

CLXXIX.—*Substitution in Aromatic Hydroxy-compounds. Part I. The Action of Nitric Acid on Gallic Acid Trimethyl Ether and Pyrogallol-carboxylic Acid Trimethyl Ether.*

By VICTOR JOHN HARDING.

It has been known for a long time that many benzenecarboxylic acids containing hydroxy-groups or their ethers when treated with nitric acid give rise to nitro-compounds in which the carboxyl group has been displaced by a nitro-group. Such well-known examples are veratric acid (Tiemann, *Ber.*, 1876, **9**, 939), piperonylic acid (Jobst and Hesse, *Annalen*, 1879, **199**, 70), gallic acid trimethyl ether (Schiffer, *Ber.*, 1892, **25**, 721), and myristicinic acid (Salway, *Trans.*, 1909, **95**, 1165). It has been observed by Oertly and Pictet (*Ber.*, 1910, **43**, 1336) that methyl hydrogen hydrastate when treated with concentrated nitric acid in acetic acid solution gives methyl nitropiperonylate:



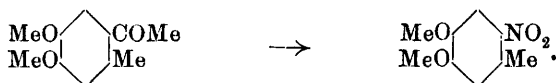
also that bromopiperonylic acid under the same conditions yields bromonitromethylenedioxybenzene:



In order to prevent this displacement of the carboxyl group it has so far been found necessary to make use of the alkyl salts when preparing the desired nitro-acid (compare Hamburg, *Monatsh.*, 1898, **19**, 599; Pollak and Feldscharek, *ibid.*, 1908, **29**, 139).

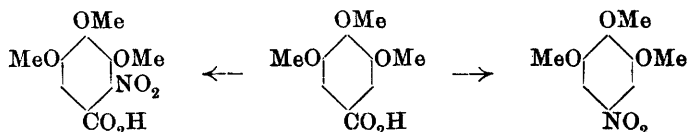
Two years ago Salway (*Trans.*, 1909, **95**, 1155) found that the ethers of aromatic hydroxy-aldehydes when acted on by concentrated nitric acid in the cold also underwent a similar reaction, the aldehyde group in part being displaced by the nitro-group. Piperonal, veratraldehyde, and myristicin aldehyde gave varying amounts of the corresponding nitrophenol ethers as well as the expected nitro-aldehydes. Anisaldehyde, however, only gave nitro-anisaldehyde, and Salway pointed out that the accumulation of methoxyl groups resulted in an increased displacement of the formyl grouping.

That acetyl groups could be similarly displaced was observed by Harding and Weizmann (*Trans.*, 1910, **97**, 1126), who by acting on 4:5-dimethoxy-*o*-methylacetophenone with nitric acid in warm glacial acetic acid solution obtained nitrohomocatechol dimethyl ether:



It was evident that these peculiar displacements were of more general occurrence than had formerly been supposed, and it was thought desirable to investigate the phenomena more closely, in order to see if any generalisation were possible, and also whether any means could be found of inhibiting the reaction, thus rendering possible the production in an easy and simple manner of the apparently more normal nitration products. In this connexion a careful study of the action of nitric acid on gallic acid trimethyl ether and the isomeric pyrogallolcarboxylic acid trimethyl ether has brought to light some interesting points.

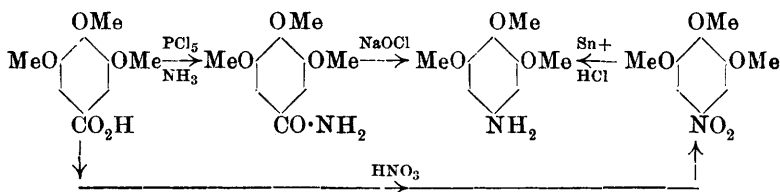
The action of nitric acid on gallic acid trimethyl ether has been investigated by Schiffer (*Ber.*, 1892, **25**, 721), who observed the displacement of the carboxyl group. Quite recently, and between the experimental results of the author and their publication, there appeared the communication of Thoms and Siebeling (*Ber.*, 1911, **44**, 2115) on the same subject. A thoroughly exhaustive examination of the products, however, does not appear to have been attempted. The action of nitric acid at 50–70°, the acid being either concentrated (D 1.4) or dilute, or in acetic acid solution, always gives a mixture of 5-nitropyrogallol trimethyl ether and nitrogallic acid trimethyl ether:



The largest yields of 5-nitropyrogallol trimethyl ether are obtained in acetic acid solution, and it is worthy of note that many of these displacements take place most readily when the nitration is carried out in that solvent. Thoms and Siebeling (*loc. cit.*), using fuming nitric acid in acetic acid solution, found that at -15° the chief product was 5-nitropyrogallol trimethyl ether, whilst on warming 5:6-dinitropyrogallol trimethyl ether was obtained, nitration of the previously-formed mononitro-compound evidently taking place. The author has also found what is probably 5:6-dinitropyrogallol trimethyl ether among the nitration products. The compound melted at 118° (Thoms and Siebeling give 119°), and was insoluble in dilute alkalis. The point, however, is being re-investigated. It does not appear to have been previously observed that nitrogallallic acid trimethyl ether is formed by the direct nitration of gallic acid trimethyl ether. The acid, however, has been prepared by Pollak and Feldscharek (*Monatsh.*, 1908, **29**, 135) by the hydrolysis of its ethyl ester, and again in exactly the same way by Thoms and Siebeling.

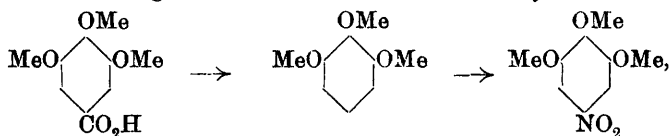
In addition to the above-mentioned compounds, there was isolated large amounts of oxalic acid, a dibasic acid, $C_{18}H_{17}O_{13}N$, and a very small amount of an acid melting at 154.5° . The question of the displacement of methoxyl groups by nitro-groups was also considered, but no evidence was obtainable that any such displacement had taken place.

The orientation of 5-nitropyrogallol trimethyl ether was accomplished by Graebe and Suter (*Annalen*, 1905, **340**, 222), thus proving that the nitro-group had displaced the carboxyl group, and that it had not arisen from the nitrogallallic acid trimethyl ether by the elimination of carbon dioxide. The following scheme shows quite clearly the proof of the position of the nitro-group:



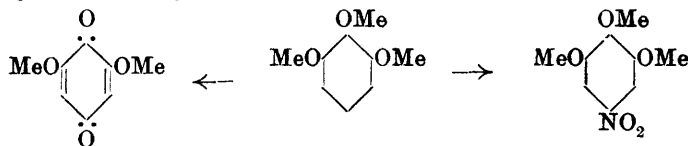
The present author has repeated this work, and confirmed it. In addition, two specimens of 5-acetylaminopyrogallol trimethyl ether were prepared from specimens of the base obtained by the two methods indicated in the diagram, and were found to be identical. Thus there can be no doubt that the action of nitric acid on gallic acid trimethyl ether results in the displacement of the carboxyl group by the nitro-group.

In considering displacements of groups of this kind by nitric acid, one obvious explanation suggests itself, namely, that the organic acid loses carbon dioxide, forming the parent phenol ether, which then undergoes substitution in the usual way:



and in the case of aldehydes and ketones that the side-chains, formyl and acetyl, undergo a preliminary oxidation to carboxyl. This view is borne out by the fact that carbethoxyl groups do not undergo this substitution. Salway (*loc. cit.*, p. 1159), however, has pointed out that, in the case of aldehydes, this view is untenable, and a consideration of the products of nitration of gallic acid trimethyl ether apparently points to the fact that it is also inadmissible in the case of organic acids, if gallic acid trimethyl ether can be taken as representative of this class of reaction.

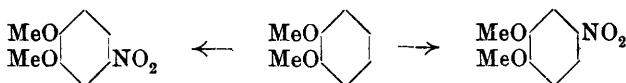
The action of nitric acid on pyrogallol trimethyl ether gives rise to a mixture of 3:5-dimethoxy-*p*-benzoquinone, as well as 5-nitropyrogallol trimethyl ether:



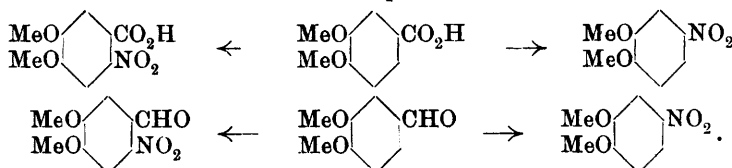
(Will, *Ber.*, 1888, **21**, 613; Schiffer, *Ber.*, 1892, **25**, 725; Graebe and Hess, *Annalen*, 1905, **340**, 232; Pollak and Goldstein, *Monatsh.*, 1908, **29**, 137). Formation of 3:5-diethoxy-*p*-benzoquinone also occurs during the nitration of pyrogallol triethyl ether (Pollak and Goldstein, *Monatsh.*, 1908, **29**, 137). If, then, there is during the production of 5-nitropyrogallol trimethyl ether from gallic acid trimethyl ether any intermediate formation of pyrogallol trimethyl ether, as such, it would be expected to show itself by the occurrence of 3:5-dimethoxy-*p*-benzoquinone among the products of nitration. This, however, is not the case; a most exhaustive search failed to reveal the presence of this quinone. Schiffer also states that the nitration of gallic acid trimethyl ether produces no quinone. It may be concluded then that the course of these reactions is one of direct substitution of the carboxyl or aldehyde group by the nitro-group.

In studying the rather scanty literature of reactions of this type, it was noticed that the substitution of the acyl group always gave rise to the same nitrophenol ether as that produced by the nitration

of the phenol ether itself. This is very clearly brought out if the substitution of veratrole is compared with that of its derivatives, veratric acid and veratraldehyde. The nitro-group enters either of the positions 4 or 5. In the case of veratrole this gives rise to the one derivative, 4- or 5-nitroveratrole:



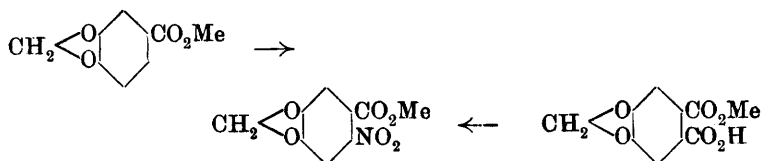
whereas in veratroles already substituted in positions 4 or 5 it gives rise to a mixture of nitro-compounds:



Homocatechol dimethyl ether and its ketone, 4:5-dimethoxy-*o*-methylacetophenone, give the same nitrohomocatechol dimethyl ether:



also methyl piperonylate and methyl hydrogen hydrastate show a similar behaviour:

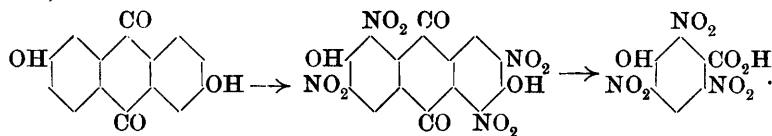


It would seem very probable from these examples that the substitution of acyl groupings by the nitro-group is conditioned by those forces in the molecule which direct the entrance of a nitro-group in the parent phenol ether, and that the substitution of the more complex group differs only in degree from that of hydrogen. That equal amounts of nitroveratric acid and nitroveratrole are not produced by the nitration of veratric acid is due to the more mobile hydrogen atom being more easily substituted than the heavier carboxyl. It must not be forgotten, however, that the carboxyl group itself exerts a definite directive influence as against that of the hydrogen atoms, but it would appear that its influence is small when compared with that of the methoxyl groups. The directive power of the two methoxyl groups in veratrole would appear to be sufficiently powerful to suppress that of certain other substi-

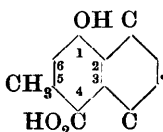
tuenta, and to cause substitution to take place in the manner described.

One consequence of the displacement of acyl groups being similar to that of hydrogen is that the substitution of the more complex groups should obey those laws which govern the ordinary substitution in the benzene ring. Just as the action of nitric acid on the hydrogen atoms of substituted benzenes results in a selective action, and by doing so has given rise to the well known ortho-, para-, and meta-rules of substitution, so ought this selective action to be observed when the more complex groups are substituted. Thus, if the carboxyl group, etc., occupies a position which would not be substituted by a nitro-group in the parent phenol ether, then that group will be inactive towards nitric acid. Cases in which the action of nitric acid has been studied in this way are few in number, and are confined to derivatives of phenol.

