

260. *The Replacement of the Diazonium by the Nitro-group. Part III. Decompositions by Cupro-cupri Sulphite.*

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Solid aryldiazonium sulphates are first prepared and their aqueous solutions decomposed by cupro-cupri sulphite suspended in saturated aqueous sodium nitrite, yields up to 65% of nitro-compound being obtained. The precipitate obtained by addition of aqueous sodium sulphite to aqueous copper sulphate appears to be more efficient than the red-violet variety hitherto used. The method is useful for the preparation of rare dinitronaphthalenes of which six examples are given.

THE solid diazonium sulphates obtained by the general method of Hodgson and Mahadevan (this vol., p. 325) are readily decomposed when added either in aqueous solution or in solid form to a saturated solution of sodium nitrite containing cupro-cupri sulphite in suspension (cf. Hantzsch and Blagden, *Ber.*, 1900, **33**, 2544; Contardi, *Annali Chim. Appl.*, 1923, **7**, 13) to give excellent yields of the corresponding nitro-compounds. In particular, the method has proved to be exceedingly serviceable for obtaining the rarer dinitronaphthalenes in excellent yield and purity, and has also worked satisfactorily with benzidine, 3 : 3'-dinitrobenzidine, and 3 : 5-dinitro-*p*-toluidine. The cupro-cupri sulphite used was prepared by the addition of aqueous sodium sulphite to an equivalent amount of aqueous copper sulphate, and the greenish yellow-brown gelatinous precipitate, when washed free from excess of either component, was stirred as a slurry into the saturated aqueous sodium nitrite. So prepared, this variety of cupro-cupri sulphite appeared to be more efficient than the red-violet crystalline precipitate obtained by the addition of aqueous ammonium sulphite saturated with sulphur dioxide to warm aqueous copper sulphate and raising the temperature to 90° for 10 minutes (Mellor, "A Comprehensive Treatise on Inorganic and Theoretical Chemistry", Vol. X, pp. 273—277).

The preparation of some solid diazonium sulphates (*e.g.*, that from 3-nitro-*p*-toluidine) involves the use of minimum amounts of acetic and sulphuric acids, and for this purpose the inverted diazotisation procedure of Hodgson and Walker (*cf.* Hodgson and Turner, *J.*, 1943, 86) has been used, *viz.*, a solution of the amine in the minimum amount of concentrated sulphuric acid is treated with solid sodium nitrite and the mixture stirred into glacial acetic acid; with 3-nitro- and 3 : 5-dinitro-*p*-toluidine, the temperature could safely be allowed to reach 40° during the addition of the sodium nitrite without loss of yield of the resulting diazonium salt.

Usually, the solid diazonium sulphate, after precipitation by ether from the diazotisation medium, is dissolved in water at 0° before the cupro-cupri sulphite treatment, but it is essential first to remove admixed acid from it by washing with alcohol or ether or both. When these precautions are observed, 2-nitro-1- and 1-nitro-2-naphthylamine, which require the glacial acetic-sulphuric acid method (Hodgson and Walker, *J.*, 1933, 1620) for their diazotisation, afford the respective diazonium sulphates, the former of which readily dissolves in cold water; both form solutions which remain stable for periods of time amply sufficient for the subsequent manipulation. If, instead of first isolating the solid diazonium sulphates, the solutions of these diazonium salts as prepared by the Hodgson and Walker method (*loc. cit.*) are diluted with water and then neutralised before the cupro-cupri sulphite treatment, diazo-oxide formation occurs rapidly and no dinitronaphthalene can be obtained (*cf.* Veselý and Dvorák, *Bull. Soc. chim.*, 1923, **33**, 319, who failed to obtain 1 : 2-dinitronaphthalene from 1-nitro-2-naphthylamine from this cause).

The co-precipitation of sodium sulphate in almost anhydrous form with the solid diazonium sulphate probably accounts for the separation of the latter in a satisfactory crystalline state free from the stickiness usually encountered in the ordinary mode of diazonium salt isolation, since any water present will be bound by the sodium sulphate.

