

**33.** *The Replacement of the Diazonium by the Nitro-group. Part II. Extension of the Method to Nitronaphthylamines, Benzidine, and 3 : 3'-Dichlorobenzidine.*

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Variations of procedure in Hodgson and Marsden's method (Part I, *J.*, 1944, 22) are described for working *in situ* and for avoidance of diazo-oxide formation as with, *e.g.*, 2-nitro-1-naphthylamine. The preparations of 4 : 4'-dinitrodiphenyl and 3 : 3'-dichloro-4 : 4'-dinitrodiphenyl are given.

The general procedure of Part I has been improved. Where it is convenient to retain the cobaltinitrite *in situ* before decomposition, the diazotisation is carried out in sulphuric acid, and in many cases by Hodgson and Walker's method (*J.*, 1933, 1620), since if chlorides are present the Sandmeyer reaction might partly occur and the final product be contaminated with a difficultly removable chloro-compound. Where the diazotised amine forms a diazo-oxide in weak acid or neutral medium, the acid solution of the diazonium salt is diluted and added rapidly to an excess of aqueous sodium cobaltinitrite at 0°, which first neutralises the acid and then forms the required complex. If formation of some diazo-oxide is unavoidable, it is readily removed from the complex by digestion with ether. Hot decompositions of the complexes occur in *ca.* 10—15 minutes at 60°, but the product is sometimes impure, and when it is of low m. p. (< 120°) there is considerable tar formation, *e.g.*, in the preparation of  $\beta$ -nitronaphthalene

The cobaltinitrite procedure has afforded a small yield (5%) of 1:2-dinitronaphthalene from 2-nitro-1-naphthylamine. Benzidine and 3:3'-dichlorobenzidine afforded 4:4'-dinitrodiphenyl and 3:3'-dichloro-4:4'-dinitrodiphenyl, respectively, in yields of ca. 40% and 65%. Tetrazotised *m*- and *p*-phenylenediamines did not behave normally towards sodium cobaltinitrite.

## EXPERIMENTAL.

*General Procedure.*—The amine (0.05 g.-mol.), finely powdered if solid, is dissolved in a hot mixture of hydrochloric acid (20 c.c., *d*, 1.18) and water (30 c.c.), the solution chilled rapidly to obtain a finely divided precipitate of hydrochloride or free base, and the mixture cooled to below 0°; a solution of sodium nitrite (4 g.) in water (20 c.c.) is then added rapidly with vigorous stirring (total volume 100 c.c.). The filtered solution is next stirred into a mixture of chalk, ice, and a little ether (to abate frothing), and filtered at the pump into a mixture of sodium cobaltinitrite (8 g.) and water (40 c.c.) contained in the filter-flask which is gently shaken during the filtration. The formation of the precipitate of aryldiazonium cobaltinitrite is complete in about 10–15 minutes; it is then filtered off, washed with water, pressed on the filter, and washed with ether to remove any diazo-oxide from the precipitate. When freshly formed, the aromatic diazonium cobaltinitrites are bright yellow, generally insoluble in water and in ether; they are obtained in good yield (generally nearly quantitative), but vary in stability even in successive preparations, for they always darken, sometimes rapidly, in the air, and cannot be stored for long, even in the dark. They are decomposed forthwith by either a hot or a cold procedure.

*Decomposition.*—(a) The moist complex is made into a slurry with water (30 c.c.) which is gradually but vigorously stirred into a mixture of sodium nitrite (15 g.), crystallised copper sulphate (15 g.), cuprous oxide (6 g.), and water (60 c.c.) at 60–70°; decomposition is complete in about 15 minutes, and the solid is removed, washed successively with water, dilute cold sodium carbonate, and water, dried, and then either extracted with a suitable solvent or steam-distilled. The products removed by solvents are usually coloured owing to the presence of traces of azo-compounds, but they can usually be purified by dissolution in sulphuric-glacial acetic acid containing a trace of nitric acid, and reprecipitation by pouring on ice and recrystallisation.

(b) The complex is stirred in the cold for 24 hours, and the solid extracted by a suitable solvent or steam-distilled. The amount of tarry matter formed is less than in method (a), so the cold procedure appears to be preferable with complexes which yield nitro-compounds melting below 120°. Filtration after diazotisation and before neutralisation, helps filtration after neutralisation and also helps to remove substances which appear to catalyse the decomposition of the complex; the latter should be removed from the solution in which it is formed as rapidly as possible since decomposition is facilitated in this medium.

