NITRATION OF *p*-DICHLOROBENZENE. 3247

CCCLXXXV.—Nitration of p-Dichlorobenzene.

By HAROLD JAMES PAGE and BENJAMIN RICHARD HEASMAN.

THE nitration of p-dichlorobenzene was first studied by Jungfleisch (Ann. Chim. Phys., 1868, [iv], **15**, 257), who showed that by the prolonged action, at the boiling point, of a mixture of fuming nitric and concentrated sulphuric acids the mononitrocompound first formed was converted into a mixture of dinitrocompounds. These he separated partially by fractional crystallisation from alcohol. Engelhardt and Latschinoff (Jahresbericht, 1870, 521) isolated two dinitrodichlorobenzenes in a state of purity from the nitration product. They showed that the less soluble (α) isomeride (m. p. 104°) was 1:4-dichloro-2:6-dinitrobenzene; to the more soluble (β) isomeride (m. p. 101°) was assigned the constitution of 1:4-dichloro-2:5-dinitrobenzene. Korner (Jahresbericht, 1875, 324) confirmed these results and gave the melting points of the α - and β -isomerides as 104.9° and 101.3°, respectively.

Considerably later, Morgan (T., 1902, 81, 1362) studied the same nitration and found that the mononitro-compound was formed quite readily; he stated, however, that the introduction of the second nitro-group "is far less readily effected" and that it is necessary to use a mixture of 10-15 per cent. oleum and an excess of fuming nitric acid at 110-115° in order to effect the further nitration. He did not attempt to purify the crude nitration product so obtained. Hartley and Cohen (T., 1904, 85, 868), working under the same conditions as Morgan, found that the separation of the two isomerides by fractional crystallisation from alcohol was difficult, and useless as a quantitative method of separation. They estimated the relative proportions of the two isomerides in the crude nitration product by reduction to diamines and separation of the latter, and concluded that the 2:6-dinitro-compound and the other isomerides were formed in the proportion of roughly 7:1. As explained below, the authors find that these conclusions are

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incorrect in so far as it is possible under suitable conditions to obtain a good yield (83 per cent.) of dinitration product containing almost equal proportions of the two isomerides. These conclusions are confirmed by the work of Sané (Inaug. Diss., "Untersuchungen über Nitrophenole," Berlin, 1910), of which the authors were unaware until the completion of their work.* Not long after the completion of this work, an investigation on the dinitro-derivatives of p-dichlorobenzene was published by Nason (J. Amer. Chem. Soc., 1918, 40, 1602). This author nitrated p-dichlorobenzene under the conditions used by Rutgers (Inaug. Diss., Bâle, 1893), involving a long nitration in the presence of a large excess of nitric acid, and claimed to have shown that all three possible dinitro-compounds were produced, the chief product being a hitherto unnoticed substance melting at 81° which she claimed to be 1:4-dichloro-2:5-dinitrobenzene. This constitution had hitherto been assigned to the isomeride melting at 101°, but Nason concluded that the constitution of the latter substance was fixed by implication as 1: 4-dichloro-2:3-dinitrobenzene.

The latter conclusion is supported by the subsequent work of Holleman and Hollander (Rec. trav. chim., 1920, 39, 435) and of Holleman, Hollander, and van Haeften (ibid., 1921, 40, 323), who showed that all three possible isomerides are present in the nitration product prepared by Jungfleisch's method (loc. cit.) and that the melting point of 1:4-dichloro-2:3-dinitrobenzene (synthesised by an alternative method) is 103°, this substance being identical with Jungfleisch's β-isomeride. The assignment by Engelhardt and Latschinoff (loc. cit.) of the constitution of 1: 4-dichloro-2:5-dinitrobenzene to this substance was thus erroneous. Holleman and Hollander (loc. cit.) synthesised the isomeride with the latter constitution, and found that it had a melting point of 119°. Nason (loc. cit.) claimed that this isomeride was the chief constituent of the dinitration product, but as the substance she isolated had a melting point of only \$1°, Holleman and Hollander's conclusion that this product was impure would seem to be justified.[†]

It would appear from the authors' results that the great preponderance of the 2:6-dinitro-compound in the nitration product, observed by all the earlier workers on the subject, is to be explained by the relatively drastic conditions employed by these workers in

^{*} This investigation was carried out during the earlier part of 1917, but owing to circumstances it could not be published before.

