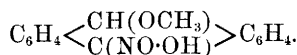


LXXIV.—CONTRIBUTIONS FROM THE LABORATORIES
OF THE HERIOT WATT COLLEGE, EDINBURGH.

Action of Nitric Acid upon Anthracene. Part II.

By A. G. PERKIN and J. E. MACKENZIE, B.Sc.

IN a previous communication to the Society (Trans., 1891, **59**, 634), an account was given by one of us of the action of nitric acid upon anthracene in the presence of ethyl and methyl alcohols. The substances thus obtained were found to be addition products of methyl and ethyl nitrates to anthracene, the formula of the former substance being $C_{14}H_{10}.CH_3.NO_3$, and its constitution being probably represented thus:—



In studying this subject further, it occurred to us that it would be a matter of interest to determine whether this reaction is a general one, and as the result of our experiments with various alcohols, we have found that in the case of propyl, isobutyl, and benzyl alcohols compounds with anthracene similar to those already described are obtained, whereas in the case of trimethylcarbinol, no such compound could be isolated, the reaction proceeding in a different manner with formation of nitrosoanthrone. As a general rule, with the alcohols already experimented with, the only products of the reaction are substances of the general formula $C_{14}H_{10}.RNO_3$. In experiments with isobutyl alcohol, however, it was found that by slightly altering the conditions, a substance is formed which, on analysis, was found to have the formula $C_{14}H_9.NO_3$. The investigation of the properties of this new compound leaves scarcely any doubt that its constitution is represented by the formula $C_6H_4 < \begin{array}{c} \overline{CO} \\ CH(NO_2) \end{array} > C_6H_4$, and we therefore propose to name it *nitroanthrone*.

This substance, on treatment with alcoholic potash, is converted into the isomeric nitroanthrole, $C_6H_4 < \begin{array}{c} C(OH) \\ C(NO_2) \end{array} > C_6H_4$.

The constitution of the two last-named substances was deduced from the fact that alcoholic ammonia or acids do not convert them into nitrosoanthrone, and further, that no nitronitrosoanthrone is formed from them by treatment with fuming nitric acid and nitrobenzene, showing that they contain no nitroso-group, and therefore probably have the above constitution.

Also included in this research is the action of nitric acid on mixtures of anthracene with pure acetone and ether. In the first place, a very good yield of anthracene methyl nitrate was obtained, showing that acetone, under the conditions used, must have yielded methyl nitrate. With methylated ether free from alcohol, a mixture of anthracene ethyl and methyl nitrates was obtained, the formation of the latter being accounted for by the presence of small quantities of methyl ether or methyl ethyl ether in the sample used. The formation of anthracene methyl nitrate is so readily detected, that this reaction might possibly be employed in proving the presence of a methyl group in methyl ketones and methyl ethers.

Anthracene Propyl Nitrate, $C_{14}H_{10}NO_2 \cdot OC_3H_7$.

In order to prepare this substance, 3 c.c. of nitric acid (sp. gr. 1.5), purified by boiling with nitrate of urea, is carefully mixed with 7 c.c. of normal propyl alcohol, and to this mixture finely powdered pure anthracene is added, until the whole becomes of a creamy consistency. The mixture is very gently warmed, when the anthracene slowly dissolves, forming a thick, pale yellow solution. This, after filtration through glass wool, is mixed with its own bulk of methyl alcohol, and allowed to stand for some hours; the hard, crystalline mass which separates is collected, pressed, washed with a little methyl alcohol, recrystallised two or three times from this solvent, and dried at 60°.

0.1300 gram of substance gave 0.3421 gram CO_2 and 0.072 gram H_2O .

0.1758 gram of substance gave 7.8 c.c. N; $t = 20^\circ$; bar. = 748 mm.

	Theory for $C_{17}H_{17}NO_3$.	Found.
C	72.08 per cent.	72.32 per cent.
H	6.00 „	6.20 „
N	4.99 „	4.94 „

As thus obtained, anthracene propyl nitrate consists of beautiful, four-sided prisms, very soluble in hot methyl alcohol, acetic acid, and benzene. It melts at 92°, and decomposes at higher temperatures with evolution of nitrous fumes and formation of anthraquinone. Chromic acid in acetic acid solution oxidises it to anthraquinone. Cold concentrated sulphuric acid dissolves it, forming a deep red solution, which quickly turns black on treatment with water, and deposits a thick, black precipitate from which nothing crystalline could be isolated. It is readily decomposed by boiling with alcoholic ammonia with formation of an orange-coloured solution, and this, on

cooling, deposits long, orange-coloured needles, melting at 144° , and having all the properties of nitrosoanthrone. Alcoholic potash produces a similar result, and in this respect anthracene propyl nitrate differs from the corresponding methyl and ethyl derivatives, which, by this treatment, yield nitrosoanthrone and pseudonitrosoanthrone (Trans., 1891, 59, 645). It is readily attacked by a mixture of nitric acid (sp. gr. 1.5) and nitrobenzene, with formation at first of a clear solution, which, on adding more of the substance, deposits crystals of nitronitrosoanthrone.

