CHAPTER III

Synthesis of some anthra α-and anthra γ-pyrones.

Theoretical

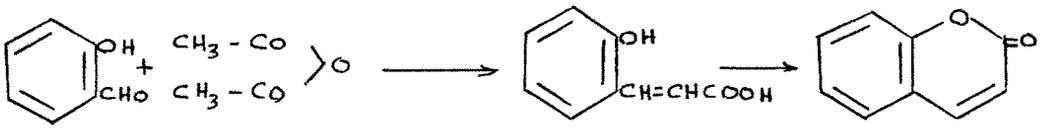
The α- and γ-pyrones found extensively in nature are the benzo α-pyrones or coumarins and the 2-phenyl benzo γ-pyrones or flavones. The coumarin derivatives are abundant in grasses, orchids, legumes and citrus fruits whereas the flavones and isoflavones are responsible for the ivory to yellow colouring matter of plants. The α- and γ-pyrone derivatives have also gained importance in recent years because of their important physiological properties. For example, Dicumarol or 3,3'-methylenebis-(4-hydroxycoumarin) is a blood anticoagulant and is responsible for the hemorrhagic sweet clover disease of cattle (Link, Feduation Proc., 1945, 4, 176). Only one intact 4-hydroxycoumarin ring appears to be necessary for activity. Thus 3-allyl-4-hydroxycoumarin,3-cinnamyl-4-hydroxycoumarin and 3-p-nitrocinnamyl-4-hydroxycoumarin are as active as dicumarol. (Grussner, Jubilee Vol. Emil Barell, Fredrick Reinhardt, Basle, 1946, p. 238). 3-Methyl-4-hydroxycoumarin shows an opposite behaviour to dicumarol and behaves like vitamin K (Meunier, Mentzer and Vinet, Helv. Chim. Acta., 1946, 29, 1291). Rutin (3-rhamnoglucoside of quercetin) shows vitamin P activity and is important in preventing capillary fragility (Couch and Krewson, U.S.Dept.Agr.Eastern Regional Research Lab., AIC-52, 1944). Other flavones,quercitrin, rhamnetin and 6,8-dihydroxyflavone (Highly, J.Am.Pharma.

Assoc., 1943, 32, 74) are reported to reduce blood pressure, and to act as diuretics (Nakamura, Ota, and Fukuchi, C.A. 1938, 32, 5833) and fish poisons (Murti, Rao and Seshadri, Proc. Indian Acad. Sci., 1947, 25A, 22 ; 1948, 27A, 33 ; Seshadri and Viswanadhan, ibid., 1947, 25A, 337). The aminomethyl derivatives of chromones and flavones are reported to act as powerful central nervous system stimulants, especially on the brain stem and to have cardiokinetic and hypertensive action (Da Re, Lucia Verlicchi, Ivo Setnikar, J.Org.Chem., 1960, 25, 1097).

Naphtha α- and γ-pyrones are not found in nature but they have been synthesised (Bartsch, Ber., 1903, 36, 1966 ; Pechmann and Welsh, ibid., 1884, 17, 1646 ; Boehm and Profft, Arch. Pharma., 1931, 269, 25 ; Bacovescu, Ber., 1910, 43, 1280 ; Robertson et al., J.Chem.Soc., 1931, 2426 ; Dey and Lakshminarayan, J.Indian Chem. Soc., 1932, 9, 149). Anthra α- and γ-pyrones have not been synthesised so far.

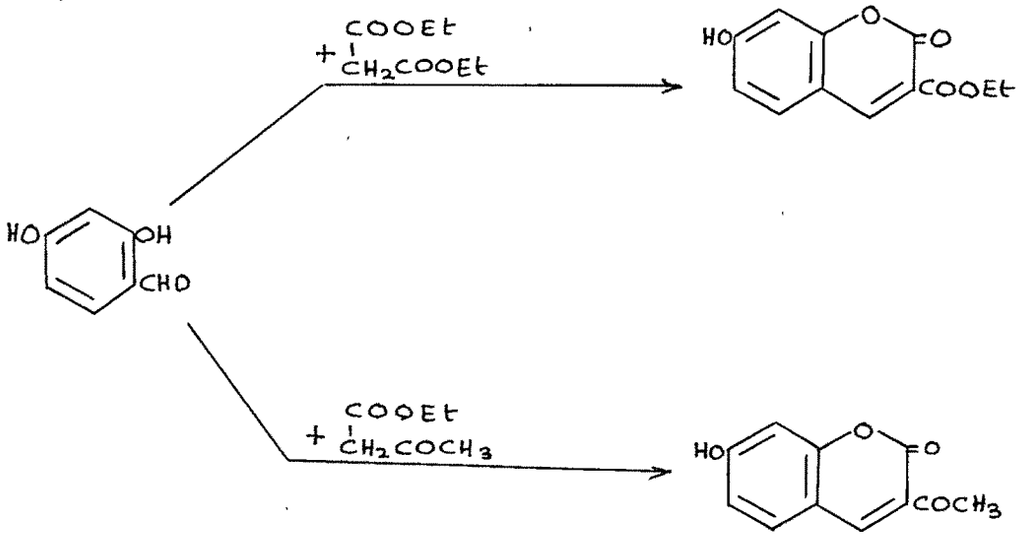
The present work deals with the synthesis of anthra α- and γ-pyrones by the Pechmann and Simonis condensation of 1- and 2-anthrol with β-ketonic esters and by the application of the Perkin, Knoevenagel, Kostanecki-Robinson acylation and the Kostanecki chalkone method to 1- and 2-anthrol derivatives. These reactions and their scope and limitations have therefore been briefly described here.

(1) Perkin reaction. Perkin reaction (J.Chem. Soc., 1868, 21, 53, 181 ; 1877, 31, 388) consists in heating an ortho-hydroxy aromatic aldehyde with the sodium salt of a fatty acid and its anhydride. Condensation occurs with the formation of a hydroxy cinnamic acid derivative which passes spontaneously into the lactone when liberated from its sodium salt.

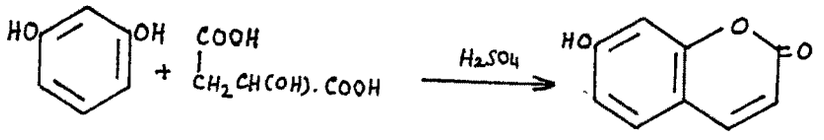


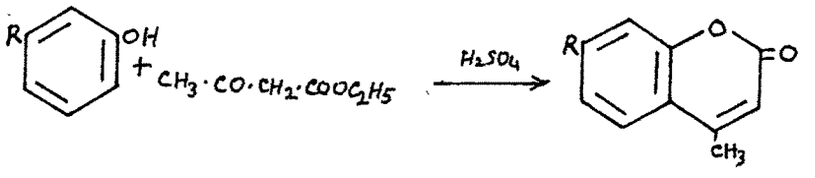
Addition of a little iodine has been reported to increase the yield of coumarin to 70% (Yanagisava and Kondo, C.A. 1922, 16, 922 ; Mizuno and Watanabe, J. Pharma.Soc.Japan., 1949, 69, 123, report only 48%). There are certain limitations to this method. It is often difficult to obtain the appropriate ortho hydroxyaldehydes from the substituted phenols. ~~α-Pyrone, unsubstituted in the pyrone ring only can be obtained with this method,~~ and the yields are also low. The method has been applied however to various phenolic aldehydes such as β-resorcylaldehyde (Pandya et al., Proc.Indian Acad.Sci., 1938, 7A, 381), phloroglucinaldehyde (Gattermann, Annalen, 1907, 357, 345 ; Heyes and Robertson, J.Chem.Soc., 1936, 1831), 2-formyl-1-naphthol and 1-formyl-2-naphthol (Dey, Rao and Sankaranarayanan, J.Indian Chem.Soc., 1932, 9, 281, 285) etc.

(2) Knoevenagel reaction. Knoevenagel (Ber., 1898, 31, 2585, 2595, 2619 ; 1904, 37, 4461) developed a method which consists in condensing ortho-hydroxy aldehydes with compounds containing reactive methylene group such as ethyl malonate, ethyl acetoacetate, cyanacetic ester etc. in the presence of piperidine, aniline and other organic amines. It affords 3-substituted coumarins in good yields. It is also very useful in proving the orthohydroxy structure of aldehydes. This method has been extensively applied for the preparation of various α-pyrone derivatives (Shah and Shah, J.Chem.Soc., 1938, 1832 ; 1939, 132, 949 ; 1940, 245 ; Pandya et al., Proc. Indian Acad. Sci., 1935, 1A, 440 et seq.).



(3) The Pechmann method (Ber., 1883, 16, 2119 ; 1884, 17, 929) consists in heating together a mixture of a phenol and malic acid or a β-ketonic ester in presence of concentrated sulphuric acid when an α-pyrone derivative is formed.





This reaction has been found to be very useful for the synthesis of coumarin derivatives and a large amount of work has been done. The course of the condensation between phenols and β-ketonic esters depends upon (i) the nature of the phenol, (ii) the nature of the β-ketonic ester and (iii) the condensing agent used.

Phenol with sulphuric acid gives only 3 % yield of 4-methylcoumarin. Phenols with electron donating groups in the meta position such as hydroxyl, methoxyl, amino, alkylamino, dialkylamino and alkyl condense more readily (Desai and Ekhlas, Proc. Indian Acad. Sci., 1938, 8A, 567). Halogenated phenols are much less effective (Clayton, J.Chem.Soc., 1908, 93, 2016). The polyhydric phenols such as resorcinol, orcinol, pyrogallol and phloroglucinol, all react very readily, whereas hydroquinone reacts less readily and catechol does not react at all. (Pechmann and

Graeger, Ber., 1901, 34, 378). α-Naphthol has about the same reactivity as phloroglucinol (Chakravarti, J. Indian Chem. Soc., 1931, 8, 407) and β-naphthol that of phenol (Chakravarti, ibid., 1932, 9, 389).

In addition to acetoacetic ester, various α- and γ- substituted acetoacetic esters and cyclic β-ketonic esters have been condensed with phenols and the corresponding substituted coumarins obtained. With reactive phenols coumarins are obtained more or less readily in all cases.

A number of reagents serve to effect condensation. The important ones are : concentrated sulphuric acid (Pechmann and Duisberg, loc.cit.), phosphorus pentoxide (Simonis and Remmert, Ber., 1914, 47, 2229), phosphorus oxychloride (Naik, Desai and Trivedi, J.Indian Chem.Soc., 1929, 6, 801) and aluminium chloride (Sethna, Shah and Shah, J.Chem.Soc., 1938, 228). The other condensing agents such as sodium ethoxide, boric anhydride, sodium acetate, ferric chloride, stannic chloride, titanium chloride and thionyl chloride, have been found to be useful only for the condensation of reactive phenols with β-ketonic esters (cf. Pechmann Reaction, Organic Reactions Vol. VII p. 19).