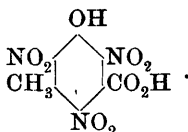
The positions in phenol reactive to nitric acid are the positions 2:4:6. Consequently it would be expected that groups occupying the positions 2:4:6 would be substituted by the nitro-group, and that those occupying the inactive positions 3:5 would remain unsubstituted; and this is found to be the case. Salicylic acid on continued nitration yields picric acid, the lighter and more mobile hydrogen atoms being first displaced, and finally the carboxyl group itself (Hübner, *Annalen*, 1879, **195**, 31; Hübner, Babcock, and Schaumann, *Ber.*, 1879, **12**, 1346; Schiff and Nasino, *Annalen*, 1879, **198**, 258; see also Beilstein, *Handbuch*, IV., 1490). Coumarin in a similar manner gives picric acid (Delaude, *Annalen*, 1843, **45**, 337), and derivatives of *p*-coumaric acid also on nitration yield *s*-trinitrophenol, for example, carthamine (Kametaka and Perkin, *Trans.*, 1910, **97**, 1419). On the other hand, anthraflavic acid on nitration gives tetranitroanthraflavic acid, and finally 2:4:6-trinitro-*m*-hydroxybenzoic acid (Schardinger, *Ber.*, 1875, **8**, 1490):



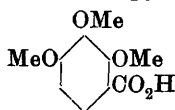
A still more striking example is the action of nitric acid on carminic acid, which contains the groupings:



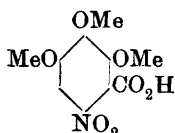
The groups occupying the active positions 2:4:6 are substituted by nitro-groups, either direct or after oxidation, whilst groups in the inactive positions 3:5 remain unsubstituted, and give rise to trinitrohydroxy-*m*-toluic acid (Kostanecki and Niementowski, *Ber.*, 1885, **18**, 253):



In order to gain more evidence on this important point it was deemed advisable to select a compound in which a carboxyl or aldehyde group occupied an inactive position in a molecule containing a large number of methoxyl groups, and to investigate the action of nitric acid on it under varying conditions. The presence of a large number of methoxyl groups would cause the carboxyl or aldehyde group to be more sensitive to the action of nitric acid (compare Salway, *loc. cit.*, p. 1159), and thus it would be possible to determine easily whether any substitution had taken place. The compound chosen was pyrogallolcarboxylic acid trimethyl ether (I):



(I.)

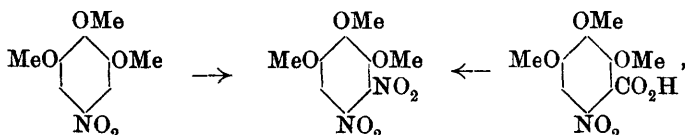


(II.)

The action of nitric acid on this compound does not appear to have been previously studied. The nitro-acid (II), however, has been prepared by Pollak and Goldstein (*Annalen*, 1907, **351**, 161) by nitrating methyl pyrogallolcarboxylate trimethyl ether, with subsequent hydrolysis.

The action of concentrated nitric acid in the cold, either alone or in acetic acid solution, results in the formation in almost quantitative yield of nitropyrogallolcarboxylic acid trimethyl ether. The use of the methyl ester of pyrogallolcarboxylic acid to prevent any possible carboxyl substitution taking place is unnecessary. The product obtained direct from the nitration of the free acid was completely soluble in sodium carbonate, and possessed the correct melting point. When, however, the action of hot nitric acid was investigated, it was found that a very small amount of a neutral substance was obtained, in addition to the nitro-acid. This melted at 118°, and was in all probability (see p. 1596) 5:6-dinitropyrogallol trimethyl ether. No trace of 6-nitropyrogallol trimethyl ether was observed. This compound has been prepared by Einhorn, Cobliner, and Pfeiffer (*Ber.*, 1904, **37**, 117), and melts at 44°

(compare also Thoms and Siebeling, *loc. cit.*). The formation of 5:6-dinitropyrogallol trimethyl ether is in accordance with the views expressed in this paper; the carboxyl group in nitropyrogallolcarboxylic acid trimethyl ether occupies the position in 5-nitropyrogallol trimethyl ether active towards a nitro-group, and is in consequence substituted:



whereas when not occupying the inactive position as in pyrogallolcarboxylic acid trimethyl ether, it remains unaffected by the nitric acid, although the isomeric gallic acid trimethyl ether undergoes substitution in a very marked manner.

