

Photochemical Transformations. Part XXXIII.¹ Photolysis of Thio- benzoic Acid *O*-Esters. Part IV.¹ Photolysis of *O*-Phenethyl Thiobenzo- ate Derivatives and the Formation of Thioketones

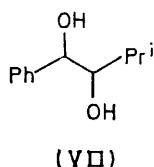
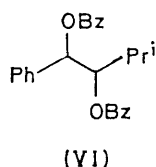
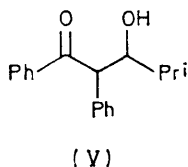
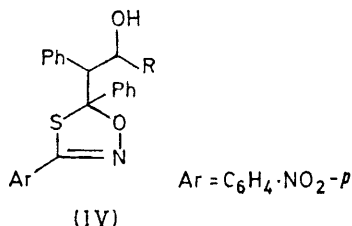
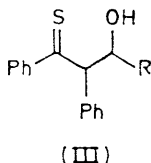
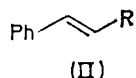
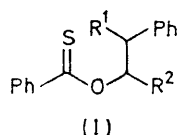
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Irradiation of *O*-1-alkyl-2-phenylethyl thiobenzoates gives styrenes and 2-alkyl-2-hydroxy-1-phenylethyl phenyl thioketones (III). The reaction proceeds *via* an oxetan (VIII), which is stable at -78° but rapidly rearranges to the thione (III) at *ca.* -20° .

DURING investigations of the photolysis of *O*-phenethyl thiobenzoates¹ we had occasion to irradiate compounds of the type (I). We now report the results of these experiments.

2,2-Diphenylethanol² was converted into its thio-*benzoate* (I; $R^1 = \text{Ph}$, $R^2 = \text{H}$) by standard procedures.³ Irradiation of the ester in dichloromethane gave 1,1-diphenylethylene as the only product (apart from thiobenzoic acid), rapidly and in high yield. Similarly, *O*-2,3-diphenylpropyl thiobenzoate (I; $R^1 = \text{CH}_2\text{Ph}$, $R^2 = \text{H}$) gave 2,3-diphenylprop-1-ene in high yield. These results are in accord with the behaviour of other *O*-phenethyl thiobenzoates.

O-1-Benzyl-2-methyl thiobenzoate (I; $R^1 = \text{H}$, $R^2 = \text{Pr}^i$) was prepared by treatment of isobutyraldehyde with benzylmagnesium chloride⁴ followed by thiobenzoylation. Irradiation of the ester in dichloro-



methane gave the styrene (II; $R = \text{Pr}^i$) (41%) and the thioketone (III; $R = \text{Pr}^i$) (29.4%). The thioketone is

¹ Part, XXXII Part III, D. H. R. Barton, M. Bolton, P. D. Magnus, K. G. Marathe, G. A. Poulton, and P. J. West, preceding paper.

² M. S. Kharasch and H. G. Clapp, *J. Org. Chem.*, 1938, **3**, 355.

³ D. H. R. Barton, C. Chavis, M. K. Kaloustian, P. D. Magnus, G. A. Poulton, and P. J. West, *J.C.S. Perkin I*, 1973, 1571.

⁴ M. T. Bogert and M. Davidson, *J. Amer. Chem. Soc.*, 1934, **56**, 185.

⁵ R. Huisgen and W. Mack, *Tetrahedron*, 1961, 583.

unstable and was fully characterised by treatment with *p*-nitrobenzonitrile oxide⁵ to give the oxathiazole (IV; $R = \text{Pr}^i$).

