

Type II Photoelimination of Thiobenzoic Acid *O*-Esters; Photolysis of Optically Active *O*-2-Phenylbutyl Thiobenzoate

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U.v. irradiation of *O*-2-phenylbutyl thiobenzoate (I) gives Norrish type II products [α -ethylstyrene (II) and thiobenzoic acid] in high yields, the quantum efficiency for the decomposition being 0.49. When the optically active thioester (+)-(S)-(I) is photolysed, the recovered starting material retains its original optical purity, which implies that the intermediate 1,4-diradical (III) is so unstable that the reverse γ -hydrogen shift to re-form structure (I) does not take place to an appreciable extent.

THIOBENZOIC acid *O*-esters undergo Norrish type II photoelimination to yield the corresponding olefins and thiobenzoic acid.^{1,2} Studies on the primary processes involved have been carried out by flash photolysis and luminescence measurements.³ The suggested mechanism is the same as for Norrish type II elimination of aromatic carbonyl compounds,⁴ *i.e.* γ -hydrogen abstraction by the n - π^* triplet thiocarbonyl group to give a 1,4-diradical, followed by either β -fission (type II cleavage) or cyclisation to oxetanethiol (isolated as its decomposition products, thioketone and aldehyde).^{3,5}

In general, photodecomposition of benzoate esters⁶ is inefficient ($\Phi_{\text{acid}} < 0.02$) in contrast to thiobenzoate *O*-esters (*e.g.* Φ 0.35 for the disappearance of *O*-phenethyl thiobenzoate^{3,5}). The intervention of a 1,4-diradical has been confirmed by the observation of racemisation of (–)-2-methylbutyl benzoate on irradiation at 253.7 nm, but only a poor yield was obtained.⁷ However, in the case of thiobenzoate *O*-esters no information is at present available as to the possibility of reversion of the 1,4-diradical to the starting thioester.

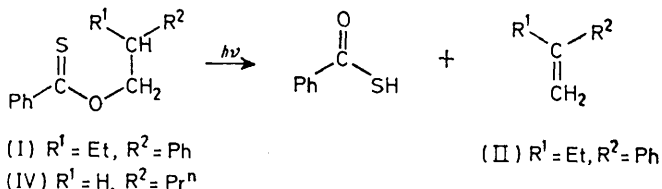
We now present some evidence that an intermediate 1,4-diradical from photolysis of a thiobenzoate *O*-ester is too unstable to allow reversion to the starting thioester, and that the reverse γ -hydrogen shift is an inefficient process in comparison with the forward reaction.

O-Alkyl thiobenzoates were prepared according to the procedure of Barton *et al.*⁵ Irradiation of *O*-2-phenylbutyl thiobenzoate (I) at –60 to –70 °C gave α -ethylstyrene (II) (66%) and thiobenzoic acid. α -Ethylstyrene (II) was identified by u.v. and n.m.r. spectral comparison with an authentic sample. The thiobenzoic acid was oxidised to dibenzoyl disulphide, the identity of which was confirmed by its i.r. spectrum and m.p.⁸ G.l.c. analysis of the reaction mixture after treatment with triethylamine showed the presence of no products other than α -ethylstyrene.

The quantum yield of the reaction is high [0.49,

measured by disappearance of the starting material absorption at 414 nm (ϵ 135)]. The value is comparable with that (0.35) for the disappearance of *O*-phenethyl thiobenzoate.³

The optically active thioester (+)-(S)-(I) was prepared and photolysed to determine whether or not the photoelimination occurs *via* a relatively stable 1,4-diradical



(III). The ester was irradiated in dichloroethane at –40 °C in the presence of triethylamine, and samples were removed at various times to determine the optical rotation of recovered starting material. Essentially no change was observed (see Table), indicating that no racemisation was occurring.

Relationship of the conversion to the optical rotation of recovered thioester (I) from photolysis of optically active thioester [(+)-(S)-(I)]

Conversion of (+)-(S)-(I) (%) ^a	0	27	29	48	66
Optical rotation ([α] _D ²⁰) of recovered (I) (°)	29.0	31.0	34.5	30.0	31.5

^a Estimated by g.l.c.

