Persulphate Oxidations. Part IX.[1] Oxidation of Biphenyl-2-sulphonamides and *o*-Phenoxybenzenesulphonamides

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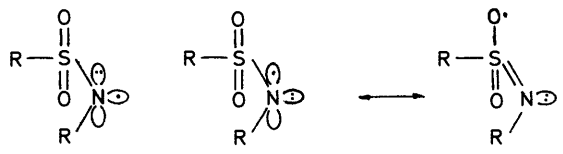
Oxidation of biphenyl-2-sulphonamides with persulphate generated sulphonamidyl radicals which cyclised intramolecularly to sultams. In contrast *N*-methyl-*o*-phenoxybenzenesulphonamidyl, similarly generated, rearranged to *o*-hydroxy-*N*-methyl-*N*-phenylbenzenesulphonamide. Oxidative cyclisation of biphenyl-2-sulphonic acid with persulphate is not practicable and gave only traces of an oxathiin.

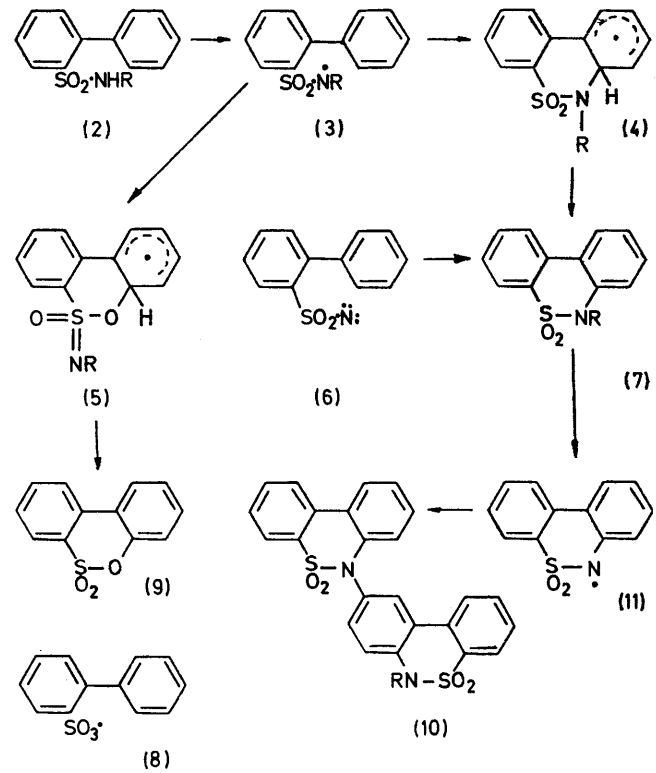
THE chemistry of sulphonamidyls ($RSO_2\dot{N}R$), as far as it is known,[2] resembles that of carboxamidyls ($RC\dot{O}NR$). These radicals have been generated mainly by photolysis or thermolysis of *N*-halogeno-sulphonamides (but not *N*-nitroso-sulphonamides [3]) and shown to add to alkenes and abstract hydrogen both intra- and inter-molecularly.[2,4] In addition, they have been suggested as intermediates in the production of sulphonamides by thermolysis [5] or photolysis [6] of arylsulphonyl azides in good hydrogen-donating solvents. The electronic structure of sulphonamidyls is not well defined; they can be depicted as either σ-radicals (1a) or as mesomeric π-radicals [(1b) ⟷ (1c)] although, unlike carboxamidyls, reactions on oxygen have not yet been observed.



(1a) (1b) (1c)

We have now undertaken an investigation of intramolecular aromatic substitution by sulphonamidyls, a reaction not previously observed for this class of radical. The sulphonamidyls studied initially were analogues of some previously examined carboxamidyls [7] in the expectation that they, like the carboxamidyls, might cyclise on both nitrogen and oxygen and so provide valuable information about their electronic structure. Comparison of these cyclisations with those of some structurally related sulphonylnitrenes has also been made.

