Anal. Calcd. for $C_{23}H_{25}NO_5 \cdot 3H_2O$: C, 61.4; H, 6.9. Found: C, 61.8; H, 7.0.

Ozonolysis of Methine XXVI; 4-Methoxyisophthalic Acid (XXVII).—A solution of 200 mg. (0.45 mmole) of methine XXVI in 150 ml. of 0.02 M methanolic sulfuric acid was ozonized at $-78°$ as described for methine XXI. Absorption of ozone ceased after 110 mole % was consumed (60 min.). The reaction mixture was boiled with 5 ml. of 30% hydrogen peroxide for 6 hours and evaporated to dryness *in vacuo*, and the oily residue was dissolved in 200 ml. of distilled water. After acidifying (pH 1) the solution with sulfuric acid, it was continuously extracted (36 hr.) with methylene chloride. The residue obtained from the methylene chloride was hydrolyzed with 5% methanolic potassium hydroxide (30 min., reflux) and the residue remaining on removal of solvent was dissolved in 25 ml. of distilled water. Acidification (congo red) with phosphoric acid and extraction with methylene chloride (4 × 25 ml.) provided 110 mg. of material which was fractionally sublimed. At 100° (50 μ), 20 mg. of a yellow gum was obtained and was discarded. Further sublimation at 140° (50 μ) gave 60 mg. of a powdery sublimate which was crystallized from water, affording 30 mg. (34%) of 4-methoxyisophthalic acid (XXVII) as colorless prisms, m.p. 274–275°; λ_{max} 217 mμ (ϵ 25,500), 253 (13,600), 293 (2,380) [reported[26] m.p. 276°; λ_{max} 217.6 mμ, (ϵ 39,000), 253 (17,000), 293 (3,240)]; ν_{max}^{KBr} 1685(s), 1722(sh) (m) cm.$^{-1}$; n.m.r. absorption in CF_3COOH, τ 5.75; C_5–H, 2.65 (d); C_6–H, 1.49 (m); C_2–H, 1.02 (d).

Dimethyl Bicyclo[2,2,2]octa-2,5-diene-2,3-dicarboxylate (VI). —A mixture of equal parts by weight of 1,3-cyclohexadiene and dimethyl acetylenedicarboxylate was allowed to stand at room temperature for 48 hr. The reaction mixture then was evaporated at room temperature and 20 mm. pressure, and a 1-g. aliquot of

the residue was applied to an alumina (30 g., neutral) column in hexane–benzene (1:1). Material eluted with hexane–benzene was distilled at 50° (50 μ) to give the pure adduct, λ_{max} 218 (ϵ 5100); $\nu_{max}^{CHCl_3}$ 1710(s), 1725(sh) cm.$^{-1}$.

Anal. Calcd. for $C_{12}H_{14}O_4$: C, 64.9; H, 6.3; OCH_3, 27.9. Found: C, 64.7; H, 6.2; OCH_3, 27.6.

Determination of pK_a's.—A suitable amount (10–20 mg.) of the base to be studied was dissolved in 25.0 ml. of benzene previously saturated with the appropriate buffer solution. This solution was then equilibrated with 25.0 ml. of benzene-saturated 0.10 M phosphate buffer, which had been adjusted (±0.01 pH unit) to the desired pH. After allowing 10–15 min. for phase separation, an aliquot (15.0 ml.) was taken from the buffer phase and concentrated *in vacuo* (40°) to *ca*. 5 ml. in order to remove all traces of benzene. The concentrate was diluted to 10.0 ml. with distilled water, and the concentration of the base (ammonium form) determined spectrophotometrically in the ultraviolet.[33] As a check, a second equilibration was carried out with the original benzene solution using fresh buffer.

Each compound was equilibrated at two values of pH and the apparent partition coefficient (P') for each pH was used to determine K_a by the equations

$$\frac{P}{P'} = 1 + \frac{(H^+)}{K_a'}; \quad K_a' = \frac{P_1'(H_1^+) - P_2'(H_2^+)}{P_2' - P_1'}$$

The precision was about $\pm 0.2 \ pK_a'$ unit.

[Contribution from the Department of Chemistry, Brandeis University, Waltham 54, Mass.]

Inhibition and Quenching of the Light-induced Reductions of Benzophenone to Benzpinacol and to Benzhydrol[1]

By Saul G. Cohen and Warren V. Sherman

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Light-induced reductions of benzophenone by 2-propanol to benzpinacol and, in the presence of sodium 2-propoxide, to benzhydrol have been studied and effects of 2-mercaptomesitylene, mesityl disulfide and naphthalene have been examined. Rates of formation of benzpinacol and of benzhydrol are nearly equal in the absence of retarders, rates of reduction of benzophenone differing by a factor of about 2. The mercaptan and disulfide retard formation of benzhydrol less efficiently than they retard formation of benzpinacol. It is concluded that radical I, $(C_6H_5)_2O\dot{C}H$, is formed during inhibition of formation of benzpinacol by sulfur compounds, and that benzpinacol is not an intermediate in the formation of benzhydrol, the latter resulting from disproportionations involving radical ion Ia, $(C_6H_5)_2\dot{C}-O^-$. Naphthalene is similarly effective in retarding formation of benzpinacol and benzhydrol, but is much less effective than the sulfur compounds in retarding formation of benzpinacol. Naphthalene must quench short-lived excited benzophenone, while the sulfur compounds react with longer-lived radicals. The reactions show linear dependence of $1/\Phi$ on concentration of quencher or retarder.

