

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, BRANDEIS UNIVERSITY, WALTHAM 54, MASS.]

## Inhibition of Light-Induced Reactions by Mercaptans and Disulfides. Benzophenone-Benzhydrol and Acetophenone- $\alpha$ -Methylbenzyl Alcohol<sup>1</sup>

BY SAUL G. COHEN, DANIEL A. LAUFER, AND WARREN V. SHERMAN

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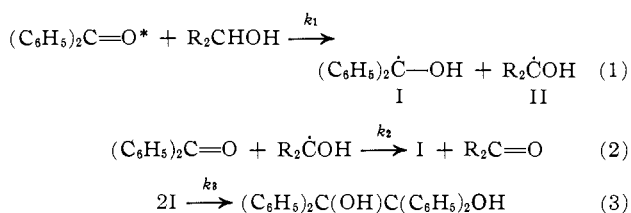
Photoreductions in benzene of  $(C_6H_5)_2C=O$  by  $(C_6H_5)_2CHOH$  and of  $C_6H_5COCH_3$  by  $C_6H_5CH(OH)CH_3$ , in which only a single intermediate radical,  $(C_6H_5)_2\dot{C}-OH$  and  $C_6H_5\dot{C}(OH)CH_3$ , respectively, is formed, are retarded by 2-mercaptomesitylene-mesityl disulfide in  $10^{-3}$ – $10^{-2}$  *M* concentration. The one radical is oxidized to ketone by disulfide, reduced to carbinol by mercaptan



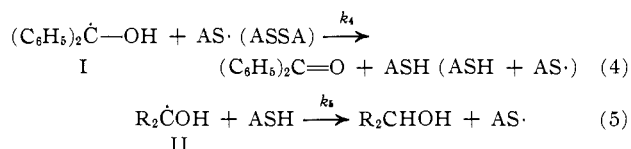
Mercaptan and disulfide show equal effectiveness, each being converted to the same mixture of the two during the irradiation. The sulfur compounds are used repeatedly, each molecule negating the chemical action of many quanta. Inhibition of photoreduction of  $(C_6H_5)_2C=O$  by  $(CH_3)_2CHOH$  leads to  $(CH_3)_2CDOH$ . Retardation of reduction of  $C_6H_5COCH_3$  in optically active  $C_6H_5CH(OH)CH_3$  leads to racemization, and in  $C_6H_5CH(OD)CH_3$  leads to  $C_6H_5CD(OH)CH_3$ . The pairs  $(C_6H_5)_2C=O$  and  $(C_6H_5)_2CHOH$ ,  $C_6H_5COCH_3$  and  $C_6H_5CH(OH)CH_3$ ,  $(C_6H_5)_2C=O$  and  $(CH_3)_2CHOH$ ,  $C_6H_5COCH_3$  and  $(CH_3)_2CHOH$  show increasing sensitivity in this order to the retarding action of the sulfur compounds, the last two pairs being quite similar. The ease of transfer of a hydrogen atom from mercaptan to the alcohol-derived radical dominates the order of reactivity in these systems. Rate constants for transfer of hydrogen from  $(CH_3)_2CHOH$  and from  $C_6H_5CH(OH)CH_3$  to triplet acetophenone, and from  $(CH_3)_2CHOH$  to triplet benzophenone, are in the range  $10^5$ – $10^6$  l. mole<sup>-1</sup> sec.<sup>-1</sup>. Rate constants for transfer of hydrogen from 2-mercaptomesitylene to acetophenone-ketyl radical and to benzophenone-ketyl radical, and from benzyl mercaptan to acetophenone-ketyl radical are in the range  $10^3$ – $10^4$  l. mole<sup>-1</sup> sec.<sup>-1</sup>.

### Introduction

We have reported that aromatic mercaptans and disulfides, in low concentration, are effective retarders and inhibitors of the photochemical reduction of benzophenone to benzpinacol by secondary alcohols,<sup>2</sup> and are somewhat less effective in retarding the reduction in alkaline medium to benzhydrol.<sup>3</sup> The reduction to benzpinacol may proceed *via* the following sequence of reactions,<sup>4</sup> starting with abstraction of hydrogen from the carbinol carbon by the lowest excited triplet<sup>5</sup> state of benzophenone.



Reduction of benzophenone to benzpinacol is retarded by physical quenchers of the triplet state of benzophenone,<sup>6,7</sup> but we have concluded that<sup>2,3</sup> retardation by the sulfur compounds results from chemical reactions which occur after the initial abstraction of hydrogen by the benzophenone triplet



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

(2) S. G. Cohen, S. Orman, and D. A. Laufer, *J. Am. Chem. Soc.*, **84**, 3905 (1962).

(3) S. G. Cohen and W. V. Sherman, *ibid.*, **85**, 1642 (1963).

(4) J. N. Pitts, Jr., R. L. Letsinger, R. P. Taylor, J. M. Patterson, G. Rectenwald, and R. B. Martin, *ibid.*, **81**, 1068 (1959).

(5) G. S. Hammond and W. M. Moore, *ibid.*, **81**, 6334 (1959).

(6) (a) W. H. Moore, G. S. Hammond, and R. P. Foss, *ibid.*, **83**, 2789 (1961); (b) G. S. Hammond and P. A. Leermakers, *J. Phys. Chem.*, **66**, 1148 (1962).

(7) W. H. Moore and M. Ketchum, *J. Am. Chem. Soc.*, **84**, 1368 (1962).

Intermediate radical I is reconverted to benzophenone by reaction with thiyl radical or disulfide and radical II is converted to alcohol by mercaptan, while disulfide and mercaptan are regenerated and function repeatedly to negate the chemical reactions of many quanta.

Support for this mechanism is given by the observations: (1) The reducing alcohol, when optically active, is racemized during irradiation in the presence of benzophenone and sulfur compound, the reduction being retarded. It is not racemized when the benzophenone is reduced normally in the absence of sulfur compounds, nor is it racemized by irradiation in the presence of the sulfur compounds in the absence of benzophenone.<sup>2</sup> (2) The sulfur compounds show equal effectiveness in retarding reduction whether present initially as mercaptan or as disulfide, and each is converted to the same mixture of the two during the inhibition. Oxidation-reduction reactions occur and radicals I and II are formed during the inhibition, but they may not lead to benzpinacol.<sup>2</sup> (3) A physical quencher, naphthalene, acting on the common precursor, triplet benzophenone, shows equal effectiveness in retarding reduction to benzpinacol and to benzhydrol. The mercaptan-disulfide system shows unequal effectiveness in retarding the two reactions, indicating that it is reacting with different chemical species<sup>3</sup> in the two reactions, the radical I and the radical ion Ia,  $(C_6H_5)_2\dot{C}-O^-$ . (4) Mercaptans do not retard, but in fact catalyze effectively by hydrogen transfer reactions, the benzophenone-sensitized light-induced decarbonylation of aldehydes.<sup>8</sup> The mercaptans thus are not quenchers for benzophenone. (5) The quencher naphthalene has no effect on the <sup>60</sup>Co- $\gamma$ -ray induced reduction of benzophenone in 2-propanol to benzpinacol, while aromatic mercaptans and disulfides are effective inhibitors.<sup>2,9</sup> The triplet state of benzophenone is not important in the high-energy radiation-induced reaction, the free

(8) J. D. Berman, J. H. Stanley, W. V. Sherman, and S. G. Cohen, *ibid.*, **85**, 4010 (1963).

(9) W. V. Sherman and S. G. Cohen, *ibid.*, **86**, 2390 (1964).

radicals are, and the sulfur compounds act *via* reactions 4 and 5.

This important mechanism of inhibition of radiation-induced reactions has now been examined in further detail: (1) Reactions have been carried out with deuterium labeling in the hydroxyl of alcohols to establish that hydrogen is removed from and returned to the carbinol carbon in inhibited reactions, as is implied by the racemization studies. (2) The reactions have been studied in systems in which only one intermediate radical is formed, *i.e.*, benzophenone-benzhydrol,<sup>6</sup> leading to radical I,  $(C_6H_5)_2\dot{C}OH$ , and acetophenone- $\alpha$ -methylbenzyl alcohol, leading to radical III,  $C_6H_5\dot{C}(CH_3)OH$ . Retardation in such systems requires that the same radical, I or III, undergo reduction by mercaptan and oxidation by thiyl radical or disulfide. The previous system led to two different radicals,<sup>5</sup> one of which (I) might be more readily oxidized, while the other (II) was more readily reduced. Experiments are now reported in these two areas, introductory ones with benzophenone, more detailed experiments with acetophenone.

### Results and Discussion

**Benzophenone-2-Propanol-OD.**—Samples of 2-propanol were prepared (a) labeled with deuterium in the hydroxyl, by hydrolysis of di-2-propyl sulfite by  $D_2O$ , characterized by  $-O-D$  absorption at 3.7 and 3.9  $\mu$ ; and (b) labeled with deuterium on the carbinol carbon, by reduction of acetone with lithium aluminum deuteride, characterized by  $C-D$  absorption bands at 4.6 and 4.8  $\mu$ . Solutions of 0.5 *M* benzophenone in 2-propanol-OD containing (i) no additive, (ii)  $1.3 \times 10^{-2}$  *M* naphthalene, and (iii)  $5 \times 10^{-3}$  *M* mesityl disulfide were degassed and irradiated for 24 hr. The 2-propanol fractions were collected and their infrared spectra were obtained against 2-propanol-OD. Distillates from i and ii showed no absorption due to  $C-D$ , while that from iii showed absorption at 4.6 and 4.8  $\mu$ . Irradiation in the presence of 0.01 *M* mesityl disulfide was carried out for 69 hr. (iv). 2-Propanol was isolated from a portion of the distillate by vapor phase chromatography; its infrared spectrum against 2-propanol-OD showed a  $C-D$  band at 4.8  $\mu$ . A portion of the distillate was oxidized to acetone, the infrared spectrum was taken against acetone, and no  $C-D$  band was observed.