Biphenyl-2-sulphonamides.—The sulphonamidyls were generated from the corresponding sulphonamides by oxidation with persulphate in boiling aqueous solution. Results obtained from biphenyl-2-sulphonamide (2; R = H) were similar to those obtained from biphenyl-2-carboxamide.[7] A cyclic amide (7; R = H) was the main product (23%), and was accompanied by smaller quantities of a dimer. The structure of the dimer (10; R = H) followed from its spectra (*M* 450; $\nu_{max.}$ 3200 cm^{-1}), which were generally similar to those of the monomeric product (7; R = H), and from its conversion on treatment with methyl iodide into a monomethyl derivative (10; R = Me), which showed no i.r.



absorption at wavenumbers greater than 3050 cm^{-1}. The *N*-methyl homologue (2; R = Me) gave a higher yield of cyclised product (7; R = Me) (42%), identical with that obtained by methylation of (7; R = H), but the phenyl derivative (2; R = Ph) yielded only a complex mixture from which none of the sultam (7; R = Ph) could be isolated.

Although these oxidations were usually effected in 0·1M-sodium hydroxide solution (1 mol. equiv.) the yield of compound (7; R = H) was similar in the absence of alkali. From this it may be deduced that oxidation to the sulphonamidyl (3) can proceed either

[1] Part VIII, P. S. Dewar, A. R. Forrester, and R. H. Thomson, preceding paper.

[2] R. S. Neale, *Synthesis*, 1970, **1**, 1, and references cited therein.

[3] J. B. F. N. Engberts, L. C. J. Van Der Laan, and Th. J. De Boer, *Rec. Trav. chim.*, 1971, **90**, 901.

[4] T. Ohashi, M. Okahara, and S. Komori, *Bull. Chem. Soc. Japan*, 1971, **44**, 1141.

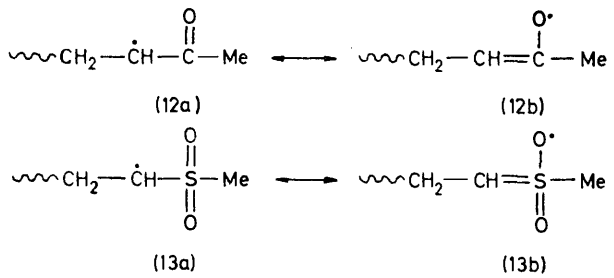
[5] D. S. Breslow in 'Nitrenes,' ed. W. Lwowski, Interscience, New York, 1970, p. 245.

[6] M. Takebayashi, T. Shingaki, and T. Mitsuyama, *Sci. Reports Osaka Univ.*, 1961, **10**, 35 (*Chem. Abs.*, 1963, **59**, 9493).

[7] A. R. Forrester, A. S. Ingram, and R. H. Thomson, *J.C.S. Perkin I*, 1972, 2847.

by hydrogen atom removal from the sulphonamide or electron removal from its anion by the sulphate radical anion. Electron abstraction from the phenyl group is also possible but the resulting radical cations would be subject to solvolysis. Once formed the sulphonamidyl (3) can cyclise to the cyclohexadienyl radical (4), which may then be aromatised by reaction with either the sulphate radical anion or, more probably, persulphate. The origin of the dimer (10; R = H), which arises by further oxidation of the sultam (7; R = H) followed by coupling *N*-to-*C* of the ensuing cyclic sulphonamidyl [presumably as indicated by (10) since coupling *ortho* to the nitrogen would be sterically less favoured], was confirmed by a separate oxidation of the sultam (7; R = H). The increase in the yield of dimer (10; R = H) (11 ⟶ 14%) at the expense of the monomer (7; R = H) (23 ⟶ 7·5%) when the sulphonamide (2; R = H) was oxidised with an excess of persulphate is thus explained.

Failure to detect the sultone (9) in these oxidations, *i.e.* the product corresponding to dibenzo[*b*,*d*]pyran-6-one in the oxidation of biphenyl-2-carboxamide,[7] may be interpreted in more than one way. Although at first sight it would seem to support the notion that sulphonamidyls are σ-radicals with the unpaired electron localised on nitrogen, it is difficult to distinguish between this possibility and a π-radical [(1b) ⟷ (1c)] which, because of the inefficiency of π-type interactions involving 2*p*–3*p* orbitals, has the unpaired electron associated almost exclusively with the nitrogen atom. In this respect it is significant that monomer reactivity [8] factors derived from copolymerisations of styrene with methyl vinyl sulphone and methyl vinyl ketone indicate that mesomeric interaction in (12a) ⟷ (12b) is much greater than in (13a) ⟷ (13b).



