32. *Experiments on the Synthesis of Substances related to the Sterols. Part XIX.*

By Robert Robinson and James Walker.

The preparation of 1-keto-7-methoxy-1 : 2 : 3 : 4 : 9 : 10 : 11 : 12-octahydrophenanthrene-b * has been improved and its conversion into the 2-carbethoxyl derivative is here described in greater detail. The *C*-methylated ester has been subjected to the Reformatsky reaction with ethyl bromoacetate, but no crystalline product could be isolated, doubtless because a complex mixture of substances and stereoisomerides was obtained. An amorphous methylimide of the anticipated composition was separated after treatment with acetic anhydride, hydrolysis, reduction with hydriodic acid and phosphorus, methylation, and heating with methylamine. 1-Keto-7-methoxy-2-methyl-1 : 2 : 3 : 4 : 9 : 10 : 11 : 12-octahydrophenanthrene-b was isolated as a by-product from the Reformatsky reaction after hydrolysis and is, of course, obtained from unchanged keto-ester.

Further work has shown that the Friedel–Crafts reaction applied to certain methoxydihydronaphthalene derivatives (or ketones which can yield these substances by ring closure and dehydration) involves, first, disproportionation with formation of related naphthalene and tetrahydronaphthalene derivatives, and second, acylation in the benzenoid nucleus or naphthalene nucleus in the *o*-position to methoxyl. The acyl group is removed by hydrolysis from the naphthalene derivatives by the action of hydriodic acid, which reagent has also been found to effect ring closure of a methoxynaphthylbutyric acid to a hydroxyketotetrahydrophenanthrene.

On hydrogenation of 1-keto-7-methoxy-1 : 2 : 3 : 4 : 9 : 10-hexahydrophenanthrene (Robinson and Schlittler, J., 1935, 1288) in ethyl acetate solution (the reaction being incomplete and being carried further in methyl-alcoholic solution) in presence of palladised strontium carbonate, a little more than one-third of the product could be isolated by way of the semicarbazone as dihydro-ketone, the remainder being converted into 7-methoxy-1 : 2 : 3 : 4 : 9 : 10 : 11 : 12-octahydrophenanthr-1-ol. The losses involved in the oxidation of this secondary alcohol to the related ketone by means of chromic acid (J., 1936, 750) or copper oxide (J., 1937, 63) are diminished by the application to this case of the reversed Pondorff method of Oppenauer (*Rec. trav. chim.*, 1937, **56**, 137).

The condensation of methoxyoctahydrophenanthrone with ethyl oxalate was repeated as previously described, anhydrous sodium ethoxide in ethereal suspension being used (J., 1936, 751), but, on heating the product for the elimination of carbon monoxide, considerable decomposition ensued. Closer examination has shown that, although our first experience proved that the reaction may proceed normally, a large proportion of a new substance is apt to be produced and this compound decomposes on heating. It is obtained from the normal product by loss of alcohol and is evidently the enolic *lactone* (I). This substance gives a ferric reaction which may be due to hydrolysis or to an enolic

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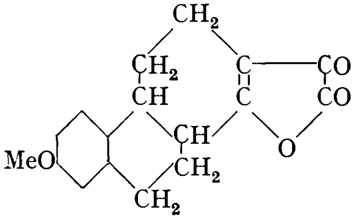
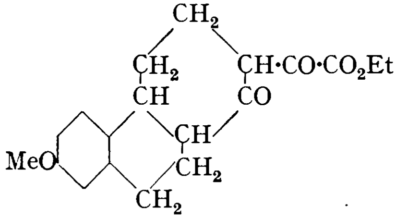
* Reasons have already been given (J., 1936, 748) for the belief that the series-b dealt with in this communication is characterised by *trans*-fusion of the two reduced benzene nuclei.

modification containing the group $:C{=}\dot{C}{-}\dot{C}{:}C(OH)\cdot$. The formation of this lactone is avoided by carrying out the condensation in benzene solution and in this way the pure

(I.)