It would seem very probable, then, by these examples that the substitution of acyl groups is governed by the same forces in the benzene nucleus which control the substitution of the hydrogen atoms in the parent phenol ether. The groups $\cdot\text{H}$, $\cdot\text{CHO}$, $\cdot\text{CO}$, $\cdot\text{CH}_3$, $\cdot\text{CO}_2\text{H}$ apparently form a series, any member of which can be substituted by the group $\cdot\text{NO}_2$. It remains to be seen how far this series can be extended, and work is in progress to determine this point. As regards the actual mechanism of the substitutions, it is of interest to note that if the nitrations are carried out in the cold in presence of a trace of hydrogen peroxide, the expected substitution does not take place. Gallic acid trimethyl ether, on treatment with concentrated nitric acid in presence of a trace of hydrogen peroxide, does not yield any 5-nitropyrogallol trimethyl ether. This interesting observation, which may turn out to be of great practical utility, is at present being studied, and the results will shortly be laid before the Society.

EXPERIMENTAL.

Action of Nitric Acid on Gallic Acid Trimethyl Ether.

In order to investigate thoroughly the action of nitric acid on gallic acid trimethyl ether, and to observe if any formation of 3:5-dimethoxy-*p*-benzoquinone occurred, the reaction was carried out under the following conditions.

I.—Fifty grams of gallic acid trimethyl ether were added in small quantities at a time to 100 c.c. of concentrated nitric acid (D 1.4). A vigorous reaction took place with rise of temperature, carbon dioxide and nitrous fumes being rapidly evolved. The temperature, however, was not allowed to rise above 50°. When

all the gallic acid trimethyl ether had been added, the reaction was completed by allowing the mixture to remain at room temperature for an hour. It was then diluted with water, and the precipitated substances were collected. The 5-nitropyrogallol trimethyl ether (A) was purified from the accompanying carboxylic acids by dissolving the latter in dilute sodium carbonate solution, and washing the residue well with water. In this way there was obtained 9.5 grams of 5-nitropyrogallol trimethyl ether. The sodium carbonate washings on acidification yielded 7 grams of an acid mixture (B) (p. 1595).

II.—Gallic acid trimethyl ether was heated with dilute nitric acid (1:4) until the vigorous reaction which set in had subsided. In this case the temperature was not allowed to rise above 70°. The solid products which separated on cooling were collected, and treated as described in method I. Fifty grams of gallic acid trimethyl ether in this manner gave 11 grams of crude 5-nitropyrogallol trimethyl ether (A) and 2 grams of an acid mixture (B).

III.—In this case gallic acid trimethyl ether was dissolved in glacial acetic acid, and an excess of nitric acid added. The reaction again was very vigorous, but the yield of neutral compounds obtained on dilution was much larger under these conditions. From 50 grams of gallic acid trimethyl ether were obtained 26 grams of crude neutral compounds (A) and 8 grams of an acid mixture (B).

The filtrates (C) from these nitration experiments were mixed and investigated as described on page 1596.

Examination of 5-Nitropyrogallol Trimethyl Ether (A).

The whole of the crude 5-nitropyrogallol trimethyl ether obtained from the above-described experiments was purified by crystallisation from absolute alcohol, from which it separated quite readily in the characteristic pale yellow needles, melting at 99°. The residues on complete evaporation of the alcohol yielded a small amount of a substance, which when crystallised from dilute acetic acid melted at 88—89°. When freshly prepared it consisted of almost colourless needles, which on drying and exposure to light were converted into a yellow, amorphous-looking powder. The amount, however, was too small to permit of further investigation, and it is very doubtful if a pure substance was isolated.

Gallamide Trimethyl Ether, $C_6H_2(OMe)_3 \cdot CO \cdot NH_2$.

This compound has been previously prepared by the methylation of gallamide (Marx, *Annalen*, 1891, 263, 250), and by passing dry

ammonia gas into a benzene solution of gallyl chloride trimethyl ether (Graebe and Suter, *Annalen*, 1905, **340**, 222). Its preparation, however, is easily effected by pouring a large excess of concentrated aqueous ammonia on to freshly prepared powdered gallyl chloride trimethyl ether, when the amide separates as a white, insoluble solid. It is collected, washed with cold water, and purified by crystallisation from 90 per cent. alcohol. It melts at (Found, N=6.7. Calc., N=6.6 per cent.)

5-Acetylaminopyrogallol Trimethyl Ether,
 $C_6H_2(OMe)_3 \cdot NH \cdot CO \cdot CH_3$.

The base 5-aminopyrogallol trimethyl ether was prepared (*a*) by the action of freshly prepared sodium hypochlorite on gallamide trimethyl ether (Graebe and Suter, *Annalen*, 1905, **340**, 222); (*b*) by the reduction of 5-nitropyrogallol trimethyl ether (Will, *Ber.*, 1888, **21**, 613).