These results support the proposed mechanism, indicating (i) the reaction of eq. 1 is irreversible as this photoreduction is usually carried out; (ii) retardation by naphthalene is due to quenching of triplet benzophenone and does not affect the free radicals I and II; (iii) retardation by sulfur compounds involves transfer of hydrogen (deuterium) from RSH (RSD) to a carbon atom of the alcohol-derived radical; and (iv) this transfer is to the carbinol carbon atom, the deuterium being removed when the recovered alcohol is oxidized to ketone.

**Benzophenone-Benzhydrol.**—The photoreduction of 0.5 *M* benzophenone by 1.0 *M* benzhydrol in benzene solution, leading to the one intermediate radical I, was studied, and the effect of mesityl disulfide was examined. The reduction of benzophenone by benzhydrol was essentially zero order over the range in which data were collected, up to 50% reaction, alone and at decreased rate in the presence of  $5 \times 10^{-3}$  *M* mesityl

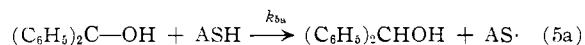
disulfide. The rates of reduction at varying concentrations of disulfide,  $0.8-8.3 \times 10^{-3}$  *M*, were determined from the extents of reduction after irradiation for 3 hr. The runs containing initially 3.4 and  $4.0 \times 10^{-3}$  *M* disulfide were found to contain 5.4 and  $6.5 \times 10^{-3}$  *M* 2-mercaptomesitylene after this irradiation. The rates of these photoreductions are summarized in Table I.

TABLE I

EFFECT OF MESITYL DISULFIDE (MSSM) ON PHOTOREDUCTION OF 0.5 *M* BENZOPHENONE BY 1.0 *M* BENZHYDROL IN BENZENE

MSSM, 10 <sup>3</sup> <i>M</i>	$-d((C_6H_5)_2C=O)/dt,$ 10 <sup>2</sup> <i>M</i> hr. <sup>-1</sup>
...	9.2
0.8	8.3
2.3	6.7
5.1	4.3
8.3	3.0

Mesityl disulfide was 80% reduced to the mercaptan during the irradiation and the mixture retarded the reduction, radical I apparently being both oxidized by thiyl radical or disulfide according to eq. 4 and being reduced to benzhydrol in reaction 5a. Cogent evidence



that one radical may undergo both reactions will be seen in the next section. The sulfur compound was less effective in retarding reduction by 1 *M* benzhydrol than by solvent 2-propanol,<sup>2</sup>  $9 \times 10^{-3}$  and  $1.2 \times 10^{-3}$  *M* thiyl group, respectively, being required to halve the rates of reduction. Since the rate constant for oxidation of radical I by thiyl radical or disulfide may be the same in the two processes (reaction 4), the lesser effectiveness of the sulfur compounds in the benzhydrol system may reflect a lower rate constant,  $k_{5a}$ , for reduction of radical I by mercaptan than that of reduction of the radical from 2-propanol (II),  $k_5$ . This might be expected, radical II being less stabilized by resonance and a more effective hydrogen abstractor. This is reflected in the higher steady-state concentration of mercaptan observed during irradiation of the benzhydrol system, an 8:1 molar ratio of mercaptan to disulfide being observed as compared with a 5:1 ratio in the benzophenone-2-propanol system.<sup>2</sup> Steady-state ratios of mercaptan and disulfide are achieved as the rates of reactions 4 and 5 or 4 and 5a become equal. A higher relative concentration of mercaptan is required when benzhydrol is the reducing agent and radical II must be reduced, and a lower proportion of disulfide remains when the two rates become equal. The rates of reaction 4' and 5a both become lower in the benzhydrol system than the rates of reactions 4 and 5 in the 2-propanol system; these reactions compete less favorably with that leading to product, reaction 3, and higher initial concentrations of sulfur compound are required to achieve the same degree of retardation as compared with the benzophenone-2-propanol system. A kinetic analysis is given below.

**Acetophenone- $\alpha$ -Methylbenzyl Alcohol.**—Ultraviolet irradiation of this system leads to the *dl*- and *meso*-forms of 2,3-diphenyl-2,3-butylene glycol and, if optically active  $\alpha$ -methylbenzyl alcohol is used, the pinacol has no optical activity and the residual alcohol

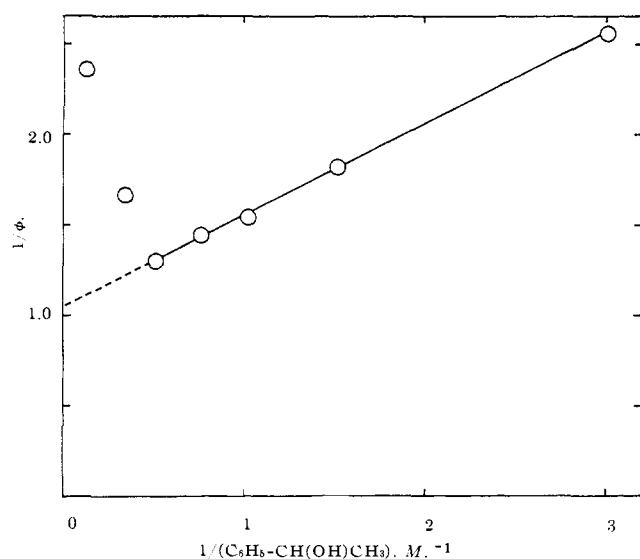
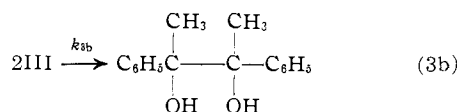
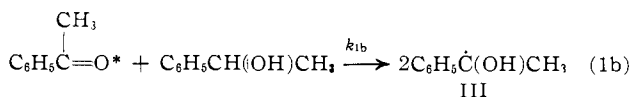


Fig. 1.—Photoreduction of 0.5 *M* acetophenone by  $\alpha$ -methylbenzyl alcohol in benzene; effect of concentration of alcohol.

is little, if at all, racemized.<sup>10</sup> Acetophenone triplet<sup>11,12</sup> and reactions analogous to those of the benzophenone-benzhydrol<sup>6</sup> system may be involved.



The kinetics of ultraviolet light induced reduction of 0.5 *M* acetophenone by 3 *M* DL- $\alpha$ -methylbenzyl alcohol in benzene were followed by measurement of concentration of residual acetophenone by infrared spectrophotometry. The reaction was zero order and the quantum yield, for unfiltered light, ferrous oxalate actinometer, was 0.60. The rates of reduction were then determined as a function of concentration of the carbinol over the range 0.33–8.30 *M*, and comparative quantum yields were calculated. The results, corrected for change in intensity of the light source, are summarized in Table II and a plot of  $1/\phi$  against  $1/(\text{C}_6\text{H}_5\text{CH}(\text{OH})\text{CH}_3)$  is given in Fig. 1.

TABLE II  
PHOTOREDUCTION OF 0.50 *M* ACETOPHENONE BY  
DL- $\alpha$ -METHYLBENZYL ALCOHOL IN BENZENE

( $\text{C}_6\text{H}_5\text{CH}(\text{OH})\text{CH}_3$ ), <i>M</i>	$-\text{d}(\text{C}_6\text{H}_5\text{COCH}_3)/\text{dt}$ , $10^2 \times \text{M hr.}^{-1}$	Quantum yield, $\phi$
0.33	0.67	0.39
.66	0.94	.55
.98	1.11	.65
1.32	1.17	.69
1.96	1.31	.77
2.94	1.08	.60
8.30 <sup>a</sup>	0.72	.42

<sup>a</sup> Pure alcohol, no benzene.

The data for solutions up to 2 *M* carbinol lie on a line which may be extrapolated to  $\phi = 1$  for high concentration of carbinol, as was found for the benzophenone-

(10) C. Weizmann, E. Bergmann, and Y. Hirschberg, *J. Am. Chem. Soc.*, **60**, 1530 (1938).

(11) G. N. Lewis and M. Kasha, *ibid.*, **66**, 2100 (1944).

(12) D. S. McClure and P. L. Hanst, *J. Chem. Phys.*, **23**, 1772 (1955).

