6.5–7.6-ppm region of isomer B is quite different from that of isomer A.

C. **1-(*o*-Hydroxyphenyl)-6-phenyl-1,5-hexadiene (13c).**—A 0.55-g sample of pure, crystalline **13c** in 180 ml of methanol was degassed in the fashion described above and irradiated for 1.5 hr with a 550-W Hanovia arc contained in a quartz well. The solvent was then removed, and the thick, orange, oily crude product was chromatographed on 50 g of alumina. Elution with ether–heptane (1:3) yielded only a trace of material, and elution with ether–methanol (6:1) yielded a yellow oil which was distilled, bp *ca.* 150° (0.1 mm), to give 0.21 g of a viscous, yellow oil: ir (liquid) 3400 cm^{-1} (ArCH); nmr (CCl_4) δ 1.2–2.7 (broad, 7, CH and CH_2), 3.12 (d, *ca.* 1, J = 1.2 Hz, ArCH), 3.23 (d, *ca.* 1, J = 2 Hz), and 6.5–7.3 ppm (m, 9, ArH). A sample of this material was treated with trifluorohexamethylsilylacetamide, and the silylated product was shown by glpc analysis to contain four components.

Registry No.—**3**, 553-86-6; **4** (R = *i*-Pr), 33316-78-8; **5a**, 13524-76-0; **5b**, 39477-78-6; **5c**, 4355-42-4; **5d**, 4374-69-0; **5e**, 39477-81-1; **6a**, 39477-82-2; **7a**, 10277-93-7; *cis*-**7b**, 39477-84-4; *trans*-**7b**, 39477-85-5; **7c**, 39477-86-6; *cis*-**7d**, 39477-87-7; *trans*-**7d**, 39477-88-8; **7e**, 39477-89-9; **8a**, 88-69-7; **8c**, 4237-44-9; *cis*-**9d**, 38281-39-9; *trans*-**9d**, 38281-40-2; **11b**, 17256-00-7; *cis*-**13a**, 39477-93-5; *trans*-**13a**, 39477-94-6; **13b**, 39477-95-7; **13c**, 39477-96-8; **17a**, 38865-45-1; **17c**, 39477-98-0; **19**, 39477-99-1; **20**, 39478-00-7; **22**, 39478-01-8; *cis*-**25**, 39478-02-9; *trans*-**25**, 39478-03-0; **26**, 39478-04-1; **27**, 39478-05-2; *cis*-**28**, 39478-06-3; *trans*-**28**, 39478-07-4; 2-keto-3-phenyl-2,3-dihydrobenzofuran, 3117-37-1; *o*-hydroxyacetophenone, 118-93-4; *o*-hydroxybenzophenone, 117-99-7; *p*-hydroxybenzophenone, 1137-42-4; 5-bromo-1-pentene, 1119-51-3; salicylaldehyde, 90-02-8; triphenylphosphine, 603-35-0; 5-bromo-1-phenyl-1-pentene, 37464-87-2; triphenyl-1-pentenylphosphonium bromide, 39478-10-9; *o*-methoxybenzaldehyde, 135-02-4; 1-phenyl-1-(*o*-hydroxyphenyl)hexane, 39478-11-0.

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Quenching and Reduction of Photoexcited Benzophenone by Thioethers and Mercaptans[1]

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Reactions of thioethers (sulfides) with excited triplet benzophenones have been studied (1) by retardation by the sulfides of photoreduction by isoborneol, (2) by quenching by naphthalene of photoreduction by the sulfides, and (3) by quenching of phosphorescence of the ketone by the sulfides. Quenching rate constants, k_{ir}, are in the range 10^7–10^9 M^{-1} sec^{-1}. They are highest for aliphatic and lowest for aromatic sulfides, and values are decreased by α branching and by electronegative substituents, and higher in acetonitrile than in benzene. Benzophenone is photoreduced by sulfides containing α H. Quantum yields are low, $\varphi \sim 0.05$–0.2, and increase with decreasing values of k_{ir}. Quenching of phosphorescence of benzophenone by mercaptans shows values of k_q in the range 10^7–10^9 M^{-1} sec^{-1}, highest for aromatic, lowest for aliphatic thiols, decreased by electron-attracting substituents. Reversible hydrogen abstraction is not important in reactions of sulfides, while probably dominant in reactions of thiols. Quenching and photoreduction by sulfides may proceed *via* a common charge transfer complex, in which a full unit of charge separation is not developed. Contributions of charge transfer, hydrogen transfer, and polarizability in quenching and reduction of excited carbonyl compounds by alcohols, ethers, amines, sulfides, and mercaptans are discussed.

The photoreduction of benzophenone to benzopinacol by alcohols proceeds by abstraction of hydrogen by the excited ketone triplet[2] from the α carbon of the alcohol, eq 1, and reduction of ground-state benzophenone by

$$(C_6H_5)_2C{=}O(T_1) + RR'CHOH \longleftrightarrow (C_6H_5)_2\dot{C}OH + RR'\dot{C}OH \quad (1)$$

the alcohol derived radical, eq 2. Such photoreduc-

$$(C_6H_5)_2C{=}O + RR'\dot{C}OH \longrightarrow (C_6H_5)_2\dot{C}OH + RR'C{=}O \quad (2)$$

tions are inhibited by mercaptans or disulfides, present in low concentration, by hydrogen transfer reactions which, in effect, catalyze disproportionation of the initially formed radicals, eq 3 and 4. Ketone and al-

$$RR'\dot{C}OH + ASH \longrightarrow RR'CHOH + AS\cdot \quad (3)$$

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

cohol are regenerated, while the sulfur compounds are regenerated in their alternate oxidation states and function repeatedly, each molecule of sulfur compound negating the effects of many quanta. Support for this mechanism was found in racemization of optically active alcohols[3] and in introduction of carbon-bound deuterium into alcohols[4] during the mercaptan-inhibited reaction, but not during uninhibited photoreduction. Mercaptans might also retard the photoreduction more directly if the excited ketone abstracted sulfhydryl hydrogen from S of mercaptan and the resulting radicals disproportionated, eq 4. At appropriate high concentrations of alcohol and low concentration of thiols the sequence of reactions, eq 1, 3, 4, can be shown to occur almost exclusively.[5]

The borneols are effective photoreducing agents for benzophenone, leading to camphor and benzopinacol

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[1] A preliminary report of part of these results has been published: J. B. Guttenplan and S. G. Cohen, *Chem. Commun.*, 247 (1969).

