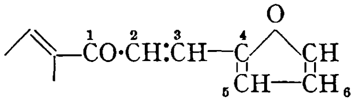
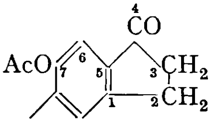
261. *Experiments on the Synthesis of Substances Related to the Sterols. Part XXI. A New Synthesis of Derivatives of Keto*cyclo*penteno-phenanthrene.*

By Robert Robinson.

2-Acetylnaphthalene, or a derivative unsubstituted in position 1, is condensed with furfuraldehyde and the resulting unsaturated ketone is then hydrolysed by aqueous-alcoholic hydrogen chloride with formation of ω-(β-naphthyl)diketoheptoic acid or a derivative thereof. This stage is analogous to the preparation of 7-phenyl-4 : 7-diketoheptoic acid (phenacyl-lævulic acid) by Kehrer and Igler (1899). Ring-closure of 1 : 4-diketones of the form $R{\cdot}CO{\cdot}CH_2{\cdot}CH_2{\cdot}CO{\cdot}CH_2{\cdot}R'$ to *cyclo*pentenones has not previously been effected but these aryldiketoheptoic acids undergo intramolecular condensation with great facility in 2% aqueous potassium hydroxide. The naphthyl-*cyclo*pentenoneacetic acids that are so produced afford the acetyl derivatives of hydroxy*cyclo*pentenonophenanthrenes when they are heated with acetic anhydride. In this synthesis the carbon skeleton is provided by the acetylnaphthalene and furfuraldehyde which are the starting points; the products are of interest as potential intermediates for the synthesis of equilenin and of substances related to other sex-hormones. The investigation is being developed in several directions, among which is a study of the products formed by catalytic hydrogenation.

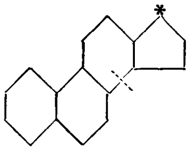
The first and the last stage are represented schematically below so as to show how the carbon atoms of furfuraldehyde are eventually arranged.

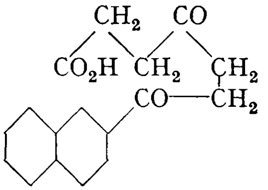




Construction of the *cyclo*pentenophenanthrene nucleus has hitherto been achieved by the final ring-closure indicated by the dotted lines in (I), but it is hard to devise a modification of known procedure which will be applicable to the synthesis of substances

(I.)

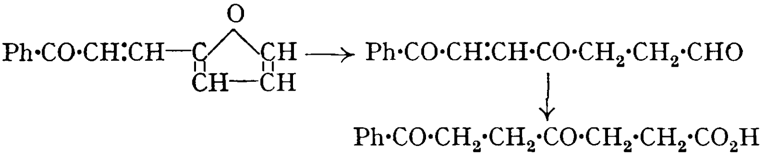




(II.)

suitably substituted in the asterisked position. At the outset it appeared that a *diketo-acid* (II) might be induced to undergo a double condensation in the directions indicated by the conformation of the chain.

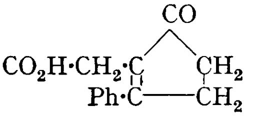
The preparation of 7-phenyl-4 : 7-diketoheptoic acid by Kehrer and Igler (*Ber.*, 1899, **32**, 1178; 1901, **34**, 1263) in a simple fashion indicated that the starting points would probably be readily accessible and this consideration made an investigation of the subject all the more desirable. Phenyldiketoheptoic acid is obtained by the hydrolysis of furfurylideneacetophenone (yield, about 50%) by means of a boiling mixture of alcohol and concentrated hydrochloric acid, the process involving hydrolytic fission of the furan ring and an oxidation-reduction :

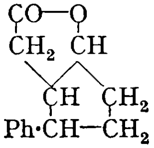


This interesting reaction has been realised in one or two further cases; it appears from the sequel to be general when the starting point is an aryl methyl ketone but it gives poor results with furfurylideneacetone (Kehrer and Igler, *loc. cit.*) and, as Mr. A. Koebner has found in this laboratory, it does not work at all with difurfurylidene*cyclo*hexanone. The diketo-acids have not previously been employed for synthetic purposes other than the synthesis of related pyrrole derivatives. Some preliminary experiments were made with the series from *furfurylideneacetoveratrone*, and as these gave favourable indications the properties of phenyldiketoheptoic acid were studied in more detail. Efforts to effect the two condensations in one operation, for example, with phosphoryl chloride, were fruitless and it was then noted that acid condensing agents led to the formation of phenylfuranpropionic acid, a substance which is being employed for another purpose and a description of which is reserved.

