CXXVII.—*The Mechanism of the Hydrogen Sulphide Reduction of Nitro-compounds.*

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In the process of reducing different nitro-compounds with ammonium sulphide, or, as it is usually effected, with hydrogen sulphide in an alcoholic solution containing ammonia, great differences are noticeable in the rate of reduction, in the conditions under which reduction takes place, and in the nature of the products formed.

Thus, mononitro-derivatives of the aromatic hydrocarbons are, as a rule, slowly attacked at the ordinary temperature, whereas 1 : 3-dinitrobenzene and 1 : 2 : 4-, 1 : 2 : 6-, and 1 : 3 : 5-dinitrotoluenes are readily and completely reduced, giving good yields of monoamino-compounds. 1 : 3 : 5-Trinitrobenzene and 1 : 2 : 4 : 6-trinitrotoluene are still more rapidly reduced with a considerable rise of temperature, and unless a trace only of ammonia is used tarry products are formed which materially affect the yields. Where more than one nitro-group is present, the process either stops or proceeds very slowly after the first nitro-group is reduced.*

It appears therefore that the greater the number of nitro-groups the more readily does the reduction take place. But this is not necessarily the case, inasmuch as dinitro- and trinitro-*m*-xylenes and dinitromesitylene can only be reduced after prolonged action of ammonium sulphide at a high temperature, whilst it is doubtful if trinitromesitylene can be reduced at all with ammonium sulphide. This is probably due to the presence of the additional methyl groups which render the nucleus more basic and the nitro-groups in some way less disposed to reduction. The slowing down of the process after one nitro-group has been reduced may be attributed to the same cause, namely, to the effect of the amino-group in rendering the nucleus more basic.

If the acidic character of the nucleus promotes reduction, the replacement of one or more of the nitro-groups by other acidic groups, such as carboxyl or sulphonic groups or the halogens, should produce a similar effect. The following observations support this conclusion.

Whereas *o*-, *m*-, and *p*-chloronitrobenzenes and 1 : 2 : 4-, 1 : 4 : 2-, 1 : 2 : 5-, 1 : 5 : 2-, 1 : 3 : 5-, and 1 : 2 : 6-chloronitrotoluenes are all slowly reduced, the 1 : 3 : 5- and 1 : 2 : 4-dichloronitrobenzenes undergo reduction readily. The same is true of the 1-chloro-3 : 5-dinitro-

* Attention was first drawn to this fact by Kolbe (*Annalen*, 1850, **76**, 38), who indicated this difference in the behaviour of the two nitro-groups in dinitrobenzene by writing the formula $\left. \begin{smallmatrix} \text{C}_6\text{H}_4 \\ \text{NO}_2 \end{smallmatrix} \right\} \text{NO}_2$.

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benzene and 1:2-chloro-4:6-dinitrotoluene, which are easily reduced. Excepting *o*-chloronitrobenzene, we have omitted from the present investigation the ortho-chloronitro-compounds, which, according to Beilstein and Kurbatoff (*Ber.*, 1878, 11, 2056), are subject to a change of quite a different character, namely, the exchange of the nitro-group for sulphur or the mercaptan (SH) group, and the same seems to be the case with the *o*-dinitro-compounds (see also Blanksma, *Rec. Trav. chim.*, 1905, 24, 46). The nitro-derivatives of the acids are not suitable for reduction, as in many cases the addition of ammonia to the alcoholic solution precipitates the ammonium salt and no reduction ensues. The methyl esters are, however, free from this objection.

Of the three isomeric methyl mononitrobenzoates, the ortho- and meta-compounds are reduced very slowly, although not equally so; the para-compound, on the other hand, is reduced quite readily. Reduction proceeds still more rapidly with the methyl esters of 1:3:5- and 1:2:4-dinitrocarboxylic acids and of the 1:2:4-, 1:4:2-, 1:3:5-, and 1:2:6-chloronitrocarboxylic acids, and finally the corresponding mononitro-esters of the three phthalic acids. The nitrosulphonic esters have not yet been examined.

It is clear, therefore, that with an increase in the number of acidic groups (NO_2 , Cl, CO_2CH_3) the reducing action of hydrogen sulphide is facilitated. Incidentally, we have been able to record differences in the rate of reduction of isomeric compounds which point to steric hindrance. Although, as stated above, the chloronitrotoluenes are reduced very slowly, it is easy to show that of the following six isomerides examined the 1:3:5-chloronitrotoluene is most rapidly reduced, the 1:2:4- and 1:2:5-compounds follow next in order of reducibility, whilst the 1:4:2-, 1:5:2-, and 1:2:6-compounds are scarcely acted on under the conditions of the experiment.

