-octanol (14.5 g, 0.11 mole, $[\alpha]^{22}\mathrm{D}$ −9.4°). The optically active carbinol was added with stirring to a suspension of 6.7 g (0.15 mole) of the sodium hydride dispersion in 25 ml of ether under hydrogen, the mixture was boiled for a few minutes, treated with 28.4 g (0.2 mole) of methyl iodide at room temperature for several hours, and filtered. The filtrate was distilled, leading to optically active methyl 2-octyl ether, 10 g (0.070 mole), 64% yield, bp 164–165°, $\alpha^{22}{}_{\mathrm{obsd}}$ −7.55°, 1 dm, $[\alpha]^{22}\mathrm{D}$ −9.35 (lit.[30] $\alpha^{14}{}_{5461}$ −3.57°, 0.5 dm). The infrared spectrum of the inactive and active ether were identical.

Irradiations were carried out n 15-mm Pyrex Thunberg tubes or sealed Pyrex tubes of similar size mounted vertically in a rotating circular turntable 4 cm from an ultraviolet source. The source was either an Osram Hg lamp, 55 w (two lamps were used designated as No. 1 and 2, respectively) or a G.E. A3 Hg lamp, 85 w. The tubes were housed in an air-cooled chamber; ambient temperature was 35–40°.

Ultraviolet absorption spectra were obtained in ethanol, unless specified otherwise, on a Cary Model 14 recording spectrophotometer. **Infrared spectra** were obtained on Perkin-Elmer Model 21 and 137 instruments. **Optical rotations** were determined on a Zeiss-Winkel polarimeter. **Vapor phase chromatography** was carried out on an Aerograph Model A-90-P instrument. **Melting points** were determined on a Gallenkamp apparatus and are uncorrected.

Procedures. Solutions of 0.50 *M* benzophenone alone and with the indicated concentrations of the sulfur compound were prepared from weighed quantities of benzophenone, 2-mercaptomesitylene, and 2-mesityl disulfide diluted with methyl 2-octyl ether in volumetric flasks. Aliquots (1 ml), were transferred to the irradiation tubes. The solutions were frozen in liquid nitrogen, degassed twice by the freeze–melt technique, and irradiated for stated periods of time. In experiments under atmospheric oxygen, the degassed tubes were opened, shaken with air, and closed for irradiation. After irradiation, the samples were analyzed for remaining benzophenone spectrophotometrically. Preliminary experiments were carried out by ultraviolet spectrometry. For infrared analyses a plot of carbonyl absorbancies at 6.0 μ *vs.* known benzophenone concentrations was constructed, and concentrations of remaining benzophenone after irradiation were determined by comparison with this curve. The plot was constructed from a number of samples prepared by diluting measured volumes of the initial 0.50 *M* benzophenone solution with methyl 2-octyl ether to a volume of 0.2 ml. To each sample a measured amount of chloroform (2 ml) was added and the spectrum was determined.

Analyses for thiol and disulfide were carried out by vapor phase chromatography. Initially, weighed amounts of 1-menthol (*ca.* 0.0020 g) were added to aliquots (1 ml) as internal standard for 2-mercaptomesitylene, and the separation was effected on a column packed with SE 30 (G.E.) 2% on Chromosorb W at 100°, detector temperature 225°. Weighed amounts of carbazole (*ca.* 0.0080 g) were added to aliquots (1 ml) as internal standard for 2-mesityl disulfide and the separation was carried out on a column packed with QF-1 1.5% on Chromosorb W, at 160°, detector temperature 270°. Analyses for both sulfur compounds were carried out before and after stated periods of irradiation, by comparison of the areas under the peaks for the compound and the standard. In later experiments analyses for thiol and disulfide were made by use of suitable calibration curves prepared from known ratios of concentration of the sulfur compounds and these standards.

Effect of 2-Mercaptomesitylene on Formation of Benzpinacol. (1). A solution (0.50 *M*) of 0.45 g (2.5 mmoles) of benzophenone in 5 ml of methyl 2-octyl ether was degassed and irradiated for 66 hr, (lamp No. 1). The precipitate was collected, washed with petroleum ether, and dried under vacuum, 0.14 g, benzpinacol, melting point and mixture melting point with an authentic sample 188–189°. Its infrared spectrum was identical with that of the authentic material. The filtrate was distilled, bp 81° (45 mm), methyl 2-octyl ether, leaving a residue 0.48 g. This was recrystallized from petroleum ether, leading to additional benzpinacol, 0.09 g, 44% total yield. The residue showed infrared absorption at 9 μ, indicative of an ether. It contained two products which we were unable to separate by column chromatography.