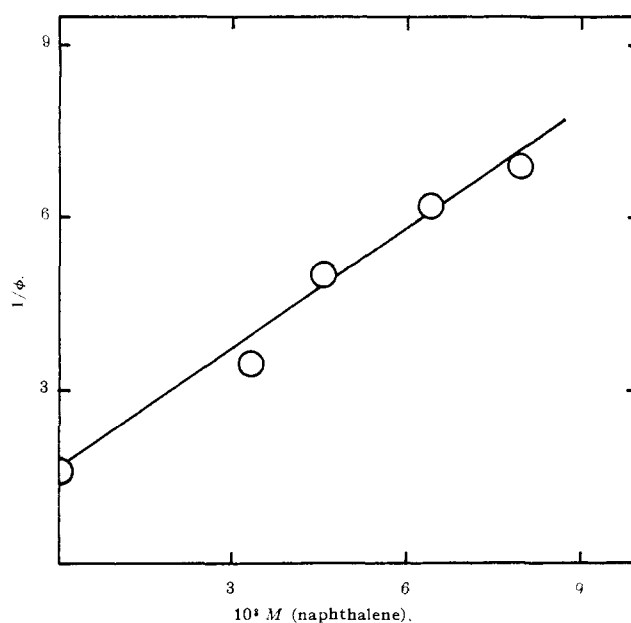


Fig. 2.—Photoreduction of 0.5 *M* acetophenone by 3 *M*  $\alpha$ -methylbenzyl alcohol in benzene; effect of naphthalene.

benzhydrol system,<sup>6a</sup> which had been studied only up to 1.0 *M* benzhydrol. At higher concentration (2.94 *M*) of  $\alpha$ -methylbenzyl alcohol and in the pure carbinol we find somewhat lower, rather than higher, rates, and these data do not lie on the extrapolated line. The deviation may be due to increased viscosity; variations in rates of photodissociation and reduction of mesityl disulfide have been attributed to changes in viscosity.<sup>13</sup> The linear portion fits an equation<sup>6a</sup> of type 6

$$1/\phi = 1 + \frac{k_{db}}{k_{1b}(\text{C}_6\text{H}_5\text{CH}(\text{OH})\text{CH}_3)} \quad (6)$$

where  $k_{db}$  refers to self- or medium-quenching of the triplet of acetophenone, and  $k_{1b}$  to abstraction of  $\alpha$ -hydrogen from  $\alpha$ -methylbenzyl alcohol by triplet acetophenone. The value of  $k_{db}/k_{1b}$  is 0.5, indicating that the photoreduction would be very low at low concentrations of carbinol. The corresponding value<sup>6</sup> for benzophenone-benzhydrol in benzene is 0.050.

The quenching effect of naphthalene<sup>14</sup> was examined. It was effective in the  $10^{-3}$  *M* range; the results are summarized in Table III and Fig. 2.

TABLE III  
EFFECT OF NAPHTHALENE ON THE PHOTOREDUCTION OF  
0.50 *M* ACETOPHENONE BY 2.94 *M* DL- $\alpha$ -METHYLBENZYL  
ALCOHOL IN BENZENE

(Naphthalene), $10^3$ <i>M</i>	$-\text{d}(\text{C}_6\text{H}_5\text{COCH}_3)/\text{dt}$ , $10^2 \text{ M hr.}^{-1}$	Quantum yield, $\phi$
0.0	1.13	0.60
3.3	0.53	.29
4.5	.36	.20
6.4	.29	.16
8.0	.26	.14

The quantum yield may be expressed by an equation of type 7

$$1/\phi = 1 + \frac{k_{db} + k_q(Q)}{k_{1b}(\text{C}_6\text{H}_5\text{CH}(\text{OH})\text{CH}_3)} \quad (7)$$

(13) Y. Schaafsma, A. F. Bickel, and E. C. Kooyman, *Tetrahedron*, **10**, 76 (1960).

(14) A. Terenin and V. Ermolaev, *Trans. Faraday Soc.*, **52**, 1042 (1955).

in which  $k_q$  is the rate constant for quenching of triplet acetophenone by naphthalene and is very large compared with  $k_{db}$ . The concentration of  $\alpha$ -methylbenzyl alcohol was essentially constant during these measurements and the linear plot of  $1/\phi$  against concentration of naphthalene, Fig. 2, is obtained.

The effect of 2-mercaptomesitylene and mesityl disulfide in retarding the photoreduction of 0.5 *M* acetophenone in 3.0 *M*  $\alpha$ -methylbenzyl alcohol was examined. The photoreductions remained zero order in the presence of the sulfur compounds and the mercaptan and disulfide had equivalent activity per thiyl group in retarding the reduction, as had been found in the benzophenone-2-propanol system.<sup>2</sup> The rate of reduction was halved by  $6 \times 10^{-3}$  *M* thiyl group, as compared with  $3 \times 10^{-3}$  *M* naphthalene in this system,  $9 \times 10^{-3}$  *M* thiyl group in the benzophenone-benzhydrol system, and  $1.2 \times 10^{-3}$  *M* thiyl group in benzophenone-2-propanol.<sup>2</sup> The results are summarized in Table IV.

TABLE IV  
EFFECT OF 2-MERCAPTOMESITYLENE (MSH) AND MESITYL DISULFIDE (MSSM) ON PHOTOREDUCTION OF 0.5 *M* ACETOPHENONE BY 3.0 *M*  $\alpha$ -METHYLBENZYL ALCOHOL IN BENZENE

(MSH) <sub>i</sub> , <sup>a</sup> 10 <sup>3</sup> <i>M</i>	(MSSM) <sub>i</sub> , <sup>a</sup> 10 <sup>3</sup> <i>M</i>	$-d(C_6H_5COCH_3)/dt$ , 10 <sup>2</sup> <i>M</i> hr. <sup>-1</sup>	Quantum yield, <sup>b</sup> $\phi$
0	0	1.08	0.60
1.25	..	1.03	.49
2.44	..	0.88	.44
5.75	..	.56	.27
9.94	..	.40	.19
20.3	..	.09	.04
..	0.76	.90	.45
..	1.50	.75	.44
..	2.00	.66	.39
..	2.04	.67	.33
..	2.51	.54	.32
..	2.66	.55	.26
..	3.01	.42	.25
..	3.51	.39	.23
..	4.02	.35	.21

<sup>a</sup> Initial concentrations of thiol or disulfide. <sup>b</sup> Quantum yields are calculated from the rates, corrected for variation in lamp output.

The equal retarding effectiveness of mercaptan and disulfide in this system is accounted for, as before,<sup>2</sup> by comparatively rapid conversion of each sulfur compound to the same equilibrium concentration of the two during irradiation. Aliquots of separate benzene solutions containing 0.5 *M* acetophenone and 3.0 *M*  $\alpha$ -methylbenzyl alcohol and (a) 0.02 *M* mesityl disulfide and (b) 0.04 *M* 2-mercaptomesitylene were irradiated and analyzed by gas chromatography for mercaptan and disulfide as a function of time of irradiation. Each type of solution was converted to the same solution, containing about 77% of the thiyl groups as mercaptan. The results are summarized in Fig. 3. Oxidation of part of the mercaptan to disulfide and reduction of part of the disulfide to mercaptan imply conversion of both acetophenone and  $\alpha$ -methylbenzyl alcohol to the radical III,  $C_6H_5\dot{C}(OH)CH_3$ , the intermediate required for formation of the pinacol, eq. 3b. Since mercaptan and disulfide do not appear to be physical quenchers for benzophenone, acetophenone, and 2-octanone,<sup>8</sup> it seems likely that reaction 1b also leads to radical III in the presence of the sulfur compounds.

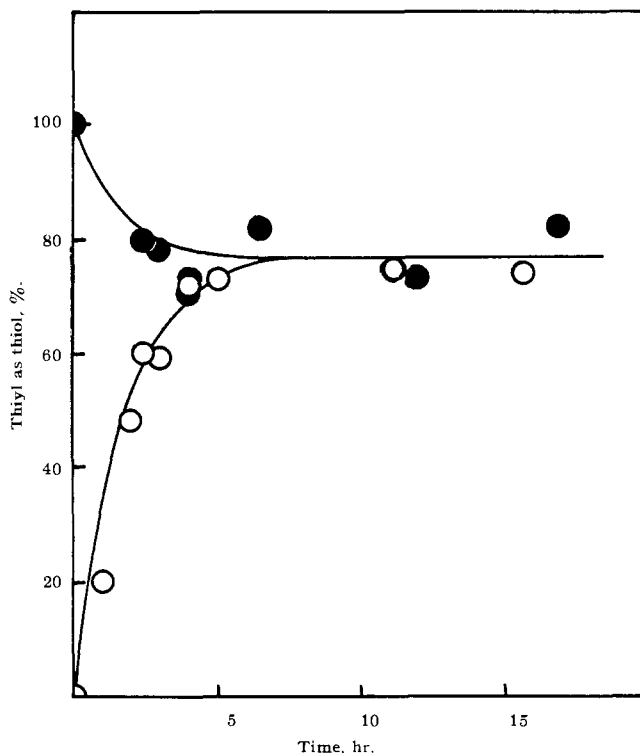
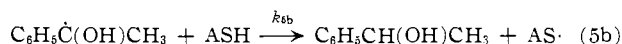
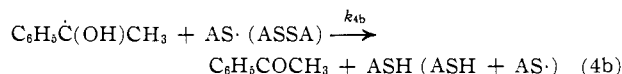


Fig. 3.—Equilibration of 2-mercaptomesitylene and mesitylene disulfide, ultraviolet irradiation of 0.5 *M* acetophenone and 3 *M*  $\alpha$ -methylbenzyl alcohol in benzene: ●, initially 0.04 *M* 2-mercaptomesitylene; ○, initially 0.02 *M* mesityl disulfide.

The retardation caused by low concentrations of the sulfur compounds may be attributed, as before,<sup>2</sup> to their repeated use and regeneration in rapid hydrogen transfer reactions, in this case converting radical III to the two starting materials, acetophenone and  $\alpha$ -methylbenzyl alcohol, eq. 4b and 5b.



Evidence for this is seen in the results of irradiation of benzene solutions of 0.5 *M* acetophenone and 3.0 *M* L-(−)- $\alpha$ -methylbenzyl alcohol. Long irradiation of this solution led to a small decrease in specific rotation of the recovered alcohol, 2°, from initial  $[\alpha]^{20}_D$  44° to final 42°. Irradiation of the alcohol and  $2.9 \times 10^{-2}$  *M* 2-mercaptomesitylene in the absence of added acetophenone led to a 4° decrease in specific rotation of the recovered alcohol, about 10% racemization; however, some acetophenone was detected in the recovered alcohol by vapor phase chromatography. Irradiation of the alcohol solution in the presence of  $1.0 \times 10^{-2}$  *M* mesityl disulfide led to a 2° decrease in specific rotation. However, when the three components were combined, 0.5 *M* acetophenone, 3.0 *M* (−)- $\alpha$ -methylbenzyl alcohol, and (a)  $2.5 \times 10^{-2}$  *M* 2-mercaptomesitylene or (b)  $1.1 \times 10^{-2}$  *M* mesityl disulfide, formation of the pinacol was strongly retarded, and 28% racemization of the alcohol occurred, the specific rotation of recovered alcohol falling in each case by 13° from an initial  $[\alpha]^{20}_D$  46°. The results are summarized in Table V.