The series of thiobenzoates (I; $R^1 = \text{H}$, $R^2 = \text{H}$, Me, Et, Bu^t , or Ph) were prepared from the corresponding alcohols in the usual way.³ Each thioester was irradiated in dichloromethane with a medium-pressure mercury lamp. The thioester (I; $R^1 = \text{H}$, $R^2 = \text{H}$) gave only styrene (II; $R = \text{H}$), with no trace of the thioketone (III; $R = \text{H}$), whereas the thioester (I; $R^1 = \text{H}$, $R^2 = \text{Me}$) gave the styrene (II; $R = \text{Me}$) (55%) and the thioketone (III; $R = \text{Me}$) (10%). The thioester (I; $R^1 = \text{H}$, $R^2 = \text{Et}$) gave the styrene (II; $R = \text{Et}$) (51%) and the thioketone (III; $R = \text{Et}$) (20%), and the ester (I; $R^1 = \text{H}$, $R^2 = \text{Bu}^t$) gave the styrene (II; $R = \text{Bu}^t$) (27%) and the thioketone (III; $R = \text{Bu}^t$) (37%). All the thioketones were purple. The thiobenzoate (I; $R^1 = \text{H}$, $R^2 = \text{Ph}$) gave no stilbene or thioketone but benzaldehyde (65%) was obtained. The ratios of thioketone to styrene in the series (I; $R^1 = \text{H}$, $R^2 = \text{Me}$, Et, Pr^i , Bu^t) were 0.176, 0.392, 0.724, and 1.38, respectively (these ratios make allowance for recovered starting material).

To determine the stereochemistry of the styrenes (II; $R = \text{Me}$, Et, Pr^i , or Bu^t) the corresponding alcohols from which the thiobenzoates were derived were dehydrated with phosphoryl chloride in pyridine⁶ to give the authentic *trans*-styrenes. These were purified by distillation on a spinning band column and their purity was checked by analytical g.l.c. They had retention times identical with those of the styrenes obtained from the photolyses. The n.m.r. spectra⁷ were also identical. The authentic *cis*-styrenes were prepared by hydrogenation of the corresponding acetylenes over 5% palladium-barium sulphate.⁸ The styrenes produced from photolysis of the thiobenzoates contained no (<1%) *cis*-isomers.

The thioketone (III; $R = \text{Pr}^i$) was degraded to determine its stereochemistry. Oxidation with ozone gave the ketone (V). Benzoylation (benzoyl chloride-pyridine) followed by treatment with *m*-chloroperbenzoic

⁶ A. Butenandt and J. Schmidt-Thomé, *Ber.*, 1938, **71**, 1487; 1939, **72**, 182; L. H. Sarett, *J. Amer. Chem. Soc.*, 1948, **70**, 1454; S. Bernstein, R. H. Lenhard, W. S. Allen, M. Miller, R. Littell, S. M. Stolar, L. I. Feldman, and R. H. Blank, *ibid.*, 1956, **78**, 5693.

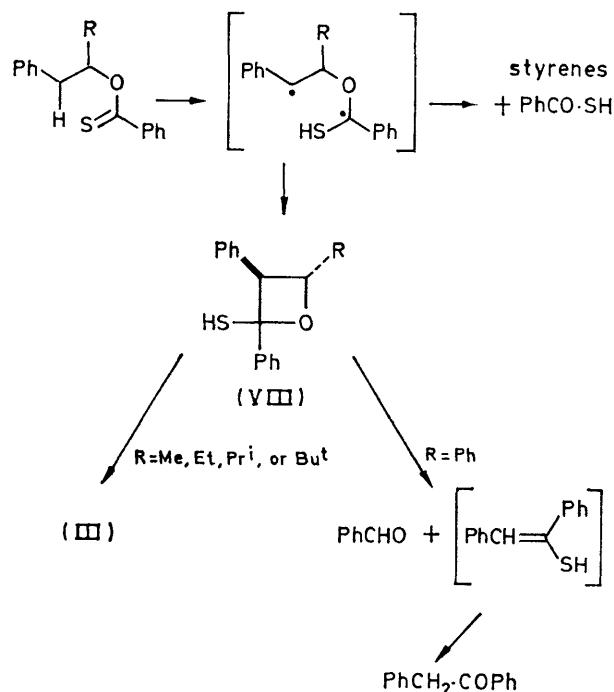
⁷ H. Rottendorf, S. Sternhell, and J. R. Wilmschurst, *Austral. J. Chem.*, 1965, **18**, 1759.