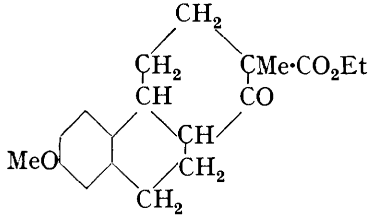


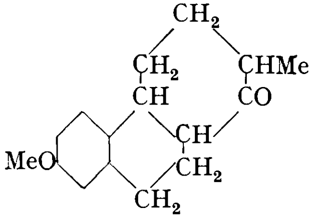
(II.)

ethoxalyl derivative (II or a related enol) may be isolated. The methylated keto-ester (III) was then obtained as already described and this underwent a rather vigorous reaction when it was treated in hot toluene solution with ethyl bromoacetate and zinc.

Hydrolysis of the product gave a mixture of acids and 1-*keto*-7-*methoxy*-2-*methyl*-1 : 2 : 3 : 4 : 9 : 10 : 11 : 12-*octahydrophenanthrene*-b (IV) in proportions indicating that about one third of the keto-ester had undergone the Reformatsky reaction. The acidic

(III.)



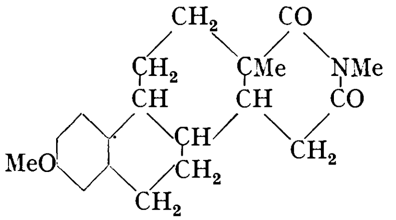


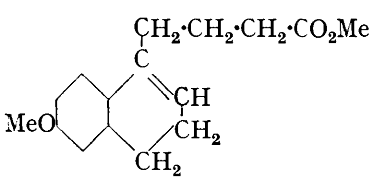
(IV.)

product was an intractable mixture and could not be crystallised. After dehydration with hot acetic anhydride the product absorbed only a few c.c. of hydrogen in the presence of a catalyst and it reduced only a trace of alkaline permanganate, the catalytic hydrogenation making very little difference in this respect. The indication was, therefore, that disproportionation to naphthalene and tetrahydronaphthalene derivatives had occurred. Obviously each of these can exist in stereoisomeric forms.

Finally the acids were heated with hydriodic acid and phosphorus, recovered, methylated, and heated with aqueous methylamine so that the water distilled and a temperature of 200° was reached. The nitrogenous products were acidic and neutral and the latter, although not distinctly crystalline, could be fractionated by means of ethyl acetate–light petroleum. An intermediate fraction of indefinite m. p. was an almost colourless solid, the analysis of which tallied well with the formula $C_{20}H_{25}O_3N$. This material is therefore regarded as a mixture of stereoisomerides of the formula (V). A further attempt will be made to utilise the keto-ester (III) for the synthesis of oestrone, although we fear that the methyl group may be in the wrong stereochemical relation to the fused alicyclic rings.

(V.)





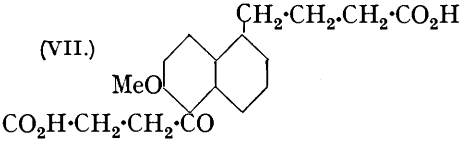
(VI.)

In continuation of experiments reported in Part XVI (Lin, Resuggan, Robinson, and Walker, J., 1937, 68; the work in this case was with the lower homologue of the dihydronaphthalene derivative and γ-carbomethoxybutyryl chloride) we have examined the condensation of the ester (VI) with β-carbomethoxypropionyl chloride in the presence of aluminium chloride. After hydrolysis of the product we were able to separate two *keto-acids*, $C_{19}H_{20}O_6$ and $C_{19}H_{24}O_6$. Both were saturated to permanganate and were clearly the result of disproportionation of the dihydronaphthalene nucleus with formation of naphthalene and tetrahydronaphthalene derivatives, followed by normal condensations. The attack of the ethenoid double bond, which we had hoped for, evidently does not take place and this conclusion applies also to the condensations described in Part XVI. The constitutions of the isomeric acids therein described are now regarded as analogous to (VII) and (VIII) below.

