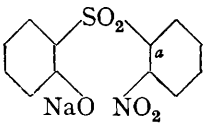
174. *Aromatic Hydroxy-sulphones.*

By Mollie E. Heppenstall and Samuel Smiles.

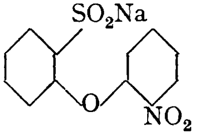
It is shown that the sodium salts of aromatic *o*-hydroxy-sulphones may be obtained in the covalent state. This tendency of sulphonyl to acquire alkali metal is evidently an important factor in promoting the intramolecular displacement of sulphonyl by phenoxyl in the rearrangement of 2-hydroxydiphenylsulphones. Examination of *o*-, *m*-, and *p*-hydroxy-derivatives of diphenyl- and phenylmethyl-sulphones has shown that the *o*- and *p*-series are distinguished by the formation of hydrates of varying stability; the character of these is discussed. 2 : 4-*Bismethylsulphonylphenol* is easily obtained from sodium hydroxide and 1-*chloro*-2 : 4-*bismethylsulphonylbenzene*; quantitative measurements showed that the reactivity of halogen in the latter is of the same order as that in 1-chloro-2 : 4-dinitrobenzene.

It has been shown that 2′-nitro-2-hydroxydiphenylsulphones (*e.g.*, as I) are converted in alkaline media (J., 1934, 422) into the sulphinic acids (*e.g.*, II), sulphonyl being displaced by phenoxyl. With sulphones containing sufficiently active hydroxyl this type of displacement takes place exclusively, but in cases where formation of the sulphinic acid proceeds slowly owing to restricted activity of the phenolic hydroxyl the accompanying formation of small amounts of the thioxin derivative (III) by displacement of the nitro-group may be detected. This preference for displacement of sulphonyl in sulphones of type (I) forms an interesting contrast with the intermolecular attack of alkaline agents on derivatives of *o*-nitro-sulphones such as (IV), which, as Loudon and his colleagues (*e.g.*, Loudon and Robson, J., 1937, 244) have shown, leads in most cases to a preferential displacement of the nitro-group.

In these cases of intramolecular rearrangement (I ⟶ II) it is evident that displacement of sulphonyl may obtain preference from the more favourable situation of the phenolic ion with respect to the carbon atom *a* than to that bearing the nitro-group. There is, however, another factor to be considered. The capture of sodium by oxygen of the displaced group is an important stage in the process and a predisposition of either nitroxyl or sulphonyl to this action would evidently favour the displacement of the group concerned. The question then arises whether nitroxyl or sulphonyl in a sulphone such as (I) is capable of behaving in this manner and, if so, whether there is likely to be sufficient difference in their behaviour to give preference to one or other of the possible types of product (II or III). Some evidence of the tendency of a nitro-group to acquire alkali metal exists in the formation of covalent alkali derivatives of *o*-nitrophenols (Sidgwick and Brewer, J., 1925, **127**, 2385), but, although nothing is yet known of the behaviour of nitrophenols of the type (I) now in question, it may be assumed that the nine-membered ring required for the formation of a covalent derivative would be attained only with difficulty.



(I.)



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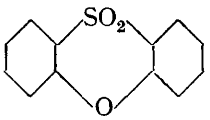
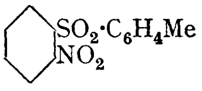


(III.)

There is no previous evidence available to show whether sulphonyl in *o*-hydroxy-sulphones is capable of acquiring alkali metal as shown in (V); experiments now described provide the required information and show that covalent alkali derivatives of this type are readily formed. Accordingly it is suggested that at least a secondary factor in favour of displacement of sulphonyl in (I) ⟶ (II) is to be found in the proximity of this group to the phenoxide, which enables it to acquire the alkali metal of the latter more readily than the less favourably placed nitro-group. The covalent sodium derivatives of *2-hydroxydiphenylsulphone* and related compounds have the usual properties of this class of substance; many of those examined are remarkable for their greater solubility in cold than in hot chloroform; the property has been used for their purification and evidently depends on the instability of hydrates in the boiling solvent. The fact that the anhydrous substances may be obtained indicates the occurrence of the alkali metal in the 2-covalent state, but in presence of moisture there is no doubt that a higher covalency is attained. Some of these sulphones, *e.g.*, (VI), showed a tendency to yield derivatives of bimolecular " acid " type, evidently containing the four-covalent metal; in fact in this case (VI) the normal derivative was not observed. With the di-*o*-hydroxy-sulphone (VII) the existence of a covalent disodium derivative would require the formation of a spirocyclic system, but attempts to obtain this substance were unsuccessful, the monosodium compound being always obtained. Analytical data cannot decide whether this product is derived from the bimolecular acid type containing the disodium derivative, but the fact that the monomethyl ether of (VII) gave a normal sodium derivative possessing properties similar to those of the product in question indicates an analogous structure for the latter. It is worth notice that the covalent state of these derivatives appears to be less stable than that of the sodium derivatives of *o*-hydroxy-ketones or -aldehydes. For example, they are decomposed by salicylaldehyde, are readily methylated in cold aqueous solution (see also Price and Smiles, J., 1928, 3156), and in alcoholic solution react normally with 2 : 4-dinitrochlorobenzene in contrast with the behaviour of sodium salicylaldehyde (Brady, J., 1932, 352).



