LXI.—*Action of Nitric Acid on Anthracene.*

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THE behaviour of anthracene towards nitric acid has been made the subject of repeated investigation at the hands of chemists, in every case with the same result, that anthraquinone, or one of its derivatives, is formed, instead of nitro-derivatives of anthracene. The reason for this lies in the fact that anthracene is more readily oxidised than nitrated, and, therefore, when treated with nitric acid, the hydrocarbon is at once converted into anthraquinone, and this, by the further action of the acid, then yields the well-known nitro-anthraquinones.

In the course of a series of experiments on anthracene derivatives, on which I have been engaged for some time, I had occasion to investigate again the action of nitric acid on this hydrocarbon, and I thus obtained a number of interesting results, a short account of which I beg to lay before the Society.

Several of the substances obtained in this investigation are closely allied to, and, in some cases, identical with, a series of derivatives obtained by Liebermann and Lindemann (*Ber.*, **13**, 1585) and Liebermann and Landshoff (*Ber.*, **14**, 467), and, in order to explain the connection between these somewhat complicated derivatives, I think it would be convenient to give a short summary of the results obtained by these chemists. When dihydroanthracene is treated with nitric acid in acetic acid solution, a colourless, crystalline substance, *hydranthracene nitrite*, $C_6H_4<\overset{\text{CH}_2}{\underset{C(NO_2)_2}{\text{C}}}>C_6H_4$, is produced. This substance, when boiled with dilute potassium hydrate solution, is decomposed, with formation of *nitrosoanthrone*,

and nitroso-oxanthranol, $C_6H_4<\overset{\text{CO}}{\underset{C(OH)(NO)}{\text{C}}}>C_6H_4$. A solution of anthracene in acetic acid, saturated with nitrogen trioxide, deposits, on standing, a precipitate of *anthracene nitrate*,

whereas, if nitrogen tetroxide is employed in the place of the trioxide, a substance $C_{14}H_{10}N_2O_4 = C_6H_4<\overset{C(OH)(NO)}{\underset{C(OH)(NO)}{\text{C}}}>C_6H_4$ is produced, which is isomeric with hydranthracene nitrate.

Alkalis decompose anthracene nitrate, with formation of *nitrosoanthrone*, $C_6H_4<\overset{\text{CO}}{\underset{CH(NO)}{\text{C}}}>C_6H_4$, and nitrosohydranthrone,

The results obtained in my investigation of the action of nitric acid on solutions of anthracene are, briefly stated, the following:—

When a solution of anthracene in nitrobenzene is treated with fuming nitric acid, the principal products of the reaction are a beautiful, yellow substance $C_{14}H_8N_2O_4$, which melts at 292° , nitrosoanthrone, $C_6H_4<\overset{\text{CO}}{\underset{CH(NO)}{\text{C}}}>C_6H_4$, and anthraquinone. The substance $C_{14}H_8N_2O_4$ was at first thought to be dinitroanthracene, as, although

it has the same composition and similar properties to Liebermann and Landshoff's nitrosoanthrone, its melting point is 30° higher than they ascribed to the latter.

At a later stage in these experiments, it became necessary to prepare a considerable quantity of nitrosoanthrone, and, in purifying this carefully, a product was ultimately obtained which melted at $288-290^{\circ}$, and was, evidently, identical with the substance $C_{14}H_8N_2O_4$ obtained by me as described above.

It seems probable that, in the formation of nitrosoanthrone by the action of nitric acid on anthracene, nitrosoanthrone is first produced, and then, by the further action of nitric acid, it is converted into nitrosoanthrone, thus:—

This hypothesis is supported by the fact that not only is nitrosoanthrone present in the product of the action of nitric acid on anthracene in nitrobenzene solution, but that this substance, when acted on by nitric acid, as is shown in the body of this paper, is almost quantitatively converted into nitrosoanthrone. Conversely, nitrosoanthrone, when subjected to the action of alkaline reducing agents, such as sodium sulphide, is reconverted into nitrosoanthrone.

