Photoelimination of a β-Keto Sulfide with a Low-Lying π–π* Triplet State

ALBERT PADWA*[1] AND DERAN PASHAYAN

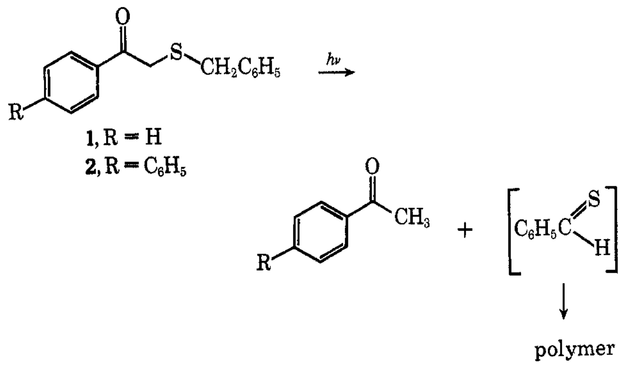
Department of Chemistry, State University of New York at Buffalo, Buffalo, New York 14214

Received March 23, 1971

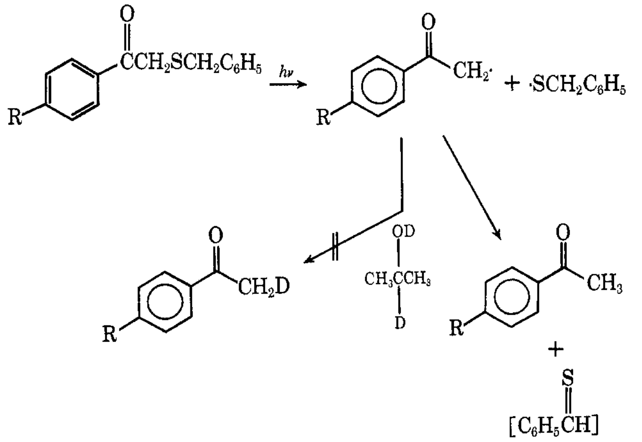
The type II photoelimination of α-benzylthioacetophenone (1) and α-benzylthio-4-acetylbiphenyl (2) has been studied. A kinetic analysis of the two systems shows that the two ketones differ in quantum efficiency and triplet reactivity. The low quantum yield and inability to quench the π–π* excited state of 2 is compatible with an electron-transfer mechanism.

The first step in the photoelimination reaction of α-amino acetophenones has been suggested to proceed by transfer of an electron from the nitrogen atom to the excited carbonyl group.[2] As a continuation of our investigations on the photochemistry of carbonyl compounds that possess a heteroatom, we sought to define the role of the nonbonding electrons of sulfur in the type II photoelimination of β-keto sulfides. It has been reported that β-keto sulfides that possess a hydrogen bearing γ carbon[3–5] undergo conversion to ketones on photolysis by a mechanism similar to that obtained in the photochemistry of alkanones (Norrish type II elimination).[6] The present work was initiated with the hope of demonstrating the importance of electron transfer in the photochemistry of α-alkyl thioaryl ketones.

The major products of the solution-phase photolysis of α-benzylthioacetophenone (1) in benzene were acetophenone and a sulfur-containing polymer. The quantum yield at 3130 Å for the production of acetophenone in benzene is 0.35. Irradiation of α-benzylthio-4-acetylbiphenyl (2) gave comparable results, with the quantum yield for ketone formation being 0.04. The sulfur-containing polymer is presumably derived by further polymerization of the initially derived thiobenzaldehyde.[7] In striking contrast to the photolytic behavior of the analogous β-keto ether system,[8] no thietanol formation was noted on photolysis of keto sulfides 1 and 2. The different behavior noted in the two systems may be related to the relative weakness of the C–S bond (65 kcal) as compared to the C–O bond (85 kcal).