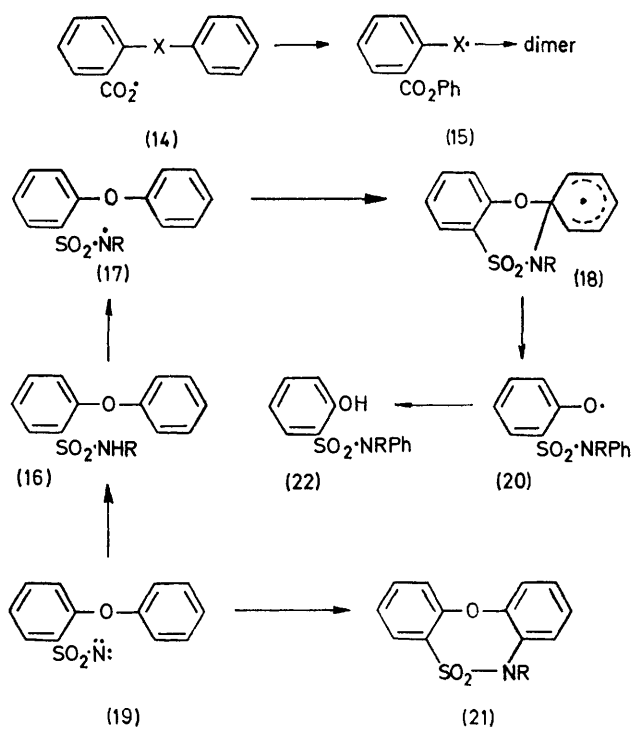
The sultam (7; R = H) was also obtained as the principal product (49%) by thermolysis of biphenyl-2-sulphonyl azide [9] in n-dodecane. However, the absence of the dimer (10; R = H) in the product mixture indicates that this cyclisation does not proceed *via* the sulphonamidyl (3; R = H). Hence we have no evidence of a mechanistic link between cyclisations of the sulphonamidyl (3) and the sulphonylnitrene (6).

Several attempts to cause oxidative cyclisation of the sulphonic acid from which the foregoing amides were derived, both by reaction with persulphate and electrochemically, met with little success. Only small quantities of the sultone (9) were formed and much unchanged acid was recovered. Since the sultone could be obtained in much higher yield [*via* (8)] by decomposition of biphenyl-2-sulphonyl peroxide (which was too unstable to be isolated), and aromatic substitution is a known [10] reaction of sulphonyloxyl radicals, we conclude that electron transfer between the arenesulphonate anion and sulphate radical anion (i) is energetically unfavourable. This observation is consistent with the experience of

$$ArSO_3^- + SO_4^{-\cdot} \rightleftharpoons ArSO_3^{\cdot} + SO_4^{=} \qquad (i)$$

others [11] who found that anodic oxidation of sulphonic acids is more difficult than that of carboxylic acids.

o-*Phenoxybenzenesulphonamides*.—Previous oxidations of *o*-phenoxy- and *o*-thiophenoxy-benzoic acids [12] with persulphate uncovered interesting rearrangements of the initial carboxyl radicals (14; X = O or S) to inherently more stable phenoxyls (15; X = O) and thiophenoxyls



(15; X = S), respectively. Hence we considered it worthwhile to extend our studies to include the oxidation of *o*-phenoxybenzenesulphonamides (16). The parent amide (16; R = H) gave no useful result; the bulk of the amide was recovered and the oxathiazepine (21; R = H) was shown to be absent from the mixture of minor products formed. However, oxidation of the homologue (16; R = Me) gave the rearranged product (22; R = Me) (8%) together with demethylated amide

[8] C. C. Price and J. Zomlefer, *J. Amer. Chem. Soc.*, 1950, **72**, 14; F. M. Lewis, C. Walling, W. Cummings, E. R. Briggs, and F. R. Mayo, *ibid.*, 1948, **70**, 1519.

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[11] A. Swelim, A. I. A. Khodair, and F. El-Sheikh, *Internat. J. Sulphur Chem.*, 1971, **6B**, 195.