 $[\]dagger$ Holleman and Hollander's conclusion is confirmed by the recent work of Macleod, Pfund, and Kilpatrick (*J. Amer. Chem. Soc.*, 1922, 44, 2260), who showed that Nason's product, of melting point 81°, was a molecular compound of the 2:3- and 2:6-dinitro-compounds.

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the nitration. The authors have found that the dinitration is by no means difficult to effect provided a nitration mixture of a suitable composition be used, but that by employing an unnecessarily long time of nitration the product does indeed contain a large excess of the 2:6-isomeride, owing apparently to the fact that the other isomerides undergo some secondary reaction, probably oxidation, more readily than the 2:6-compound, and therefore a relatively large quantity of them is destroyed during a protracted nitration. Increase of temperature has been found to have much greater effect on the rate of nitration than on this secondary reaction. The

FIG. 1.

Influence of Temperature of Nitration on the Setting Point of the Product (Experiments E and L).

The temperature during each stage of the nitration is shown against the part of the graph referring to that stage.



conditions of dinitration worked out by the authors involve the maintenance of the nitration mixture at a temperature not exceeding 85° for one hour, by which time the initial reaction has moderated, followed by a rapid increase to 120° , which is maintained for a further half hour. The results of the experiments on which the authors' conclusions and final method are based are given in Table II. A preliminary small-scale experiment, using mixed acid of 5 per cent. water content, having given incomplete dinitration, experiments A and B were designed to find out whether a more complete nitration could be effected by using a mixed acid of lower water content; they showed that this was not the case. In

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experiments B, C, and D, the proportion of nitric acid was varied; they showed that it was necessary to employ 2.5 mols. of nitric acid to 1 mol. of mononitro-compound in order to obtain a product of high setting point. In experiments E and F, the factors of time and temperature were varied within the widest possible limits; the results throw considerable light on the course of the reaction.

If the temperature coefficient of the nitration were markedly less than that of the secondary reaction, experiment E, which was a protracted one at a low temperature, should have given the better

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result. On the other hand, if the nitration were more accelerated than the other reaction by increase of temperature, experiment F, which was of short duration and in which the temperature was very rapidly raised, should have given the better result. It will be seen that the product from experiment F was of much higher setting point. The contrast between these two experiments is strikingly shown in Fig. 1, where the alterations in the setting point of the product are plotted against time for experiments E and L (the latter a still better example of a nitration under the same conditions of those of F). The remaining experiments G to L were devoted to a more detailed study of the effect of slight variations in the conditions from those used in experiment F, and the method finally

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adopted was based on the results of these experiments. In experiment H, samples of acid were taken at the end of stages 1B, 2A, and 2B, and Fig. 2 shows the rate of consumption of nitric acid and of production of nitrous acid as determined by the analyses of these samples. It was thought that under the improved conditions of experiment F as compared with experiment C it might still be possible to obtain a product of good setting point with less than $2\cdot5$ mols. of nitric acid, but it is seen from experiment K that this was not the case; although only 2 mols. of nitric acid were used at the outset, it was found necessary to add a further 0.5 mol. of nitric acid at the end of stage II in order to bring up the setting point.

It may be pointed out that as an indication of the degree of completeness of the nitration the percentage yield is of little value taken by itself, for the increase in weight caused by the further nitration of a partly nitrated product may be equalled or even exceeded by the loss due to simultaneous oxidation. This is illustrated by a comparison of experiments B and L, where the percentage yields are almost identical whereas the setting points differ by almost 20°.