A mixed melting-point determination made with specimens of the base prepared by both methods gave the same melting point as that shown by each constituent. 5-Acetylaminopyrogallol trimethyl ether is easily obtained by warming the base with acetic anhydride on the water-bath for an hour, cooling, and then pouring into water. It crystallises from alcohol in small needles, which soften at 110°, and finally melt at 127°, and contains one molecule of water of crystallisation:

0.1354 gave 0.2676 CO_2 and 0.0812 H_2O . C=53.9; H=6.6.

0.1434 „ 7.5 c.c. N_2 (moist) at 20° and 756 mm. N=5.9.

$C_{11}H_{15}O_4N \cdot H_2O$ requires C=54.3; H=6.9; N=5.7 per cent.

A direct determination of the water of crystallisation does not give a very satisfactory result, as even when kept at 100° there is considerable decomposition if the heating is continued for any length of time. The figures, however, show the presence of one molecule of water of crystallisation if the rate of the loss of water is taken into account:

0.2997, on heating at 101° for one hour, lost 0.0214.

0.2997, „ „ 101° „ two hours, „ 0.0224.

Loss at end of first hour=7.2 per cent.

„ „ second „ =8.2 „

$C_{11}H_{15}O_4N \cdot H_2O$ requires loss=7.4 per cent.

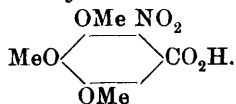
The acetyl group is not hydrolysed by warm dilute aqueous potassium hydroxide.

The same acetyl derivative is produced from specimens of base prepared by either methods (*a*) or (*b*). This was confirmed by the

method of mixed melting point. Graebø and Suter (*loc. cit.*) give the melting point of 5-acetylaminopyrogallol trimethyl ether as 124°, but no analysis of their product is given.

Examination of the Acid Mixture (B).

Isolation of Nitrogalllic Acid Trimethyl Ether,



The crude acid mixtures from the three previously described nitration experiments (p. 1593) were mixed together, and the nitrogalllic acid trimethyl ether was separated from its accompanying impurities by crystallisation from benzene, it being almost insoluble in the cold solvent. It was identified by means of its melting point (163—164°) and analysis. (Found, C=46·7; H=4·1. Calc., C=46·6; H=4·2 per cent.)

This acid has previously been described by Pollak and Feldscharek (*Monatsh.*, 1908, **29**, 139), who obtained it by the hydrolysis of its ethyl ester, a compound prepared by the nitration of ethyl gallate trimethyl ether. It seems, however, to have escaped observation that it is one of the products of the direct nitration of gallic acid trimethyl ether.

Nitrogalllic acid trimethyl ether is esterified only with great difficulty.

Nitrogallamide trimethyl ether is readily prepared by mixing nitrogalllic acid trimethyl ether with a small excess of phosphorus pentachloride in presence of a little benzene and warming slightly. A gentle reaction sets in, and at the end of two hours the semi-solid mass is poured into a large excess of concentrated aqueous ammonia, when the amide separates as a solid mass. It crystallises from alcohol in pulpy masses of needles, melting at 182—184°:

0·1339 gave 0·2323 CO₂ and 0·0529 H₂O. C=47·3; H=4·4.

C₁₀H₁₂O₆N₂ requires C=46·9; H=4·6 per cent.

Isolation of an Acid, C₁₈H₁₇O₁₃N.

The benzene mother liquors from the separation of the nitrogalllic acid trimethyl ether were evaporated to a small bulk, and an equal volume of light petroleum was added. The yellow precipitate which formed was collected and purified by crystallisation from water until further crystallisation ceased to alter its melting point. The acid separates from water in almost colourless nodules, which rapidly turn yellow on exposure to light, and melt at 136—137°:

0.1297 gave 0.2245 CO_2 and 0.0435 H_2O . $\text{C}=47.2$; $\text{H}=3.7$.

0.1591 „ 4.8 c.c. N_2 (moist) at 24° and 756 mm. $\text{N}=3.3$.

$\text{C}_{18}\text{H}_{17}\text{O}_{13}\text{N}$ requires $\text{C}=47.5$; $\text{H}=3.9$; $\text{N}=3.1$ per cent.

A determination of the basicity gave the following results:

0.1307 required for neutralisation 0.0223 NaOH , whilst the same weight of a dibasic acid, $\text{C}_{18}\text{H}_{17}\text{O}_{13}\text{N}$, requires 0.0227 NaOH .