⁸ R. Y. Mixer, R. F. Heck, S. Winstein, and W. G. Young, *J. Amer. Chem. Soc.*, 1953, **75**, 4095.

acid gave the dibenzoate (VI). Hydrolysis then gave the diol (VII). Comparison of this diol with *threo*- and *erythro*-3-methyl-1-phenylbutane-1,2-diol [prepared from the *trans*-styrene (II; R = Prⁱ) by the silver acetate-iodine method⁹] showed that it was the *threo*-isomer (n.m.r.⁹ and i.r. spectra; m.p. and mixed m.p.).

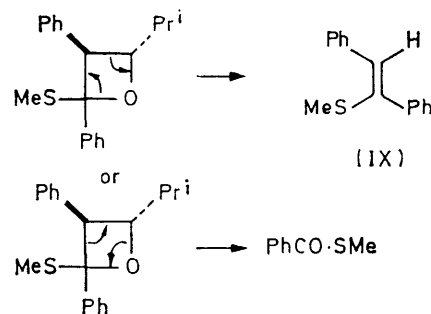
These results provide evidence for the existence of a diradical intermediate (Scheme 1) in the photoreaction of thiobenzoic *O*-esters. The 1,4-diradical can collapse to an olefin or cyclise to an oxetan. Subsequent opening of the oxetan gives thioketone (III) or benzaldehyde (if R = Ph). If R = H only styrene is formed. As the substituent R increases in size olefin formation decreases and cyclisation to oxetan increases (Thorpe-Ingold effect). The *trans*-oxetan (VIII) structure is in agreement with the formation of *trans*-styrenes and *threo*-thioketones.

In an attempt to obtain evidence for the oxetan intermediate (VIII; R = Prⁱ) a concentrated solution of the thiobenzoate (I; R¹ = H, R² = Prⁱ) was irradiated



at -78° . The solution became colourless and no thioketone was produced unless the temperature was allowed to rise to *ca.* -20° . A concentrated solution of the reaction mixture in $[^2\text{H}_8]$ toluene was examined by n.m.r. Two broad doublets at τ 5.24 and 6.09 (J 4.5 Hz) were observed as well as the aromatic proton signals. After warming the solution only the signals due to the thioketone (III; R = Prⁱ) were observed. These results are good evidence for the intermediate oxetan (VIII; R = Prⁱ) being transformed into the thioketone (III; R = Prⁱ). All attempts to trap the oxetan (VIII; R = Prⁱ) as a stable isolable derivative were unsuccessful. Treatment of a solution of the oxetan at -78° with di-

azomethane gave 1,2-diphenylvinyl methyl sulphide (IX) and *S*-methyl thiobenzoate. Both these compounds may be formed by fragmentation of the oxetan ring (Scheme 2).



The preliminary details of a study of the mechanism of the photoelimination of thiobenzoic acid have been published.¹⁰ A detailed mechanistic account will be published shortly.¹¹

EXPERIMENTAL

M.p.s were taken with a Kofler hot-stage apparatus. I.r. spectra were measured for solutions in chloroform and u.v. spectra for solutions in ethanol. N.m.r. spectra were measured for solutions in $[^2\text{H}]$ chloroform with tetramethylsilane as internal standard. Analytical g.l.c. was performed with a Perkin-Elmer F-11 instrument. All solvents were dried by standard techniques. The lamps used for the photolyses were a Philips MBU/U 125 W medium-pressure blacklight with the dark outer glass cover removed, and an HPK 125 W BA 15 D type 5720 3B/00 high-pressure mercury lamp.

