

Persulphate Oxidations. Part V.¹ † Oxidation of *o*-(Arylthio)- and *o*-(Arylsulphonyl)-benzoic Acids

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Oxidation of three *o*-(arylthio)benzoic acids with persulphate gave diaryl 2,2'-dithiodibenzoates in low yield. Oxidation of the corresponding *o*-(arylsulphonyl)benzoic acids gave only traces of the expected dibenzothiophen 5,5'-dioxides, and the radicals formed on pyrolysis of bis-*o*-(phenylsulphonyl)benzoyl peroxide reacted with solvent but did not cyclise. Persulphate oxidation of biphenyl-2-yl hydrogen oxalate gave dibenzo[*b,d*]pyran-6-one but *o*-benzyloxybenzoic acid yielded 2-phenyl-1,3-benzodioxan-4-one.

It has been reported² that persulphate oxidation of *o*-phenoxybenzoic acids gives unsymmetrical diaryl bisalicylates [*e.g.* (1) \longrightarrow (2)] in a radical rearrangement

† Continuation of the Series 'Persulphate Oxidation of Carboxylic Acids.'

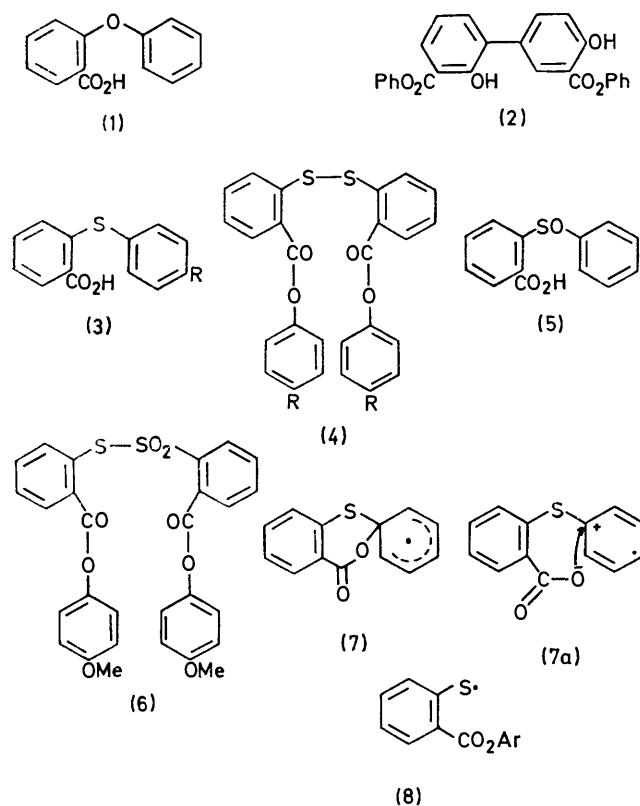
¹ Part IV, P. S. Dewar, A. R. Forrester, and R. H. Thomson, *J. Chem. Soc. (C)*, 1971, 3950.

reaction. The sulphur analogues (3) undergo a similar interesting rearrangement³ but the reaction is limited in scope. In all cases examined, oxidation under the usual

² R. H. Thomson and A. G. Wylie, *J. Chem. Soc. (C)*, 1966, 321.

³ P. M. Brown, P. S. Dewar, A. R. Forrester, A. S. Ingram, and R. H. Thomson, *Chem. Comm.*, 1970, 849.

conditions gave a large amount of acidic material and a disappointingly small neutral fraction. In the best example, compound (3; R = Me) gave the diester (4;



R = Me) in 15% yield based on starting acid consumed. Hydrolysis of the product gave *p*-cresol and 2,2'-dithio-dibenzoic acid, and its structure was confirmed by synthesis from the diacid dichloride and *p*-cresol. The parent acid (3; R = H) gave only 2.5% of the diester (4; R = H), together with starting material (44%) and the sulphoxide acid (5) (40%), and the reaction failed with the chloro-acid (3; R = Cl). Oxidation of the methoxy-analogue (3; R = OMe) yielded a little of the thiosulphonate (6) as well as a trace of the disulphide (4; R = OMe). The thiosulphonate was synthesised from the disulphide (4; R = OMe) by chlorination followed by treatment of the resulting sulphenyl chloride with base⁴ but it could not be obtained by oxidation of the disulphide with either persulphate or hydrogen peroxide.