(2). A degassed, 5-ml sample of 0.50 *M* benzophenone in methyl 2-octyl ether containing 0.030 g (0.2 mmole) of 2-mercaptomesitylene, 0.040 *M*, was degassed and irradiated for 49 hr. The solution was distilled, leading to methyl 2-octyl ether, bp 163–164°; its infrared spectrum was identical with that of an authentic sample. The residue, benzophenone, was recrystallized from petroleum ether, melting point and mixture melting point 47.7–49.0°, infrared spectrum identical with that of an authentic sample, 0.44 g, 98% recovery.

Reactions in 2-Octanol. A solution of benzophenone (9.11 g) 0.50 *M* in 2-octanol was prepared in a 100-ml volumetric flask. Samples (1 ml) of this solution were irradiated both in the presence and in the absence of air and analyzed for benzophenone. To a portion (20 ml) of the 0.50 *M* benzophenone solution in 2-octanol, 2-mercaptomesitylene (0.030 g, 0.20 mmole, 0.01 *M*) was added. To another portion (20 ml) 2-mercaptomesitylene (0.120 g) was added. Aliquots (1 ml) of the 0.010 and 0.040 *M* 2-mercaptomesitylene solutions were irradiated in the presence of air. Analyses for benzophenone were carried out by infrared spectroscopy.

Effect of Concentration of Methyl 2-Octyl Ether. Samples were prepared by mixing weighed amounts of a 0.50 *M* benzophenone solution in methyl 2-octyl ether with a 0.50 *M* benzophenone solution in benzene. From the weight of pure ether present in each sample the ether concentration was calculated. The samples (1 ml) were degassed, sealed under vacuum, irradiated for 9 hr with lamp No. 2, and analyzed for remaining benzophenone in the 300–350-mμ region.

Quenching by Naphthalene. Samples (1 ml) were prepared by mixing measured volumes of a 0.50 *M* benzophenone solution in methyl 2-octyl ether with portions of a 0.50 *M* benzophenone solution in the same solvent containing 0.0084 *M* naphthalene. The samples were degassed in Thunberg tubes, irradiated under argon with lamp No. 2 for 17.5 hr, and analyzed for remaining benzophenone at 6.0 μ.

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(29) J. Kenyon and R. A. McNicol, *J. Chem. Soc.*, **123**, 1 (1923).
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Experiments in Optically Active Methyl 2-Octyl Ether. (1). a. A solution of benzophenone (0.180 g, 0.20 *M*) in 5 ml of methyl 2-octyl ether ($\alpha^{22}_{\text{obsd}}$ −7.55°, $[\alpha]\text{D}^{22}$ −9.35°) was degassed and irradiated by lamp No. 1 in a Thunberg tube sealed to a 1-dm optical cell. The irradiation was interrupted periodically, the solution was tipped into the cell, and the optical rotation was determined. The solution was then returned into the tube and irradiation was continued. The periods of irradiation and observed rotations were: 0.0 hr, −7.21°; 9 hr, −7.26°; 32 hr, −7.28°; 125 hr, −7.17°; 147 hr, −7.16°; 226 hr, −7.18°. The mixture was distilled and the ether was recovered, 4.5 ml, bp 115–118° (70 mm), $\alpha^{22}_{\text{obsd}}$ −7.21°, $[\alpha]\text{D}^{22}$ −8.95°.

b. A solution of benzophenone (0.180 g, 0.22 *M*), 2-mercaptomesitylene (0.015 g, 0.022 *M*), and 2-mesityl disulfide (0.015 g, 0.011 *M*) in the methyl 2-octyl ether (4.5 ml) recovered from the preceding experiment was irradiated and observed as in the preceding experiment: 0.0 hr, −6.96°; 4.25 hr, −6.88°; 19.5 hr, −6.66°; 40.5 hr, −6.43°; 80.5 hr, −6.00°; 110 hr, −5.78°; 151 hr, −5.42°; 187 hr, −5.37°. The mixture was distilled and the following fractions were collected: (i) 0.4 ml, bp 120–150°; (ii) 1 ml, bp 161–165°; (iii) 3 ml, bp 164–165°. Samples ii and iii had infrared spectra identical with that of methyl 2-octyl ether. The rotation of iii was $\alpha^{23}_{\text{obsd}}$ −5.45°, $[\alpha]\text{D}^{23}$ −6.75°.