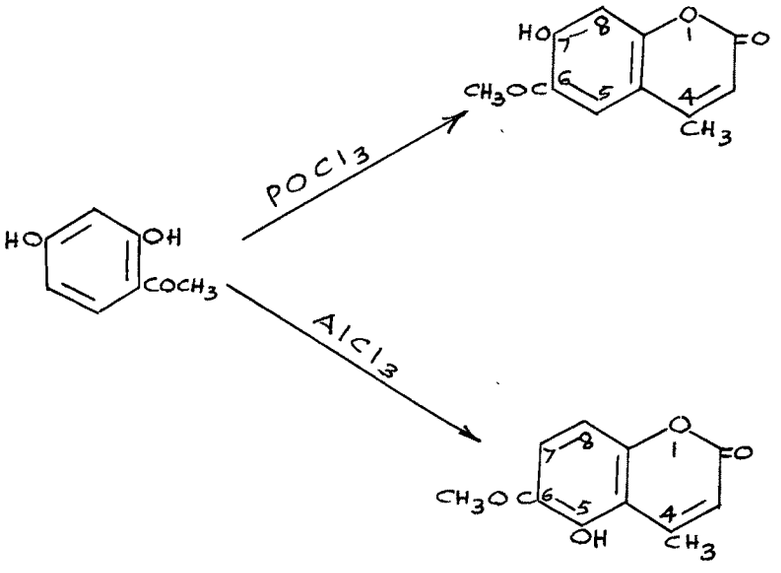
Except in very few cases sulphuric acid as the condensing agent, gives coumarins. β-Naphthol on condensation with ethyl acetoacetate gives a mixture of the coumarin and the chromone (Dey and Lakshminarayan, loc.cit.), 4-chloro-3,5-dimethyl phenol gives exclusively the chromone

(Adams and Mecorney, J.Am.Chem.Soc., 1944, 66, 802), methyl-α-resorcylate on condensation with ethyl aceto-acetate gives a mixture of the coumarin and the chromone derivatives, while α-resorcylic acid gives only the corresponding chromone derivative (Mody and Shah, Proc. Indian Acad.Sci., 1951, 34A, 77).

Phenols which are reactive and give good yields of coumarins with sulphuric acid, invariably give coumarins with phosphorus pentoxide as the condensing agent. Phenols which react with difficulty or not at all to form coumarins with sulphuric acid give chromones with phosphorus pentoxide (Chakravarti, 1932, loc.cit. ; Chakravarti and Ghosh, J. Indian Chem.Soc., 1935, 12, 622).

Aluminium chloride gives better yields than sulphuric acid in some cases and promotes the condensation with compounds like o-cresol which failed with other reagents. With some resorcinol derivatives such as methyl-β-resorcylate, 4-acylresorcinols and 4-nitroresorcinol, 5-hydroxy-coumarins are produced either exclusively or together with 7-hydroxycoumarin derivatives. (Sethna, Shah and Shah, loc.cit. ; Deliwala and Shah, Proc. Indian Acad.Sci., 1941, 13A, 352 ; Woodruff, Org. Syntheses, 1944, 24, 69)

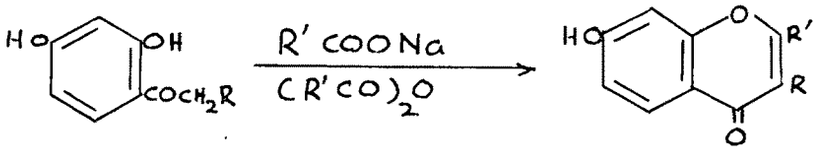
The Pechmann reaction has been reviewed in detail by Sethna and Phadake (Organic Reactions Vol.VII U.S.A. p. 1 - 58).



Mentzer et al. (Bull. Soc. Chim. France, 1953, 538) found that if a phenol was heated with β-ketonic esters at a high temperature (about 250°) without any condensing agent, chromones were produced instead of the coumarins. Desai, Trivedi and Sethna (J.M.S.University of Baroda, 1955, IV, No.2,1) found that the reaction was more rapid and better products were obtained if diphenyl ether was used as a solvent and the reaction mixture refluxed with a short condenser to remove the water formed.

(4) Kostanecki-Robinson reaction. Nagai (Ber., 1892, 25, 1284) and Tahara (Ber., 1892, 25, 1292) heated resacetophenone and paenol with sodium acetate and acetic anhydride. The products obtained were shown by Kostanecki and Rozycki (Ber., 1901, 34, 102) to be the derivatives of chromones. Since then this method of synthesis which consists in heating o-hydroxy-ketones with the sodium salts

of fatty acids and anhydrides is known as the Kostanecki method or reaction.



This method was further developed by Allan and Robinson (J.Chem.Soc., 1924, 125, 2192) who found that when an o-hydroxyketone was heated with sodium salt of an aromatic acid and its anhydride, a flavone derivative was obtained.

By using this method Robinson and his coworkers and later on a number of other workers prepared a large number of naturally occuring flavones, such as quercetin, chrysin etc.

It has been found that in the Kostanecki-Robinson reaction a coumarin, an acyl derivative of the ketone, a chromone, a 3-acylated chromone or a mixture of these may be produced.

It was observed by Bargellini (Atti R.Accad. Lineei, 1925, 2, 178, 201) and by Baker and Eastwood (J.Chem.Soc., 1929, 2900) that the use of phenylacetic anhydride and phenylacetate in the Kostanecki-Robinson reaction leads to coumarin and not chromone formation.

The Kostanecki-Robinson reaction has been extensively studied. Various simple ands substituted phenolic

ketones have been acylated using different sodium salts of fatty and aromatic acids and their anhydrides (Elderfield, Heterocyclic compounds, Vol.2, p. 176, 234). A few generalisations made by Heilbron (J.Chem.Soc., 1936, 295) may be noted.

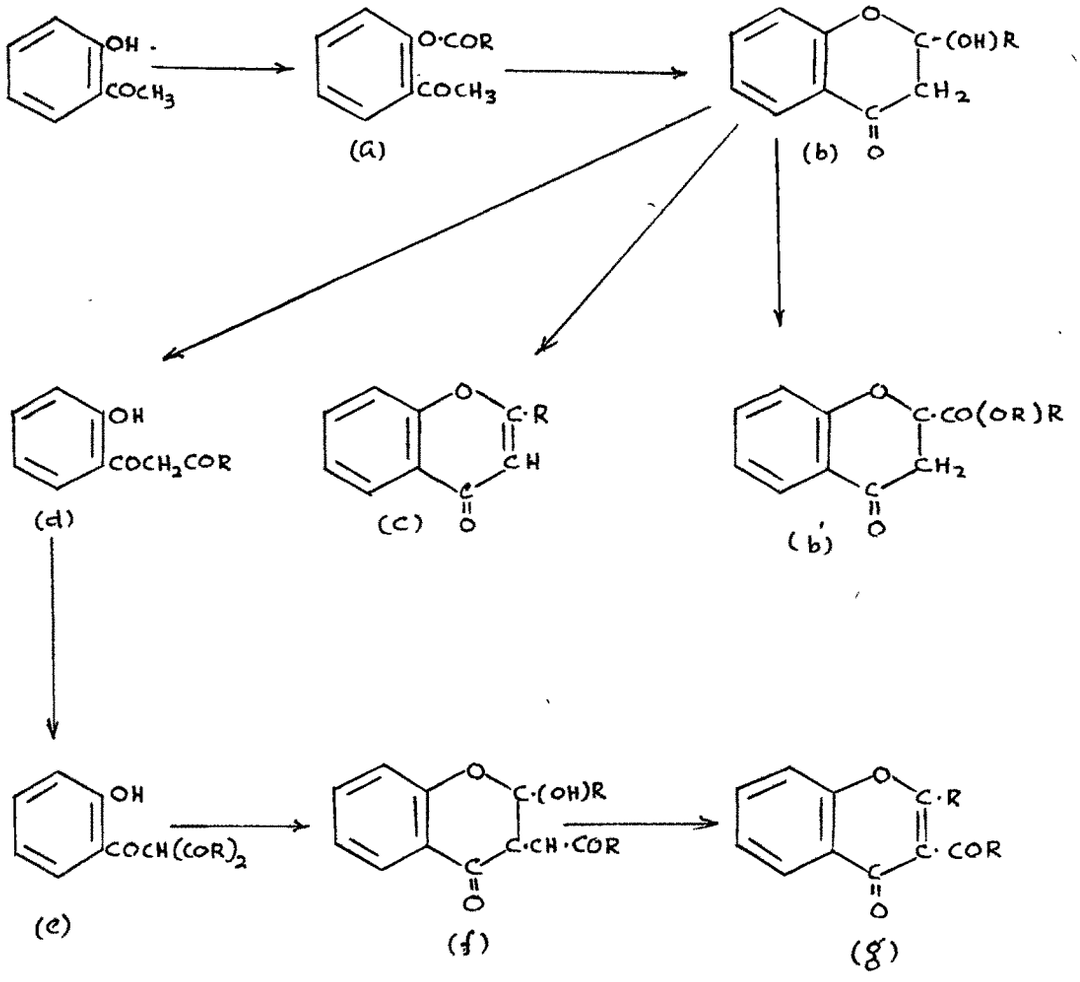
Using sodium acetate and acetic anhydride the introduction of the higher alkyl substituent in the side chain of the hydroxy-ketone favours chromone formation eg. resacetophenone gives chromone (Kostanecki and Rozycki, loc.cit.), respropiophenone also gives chromone (Canter, Curd and Robertson, J.Chem.Soc., 1931, 1263). Chadha, Mahal and Venkataraman (ibid., 1933, 1459) found that an ω-substituent in the o-hydroxy-aryl-methyl ketone favours chromone formation.

Keeping the o-hydroxy ketone the same, if the anhydride and the sodium salts of higher acids like propionic and butyric acids are taken then there is a tendency towards coumarin formation.

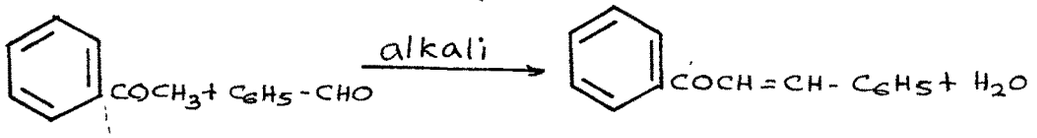
When benzoic anhydride and sodium benzoate or their derivatives are used, the products formed are always flavone derivatives. With phenylacetic anhydride or acetic anhydride and sodium phenylacetate the products formed are mostly 3-phenylcoumarin derivatives.

Baker (J.Chem.Soc., 1933, 1384) has suggested the following mechanism for the formation of chromone in the Kostanecki-Robinson reaction.