It became clear that the desired condensations must be made step-wise and that basic catalysts must be employed in the first instance. Powerful agents such as sodium ethoxide in alcoholic solution led to the formation of dark brown substances, but the desired phenyl*cyclo*pentenoneacetic acid was isolated in small yield from the mixture. Probably the condensation occurs in a few minutes and is followed by other reactions; the products were only examined after some hours. The yield was somewhat better when cold methyl-alcoholic potassium hydroxide was employed, and eventually it was discovered that a smooth and almost complete condensation occurs in dilute aqueous potassium hydroxide solution. The reaction goes slowly in the cold and requires about ½ hour at the boiling point.

(III.)

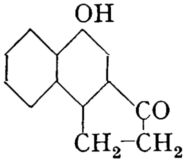


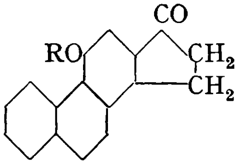


(IV.)

On reduction with sodium and alcohol 3-*phenyl*-Δ^2-cyclo*penten*-1-*one*-2-*acetic acid* (III) affords the sodium salts of a mixture of hydroxy-acids. One (or perhaps two) of these lactonise with formation of (IV), a *substance* possessing a characteristic odour; the other isomerides were encountered as a viscous oil that could not be crystallised. The Fittig α-naphthol synthesis was realised in the case of the acid (III) when it was gently heated with concentrated sulphuric acid. The substance so obtained is regarded as 4-*hydroxy*-3′-*keto*-1 : 2-cyclo*pentenonaphthalene* (V). It has the properties of a phenolic ketone and it couples with *p*-nitrobenzenediazonium acetate to a scarlet azo-compound.

(V.)



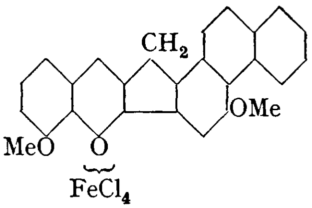


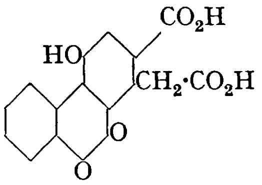
(VI.)

Furfurylidene-2-acetylnaphthalene is a source of 7-β-*naphthyl-4* : 7-*diketoheptoic acid* (II) and 3-β-*naphthyl*-Δ^2-cyclo*penten*-1-*one*-2-*acetic acid*, but the latter substance is largely sulphonated as well as dehydrated by the action of sulphuric acid. The final ring-closure in this instance is effected by means of boiling acetic anhydride, and the product, obtained in excellent yield, is the *acetyl* derivative of 4-*hydroxy*-3′-*keto*-1 : 2-cyclo*pentenophenanthrene* (VI, R = Ac). The *phenolic ketone* (VI, R = H) obtained on hydrolysis has been converted into a *methyl ether* (VI, R = Me), and a number of derivatives have been prepared among which may be mentioned the *dimethoxyphenanthra*cyclo*pentadienochromylium ferrichloride* (VII) obtained by condensation of the methyl ether with *o*-vanillin in the presence of hydrogen chloride and subsequent treatment with ferric chloride.

The oxidation of (VI, R = Ac) with chromic acid in aqueous acetic acid solution gave orange substances that were undoubtedly phenanthraquinone derivatives (see p. 1395) because of their characteristic properties and transformations, but the products were mixtures which were hard to resolve. A small quantity of an *acid*, probably (VIII), was isolated and analysed. Although the yields of phenanthraquinone derivatives in these oxidation experiments were very unfavourable, the explanation is obviously that further oxidation of the products could not be avoided, and, as the material oxidised was homogeneous, the formation of some phenanthraquinone derivative is significant and may be regarded as decisive proof of constitution. It is possible that the second ring-closure gives by-products derived from anthracene, and a search for such substances in the mother-liquors from the crystallisations is being made.

(VII.)

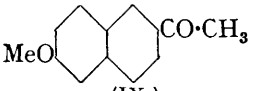




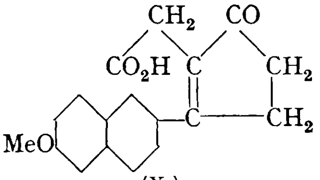
(VIII.)

The important discovery of R. D. Haworth and Sheldrick (J., 1934, 865), that 2-methoxynaphthalene can be acylated in the 6-position by means of Friedel–Crafts reactions carried out in nitrobenzene solution, makes 6-methoxy-2-acetylnaphthalene (IX) a readily accessible substance. The *furfurylidene* derivative of this ketone underwent the usual hydrolysis to a diketo-acid (with partial demethylation, see p. 1396) which afforded 3-(6′-*methoxy-β-naphthyl*)-Δ^2-cyclo*penten*-1-*one*-2-*acetic acid* (X) when its dilute solution in 2% aqueous potassium hydroxide was heated on the steam-bath.

