335. *Hydroxy-by-products in Aromatic Nitration.*

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In the nitration of nitrobenzene, phenylmethylsulphone, diphenylsulphone, and benzenesulphonyl chloride, hydroxy-by-products are formed, in amounts of 1% or more. In several cases styphnic acid is the by-product, the original substituent having been displaced. The phenomenon appears to depend, both in these instances and in the nitration of simple benzene hydrocarbons, on the entry of a hydroxyl group according to the ordinary orientation law, followed by polynitration and sometimes by the loss of the original substituent under the influence of the nitro-groups which have entered the molecule.

DURING an examination of the nitration of benzenesulphonyl chloride (Bennett and Youle, this vol., p. 887) the presence, among the products, of a polynitro-hydroxy-by-product was detected in a proportion of nearly 2% of the material. Although the production of traces of such by-products during certain nitrations has long been known, the instances recorded in the literature are all in nitrations of simple aromatic hydrocarbons. We have now examined several other nitrations from this point of view and the results are summarised in Table I, together with the facts already published.

TABLE I.

Hydroxy-by-products produced in Nitrations.

Substance nitrated.	By-product.	Yield, %.	Reference.
Benzene	Picric acid	—	Groves, *Proc.*, 1891, **7**, 91
	2 : 4-Dinitrophenol	0·03	This paper
Toluene	3 : 5-Dinitro-*p*-cresol and 3 : 5-dinitro-*o*-cresol	—	Noelting, *Ber.*, 1885, **18**, 2670; Lapworth and Mills, *Proc.*, 1898, **14**, 159
	3 : 5-Dinitro-*p*-cresol	0·7	This paper
o-Xylene	3 : 5-Dinitro-4-hydroxy-*o*-xylene and 4 : 6-dinitro-3-hydroxy-*o*-xylene	—	Noelting and Pick, *Ber.*, 1888, **21**, 3158
Chlorobenzene	Not identified	Less than 0·006	This paper
Nitrobenzene	Styphnic acid	0·5—6·5 (see table, p. 1818)	This paper
Benzenesulphonyl chloride	2 : 4 : 6-Trinitro-3-hydroxybenzenesulphonyl chloride, isolated as trinitrohydroxydiphenylamine	1·7	Bennett and Youle, *loc. cit.*
Phenylmethylsulphone	Styphnic acid	1·3	This paper
Diphenylsulphone	Styphnic acid	2·2	This paper

The main general conclusions are (1) that the by-products are all derived from hydroxy-compounds in which the hydroxyl group has entered the molecule according to the normal orientation law under the influence of the substituent originally present, whether that substituent is *op*- or *m*-directive; (2) that the amount of by-product is very much larger in the case of the *m*-directive substituents; (3) that in several cases the original substituent has been lost in the formation of the final by-product.

In the nitration of nitrobenzene styphnic acid is produced, under various conditions, in amounts up to 5—6% (Table II). This might, by itself, have been taken to involve the direct entry of two hydroxyl groups in the *o*- or *p*-position to the nitro-group, but the true explanation is evident from a consideration of the facts that styphnic acid is also the by-product from phenylmethylsulphone and diphenylsulphone, and that benzenesulphonyl chloride yields trinitro-*m*-hydroxydiphenylamine after the nitration products have been allowed to react with aniline. In these three instances it is clear that the original substituent has been displaced, in the sulphones by hydroxyl and in the sulphonyl chloride by the anilino-group, these being secondary reactions which are not surprising, since the substituent in question would in each case be under the influence of three nitro-groups in the *op*-positions. In the nitration of nitrobenzene, therefore, *m*-nitrophenol is the primary by-product and the 2 : 3 : 4 : 6-tetranitrophenol, formed from it, loses one nitro-group in an analogous manner to give styphnic acid. The formation of styphnic acid from *m*-nitrophenol was in fact recorded by Bantlin (*Ber.*, 1877, **10**, 524; 1878, **11**, 2099; compare Henriques, *Annalen*, 1882, **215**, 321), and Blanksma (*Rec. Trav. chim.*, 1902, **21**, 254) has shown that the tetranitrophenol in question is converted into styphnic acid by nitric acid.

In the course of their classic studies Holleman and de Bruyn (*Rec. Trav. chim.*, 1900, **19**, 79) recovered 1·7 grams of a slightly yellow solid by evaporating the mother-liquors after nitrating 30 grams of nitrobenzene. This, they concluded, contained 0·7 gram of dinitrobenzene, a little inorganic matter and some hydroxy-by-product, but it was not identified. They noted that the alcoholic solutions produced in their extraction analysis had a more intense colour and a higher density than were to be expected. All these points may now be attributed to the presence of styphnic acid.

The extensive production of nitrophenols in the presence of mercury catalysts is well known: picric acid, formed in yields of 40% (Wolffenstein and Boeters, *Ber.*, 1913, **46**, 586; D.R.-P. 194,883), and 2 : 4 : 6-trinitro-*m*-hydroxybenzoic acid, formed from benzoic acid in presence of mercuric nitrate (Wolffenstein and Paar, *Ber.*, 1913, **46**, 589), are the products to be expected according to the rules we have found. But Davis, Worrall, Drake, Helmkamp, and Young (*J. Amer. Chem. Soc.*, 1921, **43**, 594) conclude from their experiments that the products obtained in presence of a mercury catalyst are characteristic and are not the result merely of acceleration of some direct oxidation process. The production of trinitro-*m*-cresol from toluene and of trinitro-*m*-chlorophenol from chlorobenzene, which they record, certainly does not fall into line with the results of uncatalysed nitrations, and it would appear, therefore, that the two phenomena must be regarded as separate problems for investigation.