O-2,2-Diphenylethyl Thiobenzoate (I; R¹ = Ph, R² = H).—2,2-Diphenylethanol² (1.98 g) was added to (thiobenzoylthio)acetic acid (2.12 g) and sodium hydride (1.0 g) in dry tetrahydrofuran (95 ml). Imidazole (1.36 g) was added to the mixture and the solution was heated at reflux for 10 min. Work-up in the usual way³ gave the *thiobenzoate* (I; R¹ = Ph, R² = H) (85%), m.p. $69-70^{\circ}$ (from methanol-dichloromethane), ν_{max} (Nujol) 1208 and 1265 cm^{-1} , λ_{max} (CH_2Cl_2) 254, 291, and 406 nm (ϵ 9000, 12,500, and 115), τ 5.37 (1H, q), 4.82 (2H, m), 2.70 (8H, m), and 2.0 (2H, d) (Found: C, 79.3; H, 5.9; S, 9.9. $\text{C}_{21}\text{H}_{18}\text{OS}$ requires C, 79.2; H, 5.7; S, 10.1%).

Irradiation of O-2,2-Diphenylethyl Thiobenzoate (I; R¹ = Ph, R² = H).—The thiobenzoate (0.318 g) in dry dichloromethane (100 ml) was irradiated. The solution was extracted with *N*-sodium hydroxide solution, washed with water, dried (Na_2SO_4), and evaporated. The residue was chromatographed on silica gel GF₂₅₄. Elution with light petroleum (b.p. $40-60^{\circ}$) gave 1,1-diphenylethylene (0.16 g, 90%), ν_{max} (film) 705, 785, 910, 1423, 1497, and 1605 cm^{-1} , λ_{max} (EtOH) 250 nm (ϵ 21,400), τ 4.62 (2H, s) and 2.77 (10H, s). The basic extract after acidification and oxidation with hydrogen peroxide gave dibenzoyl disulphide (60 mg).

O-2,3-Diphenylpropyl Thiobenzoate (I; R¹ = CH_2Ph , R² = H).—Sodium hydride (1.0 g) was added slowly to a

⁹ C. A. Kingsbury, *J. Org. Chem.*, 1970, **35**, 1319.

¹⁰ D. H. R. Barton, M. Bolton, P. D. Magnus, P. J. West, G. Porter, and J. Wirz, *J.C.S. Chem. Comm.*, 1972, 632.

¹¹ J. Wirz, *J.C.S. Perkin II*, in the press.

solution of (thiobenzoylthio)acetic acid (2.12 g) in tetrahydrofuran (75 ml). Imidazole (1.36 g) and 2,3-diphenylpropan-1-ol¹² (2.12 g) were then added and the mixture was heated at reflux for 10 min. Work-up in the usual way gave the thiobenzoate (I; $R^1 = \text{CH}_2\text{Ph}$, $R^2 = \text{H}$) (3.0 g), ν_{max} (film) 1600, 1458, 1275, 1238, 782, and 708 cm^{-1} , λ_{max} (CH_2Cl_2) 253, 290, and 410 nm (ϵ 7450, 10,900, and 130), τ 6.82 (2H, d, J 6 Hz), 6.41 (1H, m), 5.12 (2H, d, J 6 Hz), 2.67 (13H, m), and 1.86 (2H, d) (Found: C, 79.5; H, 6.1; S, 9.7. $\text{C}_{22}\text{H}_{20}\text{OS}$ requires C, 79.5; H, 6.1; S, 9.6%).

Irradiation of O-2,3-Diphenylpropyl Thiobenzoate (I; $R^1 = \text{CH}_2\text{Ph}$, $R^2 = \text{H}$).—The thiobenzoate (0.332 g) in dry dichloromethane (100 ml) was irradiated in the usual way (u.v. control). The solution was extracted with *N*-sodium hydroxide, washed with water, dried (Na_2SO_4), and evaporated. Chromatography of the residue on silica gel GF₂₅₄ [elution with light petroleum (b.p. 60–80°)] gave 2,3-diphenylpropene (0.17 g), ν_{max} (film) 1612, 1603, 1500, 1460, 918, 790, 740, and 715 cm^{-1} , τ 6.18 (2H, s), 4.94 (1H, s), 4.47 (1H, s), and 2.75 (10H, s).

