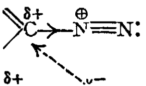
12. *The Replacement of the Diazonium by the Nitro-group. A General Method based on the Decomposition of the Aryldiazonium Cobaltinitrites.*

By Herbert H. Hodgson and Ewart Marsden.

Aryldiazonium *cobaltinitrites*, $(R\cdot\overset{\oplus}{N}_2)_3\}\overset{\ominus\ominus\ominus}{Co}(NO_2)_6$, have been prepared; they are immediately decomposed in the cold by aqueous sodium nitrite in the presence of cuprous oxide and cupric sulphate, and some even without the sulphate, to give excellent yields of aryl nitro-compounds. The reaction is held to indicate the presence of some nitrito-groups in the cobaltinitrite anion.

Previous work on the replacement of the diazonium by the nitro-group has been carried out by Sandmeyer (*Ber.*, 1887, **20**, 1495), Veselý and Dvorăk (*Bull. Soc. chim.*, 1922, **31**, 421), Orton (J., 1903, **83**, 806), Bucherer and von der Recke (*J. pr. Chem.*, 1931, **132**, 121), Hantzsch and Blagden (*Ber.*, 1900, **33**, 2544; I.G., Anm. I. 485629), and Contardi (*Ann. Chim. Appl.*, 1923, **7**, 13). In every case, however, the reactions were of limited application (cf. Saunders, "The Aromatic Diazo-compounds and Their Technical Applications," 1936, p. 158).



Since diazonium nitrites decompose in nitrous acid solution to form nitro-compounds, the mechanism of the reaction would appear to be attack of the carbon atom to which the diazonium group is attached by anionoid nitrogen (due to resonance) of the nitrito-group (inset), otherwise attack by oxygen would form the hitherto unknown, and therefore very unstable, phenyl nitrite, of which the nitrite group must immediately isomerise into the stable nitro-group. This mechanism follows on the analogy of the much greater reactivity of anionoid nitrogen (due to resonance) in nucleophilic nitrous acid (cf. Kenner, *Chem. and Ind.*, 1941, **60**, 443) than of either of its oxygens for the kationoid carbon atom. Accordingly, complex salts with diazonium kations and metallic nitrito-anions were expected to offer a means of preparing nitro-compounds by a mechanism analogous to that of the Sandmeyer reaction (Hodgson, Birtwell, and Walker, J., 1941, 770).

For this purpose, the aromatic diazonium *cobaltinitrites*, which have not hitherto been described, have been prepared. They are obtained in almost quantitative yield by the simple addition of sodium cobaltinitrite to a solution of a diazonium salt previously neutralised by calcium carbonate; they are yellow to orange crystalline substances which, when prepared from the nitro- and chloro-anilines, are stable when dry, but those from the toluidines, anisidines, and α-naphthylamine are less stable. On heating, however, the cobaltinitrites decompose, sometimes with explosive violence (*e.g.*, the complex from *p*-nitroaniline). They couple with β-naphthol in alkaline solution, and with α- and β-naphthylamine in acetic acid solution, but in hydrochloric acid they diazotise amines and nitrosate phenols by the nitrous acid formed during decomposition of the complex salt by the mineral acid.

When the solid diazonium cobaltinitrites from aniline, *o*-, *m*-, and *p*-nitroanilines and *p*-chloroaniline were added to a suspension of cuprous oxide in concentrated aqueous sodium nitrite, a vigorous evolution of nitrogen took place in the cold, and excellent yields of nitro-compounds were obtained. With the cobaltinitrites, however, from *o*- and *p*-toluidine, *o*- and *p*-anisidine, and α- and β-naphthylamine, the yields were poor, nor did the further addition of freshly precipitated copper effect any appreciable improvement; when copper sulphate was also present, however, all the diazonium cobaltinitrites as yet prepared decomposed to give yields above 60%. In the absence of sodium nitrite, cuprous oxide, either alone or in conjunction with copper sulphate, would not decompose the cobaltinitrite in the cold, although on heating there was a vigorous reaction without, however, the production of a nitro-compound; addition of sodium nitrite to the cold mixture immediately brought about formation of the relevant nitro-compound.