The reaction probably proceeds by cyclisation of the initial carboxyl radical to give the intermediate (7), followed by homolytic fission of the C-S bond to form a

thiophenoxy radical (8) which dimerises. However, the possibility that an electron is removed initially from the phenyl group to give the radical cation (7a), which is trapped by the carboxylate ion, cannot be excluded,^{5a} although sulphate radical anions prefer to add to a benzene ring.^{5b} The overall result is the migration of an aryl group from sulphur to oxygen; analogous ionic migrations have been observed in Smiles rearrangements.⁶ The initial carboxyl radical could conceivably cyclise to form a lactone, or eliminate carbon dioxide and then cyclise to form a dibenzothiophen, but these products were not detected. [Similarly, analogous products do not arise in the persulphate oxidation of the phenoxy-acid (1).]

It is difficult to account adequately for the low yields of diesters (4). Insolubility is probably a factor. *o*-(Arylthio)benzoic acids are extremely insoluble in water and much precipitation occurred during the oxidations as the pH decreased. Attempts to overcome this by use of aqueous pyridine or addition of an excess of potassium hydrogen carbonate did not increase the yield of neutral material. Attack on sulphur to form sulphoxides is also a complicating factor. This consumes persulphate and is probably a faster reaction than carboxylate ion oxidation; the use of an excess of persulphate did not improve the yields of diester (4). Ionic⁷ or radical⁸ processes may be involved in the oxidation of sulphides to sulphoxides by peroxy-compounds, and the e.s.r. spectra of radical cations ($-\overset{+}{S}-$) have been observed⁹ during the oxidation of sulphides with persulphate in concentrated sulphuric acid. Since, in the present work, sulphoxide formation was not observed below 40° it seems likely that attack on sulphur is initiated by sulphate radical anions. Alkyl sulphoxides, but not sulphones, are attacked by hydroxyl radicals,¹⁰ and also by persulphate,¹¹ with formation of alkyl radicals and sulphinic acids.

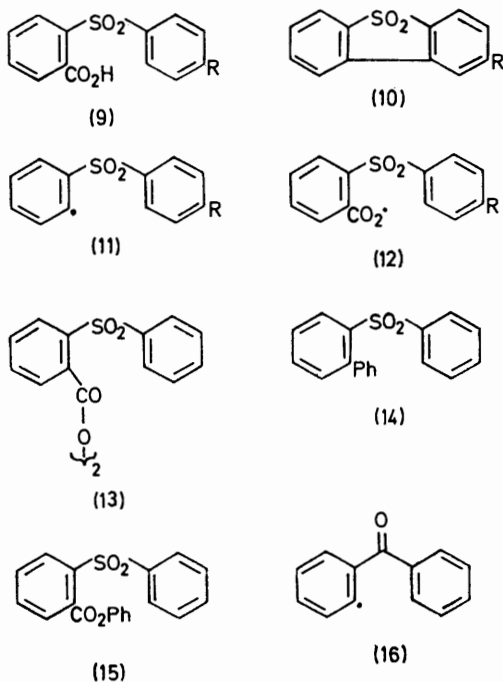
To avoid some of these complications the oxidation of the sulphone acids (9) was briefly investigated, but there were similar insolubility problems. Oxidation of the acid (9; R = H) yielded a trace of dibenzothiophen dioxide (10; R = H), and dibenzo[*b,d*]pyran-6-one; sulphonic acid was detected and starting material (41%) was recovered. The nitro-acid (9; R = NO₂) gave 1% of the dibenzothiophen (10; R = NO₂) but the methoxy-analogue (9; R = OMe) gave only a little *p*-methoxyphenol. The dibenzothiophen dioxides must be derived from the radicals (11); the reluctance of these radicals, and their precursor carboxyl radicals (12), to cyclise was further demonstrated by pyrolysis of the peroxide (13) in boiling benzene. No cyclised products were detected, the neutral material being a complex mixture from which only the sulphones (14) and (15) were isolated. Clearly, these are formed by reactions of the radicals (11;

⁴ T. Zincke and F. Farr, *Annalen*, 1912, **391**, 57.
⁵ (a) R. O. C. Norman, P. M. Storey, and P. R. West, *J. Chem. Soc. (B)*, 1970, 1087; (b) R. O. C. Norman and P. M. Storey, *ibid.*, p. 1099.
⁶ A. A. Levy, H. C. Rains, and S. Smiles, *J. Chem. Soc.*, 1931, 3264.