With regard to the composition of the crude nitration product, the authors obtained by the method of separation described below only the 2:6- and 2:3-isomerides in a state of purity, and since the quantities of these obtained accounted for almost the whole of the product, the quantity if any of the 2:5-isomeride produced by the authors' method of nitration must have been very small.

Of the three possible isomerides only one, namely, the 2:6dinitro-compound, has a labile chlorine atom. The amount of this constituent can accordingly be estimated by treatment of the crude nitration product with alcoholic ammonia in the cold for one or two days and titration of the ammonium chloride produced. An estimation by this method gave a value of 41.5 for the percentage of the 2:6-dinitro-compound.

Another method of studying the composition of the mixture is by thermal analysis. The fusion curve of a binary mixture of the pure 2:3- and 2:6-dinitro-compounds constructed from the data in Table I is of the usual shape. The eutectic mixture contains

TABLE I.

Freezing Points of Mixtures of 2:6-Dinitro- and 2:3-Dinitrop-dichlorobenzene.

2:6-Dinitro-compound %	0	20	30	35	40	41	45
F. p	$101 \cdot 2^{\circ}$	86•5°	79∙5°	75∙5°	71·7°	73∙0°	76∙5°
2:6-Dinitro-compound %	50	60	70	80	90	100	
F . p	80∙0°	87·5°	93∙0°	98∙5°	103∙0°	106·0°	

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40 per cent. of 2 : 6-dinitro-*p*-dichlorobenzene and freezes at 71.6°. As the top setting point of the crude nitration product, 69.5°, is only slightly inferior to the freezing point of the eutectic mixture, and as the percentage of the 2 : 6-dinitro-compound in the nitration mixture as determined by the method described above, namely, 41.5 per cent., is only slightly higher than that of the same compound in the eutectic, it would appear probable that the percentage of substances other than the 2:3- and 2:6-dinitro-compounds in the mixture is small.

The agreement between the authors' figure for the amount of 2:6-isomeride and that found by Sané (*loc. cit.*), namely 48.6 per cent., is tolerably satisfactory when it is remembered that Sané's method, which was to weigh the crude product of the action of aniline on the nitration product, would probably be liable to give high results.

EXPERIMENTAL.

1. Nitration of p-Dichlorobenzene. 1:4-Dichloro-2-nitrobenzene. In conformity with the results of earlier investigators, no difficulty was experienced in effecting this nitration. Nitrating acid of the following composition : H_2SO_4 58, HNO_3 36, H_2O 6 per cent. was used. To a quantity of this acid containing only a slight excess of nitric acid beyond that theoretically required, *p*-dichlorobenzene was added gradually, the whole being stirred continuously; the rate of addition was so regulated that the temperature did not exceed 70°. When the whole of the charge had been added, the mixture was heated at 100° for fifteen to thirty minutes. The nitration product was then separated and adhering acid removed by passing steam into the molten substance, beneath water. The crude, washed product so obtained had a setting point of 52° and was practically pure 1: 4-dichloro-2-nitrobenzene (the melting point of the pure substance is 54.5°).

2. Experiments on the Nitration of 1:4-Dichloro-2-nitrobenzene.— Twelve separate nitrations of this substance were carried out in which the influence of composition of nitrating acid and of the time and temperature of the nitration were studied. Particulars of the experiment are shown in Table II. The crude mononitro-compound obtained as above was used throughout; the nitrations were all carried out in a small iron nitrating pot with a working capacity of $1\frac{1}{2}$ litres, provided with mechanical stirring and jacketed so that it could be heated with high-pressure steam or cooled with water. The results of these experiments have been discussed on pp. 3249—3251.

3. Method finally adopted for the Nitration of 1:4-Dichloro-2nitrobenzene.—Nineteen hundred grams of nitrating acid of the following composition: H_2SO_4 78.5, HNO_3 16.7, H_2O 5.1 per cent.

