42. *The Action of Cuprous Oxide on Diazotised Amines. Part III. Action in Sulphuric Acid–Glacial Acetic Acid.*

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In the amines of the naphthalene series deamination by cuprous oxide in sulphuric acid–glacial acetic acid (where the amount of water is at a minimum) attains over 70% efficiency, but it falls below 40% in the benzene series. In all cases the positivity of the carbon atom to which the diazo-group is attached plays an important rôle in the deamination.

The work reported in Parts I and II (Hodgson and H. Turner, J., 1942, 748; 1943, 86) had been carried out in various solvents which themselves participated in the reaction and to that extent facilitated it. Also, work by Hodgson, Leigh, and G. Turner, (J., 1942, 744) on the decomposition of aqueous diazonium salt solutions showed that the formation of symmetrical azo-compounds predominated over deamination. It appeared therefore of interest to examine in detail the action of cuprous oxide on diazonium salts in concentrated sulphuric–glacial acetic acid solution (*i.e.*, with the minimum of water present) as effected either by Hodgson and Walker's method (J., 1933, 1620) or by an inverted modification of it, especially as a yield of 82% of 1 : 3-dinitronaphthalene had been obtained thereby from 2 : 4-dinitro-1-naphthylamine. Further, in view of its success in the deamination of substituted naphthylamines, an extension of the method to amines of the benzene series appeared to be necessary.

The mechanism of deamination, when this takes place, would seem to be the intermediate formation of the highly reactive cuprous sulphate and subsequently of nascent copper, which would make the deamination a combined reduction assisted by copper as catalyst. In the naphthalene series excellent yields of deaminated products were obtained from diazotised nitronaphthylamines, but much inferior deamination was afforded by the various aniline derivatives examined. In all cases, however, the positivity of the carbon to which the diazo-group is attached is an important factor for the efficiency of the deamination, particularly in the naphthalene series, where an almost exact parallel between positivity and deamination is obtained, as shown in the sequences: *Naphthalene series*: 2 : 4-Dinitro-1-naphthylamine > 4-chloro- and 4-bromo-2-nitro-1-naphthylamine > 2-nitro-1-naphthylamine > 4-nitro-1-naphthylamine > 2-naphthylamine. *Benzene series*: 3-nitro-4-toluidine > 2 : 5-dichloroaniline > 2-nitroaniline > 2-nitro-4-toluidine > *p*-toluidine > benzidine > *p*-nitroaniline > aniline (which gave diphenyl and only a trace of benzene).

The low yield of nitrobenzene from *p*-nitroaniline, and the formation of diphenyl from aniline, indicate that there is the competing reaction of diaryl formation in the benzene series under the experimental conditions; nevertheless, the results in the benzene series are generally in the order of the positivity of the significant carbon.

Experimental.

General Procedure.—(a) *Direct.* The amine (0·1 g.-mol.), dissolved in glacial acetic acid (150 c.c.), was added below 20° to a solution of sodium nitrite (7·7 g.) in sulphuric acid (40 c.c., *d* 1·84), and, after 30 mins.' stirring, cuprous oxide (30—35 g.) was added during 20—30 mins. If the reaction was vigorous, the temperature was maintained at 20—30° by water cooling, but if it was relatively sluggish, the temperature was allowed to rise to 40—50°. Stirring was continued for about an hour after all the cuprous oxide had been added, the end-point being when the intense yellow or red diazo-solution had changed to light or straw-yellow. Isolation of the reaction product was effected either by pouring the mixture into water, followed by steam distillation, or by the addition of more glacial acetic acid followed by filtration, dilution with water, and steam distillation.

(b) *Indirect.* The amine (0·1 g.-mol.), dissolved in the minimum of sulphuric acid (*d* 1·84), was added below 20° to the above solution of nitrosylsulphuric acid, and the mixture stirred gradually into glacial acetic acid (150 c.c.), the subsequent procedure being as above. This method was employed for 2 : 4-dinitro-1-naphthylamine especially, but is applicable to the other amines.

(c) *With suspensions*, e.g., *deamination of* 4-*chloro- and* 4-*bromo*-2-*nitro*-1-*naphthylamine.* A mixture of the amine (11·1 g. of chloro-, or 13·35 g. of bromo-; 0·05 g.-mol.) suspended in glacial acetic acid (110 c.c.) was added to a solution of sodium nitrite (4·5 g.) in sulphuric acid (30 c.c., *d* 1·84) below 20°, and stirring continued for 30 mins. to complete the diazotisation. Finely powdered commercial cuprous oxide (17 g.) was then gradually stirred into the diazonium solution during 20 mins. with external water cooling, the subsequent procedure being as above.

When the deaminated product was only slightly or not volatile in steam, the by-product if steam volatile was so removed, and the residue then crystallised from ethylene dichloride, acetone, or other suitable solvents. The results are summarised in the following table.

Amine (0·1 g.-mol.).	Deaminated product.	Yield, g.	Yield, %.
2 : 4-Dinitro-1-naphthylamine	1 : 3-Dinitronaphthalene	18·0	82·0
4-Chloro-2-nitro-1-naphthylamine	1-Chloro-3-nitronaphthalene	15·4	75·0
4-Bromo-2-nitro-1-naphthylamine	1-Bromo-3-nitronaphthalene	19·0	75·5
2-Nitro-1-naphthylamine	2-Nitronaphthalene	12·2	70·0
4-Nitro-1-naphthylamine	1-Nitronaphthalene	11·8	68·0
2-Naphthylamine	Naphthalene	6·0	47·0
3-Nitro-4-toluidine	3-Nitrotoluene	5·3	39·0
2 : 5-Dichloroaniline	1 : 4-Dichlorobenzene	5·0	35·0
2-Nitroaniline	Nitrobenzene	3·5	28·0
2-Nitro-4-toluidine	2-Nitrotoluene	3·56	26·0
p-Toluidine	Toluene	2·2	24·0
Benzidine	Diphenyl	3·5	23·0
p-Nitroaniline	Nitrobenzene	2·68	21·6
Aniline	Diphenyl (only a trace of benzene)	2·0	26·0

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