We have recently reported[2] that the aromatic mercaptans, thiophenol and 2-mercaptomesitylene, and their disulfides, when present in low concentration, 10^{-3}–10^{-2} M, are effective retarders and inhibitors of the photochemical reduction of benzophenone to benzpinacol by secondary alcohols. Similar effectiveness is shown by a thiol and its disulfide. They undergo chemical reaction and the same equilibrium mixture of the two results during the inhibition when either is used initially. When these reactions are studied in optically active 2-octanol, racemization of remaining octanol does not occur during formation of benzpinacol in the absence of inhibitor, nor does ultraviolet irradiation of the alcohol with disulfide lead to racemization; but racemization does occur when the photoreduction of benzophenone is inhibited by the mercaptan–disulfide, and at a rate comparable to the rate of photoöxidation of the alcohol by the ketone during the uninhibited reaction. We have concluded that in this situation the normal excitation of benzophenone and the abstraction of hydrogen occur, leading to the benzophenone and alcohol derived radicals I and II.

$$(C_6H_5)_2C{=}\overset{*}{O} + R_2CHOH \xrightarrow{k_1} (C_6H_5)_2\dot{C}-OH + R_2\dot{C}-OH$$
$$\text{I} \qquad\qquad \text{II} \qquad (1)$$

Normally radical II reacts with benzophenone, forming additional I and ketone, and radicals I dimerize.[3]

$$\text{II} + (C_6H_5)_2C{=}O \xrightarrow{k_2} R_2C{=}O + \text{I} \qquad (2)$$

$$2\text{I} \xrightarrow{k_3} (C_6H_5)_2\overset{|}{\underset{OH}{C}}-\overset{|}{\underset{OH}{C}}(C_6H_5)_2 \qquad (3)$$

We have proposed that in the presence of mercaptan and disulfide other reactions compete with reactions 2 and 3. Radical I is reconverted to benzophenone by thiyl radical or disulfide, and radical II is converted to starting alcohol (racemic) by mercaptan.[4]

$$(C_6H_5)_2\dot{C}-OH + AS\cdot \xrightarrow{k_4} (C_6H_5)_2C{=}O + ASH \qquad (4)$$

$$R_2\dot{C}-OH + ASH \xrightarrow{k_5} R_2CHOH + AS\cdot \qquad (5)$$

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

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

(4) Additional evidence for the latter, which will be reported in a later publication, is found in transfer of deuterium from oxygen to carbon when the inhibition is studied in O–D labeled 2-propanol.
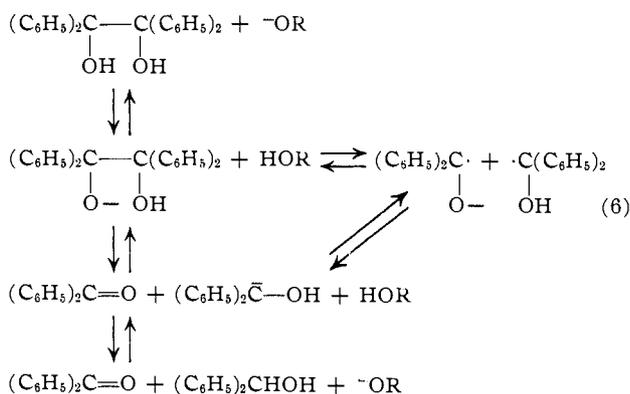
The back-reaction of radicals I and II to form benzophenone and 2-propanol, thermodynamically favorable but normally not observed for kinetic reasons, in effect is catalyzed by the mercaptan and disulfide. The latter undergo no net change in effecting this and function repeatedly, each pair negating by chemical action the ultimate chemical consequences of many quanta of both ultraviolet and ^{60}Co γ-radiation. The reported results give cogent evidence for formation of the alcohol-derived radical II in high yield during the inhibition, but only imply concomitant formation of the benzophenone derived radical I when benzpinacol is not being formed.

We have now studied a closely related system in which the subsequent reaction of radical I may not be the dimerization, reaction 3, in order to obtain evidence for its formation in the presence of the sulfur compounds. The reported effects, retardation and inhibition, are similar to those of physical quenching, and we have compared the action of a quencher, naphthalene, with those of the sulfur compounds in both systems. We anticipated that a physical quencher, acting on the excited benzophenone before chemical reaction occurs, might show similar effects in the two systems, while a chemical inhibitor, competing for the free radicals, might behave differently in the two systems.

The preparative bimolecular reduction[5] of benzophenone by 2-propanol is best carried out in the presence of a weak acid. If the solution is alkaline, the major or sole product of reduction is benzhydrol.[6] It has been proposed[6] that in these circumstances benzpinacol is formed first, and that it decomposes under the influence of the alkali to benzophenone and benzhydrol. It has not been shown that benzpinacol is formed under these conditions, but it has been shown that benzpinacol is converted by a small amount of sodium alcoholate to the intramolecular disproportionation products,[7] possibly according to the scheme

$$(C_6H_5)_2C\underset{\overset{|}{OH}}{\overset{}{—}}\underset{\overset{|}{OH}}{\overset{}{—}}C(C_6H_5)_2 + {}^-OR$$

$$\updownarrow$$

$$(C_6H_5)_2C\underset{\overset{|}{O-}}{\overset{}{—}}\underset{\overset{|}{OH}}{\overset{}{—}}C(C_6H_5)_2 + HOR \rightleftarrows (C_6H_5)_2C\cdot + \cdot C(C_6H_5)_2 \quad (6)$$
$$\underset{\overset{|}{O-}}{} \quad \underset{\overset{|}{OH}}{}$$

$$\updownarrow$$

$$(C_6H_5)_2C{=}O + (C_6H_5)_2\overset{-}{C}{—}OH + HOR$$

$$\updownarrow$$

$$(C_6H_5)_2C{=}O + (C_6H_5)_2CHOH + {}^-OR$$

As will be seen below, it appears unlikely that the reduction to benzhydrol proceeds via the pinacol.

