365. *The Preparation and Kationoid Reactivity of Dichlorodinitromethane.*

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Methods for the preparation of dichlorodinitromethane from naphthalene tetrachloride (Marignac, *Ann. Chim. Phys.*, 1853, **38**, 16; Raschig, *Ber.*, 1885, **18**, 3328) and from the potassium salt of chlorodinitromethane (Losanitsch, *Ber.*, 1884, **17**, 849) have been recorded. The alternative mode of preparation now described, by distillation of 2 : 4 : 6-trichloroaniline with nitric acid, presents advantages in yield and in accessibility of the initial material, which can be obtained from aniline in good yield by the method of Chattaway and Irving (J., 1933, 42). The method is parallel to that of Losanitsch for dibromodinitromethane (*Ber.*, 1882, **15**, 472).

The course of the reaction between dichlorodinitromethane and hydrazine hydrate is consistent with the observations and interpretations of previous workers in respect of other aliphatic halogen-substituted polynitro-compounds. Dibromodinitromethane is reduced by hydrazine in alkaline solution, one bromine atom being removed in the cold to yield a salt of bromodinitromethane, and the second bromine atom is removed at higher temperatures (Macbeth and Pratt, J., 1921, **119**, 1356); the lability of the halogen is attributed to an inductive effect originating at the two nitro-groups (Henderson and Macbeth, J., 1922, **121**, 892). Since similar considerations obtain in the case of the dichloro-compound, a parallel reaction was anticipated. It has been pointed out, however, that in analogous bromo- and chloro-compounds in which the halogen atoms are endowed with an induced positive nature the halogen in the bromo-compound, in virtue of its inherently less electronegative nature, is rendered effectively more electropositive than that in the chloro-compound; thus, for example, hydrazine removes one halogen atom from *cyclo*hexane*spiro*-4 : 4-dibromo*cyclo*hexane-3 : 5-dione, while the corresponding dichloro-compound is unattacked (Macbeth, J., 1922, **121**, 1116). It was therefore expected that the reduction of dichlorodinitromethane by hydrazine would proceed more slowly than that of dibromodinitromethane; complete extinction of the induced positive nature of the halogen, however, appeared improbable, since chloropicrin, in which the conditions are still less favourable to the manifestation of a kationoid character, slowly oxidises hydrazine in alkaline solution (Macbeth and Pratt, *loc. cit.*).

The reduction has been found to take place in accordance with these predictions. A further point of interest is that the reduction by alkaline solutions of hydrazine in the cold is arrested after the elimination of one chlorine atom, thus,

$$2CCl_2(NO_2)_2 + N_2H_4 = 2CHCl(NO_2)_2 + N_2 + 2HCl$$

whereas in the absence of excess alkali reduction continues slowly beyond this stage. This further reaction, by analogy with the reduction of dibromodinitromethane at high temperatures, is probably the slow removal of the second halogen atom, and its inhibition by alkali may be attributed to the formation of the *aci*-salt of chlorodinitromethane and the consequent removal of the inductive influence of one normal nitro-group.

Preparation of Dichlorodinitromethane.—2 : 4 : 6-Trichloroaniline (23 g.) was treated with nitric acid (200 c.c.; *d* 1·42), and the mixture gently heated for a short time and then distilled. Dichlorodinitromethane separated from the distillate as an oil, and was purified by repeated distillation in steam and dried over calcium chloride (Found : Cl, 41·0. Calc. : Cl, 40·5%). Analysis of an incompletely purified sample of the oil (Cl, 42·7%) suggested the presence of a highly chlorinated impurity in the crude product. Yield, 10 g.

Reduction with Hydrazine.—A 10% solution of hydrazine hydrate was prepared by dissolving 40·6 g. of the sulphate in water, adding 25 g. of sodium hydroxide (1 equiv.), and diluting the filtered solution to 100 c.c. 5 C.c. of a 0·4*M*-solution of dichlorodinitromethane in alcohol were introduced into a Lunge nitrometer, and 5 c.c. of the hydrazine solution added. A steady evolution of nitrogen commenced; 3·1, 8·02, and 12·7 c.c. (at N.T.P.) were liberated in 1, 3, and 7 minutes respectively, and the reaction proceeded thereafter with diminishing velocity. The reduction of 0·002 g.-mol. of dichloro- to monochloro-dinitromethane requires the liberation of 22·4 c.c. of nitrogen at N.T.P. This amount was eventually exceeded, indicating further reduction of monochlorodinitromethane; it was therefore not possible to assign experimentally a precise time for the completion of the main reaction. The second stage was, however, very slow; after 1 week the volume of nitrogen liberated was 26·3 c.c., of which 3·9 c.c. are attributable to the consecutive reaction. Its influence on the early measurements will therefore be negligible, so that for purposes of comparison the main reaction may be regarded as being 13·8%, 35·8%, and 56·7% completed in 1, 3, and 7 minutes respectively.

Dibromodinitromethane was reduced under identical conditions, 24·4, 34·5, 35·9, and 39·5 c.c. (at N.T.P.) of nitrogen being liberated in 1, 36, 68, and 170 minutes respectively. The removal of the first bromine atom being assumed to be rapid relative to the ensuing reduction of monobromodinitromethane, the former reaction is completed in 1 minute, and the second stage proceeds much more rapidly than in the case of the chloro-compound. In several trials the volume of nitrogen liberated on completion of the reaction approximated to the calculated amount for reduction to dinitromethane (44·8 c.c.), though at the ordinary temperature this amount was never quite fully realised.

The reductions were repeated under similar conditions with a 10% hydrazine solution containing excess of alkali (from N_2H_4,H_2SO_4 + 3 equivs. NaOH). 0·002 G.-mol. of dichlorodinitromethane liberated 20·6 c.c. of nitrogen at N.T.P. in 45 minutes (92% of the theoretical quantity for reduction to the monochloro-compound). 0·002 G.-mol. of dibromodinitromethane liberated 22·0 c.c. of nitrogen at N.T.P. almost instantaneously (98·2% of theoretical for reduction to monobromodinitromethane). No further increase in the volume of liberated nitrogen was observed on prolonged standing.

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