Anthracene Isobutyl Nitrate, $C_{14}H_{10}NO_2 \cdot OC_4H_9$.

The method employed in preparing this substance is similar to that described in the case of the propyl compound. There is, however, as mentioed in the Introduction, a tendency to the formation of nitroanthrone in this reaction, so that the following precautions are necessary in order to obtain a good yield of anthracene isobutyl nitrate. The anthracene must be added as rapidly as possible to the mixture of acid and alcohol, the whole warmed until solution is effected, filtered through glass wool, and, after thorough cooling, the solution is treated with about twice its bulk of low boiling petroleum. After standing for a few hours, a crystalline cake is obtained, which is collected, washed with light petroleum, and crystallised from carbon bisulphide.

The analysis of the substance dried at 60° gave the following results:—

0.1323	gram of substance	gave	0.3500	gram CO_2 ,	0.0775	gram H_2O .
0.1072	"	"	"	0.2860	gram CO_2 ;	H_2O lost.
0.1590	"	"	"	6.95	c.c. N;	$t = 19^{\circ}$; bar. = 756 mm.

	Theory for $C_{18}H_{10}NO_3$.	Found.		
		I.	II.	III.
C.....	72.72 p. c.	72.15	72.76	— p. c.
H.....	6.39 "	6.50	lost	— "
N.....	4.71 "	—	—	4.99 "

This beautiful substance crystallises in large, thick, colourless prisms, which on more than one occasion were obtained over 2 inches in length.

We are indebted to Dr. H. Marshall, of Edinburgh University, for the following examination of these crystals:—

System:—Monosymmetric.

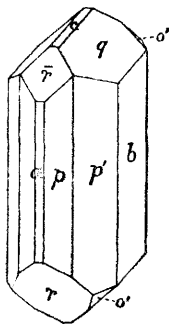
$$a : b : c = 0.8554 : 1 : 0.8563.$$

$$\beta = 74^{\circ} 39\frac{1}{2}'.$$

Forms observed:— $a = \{100\}$, $b = \{010\}$, $c = \{001\}$, $p = \{110\}$,

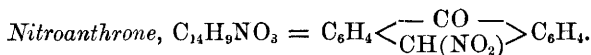
$p' = \{120\}$, $q = \{011\}$, $\bar{r} = \{101\}$, $r = \{\bar{1}01\}$, $o' = \{\bar{1}22\}$.

Figure.—Colourless, transparent prisms usually forming stellar groups, so that only one end is properly developed. They are generally long and thin, rarely short and thick. As a rule, the



prism faces are much striated longitudinally. The crystals are brittle with uneven fracture, and no well-marked cleavage. Of the forms observed c , \bar{r} , and o' occur less frequently than the others, and often only one face of o' is present.

When heated in a capillary tube, anthracene isobutyl nitrate becomes yellow at 100° , and melts at 121° with gradual decomposition. On rapid heating, it decomposes suddenly at 165° , with evolution of nitrous fumes, a strong odour of isobutyl nitrite being noticeable. It is readily soluble in hot alcohol and acetone with slight decomposition, forming yellowish-brown solutions, and also in hot benzene and carbon bisulphide, but without decomposition. Hot alcoholic potash dissolves it easily, forming a deep red solution, which when poured into water, deposits a reddish-yellow precipitate; this, on recrystallisation, forms yellow needles melting at 144° , and having all the properties of nitrosoanthrone. The filtrate from the precipitate contains a minute trace of a phenolic substance, which, however, was too small for investigation. On oxidation with chromic acid, anthracene isobutyl nitrate yields anthraquinone, and with a mixture of nitric acid and nitrobenzene, nitronitrosoanthrone.



If anthracene is *very gradually* added to a mixture of nitric acid and isobutyl alcohol, anthracene isobutyl nitrate is not formed, the reaction proceeding in a different manner. In order to investigate

this decomposition, the addition of anthracene was continued until it no longer dissolved, and the mixture then gently warmed, filtered through glass wool, and the filtrate treated with light petroleum. Crystals gradually separated, and at the end of 24 hours they were collected, washed with light petroleum, and purified by two or three crystallisations from carbon bisulphide or benzene.

