18. *The Interaction of Diazonium Salts and Acetonesulphonic Acid.*

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ACETONESULPHONIC acid, like ω-nitroacetophenone (Parkes and Williams, J., 1934, 67) and acetophenone-ω-sulphonic acid (Parkes and Tinsley, *ibid.*, p. 1861), contains a reactive methylene group and couples readily with diazonium salts in presence of sodium acetate to produce *methylglyoxalarylhydrazone-ω-sulphonates* :

$$R{\cdot}N_2Cl + CH_3{\cdot}CO{\cdot}CH_2{\cdot}SO_3Na \longrightarrow R{\cdot}NH{\cdot}N{:}C(SO_3Na){\cdot}CO{\cdot}CH_3$$

The yields are not so good as those from acetophenone-ω-sulphonic acid owing to the formation of dark red by-products.

The action of bromine upon sodium methylglyoxalphenylhydrazonesulphonate is in the main similar to its action upon the corresponding acetophenone derivative (Parkes and Tinsley, *loc. cit.*); with one molecular proportion of bromine, however, the reaction cannot be interrupted at the *p*-bromophenylhydrazone stage, and the product is a mixture of unchanged material and ω-bromomethylglyoxal-*p*-bromophenylhydrazone, the sulpho-group having been replaced by bromine. With two molecules of bromine, an almost theoretical yield of ω-bromomethylglyoxal-*p*-bromophenylhydrazone is obtained. This

compound also results from the action of one molecule of bromine upon methylglyoxal-*p*-bromophenylhydrazone-ω-sulphonic acid. The further action of bromine results in the formation of βω-dibromo-α-ketopropaldehyde-*p*-bromophenylhydrazone (compare Chattaway and Ashworth, J., 1934, 930).

$$C_6H_5\cdot NH\cdot N{:}C(SO_3Na)\cdot COMe \longrightarrow [C_6H_4Br\cdot NH\cdot N{:}C(SO_3Na)\cdot COMe] \longrightarrow C_6H_4Br\cdot NH\cdot N{:}CBr\cdot COMe \longrightarrow C_6H_4Br\cdot NH\cdot N{:}CBr\cdot CO\cdot CH_2Br$$

The action of excess of bromine on sodium methylglyoxal-2 : 4-dibromophenylhydrazone-ω-sulphonate similarly yields ββω-tribromo-α-ketopropaldehyde-2 : 4-dibromophenylhydrazone :

$$C_6H_4Br_2\cdot NH\cdot N{:}C(SO_3Na)\cdot COMe \longrightarrow C_6H_4Br_2\cdot NH\cdot N{:}CBr\cdot CO\cdot CHBr_2$$

Experimental.

Sodium Acetonesulphonate.—Monobromoacetone (Levene, "Organic Syntheses," 1930, **10**, 12) (180 g.), dissolved in 75 c.c. of alcohol, was added to 375 g. of crystallised sodium sulphite in 375 c.c. of water, the solution evaporated to dryness on the water-bath, and the residue extracted several times with boiling alcohol. Sodium acetonesulphonate separated from the extract on cooling; it was dried, and preserved over calcium chloride in a vacuum desiccator (compare Bender, *Z. Chem.*, 1870, 162).

*Sodium Methylglyoxal-*p*-bromophenylhydrazone-ω-sulphonate.*—A solution of 21 g. of *p*-bromoaniline in 5 c.c. of hot glacial acetic acid was poured into a mixture of 25 c.c. of concentrated hydrochloric acid and 25 c.c. of water with vigorous stirring. This was diazotised with 9 g. of sodium nitrite and added with stirring during ½ hour to a mixture of 20 g. of sodium acetonesulphonate, 200 g. of crystallised sodium acetate, and 200 c.c. of water at 0°. The liquid was filtered after 20 hours and the *sodium methylglyoxal-*p*-bromophenylhydrazone-ω-sulphonate* (coloured deep red by a by-product) was washed with a little warm water to remove sodium acetate, extracted with several very small quantities of hot alcohol to remove the red impurity, and crystallised from boiling alcohol (charcoal), from which it separated in fine, pale yellow needles, m. p. 224° (decomp.) (Found : N, 8·0. $C_9H_8O_4BrSNa$ requires N, 8·2%).