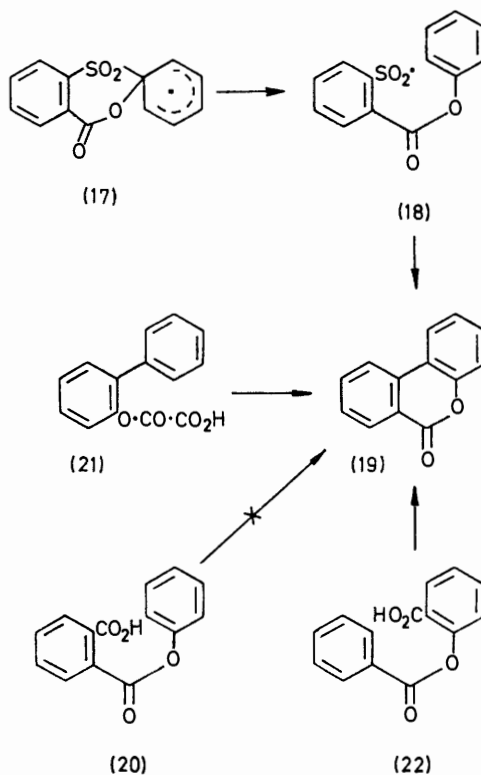
⁷ D. Barnard, L. Bateman, and J. I. Cuneen, in 'Organic Sulfur Compounds,' ed. N. Kharasch, Pergamon, New York, 1961, vol. 1, p. 229.

⁸ D. G. Pobedimskii, *Russ. Chem. Rev.*, 1971, **40**, 142.
⁹ U. Schmidt, K. Kabitzke, K. Markau, and A. Müller, *Annalen*, 1964, **672**, 78.
¹⁰ C. Lagercrantz and S. Forshult, *Acta Chem. Scand.*, 1969, **23**, 811.
¹¹ P. M. Brown and R. H. Thomson, unpublished work.

R = H) and (12; R = H) with the solvent. This contrasts with the behaviour of the radical (16), generated by persulphate oxidation of *o*-benzoylbenzoic acid,

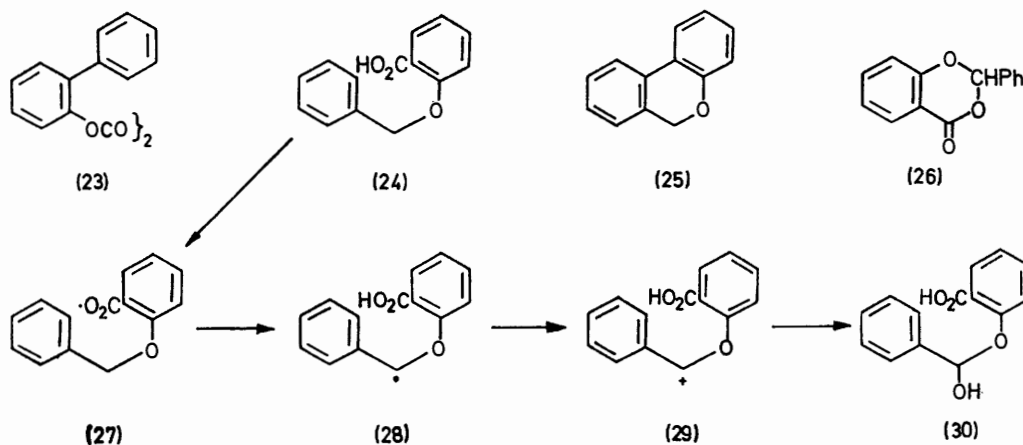


arise from the radical (18). This suggested alternative oxidative routes to dibenzo[*b,d*]pyran-6-one. In practice



which cyclises to fluorenone in 11% yield.¹² The C-CO bonds in *o*-benzoylbenzoic acid are appreciably shorter than the C-SO₂ bonds in structure (9) (1.84 Å in bis-4-bromophenyl sulphone¹³), and calculations from known bond lengths and angles suggest that the C(2)-C(2')

persulphate oxidation of monophenyl phthalate (20) did not produce compound (19) (probably owing to rapid hydrolysis to phthalic acid and phenol) but the isomer



distance in structure (16) is *ca.* 2.4 Å whereas the corresponding distance in (11) is *ca.* 4.0 Å. Obviously cyclisation of the radical (11) will be more difficult than that of (16).