According to him the first step is the esterification of the phenolic hydroxyl group (a) then ring closure to a 2-hydroxyflavanone (b) (or possibly 2-acyloxy-flavanone b'). Loss of a molecule of water with the production of chromone (c). Alternately to (c) the ring of the 2-hydroxyflavanone may open to give the diketone (d) under the influence of the sodium salt of the acid. Then acylation of the methylene carbon atom to give a triacylmethane derivative (e), ring closure to the 2-hydroxy-3-acylflavanone (f) followed by dehydration to the 3-acylchromone (g).



(5) Kostanecki's Chalkone method. Aromatic aldehydes undergo Claisen-Schmidt condensation with aromatic ketones in presence of aqueous alkali or sodium ethylate, with the formation of α,β-unsaturated ketones, called chalkones or phenyl styryl ketones (Kostanecki and Rossbach, Ber., 1896, 29, 1488).

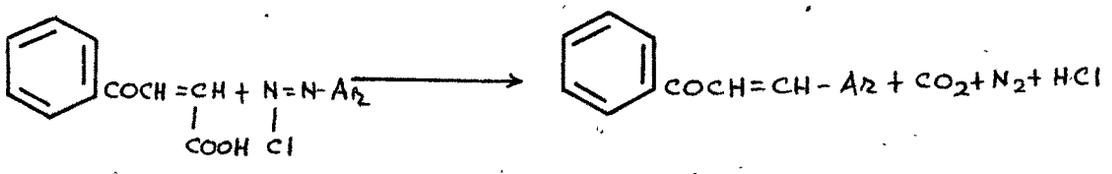


The synthesis of polyhydroxybenzylidene acetophenones became of particular interest on account of their structural relationship to the naturally occurring flavone pigments into which they may be transformed.

Alkali, used in the above reaction as the condensing agent, is generally a 40-70 % aqueous solution of potassium hydroxide (Kostanecki et al., Ber., 1896, 29, 233, 1488 ; 1898, 31, 710 ; 1899, 32, 1921). Weaker alkali such as 10-4 % or buffer with pH 7.6 to 12 leads to the formation of the flavanone or a mixture of flavanone and chalkone (Kimura, J.Ph.Soc., Japan, 1938, 58, 415). Besides alkali, hydrochloric acid in the form of dry gas in presence of a suitable solvent like ethyl acetate or methanol at 0°C (Russel et al., J.Chem. Soc., 1934, 218, 1069, 1508, 1940 ; 1937, 421 ; Lyle and Paradis, J.Amer.Chem.Soc., 1955, 77, 6667), Boron trifluoride (Breslow and Hauser, ibid., 1940, 62, 2385 ; Davey and Tiney, ibid., 1958, 1230, 2276), phosphorus oxychloride (Vyas and

Shah, Current Science, India 1949, 18, 134 ; Davey et al., loc.cit.), borax solution (Kulkarni and Jadhav, Current Science, India, 1951, 20, 42) and zinc chloride (Datta and Watson, J.Chem.Soc., 1912, 1240) have also been successfully used as the condensing agents in the synthesis of chalkones. The condensation of suitable cinnamic acid chlorides with appropriate phenols can be brought about in the presence of anhydrous aluminium chloride (Simonis and Lear, Ber., 1926, 59, 2908 ; Shinoder and Sato, J.Pharm.Soc., Japan, 1928, 48, 1933, 1791).

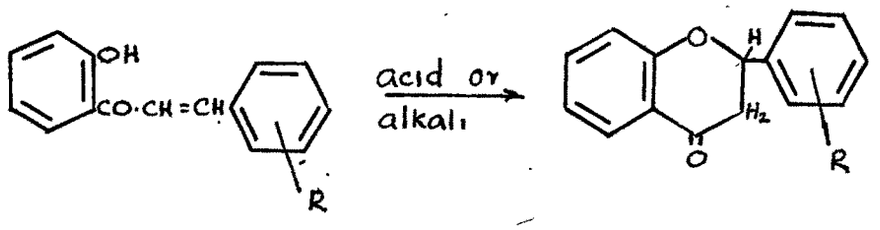
An entirely different method of preparing chalkones has been developed by Mahra and Mathur (J.Indian Chem.Soc., 1955, 32, 465 ; 1956, 33, 618). They condensed aryl-diazonium chloride with benzoyl-acrylic acid and its 3:4-dimethoxy derivative, in presence of sodium acetate and cupric chloride when decarboxylation occurred during coupling reaction resulting in the formation of chalkone.



Chalkones containing bromo-, chloro-, and nitro-groups in the aryl nucleus have been obtained in 4-22 % yield.

2-Hydroxy chalkones can be readily converted into the corresponding flavanones (2,3-dihydro-flavones) by refluxing with dilute HCl or H_2SO_4 (Kostanecki and Szabranski,

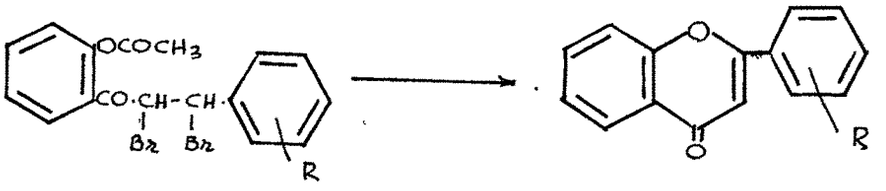
Ber., 1904, 37, 2634 ; Geissmann and Clinter, J.Amer.Chem. Soc., 1946, 68, 697 ; Seshadri et al., Proc. Indian Acad. Sci., 1948, 26A, 189 ; 1944, 20A, 274 ; 1954, 39A, 256) phosphoric acid (Dean and Nierastein, J.Amer.Chem.Soc., 1925, 47, 1680 ; Mahal, Rai and Venkataraman, J.Chem.Soc., 1935, 866) or dilute alkali (Lowenbein, Ber., 1924, 57, 1575 ; Wheeler et al., J.Chem.Soc., 1957, 1737 ; Kostanecki and Schmidt, Ber., 1900, 33, 326).



Flavones can be prepared from chalkones, chalkone dibromides or flavanones. Chalkones, on heating with selenium dioxide in isoamyl alcohol, have been converted into the corresponding flavones, isomerisation and dehydrogenation occurring simultaneously (Bargelline and Bettole, Gazetta, 1940, 70, 170 ; Rao and Seshadri Proc.Indian Acad.Sci., 1945, 21A, 130, 155, 157 ; Amin et al., Ber., 1957, 90, 1287 ; Tetrahedron, 1958, 2, 241).

Alternately, chalkone dibromide can be prepared which on treatment with ethanolic alkali (Emileaiz and Kostanecki, Ber., 1898, 31, 696 ; Auwers and Anschutz, ibid, 1921, 54, 543 ; Kostanecki et al., ibid, 1903, 36, 4235) or other basic reagents like pyridine, aqueous sodium hydroxide, sodium carbonate or alcoholic potassium cyanide (Wheeler

et al., J.Chem.Soc., 1937, 1798) cyclises to flavone.



Flavanones can be dehydrogenated to flavones by PCl_5 (Lowenbein, loc.cit. ; Hi Hon, Bull.Chem.Soc., Japan, 1927, 2, 171) or by selenium dioxide in isoamyl alcohol (Venkataraman et al., loc.cit., Nadkarni and Wheeler, J.Chem. Soc., 1938, 1320 ; Chakravarty and Dutta, J. Indian Chem. Soc., 1939, 16, 639). Various substituted flavanones can be oxidised to the corresponding substituted flavones by selenium dioxide in isoamyl alcohol (Shah and coworkers ibid., 1955, 77, 222 ; Proc. Indian Acad. Sci., 1951, 33A, 112 ; 1950, 32A, 336 ; J. Org.Chem., 1956, 21, 1408).

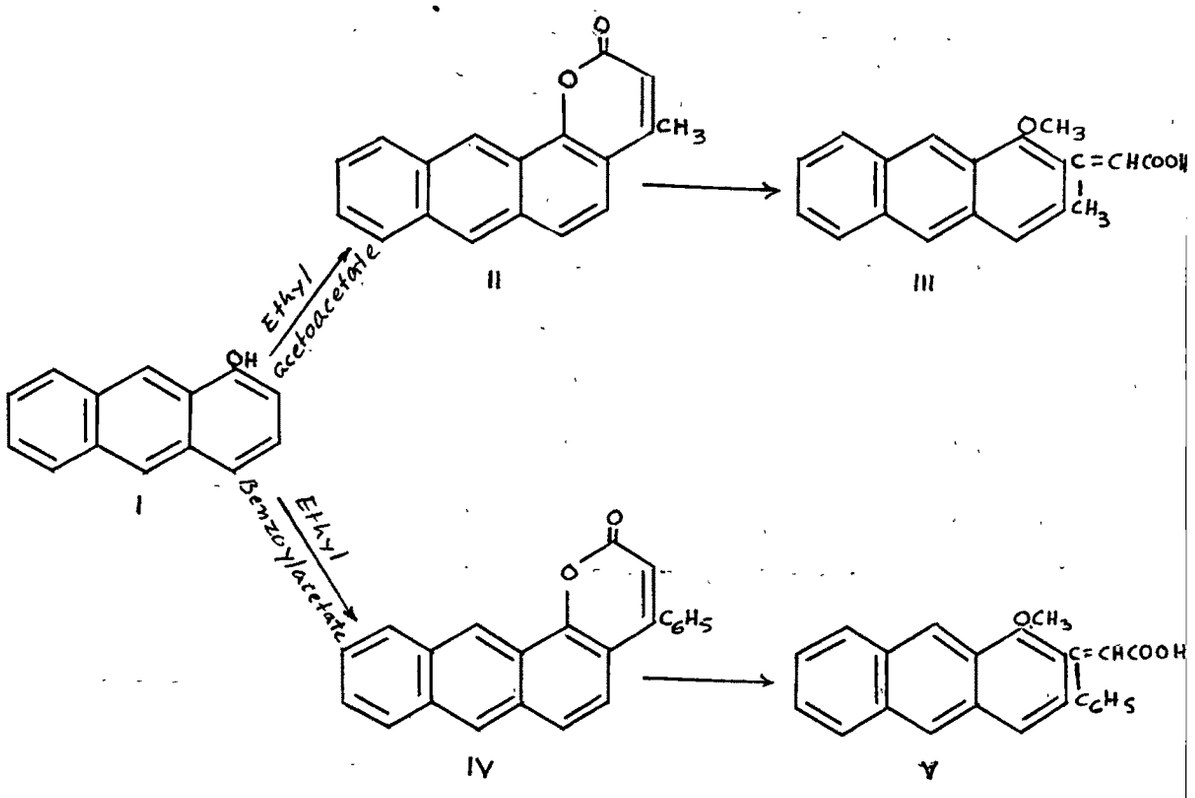
The present work may now be described.