O-1-Benzyl-2-methylpropyl Thiobenzoate (I; $R^1 = \text{H}$, $R^2 = \text{Pr}^i$).—Prepared in the usual way [sodium hydride, (thiobenzoylthio)acetic acid, *etc.*] this ester had ν_{max} (film) 2950, 1458, 1270, 1245, 710, and 695 cm^{-1} , λ_{max} (CH_2Cl_2) 250, 286, and 420 nm (ϵ 7000, 9700, and 120), τ 8.96 (6H, t), 7.88 (1H, m), 6.88 (2H, dd), 4.0 (1H, m), 2.59 (8H, m), and 1.78 (2H, dd) (Found: C, 76.4; H, 7.0; S, 11.1%; M^+ , 284.1235. $\text{C}_{18}\text{H}_{20}\text{OS}$ requires C, 76.1; H, 7.0; S, 11.3%; M , 284.1235).

Irradiation of O-1-Benzyl-2-methylpropyl Thiobenzoate (I; $R^1 = \text{H}$, $R^2 = \text{Pr}^i$).—The thiobenzoate (1.136 g) was irradiated in the usual way to give *trans*-3-methyl-1-phenylbut-1-ene (240 mg, 41%), starting material (I; $R^1 = \text{H}$, $R^2 = \text{Pr}^i$) (180 mg, 17.5%) and 3-hydroxy-4-methyl-1,2-diphenylpentane-1-thione (III; $R = \text{Pr}^i$) (334 mg, 29.4%) as purple needles, m.p. 72–74° (from degassed light petroleum), ν_{max} (Nujol) 3450 and 1220 cm^{-1} , λ_{max} (cyclohexane) 229, 234, 247, 316, and 553 nm (ϵ 9000, 8500, 5050, 12,650, and 102), τ 2.06 (2H, dd), 2.66 (8H, m), 4.83 (1H, d, J 9.5 Hz), 5.45 (1H, dd, J 9.5 and 2.5 Hz), 3.51br (1H, s, exchangeable with D_2O), 8.48 (1H, m), and 9.04 (6H, d, J 6 Hz) (Found: C, 75.4; H, 7.0; S, 11.2. $\text{C}_{18}\text{H}_{20}\text{OS}$ requires C, 76.1; H, 7.0; S, 11.3%).

The Oxathiazole (IV; $R = \text{Pr}^i$).—Triethylamine (0.06 ml) in anhydrous ether (1 ml) was added during 0.6 g to a stirred suspension of the thioketone (III; $R = \text{Pr}^i$) (128 mg) and *p*-nitrobenzohydroxamoyl chloride in ether (5 ml). The mixture was dissolved in chloroform and the solution was washed with water. Chromatography gave 5-(2-hydroxy-3-methyl-1-phenylbutyl)-3-*p*-nitrophenyl-5-phenyl-1,4,2-oxathiazole (IV; $R = \text{Pr}^i$) (122 mg, 60%), m.p. 149–151° (from benzene–light petroleum), ν_{max} (Nujol) 3450, 1390, 1360, 1290, 875, and 715 cm^{-1} , λ_{max} (EtOH) 281 and 337 nm (ϵ 14,500 and 4370) τ 2.0 (4H, dd, J 2.5 and 9.0 Hz), 2.7 (8H, m), 3.23 (2H, m), 4.03 (2H, m), 7.81br (1H, d, J 4 Hz, exchangeable with D_2O), 8.55 (1H, m), and 9.16 (6H, dd, J 7.5 and 8 Hz) (Found: C, 67.2; H, 5.5; N, 6.3; S, 7.1. $\text{C}_{25}\text{H}_{24}\text{N}_2\text{O}_4\text{S}$ requires C, 67.0; H, 5.4; N, 6.3; S, 7.1%). Another compound was isolated which from its spectral properties was considered to be a diastereoisomer of (IV; $R = \text{Pr}^i$).

