411. *Acetophenone-ω-sulphonic Acid, and the Phenylglyoxalaryl-hydrazone-ω-sulphonic Acids.*

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Acetophenone-ω-sulphonic acid was first made by Schroeter (*Annalen*, 1919, **418**, 161) from methanedisulphonic acid by a method which is rather long and involved and employs somewhat inaccessible materials.

The sodium salt can be readily prepared in quantity by the action of sodium sulphite at 100° upon ω-bromoacetophenone (compare acetonesulphonic acid; Bender, *Z. Chem.*, 1870, 162):

$$Ph{\cdot}CO{\cdot}CH_2Br + Na_2SO_3 = Ph{\cdot}CO{\cdot}CH_2{\cdot}SO_3Na + NaBr$$

The free acid, obtained by the action of dry hydrogen chloride upon a suspension of the sodium salt in dry ether, is a strong one and readily forms salts with ammonia, aniline, and phenylhydrazine, but all attempts to prepare a phenylhydrazone have failed.

The sulpho-group, like the nitro-group (this vol., p. 67), activates the methylene group in ω-substituted acetophenones, and acetophenone-ω-sulphonic acid couples readily with diazonium salts in solution in presence of sodium acetate, the corresponding phenylglyoxalarylhydrazone-ω-sulphonic acids being formed:

$$R{\cdot}N_2Cl + Ph{\cdot}CO{\cdot}CH_2{\cdot}SO_3H \longrightarrow R{\cdot}NH{\cdot}N{:}C(SO_3H){\cdot}COPh$$

The action of bromine on these compounds is similar to that upon the corresponding ω-nitrophenylglyoxalarylhydrazones (*loc. cit.*) and upon the corresponding arylazobenzoylacetones and arylazoacetoacetates (Chattaway and Lye, *Proc. Roy. Soc.*, 1932, *A*, **135**, 282; **137**, 489; J., 1933, 480) and ultimately causes the replacement of the sulpho-group by bromine. For instance, bromine converts *phenylglyoxalphenylhydrazone-ω-sulphonic acid*

into *phenylglyoxal*-p-*bromophenylhydrazone*-ω-*sulphonic acid*, and its further action first replaces the ω-sulpho-group and then brings about substitution in one ortho-position :

$$C_6H_5\cdot NH\cdot N{:}C(SO_3H)\cdot COPh \longrightarrow p\text{-}C_6H_4Br\cdot NH\cdot N{:}C(SO_3H)\cdot COPh \longrightarrow p\text{-}C_6H_4Br\cdot NH\cdot N{:}CBr\cdot COPh \longrightarrow 2:4\text{-}C_6H_3Br_2\cdot NH\cdot N{:}CBr\cdot COPh$$

As might be expected, the action of chlorine is similar to that of bromine, but more vigorous. Thus the first action of chlorine upon phenylglyoxalphenylhydrazone-ω-sulphonic acid causes the replacement of the sulpho-group by chlorine and the formation of ω-*chlorophenylglyoxal*-p-*chlorophenylhydrazone*. Under no conditions was it found possible to substitute chlorine in the para-position in the phenyl residue of phenylglyoxalphenylhydrazone-ω-sulphonic acid without replacing the sulpho-group by halogen at the same time.

Although in these ω-bromo- and ω-chloro-phenylglyoxalarylhydrazones the halogen atom in the ω-position is fairly reactive and can be replaced, for example, by an amino-group by treatment with alcoholic ammonia, the original ω-sulphonic acids are not formed on treatment with anhydrous sodium sulphite, nor is the halogen replaced by hydrogen by the action of hydriodic acid.

Experimental.

Sodium Acetophenone-ω-sulphonate.—A solution of 300 g. of ω-bromoacetophenone in 100 c.c. of alcohol was added to a solution of 500 g. of crystalline sodium sulphite in 500 c.c. of water, and the mixture evaporated to dryness on a water-bath. The resulting solid was broken into small lumps and extracted with boiling alcohol, from which, on cooling, the above *sodium* salt separated in colourless slender prisms, m. p. 260° (decomp.), excessively soluble in water, moderately so in alcohol, and insoluble in chloroform, ether, and benzene. Yield, 90% of the theoretical (Found : S, 14·5. $C_8H_7O_4SNa$ requires S, 14·4%).