Pechmann condensation of 1-anthrol with ethyl acetoacetate and ethyl benzoylacetate.

1-Anthrol (I) was condensed with ethyl acetoacetate in the presence of sulphuric acid (80 %) when a product was obtained in good yield. It was insoluble in cold dilute sodium hydroxide solution, and on treatment with alkali and dimethyl sulphate it gave an unsaturated acid. The formation of cinnamic acid derivative is a diagnostic test for coumarin derivatives (Canter and Robertson, J.Chem. Soc., 1931, 1875), hence 4'-methyl-1,2-anthra-α-pyrone (II) structure has been assigned to the condensation product, and β-methyl-β-2-(1-methoxyanthryl)-acrylic acid (III) structure to the unsaturated acid.

The same product was obtained when 1-anthrol (I) was condensed with ethyl acetoacetate using phosphorus pentoxide as the condensing agent (Simonis reaction).

1-Anthrol on condensation with ethyl benzoylacetate in the presence of both sulphuric acid and phosphorus pentoxide gave the same product to which the 4'-phenyl-1,2-anthra-α-pyrone (IV) structure has been assigned as it gave an unsaturated acid on treatment with alkali and dimethyl sulphate. The acid has been assigned the β-phenyl-β-2-(1-methoxyanthryl)-acrylic acid (V) structure.

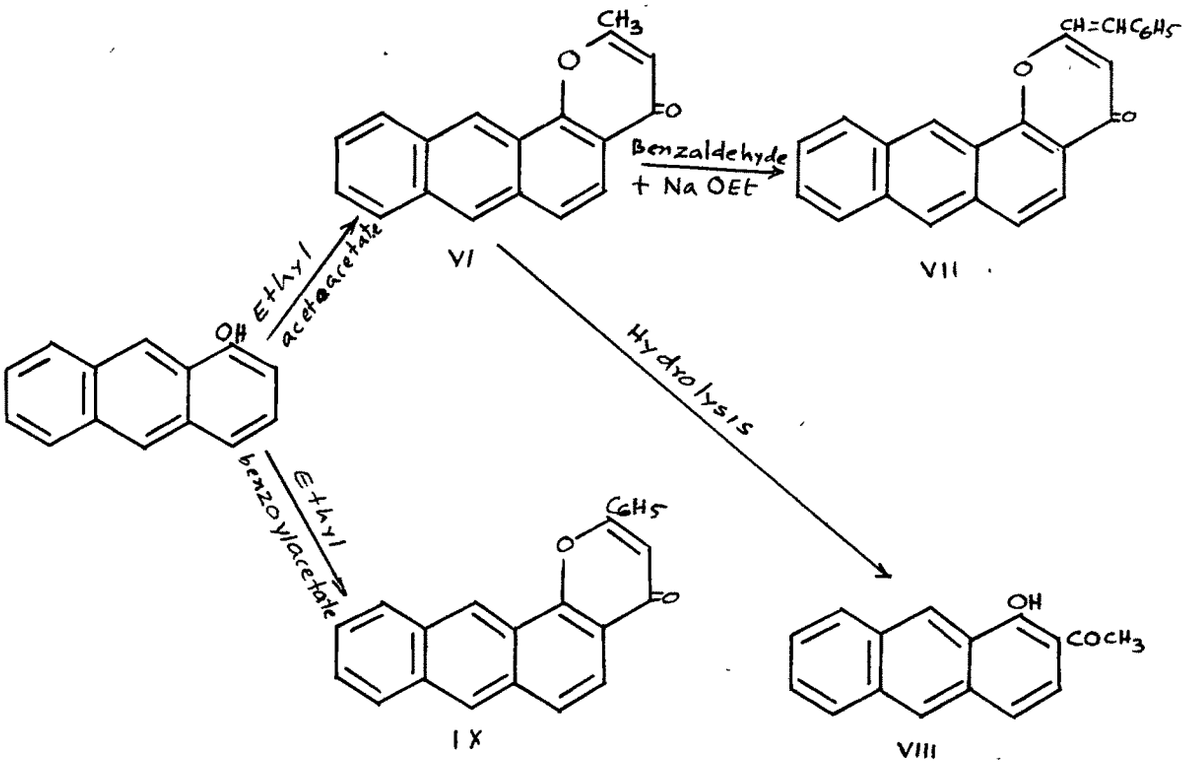


Condensation of 1-anthrol with ethyl acetoacetate and ethyl benzoylacetate at high temperature without using any condensing agent.

A solution of 1-anthrol (I) and ethyl acetoacetate in diphenyl ether was refluxed for 2 hours. On addition of petroleum ether to the cold solution, a product separated which was insoluble in cold dilute sodium hydroxide solution. It reacted with benzaldehyde in presence of sodium ethoxide to give a styryl derivative (VII). On refluxing its alcoholic solution with sodium hydroxide (10 %) for 10 hours, 2-acetyl-1-anthrol (VIII) was obtained as seen by direct comparison. The product obtained in the condensation has therefore been assigned the 2'-methyl-1,2-anthra-γ-pyrone

(VI) structure.

When ethyl benzoylacetate was used in the above reaction instead of ethyl acetoacetate, a product was obtained, which was different from 4'-phenyl-1,2-anthra-α-pyrone (IV), described before. Moreover, it was found on direct comparison to be identical with the product obtained in the Kostanecki-Robinson benzoylation of 2-acetyl-1-anthrol (described later). Hence this product has been assigned the 2'-phenyl-1,2-anthra-γ-pyrone (IX) structure.

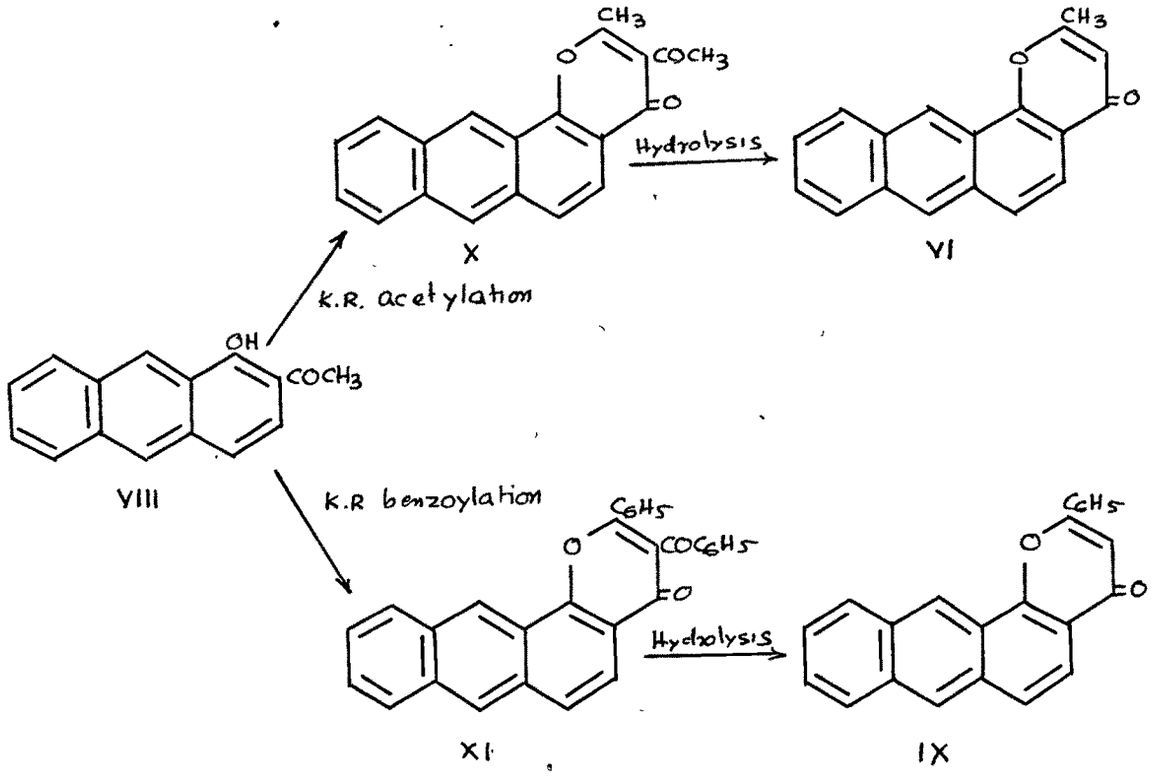


Kostanecki-Robinson acetylation and benzoylation of 2-acetyl-1-anthrol.

2-Acetyl-1-anthrol (VIII) on Kostanecki-Robinson

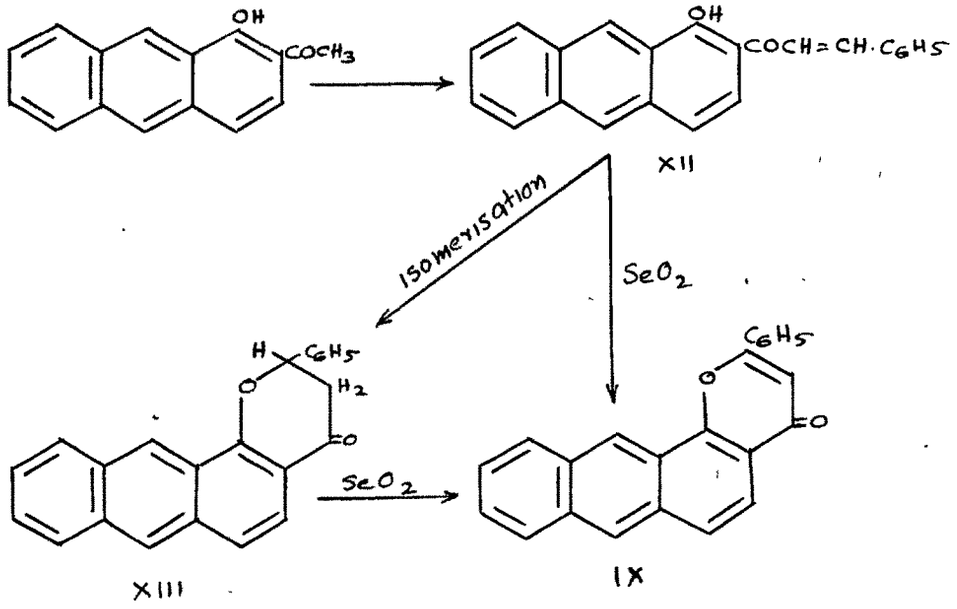
acetylation gave a product which on heating with dilute alcoholic sodium carbonate solution gave 2'-methyl-1,2-anthra-γ-pyrone (VI) (described earlier) as seen by direct comparison. The 2'-methyl-3'-acetyl-1,2-anthra-γ-pyrone (X) structure has therefore been assigned to the product isolated from the Kostanecki-Robinson acetylation.