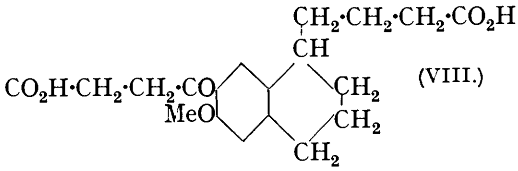
The products obtained on heating the new acid, $C_{19}H_{20}O_6$, with concentrated hydriodic acid were methyl iodide, succinic acid, and 7-hydroxy-1-keto-1 : 2 : 3 : 4-tetrahydrophenanthrene (Butenandt and Schramm, *Ber.*, 1935, **68**, 2090). A little γ-6-methoxy-1-naphthylbutyric acid was prepared by oxidation of the dihydro-acid (corresponding to VI) with alkaline permanganate, and when heated with hydriodic acid this also furnished the same hydroxyketotetrahydrophenanthrene. This novel method of ring closure gives an almost quantitative yield in the present instance and it may have considerable preparative value in other cases.

Of more significance in connection with the constitution of the acid $C_{19}H_{20}O_6$ is the removal of the succinyl residue by hydrolysis. The reaction would probably not occur if the chain were attached to the 2-, 4-, or 7-position in the naphthalene nucleus, whereas it would be anticipated if the acid were a 1-acyl-2-naphthol derivative (position 5 in the case under consideration). Specimens of 1-acetyl-2-naphthol and 3-acetyl-2-naphthol were kindly supplied by Dr. W. Baker and it was found that the former was readily hydrolysed by boiling concentrated hydriodic acid with formation of β-naphthol, whereas the latter was unchanged under the same conditions. Therefore we attribute the constitution (VII) to the acid $C_{19}H_{20}O_6$. Attempts to equate the acids $C_{19}H_{20}O_6$ and $C_{19}H_{24}O_6$ by dehydrogenating the latter were unsuccessful, but it seems very probable that $C_{19}H_{24}O_6$ is either the tetrahydro-derivative of (VII) or has the structure (VIII).

(VII.)



(VIII.)



EXPERIMENTAL.

1-*Keto*-7-*methoxy*-1 : 2 : 3 : 4 : 9 : 10 : 11 : 12-*octahydrophenanthrene*.—(A) 1-Keto-7-methoxy-1 : 2 : 3 : 4 : 9 : 10-hexahydrophenanthrene (22 g.) was hydrogenated in ethyl acetate solution (180 c.c.) under 3 atms. with a palladised strontium carbonate catalyst (16 g. of 2%) for 16 hours; the product then isolated still contained some unreduced material as shown by the colour of the precipitate obtained with Brady's reagent. Hydrogenation was completed in methyl-alcoholic solution and the product was isolated and treated in the manner described previously (J., 1936, 750), yielding the semicarbazone (9·3 g.) of the desired ketone along with methoxyoctahydrophenanthrol (13·5 g.).

(B) 7-Methoxy-1 : 2 : 3 : 4 : 9 : 10 : 11 : 12-octahydrophenanthr-1-ol (18·6 g.), dissolved in acetone (400 c.c.), was added to a solution of aluminium *tert.*-butoxide (33 g.) in dry benzene (800 c.c.) and the mixture was refluxed for 36 hours and worked up as described by Oppenauer (*loc. cit.*). The crude product had the odour of mesityl oxide and this was removed by steam-distillation; further treatment, as above, yielded the semicarbazone (9·7 g.) of the desired ketone along with unchanged secondary alcohol (7·1 g.).

The yield of ketone was not diminished when the aluminium *tert.*-butoxide was replaced by a mixture of aluminium *iso*propoxide and an equivalent amount of *tert.*-butyl alcohol. In one experiment aluminium *iso*propoxide was used without any addition of *tert.*-butyl alcohol and the yield of ketone was diminished, but, as the phenanthrol used in this experiment had been recovered from several previous ones, a more difficultly oxidisable stereoisomeride may have accumulated in it.

As described previously (*loc. cit.*), the hydrolysis of the semicarbazone yielded a mixture of a labile (oil) and a stable (solid) ketone; the latter was freed from the former by crystallisation from methyl alcohol and had the recorded properties.

