12. *Isomeric* 6 : 6'-*Di*-(2 : 4-*bistrichloromethyl*-1 : 3-*benzdioxinyl*)*sulphones.*

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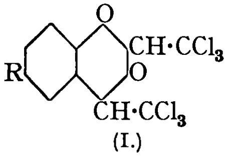
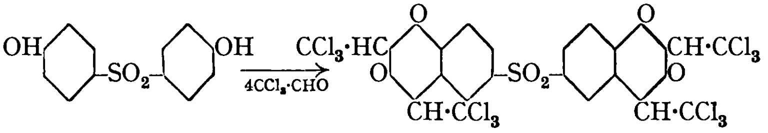
THE 2 : 4-bistrichloromethyl-1 : 3-benzdioxins (I) formed by the condensation of chloral with phenols substituted in the para-position should exist in *cis*- and *trans*-isomeric forms, but, of the compounds so far closely studied, where R = NO_2, SO_3H, or CO_2H (J., 1926, 2720; 1927, 685, 2013), only one form has been obtained. This may be due to one form only being produced in any recognisable amount under the conditions employed or to the difference in the properties of the two forms being too slight to admit of their separation.

In the case of 6 : 6'-*di*-(2 : 4-*bistrichloromethyl*-1 : 3-*benzdioxinyl*)*sulphone* (III), which is produced when chloral is allowed to condense with 4 : 4'-dihydroxydiphenylsulphone (II) under the influence of concentrated sulphuric acid, three out of the six possible *cis*- and *trans*-isomerides have been isolated by fractional crystallisation of the crude product. They are colourless well-crystallised compounds closely resembling each other in properties but melting at 215°, 240°, and 248° respectively, each lowering the melting point of the other two. They may be designated the α-, the β-, and the γ-6 : 6'-di-(2 : 4-bistrichloromethyl-1 : 3-benzdioxinyl)sulphone in order of increasing melting point. They have identical compositions and molecular weights in camphor.



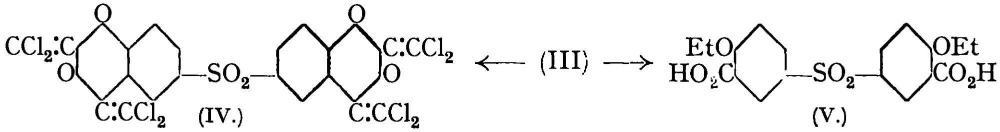
(I.)



(II.) (III.)

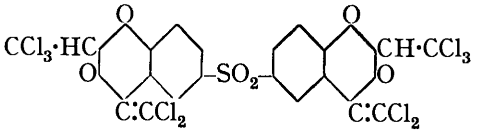
The *cis*- and *trans*-character of the isomerism is shown by the conversion of each isomeride, when warmed with the theoretical amount of alcoholic potash, into one and the same 6 : 6'-*di*-(2 : 4-*bisdichloromethylene*-1 : 3-*benzdioxinyl*)*sulphone* (IV), m. p. 215°.

When completely hydrolysed by excess of boiling alcoholic potash, and the product oxidised by alkaline permanganate, each of the three isomerides yields 4 : 4'-*diethoxy*-3 : 3'-*dicarboxydiphenylsulphone* (V), m. p. 247°, identical with the compound synthesised by converting *o*-cresol into 4 : 4′-*dihydroxy*-3 : 3′-*dimethyldiphenylsulphone* and oxidising its *diethyl* ether by permanganate.



(IV.) ⟵ (III) ⟶ (V.)

When either the α- or the γ-isomeride * is acted upon at the ordinary temperature with the theoretical amount of dilute alcoholic potash, two only of the four trichloromethyl groups are attacked and, by loss of two molecules of hydrogen chloride, corresponding isomeric α- and γ-6 : 6′-*di*(*trichloromethyldichloromethylene*-1 : 3-*benzdioxinyl*)*sulphones* are formed, melting at 241° and 250° respectively. These probably have the annexed constitution, since the behaviour of other 2 : 4-bistrichloromethyl-1 : 3-benzdioxins towards alcoholic potash sugests that in each case the trichloromethyl groups attacked are those in the 4- and 4′-positions.



EXPERIMENTAL.

6 : 6′-*Di*-(2 : 4-*bistrichloromethyl*-1 : 3-*benzdioxinyl*)*sulphone* (III).—50 G. of 4 : 4′-dihydroxydiphenylsulphone, 150 g. of chloral hydrate, and 450 c.c. of sulphuric acid (*d* 1·83) were shaken together for ½ hour and kept at the ordinary temperature with occasional shaking for 7 days. The desired sulphone together with meta- and para-chlorals separated in a solid cake. This was broken up in ice-cold water, separated, washed with hot water, and extracted with a little alcohol to remove parachlorals. The residue was dissolved in hot glacial acetic acid, metachloral remaining undissolved, and the crude product (25 g.), m. p. 200—205°, fractionally crystallised from the same solvent, the three forms then being obtained.