The uninhibited rate of reduction under the conditions of these experiments was  $1.11 \times 10^{-2}$  mole l.<sup>-1</sup> hr.<sup>-1</sup>. The average concentration of acetophenone dur-

TABLE V  
ULTRAVIOLET IRRADIATION, 3.0 M L(-)- $\alpha$ -METHYLBENZYL  
ALCOHOL, IN BENZENE, 192 HR.

Expt.	C <sub>6</sub> H <sub>5</sub> COCH <sub>3</sub> , M	Inhibitor, 10 <sup>2</sup> × M	-[ $\alpha$ ] <sub>D</sub> (-)-C <sub>6</sub> H <sub>5</sub> CH(OH)CH <sub>3</sub> - Distilled	Purified
62	0.50	0	42 <sup>oa</sup>	..
66	..	2.9 <sup>b</sup>	40 <sup>a</sup>	40 <sup>e</sup>
18A	..	1.0 <sup>d</sup>	42 <sup>a</sup>	..
18	0.52	2.5 <sup>b</sup>	28 <sup>a</sup>	31 <sup>e</sup>
85	.52	2.6 <sup>b</sup>	30 <sup>e</sup>	33 <sup>f</sup>
33	.52	1.1 <sup>d</sup>	30 <sup>e</sup>	34 <sup>f</sup>

<sup>a</sup> Initial [ $\alpha$ ]<sub>D</sub> -44°. <sup>b</sup> 2-Mercaptomesitylene. <sup>c</sup> Purified by vapor phase chromatography. <sup>d</sup> Mesityl disulfide. <sup>e</sup> Initial [ $\alpha$ ]<sub>D</sub> -46°. <sup>f</sup> Purified by treatment with phenylhydrazine.

ing the irradiation was 0.42 M,  $\epsilon$  48 at 320 m $\mu$ . In the solution containing 0.026 M mercaptan initially, 0.003 M mesityl disulfide,  $\epsilon$  2520, would be formed, indicating that 73% of the irradiation would be absorbed by the acetophenone, leading to a possible masked rate of abstraction of hydrogen of about  $0.80 \times 10^{-2}$  mole l.<sup>-1</sup> hr.<sup>-1</sup>, 1.5 moles l.<sup>-1</sup> in the 192-hr. period of irradiation, abstraction of hydrogen from about one-half of the alcohol present initially. Less racemization than this would be expected because of the initial presence of about 12% racemic alcohol<sup>15</sup> and formation of additional racemic alcohol; perhaps about 40% racemization would be expected as compared to the observed 28%. The experiment (Table V) starting with 0.011 M mesityl disulfide leads to a similar conclusion. These experiments with optically active  $\alpha$ -methylbenzyl alcohol indicate that a very substantial portion of the normal hydrogen abstraction, eq. 1b, takes place during strong retardation of pinacol formation in the presence of mercaptan disulfide and that the retardation is due to reactions 4b and 5b. The small amount of racemization which is observed in the presence of sulfur compounds and the absence of added ketone, as compared with the absence of racemization observed under these conditions in the benzophenone-2-octanol system,<sup>2</sup> may be due to easier abstraction of the benzylic hydrogen or more ready formation of acetophenone from  $\alpha$ -methylbenzyl alcohol and greater difficulty in assuring its absence during these experiments.

Additional evidence in support of retardation *via* reactions 4b and 5b is obtained from experiments with  $\alpha$ -methylbenzyl alcohol-OD. Irradiation for 192 hr. of a benzene solution of 0.5 M acetophenone and 3.0 M  $\alpha$ -methylbenzyl alcohol-OD (81% OD) led to introduction of no deuterium bound to carbon, as shown by absence of absorption at 4.7  $\mu$ , indicating that the reverse of reaction 1b does not occur directly under these conditions, for kinetic reasons. Irradiation for 192 hr. of such a solution to which had been added  $1.1 \times 10^{-2}$  M mesityl disulfide led to recovery of  $\alpha$ -methylbenzyl alcohol containing about 28 mole per cent deuterium, results similar to those of the experiments with optically active  $\alpha$ -methylbenzyl alcohol. Oxidation led to acetophenone containing no deuterium, indicating that the deuterium was probably bound to the carbinol carbon, eq. 5b. However, irradiation of 3.0 M  $\alpha$ -methylbenzyl alcohol-OD in benzene with  $1.7 \times 10^{-2}$  M 2-mercaptomesitylene and with  $1.1 \times 10^{-2}$  M mesityl disulfide led, in the absence of added acetophenone, to recovery of carbinol containing 12 and 19 mole per cent, respectively, of carbon-bound deuterium. Analysis by vapor

(15) A. J. H. Houssa, and J. Kenyon, *J. Chem. Soc.*, 2230 (1930).

phase chromatography of the  $\alpha$ -methylbenzyl alcohol-OD which we had prepared and used in these experiments indicated that it contained 1.5% acetophenone and thus the latter experiments were not carried out in the total absence of the ketone. This does not detract from the confirmation given to our mechanism of inhibition, eq. 4b and 5b, by these experiments. The difficulty due to unwanted presence of ketone had been avoided in the benzophenone study in the presence of aliphatic carbinols—optically active 2-octanol and 2-propanol-OD.

**Effect of Benzyl Disulfide.**—In another group of experiments, an aliphatic disulfide, benzyl disulfide, was examined briefly as a retarder of the acetophenone- $\alpha$ -methylbenzyl alcohol reaction. On the assumption that the reactions were zero order, single values of extent of reaction at each concentration of disulfide, after measured periods of irradiation, were converted to rates and quantum yields. This compound appeared about half as effective a retarder as the aromatic mesityl disulfide,  $5.4 \times 10^{-3}$  M disulfide being required to halve the rate of reduction. Reduction of the intermediate radical would probably be less rapid by the aliphatic mercaptan than by the aromatic. If oxidation of the intermediate radical is largely due to reaction with disulfide rather than with thiyl radical, the aromatic disulfide would be more reactive than the aliphatic. The results are summarized in Table VI.

TABLE VI  
EFFECT OF BENZYL DISULFIDE ON PHOTOREDUCTION OF 0.5 M  
ACETOPHENONE BY 3.0 M  $\alpha$ -METHYLBENZYL ALCOHOL  
IN BENZENE

Benzyl disulfide, 10 <sup>3</sup> M	-d(C <sub>6</sub> H <sub>5</sub> - COCH <sub>3</sub> )/ dt, 10 <sup>2</sup> M hr. <sup>-1</sup>	Quantum yield, $\phi$	Benzyl disulfide, 10 <sup>3</sup> M	-d(C <sub>6</sub> H <sub>5</sub> - COCH <sub>3</sub> )/dt, 10 <sup>2</sup> M hr. <sup>-1</sup>	Quantum yield, $\phi$
0	1.23	0.60	3.10	0.80	0.40
1.05	0.99	.50	4.63	.64	.36
1.56	0.97	.48	5.92	.56	.28

**Acetophenone-2-Propanol.**—Photoreduction of acetophenone in 2-propanol also leads to the *meso* and *dl* forms of 2,3-diphenyl-2,3-butylene glycol. A few experiments were carried out on the photoreduction of 0.5 M acetophenone in 2-propanol and on the effects of (a) naphthalene and (b) mesityl disulfide on this reaction. Remaining acetophenone was analyzed by ultraviolet spectrophotometry. Acetone which was formed was determined by vapor phase chromatography. One mole of acetone was formed for every two moles of acetophenone reduced. The results are summarized in Table VII.

TABLE VII  
EFFECTS OF MESITYL DISULFIDE (MSSM) AND NAPHTHALENE  
IN THE PHOTOREDUCTION OF 0.5 M ACETOPHENONE IN  
2-PROPANOL

MSSM, 10 <sup>3</sup> M	Naphtha- lene, 10 <sup>3</sup> M	-d(C <sub>6</sub> H <sub>5</sub> - COCH <sub>3</sub> )/dt, 10 <sup>2</sup> M hr. <sup>-1</sup>	MSSM, 10 <sup>3</sup> M	Naphtha- lene, 10 <sup>3</sup> M	-d(C <sub>6</sub> H <sub>5</sub> - COCH <sub>3</sub> )/dt, 10 <sup>2</sup> M hr. <sup>-1</sup>
0	0	4.6	4.9	..	0.12
0.8	..	0.80	..	2.6	3.8
1.1	..	.40	..	3.4	2.7
1.5	..	.35	..	10.5	1.7
2.5	..	.24	..	15.9	1.2

The data indicate that mesityl disulfide was quite effective in retarding photoreduction of acetophenone in 2-propanol, the rate being halved by  $1 \times 10^{-3}$  M

thiyl group, essentially the same as the concentration required to halve the rate of the benzophenone-2-propanol reaction. When only one radical is produced, as in benzophenone-benzhydrol and acetophenone- $\alpha$ -methylbenzyl alcohol, the sulfur compounds are less effective,  $9 \times 10^{-3}$  and  $6 \times 10^{-3}$  M thiyl group, respectively, being required to halve the rates. This effect was discussed in detail, above, for the benzophenone-benzhydrol reaction. The sulfur compounds are most effective when 2-propanol is the reducing agent, next with  $\alpha$ -methylbenzyl alcohol, least with benzhydrol, reflecting the ease of abstraction of hydrogen from the mercaptan by the alcohol derived radical, reactions 5.

