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# The Photoreduction of Benzophenone by Thioethers

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Ultraviolet irradiation of benzophenone in 2-propanol leads to generation of radicals $Ph_2\dot{C}OH$, (A) and $Me_2\dot{C}OH$, (B), and then to formation of pinacol and acetone.

$$Ph_2C{=}O^* + Me_2CHOH \longrightarrow Ph_2\dot{C}OH + Me_2\dot{C}OH$$

The photoexcited ketone may also abstract α-hydrogen from other hydrogen donors, *e.g.*, amines and ethers.[1–4] In these systems the derived radicals may give the three possible radical recombination products. The reaction is, however, retarded and inhibited by the presence of mercaptan or disulfide in low concentration, as rapid reactions are introduced which convert the radicals A and B into the starting materials.[5,6]

$$Ph_2\dot{C}OH + RS\cdot\ (RSSR) \longrightarrow Ph_2C{=}O + RSH\ (RSH + RS\cdot)$$

$$Me_2\dot{C}OH + RSH \longrightarrow Me_2CHOH + RS\cdot$$

On the other hand, the presence of a relatively high concentration of phenyl sulfide or other thioethers which would not readily give the thiyl radical had no effect on photoreduction of benzophenone, indicating that organic sulfur was not a quencher or desensitizer in the reaction. Thus, among aliphatic sulfides, those bearing α-hydrogen atoms are expected to reduce benzophenone photochemically, since α-hydrogen atom was found to be reactive toward abstraction by radicals. On the other hand, sulfides bearing β-hydrogen but no α-hydrogen atoms are not expected to be effective reducing agents, because such sulfides like *t*-butyl sulfide have been known to generate thiyl radicals when the β-hydrogen atom was abstracted by radicals.[7]

Thus, the photoinduced reactions of benzophenone in various aliphatic sulfides were investigated, and the above expection was found to be correct.

## Results and Discussion

Irradiation of 2 mmol benzophenone in 16 mmol dimethyl sulfide with high pressure mercury lamp for 48 hr gave benzopinacol, I, in 35% yield by decanting the unreacted dimethyl sulfide and washing the

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

[2] E. Bergman and J. Fujise, *Ann.*, **483**, 65 (1930).

[3] G. Ciamician and P. Silber, *Ber.*, **44**, 1554 (1911).

[4] S. G. Cohen and S. Atkipis, *J. Amer. Chem. Soc.*, **88**, 3587 (1966).

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

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

[7] J. A. Kampmeier, R. P, Geer, A. J. Meskin, and Rose Marie D'Silva, *ibid.*, **88**, 1257 (1966).

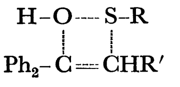
remaining solid with petroleum ether (b.p., 30—60°C). Analysis of the unreacted dimethyl sulfide solution by vapor phase chromatography (Carbowax 20M, 10% on Celite 22) indicated the formation of di(methylthio)methane, II (1.5%), 1,2-di(methylthio)ethane, III (11%), and a mixture (36%) of three diphenyl substituted products, IV, V, and VI.[8]

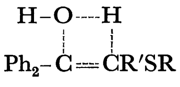
$$Ph_2C{=}O^* + CH_3SCH_3 \longrightarrow \underset{\text{I}}{Ph_2C(OH)C(OH)Ph_2}$$

$$+ \underset{\text{II}}{MeSCH_2SMe} + \underset{\text{III}}{MeSCH_2CH_2Me}$$

$$+ \underset{\text{IV}}{Ph_2C(OH)CH_2SMe} + \underset{\text{V}}{Ph_2C{=}CH_2} + \underset{\text{VI}}{Ph_2C{=}CHSMe}$$

Structures of the reaction products are determined by independent syntheses and spectra analyses. Olefins, V and VI, may be produced from $\beta$-hydroxy sulfide, and IV by elimination of the components of RSOH and $H_2O$ under vpc conditions. With regard to the mechanism of the formation of olefins from $\beta$-hydroxy sulfide, we might suppose that the elimination occurs *via* transitions C and D.


C


D

A similar olefin formation has been reported for the thermolysis of $\beta$-hydroxy sulfinamides.[9]

Photoreductions of benzophenone in diethyl sulfide and diisopropyl sulfide gave similar results. Irradiation of 2 mmol benzophenone in diethyl sulfide for 48 hr led to the consumption of 70% benzophenone and the formation of 40% pinacol I. Analysis of seaction mixture by vpc after removal of the pinacol rhowed the presence of diethyl disulfide (1.3%), 2,3-di(ethylthio)butane (20%), and a mixture (29%) of $Ph_2C(OH)CH(CH_3)SEt$ and $Ph_2C{=}CHMe$. In the reaction of benzophenone in diisopropyl sulfide, about 80% of benzophenone was consumed, and diisopropyl disulfide (3.3%), 2,3-di(isopropylthio)-2,3-dimethylbutane (13%), 1,3-di(isopropylthio) propane (9%), and a mixture (19%) of $Ph_2C{=}CMe_2$ and $Ph_2C(OH)CMe_2$-$S(i\text{-}Pr)$ were obtained together with benzopinacol (45%). Photoreaction in di-*t*-butyl sulfide led to only 8% consumption of benzophenone, and the formation of *t*-butyl mercaptan (7.2%) and a trace of di-*t*-butyl disulfide on 48 hr irradiation.