The small yield of dibenzo[*b,d*]pyran-6-one obtained in the oxidation of the acid (9; R = H) may have been formed by the sequence (17) → (18) → (19), and the sulphonic acid detected in the reaction mixture could

(22) yielded 4% of this material. Oxidation of the oxalate (23) under the usual conditions was also unsuccessful, presumably because hydrolysis to the monoaryl oxalate (21) was too slow, but when the latter was oxidised separately dibenzo[*b,d*]pyran-6-one was formed

¹² J. Russell and R. H. Thomson, *J. Chem. Soc.*, 1962, 3379.
¹³ C. C. Price and S. Oae, 'Sulfur Bonding,' Ronald Press, New York, 1962, p. 64.

in 75% yield. Coupling¹⁴ of the radicals $\text{ArO}\cdot\text{CO}$ to form the oxalate diester was not observed. An attempt to obtain the dibenzopyranone by way of the pyran (25)¹ by oxidation of *o*-benzyloxybenzoic acid (24) led to the formation of the lactone (26) (24% based on acid consumed), benzaldehyde, and a trace of salicylic acid. This suggests that the radical (28), derived from (27) or directly from (24), is further oxidised to the cation (29), which would give the lactone (26) either before or after solvolysis. In acidic solution the solvolysis product (30) would decompose to benzaldehyde and salicylic acid.

EXPERIMENTAL

T.l.c. refers to separations on silica gel plates in chloroform. Known compounds were identified by direct comparison (t.l.c., i.r. spectrum, m.p.) with authentic samples. Spectra were run for solutions in ethanol (u.v.), Nujol mulls (i.r.) and solutions in $[\text{2H}]$ chloroform (n.m.r.). Petroleum refers to light petroleum, b.p. 40–60°.

Starting Materials.—These were prepared by literature methods. The following are new. *o*-(*p*-Methoxyphenylsulphonyl)benzoic acid (action of hydrogen peroxide on the sulphide¹⁵) formed plates, m.p. 148° (from chloroform) (Found: C, 57.6; H, 4.4; OMe, 10.6. $\text{C}_{14}\text{H}_{12}\text{O}_5\text{S}$ requires C, 57.5; H, 4.1; OMe, 10.6%). *Dibiphenyl-2-yl oxalate* (from 2-hydroxybiphenyl and oxalyl chloride¹⁶) crystallised from benzene in prisms, m.p. 132–133° (Found: C, 79.5; H, 4.6. $\text{C}_{26}\text{H}_{18}\text{O}_4$ requires C, 79.2; H, 4.6%), ν_{CO} 1786 and 1762 cm^{-1} , λ_{max} 246 and 292 nm (log ϵ 4.34 and 3.42).

Bis-o-(phenylsulphonyl)benzoyl Peroxide.—*o*-(Phenylsulphonyl)benzoic acid (3 g) and thionyl chloride (5 ml) were heated under reflux for 1 h and excess of reagent was then removed *in vacuo*. The residual acid chloride in benzene (10 ml) was added to *m*-sodium hydroxide (50 ml) and hydrogen peroxide (30%; 2 ml) at 0°, and the mixture was stirred for 20 min. The precipitate was collected, dried *in vacuo* at 0°, and crystallised from chloroform–petroleum to give the peroxide as needles, m.p. 147–147.5° (53%) (Found: C, 59.7; H, 3.4; S, 12.3. $\text{C}_{26}\text{H}_{18}\text{O}_8\text{S}_2$ requires C, 59.8; H, 3.5; S, 12.25%), ν_{CO} 1812 and 1790 cm^{-1} .

