304. *The Replacement of the Diazonium by the Nitro-Group. Part IV. Decompositions involving Neutral Solutions of Diazonium Salts, with Facile Preparations of* o- *and* p-*Dinitrobenzene.*

By Herbert H. Hodgson, Fred Heyworth, and Edward R. Ward.

The neutralised solutions of the diazonium salts from 13 amines have been caused to react with sodium nitrite in the presence of either cuprous oxide and copper sulphate or cupro-cupri sulphite. Yields of nitro-compounds have been obtained which compare favourably with those from methods earlier than the cobaltinitrite method (cf. Parts I and II), and are greatest when a nitro-group is already present in the initial amine. No catalysts are necessary with diazotised *o*- and *p*-nitroaniline, where the diazonium group is replaced by the nitro-group to the extent of 70 and 76% respectively.

A NEW method for the production of nitro-compounds, here described, is based on the reaction of a neutral aqueous solution of a diazonium salt with sodium nitrite in the presence of catalysts such as a mixture of cuprous oxide and cupric sulphate or the so-called cupro-cupri sulphite prepared by mixing equivalent aqueous solutions of cupric sulphate and sodium sulphite. The method is most useful when the reaction product is steam-volatile, but the yields, though usually moderate, compare favourably with those obtained by methods earlier than that described in Part I (Hodgson and Marsden, *J.*, 1944, 22). Neutral aqueous *o*- and *p*-nitrobenzenediazonium sulphate react with sodium nitrite without catalysts, and the yields of *o*- and *p*-dinitrobenzene are unaffected when catalysts are used. The mechanism of the reaction is probably the same as that proposed by Hodgson and Ward (this vol., p. 556) for the reaction of alkaline solutions of diazo-compounds with sodium nitrite. The yields of *o*- and *p*-dinitrobenzenes are 70 and 76% respectively, and compare favourably with the 33—38% and 67—82% respectively recorded by Starkey (*Org. Synth.*, **1939**, **19**, 41).

The presence of magnesium, nickel, manganese, copper, aluminium, or zinc sulphate, or of disodium hydrogen phosphate, does not significantly improve the yield, the buffering effect of the salt being largely masked by the large excess of sodium nitrite which keeps the pH of the medium almost neutral.

The best yields are obtained with nitro-amines, indicating that ease of replacement of the diazonium by the nitro-group accompanies greater positivity of the significant carbon atom to which the diazonium group is attached (Hodgson, Leigh, and G. Turner, *J.*, 1942, 744).

In certain cases, *e.g.*, *m*-nitro-*p*-toluidine and *p*-toluidine, the decomposition begins with considerable evolution of nitrous fumes, and the first product to come over during the subsequent steam distillation is one arising from deamination, *e.g.*, *m*-nitrotoluene (ca. 15%) from *m*-nitro-*p*-toluidine, which in this particular case acts as a solvent for the 3 : 4-dinitrotoluene which follows it.

When the neutral solution of the diazonium salt cannot be prepared simply, owing to diazo-oxide formation, so that the solid diazonium sulphate has first to be made (cf. Hodgson and Mahadevan, *J.*, 1947, 325), the diazonium sulphate is sometimes insoluble or slightly soluble in the glacial acetic–sulphuric acid medium then employed, and can be removed by filtration through asbestos; *e.g.*, 4-nitro-1-naphthylamine gave a 10% yield of 4-nitro-1-naphthalenediazonium sulphate in this way.

Since the method of replacing the diazonium- by the nitro-group now given, together with those methods previously described in Parts I (*loc. cit.*), II (*J.*, 1947, 127), and III (*J.*, 1947, 1392), provide the easiest efficient techniques for this purpose, it will be convenient to review here their relative applicability. Where the amine can be diazotised in aqueous medium and where the diazonium salt is stable in neutral solution, the present method provides the simplest technique if the products so obtained are steam volatile, *e.g.*, *o*- and *p*-dinitrobenzene. Alternatively, for the above amines, the diazonium cobaltinitrite can be prepared and decomposed; seldom has difficulty been experienced in preparing the solid cobaltinitrite (as with *m*-nitro-*p*-toluidine), although the influence of steric hindrance has been indicated in Part III. For certain amines which can be diazotised in concentrated aqueous acid medium but which form diazo-oxides in neutral solution, the technique of Part II for obtaining the cobaltinitrite complex is applicable. Where the amine cannot be diazotised in aqueous medium, or where diazo-oxide formation occurs readily on neutralising the diazonium solution, the method of Part III involving the preparation of solid diazonium sulphates (Hodgson and Mahadevan, *loc. cit.*) and their subsequent decomposition by sodium nitrite–cupro-cupri sulphite can be used. This method cannot be applied, however, when difficulty is experienced in obtaining a good yield of the solid diazonium salt on solvent precipitation from nitrosylsulphuric–glacial acetic acid medium, so that, while it is excellent for preparing 1 : 2- or 1 : 4-dinitronaphthalene, it is unsatisfactory when applied to *m*-nitro-*p*-toluidine or *p*-anisidine. Only with amines which must be diazotised in concentrated acid media and whose diazonium sulphates cannot be obtained by the method of Hodgson and Mahadevan (*loc. cit.*), owing to the presence of negative groups rendering the diazonium sulphates very readily soluble in the solvent-acid medium, are suitable methods not yet available.