β-Keto sulfides that do not possess γ hydrogens are reported to give disulfides by homolysis of the carbon–sulfur bond.[9,10] Although a related mechanism can be written to account for the formation of acetophenone, we have found that irradiation of 1 or 2 in deuterio-2-propanol-2-d_1 did not lead to the incorporation of deuterium in the acetophenone produced. A mechanism involving homolytic C–S bond cleavage (see above) would be expected to lead to some deuterium incorporation by abstraction from solvent. Consequently, it would appear as though the intramolecular Norrish type II scheme is the dominant path with thioketones 1 and 2. Similar results have been noted by Caserio and coworkers with related systems.[5]



The lowest lying triplet state of 1 was demonstrated to be n–π* as evidenced from its phosphorescene emission spectrum in a methanol–ethanol glass (4:1) at 77°K. The 0–0 band of 1 corresponds to a triplet energy of 72 kcal and the vibrational spacing between the 0–0 and 0–1 band is 1660 cm^{-1}. The 77°K lifetime was determined as *ca.* 2.0 msec. In sharp contrast, the triplet energy of 2 was determined to be 61 kcal and the radiative lifetime was 0.18 sec. These observations verify that the low-lying triplet state of 2 is π–π* in nature.

Although the *p*-phenyl-substituted thioketone has a low lying $^3(\pi-\pi^*)$ state, it still is capable of undergoing photocycloelimination. This observation is somewhat unusual since the ability of an aryl alkyl ketone to undergo photoelimination is dependent on the nature of the lowest lying triplet state, with $^3(n-\pi^*)$ states being reactive and $^3(\pi-\pi^*)$ states being generally unreactive. By way of illustration, *p*-phenylbutyro-

---

[1] Fellow of the Alfred P. Sloan Foundation, 1968–1970.

[2] A. Padwa, W. Eisenhardt, R. Gruber, and D. Pashayan, *J. Amer. Chem. Soc.*, **91**, 1857 (1969).

[3] H. Hogeveen and P. J. Smit, *Recl. Trav. Chim. Pays-Bas*, **85**, 489 (1966).

[4] R. H. Fish, L. C. Chow, and M. C. Caserio, *Tetrahedron Lett.*, 1259 (1969).

[5] M. C. Caserio, W. Lauer, and T. Novinson, *J. Amer. Chem. Soc.*, **92**, 6082 (1970).

[6] N. J. Turro, "Molecular Photochemistry," W. A. Benjamin, New York, N. Y., 1965.

[7] E. Campaigne, *Chem. Rev.*, **39**, 1 (1946).

[8] F. D. Lewis and N. J. Turro, *J. Amer. Chem. Soc.*, **92**, 311 (1970).

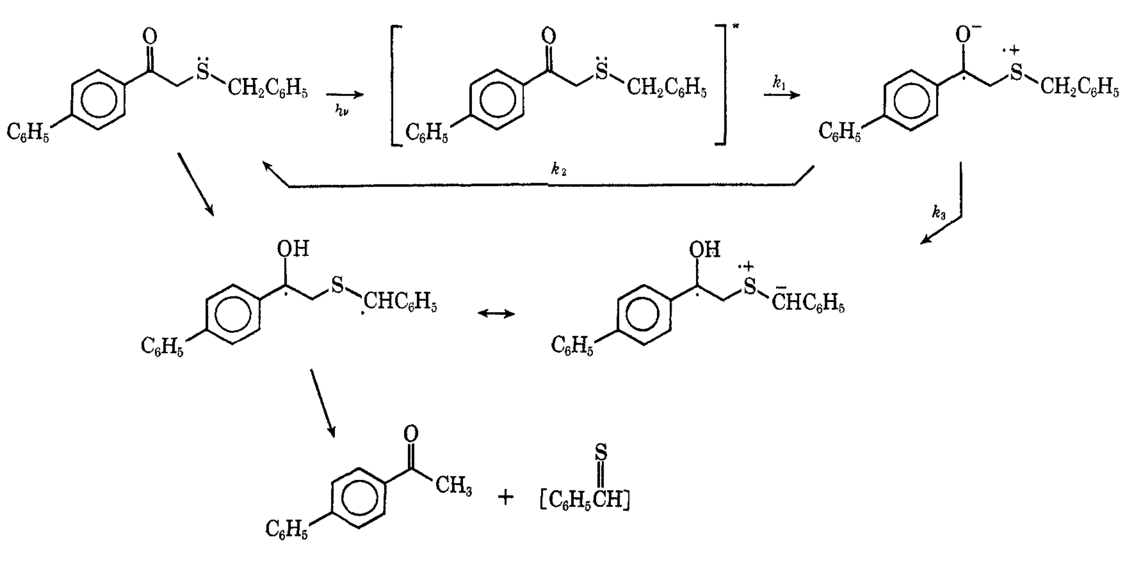
[9] J. R. Collier and J. Hill, *Chem. Commun.*, 700 (1968); 640 (1969).

