Photochemical Transformations. Part XXXII.[1] Photolysis of Thiobenzoic Acid *O*-Esters. Part III.[1, 2] Photolysis of *O*-Phenethyl Thiobenzoates and Other Thiobenzoates

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Homoallylic alcohols can be dehydrated under exceptionally mild conditions by conversion into their thiobenzoate *O*-esters and irradiation between −70° and room temperature. A variety of substrates have been dehydrated by this method.

SINCE *O*-cholestanyl thiobenzoate,[2] unlike the corresponding cholesteryl derivative, did not smoothly eliminate thiobenzoic acid on irradiation, it appeared that the transition state requires some conjugation of the newly forming double bond. *O*-2-Arylethyl thiobenzoates (I) should behave in a similar manner to *O*-cholesteryl thiobenzoate, since the incipient double bond would be conjugated with the aryl residue. A series of *para*-substituted phenethyl thiobenzoates were made and their behaviour on irradiation was studied.

O-Phenethyl thiobenzoate (II; R = H)[1] was irradiated in cyclohexane with a medium-pressure mercury lamp to give styrene in 90% yield, and, on oxidative work-up, dibenzoyl disulphide (100%). The styrene was isolated as its dibromide or (better) as its 1,3-dipolar addition product (III; R = H) with *p*-nitrobenzonitrile *N*-oxide.[3,4] The nitrile oxide was liberated *in situ* by treatment of *p*-nitrobenzohydroxamoyl chloride with triethylamine. Attempts to trap styrene as it was formed in the photoelimination reaction were unsuccessful. *p*-Nitrobenzonitrile *N*-oxide reacted rapidly with the thiobenzoic *O*-ester to give in the case of compounds (II; R = OMe or NO_2) the corresponding oxathiazoles (IV; R = OMe or NO_2).

These efforts to trap styrene as it was generated were made because the thiobenzoic acid, formed rapidly, reacts with the styrene thus preventing an accurate measurement of yield. Other 1,3-dipolar reagents such as phenyl azide and mesitonitrile *N*-oxide were unreactive. Since attempts to trap styrene *in situ* failed, methods were tried for removing the thioacid. Oxidation of the liberated thiobenzoic acid with *p*-nitrobenzoyl peroxide proved to be successful. The addition of an

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[1] Part XXXI, Part II, D. H. R. Barton, C. Chavis, M. K. Kaloustian, P. D. Magnus, G. A. Poulton, and P. J. West, *J.C.S. Perkin I*, preceding paper.

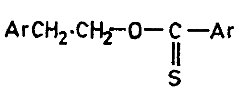
[2] Preliminary communication, S. Achmatowicz, D. H. R. Barton, P. D. Magnus, G. A. Poulton, and P. J. West, *Chem. Comm.*, 1971, 1014; Part I, *J.C.S. Perkin I*, 1973, 1567.

[3] M. S. Chang and J. U. Lowe, jun., *J. Org. Chem.*, 1967, **32**, 1577; F. Eloy and R. Lenaers, *Bull. Soc. chim. belges*, 1965, **74**, 129.

[4] R. Huisgen and W. Mack, *Tetrahedron Letters*, 1961, 583.

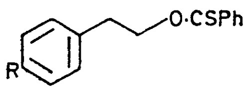
excess of triethylamine to the reaction mixture was also effective and convenient in preventing the readdition of thiobenzoic acid.

When thiobenzoic acid and styrene were mixed together in cyclohexane in the dark at room temperature a rapid reaction took place. Readdition appeared to be a thermal process. Irradiation at low temperature (−76°) resulted in an increased yield of styrene.

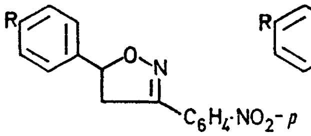


$\mathrm{ArCH_2{\cdot}CH_2{-}O{-}C({=}S){-}Ar}$

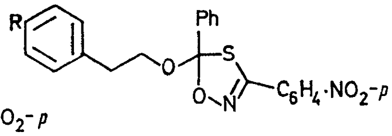
(I)



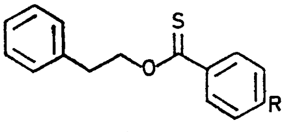
(II)



(III)



(IV)



(V)

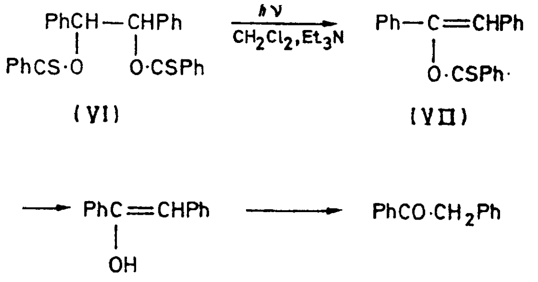
Photoreactions of the series of *O*-phenethyl thiobenzoates (II; R = OMe, NO_2, or NMe_2) gave the *p*-substituted styrenes in yields of 68·5, 79·5, and 37%, respectively. The *p*-nitro- and *p*-dimethylamino-styrenes were isolated and characterised as their adducts (III; R = NO_2 or NMe_2) with *p*-nitrobenzonitrile *N*-oxide. For the series (II; R = H, O, NO_2, or NMe_2) the times for 50% reaction (under identical conditions) were 7, 7, 47, and 13·5 min, respectively.