(2). A mixture of optically active and inactive methyl 2-octyl ether, $\alpha^{22}_{\text{obsd}}$ − 4.52°, 1 dm, was used in these experiments. Solutions were prepared as follows: (a) benzophenone (0.45 g, 0.50 *M*), 2-mercaptomesitylene (0.015 g, 0.020 *M*), and 2-mesityl disulfide (0.015 g, 0.010 *M*) in methyl 2-octyl ether (5 ml); (b) benzophenone (0.23 g, 0.50 *M*) in methyl 2-octyl ether (2.5 ml); (c) 2-mercaptomesitylene (0.0075 g, 0.020 *M*) and 2-mesityl disulfide (0.0075 g, 0.010 *M*) in methyl 2-octyl ether (2.5 ml). Each solution was irradiated in a Thunberg tube sealed to an optical cell. The optical cells were 1 dm for tube a and 0.5 dm for tubes b and c. The tubes were degassed and irradiated by lamp No. 1. The observed optical rotations after a stated periods of irradiation were: (in solution a) 0.0 hr, −4.31°; 21.5 hr, −4.06°; 54.5 hr, −3.88°; 129 hr, −3.55°; 148 hr, −3.45°; (in solution b) 0.0 hr, −2.15°; 4.3 hr, −2.16°; 14.3 hr, −2.20° (benzpinacol precipitating); 254 hr, −2.10° (decanted); (in solution c) 0.0 hr, −2.17°; 21.5 hr, −2.18°; 54.5 hr, −2.17°; 87.2 hr, −2.15°; 129 hr, −2.18°. After irradiation, the remaining methyl 2-octyl ether was recovered from each solution by distillation and the rotations were determined in a 1-dm cell at 22°: from solution a, −3.71°; from solution b, −4.04°; from solution c, −4.37°. The ether from solution b was examined by vapor phase chromatography on a 5 ft × 0.25 in. column packed with 1.5% QF-1-0065 (Dow-Corning) on Chromosorb W at three column temperatures (80, 90, 100°), detector temperature 270°. Only a single peak, corresponding to methyl 2-octyl ether, was observed. Under the same conditions (column temperature 100°), a mixture of methyl 2-octyl ether and 2-octanol are easily fractionated, giving two distinct peaks.

A mixture of optically active and inactive methyl 2-octyl ether, $\alpha^{22}_{\text{obsd}}$ −4.58°, 1 dm, was used for the preparation of two samples: (a) 2-mercaptomesitylene (0.0060 g, 0.020 *M*) and 2-mesityl disulfide (0.0060 g, 0.010 *M*) in methyl 2-octyl ether (2 ml); (b) pure methyl 2-octyl ether. The samples were placed in Thunberg tubes, degassed, and irradiated with the G.E. lamp. Sample a was irradiated for a period of 58 hr. The ether was recovered by distillation, bp 162–164°, $\alpha^{22}_{\text{obsd}}$ −4.59°, 1 dm. Sample b was irradiated for 49 hr and distilled, $\alpha^{22}_{\text{obsd}}$ −4.57°, 1 dm.

Deuterium Exchange. A solution of 2-octanone (2.0 g, 0.016 mole, Eastman Organic Chemicals) in anhydrous ether (5 ml) was added with stirring to a suspension of lithium aluminum deuteride (0.50 g, 0.03 mole) in anhydrous ether (10 ml). Water (2 ml) was added, the mixture was filtered and washed with ether, and the filtrate was dried over magnesium sulfate. The nmr spectrum of the distillate, **2-octanol-2-D** (bp 163–164°), obtained in carbon tetrachloride (10% solution) possessed a methyl singlet as compared with the doublet of deuterium-free 2-octanol, indicating absence of the carbinol C–H. **Methyl 2-octyl ether-2-D** was prepared from 2-octanol-2-D as described previously for the deuterium-free compound.

Infrared spectra were obtained in 0.5-mm sodium chloride cells for known weights of methyl 2-octyl ether-2-D in carbon tetrachloride against corresponding weights of the deuterium-free ether in the same solvent. A plot of the absorbancies of the carbon–deuterium bond at 4.75 μ *vs.* the corresponding concentrations of methyl 2-octyl ether-2-D was prepared and used in the determination of deuterium content in the ether recovered in the experiments below. From this plot, the extinction coefficient for methyl 2-octyl ether-2-D at 4.75 μ was calculated to be 9.2.

t-Butyl alcohol (18.5 g, 0.25 mole, Eastman Organic Chemicals, White Label) was added with stirring to a 54% sodium hydride dispersion in mineral oil (8.0 g, 0.33 mole, Metal Hydrides) suspended in anhydrous ether (250 ml) and was refluxed with exclusion of moisture for 1 hr. Deuterium oxide (6.6 g, 0.33 mole, Bio-Rad Laboratories) was added, and the mixture was distilled leading to ***t*-butyl alcohol-OD** (14.0 g, 0.18 mole), 72% yield, bp 83–84°. The product exhibited a weak O–H absorption band at 3.0 and a strong O–D band at 4.0 μ.