Very interesting results were obtained in the study of the action of nitric acid on a solution of anthracene in a mixture of 2 parts of nitrobenzene and 3 parts of alcohol. In this case the reaction proceeds quite differently: a beautiful, colourless, crystalline substance is produced which has the composition $C_{16}H_{15}NO_3 (= C_{14}H_{10}, C_2H_5NO_3)$, and the constitution of which is probably represented by the formula

This substance, for which I propose the name *anthracene ethyl nitrate*, is probably the ethyl derivative of anthracene nitrate,

When boiled with hydrogen iodide solution, anthracene ethyl nitrate is readily decomposed, with formation of ethyl iodide and anthracene dihydride. Boiling alkalis convert it into a substance $C_{14}H_9NO_2$, which is isomeric with nitrosoanthrone,

and also with isonitrosoanthraquinone, $C_6H_4<\overset{C(NO\dot{H})}{\underset{CO}{\parallel}}>C_6H_4$, and which, very probably, has the constitutional formula

The decomposition of anthracene ethyl nitrate by alkalis may therefore be represented by the following equation:—

This new substance, for which I propose the name pseudonitrosoanthrone, dissolves in alkalis, forming a deep orange-yellow solution; with acetic anhydride, it yields a well-characterised monacetyl derivative, $C_{14}H_8(OC_2H_3O)NO$. When treated with ammonia, or boiled with dilute sulphuric acid, anthracene ethyl nitrate is converted almost quantitatively into nitrosoanthrone.

A compound similar to anthracene ethyl nitrate is produced when methyl alcohol is substituted for ethyl alcohol in the above reaction. This has the composition $C_{14}H_{10}(CH_3\cdot NO_2)$, and is decomposed by alkalis exactly in the same way as the ethyl compound, yielding nitrosoanthrone and pseudonitrosoanthrone.

In studying these results by the side of those obtained by Liebermann and others, one cannot but be struck with the great reactive capacity of the centre portion of the anthracene molecule as distinguished from that of any other hydrocarbon which has as yet been investigated. Experiments are in progress by means of which it is hoped that this centre portion of the anthracene molecule may be to such a degree weakened that by some simple means a severance of the two benzene nuclei from the intervening portion may be brought about, in which case results of theoretical importance as bearing on the question of the constitution of anthracene might be expected.

Action of Nitric Acid on Anthracene in the Presence of Nitrobenzene.

In studying this action, finely powdered, pure anthracene was added in small portions at a time to a mixture of 1 part of fuming nitric acid, sp. gr. 1.5, and 2 parts of nitrobenzene. The anthracene quietly dissolved, and after a small quantity had been added, small, yellow needles began to appear in the solution. The addition of anthracene was continued until the whole had become of the con-

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sistency of a thin paste, but not longer, as in that case it was found that the resulting product was difficult to purify. During this addition, care was also taken to avoid rise of temperature. The whole was then thrown on to a funnel plugged with glass wool, and the filtrate placed aside for further investigation. The residue on the filter was washed two or three times with glacial acetic acid, then with alcohol, and dried. It consisted of a lemon-coloured mass of fine needles, and was further purified by one or two crystallisations from coal-tar naphtha with the aid of animal charcoal if necessary.

On analysis, numbers were obtained agreeing with the formula $C_{14}H_8N_2O_4$:—

- I. 0.2091 gram substance gave 0.0599 gram H_2O and 0.4812 gram CO_2 .
 II. 0.1653 gram substance gave 0.0480 gram H_2O and 0.3818 gram CO_2 .
 III. 0.2394 gram substance gave 20.75 c.c. N.; temp. 85° ; bar. 762.5 mm.

	Theory.	Found.		
		I.	II.	III.
C	62.99	62.77	62.99	—
H	2.99	3.18	3.22	—
N	10.44	—	—	10.57

This substance may also be prepared: *a.*—By the addition of anthracene to a mixture of 1 part of fuming nitric acid and 2 parts of pyridine neutralised with nitric acid. The details of preparation are similar to those given above.

b.—By the addition of anthracene to cold nitric acid which had been purified by boiling with nitrate of urea. In this case the anthracene did not appear to dissolve in the acid, and the product remained suspended in the liquid as a yellow mass.

c.—By the addition of anthracene ethyl nitrate to a mixture of fuming nitric acid and nitrobenzene.

