CCXXIII.—*Stereoisomerism of Disulphoxides and Related Substances. Part VII. Some Further Pairs of Isomeric Dioxides.*

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IN Part I (J., 1927, 1798) the oxidation of dimethyldithiolethane was found to give rise to two diastereoisomeric dioxides. The closely related diethyldithiolethane, studied by Beckmann in 1878 (*J. pr. Chem.*, 1878, **17**, 409), has now been investigated. By the action of hydrogen peroxide a single dioxide of m. p. 150° resulted. As this was not in agreement with the m. p. (170°) given by Beckmann, the oxidation was repeated, nitric acid being used as oxidant as in Beckmann's experiment; for the possibility was realised that different substances might preponderate in the products from two different methods of oxidation (compare preparation of the thianthrene dioxides; Fries and Vogt, *Ber.*, 1911, **44**, 756). The same dioxide of m. p. 150° was, however, again obtained, so the figure was presumably recorded erroneously by Beckmann. In neither oxidation could any second isomeride be detected.

On the other hand, the dioxide of m. p. 138—139° of ethylenedithioldiacetic acid reported by Ramberg and Tiberg (*Ber.*, 1914, **47**, 730) has been found to be a mixture of an *α-dioxide*, m. p. 147°, with a small proportion of a more soluble *β-dioxide*, m. p. 133°.

The oxidation products from *pp'*- and *oo'*-dinitrodiphenyldithiolethane (Fromm, Benzinger, and Schäfer, *Annalen*, 1912, **394**, 325) were next examined. The former yielded an *α-dioxide*, m. p. 195—197°, and a much more soluble *β-dioxide*, m. p. 174°, which alone tended to separate in combination with acetic acid. Both dioxides form unstable *compounds* with hydrochloric acid, and both are reduced to the parent disulphide by means of hydrogen bromide. Further oxidation produces the *disulphone*, m. p. 303°.

A disulphoxide of m. p. 145° derived from the *oo'*-dinitro-disulphide was described by Fromm and his colleagues. This was doubtless a mixture: our product was readily separated into an *α-dioxide*, m. p. 174°, and a more soluble *β-dioxide*, m. p. 160·5°. Each yielded the disulphide on reduction with hydrogen bromide. The *disulphone* has m. p. 265° : that described by the earlier authors, m. p. 164°, may have been incompletely oxidised.

The new disulphide, p-*nitrodiphenyldithiolethane*, prepared from thiophenol and *p*-nitrophenyl β-chloroethyl sulphide, yielded in the same way an *α-dioxide*, m. p. 173°, and a more soluble *β-dioxide*, m. p. 155°, both reducible by hydrogen bromide. The corresponding *disulphone* has m. p. 238°.

For the purpose of the study described in the following paper (Part VIII) 1 : 4-*diethylthiolbenzene* and its two *dioxides* were prepared.

The isolation of crystalline oxidation products from 1 : 3-dithiolan has been found to require careful attention to details owing to the ease with which the ring may be ruptured. The substance is a mercaptal and both it and its sulphoxides are sensitive to hydrolytic agents. The disulphide was prepared by the method of Gibson (J., 1930, 13), to whom we are indebted for advance information on this point. In addition to an amorphous substance melting at 130° (decomp.), presumably of high molecular weight, a crystalline *dioxide*, m. p. 158°, and a crystalline *trioxide*, m. p. 126°, both of which have been examined crystallographically, were obtained when the entire experiment was carried out at laboratory temperature. A careful search in several oxidations did not lead to the detection of a second dioxide, but the formation of by-products was evident, for the odour of a sulphide or mercaptan was apparent and, although no definite substance was identified in the mother-liquors, they were strongly acid.

A compound prepared by Gibson (*loc. cit.*) by the action of hydrochloric acid on dithiolan monoxide, having the carbon and hydrogen content of a dioxide, was insoluble and amorphous. It may be assumed that this is of higher molecular weight and therefore does not constitute the second isomeride expected.

The bis-sulphilimines of four disulphides have been prepared. They are all highly crystalline and apparently unaccompanied by any second substance. The sulphilimine of phenylpenthianol was found (J., 1929, 2838) to be similarly homogeneous. The bis-sulphilimines of dithian (Part II; J., 1928, 86) thus remain for the present the only case of this kind in which diastereoisomerism has been detected.

