CHAPTER II

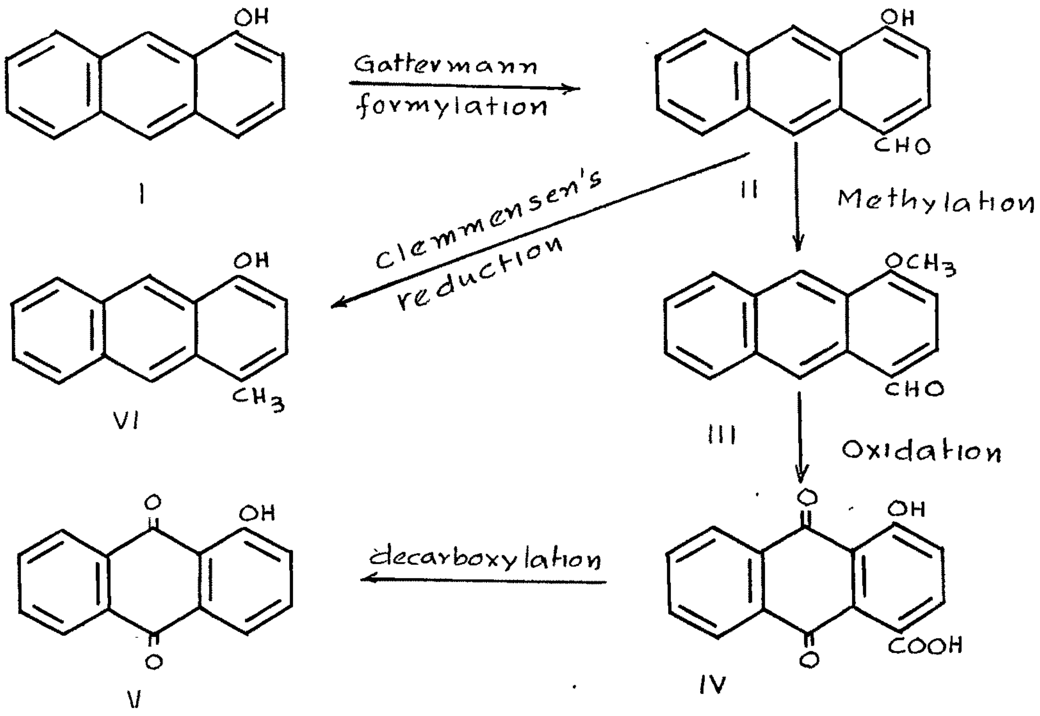
Some Reactions on 1- and 2- Anthrol

Theoretical

Gattermann reaction on 1-anthrol.

1-Anthrol (I) on Gattermann formylation afforded a product in good yield which gave a 2:4-dinitrophenylhydrazone derivative, but did not give any colour with alcoholic ferric chloride. 4-Formyl-1-hydroxyanthracene (II) structure has, therefore, been assigned to this product. The formyl derivative (II) was methylated and the methyl ether (III) was oxidised with alkaline potassium permanganate, when a hydroxy acid (m.p. 232-234°) was obtained which gave blood red colouration with alkali. On decarboxylation with copper powder in quinoline solution it gave 1-hydroxyanthraquinone (V) as seen by direct comparison with an authentic specimen prepared from 1-aminoanthraquinone according to Ullmann and Conzetti, (Ber., 1920, 53, 826). The acid is therefore 1-hydroxyanthraquinone-4-carboxylic acid (IV). This acid has been previously synthesised by Birukoff (Ber., 1887, 20, 2438) by the condensation of p-cresol with phthalic anhydride and subsequent oxidation of 4-methyl-1-hydroxyanthraquinone formed. He gave m.p.236°.

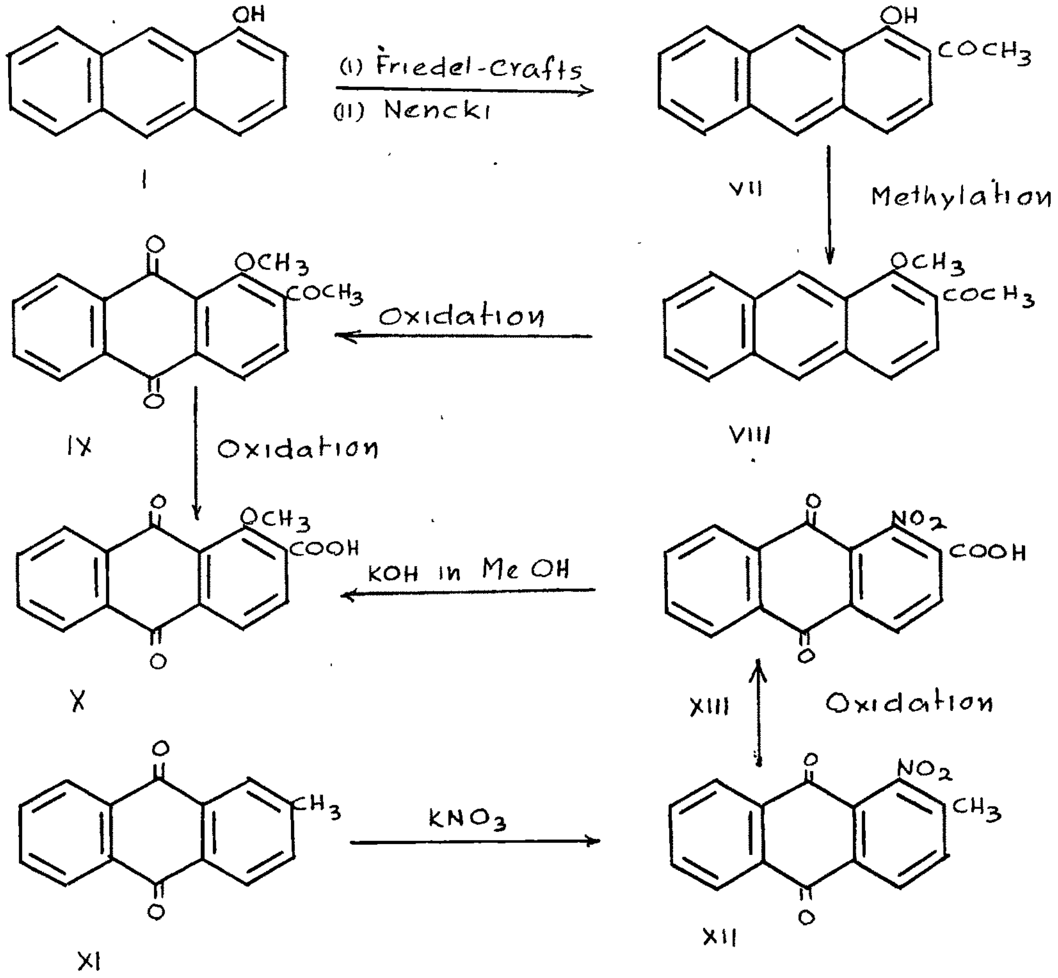
4-Formyl-1-hydroxyanthracene was reduced to 4-methyl-1-hydroxyanthracene (VI) by Clemmensen's method.



Friedel-Crafts acetylation of 1-anthrol.

1-Anthrol on Friedel-Crafts acetylation with acetic anhydride at room temperature as well as on a steam bath, afforded a product in a low yield which gave a 2:4-dinitrophenylhydrazone derivative. It has been assigned the 2-acetyl-1-anthrol (VII) structure for the following reasons : it gave a bluish violet colouration with alcoholic ferric chloride. Further, its methyl ether (VIII) on oxidation with sodium hypochlorite solution gave another ketone (IX) which gave a blood red colouration with zinc dust and alkali on warming, indicating that it was an anthraquinone derivative.. This ketone when subjected to further oxidation with the same reagent, gave an acid which was found on direct comparison to be identical with the known 1-methoxy-anthraquinone-2-carboxylic acid (X). This has been synthesised as follows:

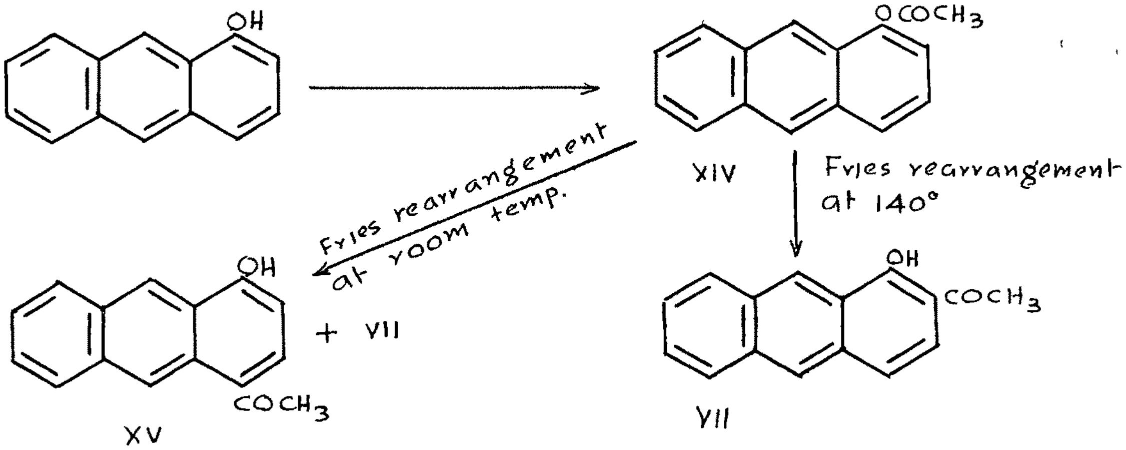
Phthalic anhydride was condensed with toluene in presence of anhydrous aluminium chloride to get p-toluyl-o-benzoic acid which on ring closure with fuming sulphuric acid gave 2-methylanthraquinone (XI). This on nitration with potassium nitrate according to Roemer and Link (Ber., 1883, 16, 695) gave 1-nitro-2-methylanthraquinone (XII). This was oxidised with a mixture of chromic anhydride and concentrated nitric acid to 1-nitroanthraquinone-2-carboxylic acid (XIII) according to Terres (Ber., 1913, 46, 1634). This was converted into 1-methoxyanthraquinone-2-carboxylic acid (X) by boiling with potassium hydroxide in methyl alcohol (Eckert and Endler, J. pr. Ch., 1921, 16, 1423. British Abstracts, 1921, 120 i, 871).



Fries rearrangement of 1-acetoxyanthracene.

1-Acetoxyanthracene (XIV) was subjected to Fries rearrangement at 140°. The product obtained was found to be identical with the ketone (VII) obtained above in the Friedel-Crafts acetylation of 1-anthrol. But when this reaction was carried out in nitrobenzene solution at room temperature, in addition to 2-acetyl-1-anthrol (VII), another product could also be isolated in a very low yield.

It gave a 2:4-dinitrophenylhydrazone, but did not give any colouration with alcoholic ferric chloride. Therefore, the 4-acetyl-1-anthrol (XV) structure has been assigned to this ketone.



1-Anthrol was subjected to Nencki acetylation when 2-acetyl-1-anthrol (VII) was obtained.

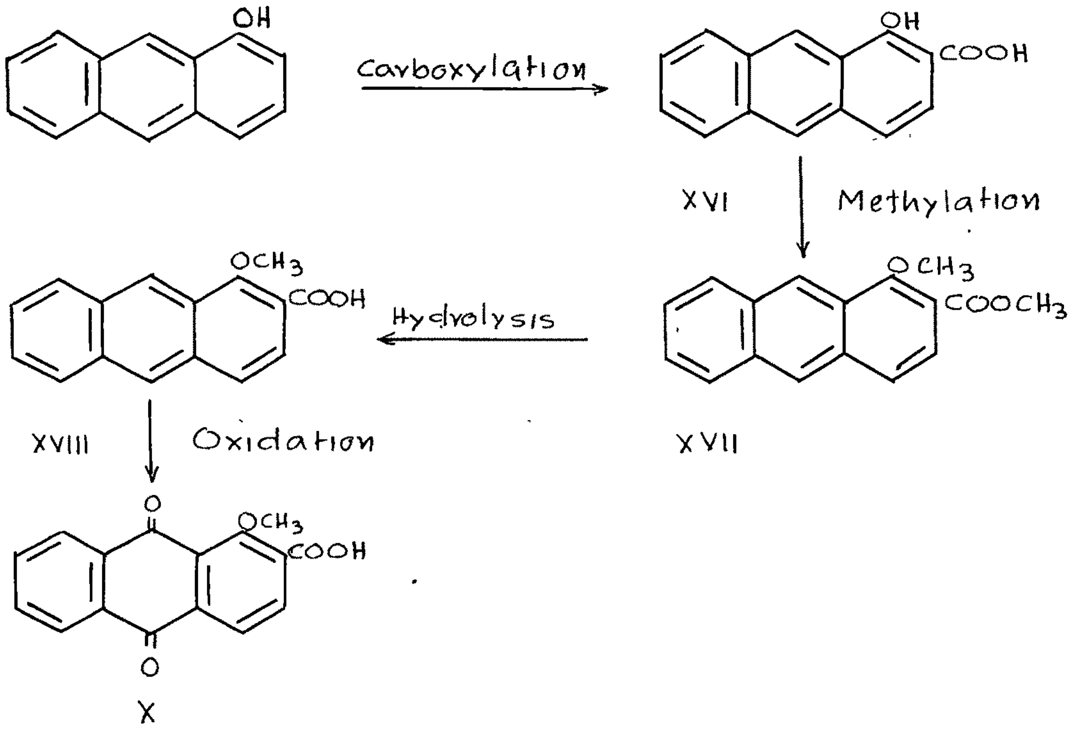
2-Acetyl-1-anthrol was required in quantity for further synthetical work and as the Friedel-Crafts and Fries ~~above~~ methods did not give a satisfactory yield on account of tarry products formed, the Nencki reaction on 1-anthrol was studied further under different conditions, and the yield of the ketone increased to about 50 % of the theoretical.

Carboxylation of 1-anthrol.

Laska and Haller (German Patent 559,333. Chem. Abstr., 1933, 27, 735) prepared an acid, m.p. 200°, by heating the alkali salt of 1-hydroxyanthracene at about 220° with carbon dioxide under pressure and assigned 1-hydroxyanthracene-2-carboxylic acid structure to this product. Kranzlein and

Corell (German Patent 564,129. Chem. Abstr., 1933, 27, 1000) claimed to have prepared the same acid by fusing what they thought was 2-carboxy-1-anthracene-sulphonic acid with alkali. They reported m.p.268°. In view of these conflicting reports it was thought of interest to study the carboxylation of 1-anthrol and establish the structure of the acid obtained.

1-Anthrol was heated with potassium bicarbonate at 120° in glycerine for 4 hours, when an acid, m.p.200°, was obtained, which gave greenish colouration with alcoholic ferric chloride. This acid on methylation with dimethyl sulphate in acetone solution in presence of potassium carbonate gave a methoxy ester, which on hydrolysis with 10 % sodium hydroxide gave a methoxy acid. This on oxidation with sodium hypochlorite solution gave 1-methoxyanthraquinone-2-carboxylic acid (X), described before. The acid is, therefore, 1-hydroxyanthracene-2-carboxylic acid (XVI) and the methoxy ester and the methoxy acid, obtained from it have the structures (XVII) and (XVIII) respectively. This confirms the 1-hydroxyanthracene-2-carboxylic acid structure assigned by Laska and Haller (loc. cit.) to their acid. The acid of Kranzlein and Corell (loc. cit.), therefore, must have some other structure.

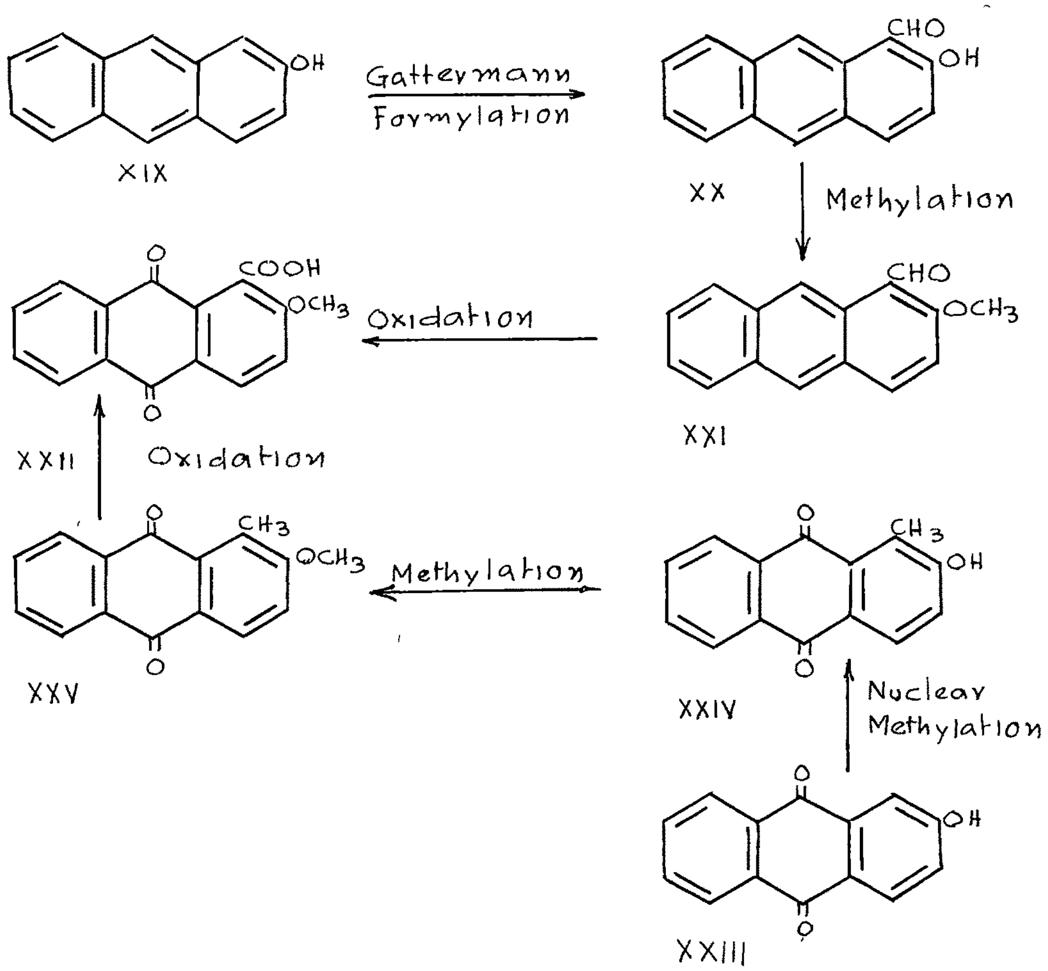

OH
Carboxylation
OH
COOH
XVI
Methylation
OCH3
COOCH3
XVII
Hydrolysis
OCH3
COOH
XVIII
Oxidation
O
OCH3
COOH
O
X

Gattermann reaction on 2-anthrol.