α-6 : 6′-*Di*-(2 : 4-*bistrichloromethyl*-1 : 3-*benzdioxinyl*)*sulphone* formed slender elongated prisms (4·0 g.), m. p. 215°, mixed m. p. 201° and 208° with the β- and the γ-form respectively (Found : Cl, 52·8; S, 4·0; C, 30·0; H, 1·3. $C_{20}H_{10}O_6Cl_{12}S$ requires Cl, 53·0; S, 4·0; C, 29·85; H, 1·25%). The β-*sulphone* also formed slender elongated prisms (0·8 g.), m. p. 240°, mixed m. p. (with γ-form) 212° (Found : Cl, 52·7; S, 3·8; C, 29·9; H, 1·4%). The γ-*sulphone* crystallised in elongated prisms (6·0 g.), m. p. 248° (Found : Cl, 52·8; S, 3·8; C, 29·8; H, 1·25%).

6 : 6′-*Di*-(2 : 4-*bisdichloromethylene*-1 : 3-*benzdioxinyl*)*sulphone* (IV).—2 G. of the α-sulphone in 500 c.c. of boiling alcohol and 0·6 g. of potassium hydroxide in 10 c.c. of alcohol were boiled together for 5 minutes. 6 : 6′-*Di*-(2 : 4-*bisdichloromethylene*-1 : 3-*benzdioxinyl*)*sulphone*, which slowly separated in woolly tufts, crystallised from acetic acid, in which it was easily soluble, in long hair-like prisms (1·1 g.), m. p. 215° (Found : Cl, 43·1; S, 5·1. $C_{20}H_6O_6Cl_8S$ requires Cl, 43·15; S, 4·9%). The β- (1 g.) and the γ-sulphone (2 g.), treated similarly, respectively yielded 0·5 g. and 1 g. of the above bisdichloromethylene compound.

α-6 : 6′-*Di*(*trichloromethyldichloromethylene*-1 : 3-*benzdioxinyl*)*sulphone*.—To 2 g. of α-6 : 6′-di-(2 : 4-bistrichloromethyl-1 : 3-benzdioxinyl)sulphone in 500 c.c. of alcohol at 30°, 0·3 g. of potassium hydroxide in 10 c.c. of alcohol was added. On standing over-night at the ordinary temperature, α-6 : 6′-*di*(*trichloromethyldichloromethylene*-1 : 3-*benzdioxinyl*)*sulphone* separated as slender colourless crystals. It crystallised from acetic acid in rhombic prisms (1·0 g.), m. p. 241° (Found : Cl, 48·4; S, 4·25. $C_{20}H_8O_6Cl_{10}S$ requires Cl, 48·6; S, 4·4%).

γ-6 : 6′-*Di*(*trichloromethyldichloromethylene*-1 : 3-*benzdioxinyl*)*sulphone*, similarly obtained from the γ-sulphone (1 g. in 250 c.c. of alcohol) and potassium hydroxide (0·3 g. in 10 c.c. of alcohol), separated in silky needles, and crystallised from alcohol in characteristic slender rhombic plates, m. p. 250° (Found : Cl, 48·9%).

Hydrolysis of Dibenzdioxinylsulphones by Alcoholic Potassium Hydroxide and Subsequent Oxidation by Permanganate : Formation of 4 : 4′-*Diethoxy*-3 : 3′-*dicarboxydiphenylsulphone* (V).—Owing to the difficulty of obtaining the β-isomeride in sufficient amount this experiment was carried out with the α-dibenzdioxinylsulphone, with the γ-dibenzdioxinylsulphone, and

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* A similar elimination of two molecules of hydrogen chloride might certainly be effected from the β-isomeride, but the isolation of this compound in a pure state is so tedious that the experiment has not been carried out.

with a mixture of approximately 1 part of the β- and 3 parts of the γ-dibenzdioxinylsulphone. An identical product was obtained in the same yield in each case.

3 G. of 6 : 6′-di-(2 : 4-bistrichloromethyl-1 : 3-benzdioxinyl)sulphone were boiled for about 1 hour with a solution of 6 g. of potassium hydroxide in 50 c.c. of alcohol until all chloroform and orthoformic ester had been evolved and a clear solution obtained, further additions of alcohol being made from time to time. The solution was then evaporated, and the residue dissolved in a little water. To the boiling aqueous solution, permanganate solution was added until present in slight excess. On filtration and acidification with hydrochloric acid 4 : 4′-*diethoxy*-3 : 3′-*dicarboxydiphenylsulphone* separated as a colourless solid. It crystallised from 20% acetic acid in long slender prisms (0·6 g.), m. p. 247° (Found : C, 54·95; H, 4·6. $C_{18}H_{18}O_8S$ requires C, 54·8; H, 4·6%).