EXPERIMENTAL.

Oxidation of Diethyldithiolethane with Hydrogen Peroxide.—The disulphide (20 g.) in glacial acetic acid was oxidised by the calculated amount of 25% hydrogen peroxide. After 24 hours, distillation in steam and evaporation of the residue to dryness on the steam-bath gave the oxidation product in quantitative yield. The *disulphoxide* crystallised from ethyl acetate in radiating bunches of small monoclinic plates with straight extinction, m. p. 150° (decomp.) (Found: S, 35·3. $C_6H_{14}O_2S_2$ requires S, 35·2%). Careful fractional crystallisation failed to reveal the presence of a second substance.

Oxidation of Ethylenedithioldiacetic Acid.—The disulphide acid, prepared as described by Ramberg and Tiberg (*loc. cit.*) and recrystallised from a little hot water, had m. p. 109°. The acid (42 g.), dissolved in acetic acid (400 c.c.), was oxidised by hydrogen peroxide (2 mols. of 25% solution in 200 c.c. of acetic acid). The solid which separated was collected after 2 days, and after several recrystallisations from 50% aqueous alcohol yielded the *α-dioxide* (20 g.), m. p. 147° (decomp.) (Found : S, 26·4. $C_6H_{10}O_6S_2$ requires S, 26·4%). It crystallises from warm water in biprisms with the extinction along the main axis. The crystals tend to develop serrated edges.

The mother-liquor of the crude α-dioxide was subjected to steam distillation and evaporated on the steam-bath. By fractional crystallisation from ethyl alcohol a relatively small amount of *β-dioxide* was isolated (1 g.), m. p. 133° (decomp.) (Found : S, 26·4%). It is much more soluble in water than the α-isomeride and crystallises in small blade-shaped plates often radiating from a point and having an oblique extinction.

Crystals with water of crystallisation were not obtained when either dioxide was recrystallised from warm water (compare Ramberg and Tiberg, *loc. cit.*).

Oxidation of pp′-*Dinitrodiphenyldithiolethane to a Pair of Disulphoxides.*—The disulphide (20 g.) was boiled with 500 c.c. of nitric acid (*d* 1·2) until the evolution of brown fumes ceased. On cooling, 7·8 g. of a *compound* containing solvent of crystallisation were obtained. The remaining oxidation product was precipitated when the solution was neutralised with potassium carbonate (total yield, 9·75 g.). The product was separated into a pair of isomeric disulphoxides by fractional crystallisation from glacial acetic acid. The *α-disulphoxide* (yield of pure substance, 1·5 g.) crystallised from acetic acid in yellow needles, m. p. 195—197° (decomp.) (Found : N, 7·9; S, 17·3. $C_{14}H_{12}O_6N_2S_2$ requires N, 7·6; S, 17·4%). It gave an unstable *monohydrochloride* when dry hydrogen chloride was passed through its solution in glacial acetic acid (Found : HCl, 7·2. $C_{14}H_{12}O_6N_2S_2,HCl$ requires HCl, 9·0%). The *β-disulphoxide* (yield, 1·8 g.) crystallised from acetic acid in bright lemon-yellow prisms as an unstable *diacetate* (Found : loss at 100°, 20·2. $C_{14}H_{12}O_6N_2S_2,2C_2H_4O_2$ requires loss at 100°, 24·0%). The non-solvated dioxide was a pale yellow powder, m. p. 174° (decomp.), and was approximately five times as soluble in glacial acetic acid as the α-isomeride (Found : N, 7·7. $C_{14}H_{12}O_6N_2S_2$ requires N, 7·6%). The β-isomeride yielded an unstable *dihydrochloride* (Found : HCl, 13·7. $C_{14}H_{12}O_6N_2S_2,2HCl$ requires HCl, 16·5%).

Isolation of the Tetroxide of pp′-*Dinitrodiphenyldithiolethane.*—The disulphide (1 g.) was oxidised in boiling glacial acetic acid with an excess of chromium trioxide (3 g.) as described by Fromm, Benzinger, and Schäfer (*Annalen*, 1912, **394**, 325). The *disulphone*, precipitated by dilution with water as a mass of almost white needles, was recrystallised from *m*-cresol; m. p. 303° (decomp.) (Found : N, 7·0. $C_{14}H_{12}O_8N_2S_2$ requires N, 7·0%).