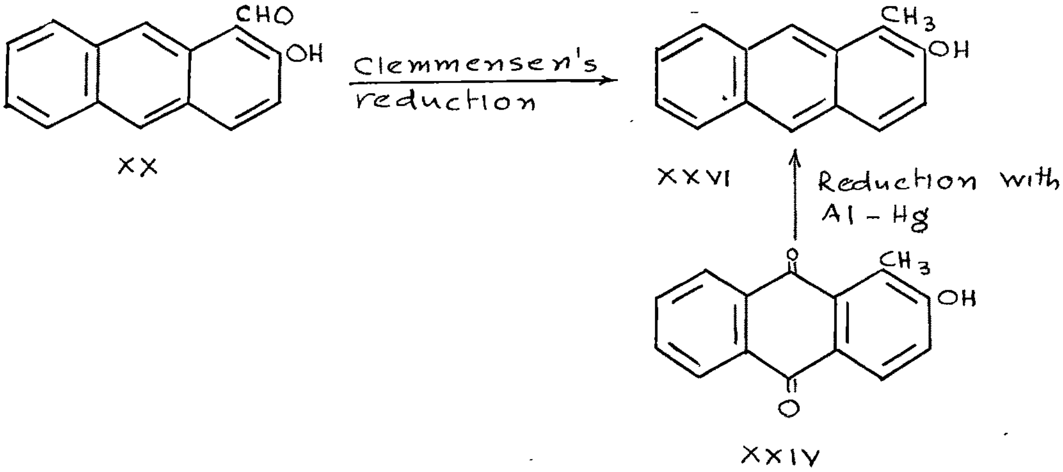
2-Anthrol (XIX) on Gattermann formylation afforded a product m.p.164° to which 1-formyl-2-anthrol (XX) structure has been assigned. Bezdzik and Friedlander (British Abstracts, 1910 i, 191) obtained it by heating anthracene indole indigo with 30 % aqueous sodium hydroxide solution. They gave the same m.p. The structure of this aldehyde was conclusively proved by the following series of reactions.

The aldehyde (XX) was methylated and the methyl ether (XXI) was oxidised with potassium permanganate in sodium carbonate solution, when an acid (XXII) was obtained which was found on direct comparison to be identical with 2-methoxyanthraquinone-1-carboxylic acid, prepared according to Ch.Marschalk (Bull.Soc.Chim., 1939, 6, 655) as follows:

1-Methyl-2-hydroxyanthraquinone (XXIV) was prepared by the action of formaldehyde on 2-hydroxyanthraquinone (XXIII), dissolved in dilute solution of sodium hydroxide in presence of sodium hydrosulphite. It was then methylated and the methyl ether (XXV) oxidised by manganese dioxide in presence of concentrated sulphuric acid below 15° to 2-methoxyanthraquinone-1-carboxylic acid (XXII). While this work was in progress, Jain and Seshadri (J.Sci. Industr. Res., 1956, 15B, 61) reported the preparation of 1-formyl-2-anthrol by the Gattermann formylation of 2-anthrol, as well as by the action of hexamine on 2-anthrol. They gave the same m.p. They proved the structure of the compound by subjecting it to Dakin oxidation when 1,2-anthradiol was obtained. The acetoxy derivative of this was oxidised by chromic acid in acetic acid and the product obtained hydrolysed to alizarin.



1-Formyl-2-anthrol (XX) on Clemmensen's reduction gave 1-methyl-2-anthrol (XXVI) identical with the product obtained when 1-methyl-2-hydroxyanthraquinone (XXIV) was reduced by aluminium amalgam and aqueous alcoholic ammonia.

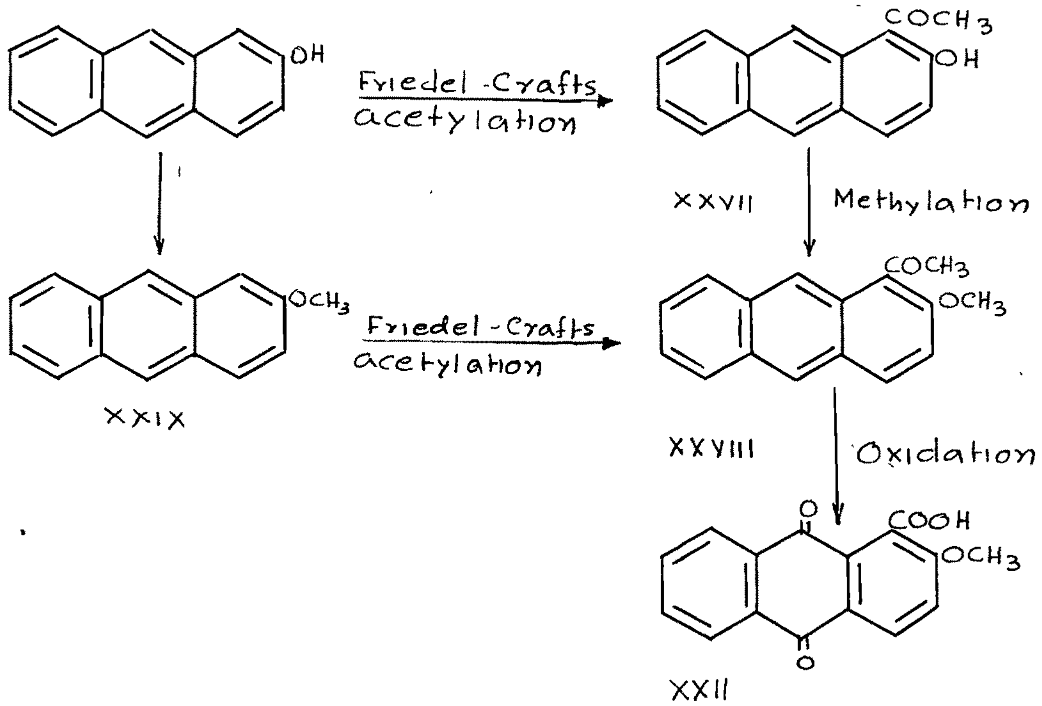


Friedel-Crafts acetylation of 2-anthrol.

2-Anthrol on Friedel-Crafts acetylation with acetic anhydride at room temperature as well as on heating on a steam bath, afforded a ketone, m.p.112-113°. It gave a 2:4-dinitrophenylhydrazone. It has been assigned the 1-acetyl-2-anthrol structure (XXVII) for the following reasons:

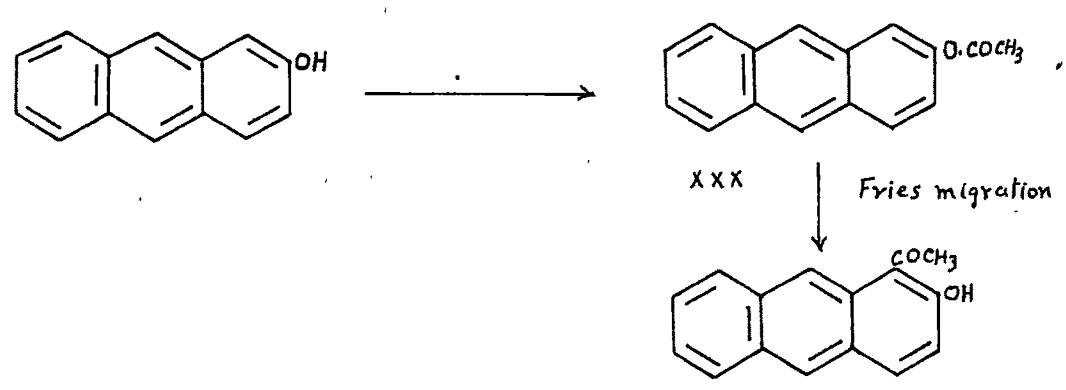
It gave a bluish colouration with alcoholic ferric chloride, which turned greenish on keeping. The ketone was methylated and the methyl ether (XXVIII) was oxidised with sodium hypochlorite solution, when an acid (XXII) was obtained, which was found on direct comparison to be identical with 2-methoxyanthraquinone-1-carboxylic acid prepared according to Ch.Marschalk (loc.cit.) as described before.