Enolic Lactone of 1-*Keto*-7-*methoxy*-1 : 2 : 3 : 4 : 9 : 10 : 11 : 12-*octahydro*-2-*phenanthroylformic Acid* (I).—1-Keto-7-methoxy-1 : 2 : 3 : 4 : 9 : 10 : 11 : 12-octahydrophenanthrene (3·76 g.) and ethyl oxalate (2·5 g.) were dissolved in pure ether (120 c.c.) and freshly prepared alcohol-free sodium ethoxide (1·5 g.) was added in lumps and then disintegrated; an orange sodium derivative soon separated. After 2 days, ether and dilute sulphuric acid were added; the cream-coloured solid then precipitated was collected and dried (0·21 g., m. p. 180—183° with decomp.). The ethereal solution was separated, dried, and evaporated; the resulting orange semi-solid material deposited a further quantity (1·2 g.) of the foregoing solid on crystallisation from alcohol. The alcoholic mother-liquors yielded a mixture (2·7 g.), which was distributed between ether and dilute sodium hydroxide solution. From the ethereal layer a further quantity of the enolic lactone (0·8 g.) was obtained. The alkaline solution afforded the ethyl ester (1·7 g.) described below on acidification and extraction with ether.

The enolic *lactone* (I) separated from alcohol in small cream-coloured prisms, m. p. 184—186° (decomp.) after softening from 180° (Found : C, 71·3; H, 5·7. $C_{17}H_{16}O_4$ requires C, 71·8; H, 5·7%). With alcoholic ferric chloride a transient green colour was developed and passed into brown, which became redder on keeping.

Ethyl 1-*Keto*-7-*methoxy*-1 : 2 : 3 : 4 : 9 : 10 : 11 : 12-*octahydro*-2-*phenanthroylformate* (II).—1-Keto-7-methoxy-1 : 2 : 3 : 4 : 9 : 10 : 11 : 12-octahydrophenanthrene (14·38 g.) and ethyl oxalate (10 g.) were dissolved in dry benzene (120 c.c.) and treated with alcohol-free sodium ethoxide (4·5 g.) in the usual way. After standing for 18 hours in the ice-chest, the clear orange solution was mixed with ether and ice-water and the alkaline layer was rapidly separated and washed with ether. The oil liberated on acidification was taken up in ether, and the extract dried and evaporated. The resulting stiff orange-yellow syrup (18·16 g.) deposited a few crystals and thus allowed recrystallisation to be effected by inoculation. The *compound* separated from ether in long colourless felted needles, m. p. 98—99° with evolution of gas (carbon monoxide) above *ca.* 138° (Found : C, 69·1; H, 6·6. $C_{19}H_{22}O_5$ requires C, 69·1; H, 6·7%). With alcoholic ferric chloride a blood-red colour was developed. The complete lack of colour in this compound contrasts with the orange colour of the analogous compound from ketomethoxyhexahydrophenanthrene in which there is a double bond in the 11 : 12-position (J., 1937, 62); the effect of conjugation through this bond with the aromatic nucleus is noteworthy.

Ethyl 1-*Keto*-7-*methoxy*-1 : 2 : 3 : 4 : 9 : 10 : 11 : 12-*octahydrophenanthrene*-2-*carboxylate*.—The above $\alpha\gamma$-diketo-ester (21 g.) was heated in three equal portions at 170° until the evolution of gas ceased (2—3 hours) and the resulting keto-ester was distilled in small portions (2—3 g. each) at 0·5 mm. (b. p. *ca.* 205°) as a pale yellow, viscous syrup (12·4 g.) giving a pure violet colour with alcoholic ferric chloride.