4 : 4′-*Dihydroxy*-3 : 3′-*dimethyldiphenylsulphone*.—50 G. of *o*-cresol (2 mols.) were gradually heated with 24 g. (1 mol.) of sulphuric acid (*d* 1·83) to 200° and maintained at this temperature for 4 hours. The red mass obtained was dissolved in dilute aqueous caustic soda (charcoal), and the solution acidified with hydrochloric acid; 4 : 4′-*dihydroxy*-3 : 3′-*dimethyldiphenylsulphone* then separated. It crystallised from 50% aqueous alcohol in colourless slender prisms with domed ends (30 g.), m. p. 268° (Found : C, 60·5; H, 5·2; S, 11·7. $C_{14}H_{14}O_4S$ requires C, 60·4; H, 5·05; S, 11·5%). It formed a diacetate, slender prisms from alcohol, m. p. 135°, and a dibenzoate, short prisms from alcohol, m. p. 182°.

4 : 4′-*Diethoxy*-3 : 3′-*dimethyldiphenylsulphone*.—To a boiling solution of 40 g. of the 4 : 4′-dihydroxysulphone in a solution of 4 g. of sodium in 100 c.c. of alcohol, 20 g. of ethyl iodide were gradually run in. After 5 hours' boiling, one-third of the alcohol was distilled off, and the residue poured into water. 4 : 4′-*Diethoxy*-3 : 3′-*dimethyldiphenylsulphone*, which separated, crystallised from acetic acid in lustrous colourless plates (14 g.), m. p. 136° (Found : C, 63·9; H, 6·5; S, 9·4. $C_{18}H_{22}O_4S$ requires C, 64·7; H, 6·6; S, 9·6%).

4′-*Hydroxy*-4-*ethoxy*-3 : 3′-*dimethyldiphenylsulphone*, of which about 3 g. were obtained from the mother-liquors of the above preparation, crystallised from acetic acid in small flattened prisms, m. p. 186° (Found : C, 62·4; H, 5·6; S, 10·3. $C_{16}H_{18}O_4S$ requires C, 62·75; H, 5·85; S, 10·45%). It formed an acetate, elongated prisms from acetic acid, m. p. 126°.

4 : 4′-*Diethoxy*-3-*carboxy*-3′-*methyldiphenylsulphone*.—To 8 g. of 4 : 4′-diethoxy-3 : 3′-dimethyldiphenylsulphone in a mixture of 80 c.c. of boiling pyridine and 60 c.c. of 30% aqueous sodium hydroxide, 5 g. of finely powdered potassium permanganate were added in small portions with frequent shaking during 1 hour. Pyridine was then removed by steam distillation, and the aqueous solution filtered and acidified when cool. 4 : 4′-*Diethoxy*-3-*carboxy*-3′-*methyldiphenylsulphone* separated as a colourless solid and crystallised from aqueous acetic acid in elongated, much flattened prisms (5·2 g.), m. p. 211° (Found : C, 58·8; H, 5·3. $C_{18}H_{20}O_6S$ requires C, 59·3; H, 5·5%).

4 : 4′-*Diethoxy*-3 : 3′-*dicarboxydiphenylsulphone*.—To 2 g. of 4 : 4′-diethoxy-3-carboxy-3′-methyldiphenylsulphone, dissolved in 40 c.c. of boiling 20% aqueous sodium hydroxide, 5% aqueous permanganate was added in small portions until present in slight permanent excess (1 hour). The solution was then filtered, evaporated to two-thirds of its volume, and acidified when cool. 4 : 4′-Diethoxy-3 : 3′-dicarboxydiphenylsulphone separated and crystallised from 20% acetic acid in long slender prisms (0·7 g.), m. p. 247°, identical with the degradation product described above.

4 : 4′-*Diethoxy*-3 : 3′-*dicarbomethoxydiphenylsulphone*, obtained by esterifying either the above dicarboxy-acid or that obtained by degradation of the dibenzdioxinylsulphones in boiling methyl alcohol and hydrogen chloride, formed colourless leaflets from alcohol, m. p. 162° (Found : S, 7·8. $C_{20}H_{22}O_8S$ requires S, 7·5%).

4 : 4′-*Dihydroxy*-3 : 3′-*dicarboxydiphenylsulphone*.—1 G. of 4 : 4′-diethoxy-3 : 3′-dicarboxydiphenylsulphone was boiled under reflux with 20 c.c. of hydriodic acid (b. p. 127°) for 6 hours. When the mixture was poured into water 4 : 4′-*dihydroxy*-3 : 3′-*dicarboxydiphenylsulphone* separated. It crystallised from 50% acetic acid in long slender colourless prisms (0·5 g.), m. p. 299°. Its aqueous solution gives an intense purple coloration with ferric chloride (Found : S, 9·6. $C_{14}H_{10}O_8S$ requires S, 9·4%).

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