Irradiation of *O*-n-pentyl thiobenzoate (IV), which has no π -electron substituent at the γ -position, at –40 °C,

⁵ (a) S. Achmatowicz, D. H. R. Barton, P. D. Magnus, G. A. Poulton, and P. J. West, *J.C.S. Perkin I*, 1973, 1567; (b) D. H. R. Barton, C. Chavis, M. K. Kaloustian, P. D. Magnus, G. A. Poulton, and P. J. West, *ibid.*, p. 1571; (c) D. H. R. Barton, M. Bolton, P. D. Magnus, K. G. Marathe, G. A. Poulton, and P. J. West, *ibid.*, p. 1574; (d) D. H. R. Barton, M. Bolton, P. D. Magnus, and P. J. West, *ibid.*, p. 1580.

⁶ (a) J. A. Barltrop and J. D. Coyle, *J. Chem. Soc. (B)*, 1971, 251; (b) J. G. Pacifici and J. A. Hyatt, *Mol. Photochem.*, 1971, 3, 267.

⁷ J. G. Pacifici and J. A. Hyatt, *Mol. Photochem.*, 1971, 3, 271.

⁸ H. E. Westlake, jun., and G. Dougherty, *J. Amer. Chem. Soc.*, 1945, 67, 1861.

¹ S. Achmatowicz, D. H. R. Barton, P. D. Magnus, G. A. Poulton, and P. J. West, *Chem. Comm.*, 1971, 1014.

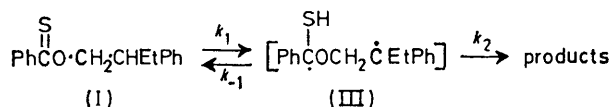
² D. H. R. Barton, M. Bolton, P. D. Magnus, P. J. West, G. Porter, and J. Wirz, *J.C.S. Chem. Comm.*, 1972, 632.

³ J. Wirz, *J.C.S. Perkin II*, 1973, 1307.

⁴ For a comprehensive review, see P. J. Wagner, *Accounts Chem. Res.*, 1971, 4, 168.

even in the presence of triethylamine, gave only polymeric material rather than pent-1-ene and thiobenzoic acid. The quantum yield for the disappearance of (IV) was *ca.* 0.01, comparable with values for the photodecomposition of typical alkyl benzoates (<0.02),⁶ even though the excited states responsible for the photoelimination are known to be different (thiobenzoates react *via* the excited triplet state,^{3,5} whereas benzoates decompose *via* the excited singlet state⁶). It has been shown that the inefficient photodecomposition of benzoate esters is not attributable to a preference for reversible 1,4-diradical formation rather than type II photoelimination.^{7,9} For example, both type II photoelimination (Φ *ca.* 0.01) and racemisation (Φ *ca.* 0.008) are very inefficient in the cases of *erythro*- and *threo*-1,2-dimethylbutyl *p*-methoxybenzoate.⁹ Similar observations have been made in the photolysis of (–)-2-methylbutyl benzoate.⁷

Thus, in contrast to the type II photoreaction of aromatic ketones,⁴ where the reverse γ -hydrogen shift is significant and lowers the efficiency of the type II elimination, both thiobenzoate *O*-esters and benzoates yield intermediate 1,4-diradicals which are too unstable to allow a reverse γ -hydrogen shift to give the starting ester, *i.e.* $k_{-1} \ll k_2$ in the Scheme.



SCHEME

The 1,4-diradical (III) formed from the $n\text{-}\pi^*$ triplet would not be expected to revert to (I) prior to racemisation, since the thioester (I) affords type II products with high efficiency (Φ 0.49), and racemisation of other types of triplet diradical is known to be faster than reversion.¹⁰ It is also improbable that the type II photoreaction proceeds in a concerted manner, in view of the observation of oxetanthiol formation by intramolecular cyclisation of analogous thiobenzoate *O*-esters.^{5d}

The greater preference of the thioester-derived diradical (III) than of the ester-derived diradical for bond cleavage rather than reverse hydrogen transfer may be explained in terms of formation of a C=O bond rather than the weaker C=S bond (energy difference *ca.* 50 kcal mol⁻¹).

