CCCLX.—*The Sulphonation of Glyoxalines. Part III.*

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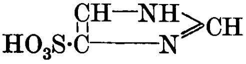
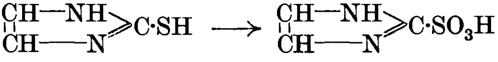
SULPHONATION of glyoxalines leads to a monosulphonic acid, which was assumed to be glyoxaline-4(5)-sulphonic acid (I) (Pyman and Ravald, J., 1920, **117**, 1429), but attempts to prove the orientation of the sulpho-group failed (Forsyth, Moore, and Pyman, J., 1924, **125**, 919). Recently, Balaban and King (this vol., p. 1858) have shown that 2-thiol-4(5)-methylglyoxaline can be oxidised to 4(5)-methylglyoxaline-2-sulphonic acid by means of hydrogen peroxide, and with the consent of these authors we have oxidised 2-thiolglyoxaline (II) to *glyoxaline-2-sulphonic acid* (III) by their method. It proves to be different from the sulphonation product of glyoxaline, which is thus shown to be glyoxaline-4(5)-sulphonic acid, as previously supposed.



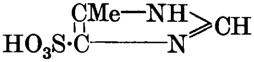
(I.)

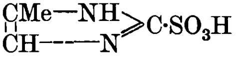


(II.) (III.)

4(5)-Methylglyoxaline has now been sulphonated, and yields a sulphonic acid which must be 4(5)-*methylglyoxaline*-5(4)-*sulphonic acid* (IV), since it is not identical with Balaban and King's 4(5)-methylglyoxaline-2-sulphonic acid (V).

(IV.)





(V.)

It resembles glyoxaline-4(5)-sulphonic acid and 2-methylglyoxaline-4(5)-sulphonic acid in being readily decomposed by cold bromine water and in failing to yield an acid chloride on treatment with phosphorus pentachloride. Like glyoxaline-4(5)-sulphonic acid, it is hydrolysed almost quantitatively by heating for 3 hours at 170° with concentrated hydrochloric acid, but glyoxaline-2-sulphonic acid is hydrolysed only to the extent of 12% under these conditions. It may be noted that all the many sulphonation and nitration products of glyoxalines which have been oriented hitherto contain the sulpho- or nitro-group in the 4- or 5-position, and there is no evidence at present that glyoxalines can be sulphonated or nitrated in the 2-position.

EXPERIMENTAL.

Glyoxaline-2-sulphonic Acid (III).—2-Thiolglyoxaline (3·21 g.) was added to Merck's perhydrol (10·92 g.) diluted with water (21·8 c.c.) at — 5° to 0°. The solution was basified with sodium hydroxide, kept at 0° for 12 hours, and acidified to Congo-red with hydrochloric acid. When the solution was concentrated, *glyoxaline-2-sulphonic acid* (2·46 g.; yield 46·2%) separated. The mother-liquor was basified with potassium carbonate, evaporated to dryness, and extracted with alcohol. This extract gave with picric acid glyoxaline picrate (0·8 g.; yield 8·4%).

Glyoxaline-2-sulphonic acid crystallises from water in colourless prisms containing $1H_2O$, which is lost in a vacuum over sulphuric acid. The dried acid softens and darkens from 285° and melts at about 303° (corr.), whilst a mixture of this acid with the monosulphonic acid formed by the sulphonation of glyoxaline—glyoxaline-4(5)-sulphonic acid, m. p. 307°—melted at 272—275°. (The latter crystallises from water in anhydrous cubes; Pyman and Ravald, *loc. cit.*) (Found: loss in a vacuum over H_2SO_4, 11·0, 11·1.

$C_3H_4O_3N_2S,H_2O$ requires H_2O, 10·8%. Found in dried acid: C, 24·3; H, 3·1; S, 21·7. $C_3H_4O_3N_2S$ requires C, 24·2; H, 2·7; S, 21·6%).

Glyoxaline-2-sulphonic acid is soluble in about 8 parts of cold water, more readily soluble in hot water, but insoluble in absolute alcohol.

The *barium* salt crystallises from water in feathery needles containing $2H_2O$, and is soluble in about 3 parts of cold water, more readily soluble in hot water, but insoluble in alcohol [Found: loss at 120°, 7·2. $(C_3H_3O_3N_2S)_2Ba,2H_2O$ requires H_2O, 7·7%. Found in dried salt: Ba, 31·3, 31·4. $(C_3H_3O_3N_2S)_2Ba$ requires Ba, 31·8%]. [Barium glyoxaline-4(5)-sulphonate crystallises from water in anhydrous octahedra; Pyman and Ravald, *loc. cit.*].

