164. *The Action of Cuprous Oxide on Diazotised Amines in Ethyl-alcoholic Acid Solution.*

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Amines can be efficiently deaminated when their diazonium salts in glacial acetic–concentrated sulphuric acid solution are decomposed by a suspension of cuprous oxide in ethyl alcohol. The method appears to be of general application.

Hodgson and Marsden's method (J., **1940**, 207) for the replacement of a diazo-group by hydrogen is of general application and almost quantitative, but it involves the preliminary isolation of a stabilised salt of the diazotised amine with a naphthalenedisulphonic acid or an acid such as oxy-Tobias acid. This preparation may be easy or difficult, and the method now described deals with the diazotised amine *in situ*. It is based on the reducing action of cuprous oxide and ethyl alcohol in conjunction with the diazotisation of the amine by Hodgson and Walker's method (J., **1933**, 1620). Ruggli, Knapp, Merz, and Zimmermann (*Helv. Chim. Acta*, 1929, **12**, 1034) have used cuprous oxide and alcohol for the reduction of 6-nitro-1-diazo-2-naphthol-4-sulphonic acid to 6-nitro-2-naphthol-4-sulphonic acid.

The efficiency of the ethyl alcohol–cuprous oxide combination for the deamination of certain derivatives of 5-nitro-1-naphthylamine (Hodgson and Turner, this vol., p. 723) indicated that the method might be of general application, and the data now included (see Table) show this to be the case. Excellent yields of deaminated products have been obtained from nitroamines and aminoanthraquinones, and good yields from amines having less pronouncedly kationoid substituents. It appears that the positivity of the carbon atom to which the diazo-group is attached is the dominant factor in the decomposition; *e.g.*, this atom in 2-nitro-1-naphthylamine (79% yield of 2-nitronaphthalene) is somewhat more positive than that in 1-nitro-2-naphthylamine (70% yield of 1-nitronaphthalene), as would be expected on the assumption of a negative inductive $(-I)$ effect of the second nucleus (Hodgson and Elliot, J., **1935**, 1850).

In the method the amine is diazotised in glacial acetic–nitrosylsulphuric acid (Hodgson and Walker, *loc. cit.*), and the solution run into a suspension of cuprous oxide in ethyl alcohol; the diazonium group is smoothly replaced by hydrogen, the deaminated product is obtained in a high state of purity and unaccompanied by azo-compounds, and diaryl or dinaphthyl production is negligible (cf. Ullman and Forgan, *Ber.*, 1901, **34**, 3803). The yields are not appreciably affected by the state of the cuprous oxide, provided it is very finely divided; the commercial variety, the yellow hydrated form, and the red powder obtained by the reduction of alkaline cupric solutions have all been found suitable. The function of the cuprous oxide may be both catalytic and direct, since it is almost completely dissolved in the reaction mixture as highly reactive cuprous sulphate. Subsequent reaction appears to be the formation of " nascent " copper, by which the decomposition of the diazonium group would be considerably facilitated; the alcohol, by its oxidation to aldehyde, participates in the reduction process, and its activity is doubtless increased by the nascent copper present (cf. the formation of aldehydes from alcohols by copper).

Although the yields of deaminated product are somewhat lower in many cases than those obtained by the Hodgson–Marsden procedure (*loc. cit.*), the present method is very convenient (especially with the less basic and the more difficultly diazotisable amines), since it is easy and rapid and is particularly useful for small quantities of amine (0·1—0·5 g.).

Experimental.

Procedure.—A solution of the amine (1/20 g.-mol.) in glacial acetic acid (80 c.c.) was added, below 20°, to a solution of sodium nitrite (4·5 g.) in sulphuric acid (30 c.c., *d* 1·84); after 30 minutes, the mixture was run into a vigorously stirred suspension of finely divided cuprous oxide (14 g.) in absolute ethyl alcohol (120 c.c.) during *ca.* 30 minutes. Evolution of nitrogen began forthwith, the temperature rose to 50—70°, and the reaction was complete in less than 5 minutes.