**Kinetic Analyses.**—From these data the absolute values of certain of the rate constants may be estimated. In the acetophenone- $\alpha$ -methylbenzyl alcohol system, from eq. 7 and the slopes of Fig. 2,  $k_q/k_{1b}(\text{C}_6\text{H}_5\dot{\text{C}}(\text{OH})\text{CH}_3) = 700$ ,  $k_q/k_{1b} = 2100$ . If quenching by naphthalene is diffusion controlled,<sup>6</sup>  $k_q \cong 10^9$  l. mole<sup>-1</sup> sec.<sup>-1</sup>, leading to  $k_{1b} \cong 5 \times 10^5$  l. mole<sup>-1</sup> sec.<sup>-1</sup> and  $k_{db} \cong 2 \times 10^5$  sec.<sup>-1</sup>. The constant  $k_d$  for decay of triplet benzophenone is about half this,<sup>16</sup>  $\sim 1 \times 10^5$  sec.<sup>-1</sup>. These latter two relative values are consistent with the relative phosphorescence decay times of excited acetophenone and benzophenone in rigid medium, 2.3 and 4.7 msec.<sup>14</sup> The value of  $k_{1a}$ , the rate constant for abstraction of hydrogen from benzhydrol by triplet benzophenone, has been reported<sup>16</sup>  $k_{1a} = 2 \times 10^6$  l. mole<sup>-1</sup> sec.<sup>-1</sup>; the lesser value of  $k_{1b} \cong 5 \times 10^5$  l. mole<sup>-1</sup> sec.<sup>-1</sup> reported here for the acetophenone- $\alpha$ -methylbenzyl alcohol reaction presumably reflects the stronger carbon-hydrogen bond in the latter carbinol, since the triplet of acetophenone would, if anything, be slightly more energetic than that of benzophenone.<sup>11</sup> The order of magnitude difference in the ratios of  $k_d/k_1$  in benzophenone-benzhydrol<sup>6</sup> and acetophenone- $\alpha$ -methylbenzyl alcohol systems, 0.05 and 0.50, respectively, arises from the combination of a more stable triplet and more easily abstracted hydrogen in the former system.

In the acetophenone-2-propanol system (Table VII), the data for the effect of naphthalene may be plotted according to eq. 7, about  $6 \times 10^{-3}$  M naphthalene being required to halve the rate of reduction,  $k_q/k_{1d}(\text{CH}_3\dot{\text{C}}\text{H}(\text{OH})\text{CH}_3) = 210$ ,  $k_q/k_{1d} = 2700$ . With the approximation<sup>6</sup>  $k_q \cong 10^9$ ,  $k_{1d} \cong 4 \times 10^5$  l. mole<sup>-1</sup> sec.<sup>-1</sup>, the rate constant for abstraction of hydrogen from 2-propanol by triplet acetophenone. The corresponding data for quenching by naphthalene of the photoreduction of benzophenone in 2-propanol<sup>3</sup> indicate that about  $4 \times 10^{-3}$  M naphthalene was required to halve the rate  $k_q/k_1(\text{CH}_3\dot{\text{C}}\text{H}(\text{OH})\text{CH}_3) = 125$ ,  $k_q/k_1 = 1600$ ,  $k_1 = 6 \times 10^5$  l. mole<sup>-1</sup> sec.<sup>-1</sup>, the rate constant for abstraction of hydrogen from 2-propanol by triplet benzophenone.

In a system in which only one intermediate radical is formed, *i.e.*, III, reactions of the type of eq. 2 may occur but do not affect the kinetics. Considering a mechanism based on eq. 1b, 3b, 4b, and 5b, an equilibrium concentration of mercaptan and disulfide is attained during the retarded reaction

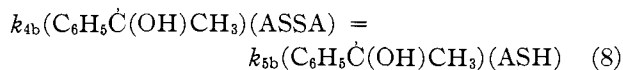
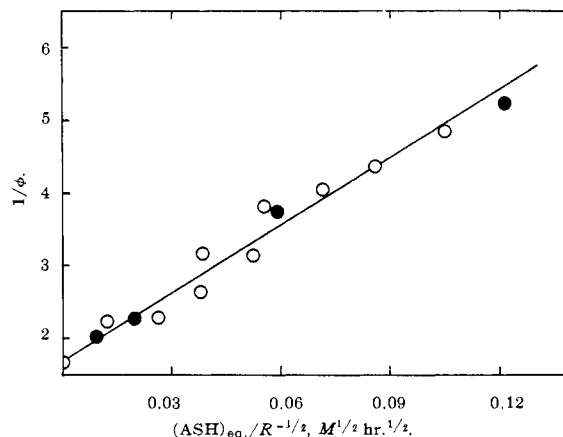
(16) J. A. Bell and H. Linschitz, *J. Am. Chem. Soc.*, **85**, 528 (1963).

Fig. 4.—Photoreduction of 0.5 M acetophenone by 3 M  $\alpha$ -methylbenzyl alcohol in benzene; effect of 2-mercaptomesitylene and mesityl disulfide: ●, 2-mercaptomesitylene; ○, mesityl disulfide.

The quantum yield for retarded pinacol formation  $\phi$  may be expressed by an equation of the form

$$\phi = \frac{k_{3b}(\text{C}_6\text{H}_5\dot{\text{C}}(\text{OH})\text{CH}_3)^2}{k_{3b}(\text{C}_6\text{H}_5\dot{\text{C}}(\text{OH})\text{CH}_3)^2 + 2k_{5b}(\text{C}_6\text{H}_5\dot{\text{C}}(\text{OH})\text{CH}_3)(\text{ASH})} \quad (9)$$

$$\frac{1}{\phi} = 1 + \frac{2k_{5b}(\text{ASH})}{k_{3b}(\text{C}_6\text{H}_5\dot{\text{C}}(\text{OH})\text{CH}_3)} \quad (10)$$

The measured rate of reduction  $R$  is

$$R = k_{3b}(\text{C}_6\text{H}_5\dot{\text{C}}(\text{OH})\text{CH}_3)^2 \quad (11)$$

and

$$(\text{C}_6\text{H}_5\dot{\text{C}}(\text{OH})\text{CH}_3) = R^{1/2}/k_{3b}^{1/2} \quad (12)$$

$$1/\phi = 1 + (2k_{5b}(\text{ASH})/k_{3b}^{1/2}R^{1/2}) \quad (13)$$

In this, (ASH) is the equilibrium concentration of mercaptan. The proportion of sulfur compound present as mercaptan probably does not vary much with initial mercaptan concentration under the conditions of our experiments. In Fig. 4 the data of Table IV and the equilibrium percentage of thiol, according to Fig. 3, are used to construct a plot of  $1/\phi$  against  $(\text{ASH})/R^{1/2}$ . A satisfactory linear plot is obtained, consistent with the proposed mechanism and eq. 13; the slope is 0.5 mole<sup>-1/2</sup> l.<sup>1/2</sup> sec.<sup>-1/2</sup> and is equal to  $2k_{5b}/k_{3b}^{1/2}$ . If, as was assumed for benzophenone-ketyl radical,<sup>16</sup> we assume that the combination of acetophenone-ketyl radicals is diffusion controlled and  $k_{3b} \cong 2 \times 10^9$  l. mole<sup>-1</sup> sec.<sup>-1</sup>, then  $k_{5b} \cong 1 \times 10^4$  l. mole<sup>-1</sup> sec.<sup>-1</sup>, the rate constant for transfer of hydrogen from mesityl mercaptan to acetophenone-ketyl radical. It has been reported recently that combination of benzophenone-ketyl radicals is somewhat slower than diffusion controlled.<sup>17</sup> If combination of acetophenone-ketyl radicals were also slower,  $k_{3b} \cong 10^8$  l. mole<sup>-1</sup> sec.<sup>-1</sup>, then  $k_{5b}$  would be lower,  $\cong 2 \times 10^3$  l. mole<sup>-1</sup> sec.<sup>-1</sup>.

The data of Table VI, for the effect of benzyl disulfide, may be dealt with similarly, leading to a linear plot of  $1/\phi$  against (thiyl)/ $R^{1/2}$ , where the total concentrations of thiyl group are used, the equilibrium concentration not having been determined. This treatment,

(17) A. Beckett and G. Porter, *Trans. Faraday Soc.*, **59**, 2038 (1963).

with the assumption that combination of the ketyl radicals is diffusion controlled, leads to  $k_{bc} \cong 5 \times 10^3$  l. mole<sup>-1</sup> sec.<sup>-1</sup> for the rate constant for transfer of a hydrogen atom from benzyl mercaptan to acetophenone-ketyl radical, and  $1 \times 10^3$  l. mole<sup>-1</sup> sec.<sup>-1</sup> on the assumption that the combination reaction is slower. The data of Table I for the effect of mesityl disulfide in retarding the photoreduction of 0.5 *M* benzophenone by 1.0 *M* benzhydrol in benzene may also be plotted according to eq. 13, leading to similar values,  $k_{ba} = 5 \times 10^3$  or  $1 \times 10^3$  l. mole<sup>-1</sup> sec.<sup>-1</sup> for transfer of a hydrogen atom from 2-mercaptomesitylene to benzophenone-ketyl radical. These relative values for  $k_{ba}$ ,  $k_{bb}$ , and  $k_{bc}$  are consistent with the anticipated greater reactivity of acetophenone-ketyl radical than that of the benzophenone radical, and the greater ease of rupture of the aromatic S-H bond than the aliphatic.

