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Photochemical Reduction of Thiobenzophenone. Reduction by Dihydroaromatic and Related Compounds

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Photochemical reduction of thiobenzophenone by 1,4-dihydrobenzene, 1,4-dihydronaphthalene, 9,10-dihydroanthracene, 1,3,5-cycloheptatriene, and acridane was studied. Relative reactivities and product analyses have revealed that the reaction is initiated by hydrogen-abstraction (one-electron-transfer followed by a proton migration) with thiobenzophenone in the n,π^* triplet state. Inability of diphenylmethane to undergo the reaction can be interpreted by means of this mechanism.

Thiobenzophenone in the n,π^* triplet state is reduced to diphenylmethanethiol (**1**) by primary and secondary aliphatic alcohols or thiols, whereas it is necessary to excite thiobenzophenone to the π,π^* singlet state in order to reduce it by hydrocarbons such as cyclohexane and diphenylmethane.[1]

$$Ph_2C{=}S \xrightarrow{589\,\mathrm{nm}} \longrightarrow {}^3(Ph_2C{=}S)_{n,\pi^*}$$

$${}^3(Ph_2C{=}S)_{n,\pi^*} + R_2CHXH \rightarrow Ph_2CHSH + R_2C{=}X$$

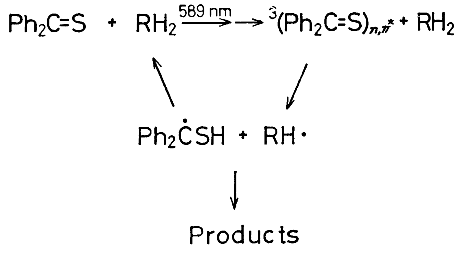
$$(X{=}O \text{ or } S;\ R{=}H, \text{ alkyl, or aralkyl})$$

The low reactivity of diphenylmethane is anomalous, since the benzenethiyl radical can abstract a hydrogen from this hydrocarbon[2] and thiobenzophenone in the n,π^* triplet state is known to behave like a thiyl radical.[3] In order to obtain further information on the reactivity of photo-excited thiobenzophenone, we studied the reactions of thiobenzophenone with various dihydroaromatic hydrocarbons and some related compounds. The results are given in this paper together with a discussion on the mechanism of the reaction.

Results and Discussion

Although the reaction of thiobenzophenone with 1,4-dihydrobenzene (**2**) does not proceed thermally, photochemical reaction takes place under the influence of light from low-pressure sodium lamps (589 nm). Thiobenzophenone in the n,π^* triplet state abstracts hydrogens from **2** yielding **1** and benzene quantitatively. A similar but slower reaction takes place with 1,4-dihydronaphthalene (**3**) giving **1** and naphthalene in 43 and 91% yields, respectively. An even slower reaction proceeds with 9,10-dihydroanthracene (**4**) giving a mixture of complex composition of products including anthracene (26%), dibenzhydryl disulfide (24 %), and **1** (17%). A similar trend of reactivity has been reported for reactions of these compounds with quinones.[4]

There is a distinct difference between dihydroaromatic hydrocarbons and diphenylmethane: the free radical produced from **2**, **3**, or **4** can eliminate a hydrogen unimolecularly yielding a stable aromatic hydrocarbon, whereas the diphenylmethyl radical has to undergo bimolecular reaction (dimerization) to form a stable molecule. Thus. reversibility of the initial hydrogen-abstraction explains the *net* reactivity of hydrocarbons toward thiobenzophenone in the n,π^* triplet state (Scheme 1).



Scheme 1.

In order to test the validity of the proposed mechanism, the reaction with 1,2-diphenylethane was carried out. The compound was found to reduce thiobenzophenone, yielding stilbene and **1**, which proves that, although thiobenzophenone in the n,π^* triplet state can abstract a hydrogen from diphenylmethane, the reverse reaction takes place faster, thus making the net reaction unrecognizable.

