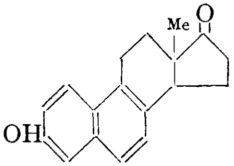
39. *Syntheses of Polycyclic Compounds related to the Sterols. Part V. Methoxy- and Hydroxy-derivatives of Phenanthrene.*

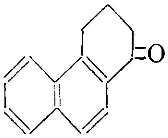
By G. A. R. KON and F. C. J. RUZICKA.

THE appearance of a recent paper by Butenandt and Schramm (*Ber.*, 1935, **68**, 2083) makes it desirable to place on record some experiments on the preparation of methoxylated derivatives of naphthalene and phenanthrene, which were to be employed in the synthesis of compounds related to equilenin (I). Other objects of the work were the preparation of compounds which might from their constitution be expected to show oestrogenic properties, and the study of the effect of changes of structure on the latter.

Cook, Dodds, and Hewett have stated (*Nature*, 1933, **131**, 205) that 1-keto-1 : 2 : 3 : 4-tetrahydrophenanthrene (II) is oestrogenic (see, however, Butenandt, *loc. cit.*) and it appeared to be of interest to examine the effect of introducing into different positions in the molecule of this compound the phenolic group characteristic of both equilenin and oestrone. The preparation of the 7-hydroxy-compound (III) has since been carried out by Butenandt (*loc. cit.*); that of the 8- and the 9-isomeride is now described. Both these compounds were obtained by the same method, starting from the appropriate methoxy-naphthylethyl alcohols, the preparation of which had been undertaken with a view to the first object of the present work. The alcohol was converted into the bromide, which was condensed with ethyl sodio- or potassio-malonate; the ester was hydrolysed, the acid decarboxylated, and the new acid cyclised :



(I.)



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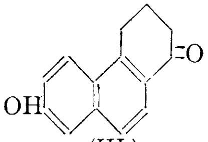

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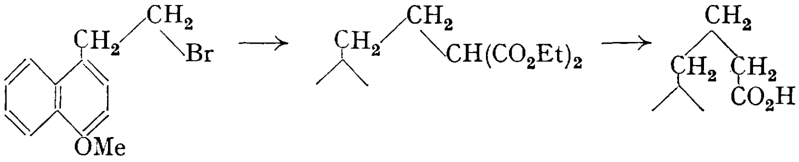

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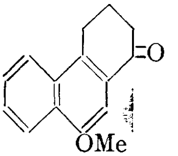
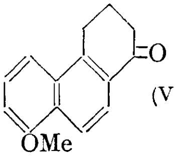


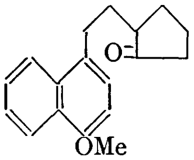


(V.)

Finally, the methoxy-ketone was converted into the free phenol.

The preparation of the 9-methoxy-compound (IV) proceeded smoothly, but when aluminium chloride was used for the final stage in the preparation of the 8-methoxy-compound, an abnormal *product*, m. p. 88—89°, was formed; it had the expected composition, but did not react with semicarbazide and gave on demethylation a *substance* of the formula $C_{14}H_{14}O_3$, not $C_{14}H_{12}O_2$. The *isomeride*, m. p. 137°, formed when stannic chloride was used in place of aluminium chloride reacted with semicarbazide and behaved normally on demethylation, yielding a *phenol* which was reconverted into the methoxy-compound, m. p. 137°, on methylation; this is therefore regarded as having the structure (V)—that of its isomeride has not yet been elucidated.

β-4-*Methoxy*-1-*naphthylethyl alcohol* was obtained by treating the Grignard reagent prepared from 1-bromo-4-methoxynaphthalene with ethylene oxide. The corresponding *bromide* was condensed with ethyl *cyclo*pentanone-2-carboxylate, and the resulting *ester* hydrolysed to α-(β′-4-*methoxy*-1-*naphthylethyl*)*adipic acid*; on pyrolysis, this acid did not give the expected substituted *cyclo*pentanone (VI), but underwent fission to 4-*methoxy*-1-*methylnaphthalene*. The corresponding alcohol should have resulted from the action of the Grignard reagent of the above bromide on *cyclo*pentene oxide (compare Fulton and Robinson, J., **1933**, **1463**), but under the conditions of the experiment the greater part was dehydrated to 4-*methoxy*-1-β-cyclo*pentenylethylnaphthalene* (VII). This was cyclised to the tetracyclic *compound* by phosphoric oxide, as shown by the formation of *cyclo*pentenophenanthrene on dehydrogenation with selenium at 320—350°, the methoxyl group being eliminated under these somewhat drastic conditions. A better result was obtained by treating the same Grignard reagent with 2-methyl*cyclo*pentanone; the *carbinol* (VIII) cyclised readily and the *methoxy-hydrocarbon* gave on dehydrogenation under carefully controlled conditions 9-*methoxy*-1 : 2-cyclo*pentenophenanthrene* (IX); the preparation of this compound was of importance because the position of the methoxyl group in the dehydrogenation product of oestrone methyl ether (Cook and Girard, *Nature*, **1934**, **133**, 377) was not known at the time; the two compounds have quite different properties.