(16; R = H). The structure of compound (22; R = Me) was established by synthesis from *N*-methylaniline and *o*-acetoxybenzenesulphonyl chloride. We presume that this phenol (22) arises by a route [(17) ⟶ (18) ⟶ (20) ⟶ (22)] analogous to that already described[12] for the conversions (14) ⟶ (15) but with the significant difference that the intermediate phenoxyl (20; R = Me) abstracts a hydrogen atom from unchanged amide either in preference to, or as well as, dimerising. We cannot be certain that dimers were not formed from compound (20; R = Me), as much intractable material was produced. We also failed to obtain authentic dimers by oxidation of the phenol (22; R = Me) with either persulphate or alkaline ferricyanide. Oxidation of compound (16; R = Et) also gave the parent sulphonamide (16; R = H) and a very small amount of the phenol (22; R = Et).

Repetition of the thermolysis of *o*-phenoxybenzenesulphonyl azide[9] in dodecane gave the oxathiazepine (21; R = Me) (7·5%), the secondary amide (16; R = $C_{12}H_{25}$) (19·4%) and the parent amide (16; R = H) (3%). The absence of the oxathiazepine (21; R = H) from the oxidation products of (16; R = H), and the absence of the phenol (22; R = H) from the thermolysis products of the azide, indicates the absence of a common intermediate in these reactions and hence that the sulphonamide (16; R = H) is not formed from the nitrene (19) in a two-step hydrogen abstraction process (*cf.* ref. 13).

EXPERIMENTAL

For general methods see Part V (p. 2842).

Starting Materials.—(i) *Sulphonamides.* These were prepared by treatment of the sulphonyl chloride[14] in benzene at 0° with either aqueous ammonia (*d* 0·880; 1·1 mol. equiv.) or the amine (1·1 mol. equiv.) (in alcohol or benzene). The mixture was stirred at room temperature for several hours, then extracted with 2M-hydrochloric acid, washed with water, dried ($MgSO_4$), and evaporated. *Biphenyl-2-sulphonamide* formed prisms, m.p. 120—121° (from chloroform–petroleum) (92%) (Found: C, 62·1; H, 4·9; N, 6·2; S, 14·1. $C_{12}H_{11}NO_2S$ requires C, 61·8; H, 4·75; N, 6·0; S, 13·7%), $\nu_{max.}$ 3370 and 3270 cm^{-1}, $\lambda_{max.}$ 234 and 276 nm (log ε 3·80 and 3·26), τ 1·77—2·09 (1H, m, H-3), 2·24—2·87 (8H, m, ArH), and 5·7br (2H, s, NH_2); *N-methylbiphenyl-2-sulphonamide* formed prisms, m.p. 122—123° (from methanol) (96%) (Found: C, 63·4; H, 5·2; N, 5·9; S, 13·1. $C_{13}H_{13}NO_2S$ requires C, 63·15; H, 5·3; N, 5·7; S, 12·9%), $\nu_{max.}$ 3340 cm^{-1}, $\lambda_{max.}$ 237sh and 279 nm (log ε 3·99 and 3·46), τ 1·75—2·0 (1H, m, H-3), 2·28—2·83 (8H, m, ArH), 6·63br (1H, q, *J* 5·5 Hz, NH), and 7·69 (3H, d, *J* 5·5 Hz, Me); *N-phenylbiphenyl-2-sulphonamide* formed prisms, m.p. 137—138° (from chloroform–petroleum) (94%) (Found: C, 70·1; H, 5·1; N, 4·7; S, 10·6. $C_{18}H_{15}NO_2S$ requires C, 69·9; H, 4·9; N, 4·5; S, 10·3%), $\nu_{max.}$ 3380 cm^{-1}, $\lambda_{max.}$ 237 and 276 nm (log ε 4·03 and 3·54), τ 1·75—2·0 (1H, m, H-3) and 2·3—3·34 (14H, m, ArH and NH); *N-methyl-o-phenoxybenzenesulphonamide* formed prisms, m.p. 90·5—91° (from aqueous methanol) (100%) (Found: C, 59·5; H, 5·3; N, 5·2; S, 12·1. $C_{13}H_{13}NO_3S$ requires C, 59·3; H, 5·0; N, 5·3; S, 12·1%), $\nu_{max.}$ 3310 cm^{-1}, $\lambda_{max.}$ 233, 283, and 290sh nm (log ε 3·91, 3·55, and 3·44), τ 2·03 (1H, q, *J* 7·5 and 2·0 Hz, H-3), 2·37—3·33 (8H, m, ArH), 5·15br (1H, q, *J* 5·5 Hz, NH), and 7·35 (3H, d, *J* 5·5 Hz, Me); *N-ethyl-o-phenoxybenzenesulphonamide* formed crystals, m.p. 92—92·5° (from aqueous methanol) (Found: C, 60·2; H, 5·3; N, 4·7; S, 11·8. $C_{14}H_{15}NO_3S$ requires C, 60·6; H, 5·45; N, 5·0; S, 11·6%). *o*-Phenoxybenzenesulphonamide formed prisms, m.p. 114·5—115·5° (from aqueous methanol) (lit.,[9] 113—114°), $\nu_{max.}$ 3260 and 3370 cm^{-1}, τ 2·09 (1H, q, *J* 7·0 and 2·0 Hz, H-3), 2·3—3·3 (8H, m, ArH), and 4·78br (2H, s, NH_2).