Stoos and Roček proposed that the enhanced reactivity of **2** in quinone-oxidation is due to a simultaneous two-hydrogen elimination assisted by the gain of aromatic stabilization energy.[5] However, "extra" stabilization energy of the cyclohexadienyl radical (24 kcal/mol) is extraordinarily large compared with that of open-chain free radicals (~15 kcal/mol).[6] In addition, if the gain of aromatic stabilization energy were to play an important role in the reactivity of these hydrocarbons, they should react faster, in contrast to observation (*vide infra*), than the corresponding nitrogen analogs since hydrocarbons can gain larger stabilization energy.[7,8] We thus propose that the oxidation of

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[1] A. Ohno and N. Kito, *Int. J. Sulfur Chem., A*, **1**, 26 (1971).

[2] S. G. Cohen and C. H. Wang, *J. Amer. Chem. Soc.*, **77**, 4435 (1955).

[3] A. Ohno, Y. Ohnishi, and G. Tsuchihashi, *ibid.*, **91**, 5038 (1969).

[4] E. A. Braude, L. M. Jackman, and R. P. Linstead, *J. Chem. Soc.*, 3564 (1954).

[5] F. Stoos and J. Roček, *J. Amer. Chem. Soc.*, **94**, 2719 (1972).

[6] G. Vincow, H. J. Dauben, Jr., F. R. Hunter, and W. V. Volland, *ibid.*, **91**, 2823 (1969).

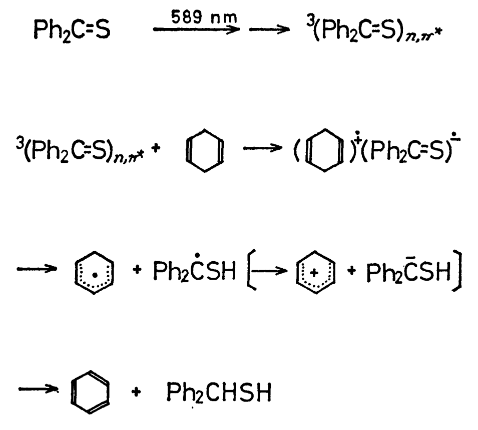
[7] G. W. Wheland, "Resonance in Organic Chemistry," John Wiley & Sons, Inc., New York, N. Y., 1955, pp 98—100.

[8] Photo-ionization potentials of **2**, **5**, and **6** are 8.82, 8.40, and 7.24 eV, respectively: D. A. Demeo and M. A. El-Sayed, *J. Chem. Phys.*, **52**, 2622 (1970); V. K. Potapov, A. D. Filyugina, D. N. Shigorin, and G. A. Ozerova, *Dokl. Akad. Nauk SSSR*, **180**, 398 (1968); *Chem. Abstr.*, **69**, 76408j (1968); N. Bordor, M. J. S. Dewar, and S. D. Worley, *J. Amer. Chem. Soc.*, **92**, 19 (1970).

1,4-dihydroaromatic hydrocarbons proceeds by successive hydrogen-eliminations.[9]

Braude and co-workers reported that cyclohexadienyl carbonium ion is involved as an intermediate of the quinone-oxidation of **2**.[10] Although we have no evidence to predict this to be the case in the reaction with thiobenzophenone, we believe that the cyclohexadienyl radical is at least one of intermediates of the reaction. The idea is based on the comparison of reactions of **2** and 1,3,5-cycloheptatriene (**5**): the photoreaction of **5** with thiobenzophenone proceeded as fast as that of **2** and products isolated from the reaction mixture were 7-(1,3,5-cycloheptatrienyl)diphenylmethanethiol (35%), 7,7′-bi(1,3,5-cycloheptatrienyl) (2%), and **1** (4%) with several unidentified materials. Formation of 7,7′-bi(1,3,5-cycloheptatrienyl) implies that the reaction involves a transient cycloheptatrienyl radical, the "extra" stabilization energy (21 kcal/mol) of which is comparable to that of the cyclohexadienyl radical.[6] On the other hand, the intermediacy of the carbonium ion is fairly well-established in the oxidation of **5**.[11] The "extra" stabilization energy is calculated to be 49 kcal/mol for cycloheptatrienyl carbonium ion,[6] which is twice as large as that of the corresponding free radical. Since it is energetically unreasonable to expect the initially formed carbonium ion to be reduced to the free radical, the free radical should be the precursor of the carbonium ion. The fact that even such a stable carbonium ion is formed *via* a free radical suggests that cyclohexadienyl carbonium ion, if any, might be formed from the corresponding free radical.