Analyses of the colourless needles thus obtained gave the following results :—

0.1107 gram of substance gave 0.2856 gram CO_2 and 0.0391 gram H_2O .

0.1946 gram of substance gave 9.6 c.c. N; $t = 24^\circ$; bar. = 751 mm.

	Theory. $\text{C}_{14}\text{H}_9\text{NO}_3$.	Found.
C.	70.29 per cent.	70.36 per cent.
H.	3.76 "	3.92 "
N.	5.85 "	5.46 "

Nitroanthrone crystallises in glistening needles, which, when heated at 100° , become violet coloured, and melt at 140° with evolution of nitrous fumes and formation of anthraquinone. It is readily soluble in hot benzene and carbon bisulphide, but more sparingly in hot alcohol, with slight decomposition and formation of a pink solution which gradually becomes reddish-brown. It is readily attacked by cold sulphuric acid with total decomposition. That the formula given at the head of this section correctly represents the constitution of this substance is rendered probable from the fact that it is not converted into nitronitrosoanthrone by the action of a mixture of nitric acid and nitrobenzene. A number of experiments were instituted with a view of converting this substance into the dinitroanthrone described by Liebermann and Landshoff (*Ber.*, **14**, 472), with negative results, as anthraquinone alone was always produced.

Action of Alcoholic Potash on Nitroanthrone.

Nitroanthrole, $\text{C}_{14}\text{H}_9\text{NO}_3$ or $\text{C}_6\text{H}_4\left\langle \begin{smallmatrix} \text{C}(\text{OH}) \\ \text{C}(\text{NO}_2) \end{smallmatrix} \right\rangle \text{C}_6\text{H}_4$.—Nitroanthrone dissolves readily in alcoholic potash forming a deep orange-red solution, which, after boiling for a few minutes and diluting with water, deposits a small quantity of crystalline matter, found on examination to consist of anthraquinone.

The filtrate, on treatment with hydrochloric acid, deposits a colourless precipitate, mixed with a small quantity of a scarlet substance. The whole was extracted with ether, the ethereal solution washed

well, evaporated nearly to dryness, and the greenish-coloured, crystalline mass which separated purified by crystallisation from carbon bisulphide. The resulting colourless needles gave the following results on analysis:—

0.1230 gram of substance gave 0.3185 gram CO_2 and 0.0462 gram OH_2 .

0.1758 gram of substance gave 8.6 c.c. N ; $t = 19^\circ$; bar. = 753 mm.

	Theory for $\text{C}_{14}\text{H}_9\text{NO}_3$.	Found.
C.....	70.29 per cent.	70.61 per cent.
H	3.76 „	4.17 „
N.....	5.85 „	5.57 „

This substance, which we propose to name *nitroanthrole*, melts at 148° with decomposition and formation of anthraquinone. It is readily soluble in hot benzene and carbon bisulphide, but only sparingly in hot methyl alcohol, with slight decomposition and formation of a pink solution. Cold dilute alkalis dissolve it somewhat sparingly, readily on warming, with formation of orange-yellow solutions. It does not yield an acetyl derivative with acetic anhydride, but on boiling with it is decomposed with formation of anthraquinone. Anthraquinone is also formed when nitroanthrole is oxidised with chromic acid or treated with nitric acid and nitrobenzene. Nitroanthrole is isomeric with nitroanthrone, and, therefore, probably has the constitution assigned to it at the head of this section.

Action of Nitric Acid on Anthracene in the presence of Trimethylcarbinol.

3 c.c. of purified nitric acid (sp. gr. 1.5) were mixed with 7 c.c. of trimethylcarbinol, and to this mixture powdered anthracene was added. It dissolved readily at first, and the solution was afterwards completed by a gentle heat. On cooling, the whole became a nearly solid mass of yellow needles, which were purified by recrystallisation from alcohol. They melted at 144° , and had all the properties of nitrosoanthrone. Analysis:—

0.1300 gram gave 7 c.c. N ; $t = 20^\circ$; bar. = 746 mm.

	Theory for $\text{C}_{14}\text{H}_9\text{NO}_2$.	Found.
N	6.27 per cent.	6.04 per cent.

Numerous experiments were instituted under varied conditions with the hope of obtaining a compound of anthracene with this

alcohol, similar to those already described, but in every case nitroso-anthrone was the sole product.

