

LXXXVIII.—*The Nitration Products of the Isomeric Dichlorobenzenes.*

By PERCIVAL HARTLEY and JULIUS BEREND COHEN.

THE progressive nitration of the dichlorotoluenes has been investigated by Cohen and Dakin (*Trans.*, 1902, 81, 1344), and the constitution of the mono- and di-nitro-derivatives has been ascertained in each case. The results show that the two nitro-groups in the dinitro-derivatives of the 6-dichlorotoluenes follow strictly the meta-law of substitution.

Since the publication of this communication, three papers on the nitration products of *o*-, *m*-, and *p*-dichlorobenzene have appeared. Morgan (*Trans.*, 1902, 81, 1378), who studied the nitration of the para-compound and confirmed the observation of Jungfleisch (*Jahresber.*, 1868, 343) that two dinitro-compounds are formed, states that "the nitration product consists chiefly of the isomeric 2:5-dinitro-1:4-dichlorobenzene, the required 2:6-dinitro-1:4-dichlorobenzene being only a by-product. This result is of interest, because it affords another illustration of the fact that, as substitution progresses, the rules governing the orientation of entrant radicles become considerably modified."

The second paper is by Blanksma and Terwogt (*Rec. trav. chim.*, 1902, 21, 286) on the derivatives of 1:3-dichloro-4:6-dinitrobenzene, the position 6 allotted to the second nitro-group being apparently based on Nietzki and Kehrman's observations (*Ber.*, 1887, 20, 3 4).

In the third paper, Blanksma (*Rec. trav. chim.*, 1902, 21, 419) deals with the products of the nitration of *o*-dichlorobenzene, and states that on nitrating *o*-dichlorobenzene only a little 1:2:4:6-dichlorodinitrobenzene is obtained, the 1:2:4:5-isomeride being formed in greater proportion.

No quantities are given, and no proof is offered that the principal product is an ortho-dinitro-compound.

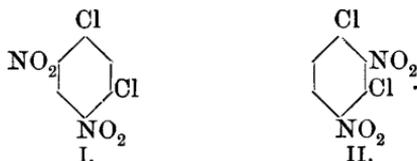
If the above facts are correct, the principal products of nitration are an ortho-dinitro-compound in the case of *o*-dichlorobenzene, a meta-dinitro-compound in the case of *m*-dichlorobenzene, and a para-dinitro-compound in the case of the para-isomeride.

On the other hand, there is an absence of data of both a qualitative and quantitative character in regard to the ortho- and para-compounds, without which any important departure from the meta-law of substitution by the entrant nitro-groups cannot be regarded as being established. We have therefore repeated the nitration of the three

dichlorobenzenes in order to obtain the required information. Before studying the dinitro-compounds, we have ascertained the position occupied by the first nitro-group in each of the three cases. The results of further nitration may be briefly summarised as follows :

The conversion of *o*-dichlorobenzene into a dinitro-compound is peculiarly difficult to effect, and after heating it at 110—120° with a large excess of fuming nitric acid mixed with double its weight of fuming sulphuric acid for 32 hours, only about 25 per cent. of the theoretical amount of the dinitro-compound (m. p. 104°) was obtained, the remainder of the product being mononitro-compound. This substance is an ortho-dinitro-compound, and the formula given by Blanksma is therefore correct.

*m*-Dichlorobenzene is wholly converted into a meta-dinitro-derivative, which, according to Nietzki and Kehrmann (*loc. cit.*), has the first of the two alternative formulæ :



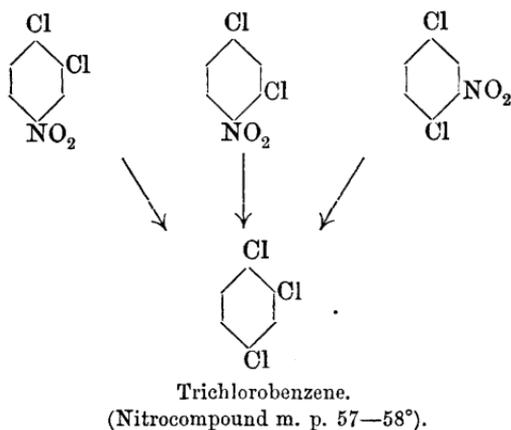
*p*-Dichlorobenzene gives two dinitro-derivatives, the meta- and para-compounds, as stated by Morgan, but we find the yield of meta-compound to be about 6 times that of the para-isomeride.

Hence, the only notable divergence from the meta-law is exhibited by *o*-dichlorobenzene. Both the resistance offered to the introduction of the second nitro-group and the position eventually occupied by it, afford a curious exception to the ordinary rule for which it is difficult to find an explanation.

#### EXPERIMENTAL.

##### *Constitution of the Mononitro-derivatives of the Dichlorobenzenes.*

The method of determining the constitution of the three mononitro-derivatives obtained by nitrating the three dichlorobenzenes was to replace the nitro-group by chlorine in the usual way. Each of the compounds gave the same trichlorobenzene, which formed a trichloronitrobenzene (m. p. 57—58°), the latter being converted into a tetrachlorobenzene (m. p. 138—139°). The mononitro-derivatives must therefore have the following formulæ :



*Nitration of o-Dichlorobenzene.*

To 10 grams of the *o*-dichlorobenzene prepared from *o*-chloronitrobenzene (Kahlbaum) was slowly added a cold mixture of 40 grams of fuming nitric acid (sp. gr. 1.5) and 75 grams of fuming sulphuric acid containing 18 per cent. of  $\text{SO}_3$ . The mixture was then heated on the oil-bath for 16 hours at 110—120°; the product, which was poured into water and left until the insoluble portion became hard, was then filtered, powdered, dried, and treated with the same quantity of acids, and for the same length of time as before. The final product was recrystallised from acetic acid and water, and yielded about a fourth of its weight of colourless, foliated crystals melting at 104°. The remainder from its low melting point (it is semi-solid at the ordinary temperature) appeared to consist mainly of unaltered mononitro-compound (m. p. 43°).