Since the series of *p*-substituted *O*-phenethyl thiobenzoates (II) reacted efficiently, with one exception (II; R = NMe_2), to give the *p*-substituted styrenes, the series of compound *p*-substituted in the thiobenzoyl residue were examined. The *p*-substituted derivatives (V; R = H, OMe, NO_2, or NMe_2) were made by the imino-ether–hydrogen sulphide[1] method. Compounds (V; R = H, OMe, or NO_2) reacted smoothly in cyclohexane to give styrene in yields of 90, 80, and 76%, respectively. Compound (V; R = NMe_2) gave only a 10% yield of styrene. For the series (V; R = H, OMe, NO_2, or NMe_2) the times for 50% reaction (under identical conditions) were 7, 8, 4, and 30 min, respectively.

To extend the scope of the photoelimination of thiobenzoic acid and to examine conjugating groups other than carbon–carbon double bonds a further series of thiobenzoic *O*-esters was studied. *meso*-Dihydrobenzoin[5] was converted into its bisthiobenzoic *O*-ester[1] (VI). Irradiation of (VI) in dichloromethane–cyclohexane with Pyrex-filtered light from a high pressure mercury vapour lamp gave deoxybenzoin (52%) ($t_{\frac{1}{2}}$ 15 min) (Scheme). The reaction presumably proceeds *via* the enol thiobenzoate (VII), which in the presence of triethylamine is converted into deoxybenzoin. We considered that replacement of the thiobenzoyl group by thionaphthoyl should shift the thiocarbonyl chromophore towards the visible region and possibly make the photoelimination proceed more readily. *O*-Phenethyl 2-thionaphthoate (VIII), prepared by treating (2-thionaphthoylthio)-acetic acid[1] with sodium hydride and 2-phenylethanol, on irradiation in dichloromethane gave styrene (85%) ($t_{\frac{1}{2}}$ 17 min). The time for reaction was longer than for compound (II; R = H). Although the π–π^* absorption of (VIII) was shifted towards the visible region, the n–π^* absorption was shifted slightly towards the ultraviolet in comparison with (II; R = H).

2-(6,6-Dimethylnorpin-2-en-2-yl)ethanol was converted into its thiobenzoic *O*-ester (IX). Irradiation of the ester (IX) gave the diene (X) (85%) ($t_{\frac{1}{2}}$ 12 min), isolated and characterised as its adduct with *p*-benzoquinone.[6] The phenylpentenoate (XI; R = H) is particularly difficult to dehydrate by conventional acid- and base-promoted eliminations. Irradiation of the derived thiobenzoate (XI; R = CSPh) gave the diene (XII; R = Bu^n) ($t_{\frac{1}{2}}$ 18 min) (78%), characterised as the acid (XII; R = H).

Other conjugating functions (a carbon–carbon triple bond or a cyclopropyl group) were also investigated. But-3-yn-1-ol was converted into its thiobenzoic *O*-ester (XIII) and irradiated at −78°. A complex mixture of products was obtained. Irradiation of *O*-but-3-enyl thiobenzoate (XIV) at −78° in dichloromethane gave butadiene, characterised as its adduct (XV) with 4-phenylbicarbamimide.[7] 2-Cyclopropylethanol, prepared by treating but-3-en-1-ol with methylene iodide in the presence of a zinc–copper couple,[8] was converted into its thiobenzoic *O*-ester (XVI). Irradiation in dichloromethane at −76° gave a complex mixture of products. Neothujol thiobenzoic *O*-ester (XVII; R =



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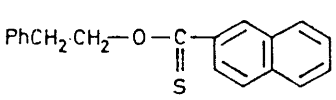
[5] J. Dale, *J. Chem. Soc.*, 1961, 910.

[6] L. J. Kitchen, *J. Amer. Chem. Soc.*, 1951, **73**, 2368; G. Ohloff, H. Farnow, and G. Schade, *Chem. Ber.*, 1956, **89**, 1549.

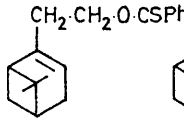
[7] R. C. Cookson, S. S. Gilani, and I. D. R. Stevens, *J. Chem. Soc.* (*C*), 1967, 1905.

[8] Y. Armand, R. Perraud, J. L. Pierre, and P. Arnaud, *Bull. Soc. chim. France*, 1965, 1893.

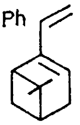
CSPh) and the corresponding thujol derivative (XVIII; R = CSPh) behaved similarly.



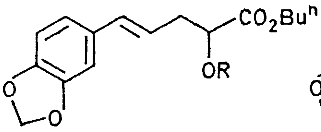
(VIII)



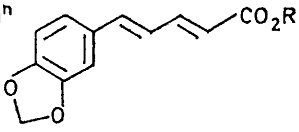
(IX)



(X)



(XI)



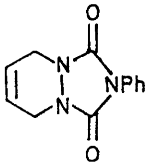
(XII)

$HC{\equiv}C{\cdot}CH_2{\cdot}CH_2{\cdot}O{\cdot}CSPh$

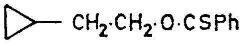
(XIII)

$CH_2{=}CH{\cdot}CH_2{\cdot}CH_2{\cdot}O{\cdot}CSPh$

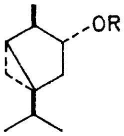
(XIV)



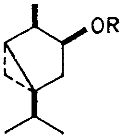
(XV)



(XVI)



(XVII)

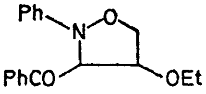


(XVIII)

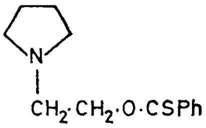
$EtO{\cdot}CH_2{\cdot}CH_2{\cdot}O{\cdot}CSPh$

(XIX)

Irradiation of *O*-2-ethoxyethyl thiobenzoate (XIX) in dichloromethane gave ethyl vinyl ether (46%; $t_{\frac{1}{2}}$ 21 min),



(XX)



(XXI)

characterised as its adduct with *N*-phenylphenacylidenamine *N*-oxide (XX). *O*-2-(Pyrrolidin-1-ylethyl) thiobenzoate (XXI), gave, on irradiation ($t_{\frac{1}{2}}$ 18 min) and acidic work-up, acetaldehyde (28%; as its 2,4-dinitrophenylhydrazone).