Oxidation of oo'-*Dinitrodiphenyldithiolethane to a Pair of Disulphoxides.*—The disulphide (7·8 g.) was oxidised by addition to boiling concentrated nitric acid, and the crude dioxide (yield, 2·4 g.), obtained by neutralisation of the solution with potassium carbonate, was separated by fractional crystallisation from 50% acetic acid into a pair of isomeric disulphoxides. The *α-disulphoxide* (yield of pure substance, 0·5 g.) crystallised from 50% acetic acid in arborescent, bright yellow needles, m. p. 174° (decomp.) (Found : C, 45·8; H, 3·5; S, 17·7. $C_{14}H_{12}O_6N_2S_2$ requires C, 45·7; H, 3·3; S, 17·4%). The *β-disulphoxide* (yield, 0·4 g.) crystallised from 50% acetic acid in clusters of bright yellow needles, m. p. 160·5° (decomp.), and was approximately four times as soluble in this solvent as the α-isomeride (Found : C, 46·0; H, 3·4; S, 17·5%). Both the α- and the β-disulphoxide showed a tendency to burn explosively in oxygen during analysis.

Isolation of the Tetroxide of oo'-*Dinitrodiphenyldithiolethane.*—The disulphide (1 g.) was oxidised by boiling with excess of chromium trioxide in glacial acetic acid. The disulphone appeared as colourless needles crystallising from glacial acetic acid; m. p. 265° (Fromm records the substance as crystallising from 75% acetic acid; m. p. 164°) (Found : N, 7·3. $C_{14}H_{12}O_8N_2S_2$ requires N, 7·0%).

Preparation of p-*Nitrodiphenyldithiolethane.*—Alcoholic solutions of thiophenol (7·3 g. in 100 c.c.) and potassium hydroxide (3·75 g. in 50 c.c.) were mixed, *p*-nitrophenyl β-chloroethyl sulphide (14·5 g. in 50 c.c. of ethyl alcohol) was added, and the whole heated for ½ hour on the steam-bath. The p-*nitrodiphenyldithiolethane* was obtained on cooling and dilution with water. It was soluble in ligroin, alcohol and acetic acid and was purified by repeated crystallisation from ethyl alcohol and finally from 75% acetic acid, giving pale yellow needles, m. p. 79—80° (Found : S, 22·1. $C_{14}H_{13}O_2NS_2$ requires S, 22·0%).

Oxidation of p-*Nitrodiphenyldithiolethane to a Pair of Disulphoxides.*—The disulphide (8·15 g.) was oxidised at 30—40° by the calculated amount of 20% hydrogen peroxide in glacial acetic acid solution. The mixture was left for 2 days, and the product obtained by neutralisation with potassium carbonate (yield, 8·8 g.). It was separated into a pair of isomeric disulphoxides by fractional crystallisation from 50% acetic acid and from ethyl alcohol. The *α-disulphoxide* (yield of pure substance, 1·5 g.) crystallised from 50% acetic acid in pale yellow, matted needles, m. p. 173°, not appreciably soluble in cold ethyl alcohol (Found : S, 20·0. $C_{14}H_{13}O_4NS_2$ requires S, 19·8%). The β-*disulphoxide* (yield, 2 g.) could be crystallised either from 50% acetic acid or from ethyl alcohol; m. p. 155° (Found : S, 20·1%).

Isolation of the Tetroxide of p-*Nitrodiphenyldithiolethane.*—The disulphide (1 g.) was oxidised by chromium trioxide in boiling glacial acetic acid to a *disulphone*, which crystallised from acetic acid in two habits (plates and needles), m. p. 238° (Found : N, 3·9. $C_{14}H_{13}O_6NS_2$ requires N, 3·9%).

Ethylation of 1 : 4-*Dithioquinol.*—Dithioquinol (5 g.) was ethylated by heating with potassium hydroxide (4 g. in 500 c.c. of ethyl alcohol) and ethyl iodide (11 g.) on the steam-bath for ½ hour. The alcohol was removed by fractional distillation and, on cooling, 1 : 4-*diethylthiolbenzene* crystallised, m. p. 46·5° (Found : S, 32·3. $C_{10}H_{14}S_2$ requires S, 32·3%).