[2] G. S. Hammond and W. M. Moore, *J. Amer. Chem. Soc.*, **81**, 6334 (1959).

[3] S. G. Cohen, S. Orman, and D. A. Laufer, *ibid.*, **84**, 3905 (1962).

[4] S. G. Cohen, D. A. Laufer, and W. V. Sherman, *ibid.*, **86**, 3060 (1964).

[5] A. Rose, Ph.D. Thesis, Brandeis University, 1971.

in equimolar yields.[6] In analogy to the racemizations, it was of interest to us to examine the equilibration of the epimeric borneol and isoborneol in mercaptan-inhibited photoreductions, a study which will be described at a later date. The process proved complex, a rather high concentration of mercaptan was required, and it became apparent that direct interaction of excited ketone with mercaptan, probably including physical quenching, was occurring in this system in addition to inhibition by the hydrogen transfer reactions. This indicated that thioethers might act as quenchers without the added complexity of transfer of sulfhydryl hydrogen. We had not considered this earlier since we had observed that diphenyl sulfide had essentially no effect on the photoreduction of benzophenone by 2-propanol.[3] We now wish to report on quenching by mercaptans and on quenching and photoreduction by thioethers, reactions analogous in some respects to those of excited ketone with tertiary amines.[7]

Experimental Section

Materials.—Acetonitrile (Matheson Coleman and Bell spectroquality), benzene (Eastman Spectrograde), benzophenone (Fisher reagent grade, mp 47–48°), and naphthalene (Baker) were used directly. Phenyl methyl sulfide (Matheson Coleman and Bell), phenylthiol (Eastman), ethyl benzyl, phenyl benzyl, di-*sec*-butyl, and di-*tert*-butyl sulfides (Aldrich), thiophene, and diphenyl sulfide (Eastman) all showed less than 1% impurity by glc and were used directly. Anisole (Eastman) was collected by glc on a 20-ft Carbowax 20M column. Di-*n*-butyl sulfide (Eastman) was collected by glc on a 6-ft 10% adipate column. *p*-Chlorothiophenol (Aldrich) was crystallized from 95% ethanol and from petroleum ether (bp 60–80°), mp 48–49°. Isoborneol (Matheson Coleman and Bell) was crystallized from ethanol–water, mp 218–220° (sealed tube). Argon was dried over Drierite.

Irradiation Procedure.—Solutions were prepared in volumetric flasks. Aliquots, 2–5 ml, were transferred to calibrated Pyrex tubes, either 12-mm-o.d. round or 10-mm-i.d. square tubes, fitted with Fisher–Porter Teflon greaseless valves. Some tubes had 1-mm quartz absorption cells sealed to side arms. Tubes were degassed by three freeze–thaw cycles, Dry Ice–acetone, 20–100 μ, and closed under argon. Studies of rates of photoreduction were carried out on a turntable holding 12 tubes 8 cm from a G.E. H85/A3 lamp. Residual benzophenone, after periods of irradiation, was determined from the absorbance at 343 nm (ϵ 133) in benzene, measured in a 1-mm cell on a Beckman DU spectrometer. In study of photoreductions retarded by naphthalene or sulfides slopes of dependence of inverse quantum yield on concentration of retarder were obtained by least-squares analysis. Intercepts, inverse quantum yields in the absence of quencher, were taken from the study of the dependence of quantum yield on the concentration of reducing agent in the absence of quencher.

Monochromatic irradiations, for determination of quantum yields by ferrioxalate actinometry,[8] were carried out on a Bausch and Lomb 38-86-01 grating monochromator, dispersion 3.2 nm/mm, Osram SP-200 mercury vapor point source, with a square tube inserted into a cell holder at the exit slit. Solutions were stirred magnetically and cooled by an air blower. At wavelengths below 366 nm a Corning 7-54 filter was placed at the exit slit to filter scattered visible light which might be absorbed by the actinometer solution. Actinometer solutions were stirred and stoppered but not degassed. Ferrioxalate solutions and sample solutions were irradiated alternately several times to minimize effects of lamp fluctuation. Solutions for which quantum yields were determined in this way were used as secondary actinometers for irradiation on the turntable.

Phosphorescence spectra were obtained with 375-nm excitation on a Farrand Mark II spectrofluorimeter. Solutions were degassed in cylindrical quartz cells, ~1 cm o.d., fitted with Teflon stopcocks. Benzophenone concentrations were 0.05–0.10 *M*, and I_0/I ratios were in the range 1–10. A correction, ~3%, was applied for apparent emission resulting from scattered excitation light. Tubes were calibrated and marked so that they could be positioned reproducibly in the cell holder. Variations in phosphorescence intensity from duplicate samples was less than 2%.

Results

In preliminary experiments quantities of sulfides leading to ~0.01 *M* solutions were diluted with a solution of 0.06 *M* benzophenone and 0.10 *M* isoborneol in benzene. Aliquots were irradiated on a turntable along with a solution containing no sulfide and rates of photoreduction were determined (Table I).