Addition of solid diazonium sulphate to the decomposition medium is not usually satisfactory, owing to formation of tar, probably because of local overheating during decomposition, while the tendency for hydroxylic by-products (phenols or naphthols as indicated by dissolution in alkalis), or small amounts of azo-compounds (as indicated by colour reactions) is enhanced.

It has been found that aryldiazonium cobaltinitrites (*cf.* Hodgson and Marsden, *J.*, 1944, 22) can be satisfactorily decomposed by adding them in aqueous suspension to the aqueous cupro-cupri sulphite-sodium nitrite mixture. Incidentally, steric hindrance appears to retard the formation of diazonium cobaltinitrites, for whereas tetrazotised 4 : 4'-dichloro-3 : 3'-diaminodiphenyl eventually affords an 85—90% yield of its tetrazonium cobaltinitrite, the formation is slow compared with that of tetrazotised benzidine.

It is of interest that the colours of 2-nitronaphthalene-1-diazonium sulphate and of 1-nitro-2-diazonium sulphate are yellow-orange and red-orange like those of the parent 2-nitro-1- and 1-nitro-2-naphthylamines.

Contardi and Mor (*Rend. Ist. Lomb. Sci. Lett.*, 1924, **57**, 646; *Annali Chim. Appl.*, *loc. cit.*), from a study of the replacement of the diazonium by the nitro-group for more than 40 different amines, conclude that the introduction of the nitro-group is facilitated when nitro-groups or halogens are present in the nucleus of the amine, and this is in accord with the viewpoint of Hodgson, Leigh, and Turner (*J.*, 1942, 744) who postulated the ease of replacement of the diazonium group to depend on the positivity of the carbon atom to which the diazonium group is attached, *viz.*, the greater the positivity, the readier the replacement by halogens or the nitro-group, and the less the positivity, the greater the proneness to attack by anionoid water with replacement of the diazonium by the hydroxyl group and formation of phenols or naphthols. The reactivity of cupri-salts for replacement of diazonium by nitro-groups as found by Contardi *et al.*, and also by Hodgson and Marsden (*loc. cit.*) for the decomposition of aryldiazonium cobaltinitrites, is evidence which supports the interpretation of the Sandmeyer reaction given by Hodgson, Birtwell, and Walker (*J.*, 1941, 770; 1942, 720).

EXPERIMENTAL.

General Decomposition Procedure as indicated by the Preparation of 1 : 4-Dinitronaphthalene.—Powdered sodium nitrite (10 g.) was stirred into sulphuric acid (50 c.c., *d* 1.84), and the mixture treated gradually below 20° (external cooling) with a solution of 4-nitro-1-naphthylamine (10 g.) in glacial acetic acid (100 c.c.), and subsequently stirred for 20 minutes. Ether (700 c.c.) was next stirred into the solution at 0°, the mixture kept for 1 hour, the crystalline precipitate (by scratching) of 4-nitronaphthalene-1-diazonium sulphate filtered off, washed free from acid with ether, and dissolved in water (100 c.c.), and the solution stirred slowly into the mixture of cupro-cupri sulphite prepared as follows. An aqueous solution of crystallised sodium sulphite (50 g.) was stirred into one of crystallised copper sulphate (50 g.), and the greenish yellow-brown precipitate filtered off, washed with water, ground into a slurry with water, and then stirred into a mixture of sodium nitrite (100 g.) in water (400

c.c.). Decomposition was very rapid (cf. Hantzsch and Blagden, *loc. cit.*), and foam was broken periodically by addition of small amounts of ether; after 1 hour's stirring, when most of the inorganic matter has passed into the dark green solution, the precipitate of crude 1 : 4-dinitronaphthalene was filtered off, washed in the sequence, water, dilute sodium hydroxide, and water, dried, and crystallised from aqueous methyl alcohol from which it separated in pale yellow needles, m. p. 133·5° (Hodgson and Hathway, *J.*, 1945, 453, give m. p. 134°) (Found : N, 13·0. Calc. for $C_{10}H_8O_4N_2$: N, 12·8%); or, it can be purified by steam distillation, which for this compound is a rather slow process. Yield of pure 1 : 4-dinitronaphthalene, 7·5 g. (ca. 65%). Usually, where a readily volatile nitro-compound is formed, the steam method of removal is the more convenient.