Hydrolysis. Glyoxaline-2-sulphonic acid (0·83 g.) and concentrated hydrochloric acid (8·3 c.c.) were heated for 3 hours at 170°, and the product was mixed with aqueous barium chloride; barium sulphate was then precipitated in quantity (0·14 g.) corresponding to the hydrolysis of 12% of the acid. After removal of the excess of barium by means of sulphuric acid, and of hydrochloric acid by means of silver hydroxide, 0·45 g. (54%) of glyoxaline-2-sulphonic acid was recovered unchanged, whilst the mother-liquor gave with picric acid glyoxaline picrate (0·1 g.; yield 6·7%). This melted at 205°, and did not depress the m. p. of an authentic specimen of glyoxaline picrate.

Sulphonation of 4(5)-*Methylglyoxaline.*—The well-dried and finely powdered sulphate from 16·76 g. of 4(5)-methylglyoxaline was added to 60—70% oleum (67·0 g.) at 0°, and the mixture heated for 6 hours at 160°. The product was diluted with water, and sulphuric acid removed by means of barium hydroxide, excess of the latter being removed by carbon dioxide. The filtered solution was evaporated to dryness, and the residue was extracted with chloroform, which removed no unchanged base, and dried at 120°; 43·44 g. of crude barium salt containing 29·2% Ba were then obtained. These figures correspond to a yield of 90·5% of barium 4(5)-methylglyoxaline-5(4)-sulphonate, but when the salt was treated with the calculated quantity of sulphuric acid pure 4(5)-methylglyoxaline-5(4)-sulphonic acid was obtained in only 60% yield, and was accompanied by small quantities of a by-product more sparingly soluble in water, which was not obtained in a pure state.

4(5)-*Methylglyoxaline*-5(4)-*sulphonic acid* (IV) crystallises from water in colourless, hexagonal plates containing $1H_2O$, which is lost at 100°. The dried acid melts at 278° (corr.) after sintering a few degrees lower. A mixture of this acid with a specimen of 4(5)-methylglyoxaline-2-sulphonic acid (m. p. 280°), for which we are indebted to Dr. King, melted at 235—240° (Found in air-dried acid : loss at 100°, 9·8, 10·0. $C_4H_6O_3N_2S,H_2O$ requires H_2O, 10·0%. Found in dried acid : C, 29·5 ; H, 4·1 ; N, 17·4 ; S, 20·2. $C_4H_6O_3N_2S$ requires C, 29·6 ; H, 3·7 ; N, 17·4 ; S, 19·8%). The acid is soluble in about 4 parts of cold water, more readily soluble in hot water, but insoluble in alcohol or ether.

The *sodium* salt crystallises from water in long, silky needles, containing $3H_2O$, and is soluble in about 2·5 parts of cold water, but insoluble in alcohol (Found in air-dried salt : H_2O, 21·7, 21·6 ; Na, 9·5, 9·6. $C_4H_5O_3N_2SNa,3H_2O$ requires H_2O, 22·7 ; Na, 9·7%). The *ammonium* salt crystallises from water in anhydrous prisms which are soluble in about 4 parts of cold water but insoluble in alcohol (Found : N, 23·3. $C_4H_9O_3N_2S$ requires N, 23·4%). The *barium* salt crystallises from 50% aqueous alcohol in long, opaque needles, containing $3H_2O$. It is soluble in 2 parts of cold water, but insoluble in alcohol [Found in air-dried salt : loss at 120°, 10·2, 10·4. $(C_4H_5O_3N_2S)_2Ba,3H_2O$ requires H_2O, 10·5%. Found in dried salt : Ba, 29·3, 29·5. $(C_4H_5O_3N_2S)_2Ba$ requires Ba, 29·8%].

Hydrolysis. 4(5)-Methylglyoxaline-5(4)-sulphonic acid (0·9 g.) was heated with concentrated hydrochloric acid (10 c.c.) for 3 hours at 170°. The product was mixed with aqueous barium chloride and gave 1·166 g. of barium sulphate corresponding to the hydrolysis of 99·8% of the acid. The filtrate was basified with sodium carbonate, filtered from barium carbonate, and evaporated to dryness. On extraction of the residue with chloroform an oil was obtained which gave with alcoholic picric acid 4(5)-methylglyoxaline picrate (0·89 g.; yield 57%; m. p. 159—160°, alone or mixed with an authentic specimen).

Bromination. To the hydrated sulphonic acid (9·62 g.) in cold water (100 c.c.), bromine (1 mol.; 2·7 c.c.) was added, and the colour of this was immediately discharged. On concentrating the solution and, on occasions, adding alcohol, various crops of crystals were obtained from which the unchanged acid (5·22 g.) and ammonium bromide (1·5 g.) were isolated. The final mother-liquor contained 1·03 g. of sulphuric acid.

Anhydrous 4(5)-methylglyoxaline-5(4)-sulphonic acid did not appear to react with phosphorus pentachloride at 160°.

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