Examination of the Filtrate (C).

The aqueous residues from the nitration of gallic acid trimethyl ether, amounting to about two litres, were combined and evaporated on the water-bath to about half their bulk, and then set aside in a cold air chamber to crystallise. After keeping overnight, a mass of crystals separated, which on collection was found to consist of oxalic acid mixed with a small amount of the acid $\text{C}_{18}\text{H}_{17}\text{O}_{13}\text{N}$ (p. 1595), the two acids being easily separated by means of warm water. A further evaporation and cooling resulted in the separation of more oxalic acid, but in this case free from the acid $\text{C}_{18}\text{H}_{17}\text{O}_{13}\text{N}$. In all, there were isolated about forty grams of oxalic acid.

Isolation of 5:6-Dinitropyrogallol Trimethyl Ether,



The remaining nitric acid was then removed by repeated evaporation and dilution, when there gradually separated a very small amount of a colourless, flocculent precipitate. This, on crystallisation from alcohol or acetic acid, melted constantly at 118° , and any further treatment failed to alter its properties. Thoms and Siebeling give the melting point of 5:6-dinitropyrogallol trimethyl ether as 119° , and state that the melting point given by Will (126°) is too high. As the compound (m. p. 118°) agreed in properties with the 5:6-dinitropyrogallol trimethyl ether described by Thoms and Siebeling (*Ber.*, 1911, **44**, 2123), this, taken in conjunction with the method of preparation and the fact that the same compound is also formed by the action of hot nitric acid on pyrogallolcarboxylic acid trimethyl ether (see p. 1597), is taken provisionally as evidence of its constitution. The point, however, will be re-investigated.

Isolation of an Acid Melting at 154.5° .—The residues after the separation of the above-described substance were evaporated to dryness, triturated with cold sodium carbonate solution, and

filtered. The filtrate on acidifying slowly deposited a small quantity of an acid, which after two crystallisations from water melted sharply at 154.5° . The amount, however, was too small to permit of further investigation.

Thus from 150 grams of gallic acid trimethyl ether there was obtained nearly 110 grams of products, and a most exhaustive search had failed to detect the presence of 3:5-dimethoxy-*p*-benzoquinone, even in the slightest trace. Under conditions identical with those obtaining in the experiments just described, the action of nitric acid on pyrogallol trimethyl ether yielded large amounts of this quinone (compare Graebe and Hess, *Annalen*, 1905, **340**, 232).

Action of Nitric Acid on Pyrogallolcarboxylic Acid Trimethyl Ether.

The action of nitric acid on pyrogallolcarboxylic acid trimethyl ether was studied under the following conditions:

I.—Two grams of acid were dissolved in excess of concentrated nitric acid, and the solution kept cold by a stream of water. There is no violent reaction, as in the case of gallic acid trimethyl ether. At the end of fifteen minutes water was added, and the clear liquid was allowed to remain for some hours in the cold air chamber, when there slowly separated a mass of faintly yellow crystals. These were found to be completely soluble in cold dilute sodium carbonate solution, and a melting-point determination showed them to consist of pure nitropyrogallolcarboxylic acid trimethyl ether.

II.—Two grams of the acid were dissolved in acetic acid, and to this solution was added the nitric acid, the whole being allowed to remain at room temperature for fifteen minutes. The crystalline product which separated on dilution was found to consist entirely of nitropyrogallolcarboxylic acid trimethyl ether. No neutral compounds were observed.

III.—The action of hot concentrated nitric acid on pyrogallolcarboxylic acid trimethyl ether, however, results in the production of a very small amount of a substance insoluble in cold dilute sodium carbonate solution, as well as the nitro-acid. From two grams of pyrogallolcarboxylic acid trimethyl ether there was obtained enough neutral substance to permit of its crystallisation and a determination of the melting point. It crystallised from alcohol in colourless needles, melting at 118° , and was found to be identical with the 5:6-dinitropyrogallol trimethyl ether obtained by the nitration of gallic acid trimethyl ether (p. 1596).

The aqueous residues from the above experiments were mixed together and evaporated on the water-bath. These separated from

the solution a further amount of 6-nitropyrogallolcarboxylic acid trimethyl ether. The mother liquors were then completely evaporated, and the small residue was extracted with cold dilute sodium carbonate solution. This on acidifying yielded a small amount of an acid, which softened at 90°, and finally melted at 100°.

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