2-Acetyl-1-anthrol (VIII) on Kostanecki-Robinson benzoylation gave a product which has been assigned the 2'-phenyl-3'-benzoyl-1,2-anthra-γ-pyrone (XI) structure. On heating with alcoholic sodium carbonate solution it gave a product which has been assigned the 2'-phenyl-1,2-anthra-γ-pyrone (IX) structure as it was found on direct comparison to be the same as the product obtained on heating 1-anthrol with ethyl benzoylacetate in diphenyl ether described earlier.



Condensation of 2-acetyl-1-anthrol with benzaldehyde in presence of alkali.

2-Acetyl-1-anthrol was condensed with benzaldehyde in presence of potassium hydroxide solution. The product obtained was assigned the 2-(1'-hydroxyanthryl-) styryl ketone (XII) structure, as it gave a reddish brown colouration with alcoholic ferric chloride and gave the acetoxy derivative. This styryl ketone was isomerised by heating its alcoholic solution with dilute sulphuric acid to 2'-phenyl-2',3'-dihydro-1,2-anthra-γ-pyrone (XIII). This as well as the styryl ketone on treatment with selenium dioxide in amyl alcohol afforded a product which was found on direct comparison to be identical with 2'-phenyl-1,2-anthra-γ-pyrone (IX) described before.



Attempted Pechmann condensation of 2-anthrol with ethyl acetoacetate.

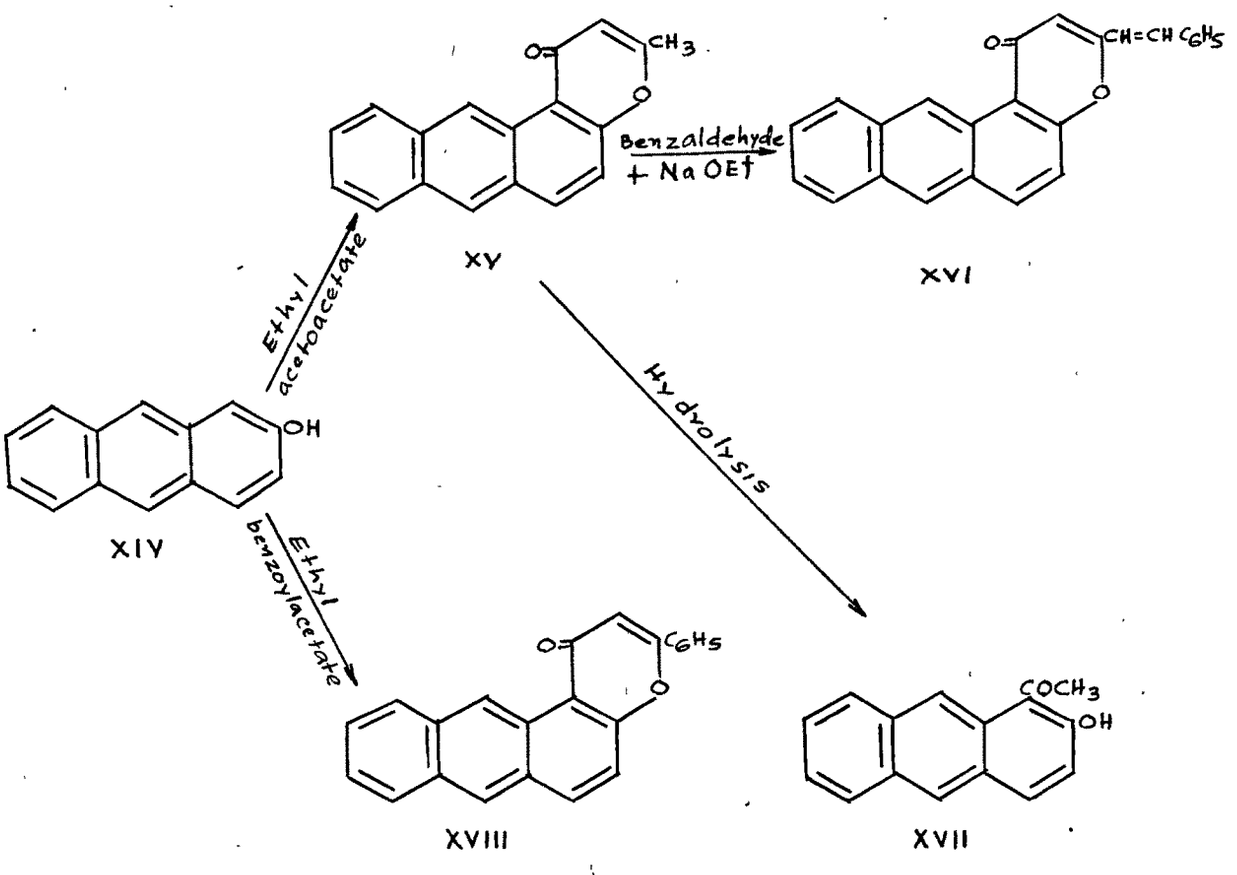
2-Anthrol (XIV) was condensed with ethyl aceto-acetate in presence of sulphuric acid (80 %), when a reddish solid was obtained, which could not be crystallised to give a product of any definite melting point. The same condensation when repeated using concentrated sulphuric acid, gave similar result. Attempts to purify the product through chromatographic method did not yield any pure product.

Condensation of 2-anthrol with ethyl acetoacetate and ethyl benzoylacetate (i) with phosphorus pentoxide as the condensing agent (Simonis reaction) and (ii) at high temperature without using any condensing agent.

2-Anthrol (XIV) was condensed with ethyl acetoacetate using phosphorus pentoxide as the condensing agent. The light brown crystalline product obtained was insoluble in cold dilute sodium hydroxide solution. It gave fluorescence with concentrated sulphuric acid. It reacted with benzaldehyde in presence of sodium ethoxide to give a styryl derivative (XVI). On alkaline hydrolysis it gave a ketone, which was found on direct comparison to be 1-acetyl-2-anthrol (XVII). Hence the condensation product has been assigned the 2'-methyl-2,1-anthra-γ-pyrone (XV) structure. The same product (XV) was obtained when 2-anthrol was condensed with ethyl acetoacetate in boiling diphenyl ether.

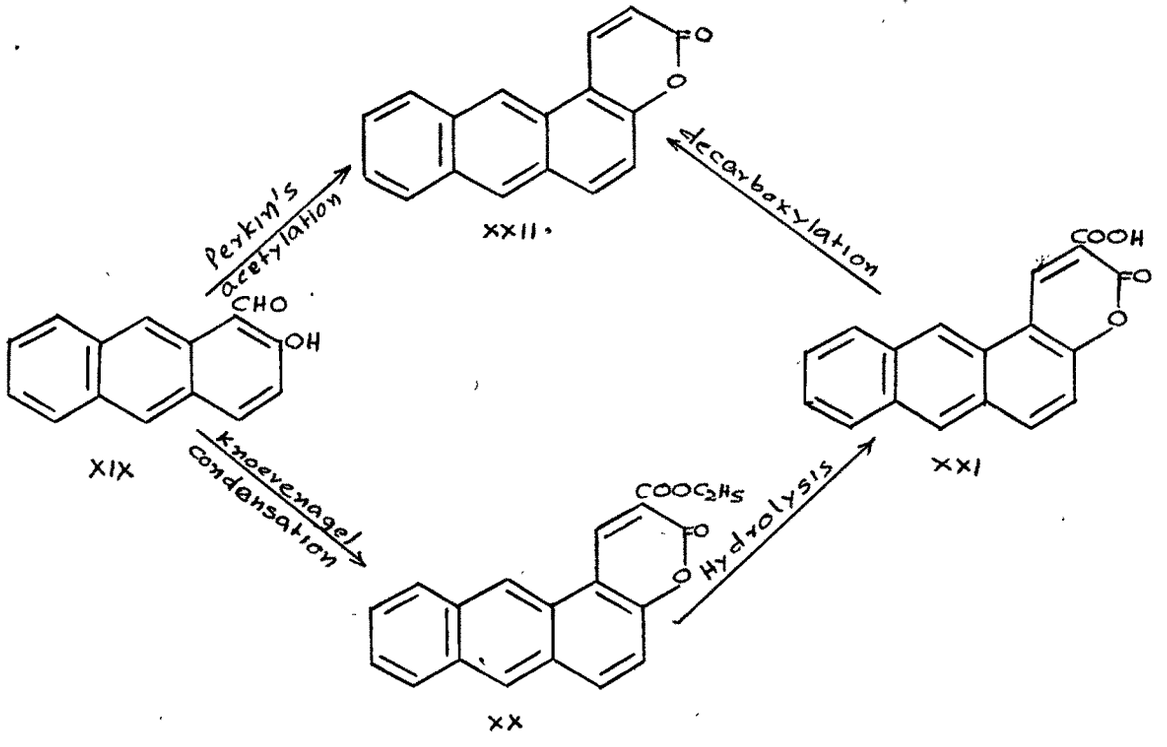
2-Anthrol on condensation with ethyl benzoylacetate in presence of phosphorus pentoxide as well as at high temperature in diphenyl ether solution gave the same product.

It has been assigned the 2'-phenyl-2,1-anthra-γ-pyrone (XVIII) structure, because the product was found on direct comparison to be identical with the one obtained from the Kostanecki-Robinson benzoylation of 1-acetyl-2-anthrol described later.



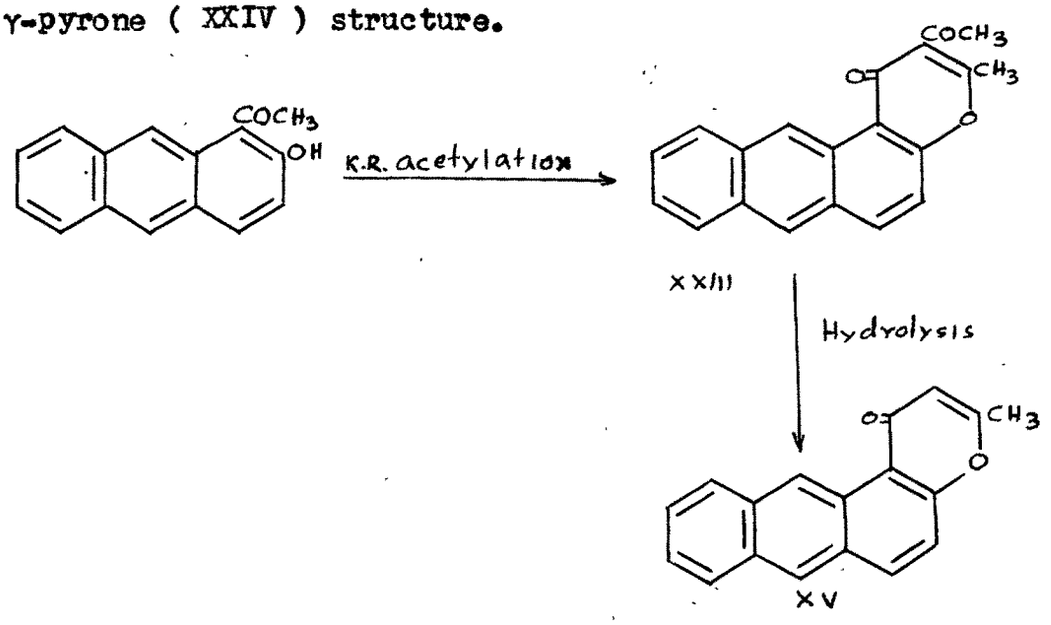
Knoevenagel condensation of 1-formyl-2-anthrol with diethyl malonate and Perkin acetylation of 1-formyl-2-anthrol.

