CHAPTER V

Synthesis of some anthraquinone derivatives.

Theoretical

Of the three stable anthracene-quinones which are known viz. 1,2-, 1,4- and 9,10-quinones, the last one known as anthraquinone is of great interest as anthraquinone derivatives are found in nature and also because it is the starting materials for the manufacture of numerous dyes.

As the present work deals with the synthesis of some anthraquinone derivatives the pattern of reactions of anthraquinone and the 1- and 2-hydroxyanthraquinones is briefly discussed here.

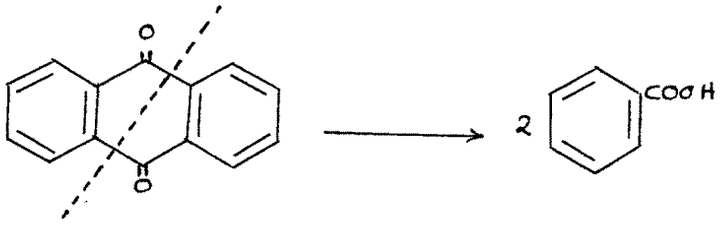
Reactions of anthraquinone.

In its reactions, anthraquinone differs greatly from anthracene. Because the meso-positions in anthraquinone are saturated, it shows no olefinic properties, also it is not a typical para-quinone. It behaves as a diketone of very low reactivity.

Anthraquinone generally does not give rise to addition compounds, except with strong acids and addition then occurs on the carbonyl groups. Thus anthraquinone dissolves readily in concentrated sulphuric acid, taking up a proton on the carbonyl group (Hammett and Deyrup, J.Am.Chem.Soc., 1933, 55, 1900).

Oxidation : Anthraquinone is fairly stable towards oxidising agents. It remains unaffected on prolonged boiling with

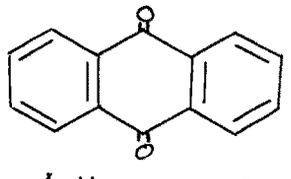
chromic acid in acetic acid or by treatment with alkaline potassium permanganate (Luck, Z.anal.Ch., 1874, 13, 251), or by alkaline hydrogen peroxide (Writz et al., Ber., 1935, 68, 1163). When one of the outer benzene rings is substituted, for example, by hydroxyl groups, oxidation is then possible, the ring carrying the substituent is destroyed and phthalic acid is obtained. Fusion with potassium hydroxide at a high temperature also breaks the middle ring of the anthraquinone molecule giving two molecules of benzoic acid (Graebe and Libermann, Ann., 1871, 160, 129).



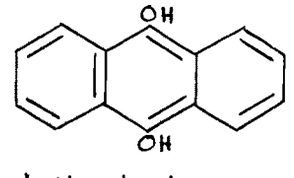
This mode of degradation is difficult with anthraquinone itself but substituted anthraquinones, eg. polyhydroxyanthraquinones such as Chrysazin and Anthrarufin, undergo oxidative fission more readily (Liebermann and Dehnst, Ber., 1879, 12, 1289). Hydroxyanthraquinones undergo simultaneous nitration and fission of the middle ring when they are treated with nitric acid (Wolffenstein and Paar, Ber., 1913, 46, 560).

Reduction : The typical quinone reagents, sulphur dioxide in water, and phenylhydrazine, do not reduce anthraquinone. More powerful reducing agents attack the diketone

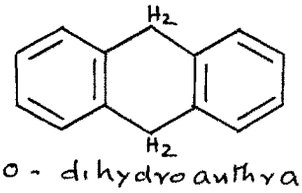
system and according to the experimental conditions employed, a wide range of very important compounds are produced. It is reduced with sodium hydrosulphite in boiling aqueous alcohol to anthrahydroquinone (Grandmoregin, Ber., 1906, 39, 3563 ; J.pr.Chem. (ii), 1907, 76, 138) ; in strongly alkaline, very dilute solution the reduction proceeds to anthrone (Battegay and Hueber, Bull.Soc.Chim., 1923, (iv), 33, 1084). It gives a green quinhydrone salt when treated with sodium amalgam in boiling aqueous alcohol. (Scholl and Bottger, Ber., 1930, 63 2120). On brief heating with hydriodic acid (d. 1.75) and phosphorus, it gives anthrone and on prolonged heating in an open vessel, it gives 9,10-dihydroanthracene (Liebermann and Topf, Ber., 1876, 9, 1201 ; Ann., 1882, 212, 1,65).



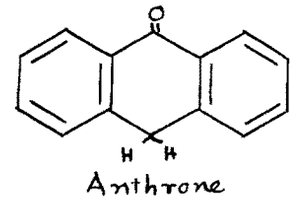
Anthraquinone



Anthrahydroquinone



9,10 - dihydroanthracene



Anthrone

On treatment with zinc dust in aqueous ammonia on ~~the water~~ a steam bath, it gives 9,10-dihydroanthranol (Perger, J.pr.Ch., 1881, (ii), 23, 137) and anthrapinacol (Schulze, Ber., 1885, 18, 3034). On boiling with zinc dust and dilute sodium hydroxide it is reduced to anthrahydroquinone (Graebe and Liebermann, Ann., 1871, 160, 121, 125, 130 ; Liebermann, Ann., 1882, 212,

1, 65 ; Manchot, Ann., 1901, 314, 177) but in presence of toluene, on boiling for 48 hours, anthracene is obtained (Martin, J.Am.Chem.Soc., 1936, 58, 1438). It is reduced to 9,10-dihydroanthracene with amalgamated zinc and hydrochloric acid (Clemmensen, Ber., 1914, 47, 681). Lithium aluminium hydride reduces it to anthrahydroquinone (Nystrom and Brown, J.Am.Chem.Soc., 1948, 70, 3738).

Halogenation : Direct halogenation is difficult. Bromine does not act on dry anthraquinone or on a solution in carbon disulphide in the cold but on prolonged heating with bromine in a sealed tube at 100° or better in presence of iodine at 160°, 2,7-dibromoanthraquinone is formed (Graebe and Liebermann, Ann.Suppl. 1870, 7, 284 ; Diehl, Ber., 1878, 11, 173 ; Grandmougin, Compt. rend., 1921, 173, 1176). When halogenation is carried out in oleum in presence of a catalyst (iodine), it effects substitution in the α i.e.1,4,5,8-positions (Bayer, G.P. 107,721 ; 228,901), and polysubstituted i.e. tetra to hepta-halogenated anthraquinones result (Eckert, J.pr.Ch. 1921 (ii), 102, 361 ; Eckert, Skiner, Monafst 1915, 36, 269). With chlorine in hot oleum, 1,4,5,8-tetrachloroanthraquinone is obtained (Schmidt, Bull.Soc.Ind. Mulhouse,1914, 84, 409). When it is treated with iodine in 70% oleum at 180°, tri-, tetra-, penta-iodo-anthraquinones and other products are formed (Eckert and Klinger, J.pr.Ch. 1929, (ii), 121, 281).

Nitration : Anthraquinone dissolves in boiling nitric

acid (d. 1.4) and deposits unchanged on cooling (Anderson, Ann., 1862, 122, 294, 301). With fuming nitric acid, 1-nitro-anthraquinone is the main product, together with small amounts of 2-nitro- and dinitroanthraquinones (Coffey, Chem.and Ind., 1953, 168). The nitration is most readily carried out in 90% sulphuric acid at temperatures round about 0° (Lauth, Compt. rend., 1903, 137, 661 ; Laurer and Oda, J.pr.Ch., 1935 (ii), 144, 176 ; Lauer, Ber., 1936, 69, 2618).

Sulphonation : Sulphonation of anthraquinone is difficult. It reacts only very slowly with sulphuric acid even at 250° but reacts with 20-40 % oleum at about 140° when β-substitution occurs. Along with the formation of anthraquinone-2-sulphonic acid which is the chief product, 2,6- and 2,7-di-sulphonic acids are also formed (Graebe and Liebermann, Ann. 1871, 160, 130). When the reaction is carried out using stronger oleum, hydroxylation occurs with the formation of hydroxyanthraquinones (Lauer, J.pr.Ch. 1931 (ii), 130, 185, 194, 214, 225, 239 ; ibid., 1932, 135, 164, 361). In the presence of a mercury salt a remarkable change in the orientation of the sulphonic acid group occurs, the reaction products being the anthraquinone-1-sulphonic acid and the 1,5- and 1,8-di-sulphonic acids (Elijinski, Ber., 1903, 36, 4194 ; Fierz David et al., Helv., 1927, 10, 197, 429 ; 1928, 11, 197 ; Org.Synth.Coll.Vol. II, 540).

Reactions of 1- and 2-hydroxyanthraquinone.

Oxidation : When 1-hydroxyanthraquinone is treated with nitric acid, it is oxidised to phthalic acid (Pechmann, Ber., 1879, 12, 2124). On fusion with alkali, it undergoes oxidative hydroxylation, giving rise to alizarin though in low yields, the main reaction product being, 1,1'-dihydroxy-2,2'-bianthraquinonyl (Bayer G.P. 167,461 ; Scholl et al., Ber., 1919, 52, 2254). With sodium nitrite in sulphuric acid in presence of boric acid, quinizarin is formed (Dimroth, and Faust, Ber., 1921, 54, 3020).

2-Hydroxyanthraquinone is oxidised to phthalic acid when it is heated with fuming nitric acid (Liebermann, Ann., 1873, 183, 145, 202, 217). On fusion with potassium hydroxide it forms alizarin, usually in presence of nitrate or chlorate (Liebermann, Ber., 1871, 4, 108 ; loc. cit., 1876 ; Graebe and Liebermann, Ann., 1871, 160, 121, 130, 141 ; Baeyer and Caro, Ber., 1874, 7, 968).