We have carried out ultraviolet irradiation of degassed 0.5 M solutions of benzophenone in 2-propanol in Pyrex tubes in the presence and absence of sodium 2-propoxide. The concentration of remaining benzophenone after measured periods of irradiation was determined in the pinacol reductions: (a) by vapor phase chromatography against an internal standard, β-naphthol; and (b) by ultraviolet absorption measurement; and in the monomolecular reduction (a) by measurement of the benzophenone:benzhydrol ratio by vapor phase chromatography, and (b) by ultraviolet absorption measurement. Approximate quantum yields were determined by comparison with a ferrioxalate actinometer. The concentrations of benzophenone and 2-propanol

(5) W. E. Bachmann, "Organic Syntheses," Coll. Vol. II, John Wiley and Sons, Inc., New York, N. Y., 1943, p. 71.

(6) W. E. Bachmann, J. Am. Chem. Soc., **55**, 391 (1933).

(7) W. E. Bachmann, ibid., **55**, 355 (1933).

were such as to lead in the pinacol reduction to expected quantum yields of nearly 1 for formation of the pinacol, nearly 2 for reduction of benzophenone.[3] The results are summarized in Table I.

TABLE I

PHOTOREDUCTION OF 0.5 M BENZOPHENONE IN 2-PROPANOL TO BENZPINACOL AND TO BENZHYDROL

Irradiation, hr.	$(CH_3)_2CHONa$, M	Benzophenone reduced mmoles	% rn.	Φ
0.5	...[a]	0.36	9	1.9
1.1	...[a]	0.88	22	2.0
2.0	...[a]	1.60	40	2.0
2.5	...[a]	2.10	49	2.1
3.0	...[a]	2.20	55	1.8
4.5	...[a]	3.41	85	1.9
1.0	0.1[b]	0.40	10	1.0
2.0	.1[b]	0.72	18	0.9
4.0	.1[b]	1.48	37	1.0
5.1	.1[b]	1.88	47	0.9
22	.1[b]	4.00	100	...

[a] Benzpinacol formed.   [b] Benzhydrol formed.

Both reductions showed zero-order kinetics. In the pinacol reaction, benzophenone was reduced at the rate of 0.10 mmole/ml./hr., 19%/hr.; in the monomolecular reduction, benzophenone was reduced at about half this rate, 0.047 mmole/ml./hr., 9.3%/hr., and this rate was insensitive to variations in the concentration of alkoxide in the range of 0.05 to 0.2 M. Benzhydrol was formed at about the same rate as benzpinacol, hydrogen being transferred at equal rates in the two reactions. The quantum yields for reduction of benzophenone were nearly 2 and 1, respectively, in the two reactions, 2 for transfer of hydrogen in both, indicating that the first step in the two processes may be the same; eq. 1. Benzhydrol and acetone were formed at equal rates, indicating that the second step in the two processes may be the same; eq. 2.

The photoreduction of benzophenone to benzhydrol was then examined in the presence of 0.01 M 2-mercaptomesitylene and of 0.009 M mesityl disulfide. Analyses of solutions after one-half hour of irradiation indicated that 70–80% of the sulfur was present as mercaptan independent of whether pure mercaptan or disulfide was used initially. Persistence of the mercaptan at this level during prolonged irradiation indicated that the alkoxide, which may react with disulfide, was not leading to irreversible transformations via derivatives of sulfenic acids. Reduction of the disulfide was even more rapid in this system than it had been[2] during the retardation of formation of benzpinacol. Reduction of disulfide to mercaptan went almost to completion when it was irradiated in 2-propanol containing 0.1 M sodium 2-propoxide in the absence of benzophenone. In the absence of alkali[2] added ketone had been required to effect the reduction. Like the reduction to pinacol, reduction to benzhydrol in the presence of mercaptan or disulfide was found to be linear with time, apparently starting at time zero, with no induction period, and proceeding with zero-order kinetics but at lower rates than in the absence of sulfur compound. Some results are summarized in Table II. Quantum yields, reflecting the effects of both masking[2] and inhibition, are calculated from the observed rates as a uniform method of comparing the rates.
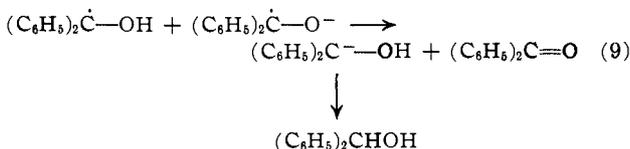
Approximate zero-order kinetics being found, the reaction was then studied for the effect of concentration of mercaptan or disulfide on the rate by determination of the extent of reduction after single stated times of irradiation at each concentration. New data for effect of the disulfide on the pinacol reduction are included for

Fig. 1.—Effect of mesityl disulfide and 2-mercaptomesitylene on the photoreduction of 0.5 M benzophenone in 2-propanol: –O–O–, reduction to pinacol; –●–●–, reduction to benzhydrol; ●, 2-mercaptomesitylene; other points refer to disulfide.

comparison in Table III and the two sets of experiments are summarized in Fig. 1.