When 2-methoxyanthracene (XXIX) was subjected to Friedel-Crafts acetylation with acetic anhydride in benzene solution at room temperature, 1-acetyl-2-methoxyanthracene (XXVIII) described above was obtained.



Fries rearrangement of 2-acetoxyanthracene.

2-Acetoxyanthracene (XXX) was subjected to Fries rearrangement at room temperature in nitrobenzene solution, when the same ketone (XXVII), described before, was obtained. Jain and Seshadri (loc.cit.) have reported that in the Fries migration of 2-anthrolacetate at 140°, a product m.p.218-219° was obtained in about 80 % yield. They assigned 1-acetyl-2-anthrol structure to this product. The reaction was repeated under the conditions given by Jain and Seshadri, but no product, m.p.219°, could be isolated, only a dark coloured product with indefinite m.p.was obtained.



XXX

XXVII

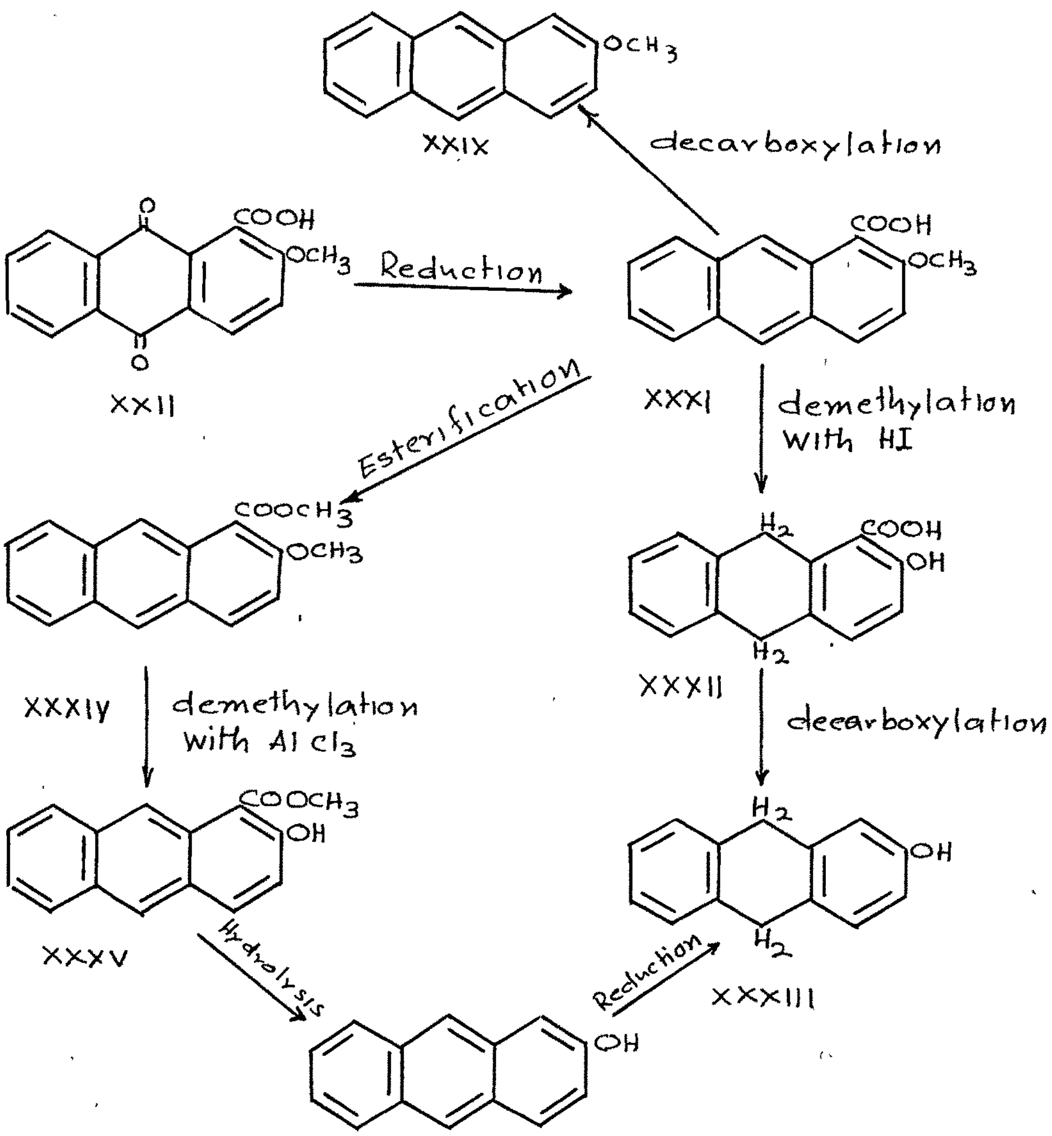
Very recently, after the work described here was published (J. Org. Chem., 1959, 24, 1783), Ferrari and Hunsberger (ibid., 1960, 25, 485) confirmed the work described here and have shown that the product obtained by Jain and Seshadri is 3-acetyl-2-anthrol. They found that Fries rearrangement of 2-anthrolacetate in nitrobenzene (0.5 hour at room temperature) produced 1-acetyl-2-anthrol in yields of about 60 %, whereas the high temperature reaction (1.5 hours at 140°, no solvent) produced 3-acetyl-2-anthrol, m.p. 226-227° dec. in yields of only 3-13 %.

Attempted synthesis of 2-hydroxyanthracene-1-carboxylic acid.

Kranzlein and Corell (loc.cit.) claim to have synthesised 2-hydroxyanthracene-1-carboxylic acid by fusing 1-carboxy-2-anthracene-sulphonic acid with alkali. In view of the discrepancy observed in the case of 1-hydroxyanthracene-2-carboxylic acid as discussed earlier, it was thought of interest to synthesise ~~it~~ this acid and establish its structure definitely. Attempts at direct carboxylation of 2-anthrol, under varying conditions, such as heating it: (i) with potassium carbonate in glycerine,

(ii) with potassium bicarbonate and water in a sealed tube at 130°, (iii) with solid potassium bicarbonate in a sealed tube at 140-150° or (iv) in toluene with metallic sodium and carbon dioxide, proved unsuccessful and so the other synthetical approaches were tried. 2-Methoxyanthraquinone-1-carboxylic acid (XXII), prepared according to Ch.Marschalk (loc.cit.), was reduced with aluminium amalgam and aqueous alcoholic ammonia. The resulting acid was 2-methoxyanthracene-1-carboxylic acid (XXXI) as on decarboxylation it gave 2-methoxyanthracene. Demethylation of the acid (XXXI) by heating with hydriodic acid in acetic anhydride solution, gave an acid, which gave a dark brown colouration with alcoholic ferric chloride. On decarboxylation 2-hydroxy-9,10-dihydroanthracene (XXXIII) was obtained, an authentic specimen of which was prepared according to Bamberger (Ber., 1893, 26, 3068) by the reduction of 2-anthrol with sodium in absolute alcohol. Hence the acid obtained on demethylation was 2-hydroxy-9,10-dihydroanthracene-1-carboxylic acid (XXXII).

Another approach was then tried. The methoxyester ~~of the acid~~ (XXXIV) was subjected to demethylation with anhydrous aluminium chloride at 80°. A product was obtained, which was insoluble in sodium bicarbonate solution, but was soluble in cold dilute sodium hydroxide solution. From this observation and the analysis it was assigned methyl-2-hydroxyanthracene-1-carboxylate (XXXV) structure. This ester was then hydrolysed with sodium hydroxide solution by keeping it overnight at room temperature. The product obtained was found to be 2-anthrol, decarboxylation having occurred simultaneously with hydrolysis.



EXPERIMENTAL

Preparation of 1-anthrol.

Potassium salt of anthraquinone-α-mono-sulphonic acid was prepared from anthraquinone according to Organic Syntheses, collective volume II, page 539. This was converted into the potassium salt of anthracene-α-mono-sulphonic acid by reduction with zinc dust and ammonia according to Schmidt (Ber., 1904, 37, 66).

Potassium salt of anthraquinone-α-mono-sulphonic acid (30 g.) was intimately mixed with finely powdered zinc dust (70 g.) and the mixture taken in a round bottom flask. Liquor ammonia (600 ml.) was added and the mixture heated gently on a water bath. The deep red solution slowly became paler in colour. After about 4 hours some more liquor ammonia (150 ml.) was added and the heating continued for 12 hours in all. The faint yellow solution obtained was then filtered hot. The potassium salt of anthracene-α-mono-sulphonic acid, salted out by adding potassium chloride, was filtered and dried. Yield 18-20 g.

The sulphonic acid on fusion with alkali according to Dienel (Ber., 1905, 38, 2862) with minor modifications as shown below gave 1-anthrol.

