# CCCLVIII.—*The Formation of Aromatic Thiosulphonic Acids from Disulphides.*

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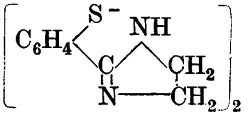
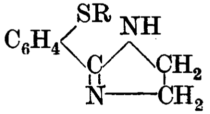
2 : 2′-*oo*′-DITHIODIPHENYL-4 : 5-DIHYDROGLYOXALINE (I) (McClelland and Warren, J., 1929, 2623) on treatment with sulphur

dioxide gave a product which is now represented as a *thiosulphonic acid* (II; R = $SO_3H$), since potassium cyanide yielded the *thiocyanate* (II; R = CN) (compare Footner and Smiles, J., 1925, **127**, 2888).

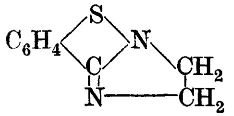
(I.)

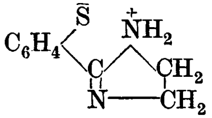




(II.)

(III.)





(IV.)

The formation of the same thiosulphonic acid by the action of sulphur dioxide on the perbromide derived from the tricyclic compound (III) (McClelland and Warren, *loc. cit.*) and on the hydrobromide of the tricyclic compound suggested that the thiosulphonic acid was formed from the disulphide (I) through the tricyclic compound, which has been shown to be a dismutation product of the disulphide (McClelland and Warren, this vol., p. 1097). Contrary to expectation, 2-*o*-thiolphenyl-4 : 5-dihydroglyoxaline (II; R = H) also gave this thiosulphonic acid, and the dihydroglyoxaline *m*- and *p*-disulphides (as I) (McClelland and Warren, *loc. cit.*) similarly gave the corresponding thiosulphonic acids. Here the improbability of the intermediate formation of a cyclic compound suggests that the disulphides studied are first reduced to the thiols, which then react to form the thiosulphonic acids.

The production of thiosulphonic acids by interaction of disulphides and sulphur dioxide does not appear to be a general reaction, since further experiment has shown that eight representative disulphides do not behave in this manner. According to patent literature (B.P. 4792, 1900) certain diamino-disulphides yield thiosulphonic acids on treatment with sulphur dioxide. Attempts to prepare a thiosulphonic acid from *pp'*-diaminodiphenyl disulphide according to this patent were unsuccessful, the sulphite of the base being obtained instead.

The presence of a strongly basic group in these reactive dihydroglyoxaline disulphides is noteworthy, and the thiols derived from them have, unlike most thiols, higher melting points than the corresponding disulphides. This anomaly might be accounted for in the *o*-compound by the tendency to dismute, but it cannot be ascribed to this cause in the *m*- and *p*-compounds, since these do not undergo dismutation (McClelland and Warren, *loc. cit.*). Moreover the thiols in question are neutral in reaction, and are sparingly soluble in non-hydroxylic organic solvents; these properties are in agreement with the betaine structure (IV) (compare Pfeiffer, *Ber.*, 1922, **55**, 1762). Further the formation of the hydriodides of the *S*-methyl bases (II; R = $CH_3$) by treatment of the thiols with methyl iodide is analogous to the formation of quaternary ammonium iodides from phenol betaines (Griess, *Ber.*, 1880, **13**, 649) and the *S*-methyl bases so obtained as well as the thiocyanates (II; R = CN) have normal physical properties. Consideration of these facts suggests that the formation of thiosulphonic acids from disulphides is dependent on their reduction to thiols capable of assuming a betaine structure and is associated with the polar character of the compounds.

## EXPERIMENTAL.

2-*Phenyl*-4 : 5-*dihydroglyoxaline*-o-*thiosulphonic Acid* (II; R = $SO_3H$).—A solution of 2-*o*-thiolphenyl-4 : 5-dihydroglyoxaline (II; R = H) (0·5 g.) in boiling ethyl alcohol was saturated with sulphur dioxide. After 24 hours the *thiosulphonic acid* (0·5 g.) had separated. It crystallised from water in colourless prisms, m. p. 228° (decomp.) (Found: S, 24·9. $C_9H_{10}O_3N_2S_2$ requires S, 24·8%), unchanged by recrystallisation from 2*N*-hydrochloric acid, and gave no precipitate with barium chloride in aqueous solution. It was decomposed by 2*N*-sodium hydroxide, yielding the disulphide (I).

2-*Phenyl*-4 : 5-*dihydroglyoxaline* o-*Thiocyanate* (II; R = CN).—A strong solution of potassium cyanide was added to a hot aqueous solution of 2-phenyl-4 : 5-dihydroglyoxaline-*o*-thiosulphonic acid, and the mixture boiled for a few minutes. The material, which separated on cooling, crystallised from water in colourless needles, m. p. 180° (Found: C, 58·9; H, 4·3. $C_{10}H_9N_3S$ requires C, 59·1; H, 4·4%). An identical product was obtained when a hot aqueous solution of the hydrobromide of the tricyclic compound (III) was mixed with an aqueous solution of potassium cyanide and cooled. The *thiocyanate* is alkaline to litmus and readily soluble in dilute hydrochloric acid.

2-*Phenyl*-4 : 5-*dihydroglyoxaline*-m-*thiosulphonic acid*, obtained from 2 : 2′-*mm*′-dithiodiphenyl-4 : 5-dihydroglyoxaline, crystallised from water in pale yellow prisms, m. p. 246° (decomp.) (Found: C, 41·8; H, 3·5. $C_9H_{10}O_3N_2S_2$ requires C, 41·8; H, 3·9%). It has similar properties to the *o*-compound.

2-*Phenyl*-4 : 5-*dihydroglyoxaline*-p-*thiosulphonic acid*, obtained from 2 : 2′-*pp*′-dithiodiphenyl-4 : 5-dihydroglyoxaline in the usual way, crystallised from aqueous acetic acid in colourless prisms, m. p. 248° (decomp.) (Found: C, 41·9; H, 4·4%). On treatment with potassium cyanide it gave 2-*phenyl*-4 : 5-*dihydroglyoxaline* p-*thiocyanate*, which formed yellow needles, m. p. above 265°, from water (Found : S, 16·3. $C_{10}H_9N_3S$ requires S, 15·8%).

The following disulphides, dissolved or suspended in alcohol, were recovered unchanged after prolonged treatment with sulphur dioxide : di-*p*-tolyl disulphide, 3 : 4 : 3′ : 4′-tetramethoxy-, 5 : 5′-dibromo-3 : 4 : 3′ : 4′-tetramethoxy-, 4 : 4′dinitro-, and 2 : 5 : 2′ : 5′-tetrabromo-diphenyl disulphides, 2-naphthol-1-disulphide, and benzyl disulphide.

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[*Received, November 4th*, 1930.]