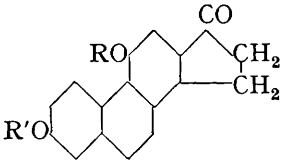
Ring-closure with boiling acetic anhydride proceeded smoothly with formation of (XI; R = Ac, R′ = Me), and a number of derivatives of this *substance* have been characterised.



(IX.)



(X.)



(XI.)

Experimental.

Furfurylideneacetoveratrone.—Aqueous sodium hydroxide (10 c.c. of 5N) was added to a solution of acetoveratrone (21 g.) and furfuraldehyde (15 g.) in warm alcohol (65 c.c.). Separation of a thick paste of crystals occurred in a few minutes. After 1 hour the product was collected, washed, and dried (25 g.), and a further quantity (4·5 g.) was recovered from the mother-liquor. The *substance* crystallised from methyl alcohol in pale yellow, glistening needles, m. p. 81°, soluble in concentrated hydrochloric acid to an orange-red solution (Found : C, 69·7; H, 5·5. $C_{15}H_{14}O_4$ requires C, 69·8; H, 5·4%). Hydrolysis by means of aqueous-alcoholic hydrochloric acid under conditions generally similar to those described below for furfurylidene-2-acetylnaphthalene gave a rather poor yield of 7-*veratryl*-4 : 7-*diketoheptoic acid.* The exact details need not be specified because the process adopted can certainly be improved without difficulty. The new acid crystallised from ethyl acetate as colourless prismatic needles, m. p. 126° (Found, in material dried at 100° in a high vacuum : C, 61·0; H, 6·1. $C_{15}H_{18}O_6$ requires C, 61·2; H, 6·2%). At an early stage in this investigation this acid was subjected to the action (or successive action) of various condensing agents, and in several cases clear evidence of the formation of a naphthol derivative was obtained.

3-*Phenyl*-Δ^2-cyclo*penten*-1-*one*-2-*acetic Acid* (III).—Furfurylideneacetophenone (Kostanecki and Podrajansky, *Ber.*, 1896, **29**, 2248; Semmler, *Ber.*, 1906, **39**, 729; Semmler and Ascher, *Ber.*, 1909, **42**, 2356) is described in the literature as an oil; a distilled specimen crystallised, and the substance can be easily recrystallised from light petroleum (b. p. 40—60°) as pale yellow needles, m. p. 47° (Found : C, 78·9; H, 5·2. Calc. for $C_{13}H_{10}O_2$: C, 78·8; H, 5·1%).

The hydrolysis to 7-phenyl-4 : 7-diketoheptoic acid was carried out by the method of Kehrer and Igler (*loc. cit.*) and the yield was 55—60%. A solution of this acid (20 g.) in water (2000 c.c.) and potassium hydroxide (40 g.) was boiled for an hour, then cooled, mixed with salt (100 g.), acidified with hydrochloric acid, and seeded with a specimen of the phenyl*cyclo*pentenoneacetic acid that had been obtained from an earlier experiment in which methyl-alcoholic potassium hydroxide had been employed. The soft, nearly colourless needles were collected and dried (18 g.). This product crystallised from benzene and from chloroform–light petroleum (b. p. 80—100°) as very pale yellow needles and prisms, m. p. 141° (Found, in material dried at 80° in a high vacuum: C, 72·3; H, 5·5. $C_{13}H_{12}O_3$ requires C, 72·2; H, 5·5%). The *acid* crystallises from benzene in a solvated condition; it is readily soluble in chloroform and acetone and moderately readily soluble in hot water, from which it separates in woolly needles. Its solution in aqueous sodium bicarbonate reduces permanganate quickly, but not instantly, the only products of the oxidation that could be recognised being benzoic and oxalic acids.

The 2 : 4-*dinitrophenylhydrazone* crystallised from acetic acid–ethyl acetate in deep red, rhombic and hexagonal prisms and prismatic needles, m. p. 273° (decomp.), soluble in aqueous sodium carbonate to an intensely orange-yellow solution (Found: C, 57·5; H, 4·2; N, 14·0. $C_{19}H_{16}O_6N_4$ requires C, 57·6; H, 4·0; N, 14·1%).