**Inhibition and Catalysis by Sulfur Compounds.**—Mercaptan-disulfide systems participate in and accelerate hydrogen atom transfer reactions, so that they may proceed more rapidly than or compete more favorably with radical combination reactions. In this way the sulfur compounds may merely catalyze hydrogen abstraction by radicals, leading to a change in identity,<sup>18</sup> and to gross change in the reaction products.<sup>19</sup> If the radical combination is a chain terminating reaction, and if one of the chain propagating steps involves transfer of a hydrogen atom, the mercaptan-disulfide may increase the rate of chain propagation as compared with termination, and catalyze the over-all process. This is observed in mercaptan catalysis of radical-induced<sup>20</sup> and light-initiated decarbonylation of aldehydes.<sup>8</sup> On the other hand, light or high energy radiation may lead to excitation and to transfer of a hydrogen atom from one species to another and to formation of two radicals. The return of the system to its initial state by an exothermic transfer of hydrogen, although thermodynamically favorable, may not occur, radical combination or other exothermic reactions being more rapid. The mercaptan-disulfide may accelerate the hydrogen transfer reaction which is involved in restoring the system to its initial state, sufficiently so that, through this same catalytic process, inhibition of the radiation-induced reaction and stabilization of the system result. The nature of these reactions, as described above and previously,<sup>2</sup> is such that the mercaptan and disulfide are regenerated and used repeatedly in these processes, a few molecules negating the consequences of many quanta.

### Experimental

**Materials.**—Benzophenone, 2-propanol, 2-mercaptomesitylene, mesityl disulfide, benzyl disulfide, and naphthalene were obtained or prepared as described previously. Benzene was Eastman Kodak Co., Spectrograde. Benzhydrol was from Eastman Kodak Co.; m.p. 66–67°. Acetophenone, Fisher Certified Reagent, was distilled under nitrogen, b.p. 48° (0.15 mm.).  $\alpha$ -Methylbenzyl alcohol, Eastman Kodak Co., was distilled under nitrogen, b.p. 52° (0.15 mm.).

**2-Propanol-OD.**—Thionyl chloride (236 g., 2 moles) and 255 g. (4.4 moles) of 2-propanol were added to refluxing methylene chloride, as described in the literature,<sup>21</sup> leading to 250 g. (1.5 moles), 75% yield, of di-2-propyl sulfite, b.p. 73–75° (40 mm.). The sulfite (83 g., 0.5 mole) and D<sub>2</sub>O (10 ml., 0.5 mole) were placed in a 250-ml. flask fitted with a magnetic stirrer, condenser,

and drying tube, and stirred for 72 hr., while immersed in an oil bath at 120°. The product was distilled, b.p. 81–82°, essentially 2-propanol-OD, showing a small O-H band at 2.93  $\mu$  and strong O-D peaks at 3.74 and 3.93  $\mu$ .

**2-Propanol-2-D.**—Acetone (15 g., 0.26 mole) was added dropwise to a suspension of 2 g. (0.05 mole) of lithium aluminum deuteride in 75 ml. of sodium-dried ether under dry nitrogen. The mixture was refluxed for 12 hr., cooled, treated with 200 ml. of 6% sulfuric acid, and distilled, leading to 2-propanol-2-D, b.p. 79–82°. The infrared spectrum, taken against 2-propanol, showed peaks at 4.63 and 4.77  $\mu$ .

**$\alpha$ -Methylbenzyl Alcohol-OD.**— $\alpha$ -Methylbenzyl alcohol (25 ml., 0.2 mole) was stirred twice with 8-ml. (0.4 mole) portions of D<sub>2</sub>O for 12 hr., extracted with ether, dried, and distilled, b.p. 50° (2 mm.). The infrared spectrum of this material showed a weak O-H band at 2.78  $\mu$ , and a strong O-D band at 3.78  $\mu$ . Comparison of the infrared spectrum with that of nondeuterated  $\alpha$ -methylbenzyl alcohol indicated 81% deuteration. The spectrum also showed absorption at 5.91  $\mu$ , indicating the presence of 1.5% acetophenone.

(-)- $\alpha$ -Methylbenzyl alcohol was prepared from the brucine salt of the acid phthalate of  $\alpha$ -methylbenzyl alcohol<sup>16</sup> and obtained in two fractions: (1)  $\alpha_{\text{obsd}} -3.73^\circ$ ,  $c$  8.01 in chloroform,  $[\alpha]_{\text{D}}^{20} -46.6^\circ$ ;  $[\alpha]_{\text{D}}^{19} -36.2^\circ$ , no solvent; reported<sup>15</sup>  $[\alpha]_{\text{D}}^{20} -40.95^\circ$ ; (2)  $\alpha_{\text{obsd}} -1.11^\circ$ ,  $c$  2.54 in chloroform,  $[\alpha]_{\text{D}}^{20} -43.9^\circ$ .

**Apparatus.**—Solutions were irradiated in 15-mm. diameter Pyrex tubes mounted vertically on a rotating circular turntable 4 cm. from an Osram Spektrallampe type Hg/1, operating at 50 v., 1.2 amp.<sup>3</sup> Solutions were degassed by the freeze-thaw method. Ambient temperature was  $32 \pm 2^\circ$ .

Infrared spectra were determined on a Perkin-Elmer Model 137 Infracord. Ultraviolet spectra were determined on a Cary Model 14 recording spectrophotometer. Optical rotations were measured with a Zeiss-Winkel polarimeter and read to  $\pm 0.02^\circ$ . Vapor phase chromatographic analyses were carried out with an Aerograph A-90-P instrument, thermal conductivity detector, helium carrier.

**Photoreduction of Benzophenone in 2-Propanol-OD.**—Benzophenone (0.91 g., 0.005 mole) was made up to 10 ml. with 2-propanol-OD. (i) An aliquot, 2 ml., was degassed and irradiated for 24 hr., and cooled for 24 hr. to allow benzpinacol to crystallize. The supernatant liquid was distilled and the infrared spectrum was taken against 2-propanol-OD, showing no band at 4.7  $\mu$ . (ii) Naphthalene (0.0032 g., 0.026 mmole) was weighed into the irradiation tube, a 2-ml. aliquot of 0.5 *M* benzophenone in 2-propanol-OD was added, and the solution was irradiated for 24 hr. The distillate was examined as above, showing no absorption at 4.7  $\mu$ . (iii) Mesityl disulfide (0.0030 g., 0.010 mmole), was weighed into the irradiation tube, dissolved in a 2-ml. aliquot of the 0.5 *M* benzophenone in 2-propanol-OD, and irradiated for 25 hr. The distillate, examined against 2-propanol-OD, showed an absorption band at 4.7  $\mu$ . (iv) Benzophenone (0.73 g., 4.0 mmoles) and 0.029 g. (0.096 mmole) of mesityl disulfide were weighed into a Thunberg tube, 8 ml. of 2-propanol-OD was added, and the solution was degassed and irradiated for 69 hr. The suspension was centrifuged and the supernatant liquid was withdrawn and distilled. The infrared spectrum of the 2-propanol fraction of the distillate, taken against 2-propanol-OD, showed peaks at 4.63 and 4.77  $\mu$ , like those of authentic 2-propanol-2-D. A sample of the 2-propanol was isolated by vapor phase chromatography and its infrared spectrum showed a peak at 4.8  $\mu$ . A portion of the 2-propanol fraction (4 ml., 0.05 mole) was refluxed in 70 ml. of dry toluene with 16 g. (0.09 mole) of fluorenone and 1.7 g. (0.007 mole) of aluminum *t*-butoxide for 12 hr. Acetone was distilled out. Its infrared spectrum against pure acetone showed no bands in the 4–5  $\mu$  region.

**Benzophenone-Benzhydrol** (Table I).—Stock solutions were prepared of 0.5 *M* benzophenone and 1.0 *M* benzhydrol in benzene. To one solution (100 ml.) mesityl disulfide was added, 0.15 g.,  $5 \times 10^{-3}$  *M*. Aliquots, 5-ml., were degassed and irradiated for stated periods. Portions, 1-ml., were diluted to 100 ml. with 2-propanol and remaining benzophenone was estimated spectrophotometrically as described previously.<sup>3</sup> Zero-order reduction of benzophenone was observed.

To examine the effects of varying concentrations of the disulfide, the required amounts of the latter were weighed directly into the irradiation tubes and aliquots of the stock benzophenone-benzhydrol solution were added. The tubes were degassed, irradiated for 3 hr., and analyzed as above. Analyses for mercaptan were made amperometrically as described before.<sup>2</sup>

(18) C. H. Wang and S. G. Cohen, *J. Am. Chem. Soc.*, **79**, 1925 (1957).

(19) A. F. Bickel and E. C. Kooyman, *Nature*, **170**, 211 (1952).

(20) E. F. P. Harris and W. A. Waters, *ibid.*, **170**, 212 (1952).

(21) W. Bissinger and F. Küng, *J. Am. Chem. Soc.*, **69**, 2158 (1947).

**Acetophenone- $\alpha$ -Methylbenzyl Alcohol in Benzene** (Tables II, III, IV, VI).—Solutions containing 0.5 *M* acetophenone and varying concentrations of  $\alpha$ -methylbenzyl alcohol were prepared by weighing the required amounts of the compounds into volumetric flasks and diluting to the mark with benzene. In experiments in which effects of concentration of quencher or retarder were studied, appropriate amounts of naphthalene, mercaptan, or disulfide were weighed into volumetric flasks and diluted to the mark with benzene solutions of 0.5 *M* acetophenone and 3 *M*  $\alpha$ -methylbenzyl alcohol.

