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Photochemical Reaction of Diaryl Thioketones in Ethereal Solutions. A Stable Transient Free-Radical

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Photochemical reactions of thiobenzophenone and its 4,4′-dimethoxy derivative in ethereal solutions such as tetrahydrofuran and diethyl ether have been studied by means of product analyses and ESR spectroscopy. It was found that the reaction involves quite stable transient free-radicals of the type $Ar_2\dot{C}SR$. The efficiency of free-radical trapping by diaryl thioketones and the reaction mechanism are discussed.

Photo-excited thiobenzophenone abstracts the hydrogen atom from an appropriate solvent through its n,π* triplet state, giving diphenylsulfhydrylmethyl radical.[1,2] The primary process of the reaction is similar to that of benzophenone[3] but products differ to a great extent. In order to obtain further insight into the photo-reaction of thiobenzophenone, we have studied ESR spectroscopy of the transient free-radicals in ethereal solutions. The results are given in this paper. Several studies have been made on detection and positive indication by ESR spectroscopy of transient free-radical species produced by continuous photo-irradiation.[4]

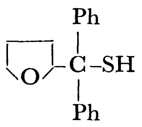
Thiobenzophenone is a good scavenger for free carbon-radicals.[5] The results of the present study also give a direct evidence for the mechanism of scavenging reactions and suggest the availability of thiobenzophenone as a spin-trapping agent.

Results and Discussion

Products. Irradiation with light (>300 nm) on thiobenzophenone in tetrahydrofuran (THF) afforded **1**, **2**, and **3** in 3.1, 35.2, and 54.5% yields, respectively. A similar reaction in diethyl ether gave **1**, **4**, and **5** in 3.6, 37.4, and 52.0% yields, respectively. Their structures were confirmed by spectral and elemental analyses. It was confirmed that no rearrangement from **3** to **2** and from **5** to **4** or *vice versa* took place under the reaction conditions. Compounds **2** and **4** were apparently resulted in by the (in-cage) combination of diphenylsulfhydrylmethyl, **6a**, and the solvent-derived free-radicals, **8**,[1] while **3** and **5** were formed by the reaction of solvent-derived free-radicals with thiobenzophenone, a potential molecular-type scavenger toward carbon-radicals.[5,6] Thus, the analyses of products suggest that the reaction involves three transient free-radicals, **6a**, **7a**, and **8**.

Ph_2CHSH

1



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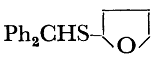

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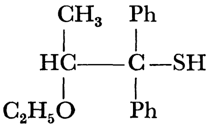
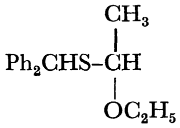


$$H\overset{CH_3}{\underset{C_2H_5O}{C}}-\overset{Ph}{\underset{Ph}{C}}-SH$$

4



$$Ph_2CHS-\overset{CH_3}{\underset{OC_2H_5}{CH}}$$

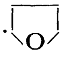
5

$Ar_2\dot{C}$–SH $Ar_2\dot{C}$–SR

6a: $Ar=C_6H_5$– **7a**: $Ar=C_6H_5$–

6b: $Ar=4\text{-}CH_3OC_6H_4$– **7b**: $Ar=4\text{-}CH_3OC_6H_4$–

(RH = solvent molecule)



8a

$C_2H_5O\dot{C}HCH_3$

8b

ESR Spectroscopy. The ESR spectrum obtained by continuous photo-irradiation on THF solution of thiobenzophenone at 25 °C is shown in Fig. 1a.