Phenyl hydrogen phthalate could not be prepared by the method of Parish *et al.*¹⁷ nor that of Thanassi *et al.*¹⁸ and was obtained as follows. Phthalic anhydride (14.3 g) and sodium phenoxide (12 g) in dried tetrahydrofuran (100 ml) were heated under reflux for 1.5 h and the solvent was then removed *in vacuo*. Benzene was added and dry hydrogen chloride was passed through the mixture for 3 h. Sodium chloride was filtered off, and petroleum was added to precipitate the ester, which formed needles, m.p. 97.5–98.5° (from chloroform–petroleum) (lit.,¹⁸ 94–96°) (11%), ν_{max} 3300–2100, 1760, and 1690 cm^{-1} . When benzene or dimethylformamide was used as solvent the reaction failed.

Persulphate Oxidations.—These were carried out as before¹ except that the solution was heated under reflux for 1 h after addition of the persulphate.

(a) Oxidation of *o*-(phenylthio)benzoic acid¹⁵ (3; R = H) (2.3 g) gave *diphenyl 2,2'*-dithiodibenzoate (4; R = H) (57

mg, 2.5%) as prisms (from aqueous acetone), m.p. 124–126° (Found: C, 67.7; H, 4.1; S, 14.3. $\text{C}_{26}\text{H}_{18}\text{O}_4\text{S}_2$ requires C, 68.1; H, 4.0; S, 14.0%), ν_{CO} 1720 cm^{-1} , λ_{max} 260 and 322 nm (log ϵ 4.31 and 4.01). The acidic fraction was a mixture of starting material (1.0 g, 43%) and *o*-(phenylsulphonyl)benzoic acid (984 mg, 40%), m.p. 161–163°, which was separated by fractional crystallisation.

The diester (4; R = H) was synthesised from diphenyl 2,2'-dithiodibenzoic acid¹⁹ by conversion into the diacid dichloride, followed by treatment with phenol (2 mol) in cold pyridine for 24 h. It was isolated by pouring the solution into 2*M*-hydrochloric acid and extraction with ether; m.p. 124–126° (from chloroform–petroleum) (77.5%).

(b) Oxidation of *o*-(*p*-tolylthio)benzoic acid²⁰ (3; R = Me) (2.44 g) gave acidic material (1.59 g) and a neutral fraction which was chromatographed (t.l.c.) and then crystallised from methanol–chloroform to give *di-p-tolyl 2,2'*-dithiodibenzoate (4; R = Me) as plates, m.p. 162–163° (130 mg, 15%) (Found: C, 68.9; H, 4.7; S, 13.5. $\text{C}_{28}\text{H}_{22}\text{O}_4\text{S}_2$ requires C, 69.1; H, 4.55; S, 13.15%), ν_{CO} 1720 cm^{-1} , λ_{max} 256 and 321 nm (log ϵ 4.30 and 3.98), identical with an authentic sample prepared as in (a). The diester (210 mg) was hydrolysed by heating under reflux with sodium hydroxide (100 mg) in ethanol (15 ml) and water (1 ml) for 1 h. After removal of the ethanol *in vacuo*, water was added, and the mixture was extracted with ether. The extract was shaken with aqueous potassium hydrogen carbonate; acidification gave 2,2'-dithiodibenzoic acid (99 mg, 75%). The dried ether layer yielded *p*-cresol (62 mg, 67%).

(c) Oxidation of *o*-(*p*-methoxyphenylthio)benzoic acid²¹ (3; R = MeO) (2.60 g) yielded acidic material (0.96 g) and a neutral fraction which was separated (t.l.c.) into (i) *bis-p-methoxyphenyl 2,2'*-dithiodibenzoate SS-dioxide (6) (59 mg, 3%), prisms, m.p. 141–142° (from chloroform–petroleum) (Found: C, 61.1; H, 4.2; S, 11.6%; *M*, 550. $\text{C}_{28}\text{H}_{22}\text{O}_8\text{S}_2$ requires C, 61.1; H, 4.0; S, 11.6%; *M*, 550), ν_{CO} 1746 and 1740sh cm^{-1} , λ_{max} 250sh, 278, and 285sh nm (log ϵ 4.21, 4.07, and 4.04), identical with material prepared later, and (ii) *bis-p-methoxyphenyl 2,2'*-dithiodibenzoate (4; R = OMe) which crystallised from chloroform–petroleum as prisms, m.p. 158–159° (6 mg, <1%) (Found: C, 64.6; H, 4.5; S, 12.15. $\text{C}_{28}\text{H}_{22}\text{O}_6\text{S}_2$ requires C, 64.9; H, 4.3; S, 12.3%), ν_{CO} 1720 cm^{-1} , λ_{max} 260, 278sh, 286sh, and 320 nm (log ϵ 4.29, 4.05, 3.97, and 4.00), identical with a sample synthesised as before from the diacid dichloride and *p*-methoxyphenol.