The results confirm the expectations noted above, the anionoid (nucleophilic) nitrito-group of the complex cobalt anion attacking the kationoid (electrophilic carbon atom of the diazonium compound. The simpler mechanism of nitrogen attack, however, would imply that the cobaltinitrite anion contained at least some of its nitrito-groups attached to the central cobalt atom by oxygen. This appears reasonable in view of the facts : (1) that the nitrito-groups in the metallic cobaltinitrites are indicated by magnetic data to be covalently linked (cf. Pauling, " Nature of the Chemical Bond," 1940, p. 116); (2) on analogy, the mixed inorganic cobalt complex salts containing both NH_3 and NO_2 groups are found in two forms, *viz.*, the red unstable nitritopentammine salts, *e.g.*, $[Co(NH_3)_5(ONO)]X_2$, and the more stable nitropentammines, *e.g.*, $[Co(NH_3)_5(NO_2)]X_2$ (cf. Emeléus and Anderson, " Modern Aspects of Inorganic Chemistry, 1943, pp. 84—86). Further, both NH_3 and NO_2 are themselves anionoid, but the introduction of NH_3 into the cobalt complex renders it kationoid, whereas the nitrito-group renders the complex anionoid. It is reasonable, therefore, to assume that reaction occurs *via* a feebly linked nitrito-group in view of the direct formation of a nitro-compound on the decomposition of a diazonium cobaltinitrite. The function of the copper compounds is to bring about the elimination of the diazonium nitrogen (cf. Sandmeyer, *loc. cit.*, and Contardi, who concluded that cupric were as effective as cuprous salts), and the rôle of the sodium nitrite would appear to be the re-formation of stable sodium cobaltinitrite, which would in consequence be the main driving force of the decomposition, since the copper compounds did not themselves effect reaction in the cold.

The excellent yields of nitro-compounds, together with the facile preparation of the intermediate diazonium cobaltinitrites, indicate this new replacement method to be of general application.

EXPERIMENTAL

Preparation and Analysis of Aromatic Diazonium Cobaltinitrites.—The amine (0·1 g.-mol.) is diazotised in either hydrochloric or sulphuric acid solution with sodium nitrite (7 g.), the volume of liquid being kept as small as possible. The diazonium solution is neutralised with calcium carbonate and filtered; finely powdered sodium cobaltinitrite (15 g.) is stirred into the filtrate, and the crystalline aryldiazonium cobaltinitrite, which separates rapidly, is filtered off, air-dried, and analysed by coupling 0·5 g. of it with β-naphthol; the resulting azo-compound is filtered off, washed with cold alcohol and water on the filter until free from β-naphthol, then with hot dilute hydrochloric acid until free from cobalt salts, and finally with water, after which it is dried, and weighed.

Replacement of the Diazonium by the Nitro-group.—The finely powdered cobaltinitrite (10 g.) is added portionwise at room temperature to a well-stirred solution of sodium nitrite (10 g.) and crystallised copper sulphate (10 g.) in water (60 c.c.) in which cuprous oxide (4 g.) is suspended. After the evolution of nitrogen, which at the outset is somewhat vigorous, is complete (sometimes only after standing overnight), the resulting nitro-compound is removed by steam (when volatile) or by extraction with a suitable solvent (*e.g.*, chloroform). Before steam distillation, the reaction mixture should be made alkaline with sodium hydroxide.

Some Aryldiazonium Cobaltinitrites.

Amine diazotised.	Colour of the cobaltinitrite.	Yield,		Arylazo-β-naphthol.	
		g.	%.	Obtained, g.	Yield, %.
Aniline	Light orange	19·2	88·5	0·5703	99·6
o-Nitroaniline	Orange	26·0	99·0	0·5581	99·7
m-Nitroaniline	Orange	22·3	89·9	0·5584	99·7
p-Nitroaniline	Orange	19·5	74·5	0·5570	99·5
p-Chloroaniline	Orange	21·2	84·0	0·5644	100·3
α-Naphthylamine	Dark orange	21·8	81·6	0·5598	100·2
β-Naphthylamine	Yellow	26·5	99·0	0·5600	100·2

[The yield of arylazo-β-naphthol is given as a percentage of that to be expected from the reaction $(RN_2)_3Co(NO_2)_6 \longrightarrow 3R{\cdot}N_2{\cdot}C_{10}H_6{\cdot}OH$.]

Decomposition of Aryldiazonium Cobaltinitrites (10 g.) *to Nitroaryls.*

Amine diazotised.	Product.	Yield, g.	Yield, %.
(*a*) By cuprous oxide only.			
Aniline	Nitrobenzone	4·3	75·5
o-Nitroaniline	*o*-Dinitrobenzene	4·3	67·4
m-Nitroaniline	*m*-Dinitrobenzene	4·6	72·0
p-Nitroaniline	*p*-Dinitrobenzene	4·8	75·0
p-Chloroaniline	*p*-Chloronitrobenzene	5·2	82·5
α-Naphthylamine	α-Nitronaphthalene	1·3	20·0
β-Naphthylamine	β-Nitronaphthalene	1·1	16·9
(*b*) By cuprous oxide–copper sulphate.			
α-Naphthylamine	α-Nitronaphthalene	4·4	68·0
β-Naphthylamine	β-Nitronaphthalene	3·9	60·0
p-Toluidine	*p*-Nitrotoluene	4·1	69·0
p-Anisidine	*p*-Nitroanisole	4·2	68·0
(*c*) By cuprous oxide–copper sulphate, but yield based on weight of amine (5 g.) taken.*			
o-Toluidine	*o*-Nitrotoluene	3·9	61·0
o-Anisidine	*o*-Nitroanisole	3·9	63·0

* These cobaltinitrites were less stable than the others, and so were not dried, but washed with water and immediately decomposed as above; hence the yields have to be calculated on the amount of amine diazotised.

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