This substance, when prepared by either of these methods and very carefully crystallised from coal-tar naphtha, forms fine, long, yellow needles, often more than an inch in length, under the microscope showing a striated appearance resembling that of nitrate of potassium. It is less soluble in coal-tar naphtha than anthraquinone, a property which renders it easy of separation from the latter, which is always formed to some extent during the reaction. It is moderately soluble in hot aniline or nitrobenzene, and slightly soluble in hot alcohol, acetic acid, and benzene. It melts at 288 – 290° , and at higher temperatures, if carefully heated, sublimes unchanged with

little or no carbonisation, but if superheated it suddenly decomposes with the formation of a cloud of black vapour, in this respect resembling the nitroanthraquinones. On exposure to sunlight, it slowly decomposes, the crystals being observed after some weeks to gradually curl up and become opaque, and on examination the product is found to consist of anthraquinone. Bromine has no action upon it in the cold, and it does not form a compound with picric acid. Cold sulphuric acid has no action upon it. When a solution of chromic acid was added to the substance suspended in glacial acetic acid, the mixture boiled for a few minutes, and water added, a white, crystalline precipitate was formed. This, after further purification, was obtained as white needles melting at 278° , and having all the properties of anthraquinone.

When added to strong fuming sulphuric acid, an energetic reaction took place. Water added to the product threw down a dirty white precipitate, which, after two or three crystallisations, appeared as white needles, consisting of pure anthraquinone. As stated in the introduction, this substance is evidently identical with *nitrosonitroanthrone*, $\text{C}_6\text{H}_4\langle\begin{smallmatrix} \text{CO} \\ \text{C}(\text{N}_2\text{O}_3) \end{smallmatrix}\rangle\text{C}_6\text{H}_4$, obtained by Liebermann and Lands-hoff by the action of alkalis on hydroanthracene nitrite.

The acid filtrate from the above substance, when treated with water and allowed to stand for a few days, became semi-solid owing to the separation of a crystalline compound. This was collected, pressed, and the residue crystallised two or three times from benzene. The product consisted of white needles melting at 278° , and having all the properties of anthraquinone.

In some cases when a larger quantity of anthracene than usual was added to a mixture of nitric acid and nitrobenzene without carefully cooling, a crystalline precipitate was obtained, and this was treated in the manner previously described. It was found to consist of a mixture of three substances, namely, nitrosonitroanthrone, anthraquinone, and a substance whose solubility in coal-tar naphtha was between the two. The yellow precipitate was first crystallised from this solvent to free it from anthraquinone, and the resulting crystalline mass very carefully fractionally crystallised from an excess of this solvent. The separation of these two substances presented no difficulty, as the point at which either commenced or finished crystallising was very sharply defined.

On analysis, the following numbers were obtained :—

- I. 0.1400 gram substance gave 0.0570 gram H_2O and 0.3872 gram CO_2 .
- II. 0.1563 gram substance gave 0.0569 gram H_2O and 0.4302 gram CO_2 .

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These numbers give the percentages required for the formula $C_{14}H_9NO_3$.

	Theory.	Found.	
		I.	II.
C	75.24	75.03	75.43
H	4.03	4.04	4.04

This substance melts at 146° and is evidently identical with the nitrosoanthrone, $C_6H_4<\frac{CO}{CH(NO)}>C_6H_4$, obtained by Liebermann and Lindemann (*Ber.*, **13**, 1555) by the action of alkalis on anthracene nitrate, $C_{14}H_{10}HNO_3$.

Action of Sodium Sulphide on Nitrosonitroanthrone.

When this was added to a boiling solution of sodium sulphide in alcohol, it quickly dissolved, forming a fine, red-violet solution, which, after a short digestion, gave no precipitate on the addition of boiling water. Hydrochloric acid, added to this solution, caused the formation of a heavy, brownish-yellow precipitate, which was collected washed, and dried. The resulting brownish-yellow powder was then digested with hot alcohol to which a few drops of aqueous potash had been added, and filtered. The filtrate, on cooling, deposited small, brownish-orange needles, which were collected, washed with hot alcohol and water, dried, and crystallised two or three times from acetic anhydride or alcohol. The yield of this substance was small, and from the residue insoluble in alcoholic potash no definite compound has been isolated.

