CCCXXV.—*The Dinitration of* m-*Dichlorobenzene.*

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THE dinitration of *m*-dichlorobenzene has long been known to give a large yield of 1 : 3-dichloro-4 : 6-dinitrobenzene (I); as pointed out by Davies and Hickox (J., 1922, **121**, 2649), a considerable quantity of mixed nitro-derivatives is also formed. This mixture gives the correct analytical figures for dichlorodinitrobenzenes, and is found to consist practically exclusively of (I) and 1 : 3-dichloro-2 : 4-dinitrobenzene (II). When the nitration of *m*-dichlorobenzene is carried out at 99° under carefully regulated conditions, the product obtained contains about 85% of (I) and 15% of (II), as shown by means of the melting-point curve. The yield of the isomeride (I) can be increased by final crystallisation from concentrated sulphuric acid.

EXPERIMENTAL.

1 : 3-Dichloro-4 : 6-dinitrobenzene, m. p. 101·0°, is obtained pure by recrystallisation of the dinitration product of *m*-dichlorobenzene from alcohol.

1 : 3-Dichloro-2-nitrobenzene (m. p. 70°), from *p*-nitroaniline after Holleman and Reiding (*Rec. trav. chim.*, 1904, **23**, 368), is heated on the water-bath for about 4 hours with three times its weight of nitric acid (*d* 1·50), and the 1 : 3-dichloro-2 : 4-dinitrobenzene (m. p. 68·0°) crystallised from alcohol.

The isomerides (I) and (II) used for obtaining the melting-point curve were prepared as above. For ordinary purposes pure (II) is more easily prepared from the mixed isomerides [freed from a large amount of (I) by means of alcohol] by crystallisation from concentrated sulphuric acid.

Körner and Contardi (*Atti R. Accad. Lincei*, **18**, i, 101) found that (II) was further nitrated by a mixture of sulphuric and fuming nitric acids; but the careful nitration of *m*-dichlorobenzene with these reagents under the conditions described below yields dinitro-compounds only.

The melting-point curve of (I) and (II) is determined in the usual manner, it being found impossible to obtain trustworthy figures for the second solidification points when a large proportion of the higher-melting isomeride is present. The solidification points obtained are as follows :—

(II), %.	First s.p.	Second s.p.	(II), %.	First s.p.	Second s.p.
0	101·0°	—	79·73	57·9°	48·2°
15·06	91·4	—	89·18	62·8	48·0
31·07	79·7	48·1°	100·00	68·0	—
49·80	62·4	48·0			

It follows from the curve (see p. 2462) that the eutectic mixture melts at about 48·1° and contains about 62% of (II).

Proportion of the Isomerides formed in the Dinitration of m-*Dichlorobenzene.*—A cold mixture of nitric acid (*d* 1·54; 170 g.) and concentrated sulphuric acid (340 g.) is treated with *m*-dichlorobenzene (50 g.), and after the first reaction is over the mixture is heated under anhydrous conditions at 99° for 1 hour with continual shaking. The cold product is treated with ice, washed free from acid, and dried in a vacuum (yield, 76·5 g. Calc. for dichlorodinitrobenzenes, 80·5 g., the small loss unavoidably occurring during the thorough washing) (Found : N, 11·9, 12·0; Cl, 29·7, 29·7. Calc. for $C_6H_2O_4N_2Cl_2$: N, 11·8; Cl, 29·8%. The chlorine was determined by Robertson's method, the Carius method giving an extremely stable nitro-compound). This mixture is referred to as Mixture A.

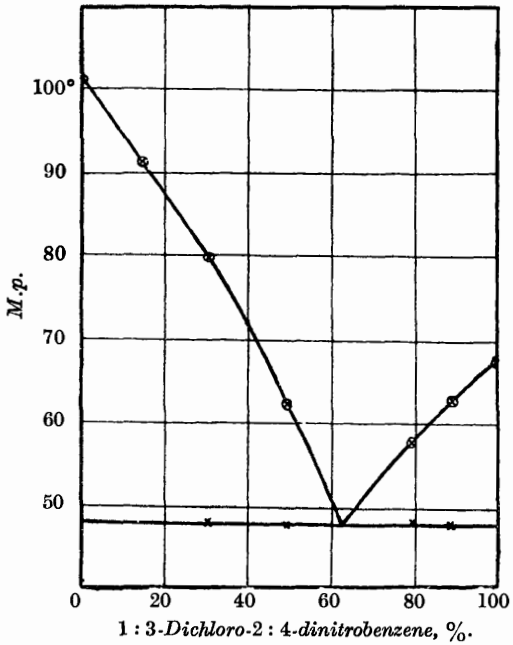
Mixture B. Mixture A (50 g.) is crystallised from alcohol, and pure (I) obtained. The total alcoholic filtrates (500 c.c.) are evaporated to dryness at room temperature under diminished pressure,

and the mixed residual nitro-compounds analysed (Found : N, 12·0; Cl, 29·8. Calc. : N, 11·8; Cl, 29·8%). Pure (I) was removed in this way in order to enable the second solidification point to be accurately determined.

The first solidification points of mixtures A and B are 91·4° and 65·8°, respectively. The second solidification point of mixture B

FIG. 1.

Melting-point curve of 1 : 3-*dichloro*-4 : 6-*dinitrobenzene and* 1 : 3-*dichloro*-2 : 4-*dinitrobenzene.*



(46·0°) is only 2·1° below that of the eutectic mixture of (I) and (II), and this indicates that the mixture produced in the nitration is almost entirely composed of (I) and (II). The melting-point curve of (I) and (II) can consequently be applied, and by its means the dinitration mixture of *m*-dichlorobenzene is found to contain about 85% of (I) and about 15% of (II).

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