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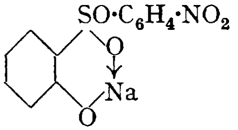

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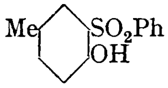
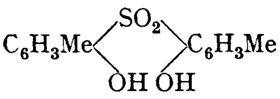
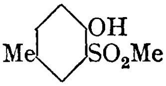


(VI.)

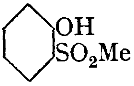


(VII.)

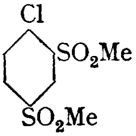
In the course of these experiments the monohydroxy-derivatives of diphenylsulphone and phenylmethylsulphone were examined. The *o*- and *p*-compounds in each series are characterised by the formation of monohydrates and are thus distinguished from the *m*-derivatives, which were obtained only in the anhydrous state. The hydrates in question show varying stability; most of them yield the anhydrous phenol when they are heated and dissolve in hot benzene with separation of water; but (VIII) yields the hydrate when exposed to air, and the hydrate of (IX) is the most stable of the series, attempts to obtain the anhydrous phenol being unsuccessful. From the fact that the hydrate of (IX) dissolves in hot benzene without separation of water it is concluded that the water in these hydrates is covalently bound. It may then be enquired whether the water of hydration is associated with hydroxyl or sulphonyl; all available evidence is contrary to the latter alternative. The tendency of sulphonyl oxygen in sulphones to form co-ordinated adducts is not great and is noticeably less than that of carbonyl oxygen; in fact at present the only undoubted evidence of it is in the sodium derivatives of *o*-hydroxy-sulphones now recorded. The addition of aluminium chloride to aromatic sulphones has been observed (Olivier, *Chem. Weekblad*, 1914, **11**, 372), but it is uncertain whether the benzene nucleus or sulphonyl is concerned in the formation of these products. Moreover, attempts to obtain boroacetates from the *o*-hydroxy-sulphones have been unsuccessful and the formation of hydrochlorides or perchlorates from the *o*- and *p*-derivatives and their methyl ethers could not be detected. In view of these facts and the circumstance that the methyl ethers do not form stable hydrates the hydration water may be regarded as associated with hydroxyl, but at present no adequate explanation can be given of the varying stability of the hydrates or of the exceptional behaviour of the *m*-derivatives.



(VIII.)



(IX.)



(X.)

In other experiments concerning the intramolecular displacement of an aromatic nucleus containing positive substituents it was found that the presence of the nitro-group led to experimental difficulties. Since the use of the methylsulphonyl group for establishing the required positive condition of the nucleus appeared likely to be an advantage owing to its stability in presence of reducing agents, the preparation of 2 : 4-*bismethylsulphonylphenol* has been more fully studied. In this connexion it is worth notice that, whilst Todd and Shriner (*J. Amer. Chem. Soc.*, 1934, **56**, 1382) have shown that the activity of halogen in *o*- or *p*-chlorophenylmethylsulphone is much more feeble than that in *o*- and *p*-chloronitrobenzene, the activity of halogen in 1-*chloro*-2 : 4-*bismethylsulphonylbenzene*, as determined by quantitative measurement, is somewhat less than but of the same order as that in 1-chloro-2 : 4-dinitrobenzene. In fact the phenol may be obtained in high yield from the reaction of alkali hydroxide with (X), and similar reagents such as aniline, piperidine, sodium ethoxide, sodium thiophenoxide, sulphinate, and sodium sulphide yielded corresponding derivatives by displacement of the halogen.