Isolation of the Products.—(1) For steam-volatile compounds, the reaction mixture was diluted with an equal volume of water and steam-distilled.

(2) For compounds readily soluble in alcohol, the liquid was filtered, the residue washed with boiling alcohol (50—100 c.c.), and the combined filtrates diluted gradually with water; the precipitate was pure after recrystallisation.

(3) For compounds non-volatile in steam and moderately soluble or insoluble in alcohol, the mixture was diluted with water (1·5 l.), and the precipitate collected, washed, dried, and extracted with ethylene dichloride or chloroform. The extract afforded the product in a high state of purity.

The yields recorded in the table are minimum yields of pure products, and can usually be increased by 3—10% by slight changes in technique, determined by trial and error. The substitution of formic for acetic acid (equal vols.) in the diazotisation usually increased the yield by *ca.* 5%.

TABLE.

Except where otherwise stated, the " oxide " mentioned is the hydrated product precipitated by alkali from cuprous chloride solution. The yellow solid was washed with water, alcohol, and ether, and vacuum-dried.

Amine.	G.-mol.	Acetic acid, c.c.	Sodium nitrite, g.	Sulphuric acid, c.c.	Cuprous oxide, g.	Alcohol, c.c.	Method of isolation of product.	Final temp.	Yield, %.
p-Toluidine	0·1	40	9	60	28 [1]	200	Dilution, separation of toluene layer, distillation.	Below 40°	45
o-Nitroaniline	0·05	40	4·5	30	14	120	(1)	60	89
m-Nitraniline	0·05	40	4·5	30	14	120	(1)	60	78
p-Nitroaniline	0·05	40	4·5	30	19	120	(1)	65	97
Anthranilic acid	0·05	40	4·5	30	14	120	(2) [2]	75	65
2 : 5-Dichloroaniline	0·05	20	4·5	30	14	120	(2) followed by (1)	62	57
3 : 5-Dinitro-*p*-toluidine	0·025	40	2·5	20	7 [3]	60	(1)	55	40
Benzidine	0·05	40	9	60	26	200	(1)	68	49 [4]
β-Naphthylamine	0·05	40	4·5 [5]	30	14	120	(1)	50	60
1-Nitro-2-naphthylamine	0·05	50	4·5	30	10 [3]	120	(2) followed by (1)	75	70
2-Nitro-1-naphthylamine	0·05	40	4·5	30	12 [3]	120	(2) followed by (1)	75	79
4-Chloro-2-nitro-1-naphthylamine	0·025	80	2·5	20	10	60	(2)	60	94
2-Iodo-4-nitro-1-naphthylamine	0·025	40	2·5	20	10	60	(2)	70	80
2 : 4-Dinitro-1-naphthylamine	0·05	70	4·5	Total 68	14 [6]	150	(3)	60	65
1-Aminoanthraquinone	0·05	80	4·5	30	14	120	(3)	75	75
2-Aminoanthraquinone	0·05	80	4·5	30	14 [1]	170	(3)	72	70

[1] Commercial oxide used. [2] The product was a mixture of benzoic acid and ethyl benzoate. After dilution, the aqueous solution was ether-extracted. Aqueous sodium hydroxide removed the acid—reprecipitated by mineral acid. Distillation of the residual ether gave the ester (2·0 c.c., b. p. 215°). [3] Precipitated red cuprous oxide used. [4] The hypophosphite method (Mai, *Ber.*, 1902, **35**, 162) gives a 60% yield of diphenyl from benzidine. [5] Excess of nitrous acid removed by urea before deamination. [6] Commercial oxide used. 2 : 4-Dinitro-*p*-toluenesulphon-1-naphthalide was hydrolysed by sulphuric acid (*d* 1·84) and diazotised *in situ* by the inverted method.

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