(ii) *Sulphonyl azides.* These were prepared by treatment of the sulphonyl chlorides in acetone at 0° with a solution of sodium azide in aqueous acetone. Biphenyl-2-sulphonyl azide formed prisms, m.p. 62—64° (from ether–petroleum) (lit.,[9] 60—61°) and *o*-phenoxybenzenesulphonyl azide formed prisms, m.p. 66—67·5° (from chloroform–petroleum) (lit.,[9] 79—80°) (Found: C, 52·7; H, 3·2; N, 15·6; S, 11·7. Calc. for $C_{12}H_9N_3O_3S$: C, 52·35; H, 3·3; N, 15·3; S, 11·65%).

Biphenyl-2-sulphonyl peroxide. The method of Bolte *et al.*[14] was used. To a solution of hydrogen peroxide (100 vol.; 5 ml) and sodium hydroxide (2 g) in water (10 ml) at −5°, biphenyl-2-sulphonyl chloride (500 mg) in tetrahydrofuran (2 ml) was added. The precipitate was collected, washed thoroughly with cold water, and sucked dry; it was shown to consist of 46% of the peroxide by titration with iodide–thiosulphate. In a second experiment the precipitate (247 mg) was added to benzene (20 ml) containing magnesium sulphate. After 2 h the solution (which gave a negative test for sulphonic acids[15]) was filtered and evaporated. Chromatography (t.l.c.) of the residue gave dibenzo[*c*,*e*][1,2]oxathiin 6,6-dioxide (9), m.p. 109—110° (20 mg, 18%), identical with an authentic specimen.[16]

Oxidations with Persulphate.—A solution of potassium persulphate (1·36 g, 0·005 mol) in water was added dropwise, with stirring, during 15 min to a solution of the substrate (0·005 mol) in 0·1M-sodium hydroxide (50 ml) at 100°. The solution was stirred and heated under reflux for a further 1·5 h, then cooled and extracted with chloroform. The extracts were washed with water, dried ($MgSO_4$), and evaporated. Products were obtained from the residue by t.l.c. or p.l.c. [chloroform or chloroform–petroleum (1 : 1) as eluant].

(i) Biphenyl-2-sulphonamide (1·167 g) gave 6*H*-dibenzo[*c*,*e*][1,2]thiazine 5,5-dioxide, m.p. 200—201° (lit.,[9] 200—202°) (197 mg, 23%); the *dimer* (10), prisms, m.p. 293—295° (from chloroform–petroleum) (96 mg, 11%) (Found: C, 62·4; H, 3·8; N, 5·9; S, 13·8%; *M*, 460·0559. $C_{24}H_{16}N_2O_4S_2$ requires C, 62·6; H, 3·5; N, 6·1; S, 13·9%; *M*, 460·0551), $\nu_{max.}$ 3200 cm^{-1}, $\lambda_{max.}$ 243sh, 260, 273sh, and 323 nm (log ε 4·43, 4·48, 4·43, and 3·92); and unchanged amide (296 mg).