Potassium hydroxide (35 g.) was taken in a nickel crucible and heated in an oil bath to about 200°. Potassium salt of anthracene-α-mono-sulphonic acid (10 g.)

was added to the molten alkali in small portions with stirring, and the temperature was then raised and maintained at 260° for three hours. The melt on cooling was dissolved in distilled water (300 ml.) and filtered. The filtrate was acidified, and the precipitated solid was filtered, washed with water and dried. It was then treated with glacial acetic acid (200 ml.) in cold and filtered. The clear filtrate was added to hot water (1000 ml.) and allowed to cool. 1-Anthrol which separated in the form of light brown shining needles was filtered, washed with water, and dried, m.p. 152°. Yield 5 g. Dienel (loc.cit.) gives m.p.150-153°.

Gattermann formylation of 1-anthrol : 4-Formyl-1-anthrol.

1-Anthrol (5 g.) was dissolved in sodium dried ether (200 ml.) in a three-necked flask provided with a mercury-sealed stirrer, and zinc cyanide (10 g.) was added. The mixture was externally cooled with ice and mechanically stirred and a rapid stream of dry hydrogen chloride gas was passed. After some time the red aldimine-hydrochloride began to separate. Hydrogen chloride was passed for two hours and the reaction mixture was then left overnight. The next day, ether was decanted and the aldimine-hydrochloride was washed with dry ether. It was then hydrolysed by refluxing with alcohol (50 % , 100 ml.) on a steam bath for about 30 minutes. The solution was filtered hot, and the product which separated on cooling, was filtered, dried, and recrystallized from benzene in yellow needles, m.p. 206°. Yield 5 g.

It did not give any colour with alcoholic ferric chloride.

<u>Analysis</u> :

3.452 mg. of the substance gave 10.162 mg. of carbon dioxide and 1.426 mg. of water.

Found : C, 81.03 % ; H, 4.66 %.

$C_{15}H_{10}O_2$ requires : C, 81.08 % ; H, 4.50 %.

<u>The 2:4-dinitrophenylhydrazone</u>. 2:4-Dinitrophenylhydrazine (0.1 g.), dissolved in alcohol containing a few drops of concentrated hydrochloric acid, was added to 4-formyl-1-anthrol (0.1 g.) dissolved in the same solvent. The mixture was heated on a water bath for 15 minutes when the 2:4-dinitrophenylhydrazone separated. It crystallised from glacial acetic acid in reddish shining needles, m.p.286°.

<u>Analysis</u> :

4.162 mg. of the substance gave 0.515 cc. of nitrogen measured at 29°C and 752 mm.

Found : N, 13.84 %.

$C_{21}H_{14}N_4O_5$ requires : N, 13.90 %.

<u>4-Formyl-1-methoxyanthracene.</u>

4-Formyl-1-anthrol (1 g.) was dissolved in dry acetone (50 ml.) and refluxed with dimethyl sulphate (0.62 g.) and anhydrous potassium carbonate (2 g.) for 20 hours. The reaction mixture was then filtered hot, and the acetone removed. The reddish yellow solid obtained was washed with dilute sodium hydroxide. It crystallised from dilute alcohol (charcoal) in yellow needles,m.p.112°. Yield 0.8 g.

Analysis :

3.690 mg. of the substance gave 10.960 mg. of carbon dioxide and 1.664 mg. of water.

Found : C, 81.05 % ; H, 5.04 %.

$C_{16}H_{12}O_2$ requires : C, 81.36 % ; H, 5.08 %.

Oxidation of 4-formyl-1-methoxyanthracene : 1-Hydroxy-anthraquinone-4-carboxylic acid.

4-Formyl-1-methoxyanthracene (0.5 g.) was suspended in sodium hydroxide solution (20 % , 20 ml.) and heated gently on a wiregauze with potassium permanganate (0.5 g.) for four hours. The reaction mixture was then filtered free of manganese dioxide. The product obtained on acidification of the filtrate with dilute sulphuric acid was washed with water and taken in sodium bicarbonate solution. The product, obtained on acidification of the alkaline extract, crystallised from dilute alcohol in yellow needles, m.p.232-234°. Birukoff (Ber., 1887, 20, 2438) gave m.p.236°.

Analysis :

2.636 mg. of the substance gave 6.472 mg. of carbon dioxide and 0.842 mg. of water.

Found : C, 67.0 % ; H, 3.57 %.

$C_{15}H_8O_5$ requires : C, 67.2 % ; H, 2.98 %.

The above acid (0.1 g.) was decarboxylated by heating its solution in quinoline (5 ml.) with a little copper powder at 210-220° till the effervescence ceased. The reaction mixture was then filtered and the filtrate treated with hydrochloric acid. The product obtained crystallised from alcohol, m.p.190°. Mixed m.p. with 1-hydroxyanthraquinone prepared according to Ullmann (Ber., 1920, 53, 829) was not depressed.

Clemmensen's reduction of 4-formyl-1-anthrol : 4-methyl-1-anthrol.

A mixture of zinc dust (5 g.), mercuric chloride (0.50 g.), concentrated hydrochloric acid (0.25 ml.) and water (8 ml.) was stirred for five minutes. The solution was then decanted and the amalgam washed with distilled water. This was suspended in dilute hydrochloric acid (8 ml., 1:1) and a solution of 4-formyl-1-anthrol (0.5 g.) in acetic acid (20 ml.) was added slowly during 30 minutes. Concentrated hydrochloric acid (1 ml.) was then added and the heating continued for further one hour. The solution was then filtered hot and the filtrate diluted with water. The product which separated, crystallised from dilute alcohol in needles, m.p.134-136°. Yield 0.2 g.

Analysis :

4.104 mg. of the substance gave 13.072 mg. of carbon dioxide and 2.148 mg. of water.

	Found	: C, 86.92 % ; H, 5.85 %.
$C_{15}H_{12}O$	requires	: C, 86.54 % ; H, 5.76 %.

Synthesis of 2-acetyl-1-anthrol.

(a) Friedel-Crafts acetylation of 1-anthrol :

A solution of 1-anthrol (1.9 g.) and acetic anhydride (1.3 g. ; 1.2 mols.) in nitrobenzene (10 ml.) was mixed with a solution of anhydrous aluminium chloride

(2.7 g. ; 2 mols.) in nitrobenzene (20 ml.), and the reaction mixture, protected from moisture, was kept for 72 hours at room temperature. It was then treated with ice and hydrochloric acid and the nitrobenzene was steam-distilled. The black product obtained was repeatedly extracted with alkali. The product obtained on acidification of the alkaline extracts crystallised from dilute acetic acid in brownish needles, m.p.182°. It gave bluish violet colouration with alcoholic ferric chloride.

Analysis :

4.058 mg. of the substance gave 12.032 mg. of carbon dioxide and 1.682 mg. of water.

Found : C, 80.92 % ; H, 4.64 %.

$C_{16}H_{12}O_2$ requires : C, 81.36 % ; H, 5.08 %.

The same ketone was obtained when the reaction mixture as above was heated on a steam bath for two hours instead of keeping at room temperature.

(b) Fries migration of 1-anthrol-acetate :

An intimate mixture of 1-anthrolacetate (Dienel, Ber., 1905, 38, 2862) (2.4 g.) and anhydrous aluminium chloride (2.7 g.) was heated in an oil bath at 140° for 3 hours. The reaction mixture was then treated with ice and hydrochloric acid and the product obtained was taken up in ether. The ethereal layer was extracted repeatedly with alkali. The product obtained on acidification of the alkaline extracts, crystallised from dilute acetic acid in brownish needles, m.p. and mixed m.p. with 2-acetyl-1-anthrol obtained above, was 182°.

(c) Nencki reaction on 1-anthrol :

The following conditions were found to give the ketone in good yield.

Anhydrous zinc chloride (25 g.) was powdered and dissolved in glacial acetic acid (25 ml.) by heating. The solution was cooled and 1-anthrol (5 g.) was added to it. The reaction mixture,protected from moisture,was then heated under reflux for 30 minutes. It was left at room temperature for 2 hours, and then added to dilute hydrochloric acid (400 ml.). The greenish coloured solid which separated, on repeated crystallisations from alcohol (charcoal), gave yellow shining needles, m.p.182°. The mixed m.p. with 2-acetyl-1-anthrol, prepared before by the Friedel-Crafts acetylation of 1-anthrol, was not depressed. Yield 3.0 g.

The 2:4-dinitrophenylhydrazone was prepared as before. It crystallised from glacial acetic acid in reddish needles, m.p.292°.

Analysis :

2.950 mg. of the substance gave 0.357 cc. of nitrogen measured at 30°C and 757 mm.

Found : N, 13.6 %.

$C_{22}H_{16}N_4O_5$ requires : N, 13.5 %.