Reduction : 1-Hydroxyanthraquinone on treatment with zinc dust in warm aqueous sodium hydroxide in carbon dioxide atmosphere is reduced to 1-hydroxyanthrahydroquinone (Meyer and Sander, Ann., 1920, 420, 113). The reduction of 1-acetoxyanthraquinone with stannous chloride and hydrochloric acid in hot acetic acid (Cross and Perkin, J.Chem.Soc., 1930, 292) or with sodium dithionate in acetic acid (Zahn, Ber., 1934, 67, 2063), affords 4-hydroxyanthrone. With hydrogen in presence of nickel catalyst (0.3 g.) in chlorobenzene at

200° and an initial pressure of 90 atmospheres, it gets reduced to 1-hydroxyanthrone ; if the reduction is effected with more nickel at 80-120° and an initial pressure of 70 atmospheres, 9,10-dihydroxy-1-keto-1,2,3,4-tetrahydroanthracene is obtained (Zahn and Koch, Ber., 1938, 71, 172). 1-Acetoxy-anthraquinone on reduction with hydrogen in presence of nickel in decalin affords 4-hydroxyanthrone (Zahn, loc.cit.).

2-Hydroxyanthraquinone is reduced by fuming hydriodic acid and phosphorus to 2-anthrol and a small amount of a hydrocarbon m.p. 63° (Liebermann, Ann., 1882, 212, 1, 20, 24, 52). When it is treated with aluminium powder and aqueous alcoholic ammonia on a steam bath, 2-anthrol and 3-hydroxyanthrone are formed (Perkin and Whatam, J.Chem.Soc., 1922, 121, 289). It is reduced to 2-anthrol when it is treated with aluminium-amalgam and aqueous alcoholic ammonia (Hall and Perkin, J.Chem.Soc., 1923, 123, 2029). On treatment with zinc dust and aqueous ammonia on a steam bath, 3-hydroxyanthrone is produced together with 2,2'-dihydroxy-9,9'-bianthryl and 3,3'-dihydroxy-10,10'-bianthronyl (Liebermann and Simon, Ber., 1881, 14, 1264 ; Liebermann loc. cit. 1882) ; if the reduction is carried out at 100° in an autoclave, 3-hydroxyanthrone is the sole product (Perkin loc.cit. 1922). When the reduction is carried out with zinc dust (excess) and alkali at 150° in an autoclave, 9,10-dihydro-2-anthrol is formed (Braun and Bayer, Ann., 1929, 472, 90). 2-Acetoxyanthraquinone on reduction with

stannous chloride and hydrochloric acid gives rise to 3-hydroxyanthrone (Cross and Perkin, J.Chem.Soc., 1930, 292). When it is distilled with zinc dust, anthracene is obtained (Graebe,loc.cit. 1871 ; Liebermann, loc.cit. 1876).

Halogenation : 1-Hydroxyanthraquinone is quite resistant towards bromine, but in presence of sodium acetate in boiling acetic acid it reacts with bromine to give 4-bromo-1-hydroxy- and 2,4-dibromo-1-hydroxyanthraquinone (Fries and Schurmann, Ber., 1919, 52, 2182). With sulphuryl chloride in nitrobenzene in presence of iodine, it gives 4-chloro-1-hydroxy- and 2,4-dichloro-1-hydroxyanthraquinone (Ullmann and Conzetti, Ber., 1920, 53, 826).

2-Hydroxyanthraquinone on boiling with sodium hypochlorite in about 10% sodium hydroxide solution gives rise to 1-chloro-2-hydroxyanthraquinone (Decker and Laube, Ber., 1906, 39, 112). It reacts similarly with sodium hypobromite, but with excess of sodium hypobromite, 1,3-dibromo-2-hydroxyanthraquinone is formed from which the α-bromine can be removed by reduction and subsequent oxidation to give 3-bromo-2-hydroxyanthraquinone (Hardacre and Perkin, J.Chem.Soc., 1929, 180). With bromine in pyridine, it produces a pyridine addition compound which on treatment with dilute hydrochloric acid gives rise to 1,3-dibromo-2-hydroxyanthraquinone (Barnett and Cook, J.Chem. Soc., 1922, 121, 1376). With iodine in pyridine, 3-iodo-2-hydroxyanthraquinone is obtained.(Hardacre and Perkin, loc.cit. 1929).

Sulphonation : 1-Hydroxyanthraquinone when treated with fuming sulphuric acid at 150°, gives rise to 1-hydroxyanthraquinone-2-sulphonic acid (Perger, J.pr.Ch. 1878, (ii), 18, 116, 159, 178 ; Georgievics, Farbenind (ii), 1905, 4, 185). When it is treated with a large excess of strongly fuming sulphuric acid and then saponified anthrarufin is obtained (Schmidt, Bull.Soc.Ind.Malhouse, 1914, 84, 409).

2-Hydroxyanthraquinone on treatment with fuming sulphuric acid at 120° forms 2-hydroxyanthraquinone-3-sulphonic acid (Perger, J.pr.Ch. 1878, (ii), 18, 116, 159, 178).

Nitration : When 1-hydroxyanthraquinone is treated with nitric acid, it gets oxidised to phthalic acid, but the borate, prepared in sulphuric acid, can be nitrated smoothly to 1-hydroxy-4-nitroanthraquinone (Gattermann, Ann., 1912, 393, 113, 163).

2-Hydroxyanthraquinone reacts with fuming nitric acid (d. 1.52) at 60-70° to give 1,3-dinitro-2-hydroxy-anthraquinone (Simon, Ber., 1881, 14, 464).

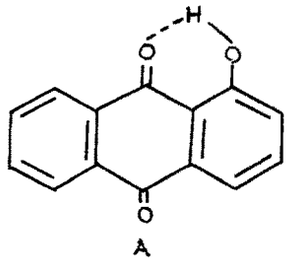
Formylation : When 2-hydroxyanthraquinone is treated with chloroform, alcohol and sodium hydroxide on a steam bath 1-formyl-2-hydroxyanthraquinone-~~1-formyl~~ is obtained (Sen and Ray, J.Indian Chem.Soc., 1932, 9, 173).

Other reactions : By the action of formaldehyde on 2-hydroxyanthraquinone in alkaline sodium hydrosulphide solution, followed by atmospheric oxidation of the leuco base,

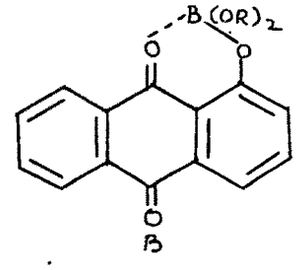
1-methyl-2-hydroxyanthraquinone is obtained (Ch.Marschalk, Bull.Soc.Chim., 1939, 6, 655).

2-Methyl-1-hydroxyanthraquinone is produced when 1-hydroxyanthraquinone, dissolved in dilute sodium hydroxide solution, is treated with sodium hydrosulphite and formaldehyde and then oxidised by air ; similarly 1-hydroxy-2-anthraquinoyl acetic acid is obtained with glyoxylic acid (Marschalk et al., Bull.Soc.Chim., 1936, 3, 1545).

1-Hydroxyanthraquinone readily forms characteristic highly coloured and fluorescent borate when treated with boric acid in concentrated sulphuric acid and orange-red boroacetate when boric acid in acetic anhydride is used (Dimroth et al., Ber., 1920, 53, 481 ; Ber., 1921, 54, 3020 ; Ann., 1926, 446, 99). From this behaviour and from spectroscopic and polarographic data (Flett, J.Chem.Soc., 1948, 1441 ; Wiles, ibid., 1952, 1938) it is concluded that hydrogen bonding occurs between the α-hydroxy group and the adjacent carbonyl group in 1-hydroxyanthraquinone (A) and that chelation occurs in the case of boric ester (B).



A

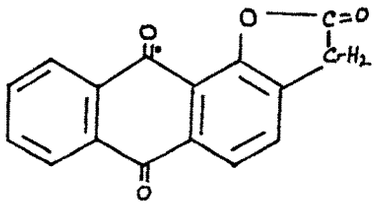


B

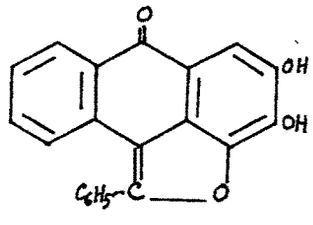
2-Hydroxyanthraquinone on warming with boroacetic anhydride merely gets acetylated (Dimroth, loc.cit., 1920).

From the foregoing account it will be seen that substitution in anthraquinone ring system is ~~difficult~~ not very facile even if it is activated by the presence of a hydroxyl group. Thus simple derivatives, which would form the starting materials for the synthesis of other compounds, such as 1-acetyl-2-hydroxyanthraquinone and 2-acetyl-1-hydroxyanthraquinone were hitherto unknown or not easily accessible. In the course of the present work attempts were made to carry out Friedel-Crafts reaction on 1-hydroxy and 2-hydroxyanthraquinone but they did not succeed, the starting materials were recovered unchanged. Fries migration of 1-acetoxyanthraquinone and 2-acetoxyanthraquinone also did not succeed. In both cases the hydroxyanthraquinones were obtained.