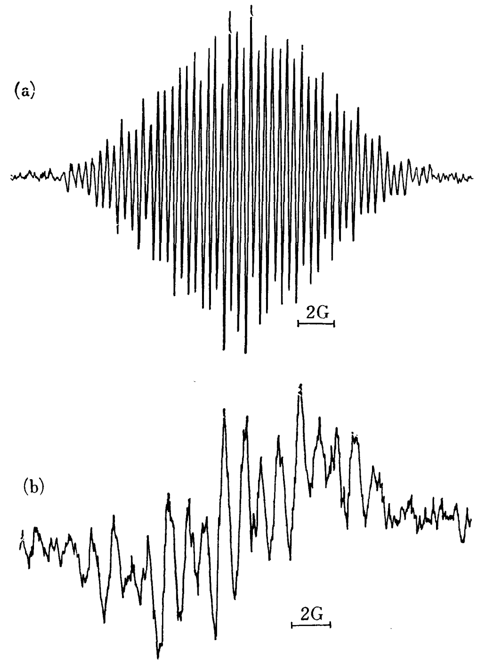


Fig. 1. Observed ESR spectra of **7a** in (a) THF and (b) MTHF.

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Table 1. Hyperfine splitting constants and g-values for photo-paramagnetic diaryl thioketones-THF system

Starting Thioketone	A_o	A_m	A_p	A_{OCH_3}	$A_{\alpha H}$	g-Value
$(C_6H_5)_2C{=}S$	2.71	0.77	3.10	—	1.16	2.0051
$(4\text{-}CH_3OC_6H_4)_2C{=}S$	2.45	0.70	—	0.35	1.05	2.0053

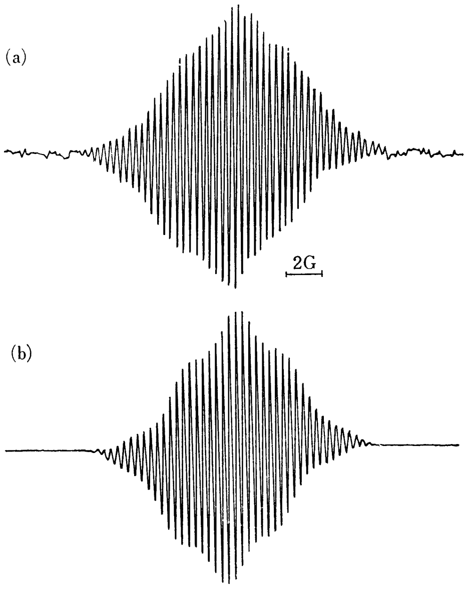


Fig. 2. (a) Observed and (b) calculated ESR spectra of **7b** in THF.

The observed spectra accord well with their computer-simulated ones[7] using the splitting constants, listed in Table 1, with a line width of 192 mG (Fig. 2). They are spectra of neither **8a**[8] nor thioketyls,[9,10] and must be those of **6** or **7**.

When the photo-reaction was carried out in 2-methyltetrahydrofuran (MTHF), the recorded spectrum distinctly showed the absence of double-splittings (Fig. 1b). Figure 3 shows the ESR spectrum of photo-irradiated thiobenzophenone in diethyl ether. The doublet-splittings of 1.12 gauss observed here are again absent when the reaction is carried out in diisopropyl ether. These results indicate unequivocally that the free-radicals detected on the spectrometer are not **6** but **7**.

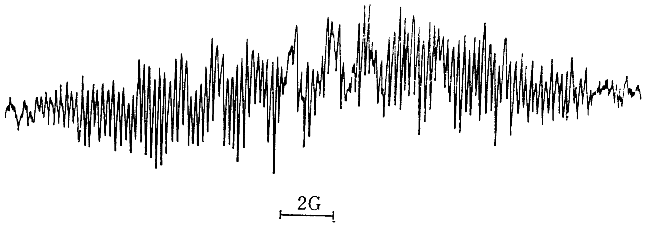


Fig. 3. Observed ESR spectrum of **7a** in diethyl ether.

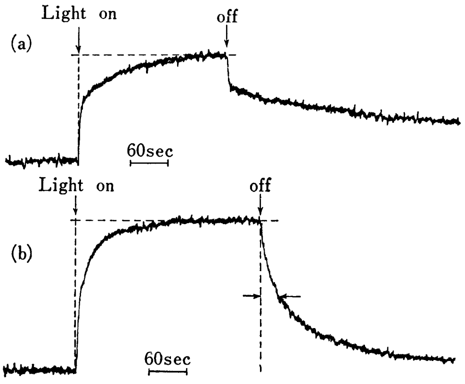


Fig. 4. The change of the intensities of ESR spectra due to the transient free-radicals during the photolyses of (a) thiobenzophenone (10.833 mM) and (b) 4,4′-dimethoxythiobenzophenone (10.173 mM) in THF at 25°C. The spectra were recorded with modulation width of 20 gauss and with response time of 0.1 sec.