[10] A. Schonberg, A. K. Fateen, and S. M. A. Omran, *J. Amer. Chem. Soc.*, **78**, 1224 (1956).

phenone has a low-lying π–π^* triplet state and has been reported to be stable to irradiation.[11]

Photolysis of **1** in degassed benzene solution in the presence of varying amounts of piperylene resulted in the linear Stern–Volmer plot shown in Figure 1. The slope of the Stern–Volmer plot equals $k_q\tau$ where k_q is the rate constant for quenching the ketone triplet by piperylene and τ is the ketone triplet lifetime. Assumption of the value of $5 \times 10^9\ M^{-1}\ \mathrm{sec}^{-1}$ for k_q[12] allows calculation of $1/\tau$ ($7.0 \times 10^9\ \mathrm{sec}^{-1}$). The large value of $1/\tau$ is very similar to the value obtained by Lewis and Turro for α-ethoxyacetophenone[8] and is indicative of a very reactive triplet state. On the other hand, photoelimination of ketone **2** could not be quenched by piperylene or 1,3-cyclohexadiene even though its quantum efficiency is one-eighth that of ketone **1**. The failure to quench the excited state implies that the reaction of the triplet of **2** is faster than diffusional control quenching ($>10^{10}\ \mathrm{sec}^{-1}$).[13] The lack of correlation between quantum yield and rate constant for photoelimination of ketones **1** and **2** is similar to the results reported by Wagner with simple alkyl phenyl ketones.[14]

The behavior of thioketone **2** is distinctly different from **1** in two regards: lower quantum efficiency and higher triplet reactivity. The difference in behavior suggests different photoelimination mechanisms for the two ketones. The sensitivity of **1** to triplet quenchers indicates direct hydrogen atom abstraction by the n–π^* state. The low quantum yield and inability to quench the π–π^* excited state of **2** suggests that the excited state interacts with an electron on sulfur (k_1) to form an ion pair or a charge-transfer complex. Once formed, the charge-transfer complex can transfer a proton from the benzylic carbon (k_3) or regenerate starting ketone by back transfer of the electron (k_2). Reverse electron transfer (k_2) accounts for the less than maximum quantum yield. This scheme is similar to the charge-transfer mechanism suggested to occur in the photoelimination of α-amino ketones[2] and for the photoreduction of ketones by amines.[15,16] In the charge-transfer complex of the thioketone system, charge destruction and quenching appears to be greater than hydrogen transfer (*i.e.*, $k_2 \gg k_3$). In the amine system, the rates of the two reactions of the complex are comparable ($k_2 \sim k_3$) and consequently the quantum efficiency of photoelimination is larger in this system. Recently Cohen and Guttenplan noted that aliphatic sulfides are good physical quenchers for excited benzophenone and have also suggested efficient interaction of the excited ketone with the nonbonding electrons of sulfur.[17]



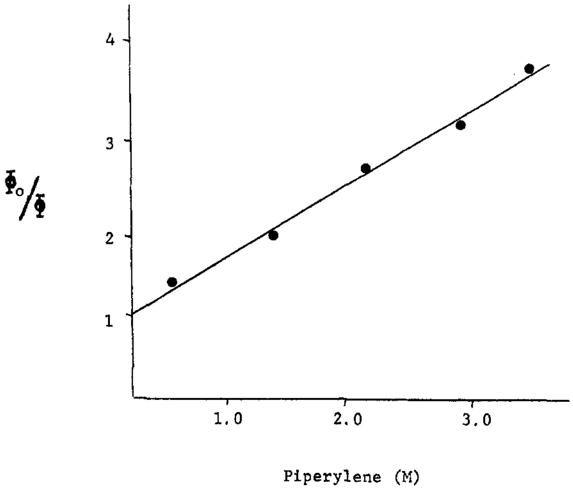


Figure 1.—Stern–Volmer plot for quenching of acetophenone formation from α-benzylthioacetophenone (1) in benzene.