On analysis, the following numbers were obtained:—

- I. 0.1318 gram substance gave 0.0532 gram OH_2 and 0.3620 gram CO_2 .
- II. 0.1650 gram substance gave 0.0628 gram OH_2 and 0.4529 gram CO_2 .

These numbers give percentages agreeing with the formula $C_{14}H_9O_2$.

	Theory. $C_{14}H_9NO_2$.	Found.	
		I.	II.
C	75.34	74.91	74.80
H	4.03	4.48	4.22

As thus obtained, it forms long, orange-yellow needles, showing a striated appearance under the microscope. It is very soluble in benzene and carbon bisulphide, somewhat less so in acetic anhydride and acetic acid, and only moderately in alcohol. It melts to an orange coloured liquid at 146° . When added to cold sulphuric acid,

a dirty green solution is produced which turns black when heated; the addition of water then throws down a black, carbonaceous precipitate. Fuming nitric acid attacks it violently with evolution of red fumes and formation of anthraquinone. When chromic acid is added to its solution in acetic acid, it reacts violently with formation of anthraquinone.

This substance is obviously identical with nitrosoanthrone, $C_6H_4<\overline{CO}>C_6H_4$, obtained by Liebermann and Lindemann (*Ber.*, **13**, 1585) by treating anthracene nitrate or nitrite with alkalis. In the formation of this substance by the action of sodium sulphide on nitrosonitroanthrone, it is probable that an intermediate substance, $C_6H_4<\overline{CH(OH)}>C_6H_4$, is first produced which dissolves in alkalis with a violet colour, and is readily oxidised on exposure to air with formation of nitrosoanthrone. This is borne out by the fact that nitrosoanthrone, although itself insoluble in alkalis, readily dissolves in the presence of a reducing agent with the formation of a violet solution.

Action of Nitric Acid on Nitrosoanthrone in the presence of Nitrobenzene.

In order to afford additional proof of the constitution of nitrosonitroanthrone, the action of nitric acid on nitrosoanthrone was carefully investigated.

When nitrosoanthrone is added to a mixture of fuming nitric acid and nitrobenzene, it slowly undergoes change, without, however, passing into solution. The addition of this substance was continued until the whole became of a pasty consistency, and the product was then filtered through glass wool, the residue washed with acetic acid and alcohol, and dried. The lemon-coloured mass which, on examination, appeared as minute needles, was further purified by crystallisation from coal-tar naphtha.

On analysis, the following results were obtained:—

0.1614 gram substance gave 0.0448 gram H_2O and 0.3717 gram CO_2 .

These numbers give percentages agreeing with the formula required for nitrosonitroanthrone.

	Theory. $C_{14}H_8N_2O_4$	Found.
C	62.69	62.80
H	2.99	3.08

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As thus obtained, it consisted of long, orange needles sparingly soluble in boiling acetic acid and coal-tar naphtha. It melted at about 290—292°. The formation of nitrosonitroanthrone by the above reaction may be represented by the equation

Action of Nitric Acid on Anthracene in the presence of Alcohol and Nitrobenzene.

If finely divided anthracene is added to a mixture of 1 part of fuming nitric acid, 2 parts of nitrobenzene, and 3 parts of alcohol by volume, it slowly dissolves in the cold, but much more readily if very gently heated.

In studying this reaction, the addition of anthracene was continued until a sample of the product set to a pasty mass of crystals on cooling. The whole was then rapidly filtered to free it from any traces of undissolved anthracene, the solution thoroughly cooled, and the crystals which separated collected, washed two or three times with a little alcohol, and strongly pressed. It was then further purified by two or three crystallisations from alcohol.