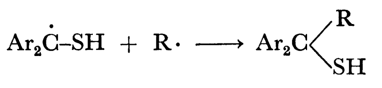
It is noteworthy that **7** is a quite stable free-radical. From the decay-curves (Fig. 4), half-lives of **7a** and **7b** (RH=THF) in THF at 25 °C are calculated to be 90 and 29 sec, respectively. Since these values are independent of initial concentrations of diaryl thioketones and irradiation time, the kinetics of the decay is of first-order in **7**. Formation of such a long-lived composite free-radical may make thiobenzophenone a useful reagent for spin-trapping.

Another paramagnetic species is detected from the reaction of thiobenzophenone (Fig. 4a). This accumulates rapidly when the light is turned on and decays instantaneously when it is shut off. We believe that this short-lived species is **6a**. If this were due to **8a**, the absence of such a phenomenon in Fig. 4b cannot be rationalized: since **7b** is less stable than **7a** under experimental conditions, the trapping of **8a** by 4,4′-dimethoxythiobenzophenone should be less effective than that by thiobenzophenone.[11] Thus, both **6a** and **7a** are more stable (or less reactive) than **6b** and **7b**, respectively. The substituent effect observed here is a general trend for the stability of benzyl-type free-radicals.[12]

Thus the mechanism of the photochemical reaction of diaryl thioketones in ethereal solutions is as follows:

$$Ar_2C{=}S \xrightarrow{h\nu} \longrightarrow {}^3(Ar_2C{=}S)_{n,\pi^*}$$

$$^3(Ar_2C{=}S)_{n,\pi^*} + RH \longrightarrow Ar_2\dot{C}\text{-}SH + R\cdot$$



$$Ar_2\dot{C}\text{-}SH + R\cdot \longrightarrow Ar_2C\begin{smallmatrix}\diagup R \\ \diagdown SH\end{smallmatrix}$$

$$Ar_2\dot{C}\text{-}SH + RH \longrightarrow Ar_2CHSH + R\cdot$$

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[7] The computer program for the simulation of spectra was supplied by The Shionogi Research Laboratory. We wish to express our cordial thanks to Dr. K. Nishikida. The program was run by IBM 360 System.

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$$\mathrm{Ar_2C{=}S + R\cdot \longrightarrow Ar_2\dot{C}{-}SR}$$

$$\mathrm{Ar_2\dot{C}{-}SR + RH \longrightarrow Ar_2CHSR + R\cdot}$$

Since the last two processes constitute a chain reaction, they suggest the possibility that the half-lives of the free-radicals do not necessarily mean the *true* values. However, we believe they are almost true, if not completely so. The concentration of **8a** is too low to be detected, indicating immediate trapping of **8a** by thiobenzophenone. Therefore, if the hydrogen-abstraction by **7** is a fast process, its steady-state concentration may also be too low to be detected after the light is shut off.

Experimental

Materials. Thiobenzophenone was prepared as reported previously.[1] 4,4′-Dimethoxythiobenzophenone was similarly prepared from the corresponding ketone in 88% yield. The thioketone was recrystallized twice from ethanol–chloroform mixture: mp 117—118 °C (lit,[13] mp 116—118 °C).

Solvents were refluxed over calcium hydride under a 50 cm column packed with helics for several days and fractionally distilled. The second distillation was performed just before use over sodium wire after being refluxed for a few hours.

Spectrometry. A 0.25—0.50 M solution of a thioketone placed in a 10 mm o.d. glass tube connected with 1.5—2.0 mm o.d. quartz tube was thoroughly degassed by the usual thawing and freezing method and sealed in a high vacuum (10^{-6} torr). The light from a 100W high-pressure mercury lamp was focused on the sample in the microwave cavity of the ESR spectrometer. The spectra of photochemically generated transient free-radicals were recorded at 25±0.3 °C (room temperature) with a X-band JES-ME-IX type spectrometer (Japan Electron Optics Laboratory Co. Ltd.) with 100 KHz field modulation. In order to obtain well resolved spectra, it was necessary to adjust concentrations of the solution and find the right moment of irradiation with respect to life-time of free-radicals.