The thiosulphonate (6) was prepared by passing chlorine into a solution of the disulphide (4; R = OMe) (185 mg) in carbon tetrachloride (25 ml) for 1 h. After removal of the solvent the residue was shaken with 0.1*M*-sodium hydroxide for 15 min, and extracted with chloroform; the extract was washed, dried, and evaporated. The product, after t.l.c., afforded the thiosulphonate (6) (74 mg, 37%), m.p. 141–142° (from chloroform–petroleum).

(d) Oxidation of *o*-(phenylsulphonyl)benzoic acid (2.62 g) (9; R = H) gave a neutral fraction which was separated into dibenzo[*b,d*]pyran-6-one, m.p. 91° (24 mg, 1%), and

¹⁴ K. Bartel, A. Goosen, and A. Scheffer, *J. Chem. Soc. (C)*, 1971, 3766.

¹⁵ W. S. Weedon and H. W. Doughty, *Amer. Chem. J.*, 1905, **33**, 386.

¹⁶ R. Adams and H. Gilman, *J. Amer. Chem. Soc.*, 1915, **37**, 2716.

¹⁷ R. C. Parish and L. M. Stock, *J. Org. Chem.*, 1965, **30**, 927.

¹⁸ J. W. Thanassi and T. C. Bruice, *J. Amer. Chem. Soc.*, 1966, **88**, 747.

¹⁹ W. G. Prescott and S. Smiles, *J. Chem. Soc.*, 1911, **99**, 640.

²⁰ J. Goldberg, *Ber.*, 1904, **37**, 4526.

²¹ K. C. Roberts and S. Smiles, *J. Chem. Soc.*, 1929, 863.

dibenzothiophen 5,5-dioxide, m.p. 228—229° (lit.,²² 233—234°) (3 mg, 0.1%). Sulphonic acids were detected in the reaction mixture with Pinacryptol Yellow,²³ but not sulphonic acids (Fast Blue B salt²⁴). Starting acid (41%) was recovered.

(e) Oxidation of *o*-(*p*-nitrophenylsulphonyl)benzoic acid²⁵ (9; R = NO₂) (3.08 g) gave neutral material which was chromatographed (t.l.c.) to yield 2-nitrodibenzothiophen 5,5-dioxide, m.p. 257—258° (lit.,²⁶ 258°) (29 mg, 1%); starting acid (84%) was recovered.

(f) Oxidation of *o*-(*p*-methoxyphenylsulphonyl)benzoic acid (2.92 g) (9; R = MeO) gave a complex mixture of neutral products (267 mg) from which *p*-methoxyphenol, m.p. 53—55° (54 mg, 4%) was isolated by t.l.c.; starting acid (63%) was recovered.

(g) Oxidation of *o*-benzyloxybenzoic acid²⁷ (2.28 g) yielded unchanged acid (1.90 g) and neutral material (100 mg) which, after t.l.c., afforded dibenzo[*b,d*]pyran-6-one (15 mg, 5%).

(h) Dibiphenyl-2-yl oxalate (1.6 g) and potassium hydroxide (0.23 g) were heated in acetone (50 ml) and water (50 ml) under reflux for 1 h; the solvent was removed *in vacuo* and the residue then extracted with ether. Shaking with sodium hydrogen carbonate solution, and acidification, yielded biphenyl-2-yl hydrogen oxalate as an oil, ν_{\max} 3680—2200, 1780, and 1750 cm⁻¹, which slowly decomposed into oxalic acid and 2-hydroxybiphenyl. This oil (1.6 g) was oxidised with persulphate in the usual way to give dibenzo[*b,d*]pyran-6-one, m.p. 92—93° (0.6 g, 79%).