TABLE I

PHOTOREDUCTION OF 0.06 *M* BENZOPHENONE BY 0.1 *M* ISOBORNEOL. EFFECTS OF ORGANIC SULFIDES

Registry no.	Sulfide Compd	*M*	R_S/R_0[a]
544-40-1	Di-*n*-butyl	0.009	0.33
6263-62-3	Ethyl Benzyl	0.007	0.44
100-68-5	Phenyl Methyl	0.008	0.62
110-02-1	Thiophene	0.010	0.66
626-26-6	Di-*sec*-butyl	0.007	0.78
831-91-4	Phenyl Benzyl	0.010	0.81
107-47-1	Di-*tert*-butyl	0.008	0.85
139-66-2	Diphenyl	0.008	0.94

[a] Ratio of rates of photoreduction in presence and absence of sulfide.

The sulfides decreased the rate of photoreduction. They do not absorb a significant fraction of the light in the concentrations used and the effect is not due to masking. The di-*n*-aliphatic sulfide was the most effective retarder. Comparison of the *n*-butyl, *sec*-2-butyl, and *tert*-butyl sulfides indicates that the effect is decreased by α branching, which might be due to less or no α H or to a steric effect.

The retarding effect appears not to be due to reversible hydrogen abstraction. Two benzene solutions, 0.0024 *M* in benzophenone, the first containing 0.14 *M* isoborneol and the second containing 0.0074 *M* di-*n*-butyl sulfide, were subject to flash excitation. Both solutions contained sufficient additive, isoborneol or sulfide, to quench ~90% of the benzophenone triplets. The solution containing the isoborneol showed an intense long-lived (~1 msec) absorption at 545 nm, consistent[9] with a high yield of ketyl radical. The solution containing the sulfide showed essentially no such absorption, indicating at least an order of magnitude less of ketyl radical.

Comparison of retardations (Table I) due to *n*-butyl and ethyl benzyl sulfides, and phenyl methyl and phenyl benzyl sulfides, indicates that the electronegative phenyl attached to α C decreases the retardation. Comparison of the effects of ethyl benzyl, phenyl benzyl, and diphenyl sulfides indicates that the aromatic group linked to S strongly decreases the retarding effect. The low retardation due to diphenyl sulfide is consistent with its having led to no detected retardation in photoreduction of benzophenone by neat 2-propanol (13 *M*).[3] Thiophene which, strictly

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[6] S. G. Cohen and R. J. Baumgarten, *J. Amer. Chem. Soc.*, **89**, 3471 (1967).

[7] S. G. Cohen and N. M. Stein, *ibid.*, **93**, 6542 (1971).

[8] C. G. Hatchard and C. A. Parker, *Proc. Roy. Soc., Ser. A*, **235**, 518 (1956).

[9] J. A. Bell and H. Linschitz, *J. Amer. Chem. Soc.*, **90**, 165 (1968).

speaking, does not lie in the class of sulfides shows moderate retarding activity.

Quantitative information about the retardation by sulfides may be obtained by detailed study of the photoreduction by the alcohol and by comparison of the effects on it of sulfides with that caused by a physical quencher of known efficiency, naphthalene. Photoreduction of 0.071 *M* benzophenone by varying concentrations of isoborneol in benzene was studied, and the concentrations and quantum yields were as follows: 0.050 *M*, φ 0.85; 0.080, 1.03; 0.10, 1.14; 0.25, 1.35; 0.50, 1.67; 1.0, 1.78. From these data a linear plot of $1/\varphi$ *vs.* $1/[\mathrm{RH}]$ may be constructed,[10] consistent with eq 5. Least-squares analysis leads to the intercept

$$1/\varphi = 1/a + k_d/ak_{ir}[\mathrm{RH}] \qquad (5)$$

0.56 and the limiting quantum yield *a*, 1.8, and to the slope 0.032 *M*. The ratio of slope to intercept is obtained, $k_d/k_{ir} = 0.057$ *M*, the ratio of rate constant for self- and solvent-induced decay of triplet to that for abstraction of hydrogen by the triplet from the carbinol carbon of isoborneol, RH.

Rates of photoreduction of benzophenone by isoborneol in benzene and in acetonitrile, as affected by naphthalene and by two sulfides, di-*n*-butyl sulfide and phenyl methyl sulfide, were determined. The results are summarized in Tables II and III. The data may be described by a Stern–Volmer relation, eq 6, in which k_q is the rate constant for quenching of the

$$1/\varphi = 1/a + k_d/ak_{ir}[\mathrm{RH}] + k_q[\mathrm{Q}]/ak_{ir}[\mathrm{RH}] \qquad (6)$$

triplet by the additive Q. The slope of the plot of $1/\varphi$ *vs.* [Q] is $k_q/ak_{ir}[\mathrm{RH}]$ and the ratio of slope to intercept is $k_q/(k_d + k_{ir}[\mathrm{RH}])$. The ratio, k_d/k_{ir}, is known from the preceding experiments and the values of k_q/k_{ir} may be calculated. The data in Table II for quenching by naphthalene lead to values of slope of 1.64×10^3 M^{-1} in benzene and 4.0×10^3 M^{-1} in acetonitrile, and to ratios of k_q/k_{ir} of 590 in benzene and 1290 in acetonitrile. The value of k_d/k_q in benzene is 0.97×10^{-4} *M*, similar to that observed with benzhydrol[10a] as reducing agent, 1.03×10^{-4} *M*.

TABLE II

RETARDATION BY NAPHTHALENE OF PHOTOREDUCTION OF 0.060 *M* BENZOPHENONE BY 0.20 *M* ISOBORNEOL

Solvent	[Naphthalene] $\times 10^3$, *M*	Quantum yield
C_6H_6[a]	1.6	0.23
C_6H_6	4.0	0.13
C_6H_6	11.0	0.052
C_6H_6	16.0	0.034
C_6H_6	21.0	0.029
CH_3CN	1.0	0.21
CH_3CN	4.1	0.057
CH_3CN	7.6	0.033
CH_6CN	19.1	0.013

[a] Rates of photoreduction of benzophenone by 0.2 *M* isoborneol in the absence of quencher are the same in C_6H_6 and in CH_3CN.