Taking account of the results obtained by Braude and co-workers[10] together with the analogy to the mechanism of reactions of dihydropyridine derivatives (*vide infra*), we would like to propose an initial electron-transfer process for the formation of cyclohexadienyl radical (Scheme 2).



Scheme 2.

In contrast to the low reactivity of **4**, the photoreaction of acridane (**6**) with thiobenzophenone proceeds instantaneously giving a clear solution with precipitation of 9,9′-biacridanyl (31% yield). However, on standing the reaction mixture at room temperature for a day or at 50 °C for an hour, regeneration of 67% of the starting thiobenzophenone was observed by spectrophotometry. The forward and reverse reactions were repeated several times, and when no more thiobenzophenone was regenerated, **1** and 9,9′-biacridanyl were isolated in quantitative yields. Thus, it is obvious that a thermally unstable intermediate is formed by the photoreaction of **6** with thiobenzophenone.

A mixture of **6** and 4,4′-dimethoxythiobenzophenone in ethanol exibits absorption maxima at 295 and 355 nm due to **6** and the thioketone, respectively. When the mixture was irradiated with light (589 nm) for a short period (within 1 min), formation of acridine was recognized by the appearance of a new maximum at 250 nm and a fine structure at about 350 nm.[12] Longer irradiation, however, caused a decrease in absorption due to acridine (Fig. 1).

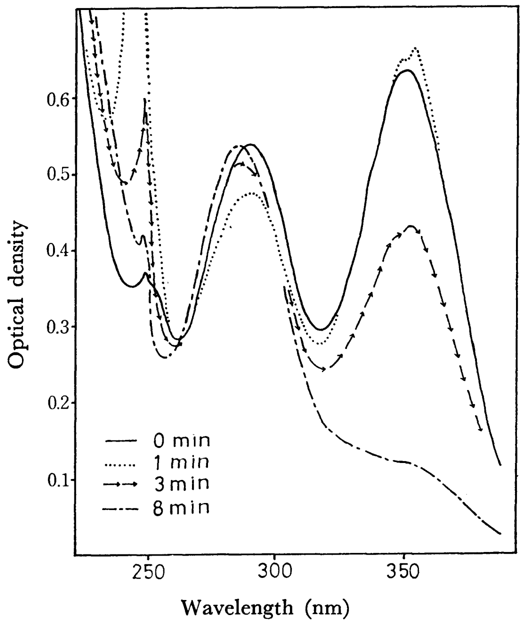


Fig. 1. Absorption spectra (in EtOH) of a mixture of acridane (1.53×10^{-5} mol/l) and 4,4′-dimethoxythiobenzophenone (1.48×10^{-5} mol/l) at different periods of photo-irradiation.

Photochemical behaviors of acridine and acridane have been studied extensively.[12–15] The present result, combined with reported ones, suggests that the most plausible mechanism for the reaction of **6** with thiobenzophenone is as follows (Scheme 3): Undoubtedly only thioketone can absorb the irradiated light. Although we failed to obtain evidence supporting

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[9] We do not intend to specify the mechanism of the hydrogen-elimination process. It might be a one-electron-proton elimination or true hydrogen-elimination. The mechanism will be discussed below.

[10] E. A. Braude, L. M. Jackman, R. P. Linstead, and G. Lowe, *J. Chem. Soc.*, 3123, 3133 (1960).

[11] P. Müller and J. Roček, *J. Amer. Chem. Soc.*, **94**, 2716 (1972).