Similar differences have been shown to exist between the three ethyl nitrobenzoates, in which the para- is more rapidly reduced than the meta-compound, and the latter more than the ortho-isomeride. Among the ethyl chloronitrobenzoates, the order of reduction is 1:3:5 and then 1:2:4, which give an appreciable amount of chloro-amino ester, after which come the 1:4:2- and 1:2:6-compounds, which give very little.

The same is true of the three chloronitrobenzenes, the para- and meta-compounds being more easily reduced than the ortho-derivative. Similar differences are again observable between the nitrophthalic esters. Methyl-5-nitroisophthalate is more rapidly reduced than the corresponding 4-nitrophthalic and 2-nitroterephthalic esters, and these again much more than the 3-nitrophthalic ester.

The result confirms the observation of Noelting and Thesmar (*Ber.*, 1902, **35**, 630) that among the polynitro-derivatives of *o*- and *m*-xylenes the nitro-group to be first reduced adjoins fewest methyl groups in the ortho-position.

The method adopted in these experiments was to dissolve 0.5 gram of material in 3 c.c. of methyl alcohol and to add in each case two drops of strong ammonia from a pipette. The solution was placed in boiling water, which was then allowed to cool, and a rapid current of hydrogen sulphide passed through the liquid for fifteen minutes. The reduction is indicated by the darkening of the liquid, which turns deep red, and, if much change occurs, sulphur is also deposited in varying quantity. Of the chloronitrotoluenes referred to above, the liquid turned red and sulphur was deposited only in the case of the 1 : 3 : 5-compound, whilst reddening of the liquid was observed in the case of the 1 : 2 : 4- and 1 : 2 : 5-compounds. No marked change was noticeable in the remaining three compounds. Of the three chloronitrobenzenes, reddening of the liquid occurred in all three cases, but sulphur was deposited only with the para- and meta-compounds and not with the ortho-compound. Of the three ethyl nitrobenzoates, immediate reddening of the solution and abundant deposition of sulphur occurred with the para-compound, a little deposit of sulphur with the meta-compound, and a faint yellow colour and no deposit of sulphur with the ortho-compound.

With the chloronitrobenzoic and nitrophthalic esters, the solution in

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each case turned dark red immediately, and sulphur was deposited. After hydrogen sulphide had been passed through for the required time, the liquid was warmed and shaken with excess of dilute hydrochloric acid, filtered, and the filtrate made alkaline with ammonia, when the amino-compound, if present, was deposited. The amount of precipitate corresponded roughly with the changes previously noted. Thus, a precipitate was formed in small quantity in the case of the 1 : 3 : 5- (largest amount), 1 : 2 : 4-, and 1 : 2 : 5-chloronitrotoluenes, but none with the remaining isomerides. A large amount of amino-ester (m. p. 86°) was obtained from methyl *p*-nitrobenzoate and an appreciable quantity from the meta-compound, but no precipitate appeared in the case of the ortho-ester. A small quantity of *p*-chloroaniline, which melted at 64° (m. p. 70°), and *m*-chloroaniline were obtained from *p*- and *m*-chloronitrobenzenes, but none from the ortho-compound. Of the four methyl chloronitrobenzoates, 0.3 gram of amino-compound was obtained from the 1 : 3 : 5-compound (m. p. 84°) and 0.08 gram from the 1 : 2 : 4-compound (m. p. 117°), but little from the other two, the quantity not being estimated. Of the four methyl nitrophthalates already referred to (p. 1259), the 5-nitroisophthalic ester gave 0.32 gram (m. p. 172°) of amino-ester, the 2-nitroterephthalic ester gave 0.04 gram (m. p. 131°), the 3-nitrophthalic ester gave a scarcely weighable amount.* The behaviour of the chloronitrotoluenes, the chloronitrobenzoic esters, and especially the nitrophthalic esters throws a little fresh light on the process known as "steric hindrance." There is no question that the phenomenon is manifested in the reduction of nitro-compounds, but it is clearly dependent to some extent on the other groups present. The theory as generally understood would anticipate a more rapid reduction of the 1 : 2 : 4- and 1 : 2 : 5- than of the 1 : 3 : 5-chloronitrotoluene, of methyl 1 : 2 : 4-chloronitrobenzoate rather than the 1 : 3 : 5-compound, and of the 1 : 2 : 4- rather than the 1 : 3 : 5-nitrophthalic esters, yet the reverse is the case. The greater reducibility of methyl 1 : 4 : 2-nitroterephthalate than of the corresponding 1 : 2 : 3-nitrophthalic ester is still more striking, for according to the theory they should exhibit no difference. The probable explanation is that the reduction of the nitro-group is not merely retarded by the juxtaposition of another group, but even when that group is in the meta- or para-position to the nitro-group and therefore out of range of its action it may influence the adjoining atom or group so as to

* In addition to the 0.32 gram of base obtained from the 5-nitroisophthalic ester, 0.112 gram of substance was separated which dissolved in strong hydrochloric acid, was precipitated by water, and gave the hydroxylamine reaction strongly. It crystallises in pale yellow needles from benzene and melts at $158-160^{\circ}$. The quantity of reduced product obtained from the 4-nitrophthalic ester amounted to 0.2 gram of liquid; but it was not pure amino-ester and contained a yellow substance, the nature of which has not been ascertained.