Quenching of benzophenone triplet by naphthalene, essentially diffusion controlled,[11] has a value of k_q in benzene[12] of 6.3×10^9 M^{-1} sec^{-1}. This leads to $k_{ir} = 1.07 \times 10^7$ M^{-1} sec^{-1} for abstraction of hydrogen by benzophenone triplet from isoborneol in benzene, $k_d = 6 \times 10^5$ sec^{-1}. A value of $k_q = 1.1 \times 10^{10}$ M^{-1} sec^{-1} for k_q in acetonitrile, based on its lower viscosity, leads to $k_{ir} = 0.9 \times 10^7$ M^{-1} sec^{-1} in this solvent, similar to the value in benzene. The data in Table III lead to values of slope, of k_q/k_{ir}, and of k_q for quenching by the sulfides, based on the values of k_{ir} determined above. Results are summarized in Table IV.

TABLE III

RETARDATION BY SULFIDES OF PHOTOREDUCTION OF 0.060 *M* BENZOPHENONE BY 0.17 *M* ISOBORNEOL

Solvent	Sulfide	[Sulfide] $\times 10^3$, *M*	Quantum yield
C_6H_6	DBS[a]	1.9	0.98
C_6H_6	DBS	4.7	0.58
C_6H_6	DBS	8.4	0.40
C_6H_6	DBS	19.0	0.22
CH_3CN	DBS	0.82	0.64
CH_3CN	DBS	3.2	0.45
CH_3CN	DBS	5.5	0.28
CH_3CN	DBS	19.0	0.12
CH_3CN	DBS	24	0.10
C_6H_6	PMS[b]	2.7	1.24
C_6H_6	PMS	7.0	1.02
C_6H_6	PMS	15.0	0.81
C_6H_6	PMS	26.0	0.68
CH_3CN	PMS	3.4	0.75
CH_3CN	PMS	7.0	0.50
CH_3CN	PMS	16.0	0.33
CH_3CN	PMS	23.0	0.27

[a] DBS = di-*n*-butyl sulfide. [b] PMS = phenyl methyl sulfide.

TABLE IV

RETARDATION BY NAPHTHALENE AND BY SULFIDES OF PHOTOREDUCTION OF 0.06 *M* BENZOPHENONE BY ~0.2 *M* ISOBORNEOL IN BENZENE AND IN ACETONITRILE

Quencher	Solvent	Slope, M^{-1}	k_q/k_{ir}	$k_q \times 10^{-8}$, M^{-1} sec^{-1}
Naphthalene	C_6H_6	1.64×10^3	590	63
Naphthalene	CH_3CN	4.0×10^3	1440	110
DBS[a]	C_6H_6	200	61	6.6
DBS[a]	CH_3CN	370	113	9.6
PMS[b]	C_6H_6	29	8.9	0.9
PMS[b]	CH_3CN	127	39	3.3

[a] Di-*n*-butyl sulfide. [b] Phenyl methyl sulfide.

The sulfides are effective retarders, and they are more efficient in acetonitrile than in benzene. Their rates are substantially less than diffusion controlled, and therefore their greater efficiency in acetonitrile may not be ascribed to the lower viscosity of this solvent. It may indicate a polar contribution to the mechanism of quenching by the thioethers.

If the thioethers act as quenchers of the ketone triplets and not by some other mechanism, such as that of eq 3 and 4, they compete with the alcohol reducing agent for the triplets, and their quenching effectiveness should depend on (a) the concentration and (b) the reactivity toward the triplet of the reducing agent. Application of eq 6 to a system containing varying concentration of isoborneol and constant concentration of

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[10] (a) W. M. Moore, G. S. Hammond, and R. P. Foss, *J. Amer. Chem. Soc.*, **83**, 2789 (1961); (b) W. M. Moore and M. D. Ketchum, *ibid.*, **84**, 1368 (1962).

[11] K. Sandros and H. L. J. Bäckstrom, *Acta Chem. Scand.*, **16**, 958 (1962).

[12] W. D. Clark, A. D. Litt, and C. Steel, *J. Amer. Chem. Soc.*, **91**, 5413 (1969).

a thioether as quencher would lead to a linear plot of $1/\varphi$ *vs.* $1/[\mathrm{RH}]$ with slope equal to $(k_\mathrm{d} + k_\mathrm{q}[\mathrm{Q}])/ak_\mathrm{ir}$. Table V contains data for two such experiments.

TABLE V

EFFECT OF CONCENTRATION OF ISOBORNEOL ON PHOTOREDUCTION IN BENZENE OF 0.071 *M* BENZOPHENONE[a]

Isoborneol	Phenyl methyl sulfide, quantum yield, φ	Ethyl benzyl sulfide, quantum yield, φ
0.050	0.50	
0.052		0.38
0.068		0.44
0.080	0.70	
0.10	0.73	0.53
0.14		0.64
0.20		0.83
0.25	1.16	
0.39		0.95
1.0	1.54	

[a] In the presence of (1) 0.0073 *M* phenyl methyl sulfide and (2) 0.0053 *M* ethyl benzyl sulfide.

The data at 0.1 *M* and higher concentration of isoborneol do lead to linear plots. For phenyl methyl sulfide the slope is 0.086 *M* and $k_\mathrm{q} = 1.5 \times 10^8\ M^{-1}\ \mathrm{sec}^{-1}$ similar to that found above by variation in concentration of sulfide. For ethyl benzyl sulfide the slope is 0.13 *M* and $k_\mathrm{q} = 3.7 \times 10^8\ M^{-1}\ \mathrm{sec}^{-1}$. This value is intermediate between the values for phenyl methyl sulfide and di-*n*-butyl sulfide in benzene (Table IV), consistent with the relative effectiveness of these three compounds as retarders (Table I). At lower concentrations of isoborneol the plots of $1/\varphi$ *vs.* $1/[\mathrm{RH}]$ deviate from linearity in the direction of high quantum yields. As will be shown below, the sulfides are also weak photoreducing agents; this contributes more importantly to the total photoreduction at low concentrations of isoborneol, and this may account for the deviation.