EXPERIMENTAL.

2-Hydroxydiphenylsulphone was prepared by Ullmann's method (*Ber.*, 1901, **34**, 1153) from 2-nitrodiphenylsulphone. Reduction of the latter was best effected by shaking it with acetic acid which had been saturated with hydrogen chloride and contained the theoretical amount of stannous chloride. The sparingly soluble stannichloride of 2-aminodiphenylsulphone was decomposed by water and yielded the base in a sufficiently pure condition for diazotisation (Ullmann, *loc. cit.*). The phenol was purified from dilute acetone; the *monohydrate* thus obtained had m. p. 82° (Found: C, 57·4; H, 4·8. $C_{12}H_{10}O_3S,H_2O$ requires C, 57·1; H, 4·8%). Ullmann (*loc. cit.*) records this m. p. for a material described as the anhydrous phenol. The latter was obtained from the hydrate by drying over phosphoric oxide under diminished pressure at 78°; it had m. p. 97° (Found: C, 61·2; H, 4·5. $C_{12}H_{10}O_3S$ requires C, 61·5; H, 4·3%). The hydrate dissolved in hot benzene with separation of water. The phenol was readily methylated by methyl sulphate in presence of cold dilute sodium hydroxide solution. 2-*Methoxydiphenylsulphone* formed prisms, m. p. 143°, from alcohol (Found: C, 62·8; H, 5·0. $C_{13}H_{12}O_3S$ requires C, 62·9; H, 4·8%). With boroacetic anhydride under usual conditions

2-*acetoxydiphenylsulphone* was obtained; this formed plates, m. p. 84°, from alcohol (Found: C, 61·2; H, 4·5. $C_{14}H_{12}O_4S$ requires C, 60·9; H, 4·3%). The *sodium* derivative was prepared from the phenol and sodium ethoxide in alcohol. The residue obtained after removal of the solvent was extracted with chloroform (Soxhlet), the product being collected from the hot medium. It formed needles, m. p. 290—293° (Found: Na, 8·9. $C_{12}H_9O_3SNa$ requires Na, 9·0%). These dissolved in cold chloroform and separated when the solution was boiled.

3-*Hydroxydiphenylsulphone*.—3-Nitrodiphenylsulphone (Olivier, *Rec. Trav. chim.*, **1916**, **35**, 110) was reduced in alcohol with stannous chloride and hydrochloric acid. The alcohol was removed and the base, liberated from the residual aqueous solution, was purified from benzene. 3-*Aminodiphenylsulphone* formed plates, m. p. 117° (Found: N, 6·0. $C_{12}H_{11}O_2NS$ requires N, 6·0%). The base, after diazotisation in 60% sulphuric acid, yielded the required phenol, which separated from water or aqueous alcohol in needles, m. p. 163° (Found: C, 61·2; H, 4·1. $C_{12}H_{10}O_3S$ requires C, 61·5; H, 4·3%). The formation of a stable hydrate was not detected. 3-*Methoxydiphenylsulphone* formed needles, m. p. 90·5°, from alcohol (Found: C, 62·4; H, 4·4. $C_{13}H_{12}O_3S$ requires C, 62·9; H, 4·8%).

4-*Hydroxydiphenylsulphone*.—4-Nitrodiphenylsulphone (Ullmann, *loc. cit.*) was conveniently obtained by heating (180°) 4-chloronitrobenzene and potassium benzenesulphinate in ethylene glycol. Reduction of the nitro-derivative and conversion of the amine into the phenol were effected as in the case of the *o*-derivative. The phenol separated from dilute alcohol as the *monohydrate* (Found: C, 57·0; H, 4·9. $C_{12}H_{10}O_3S,H_2O$ requires C, 57·1; H, 4·8%), which dissolved in hot benzene with separation of water. Dehydration in a vacuum (118°, phosphoric oxide) yielded the anhydrous phenol, m. p. 137°. This substance has been obtained by Steinkopf (*J. pr. Chem.*, **1927**, **117**, 60) and by Hilbert and Johnson (*J. Amer. Chem. Soc.*, **1929**, **51**, 1526), using other methods, but these authors did not observe the formation of a hydrate. The methyl ether had m. p. 90° (also Hilbert and Johnson, *loc. cit.*).