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affect indirectly the rate of reduction. It therefore follows that the symmetrical compounds are the most reducible. We may sum up the foregoing observations in the following empirical rule: *The rate of reduction is increased by the presence of acidic groups (NO₂, Cl, CO₂Me) and diminished by that of basic groups (CH₃, NH₂), and is further affected by steric hindrance.*

The following is a list of nitro-compounds which have been included in the scope of our inquiry and which are divided roughly into two classes, namely, (1) those which in hot methyl-alcoholic solution readily undergo reduction, and (2) those which are slowly reduced.

I.	II.
Quickly reduced.	Slowly reduced.
1 : 3-Dinitrobenzene.	<i>o</i> -Chloronitrobenzene.
1 : 3 : 5-Trinitrobenzene.	<i>m</i> - " "
1 : 3 : 5-Chlorodinitrobenzene.	<i>p</i> - " "
1 : 3 : 5-Dichloronitrobenzene.	<i>o</i> -Nitrotoluene.
1 : 2 : 4-Dichloronitrobenzene.	<i>m</i> - " "
1 : 2 : 4-Dinitrotoluene.	<i>p</i> - " "
1 : 2 : 6- " "	1 : 2 : 4-Chloronitrotoluene.
1 : 3 : 5- " "	1 : 4 : 2- " "
1 : 2 : 4 : 6-Trinitrotoluene.	1 : 2 : 5- " "
1 : 4 : 2 : 6-Chlorodinitrotoluene.	1 : 5 : 2- " "
1 : 2 : 4 : 6-Dichloronitrotoluene.	1 : 2 : 6- " "
Methyl 1 : 4-nitrobenzoate.	1 : 3 : 5- " "
" 1 : 3 : 5-chloronitrobenzoate.	2 : 4-Dinitro- <i>m</i> -xylene.
" 1 : 2 : 6- " "	Trinitro- <i>m</i> -xylene.
" 1 : 2 : 4- " "	Dinitromesitylene.
" 1 : 4 : 2- " "	Trinitromesitylene.
" 1 : 3 : 5-dinitrobenzoate.	Methyl 1 : 2-nitrobenzoate.
" 1 : 2 : 4- " "	" 1 : 3- " "
" 5-nitroisophthalate.	
" 2-nitroterephthalate.	
" 3-nitrophthalate.	
" 4- " (abnormal).	

The next point to which we directed our attention was the mechanism of the change itself.

Bamberger has shown (*Ber.*, 1894, 27, 1349) that the neutral reduction of nitro-compounds gives rise to the formation of hydroxylamine compounds. Cohen and Dakin (*Trans.*, 1902, 81, 26) obtained these compounds under certain conditions during the reduction of trinitrobenzene and trinitrotoluene with hydrogen sulphide, and incidentally Cohen and Marshall (*Trans.*, 1904, 85, 527) obtained a small quantity of a similar product from 2 : 6-dinitrotoluene. That there are at least two well-defined stages in the reduction of most nitro-compounds with ammonium sulphide follows from these experiments and from further evidence which we have since collected. Moreover, the formation of the intermediate hydroxylamine compound influences the subsequent changes in a very marked degree. In order to follow the course of the reaction, it has been necessary to examine each of these stages separately. We have succeeded in doing this by

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finding suitable methods for arresting the reduction to some extent at the hydroxylamine stage and studying the behaviour of these intermediate compounds. Thus, we have shown that some hydroxylamine compounds are very sensitive to the action of ammonia and certain organic bases, forming in some cases new crystalline compounds, in others tarry products. In both cases the diminished yield of amino-compound which is frequently experienced when much ammonia is used may be thus explained. That hydrogen sulphide in presence of a trace of ammonia will effect rapid reduction of large quantities of material was first observed in the case of 1 : 3 : 5-trinitrobenzene and 1 : 2 : 4 : 6-trinitrotoluene (*loc. cit.*). The same phenomenon, which has now been found to occur in the case of methyl 1 : 3 : 5- and 1 : 2 : 4-dinitrobenzoates and some other compounds highly charged with acidic groups, led us to suppose that the alkali acted as a catalyst.