The 2-mercaptomesitylene and mesityl disulfide showed equivalent effectiveness per thiyl group in retarding the formation of benzhydrol, as had been observed in the reduction to benzpinacol,[2] and as would be expected from the rapid conversion of the disulfide

TABLE II

PHOTOREDUCTION OF 0.5 M BENZOPHENONE TO BENZYHYDROL IN 0.11 M SODIUM 2-PROPOXIDE IN 2-PROPANOL, IN THE PRESENCE OF 2-MERCAPTOMESITYLENE (MSH) OR MESITYL DISULFIDE (MSSM)

| Irradiation, hr. | ———Additive——— | | —Benzophenone reduced[a]— | | |
	Compound	M	mmoles	% rn.	Φ
3.0	MSSM	0.0092	0.36	9	0.30
5.0	MSSM	.0092	0.64	16	.32
13.5	MSSM	.0092	1.80	45	.32
5.25	MSH	.010	1.08	27	.52
6.3	MSH	.010	1.40	35	.55
7.8	MSH	.010	1.64	41	.52
12.3	MSH	.010	2.76	69	.57
22.0	MSH	.010	4.00	100	..

[a] Analyses were by vapor phase chromatographic determination of the benzophenone:benzhydrol ratio. Benzhydrol was isolated and characterized as the reduction product.

largely to mercaptan during the irradiation. However, the sulfur compounds are considerably less effective in retarding the monomolecular reduction than they are in retarding formation of benzpinacol. The concentration of sulfur moiety sufficient to halve the rate of formation of pinacol is about 1.5×10^{-3} molar. That required to halve the rate of formation of benzhydrol is about 9×10^{-3} molar. This difference in the effectiveness of the sulfur compounds in retarding the two reductions may be confirmatory evidence that they are not acting as physical quenchers for photoexcited benzophenone, although admittedly they are present largely as mercaptan in the pinacol reaction and as mercaptide anion in the presence of alkoxide during formation of benzhydrol. Also, the formation of benz-

TABLE III

EFFECT OF 2-MERCAPTOMESITYLENE AND MESITYL DISULFIDE ON THE PHOTOREDUCTION OF 0.5 M BENZOPHENONE IN 2-PRO-PANOL TO BENZPINACOL AND TO BENZHYDROL

| Irradia-tion, hr. | NaOR, M | ———Additive———— | | —Benzophenone reduced— | | |
		Compound	$M \times 10^3$	mmoles	% rn.	Φ
2.0	..	....	...	1.60	40	2.0
2.5	..	MSSM	0.20	1.56	39	1.55
5.0	..	MSSM	1.24	1.54	38	0.75
17.5	..	MSSM	1.90	3.20	80	.48
5.0	..	MSSM	2.06	0.92	23	.45
5.0	..	MSSM	2.60	0.64	16	.35
17.5	..	MSSM	2.90	2.60	65	.39
17.8	..	MSSM	3.70	1.92	48	.28
17.5	..	MSSM	5.20	1.44	36	.22
17.5	..	MSSM	6.70	1.04	26	.16
4.0	0.10	....	...	1.48	37	1.0
3.0	.10	MSSM	1.35	0.90	22	0.75
3.0	.10	MSSM	2.90	.80	20	.68
3.0	.10	MSSM	4.15	.58	15	.48
3.0	.10	MSSM	5.60	.60	15	.50
16.0	.10	MSSM	16.0	1.34	34	.20
16.0	.10	MSSM	32.2	0.32	8	.05
12.3	.10	MSH	10.0	2.76	69	.57
16.0	.10	MSH	20.0	1.92	48	.30
16.0	.10	MSH	27.0	1.56	39	.25
16.0	.10	MSH	47.0	0.92	23	.15

hydrol at about half its normal rate, in the presence of a concentration of sulfur compound sufficient to reduce the rate of formation of benzpinacol to one-tenth its normal rate, when the reaction is carried out in the absence of alkoxide, leads us to the proposals: (1) The benzophenone-derived radical $(C_6H_5)_2\dot{C}OH$ (I) is also formed at substantial rates, while formation of benzpinacol is being strongly retarded by the sulfur compounds, and it is destroyed by reaction 4 as previously proposed.[2] (2) Benzpinacol is not formed in the presence of the high concentration of sulfur compound in the system leading to benzhydrol, and is not an intermediate in the monomolecular reduction, as had been suggested.[6]

Excited benzophenone may in the presence of alkoxide abstract hydrogen from 2-propanol, reaction 1, leading to radicals I and II, or from 2-propoxide anion, reaction 7, leading to radical I and radical ion IIa.

$$(C_6H_5)_2C{=}\overset{*}{O} + R_2CHO^- \longrightarrow (C_6H_5)_2\dot{C}{-}OH + R_2\dot{C}O^- \quad (7)$$
$$\qquad\qquad\qquad\qquad\qquad\qquad I \qquad\qquad IIa$$

In the presence of alkoxide, radicals I and II may be present in part, if not largely, as the ketyl radical ions Ia and IIa. This ionization in 0.1 N alkoxide is particularly favorable for radical I, since a $pK_a = 9.2$ has

$$(C_6H_5)_2\dot{C}{-}OH + {}^-OR \rightleftharpoons (C_6H_5)_2\dot{C}{-}O^- + HOR \quad (8)$$
$$\qquad\qquad\qquad\qquad\qquad\qquad Ia$$

been reported[8] for it. Conversion of radical I to radical Ia is more rapid than either its dimerization (reaction 3) or its destruction by thiyl radical (reaction 4). Radical II may react in its normal way, reaction 2, leading to radical I by hydrogen transfer, while IIa may be even more effective in reducing benzophenone to Ia by electron transfer, both reactions leading to acetone and finally to radical ion Ia. The concentration of radical I being lowered by its ionization, its rate of dimerization becomes small. Dimerization of radical ion Ia is slow because of the charge; for the same reason, disproportionation of Ia to form benzophenone and benzhydrol might be slow unless it is accompanied by simultaneous proton transfer from the solvent. Reduction of radical

(8) G. Porter and F. Wilkinson, *Trans. Faraday Soc.*, **57**, 1686 (1961).