2-*Methoxy*-5-*methyldiphenylsulphone* (as VI).—Aluminium chloride (18 g.) was added to a solution of 2-methoxy-5-methylbenzenesulphonyl chloride (20 g.) in benzene (100 c.c.). Subsequently (3 hrs., 15°) water was added, the excess of benzene removed by steam, and the non-volatile *sulphone* purified from alcohol; it formed plates, m. p. 140° (Found: C, 64·6; H, 5·2. $C_{14}H_{14}O_3S$ requires C, 64·1; H, 5·3%).

2-*Hydroxy*-5-*methyldiphenylsulphone* (VI).—The methyl ether (5 g.) was heated (4 hrs., 180°) with hydrobromic acid (10 c.c., *d* 1·7); the product was purified from dilute acetone. The *monohydrate* thus obtained formed needles, which were stable in moist air (Found: C, 58·5; H, 5·3. $C_{13}H_{12}O_3S,H_2O$ requires C, 58·6; H, 5·3%), but lost water at temperatures below its m. p. The anhydrous *phenol* had m. p. 139° (Found: C, 62·7; H, 4·8. $C_{13}H_{12}O_3S$ requires C, 62·9; H, 4·7%). The substance was readily methylated in dilute aqueous alkaline solution. The *sodium* derivative was obtained by evaporating an alcoholic solution of the sulphone (1 mol.) and sodium hydroxide (1 mol.) and crystallising the residue from moist chloroform; it formed needles, m. p. 260° (Found: Na, 4·3. $C_{13}H_{12}O_3S,C_{13}H_{11}O_3SNa$ requires Na, 4·4%). The same substance separated when alcoholic sodium ethoxide (0·5 mol.) was added to an alcoholic solution of the phenol (1 mol.) (Found: Na, 4·5%). The substance was soluble in warm chloroform and separated therefrom either in needles or in the colloidal state, the whole then forming a transparent jelly.

5-*Chloro*-2-*methoxydiphenylsulphone* was obtained by the interaction of 5-chloro-2-methoxybenzenesulphonyl chloride and benzene in presence of aluminium chloride (4 hrs., 40°); isolated in the usual way and purified from alcohol, it had m. p. 144° (Found: C, 55·1; H, 3·9. $C_{13}H_{11}O_3ClS$ requires C, 55·2; H, 3·9%). When heated with hydrobromic acid, it yielded 5-*chloro*-2-*hydroxydiphenylsulphone*, which crystallised from chloroform–light petroleum in needles, m. p. 139° (Found: C, 53·1; H, 3·1. $C_{12}H_9O_3ClS$ requires C, 53·6; H, 3·3%). The existence of a hydrate was not observed. Aqueous alkaline methylation readily gave the methyl ether, and the *acetyl* derivative, m. p. 134° (Found: C, 53·9; H, 3·8. $C_{14}H_{11}O_4ClS$ requires C, 54·1; H, 3·5%), was formed by treatment with boroacetic anhydride under the usual conditions. The 2 : 4-*dinitrophenyl* ether was formed in good yield during the reaction of the sodium salt with 2 : 4-dinitrochlorobenzene in hot alcohol; purified from acetic acid, it formed needles, m. p. 187° (Found: N, 6·7. $C_{18}H_{11}O_7N_2ClS$ requires N, 6·4%). The *sodium* derivative was obtained by evaporating an alcoholic solution of the sulphone (1 mol.) and sodium ethoxide (1 mol.). The residue was insoluble in water and contained the "acid" salt and the normal sodium derivative. The latter was readily removed by warm chloroform, from which it separated in needles, m. p. 247° (Found: Na, 8·0. $C_{12}H_8O_3ClSNa$ requires Na, 7·9%), sparingly soluble in hot toluene. The *lithium* derivative was obtained by evaporating an alcoholic solution of the phenol (1 mol.) and lithium hydroxide (1 mol.); it was extracted from the mass by hot chloroform and separated from the cold medium in needles, m. p. 198°. These evidently consisted of the *dihydrate* (Found: H, 3·5. $C_{12}H_8O_3ClSLi,2H_2O$ requires H, 3·8%), but they lost water in a vacuum at 118° (phosphoric oxide) (Found: Li, 2·5; H, 2·9. $C_{12}H_8O_3ClSLi$ requires Li, 2·5; H, 2·9%).