Before investigating this point, we examined the effect of traces of other bases in place of ammonia. Trinitrotoluene and methyl 1 : 3 : 5-dinitrobenzoate, which are rapidly reduced in presence of a trace of ammonia, were found to be similarly affected by traces of primary, secondary, and tertiary aliphatic amines, benzylamine, piperidine, and menthylamine, but not by the weak bases, aniline, pyridine, and phenylhydrazine.

The catalytic action of the strong bases might be explained on the assumption that previous to reduction isodynamic change of the following character occurs :

On the reduction of the nitroxyl group or its dissociated ion to the basic hydroxylamine compound, ammonia would be set free and form a fresh combination. In this way the process could continue indefinitely. The formation of an ammonium salt of a pseudo-acid of the above character would agree with the existence of a potassium compound of trinitrobenzene observed by Lobry de Bruyn and by V. Meyer (*Ber.*, 1896, **29**, 848). It is formed by the action of potassium methoxide on trinitrobenzene. The formula assigned by Lobry de Bruyn was $C_6H_3(NO_2)_3 \cdot KOCH_3 \cdot \frac{1}{2}H_2O$, whereas V. Meyer preferred to regard the alkali metal as replacing hydrogen in the benzene nucleus, thus : $C_6H_2K(NO_2)_3 \cdot CH_3 \cdot OH \cdot \frac{1}{2}H_2O$. In further support of the existence of a pseudo-acid may be mentioned the coloured solutions which ammonia and other bases give with many of the more acidic nitro-compounds. Moreover, Angeli and Angelico (*Rend. Accad. Lincei*, 1903, i 344)

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have shown that by the action of ethyl nitrate and sodium ethoxide on pyrrole salts of pyrrolenitroxyl acids are produced to which they have assigned the following formulæ :

A similar view has been expressed by Bruni and his collaborators (*Atti R. Accad. Lincei*, 1900, (v), 9, i, 273, 393, and *Gazzetta*, 1905, 34, ii, 479) from the results of an examination of the dissociation of nitro-compounds in different solvents by the cryoscopic and ebullioscopic methods. They find that the accumulation of electro-negative groups in the molecule increases the amount of dissociation. The reducibility by hydrogen sulphide conforms very closely to the amount of dissociation found by these authors. Thus, in formic acid and certain other solvents, trinitrobenzene, trinitrotoluene, trinitro-*p*-xylene, and dinitromesitylene, the isomeric chloronitrobenzenes and methyl nitrobenzoates are more or less dissociated, whilst trinitromesitylene and bromodinitromesitylene are undissociated. The authors conclude that it is not only the number of electro-negative groups present, but the specific nature of the nitro-group itself which determines the dissociation. They consider that the nitro-compounds in formic acid are dissociated only in presence of a mobile hydrogen atom in the nucleus and assign to the nitro-group the formula discussed above, $>\text{NO} \cdot \text{OH}$.

The above explanation might account for the reduction of those compounds which takes place in presence of a trace of alkali, but it cannot be applied to the reduction of nitro-compounds in general for the following reasons. 1:3-Dinitrobenzene and 1:2:4-, 1:2:6-, and 1:3:5-dinitrotoluenes and certain other nitro-compounds are only partially reduced unless a considerable quantity of ammonia is present. Ammonia in such cases obviously does not play the part of a catalyst. Moreover, a pseudo-acid of the character described necessitates a free ortho- or para-position, whereas compounds which are substituted in both ortho- and para-positions in regard to the nitro-group undergo reduction. Thus, dinitromesitylene is slowly reduced by the prolonged action of ammonium sulphide on the hot solution (Knecht, *Annalen*, 1882, 215, 98) :

Also both di- and tri-nitroxylenes, although they contain free para- and ortho-positions, are, nevertheless, not much more rapidly reduced than dinitromesitylene. A theory which does not include every case of reduction cannot be regarded as complete, and another explanation will have to be found. The action of the solvent introduces a new phase of the problem which may possibly contribute to its solution, and an investigation into the effect of various solvents on the reduction of the nitro-compounds has already been initiated.

In the experimental part which follows, we have described the formation of certain hydroxylamino- and amino-compounds which are formed during the progressive reduction of the nitro-compounds already referred to.

EXPERIMENTAL.

Reduction of 1 : 3 : 5-Chlorodinitro- and 1 : 3 : 5-Dichloronitro-benzenes.

