5. *Decomposition of Diazotised* 1 : 6-*Dinitro*-2-*naphthylamine by Precipitated Copper in Organic Solvents.*

By Herbert H. Hodgson and Harold S. Turner.

Precipitated copper deaminates 1 : 6-dinitro-2-naphthylamine without the induction period observed when cuprous oxide is used (J., 1943, 86), and in the case of methyl alcohol without production of formaldehyde. The yields obtained by both procedures are similar with methyl, ethyl, and *iso*propyl alcohol, but not with ethylene chlorohydrin.

Some comparative deaminations of 2-nitro-1-naphthylamine are included.

Previous work (J., 1942, 748; 1943, 86) on the action of cuprous oxide on diazotised amines in various media has been supplemented by an examination of the reaction of precipitated copper under the same conditions with diazotised 1 : 6-dinitro-2-naphthylamine. The copper dissolved, and, in general, where an alcohol was the solvent, oxidation to the corresponding aldehyde occurred. Methyl alcohol did not give rise to formaldehyde, nevertheless the yield of deaminated product (*ca.* 58%) was almost the same as that obtained with cuprous oxide (*ca.* 60%) (in this reaction formaldehyde is produced), so methyl alcohol again heads the list of alcohols arranged in order of decreasing efficiency. Since oxidation must occur as a complement to reduction of the diazo-compound, methyl alcohol must have been oxidised to carbon dioxide, because the formation of formic acid was never detected.

When the diazonium solution prepared in glacial acetic–sulphuric acid was decomposed in the absence of any other solvent, the amount of deamination was almost negligible (10%), and in this case, as also when methyl, ethyl, *n*-propyl, *iso*propyl, *n*-butyl, β-chloroethyl alcohol, acetone, methyl ethyl ketone, ethyl formate, or ethyl acetate was present, there was no induction period before the evolution of nitrogen (cf. Hodgson and Turner, J., 1943, 86); deamination in presence of *n*-propyl, *iso*propyl, or *n*-butyl alcohol, however, was somewhat sluggish. A short induction period was observed with *iso*butyl alcohol and a slightly longer one with amyl alcohol. Generally, it was necessary to pass steam into the diluted reaction mixture to remove alcohols or esters immiscible with water. Ethyl acetate and amyl alcohol produced tars; with ethyl formate very little gas was evolved and the reaction mixture on dilution did not give a solid precipitate, although there was the normal rise in temperature during the reaction.

The yields obtained with precipitated copper are slightly lower than those with cuprous oxide, and ethylene chlorohydrin is no longer the most efficient deaminating solvent, its place being taken by methyl alcohol.

Deaminations were also carried out with diazotised 2-nitro-1-naphthylamine in methyl, ethyl, and β-chloroethyl alcohol. The order of yields was the same as with 1 : 6-dinitro-2-naphthylamine, *viz.*, methyl > ethyl > β-chloroethyl alcohol, but the amounts were smaller than those given by the cuprous oxide procedure.

Experimental.

Precipitated Copper.—Copper was precipitated from copper sulphate solution with zinc dust, washed with water, stirred with dilute hydrochloric acid to remove zinc, washed with alcohol and ether, and stored in a stoppered bottle slightly wetted with ether.

Procedure.—The diazonium salt solution was prepared from 1 : 6-dinitro-*p*-toluenesulphon-2-naphthalide (20 g.) by combined hydrolysis and diazotisation (J., 1943, 88) and poured into a suspension of copper powder in the organic solvent (200 c.c.) at 15°. Details are given in the Table.

Deamination by Copper Powder.

Medium (200 c.c.).	Copper, g.	Max. temp.	Yield, g.	Yield, %.	M. p.	Description of product.		Remarks.
None	20	56°	1·2	10·5	163 —164°	Brown needles	(1)	
Methyl alcohol	20	65	6·55	58	165·5—166·5	Yellow needles	(1)	
Ethyl alcohol	12	65	6·5	57·5	165·5—166·5	Yellow needles	(1)	
*iso*Propyl alcohol	25	65	6·1	54·5	164·5—165·5	Light yellow needles	(1)	Reaction sluggish
n-Propyl alcohol	20	70	4·0	35·5	163·5—165·5	Yellow needles	(1)	Slow reaction
*iso*Butyl alcohol	25	58	2·9	26	163·5—164·5	Golden-brown needles	(2)	Slow reaction
n-Butyl alcohol	20	66	4·1	36·5	163·5—165	Golden-brown needles	(1)	Slow reaction
β-Chloroethyl alcohol	30	50	4·0	36	163 —165	Light brown needles	(1)	
Acetone	20	60	1·8	16	123 —133	Deep brown needles	(1)	
Methyl ethyl ketone	20	65	5·0	44·5	161·5—162·5	Golden-brown needles	(1)	
Ethyl formate	30	36	—	—	—	Water-soluble product	(1)	Slight effervescence
Ethyl acetate	30	51	—	—	—	Tar	(1)	
Amyl alcohol	30	59	—	—	—	Tar	(3)	

(1) No induction period. (2) Small induction period. (3) Induction period while temperature rose to 30°.

Deamination of 2-Nitro-1-naphthylamine —Solutions of the amine (9·4 g.) in sulphuric acid (50 c.c., *d* 1·84) and of sodium nitrite (4·5 g.) in sulphuric acid (30 c.c., *d* 1·84) were mixed in the cold and added below 20° to glacial acetic acid (100 c.c.). The diazo-solution was stirred into a suspension of copper powder (20 g.) in the alcohol (120 c.c.) at 15°; after the reaction was completed, the mixture was steam-distilled, and the 2-nitronaphthalene collected.

Medium.	Maximum temperature.	Yield. G.	Yield. %.
Methyl alcohol	65°	3·0	35
Ethyl alcohol	60	2·9	33·5
Ethylene chlorohydrin	60	2·25	26

The authors thank I.C.I. (Dyestuffs) Ltd. for gifts of chemicals.

TECHNICAL COLLEGE, HUDDERSFIELD. [*Received, July 22nd,* 1943.]