Ethyl 1-*Keto*-7-*methoxy*-2-*methyl*-1 : 2 : 3 : 4 : 9 : 10 : 11 : 12-*octahydrophenanthrene*-2-*carboxylate* (III).—Methylation of the preceding β-keto-ester was effected in the manner previously described (*loc. cit.*) with molecular potassium (1·7 g., slight excess) and a large excess of methyl iodide in benzene solution (100 c.c.). The crude product (12·82 g.) distilled as a pale yellow syrup (11·66 g.) at 200—205°/0·45 mm., $n_D^{19\cdot5^\circ}$ 1·5462; it gave no ferric reaction and the observed constants were in good agreement with those already recorded.

Reformatsky Reaction. 1-*Keto*-7-*methoxy*-2-*methyl*-1 : 2 : 3 : 4 : 9 : 10 : 11 : 12-*octahydrophenanthrene* (IV).—(A) The preceding methylated keto-ester (3·06 g.), ethyl bromoacetate (3·2 c.c.; 3 mols.), pure toluene (15 c.c.), and zinc needles (1·9 g.; 3 at.) were mixed and cautiously warmed after the addition of a crystal of iodine. A brisk reaction set in and after the spontaneous ebullition had moderated the mixture was refluxed (bath 150°) for 1 hour after the addition of more toluene (5 c.c.); a brown viscous complex then separated. Ether and dilute sulphuric acid were added to the cooled mixture and the upper layer was thoroughly washed with dilute sulphuric acid and with water. After several washings with dilute sodium carbonate solution the extract was dried and evaporated, and the crude neutral product (3·36 g.) refluxed for 7 hours with ethyl-alcoholic potassium hydroxide (7 g. of potassium hydroxide in 5 c.c. of water and 15 c.c. of alcohol). The hydrolysis product was separated into an acidic (1·05 g.) and a neutral (1·85 g.) portion in the usual way. The acidic material was a viscous reddish-brown syrup, which showed no tendency to crystallise and was quantitatively esterified by means of an excess of diazomethane (from 5 g. of nitrosomethylurea). The neutral portion was a light brown syrup which crystallised on standing. The *substance* was readily soluble in the usual solvents and recrystallisation from ether afforded fine colourless prisms, m. p. 119—120° (Found : C, 78·6; H, 8·3. $C_{16}H_{20}O_2$ requires C, 78·7; H, 8·2%).

(B) The methyl keto-ester (11·66 g.), ethyl bromoacetate (20·5 c.c.; 5 mols.), and zinc needles (12·5 g.; 5 at.) were allowed to interact as before in pure toluene (40 c.c.) and the mixture was heated for 3 hours under reflux (bath 150°) after the spontaneous reaction had moderated. The ether–toluene solution of the product was well washed with dilute sulphuric acid and then with dilute sodium carbonate solution. From the latter washings there was obtained on acidification and extraction with ether a reddish-brown gum (2·52 g.) giving a brown colour with alcoholic ferric chloride. The neutral material isolated from the ether–toluene solution after drying was a reddish-brown syrup (14·15 g.) and it was immediately hydrolysed under reflux with alcoholic potassium hydroxide (30 g. of potassium hydroxide in 20 c.c. of water and 60 c.c. of alcohol) for 5 hours. An acidic (4·2 g.) and a neutral (6·07 g.) portion were separated as before in the normal way.

The amount of ketone isolated corresponds to 7·86 g. of methyl keto-ester, indicating that 3·80 g. (or 32·6%) of the latter have undergone the Reformatsky reaction.