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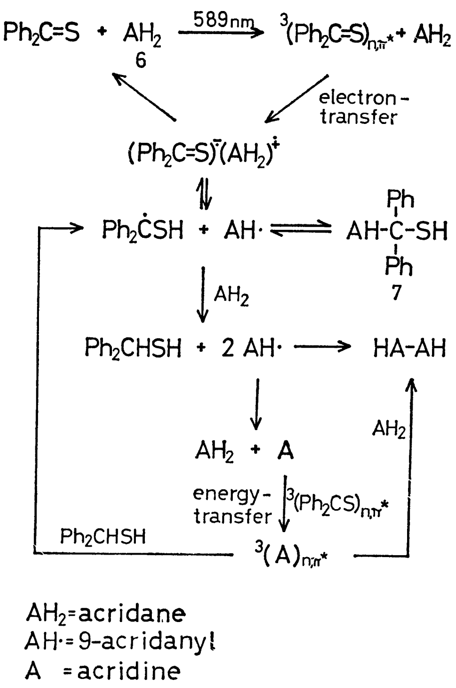
[14] R. S. Davidson, P. F. Lambeth, and M. Santhanam, *J. Chem. Soc.*, *Perkin II*, 2351 (1971).

[15] V. Zanker, E. Erhardt, and H. H. Mantsch, *Z. Phys. Chem.*, *N. F.*, **58**, 1 (1968).



Scheme 3.

the formation of the intermediate **7**, formation of 1-(9-acridanyl)ethyl alcohol by the reaction of acridine with ethanol has been confirmed.[12] There is no doubt that **7** is the thermally unstable intermediate mentioned above, because acridine semiquinone[16] and radical anion from thiobenzophenone,[17] both considered to be intermediates, are known to have absorption maxima in a visible region, whereas the present reaction mixture is transparent in this region.

The one-electron-transfer process from acridane to benzophenone has also been proposed.[14] Since thiobenzophenone is a much better electron-acceptor than benzophenone[18] and the electron-acceptability of thiobenzophenone is enhanced more in the n,π* triplet state than in the ground state,[19] the initial one-electron-transfer process from **6** to thiobenzophenone in the n,π* triplet state is most plausible for explaining the great difference in the reactivity of **4** and **6**. It should be noted that *N*-benzyl-1,4-dihydronicotinamide reacts with thiobenzophenone at room temperature in the dark, whereas **2** requires light to undergo a similar reaction. The one-electron-transfer interaction has been proposed to be a driving force of the former reaction.[20]

The photo-sensitized transformation of acridine into 9,9′-biacridanyl shown in Scheme 3 was confirmed by a separate experiment: an ethanol solution of 4,4′-dimethoxythiobenzophenone and acridine was irradiated with light (589 nm) and the decrease in intensity at the absorption maximum (250 nm) was followed spectrophotometrically.[21]

Experimental

Materials. Thiobenzophenone and 4,4′-dimethoxythiobenzophenone were prepared as reported previously.[24] 1,4-Dihydrobenzene was prepared by the Birch reduction of benzene[25]: bp 86—89 °C (lit,[26] 88 °C). Acridane was obtained by the reduction of acridine with $LiAlH_4$: mp 170 °C (lit,[27] 169 °C). 1,4-Dihydronaphthalene, 1,3,5-cycloheptatriene, 9,10-dihydroanthracene, and 1,2-diphenylethane were purified by repeated distillations or recrystallizations of commercial reagents.

*Reaction with 1,4-Dihydrobenzene (**2**).* An ampoule containing **2** (2 ml), thiobenzophenone (486 mg, 2.46 mmol), and benzene (3 ml) was degassed by the usual thawing and freezing method and sealed in a high vacuum (10^{-6} Torr). The mixture was irradiated with light from low-pressure sodium lamps[3] at room temperature until the characteristic color of thiobenzophenone completely disappeared (20 hr). Removal of the volatile materials under a reduced pressure left diphenylmethanethiol (**1**) in quantitative yield (490 mg). From the reaction mixture in ethylbenzene as a solvent, benzene (100% yield) was detected on vpc (Hitachi K-53, FID, 20% XF-1150, 2 m, 90 °C).