Estimation of Yield of Diazonium Sulphate.—The solution of the diazonium sulphate in water was made up to a definite volume, an aliquot portion stirred into the alkaline β -naphthol, the precipitated arylazo- β -naphthol removed, washed, dried, and weighed, and the corresponding amount of aryl- or naphthyl-diazonium sulphate calculated.

Preparation of 3 : 3' : 4 : 4'-Tetranitrodiphenyl.—3 : 3'-Dinitrobenzidine (5 g.) was dissolved in sulphuric acid (25 c.c., *d* 1·84), powdered sodium nitrite (5 g.) added gradually below 40°, and the mixture stirred below 20° into glacial acetic acid (50 c.c.); after 30 minutes, ether (200 c.c.) was added at 0°, the mixture kept for 1 hour, and the precipitated solid tetrazonium sulphate filtered off and dealt with as by the general method. The crude 3 : 3' : 4 : 4'-tetranitrodiphenyl was filtered off, washed with water, dilute sodium hydroxide, and finally with water, dried, extracted with boiling toluene (250 c.c.), and the extract concentrated to 25 c.c.; 3 : 3' : 4 : 4'-tetranitrodiphenyl crystallised out, m. p. 188—190°, and separated subsequently from boiling 80% acetic acid in clusters of yellow needles, m. p. 191—193° (Ullmann and Bielecki, *Ber.*, 1901, **34**, 2129, give m. p. 186°) (Found : N, 16·9. Calc. for $C_{12}H_8O_8N_4$: N, 16·8%).

Preparation of 3 : 4 : 5-Trinitrotoluene.—Solid sodium nitrite (5 g.) was stirred into sulphuric acid (25 c.c., *d* 1·84), and 3 : 5-dinitro-*p*-toluidine (5 g.) was stirred below 40° into this mixture, which was then added gradually below 20° to glacial acetic acid (50 c.c.). After 30 minutes, ether (200 c.c.) was added at 0°, and the precipitated diazonium sulphate dealt with as above. After decomposition, the crude 3 : 4 : 5-trinitrotoluene was extracted thrice with boiling toluene (150 c.c. in all), and the extract concentrated to 15 c.c.; magnificent monoclinic needles of an almost pure product separated (1·3 g., m. p. 135°) (Körner and Contardi, *Atti R. Accad. Lincei*, 1915, [5], **24**, 892, give m. p. 137·5°) (Found : N, 18·7. Calc. for $C_7H_5O_3N_3$: N, 18·5%).

Amine taken.	Nitro-compound formed.	Yield of pure compound (%).		Remarks.
		(a) With red-violet slurry.	(b) With solid.	
β -Naphthylamine	β -Nitronaphthalene	40	30	Calc. on amine taken
"	"	57	40	Calc. on diazonium sulphate isolated
2-Nitro-1-naphthylamine	1 : 2-Dinitronaphthalene	53	—	Calc. on diazonium sulphate isolated
1-Nitro-2-naphthylamine	1 : 2-Dinitronaphthalene	15	—	Calc. on diazonium sulphate isolated
4-Nitro-1-naphthylamine	1 : 4-Dinitronaphthalene	65	—	Calc. on amine taken
5-Nitro-2-naphthylamine	1 : 6-Dinitronaphthalene	55	—	" "
8-Nitro-2-naphthylamine	1 : 7-Dinitronaphthalene	45	30—40	" "
6-Nitro-2-naphthylamine	2 : 6-Dinitronaphthalene	45	—	" "
Ben-zidine	4 : 4'-Dinitrodiphenyl	16	—	" "
3 : 3'-Dinitrobenzidine	3 : 3' : 4 : 4'-Tetranitrodiphenyl	55	—	" "
3 : 5-Dinitro- <i>p</i> -toluidine	3 : 4 : 5-Trinitrotoluene	25	—	" "

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