EXPERIMENTAL

I.r. spectroscopy, g.l.c., and mass spectrometry were carried out as described in ref. 11. Optical rotations were recorded with a Yanagimoto OR-50D digital automatic polarimeter (1 cm cell).

* The accurate mass measurements were made with a Mattauch-Herzog (JMS-OSG) spectrometer.

⁹ J. E. Gano, *Chem. Comm.*, 1971, 1491.

¹⁰ L. M. Stephenson and J. J. Brauman, *J. Amer. Chem. Soc.*, 1971, **93**, 1988.

(+)-(S)-2-Phenylbutan-1-ol.—(±)-2-Phenylbutanoic acid, obtained from 2-phenylbutyronitrile,¹² was resolved by the procedure of Levene and Marker.¹³ A solution of 2-phenylbutanoic acid (26 g) and cinchonidine (26 g) in acetone was refluxed and cooled. The resulting crystals, recrystallised from 75% aqueous ethanol, melted at 112.0–112.5° (yield 9.5 g); $[\alpha]_D^{20} -59.0^\circ$ (in EtOH). The carboxylic acid, liberated by addition of hydrochloric acid, was reduced with lithium aluminium hydride to give (+)-(S)-2-phenylbutanol as a liquid, b.p. 128–133° at 20 mmHg, $[\alpha]_D^{20} 23.3^\circ$ (in EtOH) (optical yield *ca.* 70%).¹³

(+)-(S)-O-2-Phenylbutyl Thiobenzoate.—The modified procedure of Barton *et al.*^{5b} was used. Dry hydrogen chloride was introduced into an ice-cooled mixture of benzonitrile (1.5 g) and (+)-(S)-2-phenylbutanol (1.4 g). Thiolyis of the resulting solid with hydrogen sulphide gave a yellow liquid (0.8 g) which solidified; b.p. 167° at 0.5 mmHg, $[\alpha]_D^{20} 30.1^\circ$ (in EtOH). A similar procedure with benzonitrile (9 g) and (±)-2-phenylbutanol (8 g) afforded (±)-O-2-phenylbutyl thiobenzoate as a pale yellow liquid (4.5 g). The racemic and optically active esters had identical g.l.c. retention times and were purified (>95%) by chromatography on a Florisil column packed with benzene to eliminate a trace of starting alcohol. The products showed λ_{max} (CH₂Cl₂) 250, 289, and 414 nm (ϵ 7 550, 10 500 and 135); ν_{max} (film) 1 225 cm⁻¹ (C=S) (no C=O band); δ 8.00 (2 H, dd, *ortho*-protons), 7.40 (8 H, m, *meta*- and *para*-protons and other Ph), 4.70 (2 H, d, OCH₂), 3.10 (1 H, m, CH), 1.80br (2 H, m, CH₂), and 0.90 (3 H, t, Me); *m/e* (70 eV) 270 (*M*⁺), 139, 138 (PhCOSH⁺), 133 (PhCHCH₂Et⁺), 121 (PhCS⁺), 105 (PhCO⁺), 91 (C₇H₇⁺, base peak), and 77 (Ph⁺). An intense molecular ion peak (*M*⁺) was obtained by anion mass spectrometry (Found: *M*⁺, 270.0993. C₁₇H₁₈OS requires *M*, 270.1074), although the molecular formula could not be estimated by the usual cation mass spectrometry since the *M*⁺ peak was of very low intensity.* Integration of n.m.r. peaks indicated that the material was of a satisfactory degree of purity.