Aliquots (5 ml.) of a solution were pipetted into Thunberg tubes, degassed in three cycles of the freeze-melt procedure, left under argon (1 atm.), and irradiated for periods up to 100 hr. Finely divided acetophenone-pinacol precipitated in many runs. After the irradiation, residual acetophenone was determined by infrared absorption measurements, with aid of a calibration curve for each run. Aliquots (0.10–0.80 ml.) of each original solution were diluted to 5 ml. with benzene; transmittance of the acetophenone carbonyl peak at 1686  $\text{cm}^{-1}$  was measured, converted to absorbancy, and plotted against the known acetophenone concentration to furnish the calibration curve. Aliquots from each irradiated tube were also diluted to 5 ml. with benzene, the transmittance at 1686  $\text{cm}^{-1}$  was measured and converted to absorbancy, and the concentrations of acetophenone were read from the calibration curves. Ultraviolet analysis for residual acetophenone was also used in the absence of sulfur compounds, leading to results in agreement with those from infrared measurements. In these analyses the absorbancy at 320  $\text{m}\mu$  was measured and converted to the corresponding concentration with aid of a calibration curve.

The amount of radiation absorbed by the solution of 0.5 *M* acetophenone and 3 *M*  $\alpha$ -methylbenzyl alcohol in benzene was determined by use of a ferrioxalate actinometer<sup>22</sup> with unfiltered radiation from the Osram lamp. Two series of determinations were carried out,<sup>3</sup> with 8 ml. of the solution of ferric ammonium sulfate, sulfuric acid, and potassium oxalate in a Thunberg tube (1) placed in a Pyrex filter tube, and (2) placed in the Pyrex tube with the latter containing a 1-cm. layer of 0.5 *M* acetophenone and 3 *M*  $\alpha$ -methylbenzyl alcohol in benzene. After irradiation, aliquots of the ferrioxalate solution were treated with phenanthroline and analyzed for ferrous ion. From the reported<sup>23</sup> quantum yield for this photoreduction, the quantities of radiation absorbed in series 1 and 2 were calculated. The difference between these quantities is the quantity of radiation absorbed by the acetophenone solution. The mean value for the radiation absorbed was  $3.5 \times 10^{18}$  quanta/min. without the filter solution,  $1.9 \times 10^{18}$  with the filter solution, leading to  $1.6 \times 10^{18}$  quanta/min.,  $0.20 \times 10^{18}$  quanta/min./ml. The rate studies were carried out over a period of 11 months. The rate of reduction of 0.5 *M* acetophenone by 3 *M*  $\alpha$ -methylbenzyl alcohol in benzene was used as a secondary actinometer to check the output of the lamp over this period: 0.0136 *M*/hr. initially, 0.0125 *M*/hr. after 4 months, and 0.0108 *M*/hr. after 10 months, a loss of 2% per month. The quantum yield of a given reaction was calculated from the ferrioxalate actinometer value, determined in the 5th month, with the above correction applied.

**Equilibration of Mesityl Disulfide and Mesityl Mercaptan.**—Solutions of 0.5 *M* acetophenone, 3 *M*  $\alpha$ -methylbenzyl alcohol, and 0.02 *M* mesityl disulfide or 0.04 *M* mesityl mercaptan were prepared by weighing the required amounts of the reagents into 50-ml. volumetric flasks and diluting to the mark with benzene. Aliquots (5 ml.) of these solutions were pipetted into Thunberg tubes, degassed, left under argon (1 atm.), and irradiated for 1 to 17 hr. In analyses for 2-mercaptomesitylene, *p*-chloroacetophenone as internal standard was weighed into 2-ml. volumetric flasks which were filled to the mark with the irradiated solutions. These solutions were injected into the gas chromatograph using an 8 ft.  $\times$  0.25 in. column packed with 2% General Electric SE-30 on 80–100 Chromosorb W. The column was maintained at 95°, the injector at 215°, and the detector at 225°. The concentration of 2-mercaptomesitylene was determined from the peak area ratio of internal standard and mercaptan, with use of a calibration curve. In analyses for mesityl disulfide, carbazole was weighed into 2-ml. flasks and diluted to the mark with the irradiated solutions. These solutions were injected into the gas chromatograph using a 5 ft.  $\times$  0.25 in. column packed with 1.5%

QF-1 on 80–100 Chromosorb W. The column was maintained at 160°, detector 270°, and injector 360°. The concentration of mesityl disulfide was determined from the peak area ratio of standard and disulfide, with use of a calibration curve.

**Racemization Studies** (Table V).—Solutions of 3 *M* (–)- $\alpha$ -methylbenzyl alcohol in benzene, containing 0.5 *M* acetophenone, or 2-mercaptomesitylene, or mesityl disulfide, or acetophenone and one of the sulfur compounds, were prepared by weighing the appropriate compounds into 5-ml. volumetric flasks and diluting to the mark with benzene. The solutions were transferred to Thunberg tubes, degassed, and irradiated for 192 hr.

**Experiment 62.**—The irradiated solution of  $\alpha$ -methylbenzyl alcohol and acetophenone was decanted from acetophenone-pinacol and distilled, and  $\alpha$ -methylbenzyl alcohol was recovered, b.p. 50–55° (0.1 mm.), 1.39 g., 91%,  $\alpha_{\text{obsd}} -0.93^\circ$ ,  $c$  2.03 in chloroform,  $[\alpha]^{22\text{D}} -42^\circ$ . The infrared spectrum was identical with that of an authentic sample. A sample was analyzed by vapor phase chromatography and found to contain a trace of acetophenone. Analysis was on a 3 ft.  $\times$  0.5 in. column, packed with 10% Dow-Corning QF-1 on 80–100 Chromosorb W. Column, injector, and detector temperatures were 140, 290, and 220°, respectively.

**Experiment 66.**—The irradiated benzene solution of  $\alpha$ -methylbenzyl alcohol and 2-mercaptomesitylene was distilled, leading to recovered alcohol,  $\alpha_{\text{obsd}} -0.87^\circ$ ,  $c$  2.16,  $[\alpha]^{22\text{D}} -40^\circ$ . Vapor phase chromatography indicated presence of a trace of acetophenone, and led to recovered alcohol,  $\alpha_{\text{obsd}} -1.10^\circ$ ,  $c$  2.74,  $[\alpha]^{20\text{D}} -40^\circ$ ; retention time and infrared spectrum were identical with those of authentic material.

**Experiment 18A.**—The irradiated solution of  $\alpha$ -methylbenzyl alcohol and mesityl disulfide was distilled, leading to recovered alcohol, b.p. 45° (0.1 mm.),  $\alpha_{\text{obsd}} -0.95^\circ$ ,  $c$  2.26,  $[\alpha]^{21\text{D}} -42^\circ$ .

**Experiment 18.**—The irradiated solution of  $\alpha$ -methylbenzyl alcohol, acetophenone, and 2-mercaptomesitylene was distilled, leading to recovered alcohol,  $\alpha_{\text{obsd}} -0.59^\circ$ ,  $c$  2.09,  $[\alpha]^{17\text{D}} -28^\circ$ . Vapor phase chromatography indicated contamination with acetophenone. A sample of the alcohol was isolated from the chromatograph, indicated to be pure by infrared spectrum,  $\alpha_{\text{obsd}} -0.85^\circ$ ,  $c$  2.70,  $[\alpha]^{20\text{D}} -31^\circ$ .

**Experiment 85.**—The irradiated solution of  $\alpha$ -methylbenzyl alcohol, acetophenone, and 2-mercaptomesitylene was distilled, leading to recovered alcohol,  $\alpha_{\text{obsd}} -2.48^\circ$ ,  $c$  8.25,  $[\alpha]^{25\text{D}} -30^\circ$ . The infrared absorbancy at 1686  $\text{cm}^{-1}$  indicated the presence of 10% acetophenone. The distillate, 1.44 g., was treated with 5 ml. of acetic acid and 1 ml. of phenylhydrazine for 0.5 hr., and then with 7 ml. of water. Acetophenone-phenylhydrazone precipitated and was removed; the filtrate was diluted with water, extracted with ether, concentrated, and treated again in the same way with phenylhydrazine. The alcohol was again extracted with ether, washed with hydrochloric acid, water, sodium carbonate, and water, dried, and distilled, b.p. 41° (0.1 mm),  $\alpha_{\text{obsd}} -2.59^\circ$ ,  $c$  7.85,  $[\alpha]^{21\text{D}} 33^\circ$ ,  $n^{27\text{D}} 1.5258$ . The infrared spectrum indicated the presence of 1% acetophenone.

**Experiment 33.**—The irradiated solution of  $\alpha$ -methylbenzyl alcohol, acetophenone, and mesityl disulfide was distilled, leading to  $\alpha$ -methylbenzyl alcohol,  $\alpha_{\text{obsd}} -2.30^\circ$ ,  $c$  7.7,  $[\alpha]^{26\text{D}} -30^\circ$ . The infrared spectrum indicated the presence of 8% acetophenone. The material was treated twice with phenylhydrazine as described above, leading to purified  $\alpha$ -methylbenzyl alcohol,  $\alpha_{\text{obsd}} -2.57^\circ$ ,  $c$  7.6,  $[\alpha]^{21\text{D}} -34^\circ$ ,  $n^{27\text{D}} 1.5258$ . The infrared spectrum indicated the presence of 0.6% acetophenone. An authentic sample of  $\alpha$ -methylbenzyl alcohol had  $n^{27\text{D}} 1.5257$ .