Neither the ester obtained in (A) nor the acids from (B) could be induced to crystallise. The acids were refluxed with pure acetic anhydride for 30 minutes and isolated as a thick, pale brown syrup, found to be almost saturated towards potassium permanganate. On attempted catalytic reduction the volume of hydrogen absorbed was negligible. Efforts to fractionate the substance with the aid of solvents (readily soluble in chloroform and ethyl acetate; sparingly soluble in alcohol and especially in light petroleum) gave no crystalline material and as a final resource the whole material was collected and refluxed with hydriodic acid (*d* 1·7) and phosphorus, both in large excess. The isolated phenolic acids were uncrystallisable and after methylation in the usual manner the recovered methoxy-acids showed the same behaviour with solvents as the original material. An excess of aqueous methylamine was added, and the solution distilled from a gradually heated oil-bath until the temperature of the bath reached 200°. The brown residue could be separated into an acidic portion (qualitative test for nitrogen, positive), which could not be crystallised, and a neutral portion. The latter was dissolved in ethyl acetate, and a large volume of light petroleum added. The gummy precipitate (after keeping for some hours in the ice-chest) was again dissolved in ethyl acetate, and light petroleum added until turbidity occurred. The solution was kept in the ice-chest, then filtered, and an excess of light petroleum added. On keeping in the ice-chest the chalky precipitate was then obtained as an amorphous solid and repetition of the process gave a pale brownish powder which softened at 130—140° and melted up to about 170° (Found: C, 73·6; H, 7·8; N, 4·1. $C_{20}H_{25}O_3N$ requires C, 73·4; H, 7·6; N, 4·3%. $C_{20}H_{23}O_3N$ requires C, 73·8; H, 7·1; N, 4·3%). The substance was insoluble in aqueous sodium hydroxide, but on boiling it passed into solution. Methylamine was not evolved until the liquid was concentrated by distillation of most of the water.

1-*Keto*-7-*methoxy*-2-*hydroxymethylene*-1 : 2 : 3 : 4 : 9 : 10-*hexahydrophenanthrene*.—To a solution of 1-keto-7-methoxy-1 : 2 : 3 : 4 : 9 : 10-hexahydrophenanthrene (10 g.) and amyl formate (6·1 g., freshly distilled) in anhydrous ether (120 c.c.), sodium ethoxide (3·8 g., alcohol-free) was added in lumps and then disintegrated. A buff-coloured sodium derivative rapidly separated and after 14 hours at the room temperature, ice-water was added and the alkaline layer was rapidly separated, washed with ether, and acidified. The precipitated oil, which partly crystallised at once, was taken up in ether, and the extract dried and evaporated, yielding an orange crystalline solid (8 g.). Recrystallisation from aqueous acetic acid (*ca.* 65%) afforded deep yellow plates, m. p. 90—91° (Found: C, 74·7; H, 6·3. $C_{16}H_{16}O_3$ requires C, 75·0; H, 6·2%).

1-*Keto*-7-*methoxy*-2-*hydroxymethylene*-1 : 2 : 3 : 4 : 9 : 10 : 11 : 12-*octahydrophenanthrene* was prepared in a like manner from 1-keto-7-methoxy-1 : 2 : 3 : 4 : 9 : 10 : 11 : 12-octahydrophenanthrene (1·1 g.), ethyl formate (0·74 g.), and alcohol-free sodium ethoxide (0·8 g.) in anhydrous ether (40 c.c.). The aqueous alkaline solution on acidification furnished a light orange, crystalline precipitate (1·1 g., m. p. 133°), which was collected, washed, and dried. Recrystallisation from 60% aqueous acetic acid afforded light amber needles, m. p. 140—141° (Found: C, 74·6; H, 7·0. $C_{16}H_{18}O_3$ requires C, 74·4; H, 7·0%).

Neither of the above two compounds underwent smoothly the ring-fission described by Lapworth (J., 1900, 77, 1059) for hydroxymethylenecamphor (cf. Bardhan, J., 1936, 1851). With the former compound a black tar was produced and the only identifiable product was hydrogen cyanide, and with the latter compound, although there was no formation of tar, a satisfactory product was not isolable.