Photochemical Reaction of Thiobenzophenone in THF. Prior to the reaction, slow stream of argon gas was passed for 30 min through the THF (60 m*l*) solution of thiobenzophenone (613 mg, 2.59 mmol) in a Pyrex vessel. Irradiation with light from a 400W high-pressure mercury lamp (principal wavelength: 315 and 366 nm) was continued until complete decolorization of the thioketone (19 hr) took place at the temperature of running water. After excess solvent was removed, the residue was chromatographed on a column of silica-gel with elution by a mixture of *n*-hexane and benzene. The following compounds were isolated (mg, % yield, *n*-hexane : benzene ratio): diphenylmethanethiol (**1**) (16, 3.1, 2 : 8), diphenyltetrahydro-2-furylmethanethiol (**2**) (246, 35.2, 3:7), and benzhydryl tetrahydro-2-furyl sulfide (**3**) (381, 54.5, 4 : 6).

2: NMR(δ from TMS, CCl_4) 1.48—2.01 (m, 4H), 2.28 (s, 1H), 3.63—3.97 (m, 2H), 4.65—4.93 (m, 1H), and 7.02—7.55 (m, 10H); mass spectrum (*m/e*) 270 (M^+), 236, 200, 199, 198 (Ph_2CS^+, base), 165, 121, and 71; Found: C, 75.48; H, 6.60; S, 11.80%. Calcd for $C_{17}H_{18}OS$: C, 75.53; H, 6.71; S, 11.84%.

3: NMR(δ from TMS, CCl_4) 1.49—2.30(m, 4H), 3.71—4.17(m, 2H), 4.85—5.03(m, 1H), and 7.04—7.56(m, 10H), mass spectrum (*m/e*) 270 (M^+), 168, 167 (Ph_2CH^+, base), 166, 165, 151, 105, 77, and 71; Found: 75.41; H, 6.58; S, 11.81%. Calcd for $C_{17}H_{18}OS$: C, 75.53; H, 6.71; S, 11.84%.

Photochemical Reaction of Thiobenzophenone in Diethyl Ether. An ether solution (60 ml) of thiobenzophenone (580 mg, 2.93 mmol) was similarly irradiated for 30 hr. Separation on a column chromatography gave the following compounds (mg, % yield, *n*-hexane : benzene ratio): diphenylmethanethiol (**1**) (21, 3.6, 2 : 8), 1,1-diphenyl-2-ethoxypropanethiol (**4**) (298, 37.4, 3 : 7), and benzhydryl 1-ethoxyethyl sulfide (**5**) (412, 52.0, 4 : 6).

4: NMR(δ from TMS, CCl_4) 1.11 (d, 3H), 1.13 (t, 3H), 2.53 (s, 1H), 3.52 (q-q, 2H), 4.24 (q, 1H), and 7.03—7.54(m, 10H); mass spectrum (*m/e*) 272 (M^+), 238, 200, 199, 198 (Ph_2CS^+, base), 167, 165, 121, 105, and 73; Found: C, 74.81; H, 7.41; S, 11.70%. Calcd for $C_{17}H_{20}OS$: C, 74.97; H, 7.40; S, 11.75%.

5: NMR(δ from TMS, CCl_4) 1.10 (t, 3H), 1.47 (d, 3H), 3.48 (q-q, 2H), 4.50 (q, 1H), 5.23 (s, 1H), and 7.03—7.47 (m, 10H); mass spectrum (*m/e*) 272 (M^+), 236, 168, 167 (Ph_2CH^+, base), 166, 165, 105, 77, 73; Found: C, 74.79; H, 7.35; S, 11.72%. Calcd for $C_{17}H_{20}OS$: C, 74.97; H, 7.40; S, 11.75%.

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