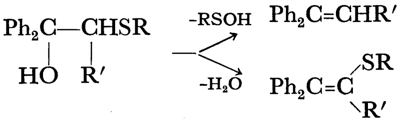
Our results can be explained by the following reaction steps analogous to those for photoreaction in alcohol.

$$Ph_2C{=}O^* + RSCH_2R' \longrightarrow Ph_2\dot{C}OH + RS\dot{C}HR'$$

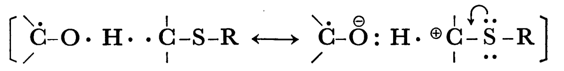
$$2\ RS\dot{C}HR' \longrightarrow RSCH(R')CH(R')SR$$

$$2\ Ph_2\dot{C}OH \longrightarrow Ph_2C(OH)C(OH)Ph_2$$

$$Ph_2\dot{C}OH + RS\dot{C}HR' \longrightarrow$$



In the thioethers, $\alpha$-C–H seems more susceptible than the $\beta$-C–H bond toward hydrogen abstraction by triplet ketone. The polar resonanced factor may contribute to stabilization of the transition state.



Low consumption of benzophenone in di-*t*-butyl sulfide is reasonably explained by the inhibiting effect of thiyl radical formed during the early stage of reaction.

$$Ph_2C{=}O^* + Me_3CSCMe_3 \longrightarrow$$

$$Ph_2\dot{C}OH + CH_2{=}CMe_2 + Me_3CS\cdot$$

$$Me_3CS\cdot + Ph_2\dot{C}OH \longrightarrow Ph_2C{=}O + Me_3CSH$$

Distribution of the olefins formed by reactions in unsymmetrical thioethers is shown in Table 1.

TABLE 1. THE FORMATION OF DIPHENYL OLEFINS IN PHOTOREDUCTION OF BENZOPHENONE IN THIOETHERS

| Thioether | Product | | Ratio A/B |
|---|---|---|---|
| | A | B | |
| *n*-PrSEt | $Ph_2C{=}CHEt$ | $Ph_2C{=}CHMe$ | 1.5 |
| *i*-PrSEt | $Ph_2C{=}CHMe$ | $Ph_2C{=}CMe_2$ | 4.0 |
| *i*-PrSMe | $Ph_2C{=}CMe_2$ | $Ph_2C{=}CH_2$ | 3.7 |

## Experimental

*Photolysis of Benzophenone in Dimethyl Sulfide.* 0.30 g of benzophenone was dissolved in 1 m*l* dimethyl sulfide. Irradiation in a Pyrex tube for 48 hr provided six products, I—VI. The course of photolysis was monitored by gas chromatography. After 40 hr the unreacted benzophenone in dimethyl sulfide was negligible. Benzopinacol was isolated by the addition of petroleum ether to the concentrated reaction mixture, and identified by comparison with authentic samples. Other products, II, III, IV, V, and VI were isolated by preparative gas chromatography. Structures of II, III, and V were identified by comparison with authentic samples. Compound IV shows NMR spectrum at 1.92 (s, 3-H), 3.30 (s, 2-H), 3.45 (s, 1-H), and 7.28 ppm (m, 10-H). VI shows NMR spectrum at 2.28 (s, 3-H), 6.40 (s, 1-H), 7.14 (s, 5-H) and 7.27 ppm (s, 5-H).

Found: C, 79.63; H, 6.12%. Calcd for $C_{15}H_{14}S$: C, 79.60; H, 6.24%.

*Formation of Diphenyl Olefins, V and VI, from IV.* Isolated compound IV by gas chromatography was reinjected into the gas chromatograph of 10% Carbowax 20M, 2 m×0.5 cm stainless column at 220°C. Two products, V and VI, were collected in the ratio 4:1, depending on the conditions of gas chromatograph. On heating the reaction mixture obtained from the photolysis of benzophenone and dimethyl sulfide at 220°C for 1 hr, IV could not be isolated by thin layer chromatography, and V and VI were found to be formed in the ratio of 1:2.5 from the analysis of gas chromatography. However, on heating IV in a Pyrex tube under the same conditions, and by direct analysis of NMR, it was found that IV was not consumed, and V and VI were not obtained.

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[8] Yields based on the consumed benzophenone.

[9] E. J. Corey and T. Durst, *J. Amer. Chem. Soc.*, **88**, 5656 (1966).

*Photolysis of Benzophenone in Thioethers.* As a typical run, a solution of 295 mg of benzophenone in 1 m*l* thioether in Pyrex tubes was irradiated with the high pressure mercury lamp for 48 hr. Precipitated benzopinacol was removed by adding the petroleum ether and washing the solid. The solvent of the reaction mixture was evaporated off *in vacuo* and the residue was analyzed directly by gas chromatography. Products isolated by gas chromatography were characterized by comparison with authentic samples.