CXXXVIII.—*The Reactions of Nitrosulphonyl Chlorides. Part I. The Reaction of Hydrazine Hydrate with* o-*Nitrosulphonyl Chlorides.*

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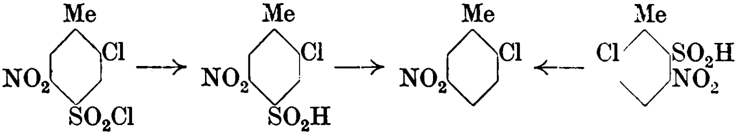
The reaction between hydrazine hydrate and 2-chloro-5-nitro-*p*-toluenesulphonyl chloride (I) in the cold gives the primary *hydrazide* R·SO$_2$·NH·NH$_2$, but from the warm mixture more than 90% of the *sulphinic acid* and the theoretical quantity of nitrogen required by the equation $2R{\cdot}SO_2Cl + 2NH_2{\cdot}NH_2,H_2O = 2R{\cdot}SO_2H + N_2 + 2H_2O + NH_2{\cdot}NH_2,2HCl$ are obtained. The hydrazide decomposes in the presence of hot aqueous hydrazine or dilute hydrochloric acid to form the sulphinic acid and the theoretical quantity of nitrogen.

It is known (Curtius and Lorenzen, *J. pr. Chem.*, 1898, **58**, 166) that benzenesulphonhydrazide is decomposed by boiling water or aqueous alkali, benzenesulphinic acid and other organic substances being produced. As there is no evidence of ring formation with *o*-nitrobenzenesulphonhydrazides, the almost quantitative production of the *o*-nitrosulphinic acid is probably due to the activating or chemical effect of the nitro-group. This influence is well shown in the properties of the *o*-nitrosulphinic acids themselves. *2-Chloro-5-nitro-*p*-toluenesulphinic acid* (II) has been kept almost unchanged for 7 years at room temperature. In hot pyridine (and in other hot solvents), however, it loses sulphur dioxide with the production of 2-chloro-5-nitrotoluene (IV) in 77% yield; under these conditions, naphthalene-β-sulphinic acid gives but 6·2% of naphthalene, and the chlorobenzene produced from *p*-chlorobenzenesulphinic acid can be detected only by its odour. 6-Chloro-3-nitro-*o*-toluenesulphinic acid (III) is so unstable that attempts to prepare it always result in the formation of (IV) in good yield (65%). *o*-Nitrobenzenesulphinic acid is of the same order of stability as (II).

m- and *p*-Nitrosulphinic acids are produced with much more difficulty than the *o*-isomeride by the action of hydrazine hydrate on the sulphonyl chloride; the difference is sufficiently great to enable an easy separation of at least one *o*-nitrosulphonyl chloride (as the sulphinic acid) from its position isomerides to be effected.



(I.) (II.) (IV.) (III.)

The product obtained by the addition of *o*- or *p*-nitrobenzoyl chloride to hydrazine hydrate contains both the primary and the secondary hydrazide; when the order of addition is reversed, the secondary hydrazide alone is formed (compare Naegli and Stefanovitsch, *Helv. Chim. Acta*, 1928, **11**, 636). In contrast with this behaviour, nitrosulphonyl chlorides have never in our experience given a secondary nitrosulphonhydrazide by direct reaction with hydrazine hydrate. Curtius and Lorenzen (*loc. cit.*), however, who dissolved their benzenesulphonyl chloride in alcohol, allude to the direct production of the secondary benzenesulphonhydrazide. It is evident that the presence of the nitro-group in the molecule makes both the nitrosulphonyl chlorides and the nitrosulphinic acids anomalous, and the study of the properties of these substances is being continued.

EXPERIMENTAL.

The preparation of 2-chloro-5-nitro-*p*-toluenesulphonyl chloride (I) (Davies, J., 1921, **119**, 860) is much simplified by the direct nitration of the crude undistilled monochlorination product from *p*-toluenesulphonyl chloride. The nitration mixture is washed with water and the mixture of sulphonyl chlorides is dried and crystallised from petroleum (b. p. 80—100°), the yield of (I) being 65% by weight of the original *p*-toluenesulphonyl chloride.