The acetyl derivative : 2-Acetyl-1-anthrol (0.5 g.) was dissolved in acetic anhydride (25 ml.) and pyridine (3 ml.) and the reaction mixture kept for 24 hours at room temperature. The product obtained on pouring the mixture in cold water crystallised from dilute alcohol (charcoal) in slightly reddish yellow needles, m.p.142°. Yield 0.4 g.

Analysis :

3.668 mg. of the substance gave 10.444 mg. of carbon dioxide and 1.608 mg. of water.

Found : C, 77.70 % ; H, 4.91 %.

$C_{18}H_{14}O_3$ requires : C, 77.71 % ; H, 5.04 %.

The benzoyl derivative : 2-Acetyl-1-anthrol (0.2 g.) was dissolved in sufficient pyridine and heated on a boiling water bath for one hour with benzoyl chloride (0.5 ml.). The reaction mixture was then added to dilute sulphuric acid. The product obtained was washed with a dilute solution of sodium hydroxide and crystallised from dilute alcohol in colourless needles, m.p.140-141°. Yield 0.1 g.

Analysis :

9.52 mg. of the substance gave 28.32 mg. of carbon dioxide and 4.28 mg. of water.

Found : C, 81.20 % ; H, 5.03 %.

$C_{23}H_{16}O_3$ requires : C, 81.17 % ; H, 4.71 %.

The methyl ether : 2-Acetyl-1-anthrol (1 g.)was dissolved in dry acetone (50 ml.) and refluxed with dimethyl sulphate (0.6 g.) and anhydrous potassium carbonate (2 g.) for 20 hours. The reddish yellow solid obtained on working up the reaction mixture as before crystallised from dilute acetone (charcoal) in yellow needles, m.p. 126°. Yield 0.8 g.

<u>Analysis</u> :

5.380 mg. of the substance gave 16.140 mg. of carbon dioxide and 2.824 mg. of water.

Found : C, 81.87 % ; H, 5.87 %.

$C_{17}H_{14}O_2$ requires : C, 81.60 % ; H, 5.60 %.

2-Acetyl-1-methoxyanthraquinone.

Sodium hydroxide (5.5 g.) in water (5.0 ml.) was added to crushed ice (50 g.) and chlorine passed through the solution until the solution was neutral to litmus. ~~Further~~ More sodium hydroxide (2.5 g.) in water (10 ml.) was then added. The solution was warmed to 65° and 2-acetyl-1-methoxyanthracene (1 g.) was added portionwise during half an hour. The temperature was then maintained at 85° for 3 hours. The separated product was filtered after cooling and crystallised from dilute acetic acid (charcoal) in orange needles, m.p.214°. Yield 0.6 g.

It gave red colour when warmed with zinc dust and alkali.

<u>Analysis</u> :

4.282 mg. of the substance gave 11.410 mg. of carbon dioxide and 1.780 mg. of water.

Found : C, 72.72 % ; H, 4.65 %.

$C_{17}H_{12}O_4$ requires : C, 72.85 % ; H, 4.32 %.

1-Methoxyanthraquinone-2-carboxylic acid.

2-Acetyl-1-methoxyanthraquinone (1.0 g.) was suspended in sodium hypochlorite solution (prepared from 5.5 g. of sodium hydroxide as described above) and the mixture heated in a water bath at 85-90° for about 3 hours. It was filtered hot, and sodium bisulphite was added after cooling the filtrate to destroy the excess of sodium hypochlorite . The solution was acidified with dilute hydrochloric acid. The product obtained crystallised from glacial acetic acid in clusters of yellow needles, m.p.254°. Mixed m.p. with an authentic sample,prepared as mentioned in the theoretical portion,was not depressed.

Fries migration of 1-anthrolacetate at room temperature : 4-Acetyl-1-anthrol, and 2-acetyl-1-anthrol.

A solution of 1-anthrolacetate (2.4 g.) in nitrobenzene (40 ml.) was mixed with a solution of anhydrous aluminium chloride (2.7 g. ; 2 mols) in nitrobenzene (20 ml.), and the reaction mixture, protected from moisture, was left for 48 hours at room temperature. It was then treated with ice and hydrochloric acid and the nitrobenzene was steam-distilled. The black product obtained was repeatedly extracted with cold dilute alkali. The product obtained on acidification of the combined alkaline extracts was dissolved in hot alcohol. On cooling, a small crop of crystals separated. These were found to be of 2-acetyl-1-anthrol. The mother liquor on dilution with water gave 4-acetyl-1-anthrol which crystallised from alcohol in yellow shining plates, m.p.260°.

It did not give any colour with alcoholic ferric chloride.

Analysis :

4.484 mg. of the substance gave 13.416 mg. of carbon dioxide and 2.220 mg. of water.

Found : C, 81.65 % ; H, 5.53 %.

$C_{16}H_{12}O_2$ requires : C, 81.36 % ; H, 5.08 %.

The 2:4-dinitrophenylhydrazone was prepared as before. It crystallised from glacial acetic acid in reddish plates, m.p.274°.

Analysis :

4.164 mg. of the substance gave 0.486 cc. of nitrogen measured at 31°C and 757 mm.

Found : N, 13.05 %.

$C_{22}H_{16}N_4O_5$ requires: N, 13.46 %.

Carboxylation of 1-anthrol : 1-Anthrol-2-carboxylic acid.

1-Anthrol (1 g.) was thoroughly mixed with potassium bicarbonate (1.8 g.) and the mixture added to anhydrous glycerine (5 ml.). The reaction mixture was heated at 120° in an oil bath for 4 hours. Carbon dioxide was bubbled through the solution during heating. The reaction mixture was then treated with water and the solution filtered. The product, obtained on acidification of the filtrate, crystallised from dilute alcohol, m.p.200° (decomp.). Läska and Haller (German Patent 559,333. Chem.

Abstr., 1933, 27, 735) give the same m.p. Yield 0.3 g.

Analysis :

3.680 mg. of the substance gave 10.162 mg. of carbon dioxide and 1.74 mg. of water.

Found : C, 75.36 % ; H, 4.52 %.

$C_{15}H_{10}O_3$ requires : C, 75.60 % ; H, 4.20 %.

Methyl-1-methoxyanthracene-2-carboxylate.

1-Anthrol-2-carboxylic acid (1 g.) was dissolved in dry acetone (50 ml.) and refluxed with dimethyl sulphate (1.1 g.) and anhydrous potassium carbonate (2 g.) for 15 hours. The reaction mixture was then filtered hot, and the acetone was removed. The product obtained crystallised from dilute alcohol (charcoal) in needles, m.p.107°.

Analysis :

3.926 mg. of the substance gave 11.08 mg. of carbon dioxide and 1.946 mg. of water.

Found : C, 77.02 % ; H, 5.54 %.

$C_{17}H_{14}O_3$ requires : C, 76.67 % ; H, 5.30 %.

1-Methoxyanthracene-2-carboxylic acid.

The above ester (0.5 g.) was refluxed on a steam bath with sodium hydroxide (10 %) for 4 hours. The solution was then filtered hot and the filtrate acidified with dilute hydrochloric acid. The product obtained crystallised from benzene in shining plates, m.p.207°.

Analysis :

3.382 mg. of the substance gave 9.512 mg. of carbon dioxide and 1.582 mg. of water.

Found : C; 76.75 % ; H, 5.23 %.

$C_{16}H_{12}O_3$ requires : C, 76.18 % ; H, 4.80 %.

1-Methoxyanthraquinone-2-carboxylic acid.

The above acid (1.0 g.) was suspended in sodium hypochlorite solution (prepared from 5.5 g. of sodium hydroxide as described before) and the mixture heated in a water bath at 85-90° for about 3 hours. It was then filtered hot and after cooling, excess of sodium bisulphite was added to destroy unreacted sodium hypochlorite. The product obtained on acidification with dilute hydrochloric acid, crystallised from glacial acetic acid in clusters of yellow needles, m.p. 254°. Mixed m.p. with an authentic sample of 1-methoxyanthraquinone-2-carboxylic acid, prepared as described before, was not depressed.

Preparation of 2-anthrol.

2Hydroxyanthraquinone was prepared from β-amino-anthraquinone by diazotization and boiling with water (Perkin, J.Chem. Soc., 1922, 122, 289). 2-Anthrol was then prepared by reducing 2-hydroxyanthraquinone with aluminium amalgam in aqueous alcoholic ammonia according to Perkin and Hall (J. Chem. Soc., 1923, 123, 2031) with slight modification in the working procedure which gave a purer product.

To a boiling solution of 2-hydroxyanthraquinone (5 g.), liquor ammonia (50 ml.), water (200 ml.) and alcohol (20 ml.), freshly prepared aluminium amalgam (from 4 g. of aluminium foil) was added. More liquor ammonia (100 ml.) was added, in portions, during twenty minutes. The heating of the mixture was continued for further one hour. The reaction mixture was then filtered, and the residue extracted with boiling ethyl alcohol (150 ml.). Hot water (100 ml.) was added to the boiling ethyl alcoholic extract. The solution was cooled and kept in a refrigerator. 2-Anthrol separated in brownish needles. It softened at 236° and melted at 248°. Yield 2.2 g. It was further purified through its acetyl derivative.