The oxidation was repeated (*a*) with an excess of per-

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[14] J. Bolte, A. Kergomard, and S. Vincent, *Tetrahedron Letters*, 1965, 1529; H. Meerwein, G. Dittmar, R. Gollner, K. Hafner, F. Mensch, and O. Steinfort, *Chem. Ber.*, 1957, **90**, 841.

[15] E. Eegriwe, *Z. analyt. Chem.*, 1937, **110**, 22.

[16] N. M. Cullinane, N. M. E. Morgan, and C. A. J. Plummer, *Rec. Trav. chim.*, 1937, **56**, 627.

sulphate (4·08 g, 0·015 mol); the yields were: thiazine dioxide (84 mg, 7·5%), dimer (157 mg, 14%), unchanged amide (31 mg); (*b*) in the absence of alkali; yields were: thiazine dioxide (211 mg, 22%), dimer (45 mg, 5%), unchanged amide (208 mg).

(ii) *N*-Methylbiphenyl-2-sulphonamide (1·235 g) gave 6-methyldibenzo[*c*,*e*][1,2]thiazine 5,5-dioxide, m.p. 110·5—111·5° (lit.,[17] 112°) (378 mg, 42·5%), identical with a specimen prepared by methylation of 6*H*-dibenzo[*c*,*e*][1,2]-thiazine 5,5-dioxide with methyl iodide in acetone, and unchanged amide (335 mg).

(iii) *N*-Phenylbiphenyl-2-sulphonamide (1·546 g) gave a complex mixture of polar products (880 mg) and unchanged amide (660 mg).

(iv) *o*-Phenoxybenzenesulphonamide (1·245 g) gave a complex mixture of polar products and unchanged amide (840 mg).

(v) *N*-Methyl-*o*-phenoxybenzenesulphonamide (1·315 g) gave o-*hydroxy*-N-*methyl*-N-*phenylbenzenesulphonamide*, needles, m.p. 62—62·5° (from ether–petroleum) (40 mg, 8%) (Found: C, 59·5; H, 5·3; N, 5·2; S, 11·9%; *M*, 263·0613. $C_{13}H_{13}NO_3S$ requires C, 59·3; H, 5·0; N, 5·3; S, 12·2%; *M*, 263·0616), $\nu_{max.}$ 3350 cm^{-1}, $\lambda_{max.}$ 235 and 290 nm (log ε 3·83 and 3·60), $\lambda_{max.}$ (EtOH–HO$^-$) 326 nm (log ε 3·71), τ 1·58 (1H, s, OH), 2·35—3·34 (9H, m, ArH) and 6·78 (3H, s, Me), *m/e* 263 (28%), 199 (17), 182 (4), 107 (100), 106 (45), and 77 (31); *o*-phenoxybenzenesulphonamide (40 mg, 3%); and unchanged amide (817 mg).

(vi) *N*-Ethyl-*o*-phenoxybenzenesulphonamide (1·386 g) gave a mixture containing starting material (889 mg), *o*-phenoxybenzenesulphonamide (71 mg, 16%), and N-*ethyl*-o-*hydroxy*-N-*phenylbenzenesulphonamide* (25 mg, 5%) as a gum (Found: *M*, 277·0767. $C_{14}H_{15}NO_3S$ requires *M*, 277·0773), $\lambda_{max.}$ 236 and 287 nm, $\lambda_{max.}$ (EtOH–HO$^-$) 324 nm.

(vii) 6*H*-Dibenzo[*c*,*e*][1,2]thiazine 5,5-dioxide (7) (231 mg) gave the dimer (10) (21 mg, 9·5%), intractable material (95 mg), and unchanged thiazine dioxide (9 mg).

(viii) Biphenyl-2-sulphonic acid, prepared *in situ* by treatment of biphenyl-2-sulphonyl chloride (1·263 g) with 0·2M-sodium hydroxide (50 ml) under reflux for 1·5 h, after oxidation with potassium persulphate (1·36 g) in water (50 ml) in the usual way, gave dibenzo[*c*,*e*][1,2]oxathiin 6,6-dioxide (trace), m.p. 110·5—111·5°. The yield of this product was not significantly increased when 4·08 g of persulphate was used.