I by radical ion Ia may be the preferred reaction leading to a carbanion and thence to the observed benzhydrol.

$$(C_6H_5)_2\dot{C}-OH + (C_6H_5)_2\dot{C}-O^- \longrightarrow$$
$$(C_6H_5)_2C^-—OH + (C_6H_5)_2C=O \quad (9)$$
$$\downarrow$$
$$(C_6H_5)_2CHOH$$

Radical I may also be reduced by radical ion IIa, the products of reaction 7 thus going on directly to benzhydrol and acetone. The intercession of the radical ions formed by the alkoxide leads by electron transfer to the carbinol and ketone, the products of radical disproportionation; the uncharged radicals lead to the pinacol by dimerization, their disproportionation requiring transfer of a hydrogen atom and being less favored. The lesser effectiveness of the sulfur compounds in retarding formation of benzhydrol as compared with their activity in the pinacol reaction may be due to one or more of several factors: (i) Reduction of radical I by radical ions Ia or IIa may be more rapid than its reaction in the absence of alkali, dimerization. (ii) The radical ions Ia and IIa may react more slowly than the radicals I and II with thiyl radical and mercaptan.

The relationship between the extent of retardation and the concentration of the sulfur compound is indicated in Fig. 1, $1/\Phi$ being approximately linear with total concentration of sulfur moiety and extrapolating to the quantum yields which are experimentally observed in the absence of inhibitor. This applies to both the bimolecular and monomolecular reductions, the slopes of the lines differing and reflecting the difference of efficiency of the inhibitor in the two reactions. This inverse dependence of quantum yield on concentration of additive is also observed with physical quenchers[9] and will be discussed below.

The action of naphthalene, a known quencher[10] of the first excited triplet of benzophenone and thus an inhibitor of its photoreduction to benzpinacol,[10] was then compared in the bimolecular and unimolecular reductions in 2-propanol. In Table IV the results of some photoreductions in the presence of 0.01 M naphthalene are summarized. Both reductions showed approximate zero-order kinetics.

TABLE IV

EFFECT OF 0.01 M NAPHTHALENE ON THE PHOTOREDUCTION OF 0.5 M BENZOPHENONE IN 2-PROPANOL TO BENZPINACOL AND TO BENZHYDROL

Irradiation, hr.	NaOR, M	Benzophenone reduced		
		mmoles	% rn.	Φ
1.5	...[a]	0.48	12	0.80
3.0	...[a]	0.88	22	.73
4.5	...[a]	1.36	34	.75
2.0	0.10[b]	0.40	10	.54
4.0	.10[b]	.76	19	.51
5.0	.10[b]	.88	22	.47
6.0	.10[b]	1.08	27	.49

[a] Benzpinacol formed. [b] Benzhydrol formed.

In Table V and in Fig. 2 the effects of varying concentration of naphthalene are summarized. Linear plots of $1/\Phi$ against concentration of naphthalene were obtained for the two reductions and the slopes of the lines differed by only 25%, the quenching appearing slightly more effective in retarding reduction to benzhydrol. This stands in contrast with the retarding action of the sulfur compounds which were about fourfold more effective in retarding reduction to benzpinacol. As described above, the sulfur compounds show dif-

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

(10) W. M. Moore and M. Ketchum, *ibid.*, **84**, 1368 (1962).
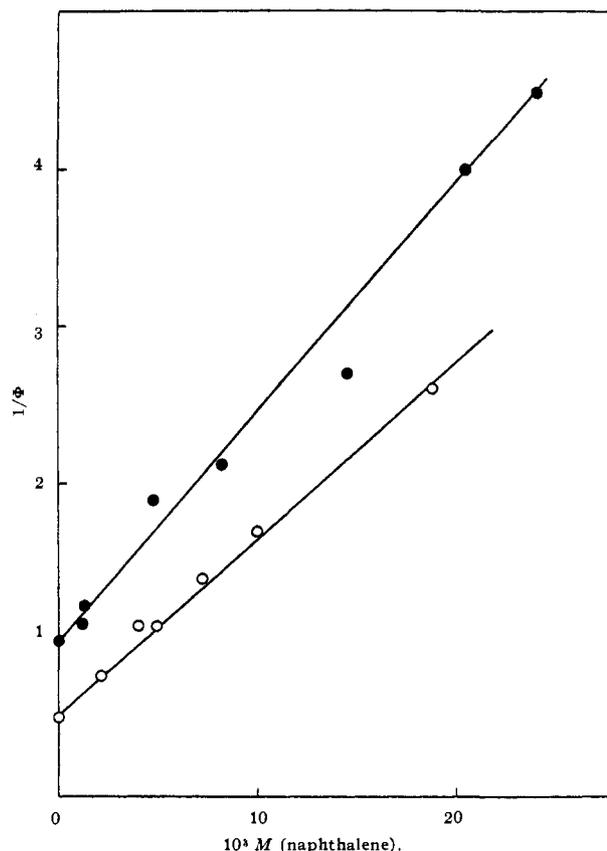
Fig. 2.—Effect of naphthalene on the photoreduction of 0.5 M benzophenone in 2-propanol: —O–O—, reduction to pinacol; —●–●—, reduction to benzhydrol.

ferent effectiveness in the two reactions because they are acting chemically and competing with different chemical reactions. The quencher had essentially the same effect in the two reactions, indicating that the physical quenching is competing with the same or similar chemical reactions in the two situations, abstraction by the excited benzophenone of the hydrogen atom from the alcohol or the alkoxide reactions 1 and 7. This provides evidence that the benzhydrol reaction does not proceed by a fundamentally different, non-radical, mechanism which can be formulated.