Lactone of 3-*Phenyl*cyclo*pentan*-1-*ol*-2-*acetic Acid* (IV).—Phenyl*cyclo*pentenoneacetic acid (15 g.) was reduced in alcoholic solution (400 c.c.) by means of sodium (40 g.); a little water was added to complete the solution of the metal. The solution was acidified with hydrochloric acid, rendered faintly alkaline again, filtered, and the alcohol removed by distillation finally under diminished pressure. Excess of hydrochloric acid was then added, and the mixture heated in the steam-bath for an hour. The product was isolated by means of ether and separated into a neutral and an acidic fraction. The former was a colourless oil, b. p. 153°/0·15 mm. (Found: C, 77·3; H, 6·9. $C_{13}H_{14}O_2$ requires C, 77·2; H, 6·9%). This substance exhibits the behaviour of a *lactone*; it possesses a highly characteristic odour. The *hydroxy-acids* constituting the acidic fraction could not be crystallised. A specimen repeatedly separated from acetic acid solution by the addition of water was dried for a long period in a vacuum over potassium hydroxide and then at 100° (Found: C, 70·6; H, 7·5. $C_{13}H_{16}O_3$ requires C, 70·9; H, 7·3%).

4-*Hydroxy*-3′-*keto*-1 : 2-cyclo*pentenonaphthalene*.—A mixture of phenyl*cyclo*pentenoneacetic acid (1·1 g.) and concentrated sulphuric acid (10 c.c.) was heated for 10 minutes in boiling water, then mixed with water (5 c.c.) without cooling and heated for 3 minutes longer. This procedure seemed necessary in order to hydrolyse a sulphonic acid. The precipitate obtained on pouring into water was collected, washed with aqueous sodium carbonate and water, and then dried (0·55 g.). The material was crystallised from alcohol (90 c.c.) and then from acetic acid and again from alcohol, being obtained as faintly yellow, well-shaped, flat, rectangular needles, m. p. 290—295° (decomp.) with previous darkening (Found, in material dried at 100°: C, 78·6; H, 5·1. $C_{13}H_{10}O_2$ requires C, 78·8; H, 5·1%). The *substance* is sparingly soluble in most organic solvents but is readily soluble in pyridine; its yellow solution in sulphuric acid exhibits an intense bluish-green fluorescence. It dissolves in aqueous sodium hydroxide to a yellow solution, but is insoluble in aqueous sodium carbonate; it exhibits no ferric reaction in alcoholic solution. On heating with chloroform and alcoholic potassium hydroxide, a dull brownish olive-green coloration is developed. As an α-naphthol derivative, it couples readily with diazonium salts to red azo-compounds. The *p*-nitrobenzeneazo-derivative separates from aqueous acetic acid as a deep red crystalline crust exhibiting a bronze lustre, m. p. 245° (decomp.). The azo-compound dissolves in sulphuric acid to a crimson solution; it is insoluble in aqueous alkalis but gives a blue-violet solution in alcoholic potassium hydroxide. The 2 : 4-*dinitrophenylhydrazone* separates in very long, slender, scarlet needles when hot acetic acid solutions of the ketone and of dinitrophenylhydrazine are mixed. This derivative darkens when heated above 200° and decomposes at 305° to a black tar without melting to a clear liquid (Found: C, 60·0; H, 3·9. $C_{19}H_{14}O_5N_4$ requires C, 60·3; H, 3·7%).

When phenyl*cyclo*pentenoneacetic acid (1 g.) was heated with sulphuric acid (5 c.c.) for a short time at 140° until the colour of the solution was a deep brownish-yellow, the addition of water gave a mauve precipitate insoluble in aqueous sodium carbonate. The substance crystallised from acetic acid in well-shaped, brownish-orange, thick hexagonal plates, which were canary-yellow by transmitted light, m. p. 290° with previous darkening. The m. p. was depressed on admixture with hydroxyketo*cyclo*pentenonaphthalene. The solution in sulphuric acid is salmon-red in colour, and has a dull green fluorescence. The substance is undoubtedly quite different from that obtained at 100°, but the analyses could not be interpreted (Found, in material dried at 100° in a high vacuum: C, 77·7, 77·8; H, 5·1, 5·1%). The substance dissolves in aqueous sodium hydroxide to an orange-yellow solution, and couples with diazo-salts with formation of crimson azo-compounds. It is perhaps formed by condensation of two molecules of the hydroxy-ketone through the indanone group, but then it must retain rather more than ½H_2O very tenaciously.

Furfurylidene-2-acetylnaphthalene.—A cold solution of sodium ethoxide (5 g. of sodium) in alcohol (200 c.c.) was added to a mixture of 2-acetylnaphthalene (100 g.), furfuraldehyde (65 c.c.) and alcohol (100 c.c.). The liquid became warm and crystallisation began in a few seconds. After 14 hours the product was collected, washed with alcohol and aqueous alcohol, and dried (140 g.). The unsaturated *ketone* crystallises from alcohol in the form of stout yellow prisms and prismatic needles, m. p. 91° (Found: C, 82·4; H, 5·0. $C_{17}H_{12}O_2$ requires C, 82·2; H, 4·8%), soluble in sulphuric acid to an orange-red solution.