1-Formyl-2-anthrol (XIX) on condensation with diethyl malonate in presence of a few drops of piperidine gave a product which was insoluble in cold dilute alkali. On hydrolysis with sodium hydroxide solution it gave an acid. The acid on decarboxylation gave a product which was found on direct comparison to be identical with the product obtained in the Perkin acetylation of 1-formyl-2-anthrol. It did not give any fluorescence with concentrated sulphuric acid and was insoluble in cold dilute alkali. It has been assigned the 2,1-anthra-α-pyrone (XXII) structure. The Knoevenagel condensation product is, therefore, ethyl-2,1-anthra-α-pyrone-3'-carboxylate (XX) and the acid obtained from it is 2,1-anthra-α-pyrone-3'-carboxylic acid (XXI).



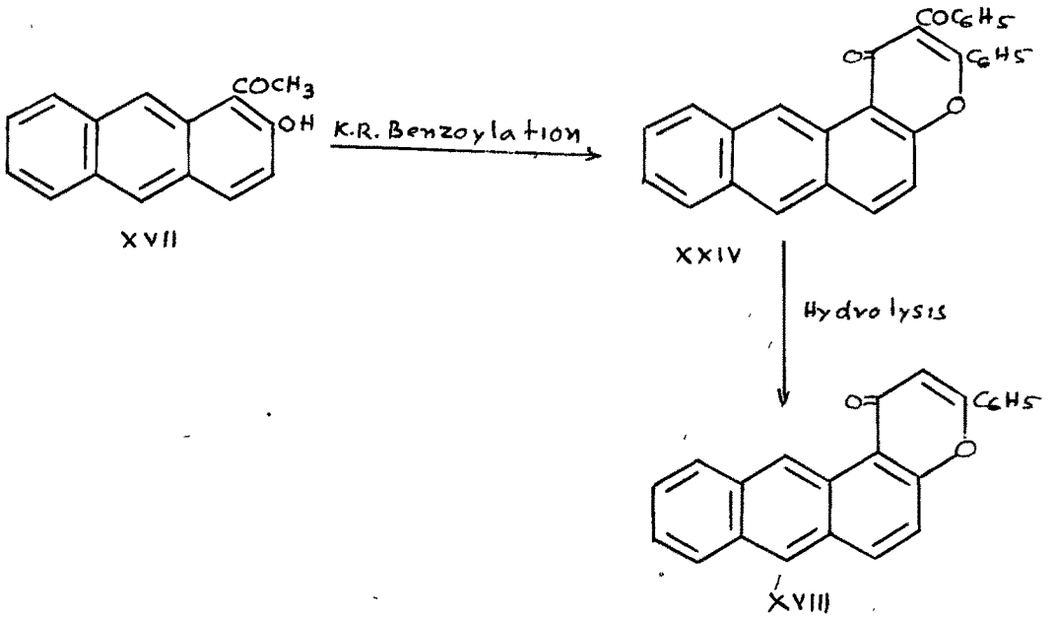
Kostanecki-Robinson acylation of 1-acetyl-2-anthrol.

1-Acetyl-2-anthrol (XVII) on Kostanecki-Robinson acetylation with acetic anhydride and sodium acetate gave a product which on heating with dilute alcoholic sodium carbonate solution gave another product which was found on direct comparison to be 2'-methyl-2,1-anthra-γ-pyrone (XV) described before. Hence the Kostanecki-Robinson acetylation product has been assigned the 2'-methyl-3'-acetyl-2,1-anthra-γ-pyrone (XXIV) structure.



Similarly 1-acetyl-2-anthrol (XVII) on Kostanecki-Robinson benzoylation gave a product which on heating with alcoholic sodium hydroxide solution gave a product which on direct comparison was found to be identical with the product obtained in the condensation of 2-anthrol with ethyl benzoylacetate in presence of phosphorus pentoxide and at high temperature as described before. 2'-Phenyl-2,1-anthra-γ-pyrone (XVIII) structure has been assigned to this product and 2'-phenyl-3'-benzoyl-2,1-anthra-γ-pyrone (XXIV)

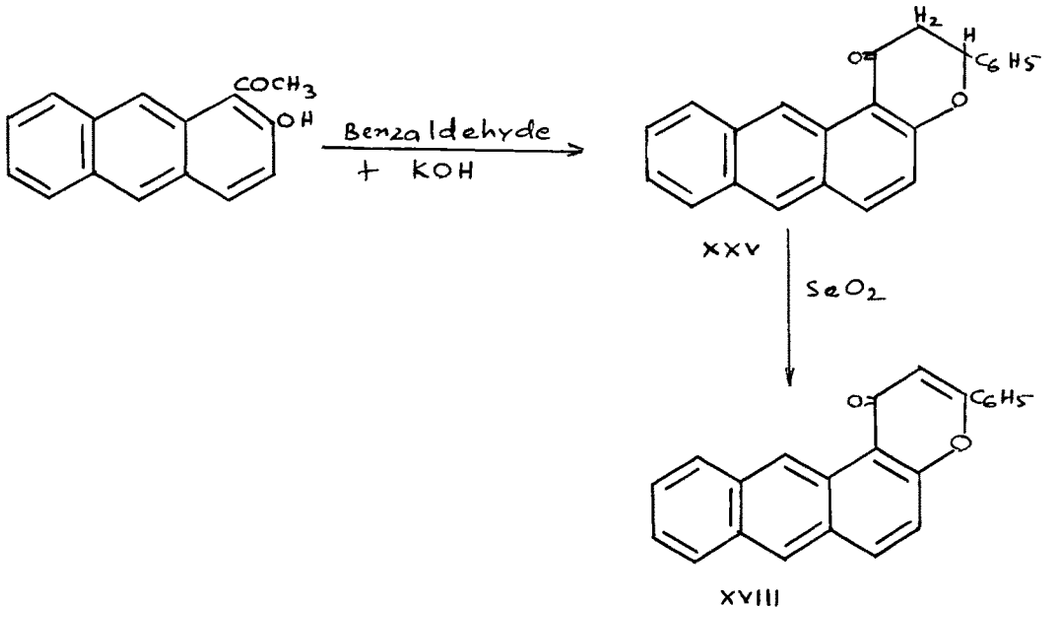
structure has been assigned to the Kostanecki-Robinson benzoylation product.



Condensation of 1-acetyl-2-anthrol with benzaldehyde in presence of alkali.

1-Acetyl-2-anthrol was condensed with benzaldehyde in presence of potassium hydroxide solution. The product obtained has been assigned the 2'-phenyl-2',3'-dihydro-2,1-anthra-γ-pyrone (XXV) structure, as it was insoluble in alkali and it did not give any colouration with alcoholic ferric chloride. Further, it did not give ~~the~~ an acetoxy derivative and remained unchanged on prolonged refluxing on a steam bath its alcoholic solution with dilute sulphuric acid. On treatment with selenium dioxide in amyl alcohol, it gave 2'-phenyl-2,1-anthra-γ-pyrone (XVIII) as seen by direct

comparison with the product described before.



EXPERIMENTAL

Condensation of 1-anthrol with ethyl acetoacetate : 4'-Methyl-1,2-anthra-α-pyrone.

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

1-Anthrol (1.94 g.) and ethyl acetoacetate (1.3 g.) were mixed together and sulphuric acid (80 % ; 20 ml.) was added gradually with shaking and external cooling. The reaction mixture was kept at room temperature for 24 hours and then poured on ice. The separated solid was filtered, washed with dilute alkali and repeatedly crystallised from alcohol (charcoal) when yellow shining needles were obtained, m.p.230°. Yield 1 g.

Analysis :

3.968 mg. of the substance gave 12.070 mg. of carbon dioxide and 1.654 mg. of water.

Found : C, 83.01 % ; H, 4.66 %.

$C_{18}H_{12}O_2$ requires : C, 83.08 % ; H, 4.62 %.

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

To a mixture of 1-anthrol (0.48 g.) and ethyl acetoacetate (0.33 g.), phosphorus pentoxide (1.0 g.) was gradually added with stirring. The reaction mixture, protected from moisture, was then heated on a steam bath for one hour. Crushed ice was then added and the residue taken up in ether. The ethereal layer was repeatedly washed with alkali (2 % ; 50 ml. in all) and then with water. The residue obtained on removing ether crystallised from

alcohol (charcoal) in yellow needles, m.p.230°. Mixed m.p. with 4'-methyl-1,2-anthra-α-pyrone,obtained before, was not depressed.

β-Methyl-β,2(1-methoxyanthryl)-acrylic acid.

4'-Methyl-1,2-anthra-α-pyrone (1 g.) was dissolved in a boiling mixture of acetone (100 ml.) and sodium hydroxide (4 % ; 20 ml.) and to this solution dimethyl sulphate (2 ml.) was added slowly with continuous vigorous shaking. More of alkali and dimethyl sulphate were added with shaking and finally the mixture was heated on a steam bath for a few minutes after making it distinctly alkaline. The product obtained on acidification with dilute hydrochloric acid, crystallised from dilute alcohol in small yellow needles, m.p.185°. It decolourised dilute potassium permanganate solution.

Analysis :

3.368 mg. of the substance gave 9.640 mg. of carbon dioxide and 1.660 mg. of water.

Found : C, 78.11 % ; H, 5.51 %.

$C_{19}H_{16}O_3$ requires : C, 78.07 % ; H, 5.48 %.

Condensation of 1-anthrol with ethyl acetoacetate in diphenyl ether without using any condensing agent :-

2'-Methyl-1,2-anthra-γ-pyrone.

1-Anthrol (0.99 g.) was dissolved in diphenyl ether (20 ml.) by warming and ethyl acetoacetate (0.65 g.) was added to it. This solution was then heated under reflux with a short air condenser (to allow the water formed to

escape) for 2 hours. The reaction mixture was then cooled and added to petroleum ether (B. range 60-80° ; 150 ml.). The solid product which separated, was filtered, washed with petroleum ether and crystallised from dilute alcohol (charcoal) in light yellow shining needles, m.p.210-211°. Yield 0.6 g.

