Photo-enethiol of *o*-Benzylthiobenzophenone

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Summary The photo-enethiol of *o*-benzylthiobenzophenone has been trapped, which implies that photoreduction of thiobenzophenone involves initial formation of $Ph_2\dot{C}SH$ instead of $Ph_2CHS\cdot$.

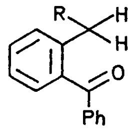
WE suggested recently that the photoreduction of thiobenzophenone in protic solvents involves hydrogen-abstraction by the thiocarbonyl sulphur atom of thiobenzophenone in the *n,π** triplet state.[1]

$$\begin{gathered} Ph_2C{=}S \xrightarrow{589nm} {}^3(Ph_2C{=}S)n,\pi^* \\ {}^3(Ph_2C{=}S)n,\pi^* \xrightarrow{RH} \underset{(I)}{Ph_2\dot{C}SH} \rightarrow \text{products} \end{gathered} \qquad (1)$$

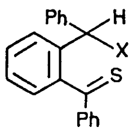
This mechanism is analogous to the corresponding reaction of benzophenone, but differs from that suggested by Oster and his co-workers,[2] where hydrogen-abstraction involves the thiocarbonyl carbon atom in *π,π** state thiobenzophenone.

$$\begin{gathered} Ph_2C{=}S \xrightarrow{360nm} (Ph_2C{=}S)\pi,\pi^* \\ (Ph_2C{=}S)\pi,\pi^* \xrightarrow{RH} \underset{(II)}{Ph_2CHS\cdot} \rightarrow \text{products} \end{gathered} \qquad (2)$$

It is well known that 2-alkylbenzophenones such as (III) and (IV) do not undergo photoreduction but form the corresponding photo-enols.[3] A similar reaction could be employed to diagnose the mechanism of photoreduction of thiobenzophenone: if the mechanism (1) is operating, irradiation of *o*-benzylthiobenzophenone (Vh) will yield the photo-enethiol, while the latter should not be produced if the reaction proceeds with the mechanism (2).



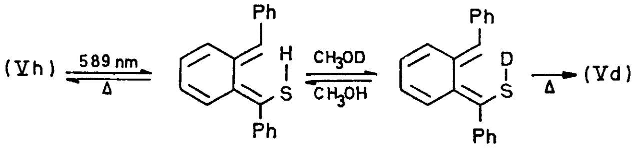
(III) R = Ph
(IV) R = H



(Vh) X = H
(Vd) X = D

When a solution of (Vh) in carbon tetrachloride was irradiated at 20° with light of 589 nm, the intense colour of (Vh) (λ_{max} in EtOH 603 nm, ε 107) disappeared within 90 min. The n.m.r. spectrum of the reaction mixture obtained at −11° has sharp singlets of equal intensity at δ 2·63 and 4·96 along with multiplets for aromatic protons. The intensity of the singlet at δ 2·63 decreases immediately after the addition of a drop of CH_3OD to the mixture, while the other peaks remain unchanged. Thus, we can assign the structure of the photo-product as (VI).

Although (VI) is sufficiently stable at −78° to be stored for several days, it reverts to (V) quantitatively within 20 h at room temperature without light. A benzyl proton in (V) recovered from (VId) has been substituted by a deuterium.



(VIh) (VId)

Similarly, when a three-component mixture of (Vh), carbon tetrachloride, and CH_3OD was subjected to irradiation, the colour of (Vh) disappeared within 90 min at 20°, while it does not even fade after 12 h at 135°. Both reactions, of course, afford (Vd). This provides further support for the photochemical conversion of (V) into (VI) and the reverse thermal reaction. On the other hand, it has been found that heating the mixture for 5 days at 135° (without light) is ineffective in introducing deuterium into (V).

This observation, coupled with previous results,[1] clearly indicates that photoreduction of thiobenzophenone involves initial hydrogen-abstraction by the thiocarbonyl sulphur atom, while thermal reduction of thiobenzophenone does not involve (I) as an intermediate.

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[1] A. Ohno and N. Kito, *Internat. J. Sulfur Chem., Part A,* 1971, **1**, in the press.
[2] G. Oster, L. Citarel, and M. Goodman, *J. Amer. Chem. Soc.,* 1962, **84**, 703.
[3] For a recent review, see A. A. Lamola and N. J. Turro, "Energy Transfer and Organic Photochemistry," Interscience Publishers, New York, 1969, pp. 222—223.