O-1-Methyl-2-phenylethyl Thiobenzoate (II; $R^1 = \text{H}$, $R^2 = \text{Me}$).—Prepared in the usual way from 1-phenylpro-

pan-2-ol this ester had ν_{max} (film) 1250 cm^{-1} , λ_{max} (cyclohexane) 252, 289, and 417 nm (ϵ 9600, 11,530, and 130), τ 1.85 (2H, dd), 2.64 (8H, m), 3.97 (1H, m), 68.8 (2H, m), and 8.58 (3H, d, J 6.5 Hz) (Found: C, 74.9; H, 6.2; S, 12.7. $\text{C}_{16}\text{H}_{16}\text{OS}$ requires C, 75.0; H, 6.3; S, 12.5%).

Irradiation of O-1-Methyl-2-phenylethyl Thiobenzoate (II; $R^1 = \text{H}$, $R^2 = \text{Me}$).—The thiobenzoate (1.024 g) was irradiated in degassed dichloromethane (400 ml) containing triethylamine (0.7 ml) in the usual way. Evaporation and chromatography gave *trans*-1-phenylprop-1-ene (II; $R = \text{Me}$) (55%) (identical with an authentic sample), unchanged starting material (15%), and 3-hydroxy-1,2-diphenylbutane-1-thione (III; $R = \text{Me}$) (10%), ν_{max} (film) 1225 cm^{-1} , λ_{max} (cyclohexane) 229, 234, 248, 316, and 553 nm (ϵ 8400, 7600, 4600, 12,600, and 76), M^+ 286. Further characterisation was not possible because of its instability.

O-1-Benzylpropyl Thiobenzoate (I; $R^1 = \text{H}$, $R^2 = \text{Et}$).—Prepared in the usual way from 1-phenylbutan-2-ol this ester had ν_{max} (film) 1250 cm^{-1} , λ_{max} (cyclohexane) 253, 291, and 421 nm (ϵ 9725, 11,250, and 120), τ 1.82 (2H, dd), 2.64 (8H, m), 4.05 (1H, m), 6.89 (2H, m), 8.23 (1H, m), and 9.03 (3H, t) (Found: C, 75.3; H, 6.7; S, 11.7. $\text{C}_{17}\text{H}_{18}\text{OS}$ requires C, 75.6; H, 6.7; S, 11.9%).

Irradiation of O-1-Benzylpropyl Thiobenzoate (I; $R^1 = \text{H}$, $R^2 = \text{Et}$).—The thiobenzoate (1.08 g) was irradiated in the usual way to give *trans*-1-phenylbut-1-ene (II; $R = \text{Et}$) (51%), starting material (9.5%), and 3-hydroxy-1,2-diphenylpentane-1-thione (III; $R = \text{Et}$) (20%), m.p. 74–77° (from degassed light petroleum under argon), ν_{max} (Nujol) 1220 and 3300 cm^{-1} , λ_{max} (cyclohexane) 229, 234, 250, 316, and 553 nm (ϵ 8100, 7600, 4600, 12,650, and 94), 5.43 τ 2.05 (2H, dd), 2.67 (8H, m), 5.00 (1H, d, J 9 Hz), (1H, m), 7.23br (1H, s, exchanged with D_2O), 8.63 (2H, m), and 9.06 (3H, t, J 6.5 Hz) (Found: C, 75.4; H, 6.5; S, 11.9. $\text{C}_{17}\text{H}_{18}\text{OS}$ requires C, 75.6; H, 6.7; S, 11.9%).

O-1-Diphenylmethyl-2,2-dimethylpropyl Thiobenzoate (I; $R^1 = \text{H}$, $R^2 = \text{Bu}^t$).—Prepared in the usual way from 3,3-dimethyl-1-phenylbutan-2-ol¹³ this ester had m.p. 51–52° (from methanol), ν_{max} (Nujol) 1230 cm^{-1} , λ_{max} (cyclohexane) 254, 293, and 421 nm (ϵ 9940, 10,500, and 125), τ 1.87 (2H, dd), 2.68 (8H, m), 3.89 (1H, m), 6.95 (2H, m), and 8.93 (9H, s) (Found: C, 76.6; H, 7.6; S, 11.0. $\text{C}_{19}\text{H}_{22}\text{OS}$ requires C, 76.7; H, 7.4; S, 10.7%).