Acetophenone-ω-sulphonic Acid.—100 G. of sodium acetophenone-ω-sulphonate were finely powdered and suspended in 500 c.c. of dry ether, and dry hydrogen chloride was passed for 12 hours. On filtration and removal of the ether by distillation in a vacuum acetophenone-ω-sulphonic acid remained as a viscous dark liquid, which solidified on standing in a vacuum over phosphoric oxide for a week. It was purified by melting it under successive small quantities of chloroform, in which it is insoluble, until the top layer of chloroform remained colourless. On cooling, the acid solidified in masses of extremely hygroscopic, flattened, rectangular prisms, m. p. 73—75°. Yield, 15% of the theoretical (Found : S, 15·1. Calc. for $C_8H_8O_4S$: S, 16·0%).

When the acid was neutralised with concentrated aqueous ammonia, the *ammonium* salt separated on cooling. It crystallised from alcohol in colourless lustrous leaflets, m. p. 207° (Found : S, 14·6. $C_8H_{11}O_4NS$ requires S, 14·7%). In a similar manner *aniline acetophenone-ω-sulphonate*, colourless lustrous leaflets from alcohol, m. p. 181° (Found : S, 10·8. $C_{14}H_{15}O_4NS$ requires S, 10·9%), and *phenylhydrazine acetophenone-ω-sulphonate*, colourless slender prisms from water, m. p. 208° (decomp.) (Found : S, 10·3. $C_{14}H_{16}O_4N_2S$ requires S, 10·4%), have been prepared.

Phenylglyoxalphenylhydrazone-ω-sulphonic Acid.—12 G. of aniline were diazotised with 9 g. of sodium nitrite in 25 c.c. of concentrated hydrochloric acid and 25 c.c. of water, and the resulting solution was slowly added to a stirred, well-cooled mixture of 30 g. of sodium acetophenone-ω-sulphonate, 300 g. of crystalline sodium acetate, and 50 c.c. of water. After 8 hours' stirring, and 24 hours' keeping in ice, the above *compound* separated. It crystallised from alcohol in light yellow, long, hair-like needles, m. p. 220° (decomp.) (Found : S, 10·5. $C_{14}H_{12}O_4N_2S$ requires S, 10·35%). Yield, 60% of the theoretical. The barium salt, prepared from aqueous solutions of the acid and barium chloride, crystallised from water in minute yellow prisms, m. p. 188° (decomp.).

In a similar manner the following have been prepared : *Phenylglyoxal*-p-*bromophenylhydrazone*-ω-*sulphonic acid*, pale yellow, very fine, hair-like crystals from alcohol, m. p. 240° (decomp.) (Found : S, 8·7; Br, 20·95. $C_{14}H_{11}O_4N_2BrS$ requires S, 8·4; Br, 21·0%).

Phenylglyoxal-2 : 4-*dibromophenylhydrazone*-ω-*sulphonic acid*, yellow, irregular, short, flattened prisms from alcohol, m. p. 245° (decomp.) (Found : S, 7·1; Br, 34·4. $C_{14}H_{10}O_4N_2Br_2S$ requires S, 6·9; Br, 34·6%). Its barium salt crystallised from water as a yellow microcrystalline solid, m. p. 270° (decomp.).

Phenylglyoxal-2 : 4 : 6-*tribromophenylhydrazone*-ω-*sulphonic acid*, which crystallised from

alcohol in a labile form as pale yellow, hair-like prisms, which gradually redissolved in the mother-liquor, whilst a stable form separated in pale yellow, irregular, rhombic plates, m. p. 210° (decomp.) (Found : Br, 44·5. $C_{14}H_9O_4N_2Br_3S$ requires Br, 44·4%).

Phenylglyoxal-p-*nitrophenylhydrazone*-ω-*sulphonic acid*, pale yellow, long prisms from water, m. p. 259° (decomp.) (Found : S, 9·2. $C_{14}H_{11}O_6N_3S$ requires S, 9·2%).