The building up of the α- and γ-pyrone ring on anthraquinone has so far not been attempted. Further, only a few cases where the furan ring has been built up on the anthraquinone ring system are known, such as, 6,7-phthaloyl-2-coumaranone (i) (Ch. Marschalk, Bull.Soc. Chim., 1942, 9, 801), and benzoin yellow (ii) (Graebe, Ber., 1898, 31, 2975).



(i)



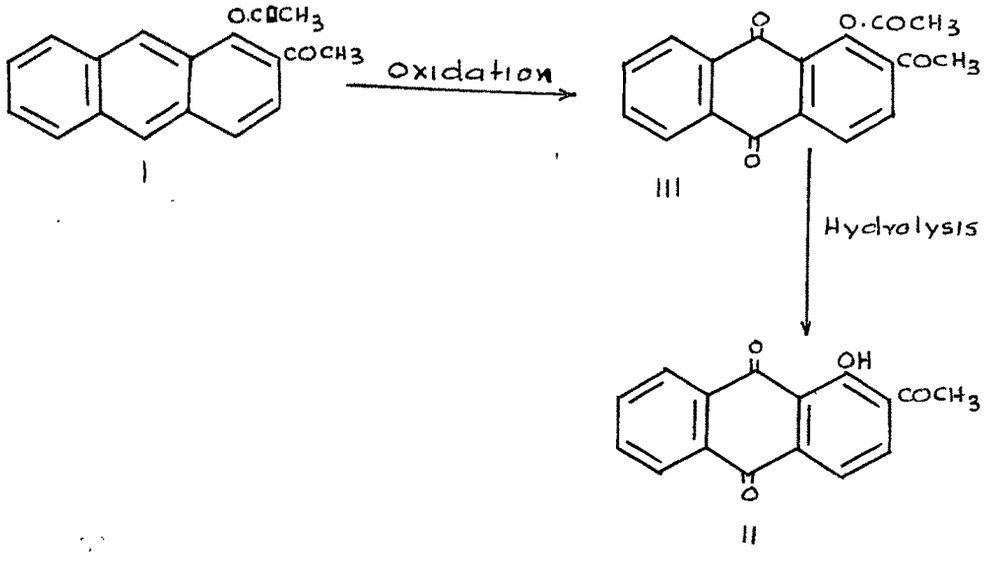
(ii)

In view of all this, it was thought of interest to study the controlled oxidation of the anthracene derivatives

described in chapters II, III and IV to see if the corresponding anthraquinone derivatives could be synthesised. This has been found possible in a number of cases. Where the oxidation affected the heterocyclic ring as in the case of the anthrafuran derivatives, intermediate anthracene derivatives were oxidised to the corresponding anthraquinone derivatives and these were then cyclised and the heterocyclic ring formed.

2-Acetyl-1-hydroxyanthraquinone.

2-Acetyl-1-hydroxyanthraquinone (II) was synthesised by oxidising 2-acetyl-1-acetoxyanthracene (I) with chromic acid in acetic acid under controlled conditions by keeping the reaction mixture at 60° for 3 hours. The product obtained was purified through its acetyl derivative (III). It gave a 2:4-dinitrophenylhydrazone and also gave greenish colouration with alcoholic ferric chloride. 1-Hydroxyanthraquinone under the same conditions does not give a 2:4-dinitrophenylhydrazone. This ketone has been previously prepared by condensing butadiene with 5-acetoxy-6-acetyl-1,4-naphoquinone by heating in a sealed tube by Spruit.(Rec. trav. Chim., 1949, 68, 304).

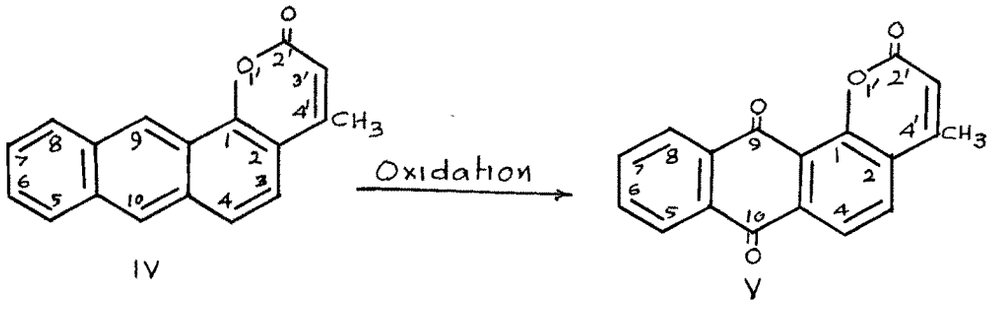


I III II

4'-Methyl-1,2(9,10-dihydro-9,10-dioxo-)anthra-α-pyrone.

4'-Methyl-1,2-anthra-α-pyrone (IV) was oxidised

with sodium dichromate in acetic acid at room temperature. The product obtained was insoluble in alkali which indicated that the pyrone ring was not oxidised. Further, it gave red colour when warmed with zinc dust and sodium hydroxide solution. It has therefore been assigned the 4'-methyl-1,2-(9,10-dihydro-9,10-dioxo-)anthra-α-pyrone structure (V).



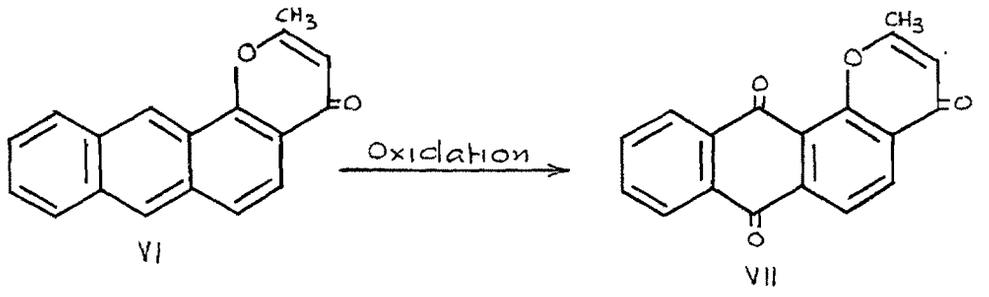
IV V

Attempts to synthesise the α-pyrone derivative (V) by condensation of 1-hydroxyanthraquinone with ethyl acetoacetate either in presence of concentrated or 80 % sulphuric acid or phosphorus pentoxide did not succeed.

2'-Methyl-and 2'-phenyl-1,2-(9,10-dihydro-9,10-dioxo-)anthra-γ-pyrone.

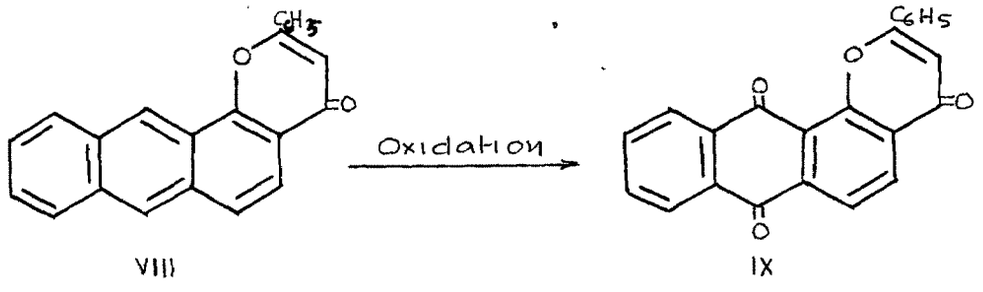
A solution of 2'-methyl-1,2-anthra-γ-pyrone (VI) in acetic acid was stirred with sodium dichromate for 2 hours at room temperature. The product obtained was insoluble in alkali indicating that the heterocyclic ring was not oxidised. Further, the product developed red colour when warmed with zinc dust and sodium hydroxide solution.

2'-Methyl-1,2-(9,10-dihydro-9,10-dioxo-)anthra-γ-pyrone (VII) structure has therefore been assigned to it.



VI VII

2'-Phenyl-1,2-anthra-γ-pyrone (VIII) was oxidised with chromic acid in acetic acid at 55° when a product was obtained which was insoluble in alkali and which developed a red colour when heated with zinc dust and sodium hydroxide solution. 2'-Phenyl-1,2-(9,10-dihydro-9,10-dioxo-)anthra-γ-pyrone (IX) structure has therefore been assigned to this product.



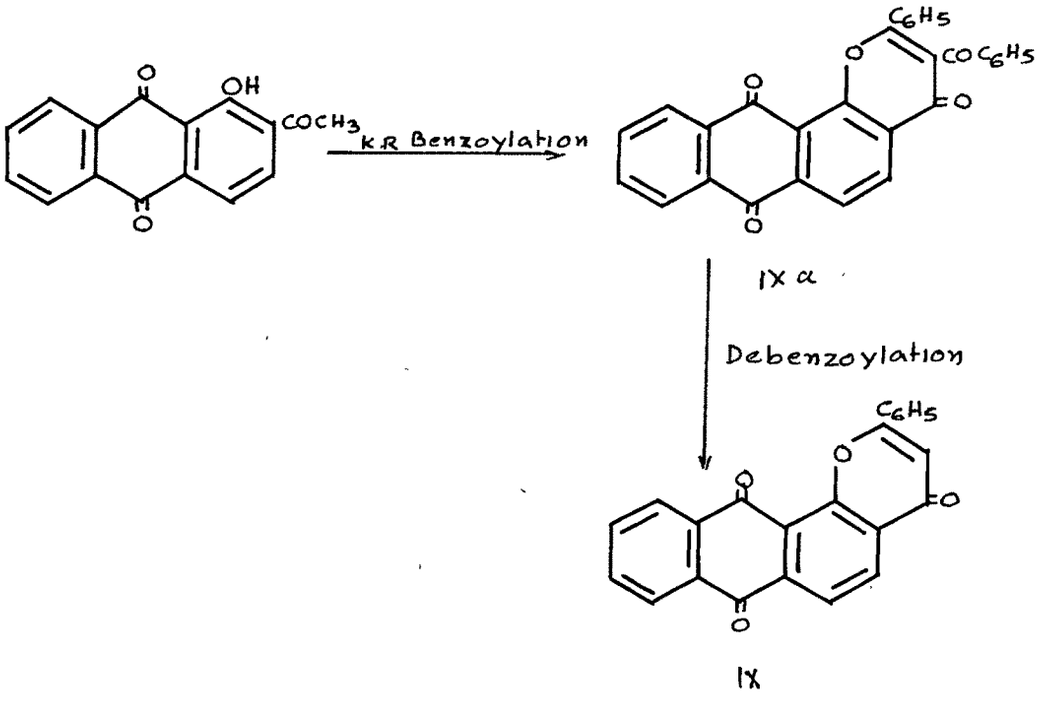
VIII IX

Kostanecki-Robinson acetylation and benzoylation of 2-acetyl-1-hydroxy-anthraquinone.