TABLE V

EFFECT OF NAPHTHALENE ON THE PHOTOREDUCTION OF 0.5 M BENZOPHENONE IN 2-PROPANOL TO BENZPINACOL AND TO BENZHYDROL

Irradiation, hr.	NaOR, M	Naphthalene, $M \times 10^3$	Benzophenone reduced		
			mmoles	% rn.	Φ
2.5	...[a]	2.1	1.28	32	1.30
2.0	...[a]	4.0	0.76	19	0.95
3.0	...[a]	5.0	1.12	28	.92
4.0	...[a]	7.3	1.12	28	.70
4.0	...[a]	10.0	0.96	24	.60
4.0	...[a]	18.7	0.60	15	.38
4.0	0.10[b]	1.3	1.32	33	.89
5.0	.10[b]	1.4	0.60	15	.81
5.0	.10[b]	4.7	1.00	25	.54
5.0	.10[b]	8.3	0.88	22	.48
16.0	.10[b]	14.6	2.20	55	.37
16.0	.10[b]	20.3	1.48	37	.25
5.0	.10[b]	24.0	0.40	10	.22

[a] Benzpinacol formed. [b] Benzhydrol formed.

Naphthalene acts as a quencher by energy transfer from excited benzophenone to the naphthalene.[10] When the quencher is

$$(C_6H_5)_2C=\overset{*}{O} + Q \xrightarrow{k_{10}} (C_3H_5)_2C=O + Q^* \quad (10)$$
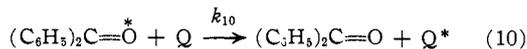
added to a solution in which in its absence negligible desensitizing by the solvent occurs, the quantum yield for benzpinacol Φ_p is given by the following simplified expressions from eq. 1, 2, 3 and 10

$$\Phi_p = \frac{k_1[R_2CHOH]}{k_1[R_2CHOH] + k_{10}[Q]} \quad (11)$$

$$\frac{1}{\Phi_p} = 1 + \frac{k_{10}[Q]}{k_1[R_2CHOH]} \quad (12)$$

Since, in our mechanism for the monomolecular reduction, reactions 8 and 9 are rapid proton and electron transfers, the same expressions lead to the quantum yields for formation of benzhydrol and to the observed linear dependence of $1/\Phi_p$ on concentration of naphthalene for this reaction also; Fig. 2.

The sulfur compounds lower the rate of formation of benzpinacol and the quantum yield by decreasing the rate of reaction 3 by entering into reactions 4 and 5 and decreasing the formation and concentration of radical I. On the assumption of negligible densitization by solvent or sulfur compound the quantum yield for formation of pinacol in the presence of sulfur compounds may be expressed as

$$\Phi_p = \frac{k_3[(C_6H_5)_2\dot{C}OH]^2}{k_3[(C_6H_5)_2\dot{C}OH]^2 + k_4[(C_6H_5)_2\dot{C}OH][AS\cdot]} \quad (13)$$

$$\frac{1}{\Phi_p} = 1 + \frac{k_4(AS\cdot)}{k_3[(C_6H_5)_2\dot{C}OH]} \quad (14)$$

Attainment of an equilibrium concentration of mercaptan and disulfide requires that the rates of reactions 4 and 5 be equal.

$$k_4[(C_6H_5)_2\dot{C}OH][AS\cdot] = k_5[R_2COH][ASH] \quad (15)$$

Equimolar quantities of benzpinacol and acetone are formed at all times in both retarded and unretarded reactions.

$$k_3[(C_6H_5)_2\dot{C}-OH]^2 = k_2[R_2\dot{C}OH][(C_6H_5)_2C=O] \quad (16)$$

$$k_3[(C_6H_5)_2\dot{C}OH]^2/k_2[(C_6H_5)_2C=O] = [R_2\dot{C}OH] \quad (17)$$

Combination of 17 and 15 leads to 18 and 19.

$$k_4[(C_6H_5)_2\dot{C}OH][AS\cdot] = k_5k_3\frac{[(C_6H_5)_2\dot{C}OH]^2[ASH]}{k_2[(C_6H_5)_2C=O]} \quad (18)$$

$$\frac{k_4[AS\cdot]}{k_3[(C_6H_5)_2\dot{C}OH]} = \frac{k_5[ASH]}{k_2[(C_6H_5)_2C=O]} \quad (19)$$

Combination of 19 and 14 leads to 20, indicating a linear

$$\frac{1}{\Phi_p} = 1 + \frac{k_5[ASH]}{k_2[(C_6H_5)_2C=O]} \quad (20)$$

ear dependence of $1/\Phi$ on the ratio of concentrations of mercaptan and benzophenone. Our studies have been carried out at a single initial concentration of benzophenone, leading to similar average concentrations in most of the experiments of Table III. The concentration of sulfur compound probably should be maintained at the present levels; variation in concentration of benzophenone would involve working at much lower concentrations, at which point absorption of light by the sulfur compounds would become important. The observed empirical dependence of $1/\Phi_p$ on concentration of total sulfur in our experiments, Fig. 1, may not be inconsistent with the derived expression (20).

The sulfur compounds may lower the rate of formation of benzhydrol by competing with reaction 9. It is more difficult to formulate this competition because of the uncertainty of the reactions involved. If they react only with radicals I and II in reactions 4 and 5 this effect is rendered less important by the conversion

of the radicals to the radical ions, and expressions of the same form as 13, 14 and 20 result. If they react with the ions, the form of the expressions may not change and the relationship of Fig. 1 might well be observed with the lower slope.

