CCCCXXII.—*Stereoisomerism of Disulphoxides and Related Substances. Part III. Some Pairs of Aromatic Disulphoxides.*

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AN examination of the products of oxidation of several aromatic disulphides of the general formulæ $Ar{\cdot}S{\cdot}C_2H_4{\cdot}SAr$ and $C_6H_4(SR)_2$ shows that in each case a pair of diastereoisomeric disulphoxides is produced.

s-Dibenzylthiolethane was oxidised by Fromm, Benzinger, and Schäfer (*Annalen*, 1912, **394**, 325) to a disulphoxide of m. p. 198°. A re-investigation of this substance shows it to be a mixture of two *isomerides* melting at 209° and 191° respectively. We have also prepared two new disulphides of the same type, namely, s-*diphenylthiolethane*, m. p. 69°, and s-*di*-p-*tolylthiolethane*, m. p. 81°, and each was oxidised by hydrogen peroxide to a mixture in about equal proportion of two isomerides : the *ethylene diphenyl disulphoxides*, α- of m. p. 166° and β- m. p. 123°; the *ethylene di*-p-*tolyl disulphoxides*, α- m. p. 174° and β- m. p. 127°.

The oxidation of *m*-dimethylthiolbenzene yields an α-*disulphoxide*, m. p. 147°, and a β-*disulphoxide*, m. p. 102°, each distinct in properties from the substance described by Zincke and Krüger (*Ber.*, 1912, **45**, 3468), which was doubtless a mixture of the two. The α-disulphoxide, m. p. 133°, of *m*-dibenzylthiolbenzene is, however, evidently identical with the disulphoxide obtained by the same authors, but we have isolated in addition a β-*disulphoxide*, m. p. 123°, from the mother-liquors of crystallisation of the former substance.

In the same way, the disulphoxide, m. p. 188°, (now α-) of *p*-dimethylthiolbenzene (Zincke and Frohneberg, *Ber.*, 1909, **42**, 2721) was found to be accompanied by a more soluble β-*disulphoxide*,

m. p. 136°, which, like its isomeride, yields a crystalline *mercurichloride.*

The members of each of these pairs of isomerides are sharply differentiated by their melting points, crystal forms and solubilities. In each case they were shown to be readily reduced to the parent disulphide, the alternative structure of a monosulphone being thereby excluded. Mixtures of the two related substances do not show a sharply depressed melting point, but in all cases melt over a range of temperature.

Negative results were obtained when attempts were made to isolate a crystalline bromide or hydrochloride of any of these disulphoxides (compare Part II, this vol., p. 86).

EXPERIMENTAL.

Condensation of Thiophenol and p-*Thiocresol with Ethylene Dibromide.*—Thiophenol (13·5 g.) in ethyl alcohol (100 c.c.) was heated on the steam-bath for 1 hour with potassium hydroxide (6·9 g. in a little water) and ethylene dibromide (11·3 g.). When the solvent had been removed in a current of steam, the residual oil solidified on cooling (yield, 14·6 g.). s-*Diphenylthiolethane,* thus obtained, crystallised from ethyl alcohol in colourless, monoclinic plates, m. p. 69° (Found: C, 68·0; H, 5·8. $C_{14}H_{14}S_2$ requires C, 68·3; H, 5·7%).

A similar operation using *p*-thiocresol (31·0 g.) gave s-*di*-p-*tolylthiolethane* (30 g.), which crystallised from ethyl alcohol in colourless, monoclinic plates, m. p. 81° (Found: S, 23·4. $C_{16}H_{18}S_2$ requires S, 23·35%).

Oxidation of the Disulphides with Hydrogen Peroxide.—In all cases to be described in this paper, the disulphide was oxidised by adding to its solution in glacial acetic acid the calculated amount of 25% hydrogen peroxide. After 24 hours the acetic acid was removed from the mixture in a current of steam, followed by evaporation to dryness on a steam-bath, the crude oxidation product being thus obtained in quantitative yield.

Isomeric Dioxides from Diphenylthiolethane.—The crude oxidation product, insoluble in water, but soluble in most organic solvents, was separated, by fractional crystallisation from toluene, into two isomerides which appear to be formed in approximately equal proportion.

The *α-disulphoxide* (yield of pure substance from 5 g. of the disulphoxide, 1·2 g.) formed colourless, monoclinic plates or tables, m. p. 166° (decomp.), from ethyl alcohol (Found: C, 60·3; H, 5·0; S, 23·3. $C_{14}H_{14}O_2S_2$ requires C, 60·4; H, 5·0; S, 23·0%). The *β-disulphoxide* (yield, 0·8 g.) separated from alcohol in colourless needles with straight extinction, m. p. 123° (decomp.), and was much more soluble in organic solvents than the preceding substance (Found : S, 22·8%).

Reduction of the Disulphoxides.—In this and each other instance the isomerides were reduced in alcoholic solution by means of zinc dust and hydrochloric acid and the product was found by its melting point and by that of a mixture with the parent disulphide to be identical with the latter.