1-Chloro-3 : 5-dinitrobenzene.—The reduction of trinitrobenzene was carried out in the manner already described (Trans., 1902, 81, 27). The amino-compound was separated from the hydroxylamine derivative by dissolving the product in strong hydrochloric acid, diluting, and filtering from the insoluble hydroxylamine base. The amino-compound was precipitated in the filtrate with ammonia. The melting point of the hydroxylamine compound is 135—137° and not 114—116° as previously given (*loc. cit.*). It crystallises from dilute hydrochloric acid or benzene in yellow needles and dissolves in concentrated ammonia giving a violet-brown solution, which is changed on heating to a tarry mass. The 3 : 5-dinitro-1-aminobenzene was converted into the corresponding chloro-compound in the ordinary way. The latter crystallises in colourless needles which melt at 55°.

1-Chloro-5-nitro-3-hydroxylaminobenzene.—Hydrogen sulphide reduces the chlorodinitro compound under precisely the same conditions as the trinitro-compound. The reduction product was poured into water, filtered, and washed; the precipitate was then boiled with dilute hydrochloric acid and the solution filtered from sulphur. On cooling the filtrate, lemon-yellow crystals of the hydroxylamine compound separated, which, after a second crystallisation, melted at 129—130°. On boiling a small quantity of the substance with strong hydrochloric acid and a few crystals of potassium iodide, iodine vapours were evolved, showing the presence of the hydroxylamine compound. After expelling the iodine, the liquid was diluted with water, which now produced no precipitate, but on adding ammonia a base was precipitated having the slightly higher melting point (130—134°) of the following amino-compound.

1-Chloro-5-nitro-3-aminobenzene.—Ammonia, when added to the

filtrate from the hydroxylamine compound, precipitated the amino-compound; this product crystallises in orange needles from alcohol, melting at 133—134°, and does not liberate iodine from potassium iodide.

1 : 3-Dichloro-5-aminobenzene.—1 : 3-Dichloro-5-nitrobenzene is reduced rapidly in the cold in presence of a trace of ammonia, and the product freed from sulphur gives the hydroxylamine reaction very distinctly. The hydroxylamine compound was not isolated, but after boiling with potassium iodide and hydrochloric acid and driving off the iodine the base was precipitated and gave the correct melting point (49—51°) for the 1 : 3-dichloro-5-aminobenzene.

*Reduction of 1 : 2 : 4 : 6-Chlorodinitro- and Dichloronitro-toluenes.
4-Chloro-2 : 6-dinitrotoluene.*

Trinitrotoluene was reduced as previously described (*loc. cit.*). The crude product, which melted at 120—160° and contained some hydroxylamine base, was at once boiled with potassium iodide and strong hydrochloric acid in order to convert the whole into the amino-compound. In this way, pure 2 : 6-dinitro-4-aminotoluene (m. p. 168—169°) was obtained. We must correct a previous statement in regard to the structure of the hydroxylamine compound. In the paper referred to (*loc. cit.*), it was stated that on boiling the hydroxylamine compound with strong hydrochloric acid a colourless, crystalline compound was precipitated which was assumed to be the 2 : 4-dinitro-6-aminotoluene. This is clearly incorrect. We have not yet determined the structure of the compound in question, but from the foregoing it is evident that it is the 4-nitro- and not the 6-nitro-group which suffers reduction. The amino-group was replaced by chlorine in the usual way; it crystallises from alcohol in colourless plates which melt at 76—77°. The structure of the chlorodinitrotoluene follows from the method of preparation and also from the fact that it gives the reaction for *m*-diamines on reduction :

M. p. 76—77°.

This contradicts an observation of Goldschmidt and Hönig (*Ber.*, 1886, **19**, 2439; 1887, **20**, 2420). In describing the nitration products of *p*-chlorotoluene, these authors obtained two mononitrotoluenes and a dinitrotoluene (m. p. 76°). From the failure of the latter to give the reaction for either *m*- or *p*-diamines, they concluded that the compound in question was 4-chloro-2 : 3-dinitrotoluene. They

further nitrated 4-chloro-2-nitrotoluene and obtained a chlorodinitrotoluene (m. p. 101°), to which the above formula of our compound is ascribed. From our experiments, the formulæ for the first of Goldschmidt and Hönig's compounds must be 4-chloro-2:6-dinitrotoluene, whilst the second is either the 4-chloro-2:3-dinitro- or, more probably, the 4-chloro-2:5-dinitro-toluene.

4-Chloro-2-hydroxylamino-6-nitrotoluene.—This substance is obtained in the usual way by reduction with hydrogen sulphide in presence of a trace of ammonia, little heat being evolved during the process. The hydroxylamine compound separated in the usual way, crystallised in yellow needles from alcohol or benzene, and then melted at 121—122°.