The dependence of the effectiveness of quenching by the sulfide on the reactivity of the alcohol reducing agent is seen in comparative experiments with isoborneol and 2-propanol. In photoreduction of 0.060 *M* benzophenone by 0.50 *M* alcohol reducing agent in benzene, the ratio of rates in the presence and absence of 0.0045 *M* di-*n*-butyl sulfide was 0.60 when isoborneol was the alcohol, 0.40 when 2-propanol was the alcohol. The greater retarding efficiency of the sulfide in reduction by 2-propanol is consistent with the lower reactivity of this alcohol toward benzophenone triplet, $k_\mathrm{ir} = 1.8 \times 10^6\ M^{-1}\ \mathrm{sec}^{-1}$,[13] as compared with $1.07 \times 10^7\ M^{-1}\ \mathrm{sec}^{-1}$ for isoborneol.

Analysis of photoreduction solutions inhibited by sulfides indicated that these compounds were not merely quenchers, since they were slowly consumed during the reactions. In a photoreduction of 0.060 *M* benzophenone by 0.18 *M* isoborneol in acetonitrile in the presence of 0.0070 *M* phenyl methyl sulfide, disappearance of benzophenone was followed at 343 nm, and formation of camphor from isoborneol and decrease in concentration of sulfide were followed by glc. After 40-min irradiation 0.024 *M* benzophenone was reduced, 0.011 *M* camphor was formed, and 0.0020 *M* sulfide disappeared. The sulfide had reduced the quantum yield from 1.25 to 0.50, preventing photoreduction of ~0.048 *M* benzophenone by isoborneol or quenching ~0.024 *M* triplet. Of this it appeared to lead to photoreduction of ~0.002 *M* triplet, indicating an efficiency or approximate quantum yield for photoreduction by phenyl methyl sulfide of ~0.08. Similarly, in a photoreduction of 0.060 *M* benzophenone by 0.17 *M* isoborneol in benzene in the presence of 0.0084 *M* di-*n*-butyl sulfide the quantum yield was reduced from 1.25 to 0.40. After 90-min irradiation 0.046 *M* benzophenone was reduced and 0.0032 *M* sulfide was consumed. This sulfide apparently prevented photoreduction of ~0.123 *M* benzophenone by isoborneol, quenching ~0.062 *M* triplet and photoreducing ~0.0032 *M* triplet. This indicates an efficiency or approximate quantum yield for photoreduction by di-*n*-butyl sulfide of ~0.05.

This interpretation was examined by study of the photoreduction of benzophenone by these sulfides. Rates of photoreduction of 0.060 *M* benzophenone by 0.077 *M* phenyl methyl sulfide in acetonitrile and by 0.19 *M* di-*n*-butyl sulfide in benzene were measured on the turntable simultaneously with a photoreduction by isoborneol of known quantum yield. The results indicated quantum yields of 0.06 and 0.05 for photoreduction by the two sulfide systems, respectively, in adequate agreement with those calculated above from consumption of the sulfides as they retarded photoreduction by isoborneol. Quantum yields were also obtained similarly for photoreduction of benzophenone by 0.049 *M* ethyl benzyl sulfide in benzene, $\varphi = 0.06$, by 0.10 *M* phenyl methyl sulfide in benzene, $\varphi = 0.13$, and by 0.088 *M* *p*-chlorophenyl methyl sulfide in benzene, $\varphi = 0.20$. These quantum yields for photoreduction by di-*n*-butyl sulfide and phenyl methyl sulfide, and probably ethyl benzyl sulfide, would differ little from high concentration limiting values, because of the high values of k_ir which characterize their reactions measured as k_q values (Table IV). *p*-Chlorophenyl methyl sulfide with an electron-attracting substituent has a lower value of k_ir, $1.7 \times 10^7\ M^{-1}\ \mathrm{sec}^{-1}$, measured below, by phosphorescence quenching, and the limiting quantum yield for photoreduction by this compound would be 0.22. It may be noted that all the values of k_ir are rather high; the quantum yields are relatively low and appear to fall with increasing values of k_ir. The stoichiometry of photoreduction by sulfides in benzene was examined briefly. Irradiation of 0.05 *M* benzophenone and 0.050 *M* benzyl ethyl sulfide for 5 hr led to reduction of 0.013 *M* benzophenone and consumption of 0.15 *M* sulfide; irradiation of 0.05 *M* benzophenone and 0.44 *M* phenyl methyl sulfide led to consumption of 0.020 *M* benzophenone and 0.021 *M* sulfide. Approximately equimolar consumption of ketone and sulfide was indicated.

The photoreduction of 0.06 *M* benzophenone by 0.019 *M* di-*n*-butyl sulfide was then examined in the presence of a quencher for this reaction, naphthalene, leading by a second procedure to the value of k_ir for interaction of the sulfide with benzophenone triplet. The following results were obtained, the first number in each pair being the concentration of naphthalene, the second the quantum yield for photoreduction: 0.0, 0.049; 0.00031, 0.046; 0.00086, 0.033; 0.0024, 0.025; 0.0060, 0.014. The plot of $1/\varphi$ *vs.* concentra-

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(13) S. G. Cohen and A. D. Litt, *Tetrahedron Lett.*, 837 (1970).

tion of naphthalene was linear, slope = $8.5 \times 10^3\ M^{-1}$, intercept = 20.5, ratio of slope to intercept 415 M^{-1}, and the rate constant for interaction of benzophenone triplet with di-*n*-butyl sulfide, $k_{ir} = 7.6 \times 10^8\ M^{-1}\ \text{sec}^{-1}$, based on k_q for naphthalene, $6.3 \times 10^9\ M^{-1}\ \text{sec}^{-1}$. The value of k_{ir} for interaction of benzophenone triplet with di-*n*-butyl sulfide used as a photoreducing agent thus proves quite similar to that found through its use as a quencher for photoreduction (Table IV), $6.6 \times 10^8\ M^{-1}\ \text{sec}^{-1}$.