*Reaction with 1,4-Dihydronaphthalene (**3**).* A benzene (10 ml) solution of thiobenzophenone (423 mg, 2.14 mmol) and **3** (284 mg, 2.19 mmol) in an ampoule was similarly irradiated. After the disappearance of thiobenzophenone (3 days), naphthalene (91% yield) was detected on vpc (20% Carbowax-20M, 2 m, 180 °C). Dibenzhydryl disulfide (48 mg, 11% yield) and **1** (180 mg, 43% yield) were isolated by subjecting the reaction mixture to column chromatography on silica gel with *n*-hexane as an eluent.

*Reaction with 9,10-Dihydroanthracene (**4**).* A mixture of thiobenzophenone (483 mg, 2.44 mmol) and **4** (440 mg, 2.44 mmol) in acetonitrile (15 ml) and ethyl ether (10 ml) was irradiated until complete decolorization of thiobenzophenone took place (one week). After the solvents were evaporated, the residue (900 mg) was chromatographed on silica gel column. Elution with *n*-hexane gave anthracene (100 mg, 26% yield), dibenzhydryl disulfide (210 mg, 24% yield), **1** (75 mg, 17% yield), and recovered **4** (45 mg). Two additional unidentified materials (200 and 150 mg) were obtained by eluting the column with a mixture of *n*-hexane–benzene (1 : 1).

Reaction with 1,2-Diphenylethane. A benzene (4 ml) solution of thiobenzophenone (40 mg) and 1,2-diphenylethane (400 mg) was irradiated for 1.5 months. The color of thiobenzophenone faded but not completely. Formation of small amounts of *trans*-stilbene, dibenzhydryl disulfide, and **1** was proved on vpc (20% XF-1150, 1 m, 180 °C) and tlc (silica gel).

*Reaction with 1,3,5-Cycloheptatriene (**5**).* A solution of thiobenzophenone (795 mg, 4.00 mmol), **5** (3 ml), and ben-

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[16] A. Kira, S. Kato, and M. Koizumi, This Bulletin, **39**, 1221 (1966).

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[19] A. Ohno, N. Kito, and N. Kawase, *J. Poly. Sci.*, *B*, *Part* **10**, 133 (1972).

[20] A. Ohno and N. Kito, *Chem. Lett.*, **1972**, 369.

[21] Both of thiobenzophenone in the n,π* triplet state and acridine in the π,π* triplet state have excitation energy of 42—45 kcal/mol.[22,23]

[22] G. N. Lewis and M. Kasha, *J. Amer. Chem. Soc.*, **67**, 994 (1945).

[23] D. E. Evans, *J. Chem. Soc.*, **1957**, 1351.

[24] N. Kito and A. Ohno, This Bulletin, **46**, 2487 (1973).

[25] C. B. Wooster, U. S., 2,182,242 (1938).

[26] F. O. Rice and A. L. Stallbaumer, *J. Amer. Chem. Soc.*, **64**, 1527 (1942).

[27] F. Bohlmann, *Chem. Ber.*, **85**, 390 (1952).

zene (5 ml) was irradiated until complete decolorization of thiobenzophenone took place (44 hr). After excess **5** and the solvent were removed, the residue was chromatograhped on a silica-gel column with a mixture of *n*-hexane–benzene (4 : 1) as an eluent. The following components were isolated: 7,7′-bi(1,3,5-cycloheptatrienyl) (17 mg, 2% yield), 7-(1,3,5-cycloheptatrienyl)diphenylmethanethiol (**8**) (550 mg, 35% yield), **1** (30 mg, 4% yield), and unidentified compounds (140 mg).

8: NMR (δ from TMS, $CDCl_3$) 2.43 (s, 1H), 2.61 (t of d, 1H), 5.44 (q, 2H), 6.14 (d or octet, 2H), 6.64 (t of d, 2H), and 7.0—7.6 (m, 10H). Mass spectrum (*m*/*e*) 290 (M^+), 257, 256, 199, 198, 179, 178, and 91 (base). IR 2570 cm^{-1} (ν_{SH}).