Isomeric Dioxides of Di-p-*tolylthiolethane.*—The oxidation product was a mixture of two substances, present in equal proportion and separated by fractional crystallisation from toluene. The *α-disulphoxide* (yield of pure substance, 1·1 g. from 9·1 g. of disulphide) may be crystallised from benzene, toluene, xylene, ethyl, butyl or amyl alcohol, or ethyl acetate, but it is insoluble in water. It separates from ethyl alcohol in small rhomb-shaped plates with diagonal extinction and a high double refraction; m. p. 173—174° (decomp.) (Found : S, 20·8. $C_{16}H_{18}O_2S_2$ requires S, 20·9%). The *β-disulphoxide* (yield, 0·9 g.) is more soluble in all solvents than its isomeride, but is insoluble in water. It separates from its highly concentrated solution in ethyl alcohol in needles with straight extinction, m. p. 126—127° (decomp.) (Found : S, 20·7%).

Isomeric Dioxides of Dibenzylthiolethane.—The crude dioxides (10·7 g. from 10·0 g. of the disulphide) were separated by crystallisation from amyl alcohol. The *α-disulphoxide* separated in small monoclinic plates from ethyl or amyl alcohol or 50% acetic acid, and in flat prisms from xylene, m. p. 209° (Found : S, 21·0. $C_{16}H_{18}O_2S_2$ requires S, 20·9%). The *β-disulphoxide* was freed from the last traces of the α-isomeride by crystallisation from xylene. It separated from xylene or amyl alcohol in feathery needles having a straight extinction, m. p. 192° (Found : S, 21·0%). The disulphoxide described by Fromm, Benzinger, and Schäfer (*loc. cit.*) had m. p. 198°.

Isomeric Dioxides of 1 : 3-*Dimethylthiolbenzene.*—The crude product of oxidation was separated by crystallisation from benzene into two substances present in approximately equal quantities : the *α-disulphoxide*, crystallising from benzene in plates with a high double refraction and a straight extinction, m. p. 147° (Found : S, 32·0. $C_8H_{10}O_2S_2$ requires S, 31·7%), and the more soluble *β-disulphoxide*, which separated from benzene in rhomb-shaped crystals with an oblique extinction, m. p. 102° (Found : S, 31·8%). The substance described by Zincke and Krüger (*loc. cit.*) had m. p. 131°.

The reduction of these two disulphoxides yielded the parent disulphide, which is a liquid. Its identity was confirmed in both cases by the preparation of the crystalline *mercurichloride* of 1 : 3-

dimethylthiolbenzene, m. p. 108° (Found : Hg, 45·5. $C_8H_{10}S_2Cl_2Hg$ requires Hg, 45·3%).

Isomeric Dioxides of 1 : 3-*Dibenzylthiolbenzene.*—Two substances, present in about equal proportion, were separated from the oxidation product by fractional crystallisation from toluene and mixtures of this solvent with petroleum of b. p. 100—120°.

The *α-disulphoxide* crystallised from toluene or ethyl alcohol in almost square plates with diagonal extinction, m. p. 133° (Found : S, 18·0. $C_{20}H_{18}O_2S_2$ requires S, 18·1%). The more soluble *β-disulphoxide* separated in minute, rhomb- or hexagonal-shaped crystals from toluene and in characteristic spherical aggregates from carbon tetrachloride; m. p. 123° (Found : S, 18·3%). The substance described by Zincke and Krüger had m. p. 131°.

Isomeric Dioxides from 1 : 4-*Dimethylthiolbenzene.*—The crude mixture was readily soluble in water and moderately easily soluble in other solvents. Crystallisation from toluene, ethyl alcohol, benzene, and ethyl acetate separated two isomeric dioxides. The α-disulphoxide (yield, 2·3 g. of pure substance from 10 g. of the disulphide) crystallised from water in rhomb-shaped plates with an oblique extinction, m. p. 183° (Found : S, 31·7. Calc. for $C_8H_{10}O_2S_2$: S, 31·7%). Zincke and Frohneberg (*loc. cit.*) gave the m. p. as 188°. The mercurichloride was obtained in silvery plates, m. p. 216° (decomp.), sparingly soluble in water (Found : Hg, 42·25. Calc. for $C_8H_{10}O_2Cl_2S_2Hg$: Hg, 42·3%). Zincke and Frohneberg give the m. p. as 220°. The *β-disulphoxide* (yield, 2·2 g.) is more soluble than its isomeride in all solvents. It crystallises in branching needles with an oblique extinction, m. p. 136° (Found : S, 31·7%), and forms a mercurichloride similar to that of the α-isomeride, but much more readily soluble in water and having m. p. 188° (decomp.).

Note on the Determination of Sulphur.—The method of Pregl ("Quantitative Organic Microanalysis," English ed., 1924, p. 102) has proved very useful on the macro-scale. Ordinary combustion tube is constricted at a point which divides it into a length of 50 cm. (for the boat and platinum catalysts) and 35 cm. (for glass beads). The acid produced is titrated with *N*/10-alkali and phenolphthalein. The time required for an analysis is less than for an ordinary combustion.

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