2 : 2′-Dihydroxy-5 : 5′-dimethyldiphenylsulphone (Tassinari, *Gazzetta*, 1889, **19**, 346) was best prepared by oxidising the sulphoxide (J., 1910, **97**, 2248) with hydrogen peroxide (3 mols.) in hot acetic acid (100°, 3 hrs.). Reaction with boroacetic anhydride yielded the *diacetyl* derivative, m. p. 211° (Found: C, 59·6; H, 5·1. $C_{18}H_{18}O_6S$ requires C, 59·7; H, 5·0%). The *sodium* derivative was prepared from an alcoholic solution of the sulphone (1 mol.) and sodium ethoxide (1 mol.). The residue obtained after removal of the solvent was extracted with chloroform (Soxhlet), the crystalline product being collected from the hot liquid. It formed needles, m. p. 190° after being dried (118°, phosphoric oxide) in a vacuum (Found: Na, 7·7. $C_{14}H_{13}O_4SNa$ requires Na, 7·7%). The substance was decomposed by salicylaldehyde, yielding the sodium derivative of the latter.

2-*Hydroxy*-2′-*methoxy*-5 : 5′-*dimethyldiphenylsulphone*.—*O*-Carbethoxy-*p*-cresol-3-sulphonyl chloride (Bennett, Lesslie, and Turner, J., 1937, 445) was added (21 g.) to *p*-tolyl methyl ether (36 g.) containing aluminium chloride (21 g.), and the mixture warmed (40—50°) until liberation of hydrogen chloride had ceased (18 hrs.). After the excess of the ether had been removed in steam the residue was hydrolysed by hot alcoholic sodium hydroxide. The product, isolated in the usual way, formed prisms, m. p. 153°, from alcohol (Found: C, 62·0; H, 5·8. $C_{15}H_{16}O_4S$ requires C, 61·6; H, 5·5%). The *sodium* derivative formed needles from alcohol; these were soluble in chloroform and sparingly so in warm benzene or toluene and had m. p. 219° (Found: Na, 7·5. $C_{15}H_{15}O_4SNa$ requires Na, 7·5%). The *lithium* derivative was prepared from the sulphone and lithium hydroxide in alcohol; it was purified by addition of light petroleum to a chloroform solution (Found: Li, 2·4; H, 5·3. $C_{15}H_{15}O_4SLi$ requires Li, 2·3; H, 5·0%).

2-*Methoxyphenylmethylsulphone* (compare IX), obtained by methylating anisole-2-sulphinic acid, formed plates, m. p. 95°, from water (Found: C, 51·3; H, 5·5. $C_8H_{10}O_3S$ requires C, 51·6; H, 5·4%). When it was heated (4 hrs., 150°) with hydrobromic acid (*d*, 1·7), it was demethylated; addition of water to the solution yielded the *hydrate* of 2-*hydroxyphenylmethylsulphone*. This was purified from hot water and formed prisms, m. p. 87·5°, which were soluble in benzene (Found: C, 44·6; H, 5·6. $C_7H_8O_3S,H_2O$ requires C, 44·2; H, 5·3%). An alcoholic solution gave a deep red colour with ferric chloride. Complete dehydration of the phenol was not effected after 8 weeks in a vacuum (15°, phosphoric oxide); a sample containing about 5% of the hydrate had m. p. 67° (appxt.).

3-Aminophenylmethylsulphone was obtained by reducing 3-nitrophenylmethylsulphone (J., 1925, **127**, 1249) with tin and hydrochloric acid. The base, isolated in the usual manner, separated from hot water in plates, m. p. 58°. Zincke (*Ber.*, 1913, **46**, 782) obtained this substance by oxidising 3-acetamidophenyl methyl sulphide and deacetylating the product and gave the m. p. 72° and that of the acetyl derivative as 137°. The acetyl derivative of the base, m. p. 58°, had m. p. 137° (Found: N, 6·7. Calc.: N, 6·6%) and yielded the original base (m. p. 58°) on deacetylation.

3-*Hydroxyphenylmethylsulphone* was obtained from the amino-derivative by diazotisation and was isolated from the solution obtained by extraction with chloroform. After purification (charcoal) it separated from benzene in needles, m. p. 82° (Found: C, 48·8; H, 5·0. $C_7H_8O_3S$ requires C, 48·8; H, 4·6%). The formation of a hydrate was not observed. Methylation in aqueous alkaline media yielded 3-*methoxyphenylmethylsulphone*, which formed plates, m. p. 47°, from water (Found: C, 51·4; H, 5·6. $C_8H_{10}O_3S$ requires C, 51·6; H, 5·4%). This substance was also obtained from 3-methoxybenzenesulphinic acid, but the preparation of the phenol from it gave unsatisfactory results.