Having obtained the above α and γ-pyrone derivatives by the oxidation of the corresponding anthracene derivatives, it was thought of interest to see whether the same products could be obtained by the Kostanecki-Robinson reaction on 2-acetyl-1-hydroxyanthraquinone as no Kostanecki-Robinson reaction has so far been attempted on the anthraquinone derivatives.

2-Acetyl-1-hydroxy anthraquinone obtained as described before, on acetylation under the conditions of the Kostanecki-Robinson reaction gave a dark coloured product in poor yield from which no pure product with definite melting point could be isolated.

However, on Kostanecki-Robinson benzoylation of 2-acetyl-1-hydroxyanthraquinone with sodium benzoate and benzoic anhydride a product was obtained which has been assigned the 2'-phenyl-3'-benzoyl-1,2-(9,10-dihydro-9,10-dioxo-) anthra-γ-pyrone (IXα) structure. On heating with sulphuric acid it gave a product which has been assigned the 2'-phenyl-1,2- (9,10-dihydro-9,10-dioxo-) anthra-γ-pyrone (IX) structure. It was found on direct comparison to be the same as the product obtained on oxidation of 2'-phenyl-1,2-anthra-γ-pyrone, described earlier.


OH
COCH3
KR Benzoylation
C6H5
COC6H5
O
O
O
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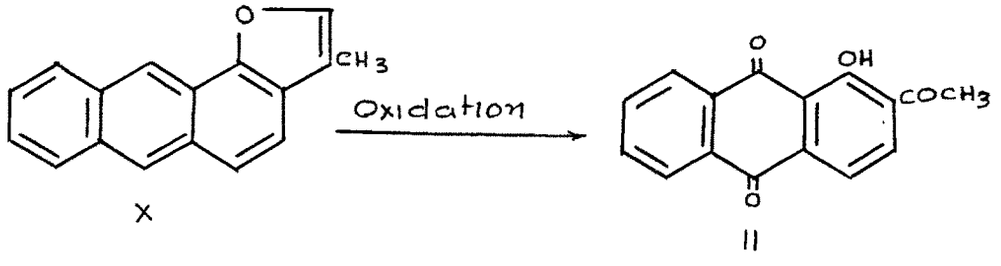
O
O
IX a
Debenzoylation
C6H5
O
O
O
O
IX

3-Methyl-(9,10-dihydro-9,10-dioxo-)anthra [1,2-b] furan.

3-Methyl-anthra [1,2-b] furan (X) was dissolved in acetic acid and oxidised with chromic acid in acetic acid at 60°. The product obtained was soluble in sodium hydroxide solution and also gave a red colour with zinc dust and alkali. It was found on direct comparison to be 2-acetyl-1-hydroxyanthraquinone.

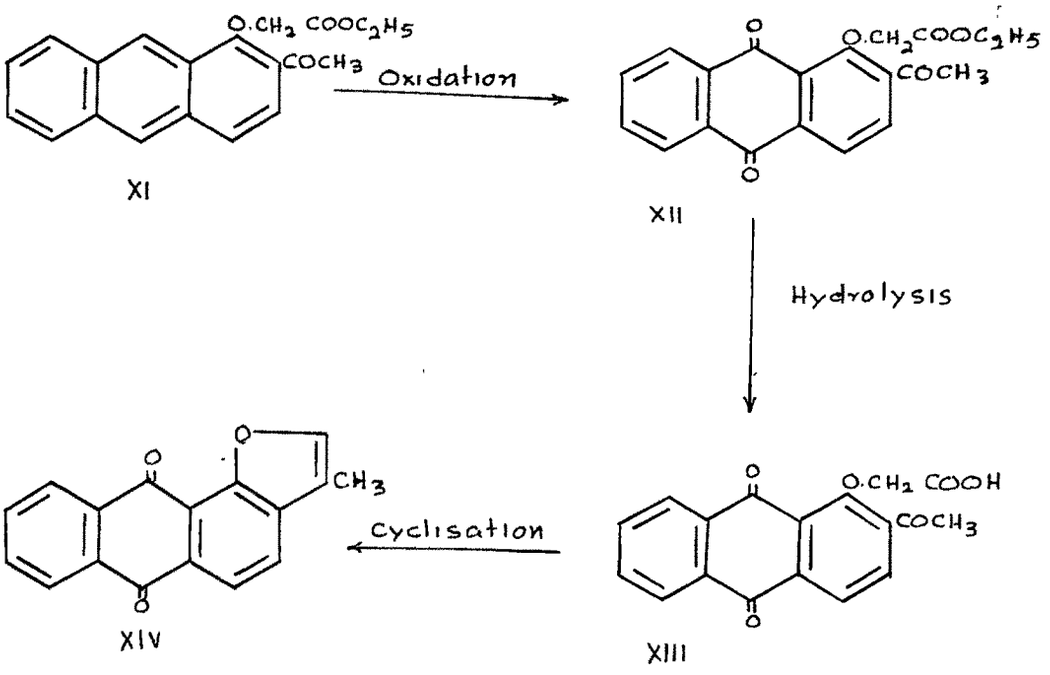


X II

As the oxidation of the 3-methyl-anthra [1,2-b] furan failed to give the corresponding anthraquinone derivative, because of the susceptibility of the furan ring to oxidation, the desired compound was synthesised as follows:

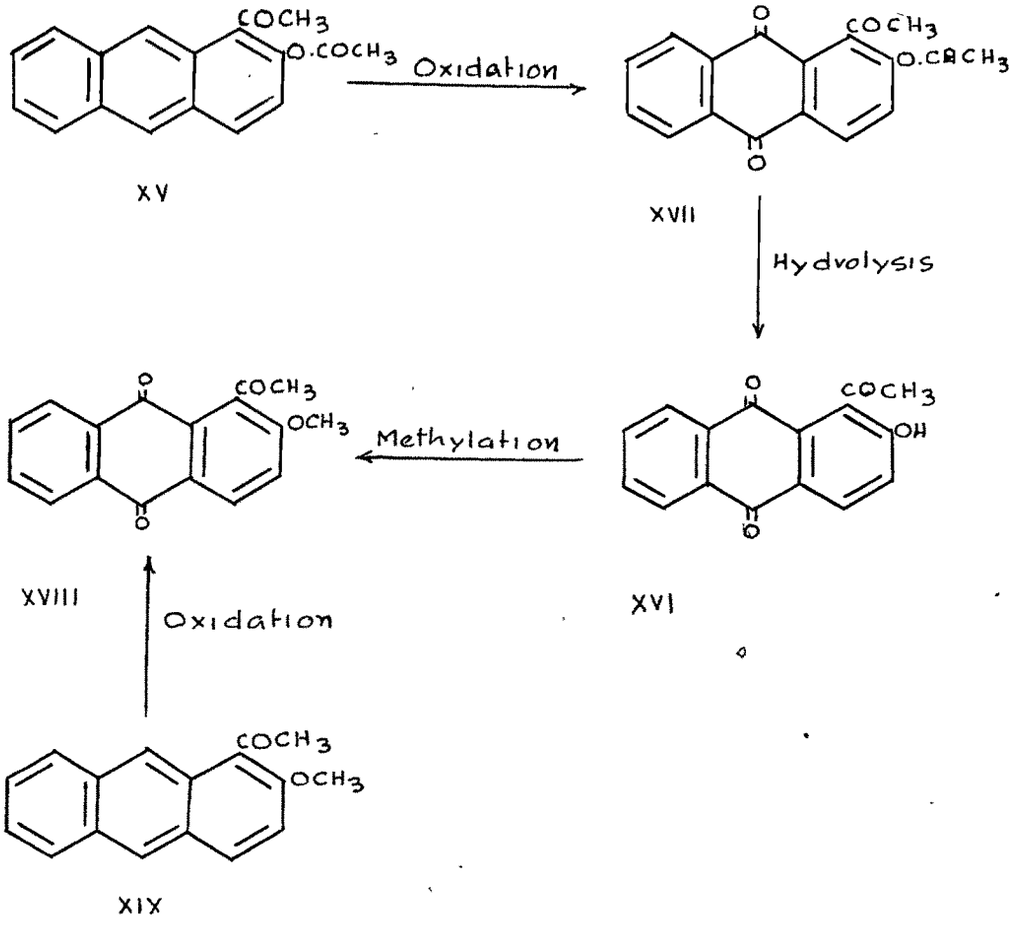
Ethyl-2-acetyl-1-anthroxyacetate (XI) prepared as described in chapter IV was subjected to oxidation with chromic acid in acetic acid. The product obtained on working up the reaction mixture was found to be insoluble in alkali and it gave a positive test for an anthraquinone derivative with zinc and alkali. It was therefore assigned

ethyl 2-acetyl-1-(9,10-dihydro-9,10-dioxo-)anthroxyacetate (XII) structure. On hydrolysis with alkali it furnished the corresponding acid (XIII) which on simultaneous ring closure and decarboxylation by boiling with acetic anhydride in the presence of anhydrous sodium acetate, furnished ~~the~~ 3-methyl-(9,10-dihydro-9,10-dioxo-)anthra [1,2-b] furan (XIV).