7-β-*Naphthyl*-4 : 7-*diketoheptoic Acid* (II).—A mixture of furfurylidene-2-acetylnaphthalene (20 g.), alcohol (200 c.c.), and hydrochloric acid (50 c.c., *d* 1·16) was refluxed for 18 hours, and the alcohol then removed by distillation, finally under diminished pressure. Concentrated hydrochloric acid (100 c.c.), acetic acid (100 c.c.), and water (200 c.c.) were added to the residue, and the whole gently refluxed (oil-bath) for 2 hours. The pale yellow aqueous solution was then separated as quickly as possible from the oil (hot water funnel or preferably decantation using several vessels), and on cooling, the diketo-acid crystallised (dried, 2·7 g.). The mother-liquor was used to extract the oil again by boiling for 1 or 2 hours, and the process repeated until very little of the acid separated. The successive crops after the first weighed 3·3, 4·5, 1·9, 0·7, and 0·2 g. (total, 14·3 g.). The increasing yield in the first three extractions suggests that a process of hydrolysis of ethyl ester or a furan derivative (*e.g.*, naphthylfuranpropionic acid) occurred. 7-β-*Naphthyl*-4 : 7-*diketoheptoic acid* crystallised from ethyl acetate and then from acetic acid containing a little water in long flat needles, m. p. 167—169° (Found, in material dried at 100°: C, 71·4, 71·6; H, 5·6, 5·7. $C_{17}H_{16}O_4$ requires C, 71·8; H, 5·6%). The solution of this acid in sulphuric acid is deep orange in colour.

The *bis*-2 : 4-*dinitrophenylhydrazone*, prepared from the acid (0·8 g.) and dinitrophenylhydrazine (1·1 g.) in acetic acid (25 c.c.) at 100°, crystallised from the hot solution in orange-red microscopic needles, yellow by transmitted light; it was washed with acetic acid and alcohol and dried at 100°, m. p. 250° (decomp.) (Found: C, 54·2; H, 4·1; N, 17·0. $C_{29}H_{24}O_{10}N_8$ requires C, 54·0; H, 3·7; N, 17·4%).

The *disemicarbazone* was obtained by the addition of semicarbazide hydrochloride to a solution of the acid in aqueous sodium carbonate; the mixture was later acidified with acetic acid. The caseous precipitate dissolved in hot alcohol and quickly separated as dense clusters of white microscopic needles which could not be redissolved; m. p. 183—184° (decomp.) (Found: N, 20·7. $C_{19}H_{22}O_4N_6$ requires N, 21·1%).

3-β-*Naphthyl*-Δ^2-cyclo*penten*-1-*one*-2-*acetic Acid.*—A mixture of naphthyldiketoheptoic acid (10 g.), water (1 l.), and potassium hydroxide (20 g.) was kept for 3 days at room temperature or, alternatively and preferably, heated at 95—100° for 1 hour. The cooled solution was acidified, and then seeded if necessary. The *acid* was collected, washed, and dried (9·4 g.). In this form the substance is sufficiently pure for the next stage, but for some other purposes it can conveniently be purified by treatment with not too much hot ethyl acetate. The substance was crystallised by solution in ethyl acetate (5 vols.) and addition of light petroleum (b. p. 60—80°, 2 vols.) and then by recrystallisation from acetone and from chloroform. It was finally obtained as colourless prismatic needles, m. p. 168—169° (Found, in material dried at 100°: C, 76·4; H, 5·2. $C_{17}H_{14}O_3$ requires C, 76·7; H, 5·2%). An alkaline solution quickly decolorises permanganate, and when the process was carried to the end in the cold, β-naphthoic acid was produced; the expected β-naphthoylpropionic acid could not be isolated.

The yellow solution in sulphuric acid becomes paler on warming and a green fluorescence is developed.

4-*Hydroxy*-3′-*keto*-1 : 2-cyclo*pentenophenanthrene and its Derivatives* (VI).—The *acetyl* derivative (VI, R = Ac) was obtained by refluxing a mixture of naphthyl*cyclo*pentenone-acetic acid (10 g.) and acetic anhydride (75 c.c.) for 30 minutes. The excess acetic anhydride (65 c.c.) was distilled off, and methyl alcohol (50 c.c.) added to the residue. The product was collected, washed with methyl alcohol, and dried at 100° (10·5 g., 90%). The addition of water to the methyl-alcoholic solution gave a small chalky precipitate which has not been examined.