4-Chloro-6-nitro-2-aminotoluene.—On boiling the hydroxylamine compound with hydrochloric acid and potassium iodide, the base was obtained, which crystallised in pale yellow needles from alcohol and melted at 95—96°.

2:4-Dichloro-6-nitrotoluene was prepared from the amino-compound by Sandmeyer's reaction and crystallised in colourless plates (m. p. 59—60°).

2:4-Dichloro-6-hydroxylaminotoluene.—*2:4-Dichloro-6-nitrotoluene* underwent reduction in presence of a trace of ammonia, and from the product the hydroxylamine derivative was separated, which crystallised from alcohol in colourless needles (m. p. 101°).

Reduction of Trinitro-m-xylene.

Trinitro-*m*-xylene is reduced very slowly even in the hot solution. After one hour, with about 0.5 gram of material, some of the trinitro-compound was still unchanged. After filtering from sulphur, water was added and the lemon-yellow precipitate was filtered and washed. It gave the hydroxylamine reaction very strongly with potassium iodide and hydrochloric acid. The hydroxylamine compound, which was not quite pure, melted at about 117—120°.

Reduction of Methyl 3:5-Dinitrobenzoate.

Methyl 3:5-dinitrobenzoate, which was prepared by Fischer and Speyer's method, melts at 107—109°, the yield of ester being about equal to the weight of acid taken. To 30 grams of the finely-powdered ester were added 100 c.c. of methyl alcohol and 1 c.c. of strong ammonia. Hydrogen sulphide was introduced for about two hours, the mixture being cooled in water or ice; the liquid became dark red, and sulphur was deposited. The mixture was then heated to boiling on the water-bath, and hydrogen sulphide was again passed into it. The product was diluted with water, filtered, and washed; strong hydrochloric acid

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was added to the orange crystalline mass, which dissolves the hydroxyl-amino- and amino-esters and leaves sulphur. The acid liquid was filtered from sulphur and the filtrate largely diluted with water. The hydroxylamino-ester was precipitated, whilst the amino-ester remained in solution, from which it was thrown down by ammonia. The quantity of the two bases obtained in four experiments varied between 12 and 15 grams of the amino-compound and 6 to 10 grams of the hydroxylamine compound.

Methyl 5-nitro-3-hydroxylaminobenzoate is a pale yellow substance, which crystallises readily from benzene or dilute hydrochloric acid in small needles and melts at $107-108^{\circ}$; it is a weak base which forms colourless salts with the strong mineral acids; these compounds are, however, dissociated on dilution, and the base is again precipitated. On boiling with strong hydrochloric acid, it is slowly converted into the amino-ester. The same result is more rapidly effected by boiling with strong hydrochloric acid and potassium iodide. Iodine is liberated, and on diluting a clear solution is obtained, from which ammonia precipitates the amino-ester, melting after recrystallisation at $157-160^{\circ}$. A partial conversion into the amino-ester is also effected by prolonged boiling with alcohol alone. When the hydroxylamine compound is dissolved in alcohol made alkaline with ammonia and hydrogen sulphide passed through the solution, it is completely transformed into the amino-ester. This fact may be taken as indicating that the hydroxylamine compound is an intermediate product in the production of the amino-ester. The hydroxylamine compound is very easily decomposed by boiling with alcoholic solutions of ammonia and organic bases. In such cases, only a small quantity of amino-compound is present in the product, which consists mainly of crystalline substances, dissolving neither in strong nor dilute hydrochloric acid. These compounds are easily obtained pure by crystallisation, but have not yet been fully examined. On analysis, the hydroxylamine compound furnished the following result:

0.2134 gave 24.85 c.c. moist nitrogen at 16° and 758 mm. $N = 13.63$.

$C_8H_8O_5N_2$ requires $N = 13.21$ per cent.

Methyl 3-Nitro-5-aminobenzoate.—The amino-ester, obtained either by direct reduction of the dinitro-ester in the manner described or from the hydroxylamine-ester, is a yellow, crystalline compound when precipitated in a fine state of division from its solution in acid; it may be crystallised from alcohol, and has then a dark red colour and melts at $158-160^{\circ}$.

0.2304 gave 28 c.c. moist nitrogen at 16° and 765 mm. $N = 14.36$.

$C_8H_8O_4N_2$ requires $N = 14.28$ per cent.

With acetyl and benzoyl chlorides, it forms colourless, crystalline derivatives, the acetyl compound melting at 165—167° and the benzoyl derivative at 178°.

The acetyl derivative was analysed with the following result :

0.2246 gave 22.9 c.c. moist nitrogen at 16° and 758 mm. $N = 11.93$.