It gave greenish fluorescence with concentrated sulphuric acid.

Analysis :

11.72 mg. of the substance gave 35.88 mg. of carbon dioxide and 5.22 mg. of water.

Found : C, 83.54 % ; H, 4.98 %.

$C_{18}H_{12}O_2$ requires : C, 83.08 % ; H, 4.62 %.

2'-Styryl-1,2-anthra-γ-pyrone.

2'-Methyl-1,2-anthra-γ-pyrone (0.1 g.) was dissolved in boiling absolute alcohol (5 ml.) and the clear hot solution treated successively with benzaldehyde (0.1 g.) and a solution of sodium ethoxide (prepared from 0.1 g. of sodium)). The reaction mixture was then allowed to stand at room temperature for 24 hours. The greenish yellow crystalline product which separated was filtered and crystallised from dilute alcohol (charcoal) in yellow shining needles, m.p.216-217°.

Analysis :

8.68 mg. of the substance gave 27.28 mg. of carbon dioxide and 3.58 mg. of water.

Found : C,85.77 % ; H, 4.62 %.

$C_{25}H_{16}O_2$ requires : C, 86.20 % ; H, 4.60 %.

Hydrolysis of 2'-methyl-1,2-anthra-γ-pyrone : 2-Acetyl-1-anthrol.

2'-Methyl-1,2-anthra-γ-pyrone (0.1 g.) was dissolved in alcohol (20 ml.) and refluxed with potassium hydroxide solution (4 g. in 5 ml. water) on a steam bath for 6 hours. The reaction mixture was then diluted with water and filtered. The product obtained on acidification of the filtrate,crystallised from dilute acetic acid (charcoal) in brownish needles, m.p.182°. Mixed m.p.with 2-acetyl-1-anthrol, described before, was not depressed.

Condensation of 1-anthrol with ethyl benzoyl-acetate : 4'-Phenyl-1,2-anthra-α-pyrone.

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

To a mixture of 1-anthrol (1.94 g.) and ethyl benzoylacetate (1.92 g.), sulphuric acid (80 % ; 20 ml.) was added gradually with shaking and external cooling. The reaction mixture was kept at room temperature for 24 hours, and then added to ice. The solid obtained was washed with a cold solution of very dilute alkali. It crystallised from ethyl acetate in needles, m.p.203°. Yield 1 g.

Analysis :

3.560 mg. of the substance gave 11.202 mg. of carbon dioxide and 1.518 mg. of water.

Found : C; 85.87 % ; H, 4.77 %.

$C_{23}H_{14}O_2$ requires: C, 85.71 % ; H, 4.35 %.

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

1-Anthrol (0.48 g.) was mixed intimately, with ethyl benzoylacetate (0.48 g.) and the mixture slightly warmed on a water bath. To this warm mixture, phosphorus pentoxide (1 g.) was gradually added with stirring. The reaction mixture, protected from moisture, was then heated on a steam bath for one hour. Crushed ice was then added and the residue taken up in ether. The ethereal layer was repeatedly washed with alkali (2 % ; 50 ml. in all) and then with water. The residue obtained on evaporating ether, crystallised from ethyl acetate in needles, m.p.203°. Mixed m.p. with 4'-phenyl-1,2-anthra-α-pyrone, described above, was not depressed.

<u>β-Phenyl-β,2 (1-methoxyanthryl)-acrylic acid</u>.

4'-Phenyl-1,2-anthra-α-pyrone (1 g.) was dissolved in a boiling mixture of acetone (100 ml.) and sodium hydroxide (10 % ; 20 ml.) and to this solution dimethyl sulphate (2 ml.) was added slowly with continuous shaking. More of alkali and dimethyl sulphate were added with shaking and finally the mixture was heated on a steam bath for a few minutes after making it distinctly alkaline. The product obtained on acidification, crystallised from dilute alcohol as yellow amorphous powder, m.p.190°. It

decolourised dilute potassium permanganate solution.

Analysis :

3.612 mg. of the substance gave 10.746 mg. of carbon dioxide and 1.544 mg. of water.

Found : C, 81.19 % ; H, 4.78 %.

$C_{24}H_{18}O_3$ requires : C, 81.35 % ; H, 5.09 %.

Condensation of 1-anthrol with ethyl benzoylacetate in diphenyl ether without using any condensing agent:-

2-Phenyl-1,2-anthra-γ-pyrone.

1-Anthrol (0.48 g.) was dissolved in diphenyl ether (10 ml.) by warming and ethyl benzoylacetate (0.48 g.) was added to it. This solution was then heated under reflux with a short air condenser (to allow the water formed to escape) for 2 hours. The reaction mixture was then cooled and added to petroleum ether (B. range 60-80° ; 100 ml.). The solid product which separated, was filtered, washed with petroleum ether and crystallised from dilute alcohol in yellow shining needles, m.p.215-216°.

Analysis :

10.26 mg. of the substance gave 32.26 mg. of carbon dioxide and 4.20 mg. of water.

Found : C, 85.81 % ; H, 4.58 %.

$C_{23}H_{14}O_2$ requires : C, 85.71 % ; H, 4.35 %.

Kostanecki-Robihson acetylation of 2-acetyl-1-anthrol : 2'-Methyl-3'-acetyl-1,2-anthra-γ-pyrone.

2-Acetyl-1-anthrol (1 g.) was heated with freshly fused and powdered sodium acetate (3 g.) and acetic anhydride (6 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 solid was obtained. On repeated crystallisations from alcohol (charcoal) it gave yellow needles, m.p.196-197°. Yield 0.2 g.

Analysis :

4.210 mg. of the substance gave 12.324 mg. of carbon dioxide and 1.704 mg. of water.

Found : C, 79.89 % ; H, 4.53 %.

$C_{20}H_{14}O_3$ requires : C, 79.50 % ; H, 4.63 %.

2'-Methyl-1,2-anthra-γ-pyrone.

2'-Methyl-3'-acetyl-1,2-anthra-γ-pyrone (0.17 g.) in alcohol (65 % ; 60 ml.) was refluxed gently with anhydrous sodium carbonate (1.5 g.) for 2 hours. The solution was then filtered hot and diluted with water. The separated crystalline solid on recrystallisation from dilute alcohol (charcoal) was obtained in shining yellow needles, m.p.210°. The mixed m.p. with 2'-methyl-1,2-anthra-γ-pyrone, described before, was not depressed.

Kostanecki-Robinson benzoylation of 2-acetyl-1-anthrol : 2'-Phenyl-3'-benzoyl-1,2-anthra-γ-pyrone.

An intimate mixture of 2-acetyl-1-anthrol (1 g.), freshly fused and powdered sodium benzoate (1.5 g.) and benzoic anhydride (5 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 alcohol (charcoal) in pale yellow needles, m.p.220-222°. Yield 0.3 g.

Analysis :

4.130 mg. of the substance gave 12.774 mg. of carbon dioxide and 1.506 mg. of water.

Found : C, 84.41 % ; H, 4.08 %.

$C_{30}H_{18}O_3$ requires : C, 84.50 % ; H, 4.22 %.

2'-Phenyl-1,2-anthra-γ-pyrone.

2'-Phenyl-3'-benzoyl-1,2-anthra-γ-pyrone (0.1 g.) was suspended in alcohol (50 % ; 40 ml.) and heated to boiling. Anhydrous sodium carbonate (2 g.) was then added and the reaction mixture refluxed gently for 2 hours. It was then filtered hot and the filtrate diluted with water. The product obtained crystallised from dilute alcohol in needles, m.p.215°. The mixed m.p. with 2'-phenyl-1,2-anthra-γ-pyrone, obtained before, was not depressed.

Condensation of 2-acetyl-1-anthrol with benzaldehyde : 2-(1'-Hydroxy-anthryl)-styryl ketone.

To a mixture of 2-acetyl-1-anthrol (1.2 g.) and benzaldehyde (2 ml.) in alcohol (50 ml.) potassium hydroxide solution (2.5 g. in 5 ml. water) was added, in small lots. The air was removed by bubbling nitrogen through the solution and the flask was corked and kept for 2 days at room temperature. The reaction mixture was then added to water. The product which separated was filtered and crystallised from alcohol in reddish brown needles, m.p.207°. Yield 0.3 g.

It gave a reddish brown colouration with alcoholic ferric chloride.

Analysis :

9.44 mg. of the substance gave 29.33 mg. of carbon dioxide and 4.08 mg. of water.

Found : C, 84.76 % ; H, 4.84 %.

$C_{23}H_{16}O_2$ requires : C, 85.19 % ; H, 4.94 %.

The acetyl derivative. A mixture of 2-(1'-hydroxy-anthryl)-styryl ketone (0.1 g.) acetic anhydride (1 ml.) and freshly fused sodium acetate (0.1 g.) was heated on a steam-bath for 5 hours. It was then added to cold water. The solid which separated was filtered, washed with water and crystallised from alcohol (charcoal) in small yellowish needles, m.p.180-181°.

Analysis :

10.76 mg. of the substance gave 32.46 mg. of carbon dioxide and 5.02 mg. of water.

Found : C, 82.30 % ; H, 5.20 %.

$C_{25}H_{18}O_3$ requires : C, 81.96 % ; H, 4.92 %.

Isomerisation of 2-(1-hydroxyanthryl)-styryl ketone : 2'-Phenyl-2',3'-dihydro-1,2-anthra-γ-pyrone.

2-(1-Hydroxyanthryl)-styryl ketone (0.1 g.) was dissolved in alcohol (100 ml.). Dilute sulphuric acid (10 % ; 10 ml.) was then added till a permanent turbidity appeared, which was redissolved by adding more alcohol. The reaction mixture was refluxed on a steam bath for 48 hours and then filtered hot and diluted with water. The product which separated crystallised from chloroform, m.p.231°.

Analysis :

10.62 mg. of the substance gave 33.00 mg. of carbon dioxide and 4.52 mg. of water.

Found : C, 84.80 % ; H, 4.76 %.

$C_{23}H_{16}O_2$ requires : C, 85.19 % ; H, 4.94 %.

2'-Phenyl-1,2-anthra-γ-pyrone.

(i) By treatment of 2-(1-hydroxyanthryl)-styryl ketone with selenium dioxide.

A mixture of 2-(1-hydroxyanthryl)-styryl ketone (0.1 g.), selenium dioxide (0.2 g.) and dry amyl alcohol (10 ml.) was heated under reflux in an oil bath at 150°

for 8 hours. The reaction mixture was then filtered hot and the product obtained on removal of the amyl alcohol was washed with a dilute solution of sodium hydroxide and crystallised from alcohol in light yellow needles, m.p. 215-216°. The mixed m.p. with 2'-phenyl-1,2-anthra-γ-pyrone, obtained before, was not depressed.