The prominence of the by-products when an electron-attracting group is present suggested the possibility that kationoid reactivity might be involved (Bradley and Robinson, J., 1932, 1254), but the orientation of the products negatives this.

Another suggestion considered was that the by-product in the nitration of benzene arose from the hydrolysis of small amounts of *o*- and *p*-dinitrobenzenes to nitrophenols. We find, however, that *o*- or *p*-dinitrobenzene can be added to the nitrating acid under similar conditions without producing any detectable trace of nitrophenols, so this hypothesis is untenable.

The suggestion was made by Armstrong and Rossiter (*Proc.*, 1891, **7**, 89) that the elements of nitric acid might be added to one double bond of the benzene molecule to yield an intermediate, which would yield the nitro-compound by loss of water, but phenol by loss of nitrous acid. Such an explanation is, however, scarcely consistent with modern views of aromatic reactivity: moreover it does not seem easy to reconcile it with the orientations of the observed products.

Experiments on the nitration of nitrobenzene under various conditions (Table II) indicate that the formation of the by-product does not depend on the presence of nitrous acid, but that it is promoted by the presence of sulphuric acid. These points will require further investigation: meanwhile we prefer to confine our conclusions to the statement that a nuclear hydroxylation takes place which appears to follow the usual rules of orientation.

EXPERIMENTAL.

General Method.—After a given substance had been nitrated, the nitration mixture was poured on ice. Then, either the whole mixture was extracted with benzene, or the liquid was extracted directly and the solid stirred several times with benzene. The mixed benzene extracts were themselves extracted with 4N-sodium hydroxide. The alkaline solution was generally shaken with a little pure benzene, to dissolve everything but nitrophenols, and acidified with dilute nitric acid at 0°. Then, either the phenols were filtered off, or the solution was ether-extracted. Purification of the small yields of crude products so obtained was sometimes difficult.

Nitration of benzene. Benzene (A.R., 454 c.c.) was stirred into a mixture of nitric acid (*d* 1·42, 304 c.c.) and sulphuric acid (96%, 332 c.c.) at 65°. A solid was isolated, m. p. 114°; mixed m. p. with 2 : 4-dinitrophenol, 114°; mixed m. p. with *p*-nitrophenol, 80° (yield, 0·03%). Comparative recrystallisation with 2 : 4-dinitrophenol showed that both substances crystallised in small, highly doubly refracting plates, with straight extinction. *o*-Dinitrobenzene and *p*-dinitrobenzene, after the same treatment, showed no trace of nitrophenols (colourless solution).

Nitration of chlorobenzene. Chlorobenzene (500 g.) was stirred at 0° with nitric acid (*d* 1·52, 1200 c.c.). The by-product finally isolated was insufficient for purification (0·03 g.) and a repetition of the experiment gave the same result.

Nitration of toluene. Toluene (100 g.) with an ordinary nitrating mixture gave an insoluble sodium salt (0·7 g.), from which dinitrocresol, m. p. 80—81°, was obtained (Found: N, 14·3. Calc.: N, 14·2%) (compare Lapworth and Mills, and Noelting, *locc. cit.*).

Nitration of nitrobenzene. Pure nitrobenzene (frozen out and twice redistilled, 100 g.) was nitrated with nitric acid (*d* 1·52, 150 c.c.) and sulphuric acid (96%, 200 c.c.). A nitrophenolic substance was isolated (2·5 g.), which after recrystallisation from water and alcohol was identified as styphnic acid (Found: C, 29·3; H, 1·9; N, 16·6. Calc.: C, 29·4; H, 1·2; N, 17·1%). It had m. p. 170—172° and, after admixture of styphnic acid, 171°. The two substances crystallised from water under similar conditions in identical and very characteristic fashion in small hexagon-shaped crystals and six-rayed stars.

TABLE II.

Yield of Styphnic Acid from Nitrobenzene nitrated under Various Conditions.

	Nitric acid.	Sulphuric acid.	Temp.	Time, hrs.	Yield, %.
1.	300 c.c., *d* 1·52	None	0°	5	0·5
2.	100 „ „	„	90	1	0·5
3.	100 „ „	10 c.c., 96%	„	5	2·5
4.	70 „ *d* 1·42	50 „ „	„	1	3·0
5.	60 g. KNO_3	150 „ „	„	2	6·5
6.	„ „	150 „ „	„	„	5·5
7.	75 c.c., *d* 1·52	75 „ 65% oleum	„	1	1·5

Nitration of phenylmethylsulphone. This sulphone (100 g.) was nitrated as described by Twist and Smiles (J., 1925, **127**, 1249) with potassium nitrate (100 g.) and sulphuric acid (600 g.). The yellow solid by-product (1·3 g.), isolated in the usual way, was crystallised twice from water and once from benzene; it formed crystals with the appearance characteristic of styphnic acid, melting at 168—172° and, after addition of styphnic acid, at 167—172° (Found: C, 29·0; H, 1·9. Calc.: C, 29·4; H, 1·2%).

Nitration of diphenylsulphone. The sulphone (80 g.) was heated with nitric acid (300 c.c., *d* 1·52) at 90°. The by-product, after successive crystallisation from water and benzene, yielded the six-rayed stars and hexagons typical of styphnic acid. It had m. p. 172—173° and 171—173° after addition of styphnic acid (Found: C, 29·2; H, 1·9%).

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