$C_{10}H_{10}O_5N_2$ requires $N = 11.77$ per cent.

When the amino-ester is hydrolysed with four times its weight of sulphuric acid (1 vol. of strong sulphuric acid and 2 vols. of water), the acid obtained melted at 209—210° (Hübner, *Annalen*, 1884, **222**, 81, gives 208°).

Methyl 3-Chloro-5-aminobenzoate.—The above compound is readily reduced by hydrogen sulphide in presence of a trace of ammonia with evolution of heat. After reduction, the alcoholic solution was filtered from sulphur and diluted with water. The yellow precipitate after filtration was boiled with dilute hydrochloric acid, and from the hot acid solution on cooling the chloroamino-ester was precipitated with ammonia and crystallised from water; it forms glistening, foliated crystals, which melt at 84—86°. No hydroxylamine compound was either detected or separated.

Reduction of Methyl 2:4-Dinitrobenzoate.

The ester was obtained by Fischer and Speyer's method, but the yield, probably owing to steric hindrance, was much smaller than in the case of the 3:5-dinitro-acid. Fifty grams of acid gave 30 grams of pure ester melting at 79—80°.

The reduction was carried out in exactly the same manner as previously described under the 3:5-dinitro-ester. The product was poured into water and filtered; from the filtrate on standing orange needles separated, which melted at 108—110°.

Methyl 2-Nitro-4-hydroxylaminobenzoate.—The substance melting at 108—110° gave the hydroxylamine reaction with hydrochloric acid and potassium iodide, and after boiling off the iodine and adding ammonia to the clear solution the amino-compound (m. p. 156—158°) was precipitated.

0.1983 gave 23.8 c.c. moist nitrogen at 19° and 737 mm. $N = 13.0$.

$C_8H_8O_5N_2$ requires $N = 13.21$ per cent.

Methyl 4-Amino-2-nitrobenzoate.—The residue left on filtration was dissolved in strong hydrochloric acid and filtered from sulphur; on dilution, a considerable quantity of yellow precipitate was produced which proved to be the amino-ester. A further quantity was precipitated by ammonia. From 30 grams of ester, 11 grams of amino-

ester were obtained. Recrystallised from dilute alcohol, it separated in the form of light brown, flat prisms melting at 157—159·5°. [View Article Online](#)

0·1452 gave 17·2 c.c. moist nitrogen at 13·5° and 748 mm. $N = 14·06$.
 $C_8H_8O_4N_2$ requires $N = 14·28$ per cent.

It forms an acetyl derivative, which crystallises from water or dilute alcohol in colourless needles (m. p. 76°), and a benzoyl derivative, which crystallises from benzene in colourless needles (m. p. 93—94°); it does not diazotise readily, and the product, after introducing chlorine, was difficult to purify.

Reduction of the Methyl Nitrophthalates.

Methyl 3-nitro-1:2-phthalate, obtained from the nitro-acid by the action of methyl iodide on the silver salt, melts at 69°. There is very little change on reduction in the cold, but on warming the liquid becomes darker and a little sulphur is deposited. Even then the reduction only proceeds slowly.

Methyl 4-nitro-1:2-phthalate was prepared from the nitro-acid by Fischer and Speyer's method and melts at 64—65°; the action was very similar to that of the foregoing compound, namely, little reduction in the cold and more energetic action on warming, with rapid separation of sulphur. As already explained, the rate of reduction is much more rapid than in the case of the previous compound, but the process is not normal, and the product contains a yellow, viscid oil, which is probably a sulphur compound.

Methyl 5-nitro-1:3-isophthalate was prepared by Fischer and Speyer's method and melts at 121°. The reduction takes place to a considerable extent in the cold, and without change of temperature; on warming, the reaction is rapid. The product was extracted with dilute hydrochloric acid and filtered. From the filtrate, the amino-compound was precipitated and melted without crystallisation at 173—175° (correct m. p. 176°). The residue on the filter gave the hydroxylamine reaction strongly. It dissolved in strong hydrochloric acid and was precipitated on the addition of water. On crystallising from benzene, it formed pale yellow needles melting at 158—160°, and after boiling with potassium iodide and hydrochloric acid and filtering in the usual way the amino-compound was precipitated and melted at 172—175° without crystallisation.

Methyl 2-Nitro-1:4-terephthalate.—The melting point of the ester is 73—74°, and not 70° as given in *Beilstein's Handbuch*. There is little action in the cold, but on heating the usual change to dark red with deposition of sulphur indicated that reduction was taking place. After pouring into water, the precipitate was collected on a filter and

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extracted with concentrated hydrochloric acid. On adding water, a portion melting at 156° was deposited, and from the solution ammonia precipitated the amino-compound, melting at 132° .