The series of *p*-substituted *O*-phenethyl thiobenzoates shows only a small variation in rate of photoreaction with marked variation in the electronic character of the *p*-substituent. It thus appears that ionic character is not being generated at either the benzylic carbon atom of the phenethyl group or the carbon atom of the thiocarbonyl group. The results are adequately explained in terms of the generation of radical character[9] at these centres. We attempted to intercept radical centres by addition of reagents such as oxygen, nitric oxide, and various stable free radicals, but without positive results.

This photoelimination offers a neutral, high yield, and extremely mild (proceeds rapidly even at —76°) synthetic method for dehydrating many homoallylic alcohols.

EXPERIMENTAL

M.p.s were taken with a Kofler hot-stage apparatus. Unless otherwise stated u.v. spectra were measured for solutions in ethanol and i.r. spectra for Nujol mulls. N.m.r. spectra were taken for solutions in deuteriochloroform at 20°, with tetramethylsilane as internal standard. All solvents were dried by standard techniques. Irradiations were carried out by use of Pyrex apparatus. The lamps used for the photolyses were a Philips MBW/U 125 W medium-pressure blacklight with the dark outer glass cover removed and an MBL 125 W high-pressure lamp. A tungsten lamp was also used where indicated.

Light petroleum refers to the fraction of b.p. 40—60°. Chromatography was carried out on acid-washed silica gel. The thermal stability of all thiobenzoates under the irradiation conditions was checked by the appropriate blank experiments. All preparations and purifications of thiobenzoates were carried out in the dark.

Irradiation of O-*Phenethyl Thiobenzoate* (II; R = H).—The thiobenzoate (II; R = H)[1] (25 mg) in cyclohexane (50 ml) was irradiated at room temperature in the usual way.[2] When the reaction was complete (7 min for 50% photolysis) the mixture was evaporated and the styrene isolated as its dibromide (90%), m.p. 74—75° (lit.,[10] 74—74·5°). Dibenzoyl disulphide (100%) was isolated from the cyclohexane solution by extraction with aqueous sodium hydroxide solution followed by oxidation in air.

The styrene was best characterised as its adduct with *p*-nitrobenzonitrile oxide[3] as follows. Triethylamine (0·5 ml) in dry ether (10 ml) was added during 1 h to a stirred mixture of styrene (0·412 g) and *p*-nitrobenzohydroxamoyl chloride (0·620 g) in ether (20 ml). The mixture was stirred at room temperature for 30 min and then chloroform (50 ml) was added. The solution was washed with water and dried (Na_2SO_4). Evaporation gave 3-p-*nitrophenyl*-5-*phenylisoxazoline* (III; R = H) (0·92 g), m.p. 129—130° (from methanol–chloroform), $\nu_{max.}$ (Nujol) 1525, 1345, and 1603 cm^{-1}, $\lambda_{max.}$ (EtOH) 310 nm (ε 16,300), τ 6·47 (2H, m), 4·23 (1H, q), 2·68 (5H, s), 2·23 (2H, d), and 1·80 (2H, d) (Found: C, 67·1; H, 4·5; N, 10·2. $C_{15}H_{12}N_2O_3$ requires C, 67·2; H, 4·5; N, 10·4%).

Irradiation of *O*-phenethyl thiobenzoate (II; R = H) in dichloromethane in the presence of either triethylamine or

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

[10] W. L. Evans and L. H. Morgan, *J. Amer. Chem. Soc.*, 1913, **35**, 54.

bis-*p*-nitrobenzoyl peroxide gave styrene (90%). Long reaction times did not effect the yield since the liberated thioacid was irreversibly removed as it was formed. Reactions at −76° gave styrene (>95%) even without additives to remove the thioacid.

O-2-(p-*Methoxyphenyl)ethyl Thiobenzoate* (II; R = OMe).—2-(*p*-Methoxyphenyl)ethanol (3·8 g) and benzonitrile (2·53 g) in dry ether (25 ml) were treated with dry hydrogen chloride gas at 0°. Work-up as usual [1] gave the *thiobenzoate* (II; R = OMe) (3·5 g, 50%), m.p. 90—91° (from methanol), $\nu_{max.}$ (CCl_4) 1232 cm^{-1}, $\lambda_{max.}$ (C_6H_{12}) 244, 278, 283, 290, and 420 nm (ε 8400, 13,150, 13,550, 11,700, and 140), τ 6·87 (2H, t, *J* 7 Hz), 6·23 (3H, s), 5·18 (2H, t, *J* 7 Hz), 2·97 (4H, ABq), 2·63 (3H, m), and 1·88 (2H, m) (Found: C, 70·2; H, 6·2; S, 11·7. $C_{16}H_{16}O_2S$ requires C, 70·6; H, 5·9; S, 11·8%).