1-Acetyl-2-hydroxyanthraquinone.

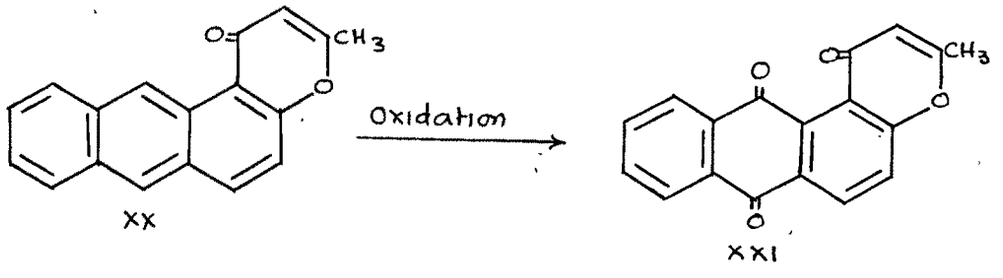
1-Acetyl-2-acetoxyanthracene (XV) was oxidised with chromic acid in acetic acid by keeping it overnight at room temperature. The crude product obtained was purified through its acetyl derivative (XVII). It (XVI) gave a 2:4-dinitrophenylhydrazone and also gave green colouration with alcoholic ferric chloride. On methylation with dimethyl sulphate, in presence of anhydrous potassium carbonate in acetone, it gave 1-acetyl-2-methoxyanthraquinone (XVIII), identical with the product obtained on oxidation of 1-acetyl-2-methoxyanthracene (XIX) in acetic acid with sodium dichromate at room temperature.



Attempts to synthesise the α-pyrone derivative by condensation of 2-hydroxyanthraquinone with ethyl acetoacetate either in presence of 80 % sulphuric acid or phosphorus pentoxide did not succeed.

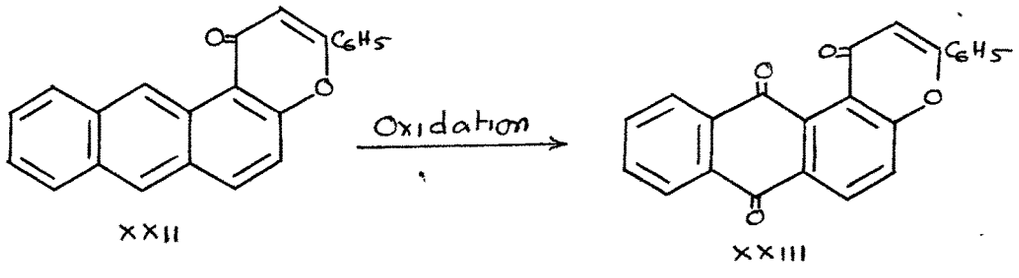
2'-Methyl- and 2'-phenyl-2,1-(9,10-dihydro-9,10-dioxo-) anthra-γ-pyrones.

2'-Methyl-2,1-anthra-γ-pyrone (XX) in acetic acid was oxidised with sodium dichromate at room temperature. The product obtained was insoluble in alkali and developed a red colour when warmed with zinc dust and sodium hydroxide solution. 2'-Methyl-2,1-(9,10-dihydro-9,10-dioxo-) anthra-γ-pyrone (XXI) structure has been assigned to this product.



XX XXI

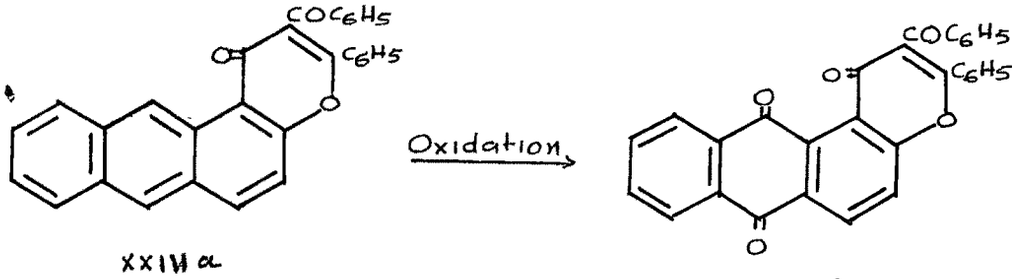
2'-Phenyl-2,1-anthra-γ-pyrone (XXII) on oxidation under similar conditions furnished a product which was insoluble in alkali and gave a red colour when warmed with zinc dust and alkali. 2'-Phenyl-2,1-(9,10-dihydro-9,10-dioxo-) anthra-γ-pyrone (XXIII) structure has been assigned to this product.



XXII XXIII

2'-Phenyl-3'-benzoyl-2,1-(9,10-dihydro-9,10-dioxo) anthra-γ-pyrone.

2'-Phenyl-3'-benzoyl-2,1-anthra-γ-pyrone (XXIIIα) in acetic acid was oxidised with sodium dichromate at room temperature. The product obtained was insoluble in alkali and developed a red colour when warmed with zinc dust and sodium hydroxide solution. 2'-Phenyl-3'-benzoyl-2,1-(9,10-dihydro-9,10-dioxo-)anthra-γ-pyrone (XXIIIβ) structure has been assigned to this product.



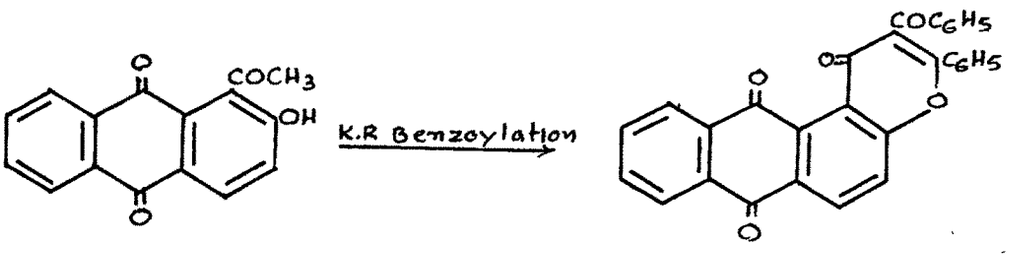
XXIII α XXIII β

Kostanecki-Robinson acetylation and benzoylation of 1-acetyl-2-hydroxyanthraquinone.

1-Acetyl-2-hydroxy anthraquinone obtained as described before on acetylation under the conditions of Kostanecki-Robinson reaction gave a dark brown coloured product in poor yield, from which no pure product with definite m.p. could be isolated.

However, on Kostanecki-Robinson benzoylation of 1-acetyl-2-hydroxyanthraquinone with sodium benzoate and benzoic anhydride a product was obtained which has been

assigned the 2'-phenyl-3'-benzoyl-2,1-(9,10-dihydro-9,10-dioxo)-anthra-γ-pyrone (XXIIIc) structure, as it was found on direct comparison to be the same as the product obtained on oxidation of 2'-phenyl-3'-benzoyl-2,1-anthra-γ-pyrone, described before.

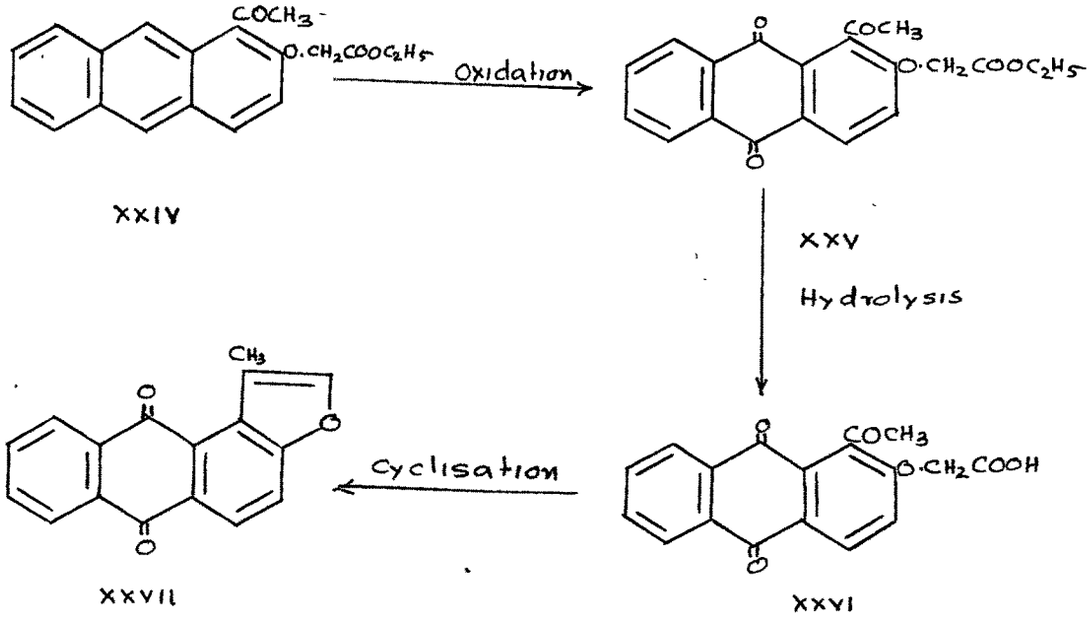


XXIII c

Synthesis of 1-methyl-(9,10-dihydro-9,10-dioxo-) anthra [2,1-b] furan.