4-*Methoxyphenylmethylsulphone*, obtained from anisole-*p*-sulphinic acid, formed plates, m. p. 121°, from water (Found: C, 51·5; H, 5·7. $C_8H_{10}O_3S$ requires C, 51·6; H, 5·4%). Demethylation with hydrobromic acid yielded 4-*hydroxyphenylmethylsulphone*, m. p. 94°, after being dried and purified from benzene (Found: C, 49·0; H, 4·8. $C_7H_8O_3S$ requires C, 48·8; H, 4·6%). It separated from water as the *hydrate*, m. p. 49° (Found: C, 44·5; H, 5·5. $C_7H_8O_3S,H_2O$ requires C, 44·2; H, 5·3%).

2-*Hydroxy*-5-*methylphenylmethylsulphone* (VIII) was obtained by demethylating 2-methoxy-5-methylphenylmethylsulphone (J., 1923, **123**, 2391) with hydrobromic acid; it separated from water as the *hydrate*, which formed thick needles, m. p. 78° (Found: C, 47·2; H, 6·1.

$C_8H_{10}O_3S,H_2O$ requires C, 47·1; H, 5·9%) and lost water in a vacuum at 50° (phosphoric oxide) (Found: H_2O, 8·7. Calc.: H_2O, 8·8%), yielding the anhydrous phenol, m. p. 89° (Found: C, 51·3; H, 5·2. $C_8H_{10}O_3S$ requires C, 51·6; H, 5·4%). The latter absorbed moisture from the atmosphere, yielding the hydrate.

5-*Chloro-2-hydroxyphenylmethylsulphone*, obtained from the methyl ether (J., 1925, **127**, 2746) by demethylation, separated from water in plates, m. p. 140° (Found: C, 40·4; H, 3·2. $C_7H_7O_3ClS$ requires C, 40·7; H, 3·4%). No hydrate was obtained.

2 : 4-*Bismethylsulphonylanisole*.—2 : 4-Bischlorosulphonylanisole (Pollak, *Monatsh.*, 1928, **50**, 55) was converted into the disulphinic acid by reaction with sodium sulphite in concentrated neutral solution. The product was removed by ether from the acidified mixture and methylated as the potassium salt in boiling alcohol with methyl iodide; the required *disulphone*, isolated in the usual manner, formed stout needles, m. p. 197°, from acetic acid (Found: C, 40·9; H, 4·5. $C_9H_{12}O_5S_2$ requires C, 40·9; H, 4·5%), which were converted into the phenol by demethylation with hydrobromic acid. Since the yields of the hydroxysulphone by this method were very poor, an alternative route to the desired phenol was taken *via* the chloro-derivative (X).

1-Chloro-2-chlorosulphonyl-4-methylsulphonylbenzene was obtained by heating (7 hrs., 150—180°) a solution of 1-chloro-4-methylsulphonylbenzene (1 mol.) in chlorosulphonic acid (5 mols.); isolated in the usual manner and purified from benzene, it formed needles, m. p. 144°. These were converted into the *anilide*, m. p. 161° (from alcohol), for analysis (Found: C, 45·2; H, 3·6; N, 4·0. $C_{13}H_{12}O_4NClS_2$ requires C, 45·1; H, 3·4; N, 4·0%).