Irradiation of O-2-(p-*Methoxyphenyl)ethyl Thiobenzoate* (II; R = OMe).—The thiobenzoate (II; R = OMe) (100 mg) in dry dichloromethane (100 ml) was irradiated at −76° in the usual way. When the reaction was complete (u.v. control; 50% reaction in 7 min), triethylamine (2 ml) was added. The mixture was allowed to warm to room temperature, then evaporated; the residue was chromatographed on thick-layer silica plates (Merck GF_{254}). Elution with light petroleum–dichloromethane (4 : 1) gave *p*-methoxystyrene (32 mg) as an oil, $\lambda_{max.}$ (EtOH) 259 nm (ε 19,000), τ 6·15 (3H, s), 4·85 (1H, dd, *J* 1·5 and 11 Hz), 4·34 (1H, dd, *J* 1·5 and 17 Hz), 3·40 (1H, d, *J* 11 Hz), 3·10 (2H, d), and 2·57 (2H, d).

Trapping *p*-methoxystyrene *in situ* with *p*-nitrobenzonitrile oxide gave 5-[2-(p-*methoxyphenyl)ethoxy*]-3-p-*nitrophenyl-5-phenyl*-1,4,2-*oxathiazole* (IV; R = OMe), m.p. 116—117° (from chloroform–cyclohexane), $\nu_{max.}$ (Nujol) 1610, 1603, 1522, 1350, and 1255 cm^{-1}, $\lambda_{max.}$ (EtOH) 302, 282, and 271 nm (ε 8800, 13,200, and 15,600), τ 7·24 (2H, t), 6·45 (3H, s), 6·18 (2H, t), 3·28 (2H, d), 2·90 (2H, d), 2·32—2·77 (5H, m), 2·24 (2H, d), and 1·79 (2H, d) (Found: C, 63·3; H, 4·7; N, 6·8; S, 7·4. $C_{23}H_{20}N_2O_5S$ requires C, 63·3; H, 4·6; N, 7·0; S, 7·4%).

O-2-(p-*Nitrophenyl)ethyl Thiobenzoate* (II; R = NO_2).—2-(*p*-Nitrophenyl)ethanol (2·67 g) and benzonitrile (1·65 g) in dry ether (25 ml) where treated with dry hydrogen chloride gas at 0°. Work-up in the usual way gave the *thiobenzoate* (II; R = NO_2) (2·62 g, 56%), m.p. 123—125° (from methanol), $\nu_{max.}$ (CCl_4) 1233 cm^{-1}, $\lambda_{max.}$ (C_6H_{12}) 272 and 418 nm (ε 19,400 and 180), τ 6·90 (2H, t, *J* 7 Hz), 5·30 (2H, t, *J* 7 Hz), 2·80 (7H, m), and 2·10 (2H, d) (Found: C, 62·5; H, 4·8; N, 4·7; S, 10·8. $C_{15}H_{13}NO_3S$ requires C, 62·7; H, 4·6; N, 4·9; S, 11·2%).

Irradiation of O-2-(p-*Nitrophenyl)ethyl Thiobenzoate* (II; R = NO_2).—The thiobenzoate (II; R = NO_2) (100 mg) in dry dichloromethane (100 ml) was irradiated in the usual way. *p*-Nitrostyrene (34 mg) was isolated, $\lambda_{max.}$ (EtOH) 299 nm (ε 13,900), τ 4·47 (1H, dd, *J* 11 and 17 Hz), 4·03 (1H, d, *J* 11 Hz), 2·40 (2H, d), and 1·72 (2H, d).

Triethylamine (0·3 ml) was added to a mixture of *p*-nitrostyrene (0·3 g) and *p*-nitrobenzohydroxamoyl chloride (0·4 g) in dichloromethane (20 ml). The mixture was left for 15 h at room temperature then poured into water. The dichloromethane layer was dried (Na_2SO_4) and evaporated to give 3,5-*bis*-p-*nitrophenylisoxazoline* (III; R = NO_2) (0·29 g), m.p. 173—174° (from methanol–chloroform), $\nu_{max.}$ (Nujol) 1603, 1525, and 1355 cm^{-1}, $\lambda_{max.}$ (EtOH) 302 nm (ε 21·200), τ 6·30 (2H, m), 4·05 (1H, dd), 1·70—2·68 (8H, m) (Found: C, 57·4; H, 3·5; N, 13·3. $C_{15}H_{11}N_3O_5$ requires C, 57·5; H, 3·5; N, 13·5%).

Irradiation of O-2-(p-*Nitrophenyl)ethyl Thiobenzoate* (II; R = NO_2) *in the Presence of* p-*Nitrobenzonitrile Oxide*.—Triethylamine (0·4 g) in dichloromethane (10 ml) was added during 90 min to the thiobenzoate (II; R = NO_2) (0·287 g) and *p*-nitrobenzohydroxamoyl chloride (0·80 g) in cyclohexane–dichloromethane (1 : 3; 150 ml) with stirring and irradiation in the usual way. The solvent was evaporated off and the residue chromatographed on thick-layer silica plates (Merck GF_{254}). Elution with light petroleum–dichloromethane (2 : 1) gave 3-p-*nitrophenyl*-5-[2-(p-*nitrophenyl)ethoxy*]-5-*phenyl*-1,4,2-*oxathiazole* (IV; R = NO_2) (130 mg), m.p. 114—117° (from chloroform–cyclohexane), $\nu_{max.}$ (Nujol) 1603, 1525, and 1357 cm^{-1}, $\lambda_{max.}$ (EtOH) 270·5 nm (ε 26,200), τ 6·91 (2H, t), 6·08 (2H, t), and 1·8—2·8 (13H, m) (Found: C, 58·2; H, 3·9; N, 9·5; S, 7·0. $C_{22}H_{17}N_3O_6S$ requires C, 58·5; H, 3·8; N, 9·3; S, 7·1%).