As the furan ring is susceptible to oxidation the title compound was synthesised as follows :

A solution of ethyl-1-acetyl-2-anthroxyacetate (XXIV) in warm acetic acid was treated with sodium dichromate and stirred for two hours at room temperature. The product obtained on working up the reaction mixture, was found to be insoluble in alkali and also gave a positive test for an anthraquinone derivative with zinc and alkali. Therefore the product formed was ethyl-1-acetyl-2-(9,10-dihydro-9,10-dioxo-) anthroxyacetate (XXV). This ester on hydrolysis with alkali furnished the corresponding acid (XXVI) which on simultaneous ring closure and decarboxylation by heating with acetic anhydride and anhydrous sodium acetate, gave 1-methyl-(9,10-dihydro-9,10-dioxo-) anthra [2,1-b] furan (XXVII).



EXPERIMENTAL

Oxidation of 2-acetyl-1-acetoxyanthracene : 2-Acetyl-1-acetoxyanthraquinone.

Chromic acid (2 g. in 10 ml. 90% acetic acid) was added slowly with constant stirring to a solution of 2-acetyl-1-acetoxyanthracene (0.5 g.) in acetic acid (25 ml.). The solution was maintained at 60-65° in a water bath and stirred at this temperature for 3 hours. It was left overnight at room temperature, added to water (300 ml.) and kept in a refrigerator. The yellow shining product (0.2 g.) which separated was dissolved after drying, in acetic anhydride (10 ml.) and pyridine (1 ml.) and kept for 24 hours at room temperature. The product which separated on adding the reaction mixture to water was filtered washed with water and crystallised from dilute alcohol in yellow needles, m.p. 167-168°.

It gave red colour when warmed with zinc dust and dilute sodium hydroxide.

Analysis :

10.60 mg. of the substance gave 27.36 mg. of carbon dioxide and 3.42 mg. of water.

Found : C, 70.43 % ; H, 3.61 %.

$C_{18}H_{12}O_5$ requires : C, 70.13 % ; H, 3.90 %.

2-Acetyl-1-hydroxyanthraquinone.

2-Acetyl-1-acetoxyanthraquinone (0.1 g.) was kept with concentrated sulphuric acid (5 ml.) for 4 hours.

The solution was then added to ice and the precipitated solid crystallised from dilute acetic acid (charcoal) in reddish yellow needles, m.p. 166°. Spruit (loc.cit.) gave m.p.166°.

It gave reddish brown colouration with alcoholic ferric chloride.

Analysis :

7.64 mg. of the substance gave 20.18 mg. of carbon dioxide and 2.66 mg. of water.

Found : C, 72.09 % ; H, 3.90 %.

$C_{16}H_{10}O_4$ requires : C, 72.18 % ; H, 3.76 %.

The 2:4-dinitrophenylhydrazone was prepared as usual. It crystallised from glacial acetic acid in reddish needles, m.p.276°.

Analysis :

5.524 mg. of the substance gave 0.626 c.c. of nitrogen measured at 31°C and 756 mm.

Found : N, 12.66 %.

$C_{22}H_{14}N_4O_7$ requires: N, 12.56 %.

Attempted Friedel-Crafts acetylation of 1-hydroxyanthraquinone.

A solution of 1-hydroxyanthraquinone (2.24 g.) and acetic anhydride (1.3 g.) in nitrobenzene (75 ml.) was mixed with a solution of anhydrous aluminium chloride (2.7 g.) in nitrobenzene (15 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 product obtained was extracted with alkali. The alkaline extract on acidification gave a product which crystallised from alcohol (charcoal) in orange yellow needles, m.p. and mixed m.p. with 1-hydroxyanthraquinone was 191°.

The reaction mixture as above, was heated at 140° for four hours. On working up as usual, a solid was obtained which crystallised from alcohol in orange yellow needles, m.p. and mixed m.p. with 1-hydroxyanthraquinone was 191°.

Attempted Fries migration of 1-acetoxyanthraquinone.

An intimate mixture of 1-acetoxyanthraquinone (0.53 g.) and anhydrous aluminium chloride (0.6 g.) was heated in an oil bath at 140° for four hours. The reaction mixture was then treated with ice and hydrochloric acid and the product obtained extracted repeatedly with alkali. The solid obtained on acidification of the alkaline extract, crystallised from alcohol (charcoal) in orange yellow needles, m.p. 191°. Mixed m.p. with 1-hydroxyanthraquinone was not depressed.

Attempted condensation of 1-hydroxyanthraquinone with ethyl acetoacetate :

(i) With sulphuric acid as the condensing agent :-

1-Hydroxyanthraquinone (0.45 g.) and ethyl acetoacetate (0.3 g.) were mixed together and sulphuric acid (80 % ; 10 ml.) was added. The reaction mixture was kept

at room temperature for 24 hours and then poured on ice. The separated solid was filtered and crystallised from alcohol (charcoal) in orange yellow needles, m.p. 191°. The mixed m.p. with 1-hydroxyanthraquinone was not depressed.

With concentrated sulphuric acid as the condensing agent instead of 80 % sulphuric acid and when the reaction mixture was heated on a steam bath for two hours after keeping it at room temperature overnight, ~~similar~~ unchanged product was obtained.

(ii) With phosphorus pentoxide as the condensing agent :-

To a mixture of 1-hydroxyanthraquinone (0.45 g.) and ethyl acetoacetate (0.3 g.), phosphorus pentoxide (1 g.) was gradually added with stirring. The reaction mixture, protected from moisture, was then heated on a steam bath for an hour. Crushed ice was then added and the residue taken up in ether. The ethereal layer was repeatedly washed with alkali and then with water. No product was obtained on removal of ether. The alkaline extract, on acidification, gave a product which crystallised from alcohol in orange yellow needles, m.p. 191°. The mixed m.p. with 1-hydroxyanthraquinone was not depressed.

(iii) With aluminium chloride as the condensing agent :-

To a mixture of 1-hydroxyanthraquinone (1.2 g.), ethyl acetoacetate (0.65 g.) in nitrobenzene (30 ml.), anhydrous aluminium chloride (0.73 g.) dissolved in

nitrobenzene (10 ml.) was added. The reaction mixture, protected from moisture, was heated in an oil bath at 120-130° for four hours. The nitrobenzene was then steam distilled and the residue obtained crystallised from alcohol (charcoal) in orange yellow needles, m.p. 191°. Mixed m.p. with 1-hydroxy-anthraquinone was not depressed.

Oxidation of 4'-methyl-1,2-anthra-α-pyrone : 4'-Methyl-1,2-(9,10-dihydro-9,10-dioxo-) anthra-α-pyrone.

To a solution of 4'-methyl-1,2-anthra-α-pyrone (0.1 g.) in acetic acid (25 ml.), sodium dichromate (0.5 g.) was added during 10 minutes with constant stirring. Some solid product immediately began separating on adding sodium dichromate. The reaction mixture was stirred for 30 minutes in all. It was then filtered and washed with water. The residue, after washing with cold dilute alkali was crystallised from acetic acid (charcoal) in reddish yellow shining needles, m.p. 319-320°.

It gave red colour when warmed with zinc dust and dilute sodium hydroxide.

Analysis :

3.442 mg. of the substance gave 9.374 mg. of carbon dioxide and 0.964 mg. of water.

Found : C, 74.32 % ; H, 3.13 %.

$C_{18}H_{10}O_4$ requires : C, 74.49 % ; H, 3.45 %.

The alkali washings did not give any product on acidification.

Oxidation of 2'-methyl-1,2-anthra-γ-pyrone :
2'-Methyl-1,2-(9,10-dihydro-9,10-dioxo-) anthra-γ-pyrone.

2'-Methyl-1,2-anthra-γ-pyrone (0.1 g.) was dissolved in acetic acid (15 ml.) and sodium dichromate (2 g.) was added in portions with continuous stirring. After stirring for two hours the reaction mixture was left overnight. The product which separated was filtered and washed with cold dilute alkali. The residue was crystallised from acetic acid (charcoal) in yellow clusters of small needles. It was recrystallised from benzene in small pale yellow needles. It starts decomposing at 283° and melts at 293°.

It gave red colour when warmed with zinc dust and dilute sodium hydroxide solution.

Analysis :

10.16 mg. of the substance gave 27.80 mg. of carbon dioxide and 3.62 mg. of water.

Found : C, 74.66 % ; H, 3.99 %.

$C_{18}H_{10}O_4$ requires : C, 74.49 % ; H, 3.45 %.

The alkali washings did not give any product on acidification.

Oxidation of 2'-phenyl-1,2-anthra-γ-pyrone :
2'-Phenyl-1,2-(9,10-dihydro-9,10-dioxo-) anthra-γ-pyrone.

