

LXXXV.—*The Reactions of Nitrosulphonyl Chlorides*
Part II. The Separation of Nitrosulphonyl Chlorides
by Means of Hydrazine Hydrate.

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DANN and DAVIES (J., 1929, 1050) have found that the difference in reactivity of the nitrosulphonyl chlorides towards hydrazine hydrate at different temperatures ($R\cdot SO_2Cl + NH_2\cdot NH_2, H_2O \longrightarrow R\cdot SO_2\cdot NH\cdot NH_2 \longrightarrow R\cdot SO_2H$) is sufficient to enable a separation of isomeric nitrosulphonyl chlorides to be effected. Thus from a mixture of 2-chloro-5-nitro-*p*-toluenesulphonyl chloride and its 6-nitro-isomeride, by the action of hydrazine hydrate at 60°, were obtained 2-chloro-5-nitro-*p*-toluenesulphonic acid (74% yield) and 2-chloro-6-nitro-*p*-toluenesulphonhydrazide (55%). This method of separation has been successfully applied in the case of the three nitrobenzenesulphonyl chlorides; each pair of chlorides, and a mixture of the three isomerides, being separable into compounds which can be converted into the component chlorides. Thus hydrazine hydrate reacted at 35° with a mixture of *o*- and *p*-nitrobenzenesulphonyl chlorides to give *o*-nitrobenzenesulphonic acid (soluble in sodium acetate solution and converted by chlorine into the sulphonyl chloride) and *p*-nitrobenzenesulphonhydrazide (insoluble), which can be chlorinated in alcohol-chloroform to give *p*-nitrobenzenesulphonyl chloride. The *o*- and *m*-nitrobenzenesulphonyl chlorides are separated at 50°, and the *m*- and *p*-chlorides at 55°. In the case of a mixture of the three nitrobenzenesulphonyl chlorides, the temperature was kept at 30—35°; the *o*-isomeride was then removed as sulphonic acid, and the resulting mixture of *m*- and *p*-nitrobenzenesulphonhydrazides treated as in the separation of the *m*- and *p*-chlorides outlined above.

In the *Annual Reports* (1929, 140) Dr. Bennett refers to the work done by Dann and Davies on "dinitrobenzenesulphonyl chloride." This compound was not mentioned in Part I of this work (*loc. cit.*), although the statement that it is an example of the "positive" reactivity of the halogen, *i.e.*, of the chlorine atom in the SO_2Cl group, is correct. 2:4-Dinitrobenzenesulphonhydrazide is described below. It is also worth noting that the order of stability of the nitrobenzenesulphonhydrazides is shown by the method of separation to be $m > p > o$, illustrating the influence of the nitro-group on the stability of the sulphonhydrazide group.

The nitrobenzenesulphonhydrazides, and especially *m*-nitrobenzenesulphonhydrazide, form easily crystallised, high-melting

hydrazones with aldehydes and ketones, and can be utilised in the isolation and identification of such compounds.

2 : 4-Dinitrobenzenesulphonhydrazide decomposes in boiling water to give *m*-dinitrobenzene, and illustrates a possible method of removing the sulphonic acid group from a benzene nucleus suitably activated.

Sprung (*J. Amer. Chem. Soc.*, 1930, **52**, 1653) has found that the order of reactivity of the isomeric chloronitrobenzenes towards sodium sulphite is $m > o > p$. In the preparations of *o*- and *p*-nitrobenzenesulphonyl chlorides from *o*- and *p*-chloronitrobenzenes, the latter compounds were condensed in alcoholic solution with sodium disulphide (and the resulting dinitrodiphenyl disulphides oxidised with fuming nitric acid to the sulphonic acids). Under the same reaction conditions, *m*-chloronitrobenzene did not react with sodium disulphide, and consequently the reactivities of the isomeric chloronitrobenzenes towards sodium disulphide are $o > m$, and $p > m$, these observations being in agreement with those of the Dutch school mentioned by Sprung.

EXPERIMENTAL.

o-Nitrobenzenesulphonhydrazide (Dann and Davies, *loc. cit.*) yields *acetone-o-nitrobenzenesulphonhydrazone*, small white prisms, m. p. 147—148° (decomp.) (Found : S, 12.6. $C_9H_{11}O_4N_3S$ requires S, 12.5%), and *piperonal-o-nitrobenzenesulphonhydrazone*, bright yellow flakes, m. p. 177—179° (decomp.) (Found : N, 11.9. $C_{14}H_{11}O_6N_3S$ requires N, 12.0%).