1-*Chloro*-2 : 4-*bismethylsulphonylbenzene* (X) was prepared from the foregoing sulphonyl chloride by two methods. (a) Reduction of the sulphonyl chloride with hydrogen iodide (5 mols., *d* 1·7) in acetic acid (100°, 30 mins.) gave a high yield of *di*-2-*chloro*-5-*methylsulphonylphenyl disulphide*, which formed needles, m. p. 253°, from acetic acid (Found: C, 37·5; H, 2·7. $C_{14}H_{12}O_4Cl_2S_4$ requires C, 37·9; H, 2·7%). This was further reduced by glucose (1 mol.) in warm aqueous alcohol containing sodium hydroxide (4 mols.) under usual conditions. After the alkaline solution of the thiol had been diluted with an equal volume of water and filtered, it was shaken with methyl sulphate. 1-*Chloro*-4-*methylsulphonyl*-2-*methylthiolbenzene* then separated; it formed needles, m. p. 107°, from alcohol (Found: S, 26·7. $C_8H_9O_2ClS_2$ requires S, 27·0%). When it was oxidised (100°, 1 hr.) in acetic acid (1 g. in 10 c.c.) with hydrogen peroxide (4 mols., 30%), the required disulphone (X) was obtained; the yield in this operation was poor (18%), the overall yield being correspondingly reduced. (b) Conversion of the sulphonyl chloride into the sulphinic acid by reduction with aqueous sodium sulphite was unsatisfactory and tedious, mainly owing to the high solubility of the acid in water, which rendered its isolation difficult. A more successful method of reduction and one which may be usefully applied to the preparation of other sulphinic acids was afforded by the reaction of the sulphonyl chloride with sodiomalonic ester. The finely powdered 1-chloro-2-chlorosulphonyl-4-methylsulphonylbenzene (1 mol.) was slowly added to a cold and stirred solution of ethyl sodiomalonate (2 mols.) in alcohol. After the mixture had been kept for 1 hour, the solvent was evaporated, water being added to the neutralised residue before extraction with ether. Evaporation of the aqueous solution gave a residue of the sodium sulphinate, which was methylated in boiling alcohol with methyl iodide, the *product* (X) being isolated in the usual manner; it had m. p. 187° after purification from acetic acid (Found: C, 35·8; H, 3·5. $C_8H_9O_4ClS_2$ requires C, 35·8; H, 3·3%).

2 : 4-*Bismethylsulphonylphenol*.—The chloro-derivative (X) was rapidly attacked by boiling aqueous or alcoholic sodium hydroxide; the *phenol* after being purified from hot water, formed clusters of needles, m. p. 220° (Found: C, 38·4; H, 3·9. $C_8H_{10}O_5S_2$ requires C, 38·4; H, 4·0%), which were soluble in aqueous sodium carbonate. When method (b) was used for the reduction of the sulphonyl chloride, 115 g. of chlorobenzene yielded 60 g. of the phenol. The activity of the halogen in 1-chloro-2 : 4-bismethylsulphonylbenzene (1) in boiling alcoholic sodium ethoxide is shown by the following data in comparison with that of the halogen in 1-chloro-2 : 4-dinitrobenzene (2) and 1-chloro-2-nitrobenzene (3); the method used was analogous to that of Todd and Shriner (*loc. cit.*). In 30 c.c. of boiling alcohol containing sodium ethoxide (0·286N) and the substance (0·005 mol.), after 15 minutes the % halogen removed was, with (1), 90·1 and, with (2), 97·6; with 0·125N-sodium ethoxide under the same conditions the % halogen removed was, with (1), 83·1, with (2), 95·5, and with (3), 16·3. Under these conditions 2 : 4-*bismethylsulphonylphenetole* was formed; it separated from alcohol in needles, m. p. 201° (Found: C, 42·8; H, 4·9. $C_{10}H_{14}O_5S_2$ requires C, 43·1; H, 5·0%). The chloro-disulphone (X) behaved similarly with other anionoid reagents. Boiling

aniline yielded 2 : 4-*bismethylsulphonyldiphenylamine*, which formed needles, m. p. 218°, from alcohol (Found : N, 4·3. $C_{14}H_{15}O_4NS_2$ requires N, 4·3%); piperidine (100°) gave (94%) N-2′ : 4′-*bismethylsulphonylphenylpiperidine*, m. p. 156° (Found : N, 4·4. $C_{13}H_{19}O_4NS_2$ requires N, 4·4%); sodium thiophenoxide in boiling alcohol gave (74%) 2 : 4-*bismethylsulphonyldiphenyl sulphide*, m. p. 232° (Found : C, 48·7; H, 4·0; S, 27·6. $C_{14}H_{14}O_4S_3$ requires C, 49·1; H, 4·1; S, 28·1%); and sodium benzenesulphinate in boiling ethylene glycol gave 2 : 4-*bismethylsulphonyldiphenylsulphone*, m. p. 270—271° (Found : C, 45·0; H, 3·7; S, 25·5. $C_{14}H_{14}O_6S_3$ requires C, 44·9; H, 3·7; S, 25·7%), which was also obtained by oxidising the sulphide with hydrogen peroxide in acetic acid.

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