O-2-(p-*Dimethylaminophenyl)ethyl Thiobenzoate* (II; R = NMe_2).—2-(*p*-Dimethylaminophenyl)ethanol (0·96 g) and benzonitrile (0·6 g) in dry dimethyl sulphoxide (10 ml) were treated with dry hydrochloric acid gas at 0°. Work-up as usual gave the *thiobenzoate* (II; R = NMe_2) (51·5 mg, 8%), m.p. 84—86° (from chloroform), $\nu_{max.}$ (CCl_4) 1240 cm^{-1}, $\lambda_{max.}$ (C_6H_{12}) 258, 290, and 420 nm (ε 12,600, 6500 and 420), τ 7·11 (6H, s), 6·91 (2H, t, *J* 7 Hz), 5·20 (2H, t, *J* 7 Hz), 3·10 (4H, ABq), 2·68 (3H, m), and 1·87 (2H, d) (Found: C, 71·5; H, 6·7; N, 4·9; S, 11·4. $C_{17}H_{19}NOS$ requires C, 71·5; H, 6·7; N, 4·9; S, 11·3%).

Irradiation of O-2-(p-*Dimethylaminophenyl)ethyl Thiobenzoate* (II; R = NMe_2).—The thiobenzoate (II; R = NMe_2) (100 mg) in dry dichloromethane (100 ml) was irradiated in the usual way. *p*-Dimethylaminostyrene (13·5 mg) was isolated, $\lambda_{max.}$ (EtOH) 293 nm (ε 19,100), τ 7·20 (6H, s), 4·94 (1H, dd, *J* 1·5 and 11 Hz), 4·43 (1H, dd, *J* 1·5 and 17 Hz), 3·42 (1H, *d*, *J* 11 Hz), 3·25 (2H, d), and 2·61 (2H, d).

Triethylamine (0·3 ml) was added to a mixture of *p*-dimethylaminostyrene (0·3 g) and *p*-nitrobenzohydroxamoyl chloride (0·4 g) in dry dichloromethane (20 ml). The mixture was stirred at room temperature for 18 h and poured into water. The dichloromethane layer was dried (Na_2SO_4) and evaporated to give 5-p-*dimethylaminophenyl*-3-p-*nitrophenylisoxazoline* (III; R = NMe_2) (0·52 g), m.p. 182—183° (decomp.) (from methanol–chloroform), $\nu_{max.}$ (Nujol) 1603, 1518, and 1355 cm^{-1}, $\lambda_{max.}$ (EtOH) 310 and 265 nm (ε 17,900 and 21,000), τ 7·04 (6H, s), 6·51 (2H, m), 4·22 (1H, dd), 3·27 (2H, d), 2·70 (2H, d), 2·10 (2H, d), and 1·68 (2H, d) (Found: C, 65·4; H, 5·3; N, 13·3. $C_{17}H_{17}N_3O_3$ requires C, 65·6; H, 5·5; N, 13·5%).

O-*Phenethyl* p-*Nitrothiobenzoate* (V; R = NO_2).—2-Phenylethanol (2·44 g) and *p*-nitrobenzonitrile (2·96 g) in dry ether (25 ml) were treated with dry hydrogen chloride gas at 0°. Work-up in the usual way gave the *thioester* (V; R = NO_2) (2·64 g), m.p. 94—94·5° (from chloroform–methanol), $\nu_{max.}$ (CCl_4) 1238 cm^{-1}, $\lambda_{max.}$ (C_6H_{12}) 256, 298, and 436 nm (ε 12,000, 13,500, and 200), τ 6·80 (2H, t, *J* 7 Hz), 5·12 (2H, t, *J* 7 Hz), 2·72 (5H, s), and 1·86 (4H, s) (Found: C, 62·7; H, 4·8; N, 4·8; S, 11·2. $C_{15}H_{13}NO_3S$ requires C, 62·7; H, 4·6; N, 4·9; S, 11·2%).

O-*Phenethyl* p-*Methoxythiobenzoate* (V; R = OMe).—2-Phenylethanol (2·44 g) and *p*-methoxybenzonitrile (2·66 g) in dry ether (50 ml) were treated with dry hydrogen chloride gas at 0°. Work-up in the usual way gave the *thiobenzoate* (V; R = OMe) (2·45 g, 45%), m.p. 79—81° (from chloroform–methanol), $\nu_{max.}$ (CCl_4) 1222 cm^{-1}, $\lambda_{max.}$ 228, 233, 260, 311, and 415 nm (ε 11,700, 11,400, 6050, 19,750, and 227), τ 6·72 (2H, t, *J* 7 Hz), 6·06 (3H, s), 5·02 (2H, t, *J* 7 Hz), 3·08

(2H, d), 2·60 (5H, s), and 1·77 (2H, d) (Found: C, 70·5; H, 5·9; S, 11·9. $C_{16}H_{16}O_2S$ requires C, 70·6; H, 5·9; S, 11·8%).

O-*Phenethyl* p-*Dimethylaminothiobenzoate* (V; R = NMe_2).—2-Phenylethanol (2·08 g) and *p*-dimethylaminobenzonitrile (2·48 g) in dry ether (50 ml) were treated with dry hydrogen chloride gas at 0°. Work-up in the usual way gave the *thiobenzoate* (V; R = NMe_2) (1·62 g, 25%), m.p. 98·5—100° (from methanol), $\nu_{max.}$ (CCl_4) 1220 cm^{-1}, $\lambda_{max.}$ (C_6H_{12}) 246, 355, and 410 nm (ε 13,000, 37,300, and 1370), τ 6·89 (6H, s), 6·75 (2H, t, *J* 7 Hz), 5·06 (2H, t, *J* 7 Hz), 3·39 (2H, d), 2·65 (5H, s), and 1·85 (2H, d) (Found: S, 11·6. $C_{17}H_{19}NOS$ requires S, 11·3%).