During the course of this work it was observed that phosphorescence of benzophenone in solution at room temperature could be used to determine values of k_{ir} or k_q for quenching of benzophenone triplet, and applications of this have been published.[12,13] This procedure has now been applied to some sulfides, allowing comparison with the values determined in the photoreduction experiments, and to some mercaptans. The latter may not be studied by the photoreduction methods. Values of k_q have been obtained from phosphorescence intensities in the absence and presence of added sulfur compound, I_0 and I, respectively, the triplet lifetime τ, 5×10^{-6} sec in benzene at 23°,[12] and application of the Stern–Volmer expression (eq 7) and are given in Table VI.

$$I_0/I = 1 + \tau_0 k_q[\mathrm{Q}] \qquad (7)$$

TABLE VI

QUENCHING OF PHOSPHORESCENCE OF BENZOPHENONE TRIPLET BY SULFIDES AND MERCAPTANS IN BENZENE AT 23°

Registry no.	Sulfur compd	k_q, M^{-1} sec^{-1}
123-09-1	*p*-Chlorophenyl methyl sulfide	2.2×10^7
	Phenyl methyl sulfide	6.0×10^7
	Di-*tert*-butyl sulfide	5.0×10^7 $(1.4 \times 10^8)^a$
	Di-*n*-butyl sulfide	8.3×10^8 $(1.7 \times 10^9)^a$
107-03-9	*n*-Propylthiol	1.3×10^7
106-54-7	*p*-Chlorophenylthiol	2.0×10^8
108-98-7	Phenylthiol	2.6×10^8
1541-10-2	2,4,6-Trimethylphenylthiol	6.8×10^8
	Isoborneol	0.9×10^7

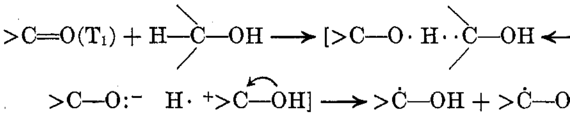
[a] Values in parentheses were measured in acetonitrile.

The value of k_q for phenyl methyl sulfide measured by phosphorescence quenching is similar to that found through its use as a quencher for photoreduction by isoborneol (Table IV). The quenching rate is decreased by the electron-attracting *p*-Cl substituent. The value for di-*n*-butyl sulfide is similar to those found through its use as a quencher (Table IV) and when studied as a photoreducing agent, quenched by naphthalene. Where measurements were made in both benzene and acetonitrile, quenching rates were higher in acetonitrile. The mercaptans prove to be efficient quenchers for benzophenone triplet. The aromatic thiols were more reactive than the aliphatic, and reactivity was decreased by the electron-attracting *p*-Cl substituent and increased by methyl substituents. The value of k_q for isoborneol is similar to that found by quenching by naphthalene of its reaction with benzophenone triplet.

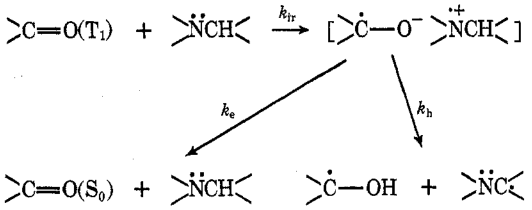
Discussion

Thioethers may be very efficient quenchers and inefficient reducing agents for excited benzophenone. The rate constants for the interaction, k_{ir}, are in the range 10^7–$10^9\ M^{-1}\ \text{sec}^{-1}$, generally higher than those for alcohols and lower than those for amines. The values are greater in acetonitrile than in benzene and indicate a polar contribution to the mechanism, which may involve interaction of triplet ketone with nonbonding electrons of sulfur. These are made less available by electron-attracting and aromatic groups, the presence of which decrease values of k_{ir}. Quantum yields for photoreduction are low, 0.05–0.20, much lower than those for alcohols and amines which may commonly be larger by an order of magnitude.

We have proposed that photoreduction by alcohols proceeds by abstraction of hydrogen from carbon α to the hydroxyl, facilitated by a polar contribution from the heteroatom,[14,15] eq 8, while photoreduction by amines proceeds *via* rapid charge transfer type interaction of triplet ketone with the n electrons of nitrogen, k_{ir}, followed either by spin inversion, charge destruction and quenching, k_e, or by hydrogen transfer and electron reorganization, k_h, eq 9.[14,16] This has been accepted as a rather common mechanism,[17] but reduction and quenching by two independent reactions leads to a similar formal kinetic scheme to that from reaction *via* a charge transfer complex, eq 9, and the two kinds of processes cannot be distinguished kinetically.[18]



(8)



(9)

In the process of eq 8 quantum yield is determined essentially by the relative values of k_r and k_d, rate constants for abstraction of hydrogen and for decay of triplet. In the process of eq 9, k_{ir} may be very high compared with k_d, and quantum yield is determined by the relative values of k_e and k_h. However polar effects are present in both processes and a single linear relationship may be observed, in reactions with a single acceptor, *i.e.*, triplet benzophenone, between value of log k_{ir} for a large variety of organic compounds—including both alcohols and amines—and the ionization potentials of these electron donors, $\mathrm{IP_D}$.[19] Polar contributions to the kinds of processes represented by eq 8 and 9 may be similar at the transition states, or the log relationship may be too crude to distinguish between them.

It is reasonable to consider that reactions of thioethers follow a course related to that of eq 9, an initial polar interaction, which will now be indicated as for-

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(14) S. G. Cohen and J. I. Cohen, *J. Phys. Chem.*, **72**, 3782 (1968).

(15) S. G. Cohen and J. I. Cohen, *J. Amer. Chem. Soc.*, **89**, 164 (1967).