Formylation of 2-anthrol : 1-Formyl-2-anthrol.

2-Anthrol (2 g.) was dissolved in sodium dried ether (200 ml.) in a three-necked flask provided with a mercury sealed stirrer, and zinc cyanide (4 g.) was added. The reaction mixture was cooled externally and mechanically stirred. A rapid stream of dry hydrogen chloride gas was then passed through the mixture for three hours. It was then left overnight. The semisolid aldimine-hydrochloride obtained on removal of ether was washed with dry ether and then hydrolysed by refluxing with alcohol (50 % ; 100 ml.) on a steam bath for about an hour. The product obtained, crystallised from alcohol (charcoal) in yellow needles, m.p. 164°. yield 1.0 g. Jain and Seshadri (J.Sci.Indust.Res., 1956, **15B**, 61) give the same m.p.

1-Formyl-2-methoxyanthracene.

1-Formyl-2-anthrol (1 g.) was dissolved in dry acetone (50 ml.) and refluxed with dimethyl sulphate (0.62 g.) and anhydrous potassium carbonate (2 g.) for 20 hours. The product obtained on working up as usual crystallised from dilute acetic acid (charcoal) in yellow needles, m.p. 178°. Yield 0.8 g.

Analysis :

3.414 mg. of the substance gave 10.140 mg. of carbon dioxide and 1.584 mg. of water.

Found : C, 81.05 % ; H, 5.19 %.
$C_{16}H_{12}O_2$ requires : C, 81.36 % ; H, 5.08 %.

Oxidation of 1-formyl-2-methoxyanthracene : 2-Methoxy-anthraquinone-1-carboxylic acid.

1-Formyl-2-methoxyanthracene (0.5 g.) was suspended in sodium carbonate solution (2.5 % ; 40 ml.) and heated gently under reflux with potassium permanganate (0.5 g.) for three hours. The reaction mixture was then filtered and the product obtained on acidification of the filtrate was purified through sodium bicarbonate solution. It crystallised from dilute acetic acid in yellow needles, m.p.277°. Mixed m.p. with an authentic sample of 2-methoxyanthraquinone-1-carboxylic acid, prepared according to Ch.Marschalk (Bull.Soc.Chim., 1939, 6, 655. Chem.Absts., 1939, 33, 5388) was not depressed.

1-Methyl-2-anthrol.

(a) By Clemmensen's reduction of 1-formyl-2-anthrol :

A mixture of zinc dust (5 g.), mercuric chloride (0.5 g.), concentrated hydrochloric acid (0.25 ml.) and water (8 ml.) was stirred for five minutes. The solution was then decanted and the amalgam washed with distilled water. This was suspended in dilute hydrochloric acid (8 ml., 1:1) and a solution of 1-formyl-2-anthrol (0.5 g.) in acetic acid (20 ml.) was added slowly during 30 minutes. Concentrated hydrochloric acid (1 ml.) was then added and the heating continued for further one hour. The solution was then filtered hot and the filtrate diluted with water. The product obtained crystallised from dilute alcohol (charcoal) in yellow granules, m.p.163°. Yield 0.2 g.

Analysis :

3.870 mg. of the substance gave 12.222 mg. of carbon dioxide and 2.008 mg. of water.

Found : C, 86.19 % ; H, 5.80 %.

$C_{15}H_{12}O$ requires : C, 86.54 % ; H, 5.76 %.

(b) By <u>the reduction of 1-methyl-2-hydroxyanthraquinone</u> :

To a boiling solution of 1-methyl-2-hydroxyanthraquinone (0.5 g.), liquor ammonia (5 ml.), water (20 ml.) and alcohol (5 ml.), freshly prepared aluminium amalgam (from 1 g. of aluminium foil) was added. More liquor ammonia (10 ml.) was added, in portions, during 20 minutes. The heating of the mixture was continued for further one hour. The reaction mixture was then filtered hot, cooled and acidified with dilute hydrochloric acid. The residue obtained,crystallised from dilute alcohol (charcoal) in yellow granuales., M.p.and mixed m.p. with 1-methyl-2-anthrol, obtained above, was 163°. Yield 0.2 g.

<u>Synthesis of 1-acetyl-2-anthrol.</u>

(a) <u>Friedel-Crafts acetylation of 2-anthrol</u> :

A solution of 2-anthrol (1.9 g.) and acetic anhydride (1.3 g. ; 1.2 mols.) in nitrobenzene (30 ml.) was mixed with a solution of anhydrous aluminium chloride (2.7 g. ; 2 mols.) in nitrobenzene (20 ml.),and the reaction mixture, protected from moisture, was kept for 72 hours at room temperature. It was then treated with ice and hydrochloric acid, and the nitrobenzene was steam-distilled. When the nitrobenzene had steam-distilled some product started coming over with the steam. The steam distillation was continued for some time and the product collected. The black residue remaining in the distilling flask was extracted with alkali, and the alkaline extract acidified with hydrochloric acid. The precipitated solid crystallised from dilute alcohol (charcoal) in yellow needles, m.p.112-113°. The solid which steam-distilled , crystallised from dilute alcohol in yellow needles, m.p. and mixed m.p.with the product obtained above by the direct crystallisation of the residue, was 112-113°. Yield 1 g. Ferrari and Hunsberger (J.Org.Chem., 1960,<u>25</u>,485) give m.p.115-116.5°.

It gave bluish colouration with alcoholic ferric chloride,which turned greenish on keeping.

<u>Analysis</u> :

4.040 mg. of the substance gave 12.028 mg. of carbon dioxide and 1.892 mg. of water.

Found : C, 81.25 % ; H, 5.23 %.

$C_{16}H_{12}O_2$ requires : C, 81.36 % ; H, 5.08 %.

The same ketone was obtained when a solution of 2-anthrol (1.9 g.) and acetic anhydride (1.3 g. ; 1.2 m mols) in nitrobenzene (30 ml.) was mixed with a solution of anhydrous aluminium chloride (2.7 g. ; 2 mols.) in nitrobenzene (20 ml.), and the reaction mixture, protected from moisture,was heated on a steam bath for two hours. The product obtained on working up the reaction mixture as above,crystallised from dilute alcohol (charcoal) in yellow needles, m.p.112-113°.

(b) Fries migration of 2-anthrolacetate.

A solution of 2-anthrol acetate (Liebermann, Hormann, Ber., 1879, 12, 589) (2.4 g.) in nitrobenzene (50 ml.) was mixed with a solution of anhydrous aluminium chloride (2.7 g. ; 2 mols.) in nitrobenzene (20 ml.), and the reaction mixture, protected from moisture, was left for 24 hours at room temperature. It was then treated with ice and hydrochloric acid and the nitrobenzene was steam distilled. The residue was taken up in ether and the ethereal layer was extracted repeatedly with alkali. The product obtained on acidification of the alkaline extracts, crystallised from dilute alcohol in yellow needles. M.p. and mixed m.p. with 1-acetyl-2-anthrol, obtained above, was 112-113°.

The 2:4-dinitrophenylhydrazone prepared as usual and crystallised from acetic acid gave m.p. 235°.

Analysis :

3.986 mg. of the substance gave 0.515 cc. of nitrogen measured at 37°C and 754 mm.

Found : N, 14.10 %.

$C_{22}H_{16}N_4O_5$ requires : N, 13.46 %.

The acetyl derivative : A mixture of 1-acetyl-2-anthrol (0.5 g.), acetic anhydride (15 ml.) and pyridine (2 ml.) was kept for 24 hours at room temperature. The product obtained on pouring the reaction mixture in water crystallised from dilute alcohol(charcoal) in colourless needles, m.p. 130°. Yield 0.4 g.

Analysis :

3.440 mg. of the substance gave 9.768 mg. of carbon dioxide and 1.370 mg. of water.

Found : C, 77.49 % ; H, 4.45 %.

$C_{18}H_{14}O_3$ requires : C, 77.71 % ; H, 5.03 %.

The benzoyl derivative, prepared from 1-acetyl-2-anthrol (0.2 g.), in pyridine and benzoyl chloride (0.5 ml.)as before,crystallised from dilute alcohol in colourless needles, m.p.110-111°. Yield 0.1 g.

Analysis :

3.220 mg. oftthe substance gave 9.596 mg. of carbon dioxide and 1.358 mg. of water.

Found : C, 81.33 % ; H, 4.72 %.

$C_{23}H_{16}O_3$ requires : C, 81.17 % ; H, 4.71 %.

The methyl ether : 1-Acetyl-2-anthrol (0.5 g.) was dissolved in dry acetone (50 ml.) and refluxed with dimethyl sulphate (0.3 g.) and anhydrous potassium carbonate (1 g.) for 20 hours. The reaction mixture was worked up as usual and the product obtained crystallised from dilute alcohol (charcoal) in small yellowish plates, m.p.99°. Yield 0.3 g.

Analysis :

3.692 mg. of the substance gave 11.096 mg. of carbon dioxide and 1.880 mg. of water.