Irradiation of O-1-Diphenylmethyl-2,2-dimethylpropyl Thiobenzoate (I; $R^1 = \text{H}$, $R^2 = \text{Bu}^t$).—The thiobenzoate (1.192 g) was irradiated in the usual way to give *trans*-3,3-dimethyl-1-phenylbut-1-ene (27%) (identical with an authentic sample) and 3-hydroxy-4,4-dimethyl-1,2-diphenylpentane-1-thione (II; $R = \text{Bu}^t$) (37%) as a purple oil, ν_{max} (film) 1215 and 3460 cm^{-1} , λ_{max} (cyclohexane) 230, 235, 247, 314, and 554 nm (ϵ 8000, 7550, 5100, 10,000, and 99), τ 2.12 (2H, dd), 2.67 (8H, m), 4.57 (1H, d, J 8 Hz), 5.66 (1H, d, J 8 Hz), 6.88br (1H, s, exchanged with D_2O), and 9.14 (9H, s) (Found: C, 76.5; H, 7.4; S, 10.7. $\text{C}_{19}\text{H}_{22}\text{OS}$ requires C, 76.4; H, 7.2; S, 10.8%).

O-1,2-Diphenylethyl Thiobenzoate (I; $R^1 = \text{H}$, $R^2 = \text{Ph}$).—Prepared in the usual way from 1,2-diphenylethanol this ester had m.p. 65–66° (from methanol), ν_{max} (Nujol) 1230 cm^{-1} , λ_{max} (cyclohexane) 250, 294, and 408 nm (ϵ 9700, 11,000, and 120), τ 1.78 (2H, dd), 2.68 (13H, m), 3.14 (1H, m), and 6.59 (2H, m) (Found: C, 79.2; H, 5.8; S, 9.8. $\text{C}_{15}\text{H}_{16}\text{OS}$ requires C, 79.2; H, 5.7; S, 10.1%).

Irradiation of O-1,2-Diphenylethyl Thiobenzoate (I; $R^1 =$

¹² H. R. Sullivan, J. R. Beck, and A. Pohland, *J. Org. Chem.*, 1963, **28**, 2381.

¹³ D. Price, D. Davidson, and M. T. Bogert, *J. Org. Chem.*, 1938, **2**, 540.

H, R² = Ph).—The thiobenzoate (1.272 g) was irradiated under the usual conditions. Treatment of the product with 2,4-dinitrophenylhydrazine in methanol gave benzaldehyde 2,4-dinitrophenylhydrazone (0.63 g, 65%).

Preparation of Authentic Styrenes (II; R = Me, Et, Prⁱ, or Bu^t).—Phosphoryl chloride (20 ml) was added dropwise to a stirred solution of the alcohol (0.1 mol) in pyridine (200 ml).⁶ The mixture was heated at reflux until g.l.c. showed the absence of starting material. The mixture was poured on crushed ice and the product was extracted with ether. The extract was washed with 3N-hydrochloric acid, saturated aqueous sodium hydrogen carbonate, and water. Evaporation of the dried (Na₂SO₄) extract and distillation (spinning band) gave the pure *trans*-styrene (II; R = Me, R = Et,¹⁴ Prⁱ,¹⁵ or Bu^t,¹⁵), retention times 7.6, 11.4, 14.0, and 15.6 min, respectively (column temp. 100°; flow rate 100 ml min⁻¹).

cis-1-Phenylbut-1-ene.—Hydrogenation⁸ of 1-phenylbut-1-yne gave *cis*-1-phenylbut-1-ene (69%), *t*_R 7.6 min, different from (II; R = Et) (similarly for the other olefins).