The following sodium salts were obtained similarly : *methylglyoxalphenylhydrazone-ω-sulphonate*, pale yellow needles, m. p. 195° (decomp.) (Found : N, 10·4. $C_9H_9O_4N_2SNa$ requires N, 10·6%); *methylglyoxal-*p*-chlorophenylhydrazone-ω-sulphonate*, lemon-yellow needles, m. p. 228° (decomp.) (Found : Cl, 11·75. $C_9H_8O_4N_2ClSNa$ requires Cl, 11·9%); *methylglyoxal-2 : 4-dichlorophenylhydrazone-ω-sulphonate*, yellow needles from methyl alcohol, m. p. 270° (decomp.) (Found : N, 8·25. $C_9H_7O_4N_2Cl_2SNa$ requires N, 8·4%); *methylglyoxal-2 : 4-dibromophenylhydrazone-ω-sulphonate*, yellow needles from methyl alcohol, m. p. 275° (decomp.) (Found : N, 6·6. $C_9H_7O_4N_2Br_2SNa$ requires N, 6·6%); *methylglyoxal-*o*-nitrophenylhydrazone-ω-sulphonate*, deep golden, microcrystalline powder, m. p. 256° (decomp.) (Found : N, 13·5. $C_9H_8O_6N_3SNa$ requires N, 13·6%); *methylglyoxal-*m*-nitrophenylhydrazone-ω-sulphonate*, pale yellow plates from glacial acetic acid, m. p. 251° (decomp.) (Found : N, 13·2%); *methylglyoxal-*p*-nitrophenylhydrazone-ω-sulphonate*, yellow prismatic needles from methyl alcohol, m. p. 265° (decomp.) (Found : N, 13·4%).

Action of Bromine upon Sodium Methylglyoxalphenylhydrazone-ω-sulphonate.—(1) *1 Mol. of bromine.* 1·6 G. of bromine (1 mol.) in a few c.c. of glacial acetic acid were added with shaking to 2·6 g. of sodium methylglyoxalphenylhydrazone-ω-sulphonate in 40 c.c. of glacial acetic acid. The deep red liquid was filtered from unchanged initial material, heated to 100°, and diluted with hot water until it was just turbid; on cooling, ω-bromomethylglyoxal-*p*-bromophenylhydrazone separated, identical with a specimen prepared by Chattaway and Lye's method (*Proc. Roy. Soc.*, 1932, *A*, **137**, 489).

(2) *2 Mols. of bromine.* When 3·2 g. of bromine were used, the other quantities being as in (1), a clear solution was obtained, from which ω-bromomethylglyoxal-*p*-bromophenylhydrazone was precipitated by dilution with hot water.

(3) *3 Mols. of bromine.* 2·6 G. of sodium methylglyoxalphenylhydrazone-ω-sulphonate in 20 c.c. of glacial acetic acid were treated with 4·8 g. of bromine in 5 c.c. of glacial acetic acid. By diluting the hot solution with hot water as above, βω-dibromo-α-ketopropaldehyde-*p*-bromophenylhydrazone was obtained; this crystallised from alcohol in bright yellow, hair-like needles, m. p. 174—175°, identical with a specimen prepared by Chattaway and Ashworth's method (*loc. cit.*).

(4) *Excess of bromine.* The action of excess of bromine upon sodium methylglyoxal-2 : 4-dibromophenylhydrazone-ω-sulphonate dissolved in glacial acetic acid was carried out in a similar manner. The product was ββω-tribromo-α-ketopropaldehyde-2 : 4-dibromophenylhydrazone, identical with a specimen prepared by Chattaway and Lye's method (*loc. cit.*).

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