Phenylglyoxal-o-*nitrophenylhydrazone*-ω-*sulphonic acid*, bright orange-yellow, minute, compact prisms from water, m. p. 238° (decomp.) (Found : S, 9·1%).

Phenylglyoxal-4-*bromo*-2-*nitrophenylhydrazone*-ω-*sulphonic acid*, yellow microcrystalline powder from water, m. p. 242° (decomp.) (Found : Br, 18·5. $C_{14}H_{10}O_6N_3BrS$ requires Br, 18·7%). Its barium salt crystallised from water as a microcrystalline powder, m. p. 238° (decomp.).

Phenylglyoxal-p-*chlorophenylhydrazone*-ω-*sulphonic acid*, pale yellow, long, slender prisms from alcohol, m. p. 240° (decomp.) (Found : S, 9·6; Cl, 10·3. $C_{14}H_{11}O_4N_2ClS$ requires S, 9·45; Cl, 10·5%).

Phenylglyoxal-2 : 4-*dichlorophenylhydrazone*-ω-*sulphonic acid*, pale yellow clusters of short flattened prisms from alcohol, m. p. 248° (decomp.) (Found : Cl, 19·1. $C_{14}H_{10}O_4N_2Cl_2S$ requires Cl, 19·0%).

Phenylglyoxal-2 : 4 : 6-*trichlorophenylhydrazone*-ω-*sulphonic acid*, pale yellow, long, slender, flattened prisms from alcohol, m. p. 217° (Found : Cl, 25·8. $C_{14}H_9O_4N_2Cl_3S$ requires Cl, 26·1%).

Action of Bromine upon Phenylglyoxalphenylhydrazone-ω-*sulphonic Acid.*—(I) *Formation of phenylglyoxal*-p-*bromophenylhydrazone*-ω-*sulphonic acid*. 1·6 G. of bromine in 3 c.c. of acetic acid were added to a solution of 3 g. of phenylglyoxalphenylhydrazone-ω-sulphonic acid in 20 c.c. of cold glacial acetic acid. The above compound separated as a yellow solid, which on crystallisation from alcohol was shown to be identical with the compound obtained by coupling acetophenone-ω-sulphonic acid with *p*-bromophenyldiazonium chloride (see above).

(II) *Formation of* ω-*bromophenylglyoxal*-p-*bromophenylhydrazone*. 3·3 G. of bromine in 3 c.c. of acetic acid were added to a solution of 3 g. of phenylglyoxalphenylhydrazone-ω-sulphonic acid in 20 c.c. of hot acetic acid. After 12 hours, the above compound separated; it crystallised from acetic acid in pale yellow needles, m. p. 197°. The same compound was obtained by similar treatment of phenylglyoxal-*p*-bromophenylhydrazone-ω-sulphonic acid with 1 mol. of bromine, and both specimens were found to be identical with an authentic specimen (J., 1933, 480).

(III) *Formation of* ω-*bromophenylglyoxal*-2 : 4-*dibromophenylhydrazone*. 6 G. of bromine in 5 c.c. of acetic acid were added to a solution of 3 g. of phenylglyoxalphenylhydrazone-ω-sulphonic acid in 20 c.c. of boiling acetic acid, and the solution was refluxed for 8 hours. On cooling, the above compound separated; it crystallised from alcohol in long, yellow, slender prisms, m. p. 124°. The same compound was obtained by similar treatment of phenylglyoxal-*p*-bromophenylhydrazone-ω-sulphonic acid with 2 mols. of bromine, or by treatment of phenylglyoxal-2 : 4-dibromophenylhydrazone-ω-sulphonic acid with 1 mol. of bromine. All three specimens were found to be identical with an authentic sample (*loc. cit.*).

Action of Bromine upon Phenylglyoxal-2 : 4 : 6-*tribromophenylhydrazone*-ω-*sulphonic Acid.*—1·2 G. of bromine were added to a solution of 3 g. of phenylglyoxal-2 : 4 : 6-tribromophenylhydrazone-ω-sulphonic acid in 20 c.c. of hot acetic acid and the whole was kept for 12 hours. ω-Bromophenylglyoxal-2 : 4 : 6-tribromophenylhydrazone slowly separated; it crystallised from acetic acid in pale yellow, large, lustrous, flattened prisms, m. p. 148°, and was found to be identical with an authentic specimen (*loc. cit.*).