Calculations based on Fig. 2 indicate that k_{10}/k_1, the ratio of rate constants for quenching by naphthalene and for abstraction of hydrogen from 2-propanol by excited benzophenone, has a value of 2900 in the reduction to pinacol, 3800 in the reduction to benzhydrol. The value of 2900 may be compared with corresponding value of 453 obtained in the study[10] of quenching by naphthalene of the reaction of excited benzophenone with benzhydrol. This indicates that the rate constants for removal of hydrogen from benzhydrol by excited benzophenone is greater than that for the removal of hydrogen from 2-propanol by a factor of 6. Comparison of the slopes of the lines in Fig. 1 and 2 indicates that the sulfur compounds are 3.7-fold more effective than naphthalene in retarding formation of benzpinacol and slightly (25%) less effective in retarding formation of benzhydrol.

It is noteworthy that, under the conditions of our experiments the sulfur compounds are this much more effective in inhibiting formation of benzpinacol than naphthalene is in preventing it by quenching, despite the fact that the quenching reaction is exceedingly rapid and thought to be diffusion controlled.[10,11] This is but an apparent paradox since the quencher must react with the relatively short-lived excited state, competing with reaction 1, in which hydrogen is transformed efficiently, leading to free radicals on which the naphthalene has no effect. The sulfur compounds need not and do not[2] react with the photo-excited benzophenone, but they react with the longer-lived free radicals and reconvert them to the starting materials. In this they may show higher effectiveness in competing with the slower later steps, reactions 2 and 3, than the quencher does in competing with reaction 1.

Some information about the rates of the reactions of the mercaptan with the radical intermediate II may be arrived at. At a concentration of mercaptan at which the pinacol reaction is half-inhibited, the rates of reactions 2 and 5 are equal, leading to 21.

$$k_2/k_5 = [ASH]/[(C_6H_5)_2C=O] = 0.002 \quad (21)$$

The specific rate of transfer of hydrogen from mercaptan to radical II, k_5, is 500 times greater than that for transfer of hydrogen from radical II to benzophenone; k_5 would have the value of a chain transfer rate constant for an aromatic thiophenol and be expected to be very high.[12] It is not possible to say whether radical I is converted to benzophenone by reaction with thiyl radical as we have indicated, reaction 4, or with the disulfide, which may also be a chain transfer agent.[12]

Experimental

Materials.—Benzophenone (Fisher) was crystallized from ethyl alcohol; m.p. 47°. Isopropyl alcohol (Fisher, spectroscopic grade) was used as solvent. 2-Mercaptomesitylene and mesitylene disulfide were prepared as described previously.[2] Naphthalene (Fisher) was used as received; m.p. 78–79°.

Apparatus.—The ultraviolet radiation source was an Osram Spektrallampe type Hg/I, operating voltage 50 volts, current 1.2 amperes. The reaction vessels, 15-mm. Pyrex Thunberg tubes, were mounted in a circular turntable and rotated slowly around the lamp. The tubes were blower cooled and were at room temperature, 25–30°, during irradiation.

Preparation of Solutions.—In the reductions to benzhydrol, a weighed quantity of sodium was dissolved in 2-propanol by warming and this solution was rinsed into a weighed quantity of benzo-

(11) G. S. Hammond, N. J. Turro and P. A. Leermakers, *J. Phys. Chem.*, **66**, 1144 (1962); G. S. Hammond and P. A. Leermakers, *ibid.*, **66**, 1148 (1962).

(12) C. H. Walling, "Free Radicals in Solution," John Wiley and Sons, Inc., New York, N. Y., 1957, pp. 319, 332.

phenone in an appropriate volumetric flask. Only freshly prepared solutions were used. For reactions in the presence of 0.01 M naphthalene, 0.01 M mercaptan or 0.01 M disulfide the required amounts of these materials were weighed into the volumetric flask along with the benzophenone. In experiments in which the effect of concentration of the quencher or the retarder was studied, appropriate amounts of naphthalene, mercaptan or disulfide were weighed directly into the Thunberg tubes, and aliquots were added from the volumetric flask. In reductions to benzpinacol, the same procedures were followed, the stock solution containing no sodium.

Photoreduction of Benzophenone to Benzpinacol.—The solution, 8 ml. of 0.5 M benzophenone in 2-propanol, with or without quencher or inhibitor, was placed in a Thunberg tube and degassed by the freeze–melt procedure. After the period of irradiation, residual benzophenone was determined either by ultraviolet absorption or by vapor phase chromatography, the two methods leading to checking results. For ultraviolet analysis, a 1-ml. aliquot was made up to 100 ml. with 2-propanol and absorptions were measured at 333, 340, 350 and 360 mμ on a Perkin–Elmer model 202 spectrophotometer. Extinction coefficients at these wave lengths were 150, 140, 108 and 68, respectively. For chromatographic analysis, β-naphthol was added as an internal standard. Weighed amounts, about 0.05 g., were dissolved in 1-ml. aliquots of the reaction solution, and the solution was analyzed on an Aerograph A-90-P instrument. A 3-foot column containing 10% fluorosilicone elastomer, Dow QF-1-0065, on 80–100 mesh Celite was used at 180°. Helium was the carrier gas and a thermal conductivity detector was used. The weight ratio of benzophenone to β-naphthol was 0.92 × the peak area ratio. Benzpinacol was also isolated and characterized as before.[2]

Photoreduction of Benzophenone to Benzhydrol.—Eight-milliliter portions were degassed in Thunberg tubes by the freeze–melt procedure, and irradiated for stated periods. The amount of benzophenone remaining was determined (a) by ultraviolet absorption as described above and (b) by vapor phase chromatography with the equipment and conditions described above. This analysis led to the residual benzhydrol–benzophenone ratio, no additional internal standard being required. The weight ratio of benzhydrol to benzophenone was 1.3 × the peak area ratio. Remaining benzophenone, determined in this way, showed agreement with that determined by ultraviolet absorption. The benzophenone and benzhydrol were separated on a preparative vapor phase chromatographic column and characterized by infrared spectrum and mixture melting points with authentic samples. Some benzhydrol was formed by thermal reaction[13] when the benzophenone was dissolved initially in warm sodium 2-propoxide-2-propanol. This was determined and a zero point correction was applied. Formation of benzhydrol in this way proceeded slowly in the dark at room temperature, but was much slower than the light-induced reaction and did not cause serious difficulty.