On analysis, the substance dried at 60° gave the following numbers:—

- I. 0.2816 gram substance gave 13.1 c.c. N; $t = 12^\circ$; bar. 740 mm.
0.1745 gram substance gave 0.0913 gram H_2O and 0.4580 gram CO_2 .
- II. 0.1557 gram substance gave 0.0770 gram H_2O and 0.4090 gram CO_2 .
- III. 0.1197 gram substance gave 0.0602 gram H_2O and 0.3138 gram CO_2 .
- IV. 0.1737 gram substance gave 0.0870 gram H_2O and 0.4577 gram CO_2 .
- V. 0.1664 gram substance gave 0.0826 gram H_2O and 0.4378 gram CO_2 .

These numbers give percentages agreeing with the formula $\text{C}_{14}\text{H}_{10}, \text{C}_2\text{H}_5\text{NO}_3$.

	Theory for $\text{C}_{14}\text{H}_{10}, \text{C}_2\text{H}_5\text{NO}_3$.	I.	II.	III.	IV.	V.
C	71.4	71.58	71.64	71.49	71.87	71.75
H	5.6	5.81	5.49	5.59	5.56	5.51
N	5.2	5.40	—	—	—	—

The determination of the molecular weight of this substance by

Raoult's method gave the following numbers, agreeing fairly well with the formula $C_{14}H_{10}, C_2H_5NO_3$.

Substance taken	1.0422 grams.
Acetic acid ,,	75.6 ,,
Melting point of the acetic acid.....	14.75° C.
,, the mixture.....	14.53 ,,
Depression of the melting point.....	0.22 ,,
Molecular weight of the substance found from the above data	244.
Theory for $C_{14}H_{10}, C_2H_5NO_3$	269.

As stated in the introduction, this new substance is a compound of anthracene with the elements of ethyl nitrate, and from a study of its properties it is probable that it has the constitution

in which case it might be looked upon as the ethyl derivative of Liebermann's anthracene nitrate, which probably has the constitution

Anthracene ethyl nitrate crystallises from alcohol in flat, white, glistening needles, which are readily soluble in benzene and chloroform, moderately so in alcohol and acetic acid. It melts at about 160° to a yellow liquid, and slightly above this point it decomposes with rapid evolution of nitrous fumes and formation of anthraquinone. This decomposition takes place slowly at temperatures below 100°, and on boiling with alcohol, acetic acid and other solvents, nitrous fumes are slowly given off and the solution becomes yellow. It is therefore necessary, when purifying this substance by recrystallisation, to conduct the operation as rapidly as possible, otherwise the product is with difficulty obtained in a colourless condition. When exposed over sulphuric acid in a vacuum, anthracene ethyl nitrate is sometimes very rapidly converted into a gummy, yellow mass. Dissolved in acetic acid and treated with chromic acid, it is converted into anthraquinone. Cold fuming nitric acid also converts it into this substance.

With a mixture of nitric acid and nitrobenzene, it behaves similarly to anthracene, nitrosonitroanthrone being formed, as was proved by the following analysis:—

0.1256 gram substance gave 0.0362 gram H_2O and 0.2888 gram CO_2 .

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	Theory for $C_{14}H_8N_2O_4$.	Found.
C	62.69	62.71
H	2.99	3.22

When boiled with strong aqueous potash, anthracene ethyl nitrate dissolves, forming a brownish-yellow solution, which, if concentrated, sets to a mass of brownish-yellow needles on cooling. The crystals dissolve in hot water, forming a yellow solution which, on the addition of acids, gives a white precipitate of a new substance which will be described below.

The solution of anthracene ethyl nitrate is coloured intensely yellow on the addition of ammonia, and, on cooling, orange-red needles are deposited. These were collected, washed with alcohol, and re-crystallised from this solvent.

The analysis gave the following results:—

- I. 0.1884 gram substance gave 0.0730 gram H_2O and 0.5197 gram CO_2 .
 II. 0.2704 gram substance gave 14.7 c.c. N ; $t = 16^\circ$; bar. = 742 mm.

	Theory for $C_{14}H_8NO_2$.	Found.
C	75.3	75.3
H	4.03	4.3
N	6.27	6.37

This substance melted at 146° , and showed all the properties of nitrosoanthrone.