The substance was crystallised from ethyl acetate and then from acetic acid and was obtained as rosettes of colourless, glistening needles, m. p. 207° (Found, in material dried at 100° in a high vacuum: C, 78·4; H, 4·9. $C_{19}H_{14}O_3$ requires C, 78·6; H, 4·8%). The yellow solution in sulphuric acid exhibits a weak green fluorescence that becomes much stronger on gentle heating.

Hydrolysis was readily effected by hot aqueous, or better, alcoholic, sodium hydroxide, and the bright yellow solution on acidification gave a colourless chalky precipitate of the free phenolic *ketone* (VI, R = H) (quantitative yield). This is very sparingly soluble in most organic solvents except pyridine, and is best crystallised from *iso*amyl alcohol. It occurs as flat, pale yellow needles which on heating darken from about 270°, soften at 300°, and melt at 310—315° to a brown tar (Found, in material dried at 100° in a high vacuum: C, 82·3; H, 4·8. $C_{17}H_{12}O_2$ requires C, 82·2; H, 4·8%). Scarlet-red azo-compounds are obtained by coupling this phenanthrol with diazo-salts of the benzene series.

The *oxime* of the hydroxy-ketone was prepared by the pyridine method; it crystallised from the reaction mixture in colourless needles, and was recrystallised from acetic acid and then from ethyl acetate; m. p. 271° (decomp.) (Found: C, 77·4; H, 4·9; N, 5·2. $C_{17}H_{13}O_2N$ requires C, 77·6; H, 4·9; N, 5·3%). The derivative is more readily soluble than other compounds mentioned in this section.

The *anisylidene* derivative of the hydroxy-ketone was prepared in a boiling alcoholic solution with the help of potassium hydroxide. The bright red solution was acidified while hot with acetic acid, intensely yellow needles being precipitated. The substance is very sparingly soluble in boiling formic and acetic acids, alcohol, and ethyl acetate. It is readily soluble in hot pyridine and nitrobenzene (pale yellow solution), but crystallisation was slow on the addition of acetic acid and alcohol respectively. The best medium is *iso*amyl alcohol, although separation was slow in this case also. The short yellow microscopic needles soften and decompose to a viscid tar at 305—310° (Found:* C, 81·8; H, 5·6. $C_{25}H_{18}O_3$ requires C, 82·0; H, 5·9%). The solution in alcoholic alkalis is red, and in sulphuric acid, crimson. The *methyl ether* (VI, R = Me) was obtained from the acetyl derivative by treating an alcoholic suspension alternately with aqueous potassium hydroxide (40%) and methyl sulphate so as to heat the solution. The stage of completion of the methylation was judged by the disappearance of the yellow colour of the alkaline solution. Water was added, and the solid collected, washed, dried and crystallised from alcohol. The colourless, short, very slender, glistening needles, m. p. 179°, were dried at 100° (Found: C, 82·1; H, 5·3. $C_{18}H_{14}O_2$ requires C, 82·4; H, 5·3%). The solutions of this substance in neutral solvents exhibit a violet fluorescence.

8 : 4′-*Dimethoxyphenanthra*cyclo*pentadienochromylium Ferrichloride* (VII).—The last-described methoxy-ketone (0·2 g.) and *o*-vanillin (0·1 g.) were dissolved in the minimum of ethyl acetate, and the solution saturated with hydrogen chloride. Crystallisation of a deep brownish-red chloride commenced in 2 minutes, and after 30 minutes the salt was collected. It crystallised from alcoholic hydrochloric acid in bronze needles. The *ferrichloride* crystallised from a mixture of formic and acetic acids, in which it is very sparingly soluble, in spherical groups of short microscopic needles which shrink at 245—248° and then gradually carbonise without melting (Found: C, 54·0; H, 3·4. $C_{26}H_{19}O_3Cl_4Fe$ requires C, 54·1; H, 3·3%). The salt is chocolate brown in mass; its red solution in sulphuric acid is not fluorescent.

*Degradation Experiments with Acetoxyketo*cyclo*pentenophenanthrene.*—Reduction by Clemmensen's method in the presence of anisole afforded a phenol which gave blue-fluorescent solutions and coupled with diazonium salts to azo-compounds; that from *p*-nitrobenzene-diazonium acetate was brownish-red, and gave a bluish-green solution in alcoholic potassium hydroxide. This phenol, which is almost cryptophenolic, was distilled with zinc dust in a stream of hydrogen, giving a hydrocarbon, m. p. about 160°, evidently not *cyclo*pentenophenanthrene. The yield was unsatisfactory and the substance appeared to be a mixture, so the investigation was not pursued.