Analysis for acetone was carried out by vapor phase chromatography on a 6-foot column containing 20% adipate resin (R. C. Polymeric B.G.A., Rubber Corporation of America) on 80–100 mesh Celite, at 60°, with helium carrier. The quantities of acetone, formed after 2.0, 3.0 and 5.0 hours irradiation, were 0.13, 0.16 and 0.26 mmole/ml.; the quantities of benzophenone reduced in these periods were 0.11, 0.16 and 0.25 mmole/ml.

Formation of benzhydrol in the disulfide-retarded reaction was demonstrated. Mesityl disulfide (0.0260 g., 0.088 mmole) was added to a standard 8-ml. aliquot, which was degassed, and irradiated for 24 hours. The solution was concentrated under vacuum to a yellow oil which did not crystallize on standing in the cold or when treated with ethanol. The oil was recovered, stored under vacuum for a day and extracted with 300 ml. of boiling

water. The extract was cooled, leading to benzhydrol, 0.23 g., 31% yield, m.p. 63–64°, mixture m.p. 65–66°.

Analyses for Mercaptan.—(i) Aliquots (8 ml.) of 2-propanol solutions, 0.5 M in benzophenone, 0.10 M in sodium 2-propoxide and 0.005 M in mesityl disulfide, were degassed, irradiated for stated periods, and analyzed for thiol[14] by amperometric titration against 0.005 M silver nitrate. At the end of 0.5, 1.0, 5.0, 10 and 19 hours irradiation, the percentages of original sulfur remaining as thiol were 80, 81, 79, 69 and 80%, respectively. Analyses by vapor phase chromatography indicated that after 6 hours, 52% of benzophenone, after 19 hours, over 90% of benzophenone, had been reduced. (ii) A similar solution, containing originally 0.011 M 2-mercaptomesitylene in place of 0.05 M disulfide, after 4.5 hours irradiation had 70% of the original sulfur remaining as thiol, as indicated by amperometric titration. (iii) The residual thiol was characterized by vapor phase chromatography. Synthetic solutions of benzophenone and 2-mercaptomesitylene were analyzed on a 3-foot column packed with 10% fluorosilicone resin QF-1 on 80–100 mesh Chromosorb W. The column oven was programmed from 120 to 180° at about 2° per minute. The mole ratio of benzophenone to 2-mercaptomesitylene was 0.66 × the peak area ratio. Irradiated solutions, similar to those described in (i) above, but containing 0.020 M disulfide, were acidified with acetic acid and the thiol was analyzed by titration and by retention time and peak area. After 2.25 hours irradiation, amperometric titration indicated 65% reduction of disulfide to thiol; the chromatography indicated 62% reduction. (iv) Aliquots of a 25-ml. solution of 0.111 g. of sodium and 0.0134 g. of mesityl disulfide in 2-propanol were degassed, irradiated for stated periods and analyzed for mercaptan by amperometric titration. After irradiation periods of 1.0, 2.0 and 4.0 hours, the percentages of original sulfur present as thiol were 62, 93 and 92%, respectively. The solution showed no mercaptan when initially prepared and after standing for 2 hours and 24 hours in the dark.

Actinometry.—The amount of radiation absorbed by the benzophenone solution was determined by use of a ferrioxalate[15] actinometer with unfiltered radiation from the Osram lamp. Freshly-prepared solutions of 4 ml. of 0.00600 M ferric ammonium sulfate in 0.1 N sulfuric acid and 4 ml. of 0.0180 M potassium oxalate were irradiated in Thunberg tubes for measured times. A 1-ml. aliquot was treated with 2 ml. of 0.1% phenanthroline and 5 ml. of a solution 0.36 N in sulfuric acid and 0.6 M in sodium acetate, diluted to 25 ml., allowed to stand for 0.5 hour and examined on a Perkin–Elmer model 202 spectrophotometer at 510 mμ. Ferrous ion concentrations were calculated from a calibration curve; from the reported[14] quantum yield of 1.2 for this photoreduction, the quantity of radiation absorbed was calculated. Three series of determinations were carried out: (1) with the reaction tube placed as usual in the irradiation equipment; (2) with the tube enclosed in a Pyrex filter tube; and (3) enclosed in the filter tube with the latter containing a 1-cm. layer of 0.5 M benzophenone in 2-propanol. The quantity of radiation absorbed by benzophenone in 2-propanol in our studies was given by 2–3. The studies were carried out using the same lamp over a period of 6 months, and during this period a solution of 0.5 M benzophenone in 2-propanol was used as a secondary actinometer, the rate of reduction of the benzophenone decreasing over this period from 19.5 to 17.5% hr.$^{-1}$, the latter value corresponding to 7.04 × 10^{16} molecules min.$^{-1}$. The results of the ferrioxalate experiments at that time were (1) 7.0 × 10^{16}, (2) 5.8 × 10^{16} and (3) 2.2 × 10^{16} quanta min.$^{-1}$. The quantum yield of the pinacol reaction, rate of reduction of benzophenone divided by 2–3, was 1.95.

(13) G. A. Swan, *J. Chem. Soc.*, 1408 (1948).

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