To a suspension of NaH (30 mg) in 30 ml of THF was added dropwise a solution of the thiol (310 mg) in 20 ml of THF at room temperature. After 2 hr, when the solution became clear, 2 ml of MeI was added and stirred for 2 hr at room temperature. The solution was acidified with 2N-hydrochloric acid and extracted with chloroform yielding 260 mg of an oil. The oil was chromatographed on a silica-gel column with the eluent of *n*-hexane-benzene (8 : 1) mixture. Triphenylethylene[28] (60 mg) and 7-(1,3,5-cycloheptatrienyl)diphenylmethyl methyl sulfide (**9**) (100 mg) were isolated.

9: NMR (δ from TMS, $CDCl_3$) 1.63 (s, 3H), 2.38 (t of t, 1H), 5.48 (q, 2H), 6.24 (d of sextet, 2H), 6.77 (t, 2H), and 7.0—7.6 (m, 10H). Mass spectrum (*m*/*e*) 304 (M^+), 256, 213, 198, 179, 165, 121, and 91 (base).

*Reaction with Acridane (**6**).* A solution of thiobenzophenone (560 mg, 2.83 mmol) and **6** (1,000 mg, 5.55 mmol) in ether (20 ml) was irradiated at the temperature of ice-water. After 30 min, the color of thiobenzophenone faded completely. From this reaction mixture, 310 mg of 9,9′-biacridanyl (31% yield) was isolated as precipitates. In a separate run, the characteristic color of thiobenzophenone reappeared, when the reaction mixture was heated at 50 °C for 1 hr. Spectroscopic observation showed that 67% of thiobenzophenone was recovered. After all the thiobenzophenone had been consumed by a repetition of the above procedure, 950 mg of 9,9′-biacridanyl (mp 260 °C (lit[29] 261—262 °C)) was isolated as precipitates. From the filtrate, additional 9,9′-biacridanyl (30 mg)(total yield; 98%) and **1** (540 mg, 97% yield) were obtained.

Formation and consumption of acridine during the reaction were followed with a Carry-14 Spectrophotometer at suitable concentrations of 4,4′-dimethoxythiobenzophenone and **6** in ethanol or ethyl ether (Fig. 1).

Photo-sensitized Reaction of Acridine. An ethanol solution of acridine (8.05×10^{-7} mol/l) and 4,4′-dimethoxythiobenzophenone (1.56×10^{-5} mol/l) was irradiated at room temperature for 2 min. The decrease in intensity at the absorption maximum (250 nm) was followed with a Carry-14 Spectrophotometer (Fig. 2).

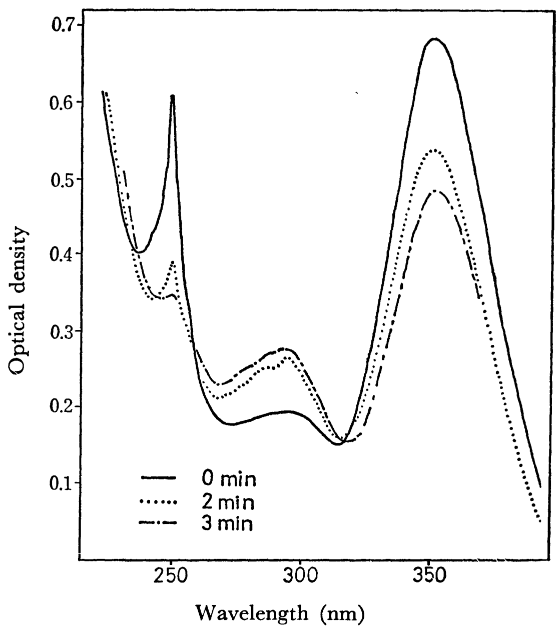

Fig. 2. Absorption spectra (in EtOH) of a mixture of acridine (8.05×10^{-7} mol/l) and 4,4′-dimethoxythiobenzophenone (1.56×10^{-5} mol/l) at different periods of photoirradiation.

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