Preliminary experiments on the oxidation of the acetyl derivative with chromic acid were conducted in acetic acid solution, aqueous acetic acid solution, and in cold acetic anhydride. In all cases orange quinones were formed in small yield. A product obtained in acetic acid solution was bright orange and readily soluble in aqueous sodium bisulphite to a lemon-yellow solution. To this was added 4 : 5-diaminoveratrole and sodium acetate. On heating, a flocculent precipitate was obtained which was extracted by a very large volume of hot benzene. The benzene was washed with bisulphite, dried, and filtered, and then exhibited the violet fluorescence characteristic of phenanthraphenazines derived from 4 : 5-diaminoveratrole. The benzene solution on evaporation gave a brownish-yellow residue, which dissolved in sulphuric acid to a brilliant magenta-coloured solution. The characteristic green fluorescence in benzene and mauve colour in sulphuric acid were obtained when 2 : 3-diaminoveratrole was used. The quinone dissolves in alcoholic potassium hydroxide to a greenish-blue solution. Efforts to repeat the experiment on a larger scale were only partly successful; the yield was unsatisfactory and the product was acidic.

* After allowance for a residue.

Chromic anhydride (30 g.), dissolved in acetic acid (300 c.c.) and water (50 c.c.), was gradually added to a boiling solution of acetoxyketo*cyclo*pentenophenanthrene (10 g.) in acetic acid (200 c.c.). When the chromic acid had been reduced, a part of the acetic acid was removed by distillation and water was added to the residue. The ochre-orange precipitate was collected, washed with water, and triturated with hot aqueous sodium bisulphite. The brown-yellow, filtered solution was acidified with sulphuric acid, and the orange precipitate collected, washed, and dried. It dissolved partly in hot acetic acid, but only a little amorphous material separated on cooling. The acetic acid filtrate from this was diluted with water, the solid isolated, and as it was then found to be an acid, dissolved in aqueous sodium carbonate and recovered by acidification. The *substance* could then be crystallised from ethyl acetate in bright orange, microscopic prisms of irregular shape (Found, in material dried at 100° in a high vacuum: C, 62·1; H, 2·9. $C_{17}H_{10}O_7$ requires C, 62·6; H, 3·0%. $C_{16}H_8O_7$ requires C, 61·5; H, 2·6%).

The substance does not melt at 350°; its solution in aqueous sodium carbonate is weak orange-yellow, and in alcoholic potassium hydroxide, dull bluish-green. It forms a phenazine derivative by condensation with *o*-phenylenediamine in acetic acid solution. The constitution of this substance is probably (VIII) but it may be mixed with the lower homologous dibasic acid. It is not identical with the phenanthraquinone derivative examined in the small-scale experiments.

Furfurylidene-6-*methoxy*-2-*acetylnaphthalene*.—The author is greatly indebted to Dr. R. D. Haworth for information regarding the preparation of 6-methoxy-2-acetylnaphthalene. When the process of Haworth and Sheldrick (*loc. cit.*) was used on a larger scale the results were found to be variable. Some modifications that have been made in this laboratory have given favourable results, and it is hoped to publish a reliable prescription in due course. The research department of Messrs. Boots Pure Drug Co. Ltd. kindly undertook the preparation of the ketone, and supplied a very pure colourless specimen, m. p. 107° (lit. 105°). The author wishes to thank Dr. F. L. Pyman, F.R.S., for the details of the method employed. A mixture of this pure ketone (35 g.), furfuraldehyde (25 g.), and methyl alcohol (250 c.c.) was heated until a clear solution was obtained, and sodium methoxide (2 g. of sodium) in methyl alcohol (50 c.c.) was then added. Crystallisation occurred in a few minutes, and next day the solid was isolated and dried at 90° (46 g. or 95%). The *substance* crystallises from acetone as pale yellow, chalky, aggregates of prisms, m. p. 113° (Found: C, 77·6; H, 5·1. $C_{18}H_{14}O_3$ requires C, 77·7; H, 5·0%). The solution in sulphuric acid is crimson.