The same decomposition takes place when anthracene ethyl nitrate in alcoholic solution is treated with pyridine and other bases, boiled in acetic acid solution with a few drops of sulphuric acid, or reduced with sodium sulphide.

Action of Alkalis on Anthracene Ethyl Nitrate.

Anthracene ethyl nitrate is readily decomposed by boiling with alcoholic potash with formation of a new substance possessing pronounced phenolic properties.

In studying this decomposition, anthracene ethyl nitrate was added to boiling dilute alcoholic potash. It rapidly dissolved, forming a dark-brown solution, and the decomposition was complete as soon as a small quantity taken out gave only a slight precipitate on diluting with water. On adding hydrochloric acid to the well-cooled product, a bulky, light-yellow precipitate was thrown down. This was collected, washed well with water, and dissolved in boiling very dilute

aqueous potash. On cooling under the tap, a small quantity of a brownish substance was deposited, which was collected, and will be referred to later.

Hydrochloric acid was added to the filtrate, and the whitish precipitate redissolved in potash, and repeatedly treated in this manner until nothing was deposited on cooling. The resulting white, amorphous product was purified by two or three crystallisations from alcohol or benzene, and analysed with the following result:—

- I. 0.1542 gram substance gave 0.0638 gram OH_2 and 0.4294 gram CO_2 .
 II. 0.1468 gram substance gave 0.0558 gram OH_2 and 0.4038 gram CO_2 .

These numbers give percentages agreeing with the formula $\text{C}_{14}\text{H}_9\text{NO}_2$.

	Theory. $\text{C}_{14}\text{H}_9\text{NO}_2$.	Found.	
		I.	II.
C	75.3	75.29	75.02
H	4.03	4.59	4.20

This substance, which I propose to call pseudo-nitrosoanthrone, is moderately soluble in alcohol, from which it crystallises in minute groups of needles, more sparingly in benzene. It melts at about $224\text{--}225^\circ$ with decomposition and evolution of nitrous fumes. The residue, on examination, was found to consist of anthraquinone. It can be crystallised from such solvents as acetic acid with but slight decomposition if the operation is rapidly performed, otherwise, after short contact with the boiling solvent, nitrous fumes are rapidly evolved and anthraquinone is formed. Chromic acid and cold nitric acid oxidise it readily to anthraquinone. It dissolves readily in alkalis, forming orange-yellow solutions. Cold sulphuric acid dissolves it with a yellow colour. When boiled with acetic anhydride, and the mass allowed to cool, colourless needles are deposited resembling anthraquinone in appearance. These were collected, purified by recrystallisation from alcohol, and analysed with the following result:—

- I. 0.1535 gram substance gave 0.0592 gram OH_2 and 0.4060 gram CO_2 .
 II. 0.1872 gram substance gave 0.0720 gram OH_2 and 0.4960 gram CO_2 .
 III. 0.1516 gram substance gave 0.0591 gram OH_2 and 0.4032 gram CO_2 .
 IV. 0.1718 gram substance gave 0.0684 gram OH_2 and 0.4564 gram CO_2 .

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	Theory. $C_{14}H_9NO_2 \cdot C_2H_5O$.	Found.			
		I.	II.	III.	IV.
C.....	72.45	72.1	72.26	72.2	72.44
H.....	4.15	4.2	4.27	4.3	4.42
N.....	5.28	—	—	—	—

This substance which, as the analyses show, is acetylpsendonitroso-anthrone, melts at 153—154°. It is moderately soluble in alcohol and acetic acid, very soluble in acetic anhydride. It is insoluble in dilute alkalis in the cold, but dissolves readily on warming, forming an orange solution. At high temperatures, or on boiling with a solvent of high boiling point, it gives off nitrous vapours, and is converted into anthraquinone. Chromic acid and nitric acid oxidise it to anthraquinone.

The brownish substance, after two or three crystallisations from alcohol, was obtained in long needles. Analysis:—

I. 0.1282 gram substance gave 0.0518 gram H_2O and 0.3524 gram CO_2 .

II. 0.2195 gram substance gave 11.3 c.c. N; $t = 16^\circ$; bar. = 760 mm.

These numbers give percentages agreeing with the formula $C_{14}H_9NO_2$.