We have also studied the photoreduction of 4-acetylbiphenyl with aliphatic sulfides. Irradiation of 0.02 *M* 4-acetylbiphenyl and 0.1 *M* di-*n*-butyl sulfide led to a high yield of pinacol. While this ketone undergoes appreciable photoreduction with aliphatic sulfides, it is not photoreduced by alcohols or hydrocarbons. This

---

[11] E. J. Baum, J. K. S. Wan, and J. N. Pitts, Jr., *J. Amer. Chem. Soc.*, **88**, 2652 (1966).

[12] P. J. Wagner and G. S. Hammond, *ibid.*, **88**, 1245 (1966).

[13] An alternate possibility is that the photoelimination of **2** proceeds by way of a n–π^* singlet state.

[14] P. J. Wagner and A. E. Kemppainen, *ibid.*, **90**, 5896 (1968).

[15] S. G. Cohen and H. M. Chao, *ibid.*, **90**, 165 (1968); S. G. Cohen and R. J. Baumgarten, *ibid.*, **89**, 3471 (1967); S. G. Cohen, N. Stein, and H. M. Chao, *ibid.*, **90**, 521 (1968).

[16] R. S. Davidson, P. F. Lambeth, F. A. Younis, and R. Wilson, *J. Chem. Soc.*, 2203 (1969); R. S. Davidson and P. F. Lambeth, *Chem. Commun.*, 511 (1968), 732 (1969).

[17] S. G. Cohen and J. Guttenplan, *ibid.*, 247 (1969).

observation provides further support for charge-transfer interaction of the nonbonding electrons on sulfur with excited π–π* triplet states.

Experimental Section[18]

α-Benzylthioacetophenone (1).—To a stirred solution containing 15 g of α-bromoacetophenone in 100 ml of benzene was added a solution containing 9.4 g of benzyl mercaptan and 8.0 g of triethylamine in 100 ml of benzene. After 12 hr the precipitated salts were filtered and the filtrate was concentrated under reduced pressure. Recrystallization of the crude solid from 95% ethanol gave 16 g (88%) of **1**, mp 85–87°. The infrared spectrum was characterized by bands at 5.99, 6.92, 7.20, 8.34, 10.00, 13.32, 14.25, and 14.65 μ. The ultraviolet spectrum (95% ethanol) had maxima at 242 mμ (ε 14,300), 278 (2000), and 330 (200). The nmr spectrum ($CDCl_3$) showed singlets at τ 6.38 (2 H) and 6.27 (2 H), and multiplets centered at τ 2.68 (8 H) and 2.10 (2 H). The mass spectrum exhibited the parent ion at m/e 274 and had major peaks at 105, 91, and 77.

Anal. Calcd for $C_{15}H_{14}OS$: C, 74.35; H, 5.82; S, 13.23. Found: C, 74.33; H, 5.77; S, 13.58.

α-Benzylthio-4-acetylbiphenyl (2).—To a stirred solution containing 15.2 g of α-bromo-4-acetylbiphenyl in 100 ml of benzene was added a solution containing 9.4 g of benzyl mercaptan and 6.5 g of triethylamine in 100 ml of benzene. After 12 hr the precipitated salts were filtered and the filtrate was evaporated to give a crude solid. Recrystallization of the solid from 95% ethanol gave 10.5 g of **2** (61%), mp 110–111°. The infrared spectrum was characterized by bands at 5.99, 6.23, 7.17, 8.38, 9.98, 12.02, 13.17, and 14.32 μ. The ultraviolet spectrum (95% ethanol) showed a maximum at 283 mμ (ε 28,000). The nmr spectrum ($CDCl_3$) showed singlets at τ 6.37 (2 H) and 6.27 (2 H) and had a multiplet centered at τ 2.60 (14 H). The mass spectrum exhibited a molecular ion at m/e 318 and had major peaks at 196, 181, 153, 91, and 77.

Anal. Calcd for $C_{21}H_{18}OS$: C, 79.21; H, 5.70; S, 10.07. Found: C, 79.06; H, 5.67; S, 9.85.