					N	II	'R.	A 7	FI (22	v	0	F	p	- I	DI	CI	II	0	R	DE	ЗE	N	ZEN	E.							
	г.	400	5-1	2.5	65-70°	20	75-80°	40	80-120°	15	120°	30	120°	30	120°	30				51.5°	60-7°	65°	64.5°	65.5°	68-5°		409	83				
	К.	400	5.1	2.0+	65-70°	20	75-80°	40	80-120°	lõ	120°	30	added the	N/A=0-5	mol. of	HNO.	120°	30]	45.6°	$50-2^{\circ}$	56.2°	69.3°		68°		395	81	20.6	0.4	3.0	
	J.	250	5-1	0 61	65-70°	20	70-85°	40	85-120°	20			120°	30					l	50.4°	63°		65-8°		68.3°		270	87				
	I.	400	5.1	2.5	60-65°	20	-70-75°	40	75-120°	20	120°	30	120°	30					-	49.5°	62.8°	64.9°	66.3°		69-2°		390	80				
	Н.	500	5.1	2.5	65°	20	70-75°	40	75-120°	20	120°	30	120°	30						50.6°	62.6°	63.5°	64.6°		70.2°		425	69	67.7	1-5(?	3.1	1 1 1
enzene.	с ^і	250	5.1	2.2	65-70°	20	70-75°	40	75-120°	15	120°	30	120°	30	120°	30	120°	30		49.9°	56°	57°	°1·6°	63° 60°	64°		260	84				V
3									•				V		m		0						V	щC								
namenan-i	F.	250	5.1	2.0 7	65-70°	20	70-75°	40	75-120	15	120°	30	120°	30	120°	30				abt. 30°	65°	67°	67°	67°	69°		247	80	9-6 9	0.4	2.2	
T-n man	Е	400	5.1	2.0	60-70°	30	10°	60	$70 - 100^{\circ}$	60	100°	60	100°	60	110°	60				bel. 36°	46°	48°	43°	41.5°	53°		391	80	68-5	0.2	1-7	
					۷		m		A°		m		A		р				Ā	р	V	р	¥	B								
	Ģ.	250	<u>5</u> .]	5-0	60-100	60			100-120	60			120°	60					57°		60°		60.7°		62.5°		255	83	1.69	0.5	2.7	1
14 667 (16 60)	ರ	250	5.1	2.2	60-85°	50			85-120°	70			120°	09							64-2°		63°		69-3°		265	86	67.8	9.0	1.8	1 40 Peter
•	в.	250	5.1	1.9	45–75°	30			$75 - 120^{\circ}$	0 6			120°	60							40°		41°		50-8°		260	84	69.2	0.2	2.3	
	Α.	250	5.Q	<u>c.1</u>	55-75°	20			75-110°	100			110°	09									43°		50·7°		255	83	6.7.9	0-2	2.1	
	riment	te (grams) *	ting % H O	d Moi. HNU ₃ to 1 moi. subst.	(Temp.	Time (mins.)	Temp.	V.Time	(Temp.	Stage 2 Time	Temp.	(Time	Temp.	Time	Stace a Temp.	Duege of Time	Temp.	(Time	setting Stage 1	nts at	of Stage 2		Stage 3		g point of dry crude product	it of dry crude product in	us	ble	osition % H _* SO ₄	vaste % HÑO.	1 % HNO ²	The shelp shows a second second
	Exp(Char	Nitr	96		Nitro	210111												Acid	poi	enc				Settin	Weig	gra	۲X %	Comp	f,	BCI	4

TABLE II.