2'-Phenyl-1,2-anthra-γ-pyrone (0.1 g.) was dissolved in acetic acid (20 ml.) and heated to 55° in a water bath. Chromic acid solution (0.5 g. dissolved in 5 ml.

of 90 % acetic acid) was added gradually with constant stirring. The solution was stirred at this temperature for 3 hours and then left overnight at room temperature. It was then filtered and the filtrate diluted with water. The solid which separated was filtered and washed with cold dilute alkali and then crystallised from acetic acid (charcoal) in small shining yellow needles, m.p. 325°.

On warming with zinc dust and alkali it gave bluish red, then violet and finally, after some time, a red colour.

Analysis :

10.40 mg. of the substance gave 30.04 mg. of carbon dioxide and 3.42 mg. of water.

Found : C, 78.83 % ; H, 3.68 %.

$C_{23}H_{12}O_4$ requires : C, 78.41 % ; H, 3.41 %.

Attempted Kostanecki-Robinson acetylation of 2-acetyl-1-hydroxyanthraquinone.

2-Acetyl-1-hydroxyanthraquinone (1 g.) was heated with freshly fused and powdered sodium acetate (3 g.) and acetic anhydride (10 ml.) in an oil bath at 180-190° for 8 hours. The reaction mixture was then poured into an excess of cold water and stirred for 2 hours when a dark reddish brown solid was obtained from which no pure product with definite m.p. could be isolated.

Kostanecki-Robinson benzoylation of 2-acetyl-1-hydroxyanthraquinone : 2'-Phenyl-3'-benzoyl-1,2-(9,10-dihydro-9,10-dioxo-)-anthra-γ-pyrone.

An intimate mixture of 2-acetyl-1-hydroxy-anthraquinone (0.6 g.), freshly fused and powdered sodium benzoate (1.8 g.) and benzoic anhydride (6 g.) was heated in an oil bath at 180-190° for 8 hours. The reaction mixture was then treated repeatedly with hot water to remove sodium benzoate and benzoic anhydride and finally washed with sodium bicarbonate solution. The residue crystallised from acetic acid (charcoal) in shining yellow needles, m.p. 275-276°. Yield 0.15 g.

Analysis :

8.68 mg. of the substance gave 24.98 mg. of carbon dioxide and 3.04 mg. of water.

Found : C, 78.53 % ; H, 3.92 %.

$C_{30}H_{16}O_5$ requires : C, 78.94 % ; H, 3.51 %.

2'-Phenyl-1,2-(9,10-dihydro-9,10-dioxo-)anthra-γ-pyrone.

2'-Phenyl-3'-benzoyl-1,2-(9,10-dihydro-9,10-dioxo)-anthra-γ-pyrone (0.1 g.) was treated with sulphuric acid (7 ml. Conc. H_2SO_4 + 2 ml. acetic acid + 1 ml. water) and heated gently on a wiregauze for 2 hours. The reaction mixture was then cooled and added to crushed ice. The separated solid was filtered, washed with a dilute solution of sodium hydroxide and crystallised from acetic acid (charcoal) in shining yellow needles, m.p. 325°. The mixed m.p. with 2'-phenyl-1,2-(9,10-dihydro-9,10-dioxo-)anthra-γ-pyrone, described before was not depressed.

Oxidation of 3-methyl-anthra [1,2-b] furan.

3-Methyl-anthra 1,2-b furan (0.1 g.) was dissolved in acetic acid (10 ml.) and chromic acid solution (0.5 g. dissolved in 5 ml. of 90% acetic acid) was added gradually with constant stirring. The reaction mixture was stirred at 60° for 2 hours and then left overnight at room temperature. It was then added to water and the residue taken up in ether. The ethereal layer was washed with alkali and finally with water. No product could be isolated on removal of ether. The sodium hydroxide extract was acidified and extracted with ether. The product obtained on removal of ether crystallised from dilute acetic acid in reddish needles, m.p. 166°. Mixed m.p. with 2-acetyl-1-hydroxyanthraquinone described earlier was not depressed.

Oxidation of ethyl-2-acetyl-1-anthroxyacetate : Ethyl-2-acetyl-1-(9,10-dihydro-9,10-dioxo-)anthroxyacetate.

Ethyl-2-acetyl-1-anthroxyacetate (0.5 g.) was dissolved in acetic acid (50 ml.) and chromic acid solution (2.5 g. in 25 ml. 90% acetic acid) was added. The reaction mixture was kept at 60° for 3 hours and then added to water. The crystalline product which separated on keeping it overnight was filtered, washed with alkali and recrystallised from dilute acetic acid (charcoal) in yellow needles, m.p. 145-146°. Yield 0.25 g.

Analysis :

10.12 mg. of the substance gave 25.24 mg. of carbon dioxide and 4.14 mg. of water.

Found : C, 68.04 % ; H, 4.58 %.

$C_{20}H_{16}O_6$ requires : C, 68.19 % ; H, 4.55 %.

2-Acetyl-1-(9,10-dihydro-9,10-dioxo-)anthroxyacetic acid.

The above ester (0.25 g.) was heated with sodium hydroxide solution (25 ml. ; 4%) at 50° in a water bath till it went in solution. The product obtained on acidification crystallised from dilute acetic acid (charcoal) in yellow shining needles, m.p.189-190°. Yield 0.2 g.

Analysis :

10.10 mg. of the substance gave 24.50 mg. of carbon dioxide and 3.56 mg. of water.

Found : C, 66.20 % ; H, 3.94 %.

$C_{18}H_{12}O_6$ requires : C, 66.68 % ; H, 3.70 %.

3-Methyl-(9,10-dihydro-9,10-dioxo-)anthra [1,2-b] furan.

A mixture of the above acid (0.2 g.), acetic anhydride (10 ml.) and freshly fused and powdered sodium acetate (1 g.) was boiled for 45 minutes. The reaction mixture was then added to cold water and the product which separated was washed with dilute sodium hydroxide. It crystallised from dilute acetic acid (charcoal) in

reddish yellow shining needles, m.p.226-227°.

Analysis :

10.56 mg. of the substance gave 30.14 mg. of carbon dioxide and 3.48 mg. of water.

Found : C, 77.91 % ; H, 3.68 %.

$C_{17}H_{10}O_3$ requires : C, 77.85 % ; H, 3.82 %.

Oxidation of 1-acetyl-2-acetoxyanthracene : 1-Acetyl-2-acetoxyanthraquinone.

1-Acetyl-2-acetoxyanthracene (0.1 g.) was dissolved in acetic acid (10 ml.) and chromic acid solution (0.5 g. dissolved in 5 ml. of 90% acetic acid) was added gradually with constant stirring. After stirring for 5 hours at room temperature the reaction mixture was left overnight. On dilution with cold water a pale yellow solid separated which was washed with alkali and dried. Yield 0.05 g. This product was then dissolved in acetic anhydride (5 ml.) and pyridine (1 ml.) and kept for 24 hours. The solid which separated on addition to water crystallised from dilute alcohol (charcoal) in yellowish white needles, m.p.200-202°.

It gave red colour when warmed with zinc dust and dilute sodium hydroxide solution.

Analysis :

10.62 mg. of the substance gave 27.30 mg. of carbon dioxide and 3.90 mg. of water.

Found : C, 70.15 % ; H, 4.11 %.

$C_{18}H_{12}O_5$ requires : C, 70.13 % ; H, 3.90 %.

1-Acetyl-2-hydroxyanthraquinone.

1-Acetyl-2-acetoxyanthraquinone (0.25 g.) was kept for 2 hours with concentrated sulphuric acid (10 ml.) and then added to crushed ice. The product obtained crystallised from dilute acetic acid (charcoal) in brownish white needles, m.p.249-250°.

It gave a pale green colouration with alcoholic ferric chloride and a red colouration when warmed with zinc dust and dilute sodium hydroxide solution.

Analysis :

9.90 mg. of the substance gave 26.10 mg. of carbon dioxide and 3.20 mg. of water.

Found : C, 71.95 % ; H, 3.62 %.

$C_{16}H_{10}O_4$ requires : C, 72.18 % ; H, 3.76 %..

The 2:4-dinitrophenylhydrazone prepared as usual crystallised from alcohol in reddish needles, m.p.260°.

Analysis :

10.40 mg. of the substance gave 1.206 c.c. of nitrogen measured at 34°C and 754 mm.

Found : N, 12.80 %.

$C_{22}H_{14}N_4O_7$ requires : N, 12.56 %.

Attempted Friedel-Crafts acetylation of 2-hydroxyanthraquinone.

A mixture of 2-hydroxyanthraquinone (1.12 g.) and acetic anhydride (0.65 g.) in nitrobenzene (100 ml.) was mixed with a solution of anhydrous aluminium chloride (1.35 g.) in nitrobenzene (10 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 product obtained was extracted with alkali. The alkaline extract on acidification gave a product which crystallised from acetic acid in yellow

needles, m.p. and mixed m.p. with 2-hydroxyanthraquinone was 303°.

The reaction mixture as above, was heated at 140° for four hours. On working up as usual, a solid was obtained which crystallised from acetic acid in yellow needles, m.p. and mixed m.p. with 2-hydroxyanthraquinone was 303°.

Attempted Fries migration of 2-acetoxyanthraquinone.

An intimate mixture of 2-acetoxyanthraquinone (0.53 g.) and anhydrous aluminium chloride (0.6 g.) was heated in an oil bath at 140° for four hours. The reaction mixture was then treated with ice and hydrochloric acid and the product obtained extracted repeatedly with alkali. The solid obtained on acidification of the alkaline extract, crystallised from acetic acid (charcoal) in yellow needles, m.p. 303°. Mixed m.p. with 2-hydroxyanthraquinone was not depressed.