(ii) By treatment of 2'-phenyl-2',3'-dihydro-1,2-anthra-γ-pyrone with selenium dioxide.

The 2'-phenyl-2',3'-dihydro-1,2-anthra-γ-pyrone (0.1 g.) in dry amyl alcohol (10 ml.) was treated with selenium dioxide (0.2 g.) as described above. On working up the reaction mixture a product was obtained which crystallised from alcohol in light yellow needles, m.p. and mixed m.p. with 2'-phenyl-1,2-anthra-γ-pyrone, obtained before, was 215-216°.

Condensation of 2-anthrol with ethyl acetoacetate : 2'-Methyl-2,1-anthra-γ-pyrone.

(i) With phosphorus pentoxide as the condensing agent (Simonis reaction) :

To a warm mixture of 2-anthrol (1.94 g.) and ethyl acetoacetate (1.3 g.), phosphorus pentoxide (2.5 g.) was gradually added with stirring. The reaction mixture, protected from moisture, was heated on a steam bath for one hour. Crushed ice was then added and the residue taken up in ether. The ethereal layer was repeatedly washed with alkali (2 % ; 200 ml. in all) and then with water. The product obtained on removal of ether, crystallised from dilute acetic acid in light brown needles, m.p.173°. Yield 0.4 g.

It gave bluish green fluorescence with concentrated sulphuric acid.

Analysis :

3.212 mg. of the substance gave 9.760 mg. of carbon dioxide and 1.284 mg. of water.

Found : C, 82.90 % ; H, 4.50 %.

$C_{18}H_{12}O_2$ requires : C, 83.08 % ; H, 4.62 %.

(ii) In diphenyl ether without using any condensing agent :

2-Anthrol (0.99 g.) was dissolved in diphenyl ether (20 ml.) by warming and ethyl acetoacetate (0.65 g.) was added to it. This solution was then heated under reflux

with a short air condenser (to allow the water formed to escape) for 2 hours. The reaction mixture was then cooled and added to petroleum ether (B. range 60-80° ; 150 ml.). The solid product which separated, was filtered, washed with a dilute solution of sodium hydroxide and crystallised from dilute acetic acid in light brown needles, m.p.173°. Yield 0.35 g. The mixed m.p. with 2'-methyl-2,1-anthra-γ-pyrone, described above, was not depressed.

2'-Styryl-2,1-anthra-γ-pyrone.

2'-Methyl-2,1-anthra-γ-pyrone (0.1 g.) was dissolved in absolute alcohol (5 ml.) and benzaldehyde (0.1 g.) and a solution of sodium ethoxide (prepared from 0.1 g. of sodium) added. The reaction mixture was refluxed on a steam bath for 15 minutes and then left overnight at room temperature. The product which separated was filtered and crystallised from absolute alcohol in long yellow needles, m.p.237-238°.

Analysis :

3.826 mg. of the substance gave 12.074 mg. of carbon dioxide and 1.582 mg. of water.

Found : C, 86.10 % ; H, 4.60 %.

$C_{25}H_{16}O_2$ requires : C, 86.20 % ; H, 4.60 %.

Hydrolysis of 2'-methyl-2,1-anthra-γ-pyrone : 1-Acetyl-2-anthrol.

2'-Methyl-2,1-anthra-γ-pyrone (0.5 g.) was heated with alcoholic potassium hydroxide (30 % ; 20 ml.)

on a steam bath for 10 hours. The solution was then diluted with water and acidified with dilute hydrochloric acid. The product was filtered and crystallised from alcohol (charcoal) in yellow needles, m.p.113°. Mixed m.p. with 1-acetyl-2-anthrol was not depressed.

Condensation of 2-anthrol with ethyl benzoylacetate : 2'-Phenyl-2,1-anthra-γ-pyrone.

(i) With phosphorus pentoxide as the condensing agent (Simonis reaction) :

To a solution of 2-anthrol (1 g.) and ethyl benzoylacetate (0.65 g.) in dry ether (10 ml.), phosphorus pentoxide (2 g.) was gradually added with stirring. The reaction mixture, protected from moisture, was warmed and the ether allowed to egaporate. It was then heated on a steam bath for one hour. Crushed ice was then added and the residue taken up in ether. The ethereal layer was repeatedly washed with alkali (2 % ; 200 ml. in all) and then with water. The product obtained on removal of ether, crystallised from dilute acetic acid (charcoal) in pale yellow needles, m.p.219°. Yield 0.2 g.

Analysis :

4.524 mg. of the substance gave 14.202 mg. of carbon dioxide and 1.958 mg. of water.

Found : C, 85.67 % ; H, 4.84 %.

$C_{23}H_{14}O_2$ requires : C, 85.71 % ; H, 4.35 %.

Knoevenagel condensation of 1-formyl-2-anthrol with diethyl malonate : Ethyl-2,1-anthra-α-pyrone-3'-carboxylate.

A mixture of 1-formyl-2-anthrol (2.22 g.), diethyl malonate (1.92 g.) and a few drops of piperidine was kept at room temperature for 4 days. The reaction mixture was then treated with dilute hydrochloric acid. The product which separated, crystallised from alcohol (charcoal) in yellow needles, m.p.194°. Yield 1.2 g.

Analysis :

3.268 mg. of the substance gave 9.016 mg. of carbon dioxide and 1.332 mg. of water.

Found : C, 75.29 % ; H, 4.56 %.

$C_{20}H_{14}O_4$ requires : C, 75.46 % ; H, 4.43 %.

2,1-Anthra-α-pyrone-3'-carboxylic acid.

The above ester (1 g.) was heated on a steam bath with sodium hydroxide (5 % ; 40 ml.) for 3 hours. The product obtained on acidification was crystallised first from dilute alcohol (charcoal) and then from benzene in fine red needles, m.p.305-306° (decomp.)

Analysis :

3.570 mg. of the substance gave 9.772 mg. of carbon dioxide and 1.174 mg. of water.

Found : C, 74.70 % ; H, 3.68 %.

$C_{18}H_{10}O_4$ requires : C, 74.48 % ; H, 3.47 %.

Decarboxylation of the acid : 2,1-Anthra-α-pyrone.

2,1-Anthra-α-pyrone-3'-carboxylic acid (0.1 g.) was decarboxylated by heating its solution in quinoline (5 ml.) with a little copper powder at 210-222°. The reaction mixture was then filtered and the filtrate treated with dilute hydrochloric acid. The product obtained crystallised from dilute alcohol (charcoal) m.p.192°. The mixed m.p.with 2,1-anthra-α-pyrone, described before, was not depressed.

Kostanecki-Robinson acetylation of 1-acetyl-2-anthrol : 2'-Methyl-3'-acetyl-2,1-anthra-γ-pyrone.

1-Acetyl-2-anthrol (1 g.) was heated with freshly fused and powdered sodium acetate (3 g.) and acetic anhydride (6 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. The solid obtained was filtered. It crystallised from acetic acid (charcoal) in yellow needles, m.p.252-253°. Yield 0.4 g.

Analysis :

4.016 mg. of the substance gave 11.714 mg. of carbon dioxide and 1.746 mg. of water.

Found : C, 79.60 % ; H, 4.86 %.

$C_{20}H_{14}O_3$ requires : C, 79.50 % ; H, 4.63 %.

2'-Methyl-2,1-anthra-γ-pyrone.

2'-Methyl-3'-acetyl-2,1-anthra-γ-pyrone (0.5 g.) suspended in alcohol (50 % ; 50 ml.) was refluxed with sodium carbonate (2 g.) for 2 hours. The reaction mixture was then diluted with water and filtered. The product obtained crystallised from dilute acetic acid in needles, m.p.173°. The mixed m.p. with 2'-methyl-2,1-anthra-γ-pyrone, described before, was not depressed.

Kostanecki-Robinson benzoylation of 1-acetyl-2-anthrol : 2'-Phenyl-3'-benzoyl-2,1-anthra-γ-pyrone.

An intimate mixture of 1-acetyl-2-anthrol (1 g.) freshly fused and powdered sodium benzoate (1.5 g.) and benzoic anhydride (5 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 excess of benzoic anhydride and finally washed with sodium bicarbonate solution. The residue crystallised from acetic acid (charcoal) in small yellow needles, m.p.270°. *Yield 0.5 g.*

Analysis :

4.354 mg. of the substance gave 13.406 mg. of carbon dioxide and 1.624 mg. of water.

Found : C, 84.03 % ; H, 4.17 %.

$C_{30}H_{18}O_3$ requires : C, 84.50 % ; H, 4.22 %.

2'-Phenyl-2,1-anthra-γ-pyrone.

2'-Phenyl-3'-benzoyl-2,1-anthra-γ-pyrone (0.2 g.) was refluxed with alcoholic sodium hydroxide (5 % ; 20 ml.)

on a steam bath for one hour. The reaction mixture was filtered hot and diluted with water. The product which separated, crystallised from dilute acetic acid (charcoal) in pale yellow needles, m.p.219°. The mixed m.p. with 2'-phenyl-2,1-anthra-γ-pyrone, described before, was not depressed.

Condensation of 1-acetyl-2-anthrol with benzaldehyde : 2'-Phenyl-2',3'-dihydro-2,1-anthra-γ-pyrone.

To a mixture of 1-acetyl-2-anthrol (1.2 g.) in ethyl alcohol (50 ml.) and benzaldehyde (2 ml.), potassium hydroxide solution (2.5 g. in 5 ml. water) was added in small lots. The air was removed by bubbling nitrogen through the solution and the flask was corked and kept for 2 days at room temperature. The solution was then diluted with water and acidified. The residue was taken in ether and the ethereal layer was washed first with sodium bicarbonate solution then with sodium hydroxide solution and finally with water. The residue obtained on removal of ether crystallised from alcohol in yellowish plates, m.p.192°. Yield 0.4 g.

It ~~does~~ did not give any colouration with alcoholic ferric chloride.

Analysis :

3.686 mg. of the substance gave 11.450 mg. of carbon dioxide and 1.670 mg. of water.

Found : C, 84.77 % ; H, 5.07 %.

$C_{23}H_{16}O_2$ requires : C, 85.19 % ; H, 4.94 %.

Treatment of 2'-phenyl-2',3'-dihydro-2,1-anthra-γ-pyrone with selenium dioxide : 2'-Phenyl-2,1-anthra-γ-pyrone.

A mixture of the above γ-pyrone (0.1 g.), selenium dioxide (0.2 g.) and dry amyl alcohol (10 ml.) was heated under reflux in an oil bath at 150° for 8 hours. The reaction mixture was then filtered hot and the product obtained on removal of the amyl alcohol was washed with a dilute sodium hydroxide solution. It crystallised from dilute acetic acid in pale yellow needles, m.p.219°. The mixed m.p. with 2'-phenyl-2,1-anthra-γ-pyrone, described before, was not depressed.