(i) Oxidation of *o*-benzyloxybenzoic acid (2.28 g) (22) gave, besides unchanged acid (1.62 g), benzaldehyde (20 mg) (2,4-dinitrophenylhydrazone, m.p. 237°), and 2-phenyl-1,3-benzodioxan-4-one (26), m.p. 63.5—64.5° (lit.,²⁸ 60°) (from aqueous ethanol) (160 mg, 24%), ν_{CO} 1745 cm⁻¹, λ_{\max} 238 and 302 nm (log ϵ 3.85 and 3.36), τ (CDCl₃) 1.84—3.10 (9H, m, ArH) and 3.52 (1H, s, O·CHPh·O). The yields of the dioxan and benzaldehyde were not increased by using an excess of persulphate, but salicylic acid (90 mg) was isolated from the acidic material by fractional crystallisation.

²² H. Gilman and J. F. Nobis, *J. Amer. Chem. Soc.*, 1945, **67**, 1479.

²³ J. Borecký, *J. Chromatog.*, 1959, **2**, 612.

²⁴ L. Gringras and G. Sjöstedt, *Acta Chem. Scand.*, 1961, **15**, 435.

²⁵ F. Mayer, *Ber.*, 1909, **42**, 3046.

*Decomposition of Bis-*o*-(phenylsulphonyl)benzoyl Peroxide.*—A solution of the peroxide (1.21 g) in benzene (70 ml) was thoroughly degassed, boiled under reflux for 8 h, and extracted with aqueous potassium hydrogen carbonate to give *o*-(phenylsulphonyl)benzoic acid (32%) on acidification. The neutral material was chromatographed on a column of silica, with petroleum, benzene, and chloroform as successive eluants, and appropriate fractions were further purified by t.l.c. to give (i) *biphenyl-2-yl phenyl sulphone* (14), needles, m.p. 72.5—73.5° (from petroleum) (200 mg, 15%) (Found: C, 73.8; H, 4.7; S, 10.9. C₁₈H₁₄O₂S requires C, 73.5; H, 4.8; S, 10.9%), λ_{\max} (CHCl₃) 250 and 276 nm (log ϵ 4.36 and 3.94), identical with material synthesised as follows. 2-Bromobiphenyl was condensed with copper(i) thiophenoxide²⁹ to give biphenyl-2-yl phenyl sulphide, b.p. 200—210° at 9 mmHg, and this (2 g) was heated in acetic acid (25 ml) with 3% hydrogen peroxide (5 ml) at 80° for 2 h. The solvent was removed *in vacuo* and the residue was chromatographed (p.l.c.) on silica gel in chloroform to give the sulphone as needles, m.p. 72.5—73.5° (from petroleum) (76%).

The second product (ii) of the decomposition was *phenyl o*-phenylsulphonylbenzoate (15), prisms, m.p. 137—137.5° (from chloroform-methanol) (30 mg, 2%) (Found: C, 67.5; H, 4.2; S, 9.5. C₁₉H₁₄O₄S requires C, 67.45; H, 4.2; S, 9.5%), ν_{CO} 1750 cm⁻¹, λ_{\max} 240, 269, and 276 nm (log ϵ 4.10, 3.53, and 3.47), identical with synthesised material. No diphenyl sulphone was detected. The ester was prepared by heating *o*-phenylsulphonylbenzoic acid (1 g) under reflux with thionyl chloride (2 ml) for 1 h; after removal of excess reagent the residue was shaken for 15 min with phenol (360 mg) in 10% sodium hydroxide solution (6 ml). The product was collected and crystallised from chloroform-methanol; m.p. 137—137.5° (65%).

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²⁶ N. M. Cullinane, C. G. Davies, and G. I. Davies, *J. Chem. Soc.*, 1936, 1435.

²⁷ A. Einhorn, L. Rothlauf, and R. Seuffert, *Ber.*, 1911, **44**, 3309.

²⁸ D. T. Mowry, *J. Amer. Chem. Soc.*, 1947, **69**, 2362.

²⁹ R. Adams, W. Reifschneider, and M. D. Nair, *Croat. Chem. Acta*, 1957, **29**, 277.