

### 239. *Replacement of the Diazonium by the Cyano-group in Neutral Solution.*

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The preparation of cyanides and dicyanides from diazonium and bisdiazonium compounds in neutral solution is described, together with a comparison of the catalytic efficiencies of potassium cupro- and nickelo-cyanides in decompositions of diazonium compounds.

PREVIOUS applications of the Sandmeyer reaction to the preparation of cyanides from diazo-compounds have been limited to monodiazonium salts, mainly in acid solution, although Clarke and Read (*J. Amer. Chem. Soc.*, 1924, **66**, 1001) neutralised their diazonium salt solutions with sodium carbonate before adding them to the cyanide mixture to avoid the subsequent evolution of hydrogen cyanide, and benzene was also added to remove the product from the reaction phase immediately it was formed. Korczynski, Mrczynski, and Vielan (*Rocz. Chem.*, 1921, **1**, 140; cf. also, Korczynski and Fundrich, *Compt. rend.*, 1926, **183**, 421) found that replacement of the copper cyanide as catalyst by nickel cyanide gave somewhat better yields of cyanides, and the improved efficiency was attributed to the greater solubility of the nickel cyanide than of cuprous cyanide in the solution of the excess of potassium cyanide. Other metallic cyanides, such as those of iron, chromium, manganese, zinc, molybdenum, cadmium, and tin, were found to be without catalytic effect. Ashley, Barber, Ewin, Newbery, and Self (*J.*, 1942, 113) and Barber (*J.*, 1943, 79) have investigated the isolation process and the preparation of the cuprous catalyst.

We prepared the cyanides in neutral solution, and compared the relative efficiencies of potassium cupro- and nickelo-cyanides under these conditions. Further, the preparation of dicyanides direct from bisdiazotised homonuclear diamines is described for the first time; although Hodgson and Walker (*J.*, 1935, 530) described the bisdiazotisation of *o*-, *m*-, and *p*-phenylenediamine and their direct conversion into the respective dichlorobenzene, and Schoutissen (*J. Amer. Chem. Soc.*, 1933, **55**, 4531) reported a method for the bisdiazotisation of *m*- and *p*-phenylenediamine and their subsequent direct conversion into dihalogenobenzenes, yet the corresponding dicyanides could not be prepared until Hodgson and Walker (*J.*, 1933, 1620) overcame the difficulty of bisdiazotising the homonuclear diamines, and Hodgson and Mahadevan (*J.*, 1947, 325) isolated the bisdiazonium sulphates in solid form, thereby permitting the use of neutral solutions of these compounds. With nickel cyanide, which was much more efficient than cuprous cyanide, as catalyst, *m*- and *p*-dicyanobenzene were obtained from their respective bisdiazonium salts in 17% and 42% yields, and identified respectively by comparison with an authentic specimen, and by hydrolysis to terephthalic acid. An 8% yield of 2:4-dicyanotoluene was obtained from *m*-tolylene-2:4-diamine, but dicyanides could not be obtained from *o*-phenylenediamine and 4-nitro-*o*-phenylenediamine.

Korczynski *et al.* (*loc. cit.*) compared the yields of *p*-bromocyanobenzene and *o*-cyanoanisole from *p*-bromoaniline and *o*-anisidine with cuprous and nickel cyanide, respectively, and this

comparison has now been extended to the diazonium sulphates from twelve amines after neutralisation with calcium carbonate. The comparison confirms their result for *o*-anisidine under the conditions employed, but affords variable data for other amines; for with diazotised aniline and *p*-anisidine, both catalysts are equally effective, but diazotised *o*- and *p*-nitroaniline, *o*- and *p*-chloroaniline, and *o*- and *p*-toluidine give the best yields with the cuprous catalyst, and  $\beta$ -naphthylamine with the nickel salt, but diazotised *m*-nitro- and *m*-chloro-aniline only react with the cuprous catalyst.

Sandmeyer had originally carried out the reaction by the addition of the diazonium solution to the boiling aqueous potassium cuprocyanide, but Clarke and Read (*loc. cit.*) recommended 20—30° as the optimum temperature range; it has now been found that 70—80° is better for most of the decompositions, and, whereas Barber (*loc. cit.*) states that any temperature between 30° and 90° is equally suitable, the yields under the present conditions are favoured by hot decomposition: in contrast to the claim of Clarke and Read, *p*-toluidine gives an improved yield of *p*-cyanotoluene at 70—80°.