	Theory. $C_{14}H_9NO_2$.	Found.	
		I.	II.
C.....	75.3	74.97	—
H.....	4.03	4.45	—
N.....	6.28	—	6.00

This substance has therefore the same composition as nitroso-anthrone, with which it is in every respect identical. It melts at 146°, crystallises in the same way, and shows all the properties of this substance.

As stated in the introduction, pseudonitrosoanthrone is isomeric with nitrosoanthrone, $C_6H_4 \langle \begin{smallmatrix} \text{CO} \\ \text{CH(NO)} \end{smallmatrix} \rangle C_6H_4$, and with isonitroso-anthraquinone, $C_6H_4 \langle \begin{smallmatrix} \text{CO} \\ \text{C(NO H)} \end{smallmatrix} \rangle C_6H_4$, and it therefore probably has the constitution $C_6H_4 \langle \begin{smallmatrix} \text{C(OH)} \\ \text{C(NO)} \end{smallmatrix} \rangle C_6H_4$. This formula accounts for the phenolic nature of the substance, and the fact that it forms an acetyl compound, which latter would be represented by the formula $C_6H_4 \langle \begin{smallmatrix} \text{C(O} \cdot \text{C}_2\text{H}_5\text{O)} \\ \text{C(NO)} \end{smallmatrix} \rangle C_6H_4$.

The production of nitrosoanthrone by the reducing action of sodium sulphide may be represented thus:—

Action of Hydrogen Iodide on Anthracene Ethyl Nitrate.

In studying this action, 5 grams of anthracene ethyl nitrate was mixed with 50 c.c. of aqueous hydrogen iodide (sp. gr. 1.96), and distilled gently from a retort. The dark-coloured distillate, on mixing with water, deposited a quantity of a heavy liquid, which was mechanically separated, mixed with water containing a trace of sulphurous acid, and the whole distilled. The heavy oil which separated from the aqueous distillate was collected, dried over calcium chloride, and distilled from a small Wurtz flask. It showed the boiling point of ethyl iodide (72°), with which it was identical, as the following analysis shows:—

0.1070 gram of substance, heated at 180° with nitric acid and nitrate of silver, gave 0.1608 gram AgI = 81.2 I per cent.
Theory, C₂H₅I = 81.4 I per cent.

The residue in the retort was mixed with water and sufficient sulphurous acid to remove excess of iodine, the brownish-coloured substance collected, well washed with water, dried on a porous plate, and recrystallised from alcohol.

In this way, beautiful plates were obtained which melted at 106–108°, and showed all the properties of dihydroanthracene. Analysis:—

0.1634 gram substance gave 0.1004 gram H₂O and 0.5592 gram CO₂.

	Theory.	
	$\text{C}_6\text{H}_4 \left\langle \begin{array}{c} \text{CH}_2 \\ \\ \text{CH}_2 \end{array} \right\rangle \text{C}_6\text{H}_4.$	Found.
C	93.33 per cent.	93.33 per cent.
H.	6.66 „	6.83 „

This experiment shows, therefore, that anthracene ethyl nitrate, when boiled with aqueous hydrogen iodide, is decomposed into dihydroanthracene and ethyl iodide, most of the nitrogen being evolved as nitrous fumes.

Anthracene Methyl Nitrate,

This substance is produced in a similar manner to the ethyl compound already described, to which it also bears the greatest resemblance. It crystallises from alcohol in glittering plates which melt at about 183° with decomposition and formation of anthraquinone. The analysis gave the following results:—

	Theory. $\text{C}_{14}\text{H}_{10}, \text{CH}_3\text{NO}_3.$	Found.
C.....	70·59 per cent.	70·36 per cent.
H.....	5·10 „	5·39 „

Anthracene methyl nitrate is decomposed by alkalis, yielding a mixture of nitrosoanthrone and pseudonitrosoanthrone. The latter melted at $224\text{--}225^\circ$, the acetyl derivative at 153° , and in its properties was found to be exactly similar to the compound obtained by the action of alkalis on anthracene ethyl nitrate.