Blanksma's method consists in heating the dichlorobenzene with a mixture of 4 times its weight of fuming nitric acid and 6 times its weight of concentrated sulphuric acid for one hour on the water-bath, and he obtained a product melting at 110°. We cannot confirm his results, for in some preliminary experiments carried out in a similar manner with the addition of a stirring apparatus to keep the acid and dichlorobenzene well mixed, the product did not solidify after heating on the water-bath for a week.

The compound melting at 104° was reduced to the diamine with tin and hydrochloric acid; this base gave the phenanthraquinone test for ortho-diamines, but no reaction with nitrous acid, thus showing the absence of a meta-diamine. The original compound must therefore be 1 : 2-dichloro-4 : 5-dinitrobenzene.

*Nitration of m-Dichlorobenzene.*

The *m*-dichlorobenzene prepared from *m*-nitroaniline was nitrated in the manner described in the case of the *o*-compound, the mixture being heated for 8 hours at 110—120° and then poured into water. A theoretical yield of crude dinitro-compound (m. p. 80—90°) was obtained (the mononitro-compound melts at 33°). After one crystallisation from alcohol it melted at 99—100°, and at 103° after a second crystallisation. Fifty to sixty per cent. of the pure substance was thus obtained. No other product could be isolated from the mother liquor, and the absence of any ortho-dinitro-compound, which is the only other possible product, was assured by reducing the crude dinitro-compound and applying the phenanthraquinone test. A second nitro-group occupying a meta-position to the first leaves a choice between two formulæ, as already stated. We attempted to confirm Nietzki and Kehrman's formula by nitrating 1:3-dichloro-2-nitrobenzene, which can only give formula II on p. 866, but have not yet obtained this substance in a pure state.

*Nitration of p-Dichlorobenzene.*

The nitration of *p*-dichlorobenzene was conducted in two steps. The pure mononitro-compound (m. p. 54°) was first prepared and then treated as described by Morgan (*loc. cit.*). The product, which slowly solidified when poured into water, was filtered and dried, the treatment with acid being repeated to ensure complete nitration. An attempt was made to separate the two dinitro-derivatives by fractional crystallisation from alcohol, but although the pure dinitro-compounds were eventually obtained, the process proved to be useless as a quantitative method of separation. The meta-dinitro-compound crystallises from alcohol in large, colourless plates (m. p. 101—102°) (Engelhardt and Latschinow, *Zeitsch. für Chemie*, 1870, 234, give 101°). The para-compound crystallises in long prisms which melt at 105—106° (E. and L. give 104°). The positions of the nitro-groups were confirmed by reduction and the application of the usual tests for diamines.

The quantitative method which we have employed for estimating the two dinitro-compounds in the mixture is to reduce them to the diamines, as described by Morgan, but, instead of using water, the separation of the bases was effected by means of alcohol, in which the para-compound is very slightly soluble. Tin and hydrochloric acid were used for reduction as giving a cleaner product than the iron and hydrochloric acid employed by Morgan. The reduction product

was made alkaline and at once extracted with chloroform. After dehydrating and removing the chloroform, the bases crystallised usually with a red tint, which became deeper the longer the product was exposed to the air. As the quantitative estimation of the original dinitro-compounds depends in the first instance on a quantitative yield of diamine, the reduction product was weighed in each case and a yield of 88, 90, and 95 per cent. respectively of the theoretical quantity was obtained in 3 experiments with 5, 15, and 20 grams of material. The reduction product was extracted with a small quantity of warm alcohol and filtered from the undissolved portion. The crystals which separated from the mother liquor on cooling were also removed by filtration. Both these portions consist of nearly pure para-diamine, which melts at 164°. The mother liquor was then evaporated, the various fractions weighed, and the melting points ascertained. The melting point of the pure meta-diamine is given as 99—100°.

The following are the results of 3 experiments :

Weight of the mixed bases.	Less soluble fraction.	M. p.	More soluble fraction.	M. p.	Per cent.	
					Less sol. fraction.	More sol. fraction.
(1) 10 grams	1.1 grams	161—163°	4.3 grams	85—89°	14	80
	0.3 „	159—161	1.2 „	75—80		
	— „	—	2.5 „	68—72		
	1.4 „	—	8.0 „	—		
(2) 8 „	0.8 „	162	1.4 „	85—90	12	79
	0.15 „	161—162	0.6 „	70—75		
	— „	—	2.8 „	70—75		
	— „	—	1.5 „	64—70		
	0.95 „	—	6.3 „	—		
(3) 8 „	1.1 „	163	not estimated	—	13.7	—

The results are fairly concordant. In the 3 experiments, 14, 13.7, and 12 per cent. of the mixed bases consist of nearly pure para-compound. It was thought at first that the low melting point of the more soluble portion might be due to the presence of a small amount of the para-compound or of dichloroaniline obtained from dichloronitrobenzene in the crude dinitro-product, but we found that even the most fusible fraction could be easily purified by removing a small

quantity of resinous matter which appears to be formed by the atmospheric oxidation of the base and is insoluble in water.

All the fractions may be purified with very little loss by either distilling in steam, crystallising from hot water, or dissolving in hydrochloric acid, filtering from impurities, and reprecipitating the base.

In conclusion, we wish to thank Mr. R. Barton for his help in conducting some of the preliminary experiments.

THE UNIVERSITY OF LEEDS.

---