Irradiation of O-*Phenethyl* p-*Substituted Thiobenzoates*.—Irradiation of compound (V; R = OMe) (100 mg) in the usual way gave styrene [80%; characterised as the isoxazoline (III; R = H)]. Similarly (V; R = NO_2) gave styrene (76%; characterised as the isoxazoline) and (V; R = NMe_2) gave styrene (10%; characterised as the isoxazoline).

OO′-meso-1,2-*Diphenylethylene Bisthiobenzoate* (VI).—(Thiobenzoylthio)acetic acid (107 g) in dry tetrahydrofuran (50 ml) was treated with sodium hydride (0·8 g). When the effervescence had ceased, imidazole (1·1 g) was added, followed by *meso*-dihydrobenzoin (0·856 g). The mixture was heated at reflux for 10 min, then diluted with water and filtered. The filtrate was extracted with ether. The extract was washed with 6N-hydrochloric acid, saturated aqueous sodium hydrogen carbonate solution, and water, dried (Na_2SO_4), and evaporated. The residue was combined with the material obtained by filtration and dissolved in chloroform. The solution was preadsorbed on grade III alumina and chromatographed on grade III alumina (200 g) with light petroleum (b.p. 60—80°) as eluant to give the *bisthioester* (VI) (1·2 g, 65%), m.p. 193—195° (from methanol), $\nu_{max.}$ (Nujol) 1215 cm^{-1}, $\lambda_{max.}$ (C_6H_{12}) 284, 282, and 420 nm (ε 16,900, 22,200, and 265), τ, 1·90 (4H, m), 2·78 (16H, m), and (3·36 (1H, d) (Found: C, 73·8; H, 4·8; S, 13·9. $C_{28}H_{22}O_2S$ requires C, 74·0; H, 4·9; S, 14·1%).

Irradiation of the Bisthiobenzoate (VI).—The thiobenzoate (VI) (334 mg) in dichloromethane (1 ml) and cyclohexane (300 ml) was irradiated in the usual way. Triethylamine (1 ml) was added at the beginning of the irradiation. Work-up gave deoxybenzoin (52%), m.p. 55—56° (from methanol), $\nu_{max.}$ (Nujol) 1695 cm^{-1}, τ, 1·71 (2H, m), 2·45 (8H, m), and 5·50 (2H, s).

O-*Phenethyl* 2-*Thionaphthoate* (VIII).—Carbon disulphide (2·5 ml) in ether (5 ml) was added dropwise to a cooled solution (−78°) of 2-lithionaphthalene [from 2-bromonaphthalene (3·7 g) and lithium (0·3 g)]. After 2 h the solution was warmed to 0° and the lithium salt of the dithioacid was dissolved in water (20 ml) and treated with sodium chloroacetate (0·9 g). The precipitated solid was filtered off, treated with 2N-hydrochloric acid, and extracted with ether. Drying (Na_2SO_4) and evaporation gave 2-(thionaphthoylthio)acetic acid (15%), m.p. 145—147° (lit.,[11] 147—148°). 2-Phenylethanol (0·348 g) in dimethoxyethane (3 ml) was added dropwise to a cooled (0°) suspension of sodium hydride (0·35 g of a 50% dispersion) in dimethoxyethane (10 ml). After 0·5 g at reflux the mixture was cooled at 0° and 2-(thionaphthoylthio)acetic acid (0·362 g) in dimethoxyethane (5 ml) was added. Work-up in the usual way gave O-*phenethyl* 2-*thionaphthoate* (VIII) (0·175 g), m.p. 69—70° (from light petroleum), $\lambda_{max.}$ 420, 312, 261, 250, and 217 nm (ε 85, 14,700, 23,000, 25,000, and 36,200), τ 7·6 (2H, t), 5·9 (2H, t), 3·5 (5H, s), and 3·4—2·2 (7H, m) (Found: C, 78·1; H, 5·6; S, 10·8. $C_{19}H_{16}OS$ requires C, 78·1; H, 5·5; S, 10·9%).

Irradiation of O-*Phenethyl* 2-*Thionaphthoate* (VIII).—Irradiation of the thionaphthoate (VIII) (100 mg) in dichloromethane (100 ml) in the usual way gave styrene (85%), isolated and characterised as the adduct (III; R = H), identical with an authentic sample.

2-(6,6-*Dimethylnorpin*-2-*en*-2-*yl*)*ethyl Thiobenzoate* (IX).—Sodium hydride (1·2 g) was added to 2-(6,6-dimethylnorpin-2-en-2-yl)ethanol (1·66 g) in dry dimethoxyethane (75 ml) and the mixture was heated to 60° for 5 min. To this mixture at room temperature was added (thiobenzoylthio)acetic acid (2·12 g) in dry dimethoxyethane (40 ml), and the mixture was left for 15 min. Work-up in the usual way gave the *thiobenzoate* (IX) (2·63 g, 92%), $\nu_{max.}$ (liq.) 1235 and 1273 cm^{-1}, $\lambda_{max.}$ (EtOH 241 and 286 nm (ε 9100 and 11,050), τ 9·17 (3H, s), 8·70 (3H, s), 7·78 (6H, m), 7·42 (2H, m), 5·31 (2H, t), 4·58br (1H, s), 2·60 (3H, m), and 1·80 (2H, d) (Found: C, 75·3; H, 7·7; S, 11·0. $C_{18}H_{22}OS$ requires C, 75·5; H, 7·7; S, 11·2%).