Anthracene Benzyl Nitrate, $C_{14}H_{10}NO_2 \cdot OC_7H_7$.

This may be prepared in a similar manner to the analogous compounds previously described. The semi-solid, crystalline mass obtained is washed with a little methyl alcohol, pressed, and further purified by crystallisation from alcohol. Analysis gave the following results:—

0.1312 gram of substance gave 0.3669 gram CO_2 and 0.0654 gram OH_2 .

0.1396 gram of substance gave 5.6 c.c. N; $t = 20^\circ$; bar. = 744 mm.

	Theory for $C_{21}H_{17}NO_3$.	Found.
C.....	76.13 per cent.	76.26 per cent.
H.....	5.13 "	5.53 "
N.....	4.23 "	4.49 "

Anthracene benzyl nitrate crystallises from alcohol in beautiful, glistening needles. It is only sparingly soluble in alcohol, but very soluble in hot carbon bisulphide and benzene. When heated, it becomes yellow at 125° , melts at 138° , and decomposes rapidly at 150° , with evolution of nitrous fumes and formation of anthraquinone. In its reactions it exactly resembles the corresponding derivatives of anthracene already described.

Action of Nitric Acid on Anthracene in the presence of Acetone and Ether respectively.

The acetone used for this experiment was Kahlbaum's pure acetone prepared from the bisulphite compound. Anthracene was added to a mixture of acetone and nitric acid, and the product crystallised from alcohol. The analysis of the beautiful, colourless, crystalline mass thus obtained gave the following result:—

0.1209 gram of substance gave 0.3148 gram CO_2 and 0.0615 gram H_2O .

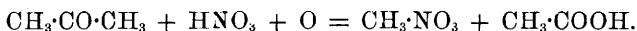
0.1381 gram of substance gave 6.6 c.c. N; $t = 18^\circ$; bar. = 747 mm.

	Theory for $C_{14}H_{10} \cdot CH_3NO_3$.	Found.
C.....	70.58 per cent.	71.00 per cent.
H.....	5.09 "	5.64 "
N.....	5.49 "	5.42 "

This substance melts with decomposition at 183° , and is identical with the anthracene methyl nitrate previously obtained by the action

of nitric acid on anthracene in the presence of methyl alcohol (Trans., 1891, 59, 648).

As the yield of the substance obtained in this way was large, its formation cannot be accounted for by the accidental presence of any traces of methyl alcohol in the acetone employed. In order that anthracene methyl nitrate may be formed in this reaction, it is necessary to suppose that the acetone is decomposed by the nitric acid into methyl nitrate and acetic acid, thus:—



The former then in the moment of its formation combines with the anthracene, forming anthracene methyl nitrate.

We propose to experiment on the action of nitric acid on other ketones in the presence of anthracene, with the view to determine whether the above interesting reaction is a general one.

Action of Nitric Acid on Anthracene in the presence of Ether.

The ether employed in this experiment was ordinary methylated ether, which had been carefully freed from alcohol by repeated treatment with sodium.

On adding anthracene to a mixture of ether, nitrobenzene, and nitric acid, a substance soon separated which, after collecting on a plug of glass wool and recrystallisation from alcohol, was obtained in thin leaflets melting at 152°, and having all the properties of anthracene ethyl nitrate (Trans., 1891, 59, 642).

An analysis gave the following result:—

0.1376 gram gave 6.9 c.c. N; $t = 25^\circ$; bar. = 746 mm.

	Theory for $\text{C}_{14}\text{H}_{10}\cdot\text{C}_2\text{H}_5\text{NO}_3$.	Found.
N	5.20 per cent.	5.49 per cent.

The acid mother liquors from this substance, on standing, deposited a small quantity of crystalline matter melting at 183°, and found to be anthracene methyl nitrate.

0.1472 gram gave 7.2 c.c. N; $t = 20^\circ$; bar. = 743 mm.

	Theory $\text{C}_{14}\text{H}_{10}\cdot\text{CH}_3\text{NO}_3$.	Found.
N	5.49 per cent.	5.46 per cent.

The presence of the latter substance is accounted for by the fact that the ether employed contained small quantities of methyl ether or methyl ethyl ether. As anthracene methyl nitrate is far more insoluble in alcohol and other solvents than anthracene ethyl nitrate,

the experiment is interesting, as indicating that, under these conditions, anthracene methyl nitrate is formed less readily than the ethyl derivative.

We hope to continue these experiments in various directions, and also propose to study the action of fuming nitric acid on ketones, as this subject has evidently not been sufficiently investigated.