Oxidation of 1-acetyl-2-methoxyanthracene : 1-Acetyl-2-methoxyanthraquinone.

1-Acetyl-2-methoxyanthracene (0.5 g.) was dissolved by slight warming in acetic acid (25 ml.) and sodium dichromate (2 g.) was added in portions with constant stirring. The reaction mixture was stirred for 2 hours and then added to cold water (200 ml.). The product which separated was filtered, washed with alkali and crystallised first from dilute acetic acid (charcoal) and then from dilute alcohol in pale yellow needles, m.p. 215-216°.

It gave red colour when warmed with zinc dust and

dilute sodium hydroxide solution.

Analysis :

3.320 mg. of the substance gave 8.904 mg. of carbon dioxide and 1.216 mg. of water.

Found : C, 73.2 % ; H, 4.1 %.

$C_{17}H_{12}O_4$ requires : C, 72.9 % ; H, 4.3 %.

The same product was obtained when 1-acetyl-2-hydroxyanthraquinone (0.1 g.) was methylated in acetone (50 ml.) solution with dimethyl sulphate (0.06 g.) in presence of potassium carbonate (1 g.) by refluxing on a steam bath for 15 hours.

Attempted condensation of 2-hydroxyanthraquinone with ethyl acetoacetate :

(i) With sulphuric acid as the condensing agent :-

2-Hydroxyanthraquinone (0.45 g.) and ethyl acetoacetate (0.3 g.) were mixed together and sulphuric acid (80 % ; 10 ml.) was added. The reaction mixture was kept at room temperature for 24 hours and then poured on ice. The separated solid was filtered and crystallised from acetic acid (charcoal) in yellow needles, m.p. 303°. The mixed m.p. with 2-hydroxyanthraquinone was not depressed.

(ii) With phosphorus pentoxide as the condensing agent :-

To a mixture of 2-hydroxyanthraquinone (0.45 g.) and ethyl acetoacetate (0.3 g.), phosphorus pentoxide (1 g.) was gradually added with stirring. The reaction

mixture, protected from moisture, was then heated on a steam bath for two hours. Crushed ice was then added and the residue taken up in ether. The ethereal layer was repeatedly washed with alkali and then with water. No product was obtained on removal of ether. The alkaline extract, on acidification, gave a solid which crystallised from acetica acid in yellow needles, m.p. 303°. The mixed m.p. with 2-hydroxyanthraquinone was not depressed.

Oxidation of 2'-methyl-2,1-anthra-γ-pyrone : 2'-Methyl-2,1-(9,10-dihydro-9,10-dioxo-) anthra-γ-pyrone.

2'-Methyl-2,1-anthra-γ-pyrone (0.1 g.) was dissolved in acetic acid (15 ml.) and sodium dichromate (2 g.) was added in portions with continuous stirring. The reaction mixture was stirred for 2 hours and then left overnight. The product which separated on adding the reaction mixture to cold water was washed with cold dilute alkali. The residue thus obtained crystallised from dilute acetic acid (charcoal) in yellowish white needles, m.p. 251°.

It gave red colour when warmed with zinc dust and dilute sodium hydroxide solution.

Analysis :

5.382 mg. of the substance gave 14.636 mg. of carbon dioxide and 1.626 mg. of water.

Found : C, 74.21 % ; H, 3.38 %.

$C_{18}H_{10}O_4$ requires : C, 74.49 % ; H, 3.45 %.

The alkali washings did not give any product on acidification.

Oxidation of 2'-phenyl-2,1-anthra-γ-pyrone : 2'-Phenyl-2,1-(9,10-dihydro-9,10-dioxo-) anthra-γ-pyrone.

2'-Phenyl-2,1-anthra-γ-pyrone (0.1 g.) was dissolved in acetic acid (10 ml.) and chromic acid solution (0.5 g. dissolved in 5 ml. of 90 % acetic acid) was added gradually with constant stirring. Immediately some solid product began to separate. The solution was stirred for two hours and then added to cold water (250 ml.) and kept in a refrigerator. The next day, the yellow solid which separated was filtered, washed with cold dilute alkali and crystallised from alcohol (charcoal) in needles, m.p. 266-267°.

It gave red colour when warmed with zinc dust and dilute sodium hydroxide solution.

Analysis :

10.50 mg. of the substance gave 30.02 mg. of carbon dioxide and 3.58 mg. of water.

Found : C, 78.01 % ; H, 3.81 %.

$C_{23}H_{12}O_4$ requires : C, 78.41 % ; H, 3.41 %.

The alkali washings did not give any product on acidification.

Oxidation of 2'-phenyl-3'-benzoyl-2,1-anthra-γ-pyrone : 2'-Phenyl-3'-benzoyl-2,1-(9,10-dihydro-9,10-dioxo-) anthra-γ-pyrone.

2'-Phenyl-3'-benzoyl-2,1-anthra-γ-pyrone (0.1 g.) was dissolved in acetic acid (25 ml.) by warming and sodium dichromate (1 g.) was added in portions with continuous stirring. The reaction mixture was stirred for

2 hours and then left overnight. The product which separated on adding the reaction mixture to cold water was washed with cold dilute alkali. The residue thus obtained crystallised from dilute acetic acid (charcoal) in small yellow needles, m.p. 253 - 254°.

It gave red colour when warmed with zinc dust and dilute sodium hydroxide solution.

Analysis :

4.122 mg. of the substance gave 11.882 mg. of carbon dioxide and 1.282 mg. of water.

Found : C, 78.66 % ; H, 3.48 %.

$C_{30}H_{16}O_5$ requires: C, 78.94 % ; H, 3.51 %.

Kostanecki-Robinson acetylation of 1-acetyl-2-hydroxyanthraquinone.

1-Acetyl-2-hydroxyanthraquinone (1 g.) was heated with freshly fused and powdered sodium acetate (3 g.) and acetic anhydride (10 ml.) in an oil bath at 180-190° for 8 hours. The reaction mixture was then added to an excess of cold water and left overnight. From the dark brown solid obtained no pure crystalline product with definite m.p. could be isolated.

Kostanecki-Robinson benzoylation of 1-acetyl-2-hydroxyanthraquinone : 2'-Phenyl-3'-benzoyl-2,1-(9,10-dihydro-9,10-dioxo-)anthra-γ-pyrone.

An intimate mixture of 1-acetyl-2-hydroxy-anthraquinone (0.8 g.) freshly fused and powdered sodium benzoate (2.4 g.) and benzoic anhydride (8 g.) was

heated in an oil bath at 180-190° for 8 hours. The reaction mixture was then treated repeatedly with hot water to remove sodium benzoate and benzoic anhydride and finally washed with sodium bicarbonate solution. The residue obtained was dried and treated with concentrated sulphuric acid (10 ml.) and left overnight at room temperature. The solution was then added to crushed ice. The separated solid was filtered and washed with dilute sodium hydroxide solution. The residue crystallised from acetic acid (charcoal) in yellow needles, m.p. 253-254°. / yield 0.2 g. The mixed m.p. with 2'-phenyl-3'-benzoyl-2,1-(9,10-dihydro-9,10-dioxo-)anthra-γ-pyrone, described before, was not depressed.

Oxidation of ethyl-1-acetyl-2-anthroxyacetate :

Ethyl-1-acetyl-2-(9,10-dihydro-9,10-dioxo-)anthroxyacetate.

Ethyl-1-acetyl-2-anthroxyacetate (0.3 g.) was dissolved in warm acetic acid (30 ml.) and sodium dichromate (3 g.) was added in portions with continuous stirring. The reaction mixture was stirred for 2 hours and then added to cold water. The product which separated was washed with alkali and crystallised from alcohol (charcoal) in straw coloured needles, m.p. 164-165°. Yield 0.15 g.

Analysis :

10.52 mg. of the substance gave 26.36 mg. of carbon dioxide and 4.48 mg. of water.

Found : C, 68.39 % ; H, 4.76 %.

$C_{20}H_{16}O_6$ requires : C, 68.19 % ; H, 4.55 %.

1-Acetyl-2-(9,10-dihydro-9,10-dioxo-)anthroxyacetic acid.

The above ester (0.15 g.) was hydrolysed by keeping it with sodium hydroxide solution (10 ml. ; 4 %) overnight at room temperature. The solution was then filtered and the residue was treated with water to dissolve the sodium salt of the acid which had separated. The product obtained on acidification of the combined filtrates, crystallised from dilute alcohol (charcoal) in yellowish green shining plates, m.p.256-257° (efferv.). Yield 0.1 g.

Analysis :

10.22 mg. of the substance gave 24.84 mg. of carbon dioxide and 3.46 mg. of water.

Found : C, 66.33 % ; H, 3.79 %.

$C_{18}H_{12}O_6$ requires : C, 66.68 % ; H, 3.70 %.

1-Methyl-(9,10-dihydro-9,10-dioxo-)anthra[2,1-b]furan.

A mixture of the above acid (0.2 g.), acetic anhydride (10 ml.) and freshly fused and powdered sodium acetate (1 g.) was boiled for 45 minutes. The reaction mixture was then added to cold water and the product which separated was washed with dilute sodium hydroxide and crystallised from alcohol (charcoal) in pale yellow plates, m.p. 208-209°.

Analysis :

9.86 mg. of the substance gave 27.98 mg. of carbon dioxide and 3.42 mg. of water.

Found : C, 77.43 % ; H, 3.88 %.

$C_{17}H_{10}O_3$ requires : C, 77.85 % ; H, 3.82 %.