Irradiation of the Thiobenzoate (IX).—The thiobenzoate (IX) (100 mg) in cyclohexane (75 ml) was irradiated in the usual way to give 6,6-dimethyl-2-vinylnorpin-2-ene (X) (85%), isolated as its adduct with *p*-benzoquinone, m.p. 136° (lit.,[6] 136°), identical with an authentic sample.

Butyl 5-(3,4-*Methylenedioxyphenyl*)-2-*thiobenzoyloxypent*-4-*enoate* (XI; R = CSPh).—Sodium hydride (30 mg) and the hydroxy-acid (XI; R = H) (37 mg) in dry dimethoxyethane (5 ml) were heated at reflux for 40 min. To the stirred mixture at room temperature was added (thiobenzoylthio)acetic acid (25 mg) and the mixture was left for 10 min. Work-up in the usual way gave the thiobenzoate (XI; R = CSPh) (40 mg) as a yellow oil, $\nu_{max.}$ 1210, 1255, and 1745 cm^{-1}, $\lambda_{max.}$ (EtOH) 248 and 287 nm (ε 8300 and 13,900).

Irradiation of the Diester (XI; R = CSPh).—The thiobenzoate (XI; R = CSPh) (38 mg) and triethylamine (0·1 ml) in dry dichloromethane (50 ml) were irradiated in the usual way. The mixture was evaporated, the residue was dissolved in ethanol, and conc. hydrochloric acid (0·5 ml) was added. After 15 min at room temperature the mixture was diluted with water (40 ml) and filtered. 5-(3,4-Methylenedioxyphenyl)penta-2,4-dienoic acid (XII; R = H) (12·8 mg), m.p. 224—226° (from ethanol–water), was isolated.

O-*But*-3-*ynyl Thiobenzoate* (XIII).—Sodium hydride (1·20 g) was added to but-3-yn-1-ol (0·7 g) in dry dimethoxyethane (50 ml). The mixture was warmed to 60° for 5 min, then cooled to −25° and (thiobenzoylthio)acetic acid (2·12 g) in dry dimethoxyethane (15 ml) was added dropwise over 3 min. Work-up in the usual way gave the *thiobenzoate* (XIII) (1·42 g) as a yellow liquid, $\nu_{max.}$ (film) 1230, 1275, and 3290 cm^{-1}, $\lambda_{max.}$ (CH_2Cl_2) 420, 290, and 248 nm (ε 180, 12,700, and 7200), τ 7·98 (1H, t, *J* 2·5 Hz), 7·23 (2H, t), 5·26 (2H, t, *J* 6·5 Hz), 2·68 (3H, m), and 1·82 (2H, m) (Found: C, 69·3; H, 5·30; S, 16·7. $C_{11}H_{10}OS$ requires C, 69·5; H, 5·3; S, 16·6%). Irradiation at −70° gave a large number of compounds and was not investigated further.

O-*But*-3-*enyl Thiobenzoate* (XIV).—But-3-en-1-ol (0·72 g), prepared by hydrogenation of but-3-yn-1-ol, was treated with sodium hydride (1·20 g) in dry dimethoxyethane (50 ml). Addition of (thiobenzoylthio)acetic acid (2·12 g) and work-up in the usual way gave the thiobenzoate (XIV)

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[11] K. A. Jensen and C. Pedersen, *Acta Chem. Scand.*, 1961, **15**, 1087.

(1·59 g) as a yellow liquid, $\nu_{max.}$ (film) 1235 and 1273 cm^{-1}, $\lambda_{max.}$ (CH_2Cl_2) 287 and 248 nm (ε 11,700 and 7200), τ 7·37 (2H, q), 5·28 (2H, t), 4·82 (2H, m), 4·18 (1H, m), 2·62 (3H, m), and 1·83 (2H, m).

*Irradiation of But-*3*-enyl Thiobenzoate* (XIV).—The thiobenzoate (XIV) (0·48 g) in dichloromethane (100 ml) was irradiated at −70°. When the reaction was complete ($t_{\frac{1}{2}}$ 14 min) a slight excess of 4-phenyl-1,2,4-triazoline-3,5-dione [7] was added and the mixture was left for 1 h. Evaporation and chromatography on alumina (grade III) gave the adduct (XV) (80 mg, 18%), m.p. 160—161° (identical with an authentic sample).[7]

O-2-*Cyclopropylethyl Thiobenzoate* (XVI).—Sodium hydride (1·20 g) was added to 2-cyclopropylethanol [8] (0·86 g) in dry dimethoxyethane (50 ml) and the mixture was warmed to 60° for 5 min. Addition of (thiobenzoylthio)-acetic acid (2·12 g) in dry dimethoxyethane (20 ml) followed by work-up in the usual way gave the thiobenzoate, (XVI) (1·90 g) as a yellow liquid, $\nu_{max.}$ (film) 695, 760, 1115, 1235, 1272, and 1475 cm^{-1}, $\lambda_{max.}$ (CH_2Cl_2) 248, 287, and 420 nm (ε 7200, 12,500, and 160), τ 9·20—10·0 (5H, m), 8·20 (2H, q, *J* 7 Hz), 5·15 (2H, t, *J* 7 Hz), 2·63 (3H, m), and 1·83 (2H, dd). Irradiation gave a complex mixture of products that was not investigated further.

O-*Neothujyl Thiobenzoate* (XVII; R = CSPh).—Neothujyl thiobenzoate (XVII; R = CSPh), prepared by the (thiobenzoylthio)acetic acid route, had, $\nu_{max.}$ (film) 700, 783, 1240, 1280, 1563, and 2920 cm^{-1}, $\lambda_{max.}$ (CH_2Cl_2) 249, 287, and 420 nm (ε 7100, 11,900 and 130), τ 8·6—9·9 (12H, m), 7·2—8·4 (4H, m), 4·42 (1H, d), 2·59 (3H, m), and 1·83 (2H, dd) (Found: M^+, 274·1385. Calc. for $C_{17}H_{22}OS$: *M*, 274·1391). Irradiation in the usual way gave a complex mixture.