The portion melting at 156° was recrystallised from benzene and formed pale yellow, spear-shaped clusters (m. p. 157°) which gave the hydroxylamine reaction, and was converted by the usual method into the amino-compound melting without crystallisation at 131° . The amino-compound crystallises in colourless, shining leaflets from dilute alcohol and melts at $131-132^{\circ}$.

Reduction of the Methyl Nitrobenzoates.

The method of reduction of the three isomeric esters has already been described in the introduction; the following additional details may be recorded. The ortho-ester is a liquid, the meta-ester melts at 80° , and the para-ester at $94-95^{\circ}$. The amino-compound derived from the para-ester crystallises in lustrous, flattened prisms and melts at 86° .

Reduction of 1:2-Dichloro-4-nitrobenzene.

After reduction in the ordinary way, the hot alcoholic solution was filtered from sulphur, and on cooling yellow crystals separated which, after recrystallisation from alcohol, melted at $138-140^{\circ}$; this substance did not give the hydroxylamine reaction and its constitution was not ascertained. Dilute hydrochloric acid was then added to the filtrate and the unchanged nitro-compound removed with ether. From the aqueous portion after extraction, ammonia precipitated the crystalline base which, without purification, melted at $69-70^{\circ}$ (corr. 71.5°). The base amounted to about half of the original material, the remainder being unchanged substance and the compound melting at $138-140^{\circ}$.

Reduction of 1:3-Dichloro-5-nitrobenzene

(see p. 1265).

Reduction of the Chloronitrotoluenes.

The six isomeric chloronitrotoluenes referred to in the introduction were prepared from the corresponding nitrotoluidines by well-known methods. Some slight modifications were introduced into the preparation of 1:3:5-dinitrotoluene which may be useful to record, and from it the corresponding chloronitro-derivative was obtained. After nitrating *p*-acetotoluidide in the manner described by Städel (*Annalen*, 1883, 217, 189), the dinitro-compound was recrystallised and hydrolysed on the water-bath with 15 parts of sulphuric acid (5 vols. of concentrated acid to 10 vols. of water) instead of boiling with caustic

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potash, which gives a less pure product. In place of using nitrosylsulphate for diazotising, as recommended by Hönig (*Ber.*, 1887, 20, 2418), the dinitrotoluidine can be much more easily converted into dinitrotoluene as follows:

One part of finely divided substance suspended in 20 vols. of absolute alcohol and 5 vols. of strong sulphuric acid are heated on the water-bath and 3 parts of powdered sodium nitrite gradually introduced. When effervescence ceases, water is added and the dinitrotoluene filtered and recrystallised from alcohol. A theoretical yield of pure dinitro-compound melting at 92–93° was thus obtained. The 1:3:5-nitrotoluidine was prepared by reduction with hydrogen sulphide in presence of ammonia in the usual way. The chloronitro-compound melted at 58–60° after crystallisation from alcohol, and not at 55° as given by Hönig.

Preparation and Reduction of the Methyl Chloronitrobenzoates.

Methyl 2-Chloro-6-nitrobenzoate.—The acid was obtained by the oxidation of 2-chloro-6-nitrotoluene with nitric acid in a sealed tube; when pure, it melts at 161°. The silver salt crystallises from water in needles. The methyl ester was obtained in the usual way from the silver salt and methyl iodide, and crystallises from ether in colourless needles which melt at 80–82°.

Methyl 3-chloro-5-nitrobenzoate, obtained by Sandmeyer's method from the corresponding amino-ester described on p. 1268, crystallises from dilute alcohol in colourless needles and melts at 79–80°.

Methyl 2-chloro-4-nitrobenzoate was prepared by first oxidising the corresponding chloronitrotoluene with nitric acid in a sealed tube. The resulting acid was purified by crystallising from benzene, from which it separates in rhomboidal plates containing benzene of crystallisation. The acid from which the benzene has been removed on the water-bath melts at 140–142°; it was converted into the silver salt, which separates from water, in which it is moderately soluble, in colourless needles. The methyl ester melts at 73–75°.

Methyl 4-chloro-2-nitrobenzoate was prepared in the same manner as the preceding compound. The acid obtained by oxidation with nitric acid from the chloronitrotoluene is very impure, but can be purified by repeated crystallisation from water and then from benzene; it crystallises in large plates and melts at 140–142°. The methyl ester prepared from the silver salt melts at 41–43°. All the above esters exhibit very little difference in their behaviour with hydrogen sulphide in presence of ammonia. The colour of the solution in methyl alcohol reddens instantly, and shortly afterwards sulphur is deposited in quantity.

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