Found : C, 82.02 % ; H, 5.69 %.

$C_{17}H_{14}O_2$ requires : C, 81.60 % ; H, 5.60 %.

Friedel-Crafts acetylation of 2-methoxyanthracene : 1-Acetyl-2-methoxyanthracene.

2-Methoxyanthracene was prepared by dissolving 2-anthrol (1.0 g.) in dry acetone (100 ml.) and refluxing with dimethylsulphate (0.6 g.) and anhydrous potassium carbonate (2 g.) for 20 hours on a water bath. The product crystallised from dilute alcohol (charcoal) in colourless plates, m.p.175° (Liebermann, Hagen, Ber., 1882, 15, 1427, 1794).

A solution of 2-methoxyanthracene (1.04 g.) and acetic anhydride (0.65 g. ; 1.2 mols.) in dry benzene was mixed with anhydrous aluminium chloride (1.4 g. ; 2 mols.) in dry benzene. The reaction mixture, protected from moisture, was kept for 72 hours at room temperature. It was then treated with ice and hydrochloric acid and the benzene steam-distilled. The product was taken up in ether and the ethereal layer washed with dilute sodium hydroxide solution and then with water. After drying the ether extract with anhydrous sodium sulphate the ether was removed. The residue obtained crystallised from dilute alcohol (charcoal) in yellowish plates, m.p.99-100°. Mixed m.p. with the methyl ether of 1-acetyl-2-anthrol, obtained before, was not depressed.

Sodium hypochlorite oxidation of 1-acetyl-2-methoxyanthracene : 2-Methoxyanthraquinone-1-carboxylic acid.

To a solution of sodium hypochlorite (prepared from 5.5 g. of sodium hydroxide as described before) , 1-acetyl-2-methoxyanthracene (1 g.) was added portionwise during 30 minutes at 65°. The temperature was then raised to 85° and was maintained for three hours. The product which separated was found to be a chlorinated product. This was filtered and sodium bisulphite was added to the filtrate to destroy the excess of sodium hypochlorite. The solution was then acidified with dilute hydrochloric acid. The product obtained was dissolved in sodium bicarbonate solution and filtered. The product obtained on acidification of the filtrate crystallised from acetic acid in small yellow needles. M.p. and mixed m.p. with 2-methoxyanthraquinone-1-carboxylic acid, prepared according to Ch.Marschalk (loc.cit.) was 276-277°.

Attempted carboxylation of 2-anthrol.

(a) 2-Anthrol (1 g.) was thoroughly mixed with potassium bicarbonate (1.8 g.) and the mixture added to anhydrous glycerine (15 ml.). The reaction mixture was heated at 120° in an oil bath for seven hours. Carbon dioxide was bubbled through the solution during heating. The reaction mixture was then treated with water and the solution was filtered. The residue was of 2-anthrol. The filtrate on acidification gave no product. No product was obtained from the ether extract of the filtrate.

(b) A mixture of 2-anthrol (1 g.), potassium bicarbonate (2.5 g.) and water (9 ml.) was heated in a sealed tube at 120-130° for 5 hours. On working up the reaction mixture as usual no acid could be isolated.

(c) 2-Anthrol (1 g.) was intimately mixed with potassium bicarbonate (5 g.) and heated without water in a sealed tube at 140-150° for 6 hours. On working up the reaction mixture no acid was found to be formed.

(d) 2-Anthrol (1 g.) was dissolved in dry toluene (75 ml.) and finely pulverized sodium (0.12 g.) was added to it. It was then heated to boiling, protected from moisture, and a current of dry carbon dioxide was passed through the solution. After heating for about 3 hours, the reaction mixture was worked up. No acid was found to have been formed.

In all the above cases unchanged 2-anthrol was recovered.

Reduction of 2-methoxyanthraquinone-1-carboxylic acid : 2-Methoxyanthracene-1-carboxylic acid.

To a boiling solution of 2-methoxyanthraquinone-1-carboxylic acid (0.5 g.) (prepared according to Ch.Marschalk, loc.cit.) in alcohol (35 ml.), water (25 ml.) and a few drops of liquor ammonia, freshly prepared aluminium-mercury couple (from 1 g. of aluminium foil) was introduced, and more liquor ammonia (30 ml.) was added during 20 minutes. After refluxing for further

30 minutes the solution was filtered hot and the filtrate acidified. The product obtained was purified through sodium bicarbonate solution and then crystallised from alcohol in shining greenish yellow plates, m.p.191°. Yield 0.3 g.

The alcoholic solution gave bluish fluorescence. It did not give colouration with alcoholic ferric chloride.

Analysis :

4.366 mg. of the substance gave 12.150 mg. of carbon dioxide and 1.856 mg. of water.

Found : C, 75.95 % ; H, 4.75 %.

$C_{16}H_{12}O_3$ requires : C, 76.19 % ; H, 4.76 %.

Decarboxylation of the above acid :

2-Methoxyanthracene.

The above acid (0.1 g.) was decarboxylated by heating its solution in quinoline (5 ml.) with a little copper powder at 210-220°, till the effervescence ceased. The reaction mixture was then filtered and the filtrate treated with hydrochloric acid. The product obtained crystallised from alcohol in light brownish plates, m.p.175-176°. Mixed m.p. with 2-methoxyanthracene prepared according to Liebermann (loc.cit.) was not depressed.

Demethylation of 2-methoxyanthracene-1-carboxylic acid with hydriodic acid : 2-Hydroxy-9,10-dihydro-anthracene-1-carboxylic acid.

To a cooled solution of 2-methoxyanthracene-1-carboxylic acid (0.3 g.) in acetic anhydride (10 ml.) hydriodic acid (3 ml.) was added drop-wise with constant shaking. The reaction mixture was left at room temperature for 48 hours, with occasional stirring with a magnetic stirrer. The reaction mixture was then poured into ice. The precipitate was filtered and taken up in ether. The ethereal solution was extracted with sodium bicarbonate solution. On acidification of the alkaline extract, a product was obtained which crystallised from benzene in faint yellowish crystals, m.p.216-218°.

Analysis :

6.338 mg. of the substance gave 17.356 mg. of carbon dioxide and 2.942 mg. of water.

Found : C, 74.73 % ; H, 5.13 %.

$C_{15}H_{12}O_3$ requires : C, 75.00 % ; H, 5.00 %.

Decarboxylation of the above acid : 9,10-dihydro-2-anthrol.

The above acid (0.1 g.) was decarboxylated by heating its solution in quinoline (5 ml.) with a little copper powder at 210-220°, till the effervescence ceased. The reaction mixture was then filtered and the filtrate treated with dilute hydrochloric acid. The product obtained crystallised from dilute alcohol, m.p.

129°. The mixed m.p. with 9,10-dihydro-2-anthrol, prepared according to Bamberger (Ber., 1893, 26, 3068) was not depressed.

Esterification of 2-methoxyanthracene-1-carboxylic acid: Methyl-2-methoxy-anthracene-1-carboxylate.

2-Methoxyanthracene-1-carboxylic acid (1 g.) was dissolved in dry acetone (100 ml.) and refluxed with dimethyl sulphate (0.6 g.) and anhydrous potassium carbonate (2 g.) for 15 hours. The reaction mixture was then filtered hot and the acetone ~~allowed to evaporate~~ removed. The product remaining after washing with sodium bicarbonate, crystallised from dilute alcohol in yellow plates, m.p. 127-128°.

Analysis :

5.370 mg. of the substance gave 15.173 mg. of carbon dioxide and 2.711 mg. of water.

Found : C, 77.11 % ; H, 5.64 %.

$C_{17}H_{14}O_3$ requires : C, 76.67 % ; H, 5.30 %.

Demethylation of methyl-2-methoxyanthracene-1-carboxylate with aluminium chloride : Methyl-2-hydroxy-anthracene-1-carboxylate.

The above ester (0.5 g.) was intimately mixed with anhydrous aluminium chloride (0.5 g.) and heated at 80° for 8 hours, and then kept overnight at room temperature. The reaction mixture was then added to ice and hydrochloric acid. The residue obtained, was taken up in ether. The ethereal layer, after washing with sodium bicarbonate solution, was extracted with dilute alkali. On acidification of the alkaline extract a product was obtained which crystallised from dilute alcohol in shining yellow needles, m.p.110°.

Analysis :

4.360 mg. of the substance gave 12.142 mg. of carbon dioxide and 1.896 mg. of water.

Found : C, 76.00 % ; H, 4.86 %.

$C_{16}H_{12}O_3$ requires : C, 76.18 % ; H, 4.80 %.

Attemoted hydrolysis of methyl-2-hydroxyanthracene-1-carboxylate.

The above ester (0.1 g.) was dissolved in alcohol (5 ml.) and kept overnight at room temperature with sodium hydroxide solution (5 ml. ; 20 %). The next day, the solution was diluted with water and acidified. The product obtained did not dissolve in sodium bicarbonate solution. It crystallised from dilute alcohol in needles, m.p.252°. Mixed m.p. with 2-anthrol was not depressed.