*Reaction between 2-Chloro-5-nitro-*p*-toluenesulphonyl Chloride and Hydrazine Hydrate.*—(I) *The sulphonyl chloride added to the hydrazine hydrate.* A solution of the sulphonyl chloride (21·6 g., 1 mol.) in benzene (30 c.c.) is added during 10 minutes to hydrazine hydrate (10 g. of 100%, 2¼ mols.) in absolute alcohol (40 c.c.) with thorough shaking and intermittent cooling, but the temperature is allowed to reach 40°; a brisk evolution of nitrogen then occurs. After 4 hours, the precipitate of sulphinic acid is collected, stirred with cold dilute hydrochloric acid (60 c.c.), dissolved in dilute sodium hydroxide solution, and recovered (16·5 g., 87·6% yield), m. p. 129—131°.

(2) *The hydrazine hydrate added to the sulphonyl chloride.* The sulphonyl chloride (20 g.) is dissolved in ether or benzene (70 c.c.), and the hydrazine hydrate (without solvent) added in the cold. The precipitate is collected and heated with a little water, and the sulphinic acid purified as described above. Yield, 17 g. (97·5%); m. p. 125—128°.

Estimation of the nitrogen produced in the reaction. The sulphonyl chloride (0·4091 g.) in about 3 c.c. of benzene was mixed with 0·17 c.c. of hydrazine hydrate and 2 c.c. of alcohol and warmed, the usual apparatus, consisting of a small flask, a small tube, and a nitrometer, being employed. 17·61 C.c. of nitrogen (measured at 17° and 756 mm.) were obtained, corresponding to 0·49 mol. of nitrogen per mol. of sulphonyl chloride. In another experiment the nitrogen was shown, by sparking with oxygen, to be free from hydrogen. The product did not contain an amino-group, and ammonia was not produced in the reaction.

2-*Chloro*-5-*nitro*-p-*toluenesulphinic acid* (II) consists of very pale yellow needles, m. p. 131·5° (Found : C, 35·7; H, 2·8; N, 5·95, 6·05, 6·1; Cl, 15·4; equiv., 238·8; *M*, cryoscopic in phenol, 215, 219. $C_7H_6O_4NClS$ requires C, 35·6; H, 2·5; N, 6·0; Cl, 15·1%; *M* and equiv., 235·5). It is very soluble in the common organic solvents except light petroleum, readily soluble in hot and sparingly soluble in cold water, from which it is almost entirely precipitated by the addition of concentrated hydrochloric acid. When the sulphinic acid (10 g.) is heated with pyridine (50 c.c.) on the water-bath for 50 hours, and the product diluted with water, 2-chloro-5-nitrotoluene (m. p. 44°; 5·0 g.) is obtained; the yield is increased to 5·6 g. (77%) by steam distillation after acidification of the filtrate (Found: C, 49·2; H, 3·4. Calc.: C, 48·9; H, 3·6%).

2-*Chloro*-5-*nitro*-p-*tolylmethylsulphone* is made from the sulphinic acid in small yield by methylation with methyl sulphate and sodium hydroxide, but in 50% yield together with only a small quantity of 2-chloro-5-nitrotoluene by shaking in the cold a suspension of the silver salt in methyl alcohol–methyl iodide for several hours. It separates from alcohol in colourless needles, m. p. 145—146°, and is extremely stable and difficult to oxidise completely either in a combustion tube or with nitric acid (Found: C, 37·9; H, 3·3; N, 5·7, 5·8. $C_8H_8O_4NClS$ requires C, 38·5; H, 3·2; N, 5·6%).

o-Nitrobenzenesulphinic acid is produced in 80% yield by method (1) above, the temperature being allowed to reach 60°; it is extracted from the hydrochloric acid solution with ether and obtained in thick, light yellow crystals, m. p. 138—139° (Claasz, *Annalen*, 1911, **380**, 311, gives m. p. 134°). The silver salt and methyl-alcoholic methyl iodide give the sulphone, m. p. 105° (compare Claasz, *Ber.*, 1912, **45**, 1020, 1023).

The Production of Nitrosulphonhydrazides.—2-*Chloro*-5-*nitro*-p-*toluenesulphonhydrazide*. A solution of the corresponding sulphonyl chloride (21·6 g.; 1 mol.) in benzene (65 c.c.) at 0° is very slowly added with stirring to hydrazine hydrate (10 g.; 2¼ mols.) in absolute alcohol (50 c.c.) in a freezing mixture, the temperature being kept below 3°. After ½ hour, the precipitate is collected, washed with alcohol, well stirred with cold water until it is free from chloride, and dried in a vacuum over phosphoric oxide (yield, 20·8 g., 98%). The *sulphonhydrazide* forms colourless felted needles, m. p. 110—113° with brisk effervescence (Found: N, 15·95, 15·8. $C_7H_8O_4N_3ClS$ requires N, 15·8%). It is soluble in dilute acids and alkalis, practically insoluble in cold water and cold alcohol, slightly soluble in hot alcohol. It is unstable to heat, especially in hydroxylic solvents, but can be recrystallised by adding it to boiling methyl alcohol and rapidly decanting or filtering the solution into a cold vessel.