**Deuterium Exchange.**—Solutions of 3 *M*  $\alpha$ -methylbenzyl alcohol-OD, with and without 0.5 *M* acetophenone and inhibitor, were prepared by weighing the appropriate compounds into 5-ml. volumetric flasks and diluting to the mark with benzene. The solutions were transferred to Thunberg tubes, degassed, left under argon, and irradiated for 192 hr. The irradiated solutions were transferred to a microdistillation apparatus, benzene was distilled off, b.p. 80°, and the high boiling  $\alpha$ -methylbenzyl alcohol-acetophenone fractions were collected, b.p. 45–50° (0.1 mm.). The distillates were stirred with 4 ml. (0.2 mole) of water for 12 hr. The alcohol fraction was extracted with ether and dried. The ether was evaporated, and treatment with water was repeated. The water-equilibrated high-boiling fractions were distilled, b.p. 45–50° (0.1 mm.), and examined in the infrared. An Irtran-2 cell was filled with the distillate and balanced against a similar cell filled with authentic  $\alpha$ -methylbenzyl alcohol, and the difference spectrum of the distillate was recorded.

(22) C. G. Hatchard and C. A. Parker, *Proc. Roy. Soc. (London)*, **236**, 518 (1956).

(23) I. M. Kolthoff and W. E. Harris, *Ind. Eng. Chem., Anal. Ed.*, **18**, 161 (1946).



Solution a, originally containing 3.0 *M*  $\alpha$ -methylbenzyl alcohol-OD, 0.50 *M* acetophenone, and 0.011 *M* mesityl disulfide, was treated in this way. The difference spectrum showed C-D absorption at 4.7  $\mu$ , absorptancy 0.14. The infrared spectrum indicated the presence in the distillate of 15% acetophenone, 85%  $\alpha$ -methylbenzyl alcohol. The extinction coefficient of the C-D bond was estimated to be 7.0 from examination of the infrared spectrum of 2-octanol-2-D in chloroform. On this basis the concentration of  $\alpha$ -methylbenzyl alcohol- $\alpha$ -D in the distillate was estimated to be 2.0 *M*, 28% deuterium exchange. In another similar run the recovered distilled  $\alpha$ -methylbenzyl alcohol (1.05 g., 0.0086 mole) was diluted to 10 ml. with pyridine and treated with a solution of 2 g. (0.02 mole) of chromium trioxide in 20 ml. of pyridine at room temperature for 16 hr. The mixture was filtered, diluted with water, and extracted with ether. The extract was washed with 6 *N* hydrochloric acid, and with water, dried, and distilled, leading to acetophenone, b.p. 40° (0.1 mm.), 0.43 g., 42% yield. A difference spectrum against acetophenone showed no infrared absorption at 4.7  $\mu$ .

Solution b, containing initially 3.0 *M*  $\alpha$ -methylbenzyl alcohol-OD and 0.5 *M* acetophenone in benzene, was irradiated and treated in the same way. The difference spectrum of the recovered, water-equilibrated  $\alpha$ -methylbenzyl alcohol showed no C-D absorption at 4.7  $\mu$ .

Solution c, containing initially 3.0 *M*  $\alpha$ -methylbenzyl alcohol and 0.017 *M* 2-mercaptomesitylene, was irradiated and worked up in the same way. The difference spectrum of the recovered water-equilibrated  $\alpha$ -methylbenzyl alcohol showed absorption at 4.7  $\mu$ , indicating 12% deuterium exchange. Solution d, 3.0 *M*  $\alpha$ -methylbenzyl alcohol and 0.011 *M* mesityl disulfide, led, after irradiation and work-up, to recovered alcohol with absorption at 4.7  $\mu$ , indicating 19% deuterium exchange.

**Acetophenone-2-Propanol** (Table VII).—Aliquots (5 ml.) of 0.5 *M* acetophenone in 2-propanol were transferred to Thunberg tubes, degassed, and irradiated for 3 to 24 hr. The rate of reaction of acetophenone was followed by ultraviolet spectrophotometry and by vapor phase chromatography. The rate of formation of acetone was followed by vapor phase chromatography. In ultraviolet analyses for acetophenone, the irradiated solutions were diluted, absorbancies were measured at 310, 320, and 330 m $\mu$ , averaged, and converted to concentrations from a calibration curve. Chromatographic analyses for acetophenone were made with *p*-chloroacetophenone as internal standard, with a 3 ft.  $\times$  0.5 in. column packed with 10% Dow-Corning QF-1 on 80-100 Chromosorb W. Column, detector, and injector temperatures were 150, 200, and 305°, respectively. Analyses for acetone were carried out with 2-butanol as internal standard, with a 6 ft.  $\times$  0.25 in. column packed with 20% adipate resin (R. C. Polymeric B.G.A., Rubber Corporation of America) on 80-100 Celite. Column, detector, and injector temperatures were 50, 100, and 130°, respectively.

**Acetophenone-Pinacol**.—(a) Acetophenone (120 ml., 1 mole) was diluted to 1 l. with 2-propanol and irradiated under nitrogen for 192 hr. with a Hanovia mercury arc 100 w. 16A-13 lamp with an interposed Vycor heat shield. 2-Propanol was removed and unreacted acetophenone was distilled out, b.p. 46° (0.1 mm.), 80 ml. The pinacol residue, 40 g., 100% yield, was triturated with 60-110° petroleum ether, and the insoluble fraction was crystallized three times from 60-110° petroleum ether, leading to 10 g. of the *meso* diastereomer, m.p. 123-124°, reported<sup>10</sup> 123°. The remainder was a mixture of the diastereomers, melting over a range.

(b) Samples of the pinacol were isolated from the kinetic runs under conditions examined. Yields were determined, and the products were characterized by infrared spectra.

[CONTRIBUTION FROM THE KEDZIE CHEMICAL LABORATORY, MICHIGAN STATE UNIVERSITY, EAST LANSING, MICH.]

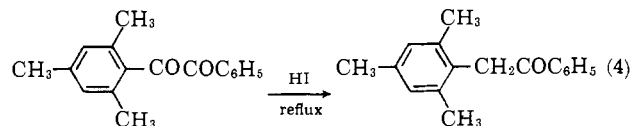
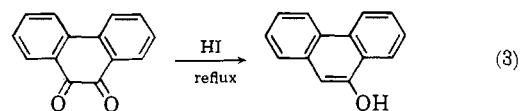
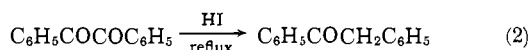
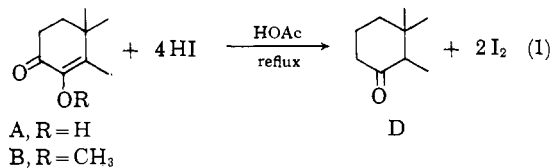
## A Versatile Ketone Synthesis. The Reduction of $\alpha$ -Diketones and $\alpha$ -Ketols by Hydriodic Acid<sup>1</sup>

BY WILLIAM REUSCH AND RONALD LEMAHIEU

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When treated with hydriodic acid in refluxing acetic acid,  $\alpha$ -diketones and  $\alpha$ -ketols are reduced to saturated ketones. This provides a general ketone synthesis, which in certain cases may be used to shift a carbonyl group to an adjacent position. Thus, 4-acetoxystrophan-3-one was converted to strophan-4-one; 3,5,5-trimethylcyclohexane-1,2-dione gave 2,4,4-trimethylcyclohexanone and 2,4,4-trimethylcyclohex-2-en-1-one in a ratio of 4:1; 3,3-dimethylcyclohexane-1,2-dione gave 3,3-dimethylcyclohexanone; 4-hydroxy-4-ethyl-3-hexanone gave 4-ethyl-3-hexanone; and both sebacoin and sebacil were reduced to cyclodecanone. Since benzoin and benzil require more vigorous conditions for reduction to deoxybenzoin and since pivaloin cannot be reduced at all, we suggest an enolic carbonium ion intermediate to explain these findings.

In a recent paper<sup>2</sup> we described the reduction of cholestan-3,4-dione and the derived enol methyl ethers to cholestan-4-one by hydriodic acid in refluxing acetic acid (eq. 1). Hydrogen iodide is well known for its ability to reduce a variety of organic substrates including aryl olefins, arylcarbinols, aryl ketones, benzils, glycols,  $\alpha$ -haloketones, and  $\alpha,\beta$ -epoxyketones. In some of these reactions the reduction is believed to proceed by a direct hydride transfer from hydrogen iodide to a carbonium ion intermediate.<sup>3</sup> At first, reaction 1 appeared to parallel the reduction of substituted benzils reported by Japp, Klingeman,<sup>4</sup> and Fuson<sup>5</sup> (reactions 2, 3, and 4); however, the conditions required for satisfactory reduction of these latter compounds are more vigorous than those employed in the reductions of A and the aliphatic  $\alpha$ -diketones dis-



(1) Abstracted in part from the Ph.D. thesis of R. LeMahieu, Michigan State University, August, 1963.

(2) W. Reusch and R. LeMahieu, *J. Am. Chem. Soc.*, **85**, 1669 (1963).

(3) N. Deno, N. Friedman, J. Hodge, F. Mackay, and G. Saines, *ibid.*, **84**, 4713 (1962).

(4) F. Japp and F. Klingeman, *J. Chem. Soc.*, **63**, 770 (1893).

(5) R. Fuson and P. Hoch, *J. Am. Chem. Soc.*, **71**, 1585 (1949).

cussed in this paper. Thus, an acetic acid solution of benzil containing 4 to 5 equivalents of 48% hydriodic acid gave, after 1 hr. at reflux, an excellent yield of