Coirradiation of 4-Acetylbiphenyl with Di-*n*-butyl Sulfide.—A solution containing 4.0 g of 4-acetylbiphenyl and 20 g of di-*n*-butyl sulfide in 250 ml of benzene was irradiated for 3 hr with a 550-W Hanovia lamp using a Pyrex filter. Removal of the solvent left a crude solid which was recrystallized from ethyl acetate to give 1.9 g (47%) of 1,2-dibiphenyl-1,2-dimethylethane-1,2-diol, mp 223–225°. The infrared spectrum of this material was identical with that of the pinacol prepared by the reaction of aluminum amalgam with 4-acetylbiphenyl.

Anal. Calcd for $C_{28}H_{26}O_2$: C, 85.24; H, 6.64. Found: C, 84.96; H, 6.65.

Quantum Yield Determinations.—All quantitative measurements were made on a rotating assembly with a central light source (internal water-cooled mercury arc lamp, Hanovia type L-450-W). Samples in 13-mm Pyrex ampoules were placed in holders on the assembly approximately 6 cm from the immersion well. The light was filtered by circulation of a solution containing 46 g of nickel sulfate hexahydrate and 14 g of cobaltous sulfate heptahydrate per 100 ml of water through the inner jacket.[12] This solution permitted the following wavelength distribution to pass through: 6%, 2967; 20%, 3025; 62%, 3130, 3340 Å. All studies were made at room temperature. Samples in 13-mm Pyrex test tubes were degassed to 5×10^{-3} mm in three freeze–thaw cycles and then sealed. Benzophenone–benzhydrol actinometry was used for quantum yield determinations. An actinometer quantum yield of 0.69 was used when the concentration of benzophenone and benzhydrol in benzene was 0.1 *M*.[19] Reliably reproducible output rates of 4.86×10^{16} quanta sec were recorded. After the irradiation the degree of reaction was determined by vapor phase chromatography (6 ft × 0.25 in. 10% SE-30 methylsilicone gum rubber on Diatoport S). The conversions were run to 15% or less. The mass balance in these runs was generally better than 96%. For the quenching studies samples were prepared and analyzed as for quantum yield determinations except that varying amounts of piperylene were added to the solutions. Five concentrations of piperylene, in addition to blanks containing no piperylene, were used for the Stern–Volmer plot.

Phosphorescence Emission Studies.—The emission spectra were made on an Aminco-Bowman spectrophotofluorometer with a phosphoroscope and transmission attachments. The spectrophotofluorometer was equipped with a 1P21 photomultiplier and a high-pressure xenon lamp, as supplied by the manufacturer. All emission spectra were recorded using EPA (ethyl ether–isopentane–ethanol, 5:5:2 volume ratio) as solvent. The solvent was checked for emission each time a spectrum was recorded. No interference due to solvent was found at any time. All compounds having relatively long radiative lifetimes were recorded on a xy plotter. Samples having short radiative lifetimes (<100 msec) were measured by photographing the decay curve on an oscillograph. The chopper was rotated manually to obtain the decay curve. The logarithmic intensities of the decay curve were plotted *vs.* time and the slope of the line at a logarithmic value of 2.303 gave the mean lifetime (τ_0).

Registry No.—**1**, 2408-88-0; **2**, 31593-31-4; 1,2-dibiphenyl-1,2-dimethylethane-1,2-diol, 10426-00-3.

Acknowledgment.—Support of this work by the Petroleum Research Fund, administered by the American Chemical Society, is gratefully acknowledged.

---

[18] Nmr spectra were recorded on a Varian A-60 spectrometer using carbon tetrachloride as solvent. Infrared spectra were obtained on a Perkin-Elmer Infracord spectrophotometer, Model 137. The ultraviolet absorption spectra were measured with a Cary recording spectrophotometer, using 1-cm matched cells. Elemental analyses were performed by Scandinavian Microanalytical Laboratory, Herlev, Denmark. Gas–liquid partition chromatographic analyses and preparative separations were carried out using an F & M Model 5720 instrument equipped with a 6 ft × 0.25 in. 20% Apiezon M on 60–80 mesh Chromosorb W column. Irradiations were carried out using Hanovia 450- and 550-W, medium-pressure mercury lamps with water-cooled quartz immersion wells.

[19] W. M. Moore, G. S. Hammond, and R. P. Foss, *J. Amer. Chem. Soc.*, **83**, 2789 (1961).