Oxidation of 1 : 4-*Diethylthiolbenzene to a Pair of Disulphoxides.*—The disulphide (3·4 g.) was oxidised in glacial acetic acid by the gradual addition of the calculated amount of 20% hydrogen peroxide. The mixture was left for 24 hours, and the acetic acid removed by distillation in a current of steam; the solution was evaporated to dryness on the steam-bath (yield, 4 g.). The product was separated into a pair of isomeric disulphoxides by fractional crystallisation from ethyl acetate. The α-*disulphoxide* (yield of pure substance, 0·3 g.) crystallised from ethyl acetate in shining rhomb-shaped plates, m. p. 155° (Found : S, 28·0. $C_{10}H_{14}O_2S_2$ requires S, 27·8%). The β-*disulphoxide* (yield, 0·4 g.) was approximately four times as soluble in ethyl acetate as the α-isomeride, and crystallised in small dull nodular aggregates, m. p. 134° (Found : S, 28·0%).

Isolation of a Di- and a Tri-oxide of 1 : 3-*Dithiolan.*—(a) *Oxidation of* 1 : 3-*dithiolan by hydrogen peroxide.* Dithiolan (10 g.) was oxidised in glacial acetic acid solution (100 c.c.) by the addition of 25% hydrogen peroxide in amount calculated to give a disulphoxide. The acid was removed by distillation in a current of steam, and evaporation of the residue gave an amorphous, almost insoluble, white compound, m. p. 128° (decomp.) (Found : S, 63·2. $C_3H_6O_2S_2$ requires S, 46·4%).

(b) *Oxidation of* 1 : 3-*dithiolan with perhydrol.* Dithiolan (30 g.) was oxidised in pure, mineral acid-free glacial acetic acid solution by the addition of 25% perhydrol in amount calculated to give a dioxide. The mixture was left for 24 hours, and the acid removed by evaporation at laboratory temperatures under reduced pressure. The resulting white crystalline solid was extracted with cold water, leaving an amorphous residue. Evaporation of the aqueous solution at laboratory temperature in vacuum desiccators gave deposits of a crystalline *dioxide*, m. p. 157—158·5° (decomp.) (Found: S, 46·2. $C_3H_6O_2S_2$ requires S, 46·4%). It crystallised from benzene in flakes and from water in crystals suitable for goniometric measurement. The crystals were monoclinic with axial ratios $a : b : c = 1·4835 : 1 : 0·7072$, and axial angle $\beta = 58° 56'$. The following is a list of forms and mean angular values obtained with four crystals :

	a(100).	*m*(100).	*c* (001).	*p* (111).
ϕ	0° 0′	51° 48′	0° 0′	86° 5′
ρ	90° 0′	90° 0′	31° 4′	35° 20′

The usual habit of crystals from water is shown in Fig. 1, a combination of forms *m*, *c*, and *p* being observed.

Further deposits of crystals proved to be the *trioxide*, m. p. 128° (decomp.) (Found: S, 41·5. $C_3H_6O_3S_2$ requires S, 41·5%). A few crystals of what was apparently a third substance were noticed, but goniometric examination showed that they were identical with the trioxide. The trioxide is orthorhombic with axial ratios $a:b:c = 0·6156 : 1 : 1·0319$. The forms and mean angular values observed with three crystals were :

FIG. 1.

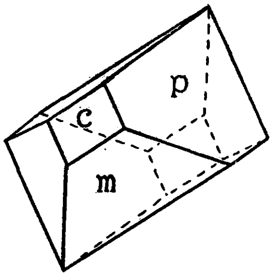
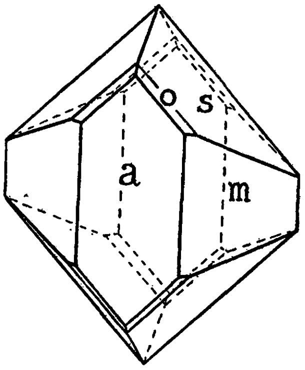


FIG. 2.



	a (100).	*m* (110).	*o* (111).	*s* (122).
ϕ	9° 9′	31° 37′	31° 37′	50° 54′
ρ	90° 0′	90° 0′	63° 0′	53° 3′

The habit of some crystals from water was octahedral (Fig. 2) with *a*, *m*, and *s* equally developed. In other crystals the habit was prismatic with *m* large and *s* forming a terminal pyramid, *o* being minute and *a* absent. The extinctions were found to be straight on *a* and *m*.

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