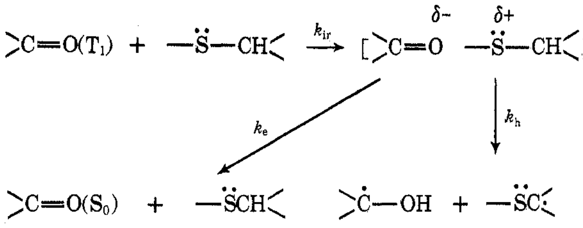
(16) S. G. Cohen and H. M. Chao, *ibid.*, **90**, 165 (1968).

(17) S. G. Cohen, A. Parola, and G. H. Parsons, Jr., *Chem. Rev.*, **73**, 141 (1973).

(18) S. G. Cohen, G. A. Davis, and W. D. K. Clark, *J. Amer. Chem. Soc.*, **94**, 869 (1972).

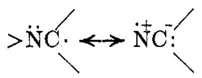
(19) J. B. Guttenplan and S. G. Cohen, *ibid.*, **94**, 4040 (1972).

mation of partial charges, leading then either to quenching or to reduction, eq 10. This formulation,


(10)

as with amines, is consistent with high values of k_{ir} and low sensitivity to diffusion-controlled physical quenchers and allows for very low quantum yields. Triplet–triplet energy transfer, leading to quenching and to inefficient photoreduction, appears not to be a feasible mechanism. Sulfides absorb at much higher energy than benzophenone and their triplet energies are likely to be quite high. Also, the low quantum yields may apparently not be attributed to rapid disproportionation of products formed in an efficient initial hydrogen abstraction. Such a sequence might regenerate starting materials and lead to a low observed quantum yield, but the flash photolysis experiment with di-*n*-butyl sulfide indicates that this is not occurring. Study of photoreduction by an optically active amine indicated that this reversible hydrogen abstraction was not important in that photoreduction,[15] but deuterium-labeling experiments indicated that it did occur in photoreduction by an ether.[20]

The value of k_{ir} for reaction of di-*n*-butyl sulfide with excited benzophenone lies on the same linear plot of log k_{ir} *vs*, IP_D as do many amines,[19] supporting a process such as that of eq 10. However factors which affect the characteristics of these reactions of sulfides may differ from those affecting amines. The low quantum yields, corresponding to low k_h/k_e ratios, may result from low k_h and may indicate that S does not facilitate transfer of H and stabilization of radicals as effectively as N. Radical character α to N may be stabilized by resonance, which lowers the transition state energy for the hydrogen transfer. Such a contribution would be



less from S due to diminished overlap between orbitals of different principal quantum number. It may also be that k_e is higher for thioethers than for amines.

The nature of the initial complex indicated in eq 10 is not clear. The enthalpy for formation of a full charge transfer complex in a hydrocarbon solvent, ΔH_c, may be calculated[21] from

$$\Delta H_c = -\Delta E_{0,0} + [E(D/D^+) - E(A^-/A)] + 0.13 \text{ eV} \quad (11)$$

where $E(D/D^+)$ is the oxidation potential of the donor sulfide, $-E(A^-/A)$ is the reduction potential of the ground state acceptor ketone, and $\Delta E_{0,0}$ is the excitation energy. Oxidation potentials of thioethers do not appear to be reported, but they may be related to ionization potentials,[21] IP_D, by

$$IP_D = E(D/D^+) - \Delta G_{solv}(D^+) + C \quad (12)$$

in which $-\Delta G_{solv}(D^+)$ is the free energy for process 13,

$$D^+_g + D_s \rightleftarrows D^+_s + D_g \quad (13)$$

and C reflects the reference electrode. Comparison of oxidation potentials[22] and ionization potentials[23] of compounds of similar size indicates a value of ~6.5 eV for $[-\Delta G_{solv}(D^+) + C]$ against saturated calomel electrode. The ionization potential of di-*n*-butyl sulfide is 8.3 eV, and $E(D/D^+) \simeq 1.8$ eV. With values of -1.73[24] and 2.97 eV[25] for the reduction potential and triplet energy, respectively, of benzophenone, AH_c is ~15 kcal/mol above triplet benzophenone. The entropy of complex formation is also unfavorable, -18 eu,[26] and the resulting free energy of activation would lead to rate constants much lower than those observed in this work. Thus a complex involving transfer of a full unit of charge is not involved in this process. The effect on k_{ir} of change in solvent from hydrocarbon to acetonitrile is also much less in these reactions than when a full charge is formed.[27]

A similar calculation for the interaction of benzophenone triplet with amines led to a similar conclusion;[19] the observed rates were far too high to be due to transfer of a full unit of charge, and the solvent effects were also too small. It was proposed that the interaction involved development of a partial charge and partial transfer of hydrogen, and this chemical reactivity contributed to the high value of k_{ir}. Quinuclidine, in which the bridgehead nitrogen may not facilitate hydrogen transfer well, is an inefficient photoreducing agent and has a value of k_{ir} an order of magnitude lower than would be predicted from its ionization potential.[19] On the other hand, electron donors which have very easily transferred hydrogen, phenols, anilines, and aromatic thiols, show quenching rates which are higher than would be predicted from the linear relation between log k_{ir} and IP_D. These indications that interaction with n electrons and partial transfer of hydrogen both contribute to the value of k_{ir} support the proposal that the quenching and hydrogen abstraction processes proceed *via* a common intermediate.

The aliphatic sulfides show values of k_{ir} consistent with their ionization potential,[19] but their chemical reactivity is low and partial transfer of hydrogen may not contribute substantially to the high quenching activity. The greater polarizability or heavy atom effect of sulfur, with increased spin–orbit coupling, may enhance intersystem crossing from excited triplet to ground state singlet, in effect increasing k_e, eq 10. The effect need not be a very large one, since with aliphatic amines quenching and hydrogen transfer, k_e and k_h, are already delicately balanced and may be processes of similar rate.

Quenching interactions may involve charge transfer,

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[21] D. Rehm and A. Weller, *Z. Phys. Chem., Neue Folge*, **69**, 183 (1970), and references cited therein.