O-*n*-Pentyl Thiobenzoate (IV).—The thioester (IV) was similarly prepared as a yellow liquid, b.p. 138–143° at 4 mmHg; ν_{max} (film) 1 230 cm⁻¹ (no C=O band); δ 8.15 (2 H, dd, *ortho*-protons), 7.40 (3 H, m, *meta*- and *para*-protons), 4.60 (2 H, t, OCH₂), 1.90–1.50 (6 H, m, [CH₂]₃), and 0.95 (3 H, t, Me); *m/e* (70 eV) 208 (*M*⁺), 175 (*M*⁺ – SH), 138, 139 (PhCOSH⁺), 121 (PhCS⁺), 105 (PhCO⁺, base peak), 91 (C₇H₇⁺), 77 (Ph⁺), 71 (C₅H₁₁⁺), 57 (C₄H₉⁺), and 43 (C₃H₇⁺) (Found: *M*⁺, 208.088. C₁₂H₁₆OS requires *M*, 208.0918). Integration of n.m.r. peaks and the presence of a single peak on g.l.c. analysis indicated that the material was of satisfactory purity.

Photolysis of (±)-2-Phenylbutyl Thiobenzoate (I).—The thioester (I) (1.0 g) in dry dichloromethane (150 ml) was irradiated at –60 to –70 °C in the usual way.⁵ After 11.5 h triethylamine (5 ml) was added. After the mixture had warmed to room temperature it was extracted with 2*N*-sodium hydroxide, and the alkaline layer was neutralised with (1*N*-HCl) and extracted with benzene. The benzene extract (dried over Na₂SO₄) was evaporated, and the isolated thiobenzoic acid was oxidised with a mixture of aqueous

¹¹ Y. Ogata, K. Takagi, and Y. Takayanagi, *J.C.S. Perkin I*, 1973, 1244.

¹² J. V. Murray and J. B. Cloke, *J. Amer. Chem. Soc.*, 1946, **68**, 126.

¹³ P. A. Levene and R. E. Marker, *J. Biol. Chem.*, 1933, **100**, 685.

hydrogen peroxide (1 ml) and hydrochloric acid (1 ml) to give dibenzoyl disulphide as plates, m.p. 131—133° (from methanol) (lit.,⁸ 134—135°), showing i.r. absorptions identical with those of authentic material. The remaining organic solution (dried over Na₂SO₄) was evaporated and the product chromatographed on a Florisil slurry packed in light petroleum. Elution with light petroleum gave α -ethylstyrene as an oil (80 mg, 66%); λ_{max} (MeOH) 240 nm (lit.,¹⁴ 240 nm); δ (CCl₄) 7.25 (5 H, m, Ph), 5.22 (1 H, m) and 5.03 (1 H, m) (=CH₂), 2.48 (2 H, q, CH₂), and 1.08 (3 H, t, Me). Elution with benzene then gave the starting thioester (0.75 g), identified by comparison (u.v. and g.l.c.) with authentic material.

Irradiation of (+)-(S)-2-Phenylbutyl Thiobenzoate (I). A solution of the thioester (360 mg) and triethylamine (5 ml) in dichloromethane (120 ml) was irradiated with Pyrex-filtered u.v. light ($\lambda > 300$ nm) at -40 °C. Samples (15 ml) were removed at intervals (15 min) and evaporated *in vacuo*. The products were diluted with ethanol (2 ml) and their optical rotations were determined. The content of remain-

ing thioester was analysed by g.l.c. (cinnamyl alcohol as internal standard).

Measurement of the Quantum Yield for Photolysis of the Thioester (I).—A dilute solution of (I) (7.4×10^{-3} M) in dichloromethane, in a 10 mm thick quartz cell, was irradiated in an optical train with three quartz lenses in conjunction with a Halos HIP high-pressure lamp (300 W) through a colour filter (Corning 5-59) which transmits light of $\lambda 420 \pm 70$ nm. The samples were degassed by three freeze-thaw cycles at less than 10^{-3} mmHg and the tubes were then sealed. These samples were irradiated to less than 10% conversion simultaneously with a potassium ferrioxalate actinometer.¹⁵ After irradiation, the concentrations of remaining thioester (I) were determined spectrophotometrically at 414 nm.

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¹⁴ C. G. Overberger and D. Tanner, *J. Amer. Chem. Soc.*, 1955, **77**, 369.

¹⁵ C. H. Hatchard and C. A. Parker, *Proc. Roy. Soc., Ser. A*, 1956, **235**, 518.