Pyrolysis of Azides.—(i) Biphenyl-2-sulphonyl azide (500 mg) and n-dodecane were heated at *ca.* 160° for 18 h. The dodecane was then distilled off and the residue was chromatographed (p.l.c.) in dichloromethane to give 6*H*-dibenzo[*c*,*e*][1,2]thiazine dioxide (7), m.p. 200—201° (220 mg, 50%).

(ii) *o*-Phenoxybenzenesulphonyl azide (900 mg) and n-dodecane (5 ml) were heated at *ca.* 130° for 30 h. After removal of the dodecane the residue was chromatographed (p.l.c.) in petroleum–ether (9 : 1) to give *N*-n-dodecyl-*o*-phenoxybenzenesulphonamide [9] (158 mg, 19%) as an oil, $\nu_{max.}$ 3300 cm^{-1}, τ 1·9—2·26 (1H, m, ArH), 2·42—3·32 (8H, m, ArH), and 7·8—9·4 (25H, m, CH_2,CH_3); 6*H*-dibenz-[1,4,5]oxathiazepine 5,5-dioxide,[9] m.p. 140—141° (36 mg, 7·5%); *o*-phenoxybenzenesulphonamide, m.p. 120—121° (14 mg, 3%); and unchanged azide (363 mg).

Electrolysis of Biphenyl-2-sulphonic Acid.—A solution of the acid, prepared by treatment of biphenyl-2-sulphonyl chloride (1·008 g) with 0·1M-sodium hydroxide solution (80 ml) under reflux for 1·5 h, was electrolysed for 2 h between platinum electrodes (2 × 1 cm, separated by 4 mm) with a current of 1·5 A. The cell was so designed that the aqueous solution was continuously extracted with benzene during the electrolysis. The aqueous phase was extracted with ether and the ether extracts were combined with the benzene solution and evaporated. Chromatography (t.l.c.) of the residue in dichloromethane–petroleum gave 6*H*-dibenzo[*c*,*e*][1,2]oxathiin 6,6-dioxide (9) (7 mg, 1%).

Methylation of 6H-*Dibenzo*[c,e][1,2]*thiazine Dioxide* (7).—The thiazine dioxide (150 mg), methyl iodide (1 ml), potassium carbonate (1 g), and acetone (10 ml) were stirred and heated under reflux for 2·5 h. Work-up and crystallisation from chloroform–petroleum gave 6-methyldibenzo-[*c*,*e*][1,2]thiazine dioxide, m.p. 110·5—111·5° (110 mg, 69%).

Methylation of the Dimer (10).—The crude product obtained after methylation as in the preceding experiment was chromatographed (t.l.c.) in chloroform to give 9-(*dibenzo*[c,e][1,2]*thiazin*-6-*yl*)-6-*methyldibenzo*[c,e][1,2]*thiazine tetraoxide* as prisms, m.p. 249·5—250° (from chloroform–petroleum) (66%) (Found: C, 63·5; H, 3·8; N, 6·2; S, 13·3%; *M*, 474·0694. $C_{25}H_{18}N_2O_4S_2$ requires C, 63·3; H, 3·8; N, 5·9; S, 13·5%; *M*, 474·0708), $\lambda_{max.}$ 245, 260sh, and 310 nm (log ε 4·64, 4·61, and 4·13), τ 1·7—3·3 (15H, m, ArH) and 6·59 (3H, s, Me), *m/e* 474 (100%), 410 (21), 346 (82), and 331 (50).

o-*Hydroxy*-N-*methyl*-N-*phenylbenzenesulphonamide*. — A solution of *o*-acetoxybenzenesulphonyl chloride [18] (3 g) and *N*-methylaniline (2·8 g) in benzene (10 ml) was heated under reflux for 1·5 h, then diluted with benzene, washed with water, and evaporated to dryness. The residue was treated with a solution of potassium hydroxide (10 g) in water–ethanol (1 : 1; 100 ml) and the mixture was heated under reflux for 30 min. The alcohol was removed *in vacuo*, and the remaining aqueous solution was extracted with ether, then acidified. The oil which separated was extracted into ether, and the extracts were washed with water and dried ($MgSO_4$). Evaporation gave an oil which, after distillation (b.p. *ca.* 170° at 0·65 mmHg), solidified to give the product, m.p. 62—63·5° (from ether–petroleum) (2·13 g, 63%).

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