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[23] J. L. Franklin, J. G. Dillard, H. M. Rosenstock, J. T. Herron, K. Draxl, and F. H. Field, "Ionization Potentials, Appearance Potentials and Heats of Formation of Gaseous Positive Ions," U. S. Department of Commerce, National Bureau of Standards, Washington, D. C., 1969.

[24] M. Peover in "Electroanalytical Chemistry," Vol. 2, A. J. Bard, Ed., Marcel Dekker, New York, N. Y., 1967, p 9.

[25] J. G. Calvert and J. N. Pitts, Jr., "Photochemistry," Wiley, New York, N. Y., 1966, p 298.

[26] H. Knibbe, D. Rehm, and A. Weller, *Ber. Bunsenges. Phys. Chem.*, **73**, 839 (1969).

[27] H. Leonhardt and A. Weller, *ibid.*, **67**, 791 (1963).

partial hydrogen transfer, and polarization. Since there may be a polar effect on hydrogen transfer,[14] all three factors may be related to ionization potential, and many compounds show a linear relation between log k_{ir} and IP_D.[19] The absolute value of k_{ir} depends as well on the acceptor and this has been formulated, eq 14, in a relation derived from eq 11. While for a single

$$\log k_{ir} \simeq -{}^3\Delta E_{0,0} + IP_D - E(A^-/A) + C' \qquad (14)$$

acceptor and a series of donors log $k_{ir} \simeq IP_D$, for a single donor and series of acceptors log $k_{ir} \simeq -{}^3\Delta E_{0,0} - E(A^-/A)$.[28] The relative importance of the several possible factors in a particular interaction will be affected by the properties of the donor–acceptor pair. The extent to which hydrogen donation will contribute will depend on the triplet energy of the acceptor and the C–H bond strength in the donor. Interactions with phenols, anilines, or aromatic thiols will show much hydrogen transfer, and this effect will be greater if the acceptor has high triplet energy. The extent to which electron transfer will contribute will depend on the reduction potential and anionic stability of the acceptor and the oxidation or ionization potential of the donor. Interactions of an acceptor of favorable reduction potential such as fluorenone will show much electron transfer, and this effect will be greater if the donor does not have readily transferred hydrogen, such as di-*tert*-butyl sulfide or quinuclidine. The extent to which polarizability will contribute will depend on atomic size in the donor–acceptor pair and the oxidation and reduction potentials. Where electron-attracting substituents in the donor lower the charge transfer and polarization contributions to the transition state, hydrogen transfer contributions may become proportionally more important. This may account for the inverse relationship between k_{ir} and quantum yield for photoreduction observed in reactions of the thioethers.

Values of rate constants for interaction of mercaptans with excited ketones have not been accessible through study of them as reducing agents or quenchers. These compounds have readily extractable sulfhydryl hydrogen, but they are not photoreducing agents for ketones. When the abstraction occurs, it is followed efficiently by exothermic disproportionation and regeneration of ground state ketone and mercaptan, eq 4. Although mercaptans retard photoreduction by alcohols[3,4] and amines,[15] such study does not lead to values of k_q since the retardation may be due largely or wholly to hydrogen transfer reaction eq 3 and 4. They do interact with excited ketone, and values of k_q, now determined by quenching of phosphorescence (Table VI), indicate high reactivity, $k_q \simeq 10^7$–10^9 M^{-1} sec^{-1}. The greater reactivity of the aromatic as compared with aliphatic thiols, opposite to what is observed in the sulfides, indicates that hydrogen transfer from thiol to triplet contributes importantly to the quenching interaction. This would be favored by greater stability of aromatic thiyl radical. This effect may account for the values of k_q for aromatic thiols being greater than would be indicated by their ionization potentials. Decrease and increase in reactivity by electron-withdrawing and -donating substituents, respectively, while small, indicate some polar contribution to the interaction. This may be an effect on interaction of triplet with *n* electrons of S or an effect on the polar contribution to the hydrogen transfer.

The values of k_q for mercaptans now allow approximate calculation of the relative importance of retardation of photoreduction by mercaptans by the two processes, quenching of excited ketone, and catalysis of disproportionation, eq 3 and 4. For the aromatic thiol with highest value of k_q, 6.8×10^8 M^{-1} sec^{-1} (Table VI), in photoreduction by neat, 13 M 2-propanol, for which $k_r = 1.8 \times 10^6$ M^{-1} sec^{-1}, at 0.005 M thiol about 13% of the retardation may be due to direct interaction of mercaptan and ketone triplet, the remainder due to the hydrogen transfer reactions, eq 3 and 4.

A comparison may be made of interaction and subsequent reaction of excited carbonyl compounds with compounds of O, N, and S. Because of the high electronegativity of O, interaction apparently does not take place at the n electrons, but starts with abstraction of H from α C, and is facilitated by a polar contribution in the transition state, eq 8. Alcohols are not quenchers, but ethers may exhibit disproportionation of the radicals formed by hydrogen transfer. High O–H and lower α-C–H bond energies strongly favor abstraction of α C–H. With amines lower electronegativity and ionization potentials leads to interaction at the n electrons, and interaction between the n electrons and an unpaired electron on adjacent C facilitates transfer of α C–H to excited carbonyl, but the amines may also quench, eq 9. With mercaptans, polarizability and low ionization potential lead to interaction at S, and low S–H bond energy and low capacity of S to stabilize an adjacent radical lead to transfer of sulfhydryl hydrogen to excited ketone. With sulfides, the polarizability of S and low stabilization of the α-carbon radical lead to interaction at S and then largely to quenching, and to little transfer of hydrogen.

Registry No.—Benzophenone, 119-61-0; isoborneol, 124-76-5; naphthalene, 91-20-3.

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[28] J. B. Guttenplan and S. G. Cohen, *Tetrahedron Lett.*, 2163 (1972).