Nitration of Mononitro-n-dichlorohonzone

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(obtained by mixing 96 per cent. sulphuric acid and 90 per cent. nitric acid in the proportions of 2,400 c.c. to 665 c.c.) were placed in the nitrating pot and heated at 60°. Four hundred grams of crude 1:4-dichloro-2-nitrobenzene were added gradually in the course of twenty minutes, with constant stirring, the temperature being kept below 75° by water cooling. The mixture was then heated at 75-85° for forty minutes, after which the temperature was raised to 120° in fifteen minutes and this temperature maintained for a further eighty minutes. A sample of the crude, washed product showed a setting point of 65°. The temperature was allowed to fall to 80°, after which 275 c.c. of water were slowly run in with stirring as before, the temperature being allowed to rise to 90°. The mixture was allowed to settle and the molten nitration product separated and washed by covering it with boiling water and blowing steam through it until the wash waters were no longer acid. It was then allowed to solidify, and the solid cake wiped dry from adhering moisture and dried in the molten state at 100° for a few hours. The setting point of the product was 69.5° and the yield was 83 per cent. of the theoretical.

4. Description of the Crude Nitration Product.—The product obtained as above is a practically white solid of very hard consistency. The vapours produced by the molten substance are extremely irritating to the eyes, nose, and throat. An irritating rash is liable to develop if the solid substance or its solution or vapour come into contact with the skin. The density of the fused solid is d_{av}^{10} ·1·72. When the fused substance is slowly cooled, the liquid clouds at 69·6° and finally gives a setting point of 69·5°.

5. Separation and Purification of 1:3-Dichloro-2:6-dinitrobenzene and 1:4-Dichloro-2:3-dinitrobenzene.-The separation and isolation in a state of purity of the two isomeric dinitro-compounds at first presented some difficulties. As already noted by Hartley and Cohen (loc. cit.), the difference in the solubilities of the two isomerides in alcohol was so small that their separation by fractional crystallisation from this solvent was a very tedious and protracted operation. A method whereby the separation could be rapidly and conveniently effected was found in the fractional precipitation of the two isomerides from their benzene solution by means of light petroleum. The crude nitration product was dissolved in benzene to form a concentrated solution. Sufficient light petroleum was added to precipitate about half of the dissolved substance, which was filtered off. The material in the motherliquor was recovered. Each of the two fractions was then separately dissolved in benzene and precipitated with light petroleum as before. The mother-liquor from the treatment of the less soluble fraction

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was evaporated and the residue added to the precipitate from the treatment of the more soluble portion. This process was continued two or three times until the products consisted of a less soluble and a more soluble fraction, the melting points of each of which were over 95°, together with a small quantity of residues in the motherliquors. These two fractions were then separately recrystallised from carbon tetrachloride. The purified product obtained from the less soluble fraction had a constant melting point of 105-106° and was thus 1: 4-dichloro-2: 6-dinitrobenzene, whilst similar recrystallisation of the other fraction readily gave a product with a constant melting point of 101-102°. These values are in good agreement with those found by Engelhardt and Latschinoff (loc. cit.), Hartley and Cohen (loc. cit.), and Holleman and Hollander (loc. cit.). These pure substances were isolated in practically equal quantities and the amount of material remaining in the mother-liquors after as much as possible of the two isomerides had been separated in a state of purity was very small. This residual material was not specially examined for the presence of 1:4-dichloro-2-5-dinitrobenzene, but if this substance were present it must have been in considerably smaller quantity than the other isomerides. It may also be noted that the 2:6-isomeride is more volatile than the 2:3- and that if the crude substance is kept in the molten condition for long, the loss of the 2:6-isomeride is sufficient to bring about appreciable changes in the composition and the setting point of the mixture. This had particularly to be borne in mind in the experiments from the results of which the fusion curve was constructed.

Summary.

The authors have studied the nitration of p-dichlorobenzene and have shown that when the nitration is conducted in two stages the 1:4-dichloro-2-nitrobenzene first produced can after separation be quite readily further nitrated to give a mixture consisting almost entirely of 2:6- and 2:3-dinitro-1:4-dichlorobenzenes in about equal proportions.

A convenient method for the isolation of these two isomerides in a state of purity is described.

In conclusion, the authors wish to express their thanks to the Director of Artillery for permission to publish this work.

Research Department, Royal Arsenal, Woolwich.

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