In hot alcoholic solution the hydrazide reacts with salicylaldehyde and cinnamaldehyde to form salicylidene- and cinnamylidene-azine, m. p. 216° and 166°, respectively. There is, however, evidence of the formation of the sulphonhydrazones, but these compounds are difficult to obtain pure when made in this medium. A warm anisole solution of the hydrazide and cinnamaldehyde give *cinnamaldehyde*-

2-*chloro*-5-*nitro*-p-*toluenesulphonhydrazone*, dark red leaves, m. p. 95°. The melting point rises with keeping (Found : N, 11·4, 11·3. $C_{16}H_{14}O_4N_3ClS$ requires N, 11·1%). The formation of this hydrazone, the fact that the hydrazide cannot be obtained pure from methyl alcohol rich in acetone, and the reduction of Fehling's solution in the cold all indicate that the constitution of the hydrazide is normal.

o-*Nitrobenzenesulphonhydrazide* is relatively unstable. The temperature should be kept below 0° during its preparation, and the sulphonhydrazide, which is fairly readily soluble in water, should be washed with sodium acetate solution. In this way almost colourless prisms, m. p. 101° (decomp.), are obtained in 82% yield (Found : N, 19·0. $C_6H_7O_4N_3S$ requires N, 19·35%). Claasz (*Ber.*, 1911, **44**, 1417) obtained from the action of aqueous alkali and hydrazine on *o*-nitrobenzenesulphonyl chloride exclusively potassium *o*-nitrobenzenesulphonate and azimidol.

6-*Chloro*-4-*nitro*-o-*toluenesulphonhydrazide*, colourless needles, m. p. 127°, and 2-*chloro*-6-*nitro*-p-*toluenesulphonhydrazide*, m. p. 125°, plates, moderately easily soluble in cold alcohol, are both prepared in the usual way in excellent yield (Found respectively : N, 16·0, 16·0. $C_7H_8O_4N_3ClS$ requires N, 15·8%).

The Action of o-*Nitrobenzoyl Chloride on Hydrazine Hydrate*.—*o*-Nitrobenzoyl chloride (9·3 g., 1 mol.), dissolved in benzene (25 c.c.), is slowly added with vigorous stirring to hydrazine hydrate (5·1 g., 2 mols.) in benzene (30 c.c.). The precipitate is collected when cold and extracted twice with boiling water (50 c.c.), from which *o*-nitrobenzoylhydrazide (1·3 g.), identified by comparison with an authentic specimen, crystallises on cooling. The precipitate insoluble in water crystallises from nitrobenzene in minute needles (m. p. 298°, 5·8 g.), which become brown on prolonged exposure to light (Found : C, 50·8; H, 3·1; N, 17·4. Calc. for $C_{14}H_{10}O_6N_4$: C, 50·9; H, 3·0; N, 17·0%). This *NN'*-di-*o*-nitrobenzoylhydrazine is recognised as such by its inertness to cold Fehling's solution and by its inability to form hydrazones. It is undoubtedly the substance (m. p. higher than 250°) prepared from the *o*-nitrobenzoylhydrazone of acetoacetic ester (Beilstein, "Organische Chemie," IVth edition, vol. IX, p. 375).

p-Nitrobenzoyl chloride, similarly treated, gives 3·5 g. of *p*-nitrobenzoylhydrazide, m. p. 217°, sparingly soluble in boiling water and crystallising from alcohol in minute, pale yellow needles. *Benzaldehyde*-p-*nitrobenzoylhydrazone* is almost insoluble in cold alcohol, and its formation in alcoholic solution is a delicate test for benzaldehyde: one drop of benzaldehyde added to a hot alcoholic solution of the hydrazide yields a copious precipitate of very faintly yellow needles, m. p. 259° (Found : C, 62·9; H, 3·9. $C_{14}H_{11}O_3N_3$ requires C, 62·4; H, 4·1%).

NN′-*Di*-p-*nitrobenzoylhydrazine* (4·0 g.) crystallises from nitrobenzene in very pale yellow needles, m. p. 291° (Found : C, 50·4; H, 3·3%). It forms a very sparingly soluble scarlet salt.

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