Since *o*-nitrobenzenesulphonhydrazide is unstable at the ordinary temperature, the following method had to be adopted for the preparation of these *o*-nitrobenzenesulphonhydrazones. The *o*-nitrobenzenesulphonhydrazide was prepared in ice-cold solution and washed with ice-water (approximate dry yield, 80%), the cold solid added to the aldehyde or ketone (1 mol.) in alcohol, and the whole boiled for a minute and cooled; the hydrazone then crystallised. For the *p*- and *m*-nitrobenzenesulphonhydrazones the solid hydrazide and the aldehyde or ketone were simply heated together, alone or in alcoholic solution.

p-Nitrobenzenesulphonyl chloride was prepared after Blanksma (*Rec. trav. chim.*, 1900, **19**, 111), Wohlfahrt (*J. pr. Chem.*, 1902, **66**, 553), and Bell (*J.*, 1928, 2776). Alternatively, the sulphonic acid may be isolated (m. p. 109—111°; compare Blanksma, *Rec. trav. chim.*, 1901, **20**, 121, who gives m. p. 95°) and converted by phosphorus pentachloride into the sulphonyl chloride, or the ammonium salt treated with chlorosulphonic acid.

p - Nitrobenzenesulphonhydrazide. — *p* - Nitrobenzenesulphonyl

chloride (4.43 g.; 1 mol.) in benzene (12 c.c.) was gradually added with stirring to hydrazine hydrate (1.95 c.c.; 2 mols.) in absolute alcohol (15 c.c.). The temperature was kept below 40°; no nitrogen was evolved. The product was mixed with *N*/2-sodium acetate solution (20 c.c.), the benzene removed in a stream of air, and the precipitate ground with water containing a trace of sodium acetate until free from chloride (3.7 g.); m. p. 150—152° (decomp.). It is almost insoluble in cold water, and sparingly soluble in cold alcohol. It is unchanged by rapidly effected crystallisation from alcohol, but is decomposed by boiling alcohol to give the sulphinic acid. It forms faintly yellow, compact prisms which seem colourless when powdered (Found: C, 33.2; H, 3.2. $C_6H_7O_4N_3S$ requires C, 33.2; H, 3.2%).

Acetone-p-nitrobenzenesulphonhydrazone forms small white needles, m. p. 169—171° (decomp.) (Found: N, 16.5. $C_9H_{11}O_4N_3S$ requires N, 16.3), *benzaldehyde-p-nitrobenzenesulphonhydrazone*, small glistening plates, m. p. 142—144° (decomp.) (Found: N, 13.6. $C_{13}H_{11}O_4N_3S$ requires N, 13.8%), and *piperonal-p-nitrobenzene sulphonhydrazone*, golden flakes, m. p. 189—190° (decomp.) (Found: N, 12.3. $C_{14}H_{11}O_6N_3S$ requires N, 12.0%).

m-Nitrobenzenesulphonhydrazide was similarly prepared in more than 90% yield, and consisted of colourless prisms, m. p. 130° (decomp.). It is stable in boiling alcohol (Found: C, 33.1; H, 3.2%).

m-Nitrobenzenesulphonhydrazones of (a) acetone, small rectangular prisms, m. p. 148—150° (decomp.) (Found: S, 12.6; N, 16.7%), (b) methyl ethyl ketone, small white flakes, m. p. 124—125° (decomp.) (Found: N, 15.7. $C_{10}H_{13}O_4N_3S$ requires N, 15.5%), (c) benzaldehyde, white needles, m. p. 150—151° (decomp.) (Found: N, 13.9%), (d) piperonal, bright yellow microcrystals, m. p. 173—175° (decomp.) (Found: N, 11.8; S, 9.3. $C_{14}H_{11}O_6N_3S$ requires N, 12.0; S, 9.2%), were prepared.

2:4-Dinitrobenzenesulphonyl Chloride.—2:4-Dinitrobenzenesulphonic acid was prepared after Willgerodt and Mohr (*J. pr. Chem.*, 1886, **34**, 116) and Blanksma (*Rec. trav. chim.*, 1905, **24**, 322), and converted by phosphorus pentachloride into 2:4-dinitrobenzenesulphonyl chloride, m. p. 102° (compare Willgerodt and Mohr, *loc. cit.*, p. 123).

2:4-Dinitrobenzenesulphonhydrazide was prepared as above at —10°. It forms light yellow plates, m. p. 110° (decomp.); yield, 1.2 g. (Found: S, 12.4; *M*, 263.5. $C_6H_6O_6N_4S$ requires S, 12.2%; *M*, 262). It is practically insoluble in cold water and in cold alcohol, but is soluble in ether. It is very unstable to heat, evolving nitrogen.