The following solutions, prepared in 1:1 methyl 2-octyl ether (1 ml) and *t*-butyl alcohol-OD (1 ml), were degassed and irradiated in Thunberg tubes with lamp No. 1 (samples a and b for 225 hr, sample c for 355 hr): (a) 0.020 *M* 2-mercaptomesitylene; (b) 0.25 *M* benzophenone; (c) 0.25 *M* benzophenone and 0.010 *M* 2-mesityl disulfide. Methyl 2-octyl ether, recovered from sample c, placed in a 0.5-mm cell *vs.* pure ether, exhibited a strong C–D absorption band at 4.7 μ, indicating the presence of 0.36 *M*, 6.4% deuterated compound. Ether recovered from samples a and b did not show definite absorption at 4.7 μ.

The following irradiations were with the G.E. lamp. (a) A solution of 0.091 g (0.25 *M*) of benzophenone and 0.0060 g (0.020 *M*) of 2-mercaptomesitylene in 1 ml of methyl 2-octyl ether and 1 ml of *t*-butyl alcohol-OD was degassed, irradiated for 48.5 hr, and distilled. *t*-Butyl alcohol (bp 82–84°) and methyl 2-octyl ether (bp 162–164°) were recovered. The infrared spectrum of the ether, taken against the pure ether, showed C–D absorption at 4.75 μ, absorbancy 0.192, corresponding to 0.40 *M*, 7.1% deuterated ether.

(b) A solution (0.25 *M*) of benzophenone in 1 ml of methyl 2-octyl ether and 1 ml of *t*-butyl alcohol-OD was irradiated for 48 hr and distilled, leading to methyl 2-octyl ether, with absorption at 4.75 μ, absorbancy 0.044, corresponding to 0.087 *M*, 1.6% deuterated ether.

(c) A solution of 0.0060 g (0.020 *M*) of 2-mercaptomesitylene and 0.0060 g (0.010 *M*) of 2-mesityl disulfide in 1 ml of methyl 2-octyl ether and 1 ml of *t*-butyl alcohol-OD was irradiated for 58 hr, and distilled. The recovered methyl 2-octyl ether showed minor absorption at 4.75 μ.

(d) A solution of 1 ml of methyl 2-octyl ether and 1 ml of *t*-butyl alcohol-OD was irradiated for 48 hr, distilled, and examined. The recovered ether, bp 162–164°, showed no absorption at 4.75 μ.

(e) A solution of benzophenone and 2-mercaptomesitylene in methyl 2-octyl ether and *t*-butyl alcohol-OD, identical with that of a, was degassed, irradiated for 51 hr, and distilled. *t*-Butyl alcohol was collected (bp 82–84°) and purified by vapor phase chromatography on a 7 ft × 0.25 in. column packed with 20% adipate resin on Chromosorb W. Its infrared spectrum was obtained in a 0.5-mm cell against *t*-butyl alcohol, and showed C–D absorption.

(f) A solution of 0.5 *M* benzophenone and 0.04 *M* 2-mercaptomesitylene in 1 ml of *t*-butyl alcohol-OD was irradiated for 51 hr. The *t*-butyl alcohol was distilled (bp 82–84°) and the infrared spectrum was taken against *t*-butyl alcohol in a 0.5-mm cell. Possible absorption at 4.75 μ was masked by strong O–D absorption at 4–4.5 μ. The alcohol (0.44 g, 5.8 mmoles) was dissolved in ether, heated in 0.28 g (5.8 mmoles) of 54% sodium hydride, then with water, and distilled. The recovered alcohol (bp 82–84°) showed strong C–D absorption at 4.7 μ.

Degradation of Methyl 2-Octyl Ether-2-D. The partially deuterated methyl 2-octyl ether recovered from solution a, above, was refluxed with 57% hydriodic acid (5 ml, Fisher reagent) for 3 hr. Water (10 ml) was added and the mixture was distilled until 7 ml was collected. The distillate was treated with sodium thiosulfate and the lower layer was separated, 2-octyl iodide (1.0 g, 4.1 mmoles), 74% yield. The infrared spectrum of the iodide was obtained *vs.* a sample prepared in the same manner from deuterium-free methyl 2-octyl ether, and exhibited C–D absorption at 4.75 μ. The partially deuterated iodide was added to a solution of trimethylamine oxide (0.31 g, 4.1 mmoles) in chloroform (15 ml) and refluxed for 24 hr. Infrared spectra obtained on aliquots from the reaction mixture during this period indictated progressive formation of a carbonyl compound with absorption at 5.85 μ. The solution was subsequently shaken with 2 *N* hydrochloric acid (15 ml) and the chloroform layer was washed with 5% sodium bicarbonate, dried over sodium sulfate, and concentrated. The residue was fractionated by vapor phase chromatography on a column packed with 20% SE 30 (G.E.) on Chromosorb W. The infrared spectrum of the collected ketonic product was obtained *vs.* authentic 2-octanone and exhibited very slight evidence of carbon-bound deuterium.