Condensation of Methyl γ-(6-*Methoxy*-3 : 4-*dihydro*-1-*naphthyl*)*butyrate* (VI) *with* β-*Carbomethoxypropionyl Chloride in the Presence of Aluminium Chloride.*—A mixture of methyl methoxydihydronaphthylbutyrate (6 g.), carbomethoxypropionyl chloride (6·8 g.), and carbon disulphide (25 c.c.) was rapidly added to a mechanically stirred mixture of powdered aluminium chloride (12·3 g.) and carbon disulphide (75 c.c.) cooled in melting ice. After 3 hours' stirring, the mixture was kept for 12 hours; the carbon disulphide was then decanted, and ice added in order to decompose the complex. Steam was passed for 5 minutes, and the product (10 g.) isolated by means of ether. The product was hydrolysed with aqueous alcoholic potassium hydroxide, remethylated with methyl sulphate and potassium hydroxide, and again hydrolysed and isolated as mixed acids (6 g.), which partly crystallised. The paste was triturated with acetone, and the solid collected and thrice crystallised from acetone; it formed colourless rod-like needles, m. p. 163—164° (Found: C, 65·9, 65·6; H, 6·9, 7·1; MeO, 8·4. $C_{19}H_{24}O_6$ requires C, 65·5; H, 6·9; 1MeO, 8·9%). The *acid* was very sparingly soluble in hot benzene and cold acetone. It was saturated to permanganate, and with 2 : 4-dinitrophenylhydrazine it gave an orange derivative, soluble in aqueous sodium carbonate. Heated with acetic anhydride, it furnished a red insoluble resin. When it was heated with platinum-black or with selenium, extensive decomposition occurred and the corresponding de-tetrahydro-derivative could not be obtained. The first acetone mother-liquor afforded a further quantity of this acid (total yield, 2·3 g.) by treatment with light petroleum and then crystallisation of the insoluble portion from ethyl acetate. The later acetone mother-liquors were concentrated and on keeping in the ice-chest deposited a pale yellow crust of prisms, m. p. 140—147° (1·8 g.). The substance, recrystallised from chloroform, in which it was sparingly soluble, formed colourless prismatic needles, m. p. 155—157° (mixed with $C_{19}H_{24}O_6$, m. p. 140—144°); recrystallisation from ethyl acetate–benzene then gave elongated prisms with pointed ends (Found in material dried at 100°: C, 67·5, 67·5; H, 6·2, 5·9. $C_{19}H_{20}O_6$ with 4·6% C_6H_6 requires C, 67·5; H, 5·9%. The presence of benzene was confirmed by Ramsden's test. Found in material dried at 120° in a high vacuum: C, 66·5, 66·6; H, 6·0, 6·0. $C_{19}H_{20}O_6$ requires C, 66·3; H, 5·8%). This *acid* was saturated to alkaline permanganate and formed an alkali-soluble orange derivative with dinitrophenylhydrazine. In a subsequent experiment the crude mixture of acids (11 g.) was more oily than in the first case and it was accordingly thoroughly extracted with boiling light petroleum (b. p. 60—80°); the magma then hardened. This was dissolved in acetone and seeded with the acid $C_{19}H_{24}O_6$; the filtrate from the crystals of this substance (3·4 g.) was mixed with 2 vols. of benzene and 1 vol. of chloroform; the acid $C_{19}H_{20}O_6$ then separated in a nearly pure form (3·6 g.). It is noteworthy that in the above separation the tetrahydro-acid was the first to crystallise, whereas in the isomeric series previously described the naphthalene acid was much the more sparingly soluble of the two acids obtained. The acid (0·5 g.), m. p. 155—157°, was boiled with hydriodic acid (*d* 1·7, 5 c.c.) in a stream of carbon dioxide for ½ minute; the formation of methyl iodide was recognised by means of alcoholic silver nitrate. The solution was mixed with water and sulphurous acid; a pale yellow precipitate was then obtained (0·3 g.).

The substance crystallised from chloroform in dense clusters of colourless needles, m. p. 232°, and was again crystallised from aqueous acetic acid (Found in material dried at 100°: C, 71·3; H, 5·9. $C_{14}H_{12}O_2,C_2H_4O_2$ requires C, 70·6; H, 5·9%). On methylation, methoxytetrahydrophenanthrone was obtained; it was converted into its 2 : 4-dinitrophenylhydrazone, which crystallised from pyridine in red needles, m. p. 304° (decomp.) alone or mixed with a specimen previously examined and analysed (J., 1936, 750). The hydriodic acid aqueous solution was saturated with salt and extracted with ether; succinic acid was thus isolated and recognised as succinanil and by the fluorescein reaction.

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