7-(β-6′-*Methoxynaphthyl*)-4 : 7-*diketoheptoic Acid*.—This acid was prepared like 7-β-naphthyl-4 : 7-diketoheptoic acid. The unsaturated ketone (14 g.) was hydrolysed by refluxing with a mixture of alcohol (240 c.c.) and concentrated hydrochloric acid (60 c.c.). After removal of the solvent, concentrated hydrochloric acid (80 c.c.), acetic acid (100 c.c.) and water (200 c.c.) were added, and the successive extractions gave crops of 1·5, 1·95, 2·55, 1·2, 0·95, and 0·45 g. (2 crops) (total, 8·6 g.). After crystallisation this acid had m. p. 138—140°, and was found to contain a small proportion of demethylated material. It was shaken with methyl sulphate and aqueous sodium hydroxide in the cold until the diazo-coupling test was negative, and then recovered. The *product* was crystallised from equal parts of acetic acid and water and obtained as pearly laminæ, m. p. 142—143° (Found, in material dried at 100°: C, 68·7; H, 5·8. $C_{18}H_{18}O_5$ requires C, 68·8; H, 5·7%). The solution in sulphuric acid is intensely orange in colour. The formation of a red bisdinitrophenylhydrazone was noted.

3-(6′-*Methoxy*-β-*naphthyl*)-Δ^2-cyclo*penten*-1-*one*-2-*acetic Acid* (X).—This and the other substances described below were obtained by the methods used for the series lacking the methoxyl group. The pure methylated diketo-acid gave an almost quantitative yield of the unsaturated acid, which crystallised from glacial acetic acid in yellow, glistening, prismatic needles containing solvent of crystallisation. It was recrystallised from aqueous acetic acid, and obtained as long straw-coloured needles, m. p. 204—205° (Found, in material dried at 100° in a high vacuum: C, 72·7; H, 5·4. $C_{18}H_{16}O_4$ requires C, 72·9; H, 5·4%). The *acid* is sparingly soluble in hot ethyl acetate. Its canary-yellow solution in sulphuric acid exhibits green fluorescence after keeping for a few seconds. Permanganate is quickly, but not instantaneously, reduced by a solution of the acid in aqueous sodium bicarbonate. For many purposes, such as the preparation of the dimethoxy-compound described below, the methylation of the diketo-acid is unnecessary; the crude diketo-acid (12 g., crystallised from acetic acid but not methylated) gave crude unsaturated acid (11·2 g.). On methylation by means of sodium hydroxide and methyl sulphate in aqueous or methyl-alcoholic medium, followed by crystallisation, the pure acid was obtained. By crystallisation alone the crude acid (5 g.) gave the pure acid (3·8 g.); the mother-liquors contained a mixture which was conveniently methylated and so recovered as the methoxy-acid (0·7 g.).

4-*Hydroxy*-7-*methoxy*-3′-*keto*-1 : 2-cyclo*pentenophenanthrene* (XI; R = H, R′ = Me).—The crude unsaturated acid (5 g.) was refluxed with acetic anhydride (50 c.c.) for ½ hour, the mixture cooled, and water (25 c.c.) added. When the acetic anhydride had been decomposed, the *acetyl* derivative (XI; R = Ac, R′ = Me) was collected, washed, and dried (4·05 g., m. p., 243°). When the pure methylated acid was employed the yield was almost quantitative, and the product crystallised from acetic acid in nearly colourless, slender needles, m. p. 254° after shrinking at 250° (Found, in material dried at 100°: C, 75·1; H, 5·0. $C_{20}H_{16}O_4$ requires C, 75·0; H, 5·0%). The *ketone* (XI; R = H, R′ = Me) is sparingly soluble in most organic solvents; it crystallises in pale yellow, glistening plates when acetic acid is added to its solution in pyridine. The crystals were washed with alcohol and dried at 100° (Found: C, 77·5; H, 5·0. $C_{18}H_{14}O_3$ requires C, 77·7; H, 5·0%). On heating, the substance darkens at 268°, softens at 285°, and melts at 293—299° to a brown tar. The potassium salt crystallises from alcohol in orange needles, and the alcoholic solution of the phenol exhibits a feeble bluish-violet fluorescence. The *p*-nitrobenzeneazo-derivative is deep red, and dissolves in alcoholic sodium hydroxide with a rich violet colour; in sulphuric acid the coloration is bluish-magenta.

The *methyl ether* (XI; R = R′ = Me) crystallised from pyridine–ethyl alcohol and then from *cyclo*hexanone–alcohol as pale yellow, flat needles, m. p. 200—201° after softening at 195° (Found: C, 77·7; H, 5·3. $C_{19}H_{16}O_3$ requires C, 78·1; H, 5·5%). The alcoholic solution exhibits a violet fluorescence. 4 : 7-Dihydroxy-3′-keto-1 : 2-*cyclo*pentenophenanthrene has been obtained by demethylation of the above acetyl derivative of the monomethyl ether and also by full demethylation of the diketo-acid and processes similar to those described. Its properties will be described in a later paper.

DYSON PERRINS LABORATORY, OXFORD UNIVERSITY.

[*Received, July* 6*th*, 1938.]