

**137.** *The Deamination of 2 : 6-Dichloro-4-nitroaniline.*

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The treatment of diazotised 2 : 6-dichloro-4-nitroaniline with ethyl alcohol results in the formation of either 3 : 5-dichloro-1-nitrobenzene or 2 : 2' : 6 : 6'-tetrachloro-4 : 4'-dinitrodiphenyl according to the conditions of the experiment. The critical factor appears to be the polarity of the nuclear carbon atom to which the diazonium group is attached, and the optimum

Experimental conditions for hydrocarbon formation are found to be in harmony with the theoretical considerations.

REMOVAL of the amino-group from 2:6-dichloro-4-nitroaniline has been described by Beilstein and Kurbatow (*Annalen*, 1879, 196, 228), Holleman and Reiding (*Rec. Trav. chim.*, 1904, 23, 366), and Holleman and de Mooy (*ibid.*, 1915, 35, 8), the last workers recording a 73% yield of 3:5-dichloro-1-nitrobenzene; it has not been possible to repeat this result. Yields were erratic, but usually about 10% of the theoretical quantity of 3:5-dichloro-1-nitrobenzene was obtained together with 2:2':6:6'-tetrachloro-4:4'-dinitrodiphenyl. The best yields of 3:5-dichloro-1-nitrobenzene were obtained when the following conditions were observed: (a) low temperature; (b) slow rate of diazotisation; (c) the presence of a little water.

To explain these results it will be seen that in 2:6-dichloro-4-nitrobenzenediazonium sulphate both the inductive ( $-I$ ) and mesomeric ( $-M$ ) effects of the nitro-group produce positivity at the carbon atom to which the diazonium radical is attached. The inductive effect ( $-I$ ) of the chlorine atoms operating from the two ortho-positions produce positivity but, on the other hand, the mesomeric effect ( $+M$ ) will tend to reverse the polarity of the nuclear carbon atom. The combined effect of these substituents is to produce an intermediate state of positivity whereby both diaryl and hydrocarbon formation are possible (cf. Hodgson, Leigh, and Turner, *J.*, 1942, 744). Moreover, this state seems to be critical, since small changes in the experimental conditions produce considerable variation in the relative proportions of the products.

Waters (*J.*, 1942, 266) has shown that diaryl formation may operate through the un-ionised diazo-compound  $\text{Ar}-\text{N}=\text{N}-\text{X}$  rather than through the ionised diazonium salt  $\text{Ar}-\text{N}\equiv\text{N}^{\oplus}\text{X}^{\ominus}$ , and therefore conditions which favour the preservation of the latter structure will increase the yield of hydrocarbon at the expense of that of the diaryl. When deamination is carried out by ethyl alcohol in concentrated sulphuric acid, ionisation is inhibited and diaryl formation predominates. On the introduction of a little water, ionisation takes place and increased hydrocarbon formation results. Furthermore, the stability of the diazonium salt is increased by low temperature and slow rate of diazotisation, thus reducing the likelihood of diaryl formation.

Deamination by Hodgson and Turner's method (*J.*, 1942, 748), although performed in the absence of water, gave excellent yields of hydrocarbon with negligible quantities of diaryl. This suggests either that the diazonium ion is maintained in the presence of glacial acetic acid, or more likely (*vide* Hodgson and Turner, *loc. cit.*) that the cuprous oxide acts catalytically as well as functioning as a reducing agent.

#### EXPERIMENTAL.

*Deamination by Ethyl Alcohol and Sulphuric Acid.*—(a) Ethyl alcohol (37.5 c.c.), concentrated sulphuric acid (18 c.c.), and dry, powdered 2:6-dichloro-4-nitroaniline (10 g.) were mixed in a flask with reflux condenser. Finely powdered sodium nitrite (3.6 g.) was slowly added with agitation and cooling. The mixture was heated on the water-bath for 1 hour, and next day was steam-distilled. The crude 3:5-dichloro-1-nitrobenzene had m. p.  $60^{\circ}$  (4.5 g., 41%). Recrystallisation from 50% alcohol raised the m. p. to  $65-66^{\circ}$  (lit.  $65^{\circ}$ ) (yield 4.0 g., 46%).

(b) Ethyl alcohol (75 c.c.), concentrated sulphuric acid (36 c.c.), and 2:6-dichloro-4-nitroaniline (21 g.) were treated with sodium nitrite (7.2 g.). The mixture was mechanically stirred but no special precautions were taken to keep the temperature low. No 3:5-dichloro-1-nitrobenzene was obtained, but distillation with superheated steam gave a yellow substance, difficult to purify, m. p.  $148-158^{\circ}$ . This, recrystallised from boiling trichloroethylene, yielded 2:2':6:6'-tetrachloro-4:4'-dinitrodiphenyl as a yellow amorphous power, m. p.  $184^{\circ}$  with a tendency to sublime and decompose [Found: N, 7.20; Cl, 37.40; *M* (Rast), 382.  $\text{C}_{12}\text{H}_4\text{O}_4\text{N}_2\text{Cl}_4$  requires N, 7.33; Cl, 37.17%; *M*, 378].

Similar experiments produced 3:5-dichloro-1-nitrobenzene in yields of 14 and 23%.

(c) 2:6-Dichloro-4-nitroaniline (53 g.) was dissolved in warm concentrated sulphuric acid (93 c.c.). Ethyl alcohol (190 c.c.) was slowly added with cooling, causing the precipitation of the sulphate of the base in a finely divided state. Additional ethyl alcohol (40 c.c.) was added to render the mixture more fluid. The flask was cooled in ice-water and sodium nitrite (38 g. in saturated aqueous solution) added very slowly over a period of 24 hours, with mechanical stirring. After 1 hour on the water-bath at  $100^{\circ}$  the mixture was steam-distilled. Yield of recrystallised 3:5-dichloro-1-nitrobenzene, 30 g. (61%); m. p.  $63-64^{\circ}$  (lit.  $65^{\circ}$ ).

*Deamination by Hodgson and Turner's Method* (*loc. cit.*)—2:6-Dichloro-4-nitroaniline (2 g.) was dissolved in hot glacial acetic acid and rapidly cooled to room temperature. Finely powdered sodium nitrite (0.9 g.) was gradually added to ice-cold concentrated sulphuric acid (7 c.c.) with vigorous stirring, and the mixture then heated on the water-bath to complete solution. The acetic acid solution of the amine was slowly added to the nitrosylsulphuric acid cooled in ice and mechanically stirred. The diazotised mixture was gradually run into a suspension of finely pulverised cuprous oxide (2.8 g.) in ethyl alcohol (25 c.c.), with constant stirring. After being stirred for thirty minutes, the reaction mixture was diluted with an equal volume of water and distilled to remove ethyl alcohol and ethyl

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acetate. Steam distillation of the residue gave 3 : 5-dichloro-1-nitrobenzene (1.12 g., 60%); m. p. after recrystallisation from alcohol, 65° (lit. 65°).

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