In a similar manner to the above have been obtained : ω-Bromophenylglyoxal-*p*-nitrophenylhydrazone, pale yellow, long, slender prisms from acetic acid, m. p. 247° (decomp.), which was found to be identical with an authentic specimen (*loc. cit.*).

ω-*Bromophenylglyoxal*-o-*nitrophenylhydrazone*, pale yellow, hair-like needles from alcohol, m. p. 128° (Found : Br, 22·8. $C_{14}H_{10}O_3N_3Br$ requires Br, 23·0%).

ω-*Bromophenylglyoxal*-4-*bromo*-2-*nitrophenylhydrazone*, orange-yellow, rhombic plates from acetic acid, m. p. 185° (Found : Br, 37·7. $C_{14}H_9O_3N_3Br_2$ requires Br, 37·5%).

Action of Excess of Bromine upon Phenylglyoxal-o-*nitrophenylhydrazone*-ω-*sulphonic Acid. Formation of* ω-*Bromophenylglyoxal*-4-*bromo*-2-*nitrophenylhydrazone.*—6 G. of bromine in 5 c.c. of acetic acid were added to a solution of 3 g. of phenylglyoxal-*o*-nitrophenylhydrazone-ω-sulphonic acid in 50 c.c. of boiling acetic acid, and the solution was refluxed over-night. On careful addition of water to the resulting solution the above compound separated as an orange-yellow solid, which on crystallisation was shown to be identical with the compound obtained by the action of 1 mol. of bromine upon phenylglyoxal-4-bromo-2-nitrophenylhydrazone-ω-sulphonic acid.

Action of Chlorine upon Phenylglyoxalphenylhydrazone-ω-sulphonic Acid.—(I) *Formation of ω-chlorophenylglyoxal*-p-*chlorophenylhydrazone.* 5 G. of phenylglyoxalphenylhydrazone-ω-sulphonic acid were dissolved in 20 c.c. of cold acetic acid and a slow stream of chlorine was passed for 5 minutes. On addition of water the above *compound* separated as a pale yellow solid. It crystallised from alcohol in colourless, long, slender prisms, m. p. 133° (Found : Cl, 24·5. $C_{14}H_{10}ON_2Cl_2$ requires Cl, 24·2%). This compound was also obtained by the action of chlorine upon phenylglyoxal-*p*-chlorophenylhydrazone-ω-sulphonic acid under similar conditions.

(II) *Formation of ω-chlorophenylglyoxal*-2 : 4-*dichlorophenylhydrazone.* A rapid stream of chlorine was passed through a solution of 5 g. of phenylglyoxalphenylhydrazone-ω-sulphonic acid in 20 c.c. of hot acetic acid for 15 minutes. On addition of water the above *compound* separated as a yellow solid. It crystallised from alcohol in colourless, hair-like prisms, m. p. 106° (Found : Cl, 32·3. $C_{14}H_9ON_2Cl_3$ requires Cl, 32·5%). This compound was also obtained by the action of chlorine upon phenylglyoxal-*p*-chlorophenylhydrazone-ω-sulphonic acid and upon phenylglyoxal-2 : 4-dichlorophenylhydrazone-ω-sulphonic acid under similar conditions.

Action of Chlorine upon Phenylglyoxal-2 : 4 : 6-*trichlorophenylhydrazone-ω-sulphonic Acid.*—5 G. phenylglyoxal-2 : 4 : 6-trichlorophenylhydrazone-ω-sulphonic acid were dissolved in 20 c.c. of hot glacial acetic acid and a rapid stream of chlorine was passed for 15 minutes. On addition of water *ω-chlorophenylglyoxal*-2 : 4 : 6-*trichlorophenylhydrazone* was precipitated as a yellow solid. It crystallised from alcohol in colourless, long, slender prisms, m. p. 119° (Found : Cl, 39·3. $C_{14}H_8ON_2Cl_4$ requires Cl, 39·2%).

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