## EXPERIMENTAL.

*Comparison of the Catalytic Efficiencies of Sodium Cupro- and Nickelocyanides at 30—40°.—General procedure.* The amine (2.0 g.) was diazotised in a solution of sulphuric acid (6 c.c., *d* 1.84) and water (10 c.c.) by addition of a solution of sodium nitrite (1.5 g.) in water (7 c.c.), with crushed ice (10—20 g.) to keep the temperature at 0°. Excess acid was removed by addition of the mixture to powdered calcium carbonate (10 g.) and ice (10 g.), and the filtered solution was run into the relevant decomposition mixture (a) or (b) at 30—40°: (a) potassium cuprocyanide was prepared by dissolution of cuprous cyanide (made according to Barber's directions, *J.*, 1943, 79) in potassium cyanide (10 g.) and water (25 c.c.); (b) potassium nickelocyanide was prepared by addition of a solution of crystallised nickel sulphate (7 g.) in water (20 c.c.) to one of potassium cyanide (10 g.) in cold water (25 c.c.). After the evolution of nitrogen had ceased, the cyano-compound was removed by steam-distillation, and filtered off from the distillate if solid or ether-extracted if liquid, then weighed and identified. The results are given in the following table.

Amine.	Yield of cyano-compound, %.		Amine.	Yield of cyano-compound, %.	
	Catalyst (a).	Catalyst (b).		Catalyst (a).	Catalyst (b).
Aniline .....	17.5	17.5	<i>p</i> -Chloroaniline ...	51	32
<i>o</i> -Nitroaniline .....	65	40	<i>o</i> -Anisidine .....	60	72
<i>m</i> -Nitroaniline ...	28	0	<i>p</i> -Anisidine .....	45	36
<i>p</i> -Nitroaniline ...	67	48	<i>o</i> -Toluidine .....	48	27
<i>o</i> -Chloroaniline ...	67	46	<i>p</i> -Toluidine.....	45	36
<i>m</i> -Chloroaniline ...	28	Trace	$\beta$ -Naphthylamine	14.5	25

*Comparison of Decompositions at 20—30° and at 70—80°.—Method.* The sodium cuprocyanide used in these experiments was prepared by dissolving cuprous cyanide (10 g.) in a solution of sodium cyanide (20 g.) in water (50 c.c.), dividing the mixture in two equal parts, and stirring into each half, at the appropriate temperature, a solution of the neutralised diazotised amine (10 g.). The results are compared below:

Amine.	Yield, %.		Amine.	Yield, %.	
	at 70—80°.	at 20—30°.		at 70—80°.	at 20—30°.
<i>o</i> -Toluidine .....	45	18	<i>o</i> -Chloroaniline .....	67	Small
<i>p</i> -Toluidine .....	48	Small	<i>m</i> -Chloroaniline ...	28	21
<i>m</i> -Nitroaniline .....	23	7	<i>p</i> -Chloroaniline .....	51	14
<i>p</i> -Nitroaniline .....	21	14			

*Simultaneous Replacement of Two Homonuclear Diazonium by Two Cyano-groups.—p-Phenylenediamine.* The amine (5 g.), dissolved in cold glacial acetic acid (50 c.c.), was added to an ice-cold solution of sodium nitrite (7 g.) in sulphuric acid (40 c.c., *d* 1.84), the mixture being kept until diazotisation was complete, after which dry ether (250 c.c.) was stirred into it, the solid bisdiazonium compound was filtered off, washed with ether (250 c.c.), dissolved in water (30 c.c.) at 0°, and the solution stirred quickly into one of cuprous cyanide (20 g.) and sodium cyanide (30 g.) in water (100 c.c.) at 30°. On steam-distillation, *p*-dicyanobenzene passed over (0.05 g.). On repetition, but with potassium nickelocyanide as catalyst [prepared by adding a solution of crystallised nickel sulphate (20 g.) in water (60 c.c.) to one of potassium cyanide (50 g.) in water (150 c.c.)], *p*-dicyanobenzene (2.5 g., 42.2% yield) passed over on steam-distillation; m. p. 220°, raised to 222° by recrystallisation from acetic acid, and hydrolysed by alcoholic potassium hydroxide followed by acidification to terephthalic acid (2.0 g.) (unmolten at 300°). This acid, on dissolution in methanol with subsequent passage of dry hydrogen chloride, afforded the methyl ester, m. p. 140° (Schwanert, *Annalen*, 1864, 132, 269, gives m. p. 140°).

*m-Phenylenediamine.* After procedure as above, steam-distillation afforded *m*-dicyanobenzene (1.5 g., 25.4% yield), m. p. 158—160°, which on recrystallisation from ethanol gave colourless crystals, m. p. 159—160° (lit., m. p. 160°).

*m-Tolylene-2:4-diamine.* This diamine (2 g.), when treated as above, afforded 2:4-dicyanotoluene (0.01—0.1 g.) on steam-distillation; it separated from ethanol in colourless crystals, m. p. 142—144° (lit., m. p. 144—145°) (Found: N, 20.0. Calc. for C<sub>8</sub>H<sub>8</sub>N<sub>2</sub>: N, 19.7%).

*p-Tolylene-2:5-diamine.* This base (2 g.) similarly afforded 2:5-dicyanotoluene, m. p. 150—152°

(Found: N, 20.0%), which was hydrolysed by boiling aqueous 65% sulphuric acid to toluene-2:5-dicarboxylic acid, m. p. 328—330° (lit., m. p. 328—330°).

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