*Examples of some monoamines.*

Amine diazotised.	Product.	Yield, %, calc. on amine.	
		Method (a).	Method (b).
2-Naphthylamine	2-Nitronaphthalene	45	—
4-Bromo-1-naphthylamine	4-Bromo-1-nitronaphthalene	—	10
2:4-Dibromo-1-naphthylamine	2:4-Dibromo-1-nitronaphthalene	—	2
2-Nitro-1-naphthylamine	1:2-Dinitronaphthalene	5	5
1-Nitro-2-naphthylamine	1:2-Dinitronaphthalene *	Traces	Traces
4-Nitro-1-naphthylamine	1:4-Dinitronaphthalene	15	30
5-Nitro-1-naphthylamine	1:5-Dinitronaphthalene	30	—
5-Nitro-2-naphthylamine	1:6-Dinitronaphthalene	—	40
6-Nitro-2-naphthylamine	2:6-Dinitronaphthalene	40	50
8-Nitro-2-naphthylamine	1:7-Dinitronaphthalene	45	40

\* Cf. Veselý and Dvorák (*Bull. Soc. chim.*, 1923, **33**, 319), who failed to obtain this compound.

2-Nitro-1- and 1-nitro-2-naphthylamine were diazotised by Hodgson and Walker's method (*loc. cit.*) and the diluted, filtered solution treated with a large excess of sodium cobaltinitrite.

2:4-Dibromo-1-nitronaphthalene crystallised from methyl or aqueous methyl alcohol in sandy microparallelepiped, *m. p.* 102° (Found: N, 4.4.  $C_{10}H_5O_2NBr_2$  requires N, 4.2%), which were slightly volatile in steam, and dissolved in boiling aqueous alkali to give a yellow solution.

*Examples of Some Diamines.*—*Benzidine.* The dihydrochloride (7 g.) was stirred into a solution of hydrochloric acid (8 c.c., *d*, 1.18) and water (40 c.c.) and tetrazotised by addition of sodium nitrite (5 g.) in a little water below 8°; the mixture was neutralised with calcium carbonate as before, filtered, and the filtrate poured on sodium cobaltinitrite (8 g.) dissolved in iced water; the yield of the brilliant yellow complex was 11.5 g., *i.e.*, almost quantitative. The decomposition product obtained as above from the complex (5 g.) was washed repeatedly with water and cold sodium carbonate solution, and then boiled with 15% aqueous hydrochloric acid to remove copper salts, after which it was crystallised from boiling glacial acetic acid; yield of 4:4'-dinitrodiphenyl, ca. 20% (method a) and ca. 40% (method b); *m. p.* 233–235° (Willstätter and Kalb, *Ber.*, 1906, **39**, 3478, give *m. p.* 234–235°). The cobaltinitrite complex remained unaffected after two weeks' exposure to the air in daylight.

3:3'-Dichlorobenzidine. This compound (5 g.) was dissolved in a mixture of hydrochloric acid (10 c.c., *d* 1.18) and water (30 c.c.), the solution chilled rapidly, and treated below 5° with sodium nitrite (4 g.) in a little water; after neutralisation as before, the filtered solution of the tetrazo-compound was stirred with sodium cobaltinitrite (7 g.) in iced water. The yellow-orange complex (9.7 g.) was formed gradually (15 minutes) and, when removed, darkened only slightly on the surface when kept in air for 3 days. The complex (5 g.) was stirred into a cold solution of crystallised copper sulphate (8 g.) and sodium nitrite (5 g.) containing red cuprous oxide (2 g.) in suspension, decomposition being very vigorous

during the first 5 minutes with considerable frothing; the mixture was subsequently stirred for 24 hours. The **3**: 3'-dichloro-4 : 4'-dinitrodiphenyl formed (2.1 g.) was isolated as above; it crystallised three times from boiling glacial acetic acid as cream micro-needles, m. p. 226—230° (Found : N, 7.1.  $C_{12}H_6O_4N_2Cl_2$  requires N, 6.9%).

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