O-*Thujyl Thiobenzoate* (XVIII; R = CSPh).—Sodium hydride (0·5 g) was added to thujol (0·5 g) in dry dimethoxyethane (25 ml) and the mixture was heated at reflux for 1 h. (Thiobenzoylthio)acetic acid (0·7 g) was added at room temperature and the mixture was left for 15 min. Work-up in the usual way gave the *thiobenzoate* (XVIII; R = CSPh) (0·69 g) as a yellow liquid, $\nu_{max.}$ (film) 700, 783, 1240, 1280, 1563, and 2920 cm^{-1}, $\lambda_{max.}$ (CH_2Cl_2) 249, 287, and 420 nm (ε 7200, 11,800, and 120), τ 8·6—9·9 (12H, m), 7·2—8·4 (4H, m), 4·42 (1H, d), 2·59 (3H, m), and 1·83 (2H, dd) (Found: M^+, 274·1385. $C_{17}H_{22}OS$ requires *M*, 274·1391). Irradiation in the usual way gave a complex mixture.

O-2-*Ethoxyethyl Thiobenzoate* (XIX).—Sodium hydride (0·5 g) was added to 2-ethoxyethanol (0·9 g) in dry dimethoxyethane (50 ml) and the mixture was warmed to 60° for 5 min. At room temperature (thiobenzoylthio)acetic acid (2·1 g) in dry dimethoxyethane (15 ml) was added and the mixture was left for 15 min. Work-up in the usual way gave the *thiobenzoate* (XIX) (2·0 g, 95%) as a yellow oil, $\nu_{max.}$ (film) 1250, 1273, 1310, and 1458 cm^{-1}, $\lambda_{max.}$ 258, 287, and 418 nm (ε 7200, 11,000, and 140), τ 8·77 (3H, t), 6·43 (2H, q), 6·08 (2H, t), 5·13 (2H, t), 2·48 (3H, m), and 1·70 (2H, m) (Found: C, 62·8; H, 6·6; S, 15·1. $C_{11}H_{14}O_2S$ requires C, 62·8; H, 6·7; S, 15·2%).

Irradiation of O-2-*Ethoxyethyl Thiobenzoate* (XIX).—2-Ethoxyethyl thiobenzoate (XIX) (1·0 g) in dry dichloromethane (100 ml) was irradiated in the usual way in the presence of triethylamine. When the reaction was complete ($t_{\frac{1}{2}}$ 21 min) *N*-phenylphenacylidenamine *N*-oxide (1·30 g) was added, and the mixture was left overnight. Evaporation and chromatography of the residue on alumina (grade III), eluting with dichloromethane–light petroleum (4 : 1), gave 3-benzoyl-4-ethoxy-2-phenylisoxazolidine (XX) (0·29 g), identical with an authentic specimen. The yield of ethyl vinyl ether, determined by bromine titration, was 46%.

N-Phenylphenacylidenamine *N*-oxide (0·45 g) in dichloromethane (10 ml) was added to ethyl vinyl ether (0·50 g) in dichloromethane (30 ml). The mixture was stirred overnight at room temperature and evaporated to give the *isoxazolidine* (XX) (0·506 g), m.p. 114—115° (from chloroform–cyclohexane), $\nu_{max.}$ (Nujol) 700, 870, 1130, 1160, and 1675 cm^{-1}, τ 7·79 (3H, t), 7·27 (2H, q), 6·28 (2H, m), 5·45 (1H, dd), 4·57 (1H, dd), 2·72 (8H, m), and 1·75 (2H, dd) (Found: C, 72·6; H, 6·4; N, 4·7. $C_{18}H_{19}NO_3$ requires C, 72·7; H, 6·4; N, 4·7%).

O-2-(*Pyrrolidin-*1*-yl*)*ethyl Thiobenzoate* (XXI).—Sodium hydride (1·20 g) was added to 2-(pyrrolidin-1-yl)ethanol [12] (1·15 g) in dry dimethoxyethane (25 ml) and the mixture was heated at reflux for 10 min. At room temperature (thiobenzoylthio)acetic acid (2·12 g) in dry dimethoxyethane (30 ml) was added and the mixture was left for 15 min. Work-up in the usual way gave the *thiobenzoate* (XXI) (2·01 g) as a yellow liquid, $\nu_{max.}$ (film) 1235, 1275, and 1460 cm^{-1}, $\lambda_{max.}$ (cyclohexane) 287·5 and 247 nm (ε 12,000 and 7800), τ 8·12 (4H, m), 6·98 (2H, t), 6·42 (4H, m), 5·33 (2H, t), and 2·72 (5H, s) (Found: C, 66·1; H, 7·1; N, 5·7; S, 13·4. $C_{13}H_{17}NOS$ requires C, 66·4; H, 7·3; N, 6·0; S, 13·6%).

Irradiation of the Thiobenzoate (XXI).—Irradiation of the thiobenzoate (XXI) (1·0 g) in dry dichloromethane (100 ml) at −70° in the usual way gave, after work-up with 2,4-dinitrophenylhydrazine (0·85 g) in conc. hydrochloric acid (15 ml) and ethanol (20 ml), acetaldehyde 2,4-dinitrophenylhydrazone (0·23 g) (identical with an authentic sample).

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[12] W. Reppe, *Annalen*, 1955, **596**, 1.