Oxidation of 3-Hydroxy-4-methyl-1,2-diphenylpentane-1-thione (III; R = Prⁱ).—The thione (0.986 g) in dry dichloromethane (500 ml) was treated with ozone at room temperature. When the purple colour disappeared the solution was evaporated and the residue chromatographed on silica gel GF₂₅₄ (thick plates) to give 3-hydroxy-4-methyl-1,2-diphenylpentan-1-one (V) (573 mg), m.p. 120–123° (from dichloromethane–light petroleum), *v*_{max} (Nujol) 1678 and 3300 cm⁻¹, *τ* 2.01 (2H, dd), 2.65 (8H, m), 5.20 (1H, d, *J* 8.5 Hz), 5.73 (1H, dd, *J* 8.5 and 2.5 Hz), 6.83 (1H, s, exchangeable with D₂O), 8.54 (1H, m), 9.04 (6H, dd, *J* 6.5 and 2.5 Hz). Benzoylation of the product (V) with benzoylchloride (1 ml) in pyridine (5 ml) gave the *benzoate* (71%), m.p. 162–165° (from methanol), *v*_{max} (Nujol) 1715 and 1675 cm⁻¹, *τ* 1.96 (4H, m), 2.64 (14H, m), 3.86 (1H, dd, *J* 10 and 2.5 Hz), 4.85 (1H, d, *J* 10 Hz), 8.25 (1H, m), and 9.01 (6H, dd, *J* 6 and 6 Hz) (Found: C, 80.9; H, 6.5. C₂₅H₂₄O₃ requires C, 80.6; H, 6.5%).

Baeyer–Villiger Oxidation of 3-Benzoyloxy-4-methyl-1,2-diphenylpentan-1-one.—The ketone (0.372 g) and *m*-chloro-

perbenzoic acid were heated overnight in dry dichloroethane (10 ml). The mixture was cooled and the crystalline mass that separated was filtered off and chromatographed on silica gel GF₂₅₄ (thick plates) to give 3-methyl-1-phenylbutane-1,2-diyl dibenzoate (VI) (49%) as an oil, *v*_{max} 1710 and 1720 cm⁻¹, *τ* 2.07 (4H, m), 2.62 (11H, m), 3.76 (1H, d, *J* 9 Hz), 4.39 (1H, dd, *J* 4 and 8 Hz), 8.18 (1H, m), and 8.89 (6H, dd). Treatment of the dibenzoate (VI) with lithium aluminium hydride in anhydrous ether in the usual way gave *threo*-3-methyl-1-phenylbutane-1,2-diol (VII) (77%), m.p. 74–75° (from hexane–ether), identical with an authentic sample⁹ [prepared by treatment of *trans*-3-methyl-1-phenylbut-1-ene (II; R = Prⁱ) with silver acetate–iodine–acetic acid–water, followed by lithium aluminium hydride]. The *erythro*-isomer,⁹ prepared in the usual way, had m.p. 102–103°.

Irradiation of the Thiobenzoates (I; R¹ = H, R² = H, Me, Et, Prⁱ, or Bu^t) at –78°.—The thiobenzoate (1 mmol) in dry degassed dichloromethane (400 ml) at –78° was irradiated in the usual way. When the reaction was complete (u.v. control) thioketone (III) formation was induced by warming to room temperature. Results are in the Table.

Compound (I; R ¹ = H)	Yield of thione (%)	Yield of styrene (%)
R ² = H	10	81
R ² = Me	32	61
R ² = Et	45	52
R ² = Pr ⁱ	55	42
R ² = Bu ^t	75	25

Attempted Trapping of the Intermediate (VIII; R = Prⁱ) *with Diazomethane*.—Irradiation of the ester (I; R¹ = H, R² = Prⁱ) (1.3 g) at –78° followed by treatment of the solution at –78° with an excess of diazomethane gave the styrene (II; R = Prⁱ), 1,2-diphenylvinyl methyl sulphide (11%) (identical with an authentic sample),¹⁶ and *S*-methyl thiobenzoate (35%) (identical with an authentic sample).

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