Since the diazonium group in alkaline and neutral media is so very susceptible towards sodium nitrite with group replacement, while in acid media free nitrous acid is very reactive, especially towards phenols (if present as in diazo-decompositions), it is desirable in all diazotisations to remove any excess of nitrous acid as a precautionary measure before subsequent work.

EXPERIMENTAL.

Preparation of o- *and* p-*Dinitrobenzene.*—*o*- or *p*-Nitroaniline (25 g.) is dissolved in a mixture of sulphuric acid (25 c.c., *d* 1·84) and water (55 c.c.), and the solution cooled to 0° with vigorous stirring to obtain a finely divided precipitate, after which crushed ice (40 g.) is introduced, followed by a solution of sodium nitrite (25 g.) in water (50 c.c.) added in one batch. The mixture is then poured on powdered calcium carbonate (50 g.) and ice, and stirred until frothing ceases, after which it is stirred portionwise into a solution of sodium nitrite (250 g.) in water (200 c.c.) at 50°, and finally heated at 70° for 10 minutes. The *o*- or *p*-dinitrobenzene so formed is steam distilled from the mixture (21·3 g. of *o*- and 23 g. of *p*-dinitrobenzene, *i.e.*, yields of 70% and 76% respectively); the m. p.s of the very pale yellow products are 117° and 173° respectively, indicating that they are pure. Further amounts may be recovered from the cold filtered steam distillate by solvent extraction (*ca.* 3—5%).

General Procedure for Other Amines.—The amine (0·05 g.-mol.) is diazotised with the minimum quantity of dilute hydrochloric or sulphuric acid either in the usual way or as for *p*-nitroaniline above should this process be necessary, and a neutral solution of the diazonium salt is obtained by addition to calcium carbonate at 0°. In the event of the instability of this neutral solution, *e.g.*, with *p*-toluidine and 4-nitro-1-naphthylamine, the neutral mixture is stirred forthwith into a hot solution of sodium nitrite (50 g.) and crystallised copper sulphate (5 g.) in water (50 c.c.) containing cuprous oxide (3 g.) in suspension. In the more stable cases, the neutralised solution is filtered, and either decomposed as above or added to a mixture of cupro-cupri sulphite prepared by addition of an aqueous solution of crystallised sodium sulphite (25 g.) to one of crystallised copper sulphate (25 g.). If the reaction product is volatile in steam, it is removed thereby, and, if not, the hot mixture is filtered from the solid product which is then dried and extracted with a suitable solvent such as ethanol and glacial acetic acid: a typical example is as follows.

Preparation of 1 : 4-*dinitronaphthalene.* 4-Nitro-1-naphthylamine (10 g.) is stirred into a mixture of hydrochloric acid (20 c.c., *d* 1·18) and water (20 c.c.); crushed ice (30 g.) is then added to reduce the temperature to 0°, and then a solution of sodium nitrite (5 g.) in the minimum quantity of water is added in one batch. When diazotisation is complete, the liquor is filtered, the filtrate stirred into calcium carbonate (10 g.), and the neutralised mixture stirred immediately into one of sodium nitrite (75 g.), cuprous oxide (10 g.), crystallised copper sulphate (15 g.), and water (100 c.c.), which is just below the boiling point. Decomposition is immediate, and, after cooling, the solids are filtered off, washed with water, dilute sodium hydroxide, and water, dried, and extracted with boiling ethanol (250 c.c.). The extract is boiled with charcoal, filtered, and concentrated; 1 : 4-dinitronaphthalene (m. p. 128—130°) then crystallises out; yield, 2·9 g. (25%). The compound is obtained pure by one crystallisation from alcohol (charcoal).

Amine diazotised.	Product.	Yield, %.	Remarks.
Aniline	Nitrobenzene	35	Small amount of diphenyl formed.
o-Nitroaniline	*o*-Dinitrobenzene	70	Volatile in steam.
p-Nitroaniline	*p*-Dinitrobenzene	76	,, ,,
m-Chloroaniline	*m*-Chloronitrobenzene	12	,, ,,
p-Chloroaniline	*p*-Chloronitrobenzene	35	,, ,,
m-Toluidine	*m*-Nitrotoluene	13	,, ,,
p-Anisidine	*p*-Nitroanisole	16	,, ,,
o-Nitro-*p*-toluidine	2 : 4-Dinitrotoluene	30	,, ,,
m-Nitro-*p*-toluidine	3 : 4-Dinitrotoluene	45	Nitrous fumes and some deamination.
β-Naphthylamine	β-Nitronaphthalene	15	
Benzidine	4 : 4′-Dinitrodiphenyl	10	Obtained by acetic acid extraction.
4-Nitro-1-naphthylamine	1 : 4-Dinitronaphthalene	25	Obtained by ethanol extraction.
5-Nitro-2-naphthylamine	1 : 6-Dinitronaphthalene	15	,, ,, ,,

The authors are indebted to the Huddersfield Education Authority for a Research Scholarship to F. H., to the Department of Scientific and Industrial Research for a Senior Research Award to E. R. W., and to Imperial Chemical Industries Ltd., Dyestuffs Division, for gifts of chemicals.

TECHNICAL COLLEGE, HUDDERSFIELD. [*Received, November 3rd,* 1947.]