2:4-Dinitrobenzenesulphinic Acid.—If 2:4-dinitrobenzene-

sulphonhydrazide is heated with aqueous hydrazine or with dilute hydrochloric acid, a brisk evolution of nitrogen occurs, and 2:4-dinitrobenzenesulphinic acid is precipitated from the solution by the addition of concentrated hydrochloric acid. It forms white tufts, m. p. 196° (Found: S, 13.2; M, 243. Calc. for $C_6H_4O_6N_2S$: S, 13.8%; M, 232. Calc. for $C_6H_4O_6N_2S, \frac{1}{2}H_2O$: S, 13.3%; M, 241).

By boiling either 2:4-dinitrobenzenesulphonhydrazide or the sulphinic acid in aqueous solution, a quantitative yield of *m*-dinitrobenzene was obtained.

The hydrazides, purified as above by washing with sodium acetate solution, may more conveniently be freed from hydrazine hydrochloride by simple washing with water, but the above detailed conditions approximate to those employed in separating a hydrazide from a sulphinic acid (*vide infra*). The preparation of the hydrazides is equally well effected by adding the hydrazine hydrate to the sulphonyl chloride solution (instead of vice versa), but very efficient stirring is necessary, and in separating the isomerides the former method is preferable.

Conversion of Sulphonhydrazides into Sulphonyl Chlorides.—*p*(or *m*)-Nitrobenzenesulphonhydrazide was suspended in rectified spirits and chloroform, ice added, and chlorine passed through the mixture. After a short time, the chloroform solution was separated, washed with water, dried, and allowed to evaporate. The *p*(or *m*)-nitrobenzenesulphonyl chloride crystallised in good yield. Thus 0.8 g. of the *p*-hydrazide gave 0.67 g. of the *p*-chloride, m. p. $75-77^{\circ}$; and 0.5 g. of the *m*-hydrazide gave 0.45 g. of the *m*-chloride, m. p. $59-60^{\circ}$.

Separation of o- and p-Nitrobenzenesulphonyl Chlorides.—A mixture of *o*- and *p*-nitrobenzenesulphonyl chlorides (3 g. of each) in benzene (12 c.c.) was slowly added with mechanical stirring to hydrazine hydrate (3 c.c.) in absolute alcohol (12 c.c.) cooled in ice. After a short time, the temperature of the water-bath was raised to and maintained at 35° till effervescence ceased. The reaction mixture was cooled, *N*/2-sodium acetate solution (35 c.c.) added, the mixture stirred, the liquid filtered, and the precipitate washed with ice-water till free from chloride. The dry *p*-nitrobenzenesulphonhydrazide (2.4 g.) had m. p. $145-147^{\circ}$. Chlorinated as above, it gave *p*-nitrobenzenesulphonyl chloride (1.8 g.), m. p. $75-77^{\circ}$. Recrystallised from benzene-light petroleum (b. p. $40-60^{\circ}$), this had m. p. $77-79^{\circ}$, mixed m. p. with pure chloride, $78-79^{\circ}$; the sulphonamide obtained from it had m. p. 177° .

The sodium acetate solution containing the *o*-nitrobenzenesulphinic acid was separated from the benzene, dilute hydrochloric acid, rectified spirits, and chloroform were added, and chlorine was

passed through the liquid. The chloroform solution was separated, washed with water, and dried, and the *o*-nitrobenzenesulphonyl chloride (2.2 g.) crystallised; m. p. 63—65°. Recrystallised, it had m. p. 66—68° and mixed m. p. 67—68°; the sulphonamide had m. p. 189—190°.

Separation of o- and m-Nitrobenzenesulphonyl Chlorides.—*o*- and *m*-Nitrobenzenesulphonyl chlorides (3 g. of each) in benzene (12 c.c.) were added to hydrazine hydrate (3 c.c.) in absolute alcohol as above. The temperature of the bath was kept below 50° till effervescence ceased; the reaction mixture was then treated as above. The resulting *m*-nitrobenzenesulphonhydrazide (2.4 g.) had m. p. 124—126°. Chlorination gave *m*-nitrobenzenesulphonyl chloride (1.6 g.), m. p. 59—62°, rising to 60—62° on crystallisation. The acetate extract was treated as in the above separation; the *o*-nitrobenzenesulphonyl chloride (1.7 g.), m. p. 65—66°, resulted (purified, it had m. p. 66—67°).

Separation of m- and p-Nitrobenzenesulphonyl Chlorides.—The sulphonyl chlorides (3 g. of each) in benzene (12 c.c.) were added as above to hydrazine hydrate (3 c.c.) in absolute alcohol (10 c.c.), and in this case the temperature of the bath was kept at 55° till decomposition ceased. The cooled mixture was treated with acetate solution as before, and the washed *m*-nitrobenzenesulphonhydrazide (m. p. 125—127°, decomp.; 2.5 g.) chlorinated as above, giving *m*-nitrobenzenesulphonyl chloride, m. p. 58—60°. Chlorination of the acidified acetate extract gave *p*-nitrobenzenesulphonyl chloride, m. p. 78—79° (1.6 g.).

Separation of o-, m-, and p-Nitrobenzenesulphonyl Chlorides.—A mixture of *o*-, *m*-, and *p*-nitrobenzenesulphonyl chlorides (3 g. of each) in benzene (15 c.c.) was added slowly with stirring to hydrazine hydrate (4.5 c.c.) in absolute alcohol (12 c.c.), well cooled. After 30 minutes, the temperature of the bath was raised and maintained at 30—35° till effervescence ceased. The reaction mixture was cooled and *N*/2-sodium acetate solution (35 c.c.) added, the whole stirred, the liquid filtered, and the precipitate washed with ice-water. The acidified filtrate was chlorinated, giving *o*-nitrobenzenesulphonyl chloride (2.1 g.), m. p. 64—67°. The mixture of *p*- and *m*-nitrobenzenesulphonhydrazides was left over-night to dry in a gentle heat, and then stirred with benzene (10 c.c.), absolute alcohol (10 c.c.), and hydrazine hydrate (1 c.c.) at 40—45° till effervescence ceased. From this reaction mixture were obtained in the usual manner, *p*-nitrobenzenesulphonyl chloride (1.2 g.), m. p. 78—79°, and *m*-nitrobenzenesulphonyl chloride (1.4 g.), m. p. 57—59°.

In the above separations the sulphinic acids formed may be separated and identified, but this is not necessary, and the direct

conversion into the sulphonyl chlorides prevents loss of some of the product. The use of aqueous solutions of hydrazine hydrate alters the temperature conditions required for the above separations, and it is advisable to use 100% hydrazine hydrate.

Separation of 2-Chloro-5-nitro-p-toluenesulphinic Acid from a Mixture of 2-Chloro-5-nitro-p-toluenesulphonyl Chloride and 2-Chloro-6-nitro-p-toluenesulphonyl Chloride.—2-Chloro-5-nitro-p-toluenesulphonyl chloride (6.8 g.) and the 6-nitro-isomeride (5.0 g.) were mixed (11.8 g.; 1 mol.) in benzene (16 c.c.), and the solution gradually added to hydrazine hydrate (5.3 c.c.) in absolute alcohol (25 c.c.). The temperature was maintained at 40–55° during the reaction, and then raised to 60°. After cooling, 2*N*-sodium acetate (20 c.c.) was added, and the benzene and some of the alcohol were removed in a stream of air. The precipitate was ground and washed with water containing a little sodium acetate. The 2-chloro-6-nitro-p-toluenesulphonhydrazide produced had m. p. 121–124°, mixed m. p. with pure hydrazide, 123–125° (yield, 2.7 g. = 55%).

The filtrate was strongly acidified with hydrochloric acid, and the 2-chloro-5-nitro-p-toluenesulphinic acid collected next day; m. p. 126–129°. Purification by solution in alkali and precipitation with acid gave the pure sulphinic acid, m. p. 130–131° (yield, 4.4 g. = 74%).

Note.—Since the completion of this paper, there has appeared the pamphlet "Nitro-benzolsulphonhydraziden" by A. A. M. Witte. This thesis contains a description of some *o*-, *m*-, and *p*-nitrobenzenesulphonhydrazones of aldehydes and ketones. In general there is agreement (to $\pm 4^\circ$) between Witte and us on the melting points of these derivatives, but in some cases his analyses are not quite satisfactory. For example, benzaldehyde-*p*-nitrobenzenesulphonhydrazone, m. p. (Witte) 142°, (D., S. and T.) 142–144° (decomp.); N estimation, (Witte) 13.11, (D., S. and T.) 13.55. Theory requires 13.77%. Again, for acetone-*m*-nitrobenzenesulphonhydrazone, Witte gives m. p. 153° (decomp.) and N, 16.86. We give m. p. 148–150° (decomp.) and N, 16.69; S, 12.57. Theory requires N, 16.34; S, 12.45%.

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