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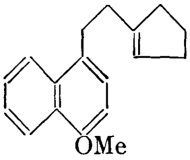

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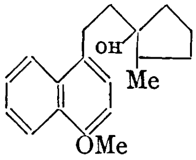
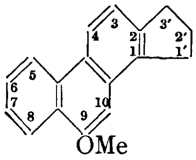


(VIII.)



(IX.)

9-*Methoxy*-3′-*methyl*-1 : 2-cyclo*pentenophenanthrene*, which was required for crystallographic work, was similarly prepared from 2 : 5-dimethyl*cyclo*pentanone.

β-5-*Methoxy*-1-*naphthylethyl alcohol* was prepared in the same way as the 4 : 1-compound, starting from 1-bromo-5-methoxynaphthalene (Fuson, *J. Amer. Chem. Soc.*, 1924, **46**, 2785), the preparation of which has been modified. 8-*Methoxy*-1 : 2-cyclo*pentenophenanthrene* was synthesised from this by a method similar to that described above and was also found to differ appreciably from the isomeride derived from equilenin; these compounds, unlike *cyclo*pentenophenanthrene and its 3′-methyl derivative, depress each other's m. p. and their identification is therefore more certain.

The results of the biological tests now being carried out on some of the compounds described will be reported elsewhere.

EXPERIMENTAL.

β-4-*Methoxy*-1-*naphthylethyl Alcohol*.—To an ice-cold Grignard reagent, prepared at room temperature from 124 g. of 1-bromo-4-methoxynaphthalene (Fourneau, Tréfouel, and Tréfouel, *Bull. Soc. chim.*, 1928, **43**, 454) and 12·9 g. of magnesium activated with iodine in 500 c.c. of ether, were added 28 g. of ethylene oxide in 250 c.c. of ether. The mixture was mechanically stirred during the addition, then allowed to attain room temperature, and finally warmed under reflux, and the ether distilled off. The mass was decomposed with ice and hydrochloric acid, and the products taken up in ether, dried, and distilled. There was a considerable low fraction, b. p. 110—150°/2 mm. (mainly α-naphthyl methyl ether), then the *alcohol* distilled at 190°/2 mm.

(60 g.) and solidified; m. p. 87° after repeated crystallisation from benzene–petroleum (Found: C, 76·8; H, 7·0. $C_{13}H_{14}O_2$ requires C, 77·1; H, 7·0%).

Bromide. Heating with 33% hydrogen bromide in acetic acid under pressure, or with hydrobromic acid and sulphuric acid, failed to convert the alcohol satisfactorily into the bromide, the product generally containing unchanged alcohol. Finally, 20 g. of the alcohol in 120 c.c. of benzene were vigorously stirred during the slow addition of 25 g. of phosphorus tribromide in 70 c.c. of benzene, the mixture being then warmed under reflux for 2 hours; 17 g. of the *bromide* were obtained as a yellow oil, b. p. 161°/1·2 mm. (Found: Br, 30·2. $C_{13}H_{13}OBr$ requires Br, 30·2%).

Ethyl 2-(β-4-*Methoxy*-1-*naphthylethyl*)cyclo*pentanone*-2-*carboxylate*.—4·7 G. of "molecular" potassium were treated with 18 g. of ethyl *cyclo*pentanone-2-carboxylate in 70 c.c. of dry xylene, warming on the steam-bath for 45 minutes completing the reaction; 17 g. of the above bromide were then added and the mixture was boiled under reflux (oil-bath) for 48 hours. The *ester*, isolated in the usual manner, was a very viscous, yellow oil, b. p. 235—248°/1·2 mm. (Found: C, 73·6; H, 7·3. $C_{21}H_{24}O_4$ requires C, 74·0; H, 7·3%).

α-(β′-4-*Methoxy*-1-*naphthylethyl*)*adipic Acid*.—The above ester was boiled with twice its weight of potassium hydroxide in 40% aqueous solution, together with enough alcohol to give a homogeneous solution, for 16 hours, the alcohol being allowed to distil off slowly. The *acid* was isolated by acidification and extraction with ether and slowly solidified on keeping and scratching; m. p. 178° after crystallisation from alcohol (Found: C, 68·7; H, 6·6. $C_{19}H_{22}O_5$ requires C, 69·0; H, 6·7%).

Pyrolysis. The crude acid was heated with a trace of baryta under 450 mm. by means of an air-bath; a liquid distilled at 200—240°. In another experiment at atmospheric pressure, the product boiled at 330—360°, 121°/0·8 mm. on redistillation (21 g. from 50 g. of ketonic ester) and consisted of 4-*methoxy*-1-*methylnaphthalene* (Found: C, 83·7; H, 7·1. $C_{12}H_{12}O$ requires C, 83·7; H, 7·0%). The same substance was synthesised by the action of methyl iodide on the Grignard reagent prepared from 1-bromo-4-methoxynaphthalene; it can be characterised by means of the picrate, m. p. 146—147°, the *s*-trinitrobenzene complex, m. p. 169°, and the trinitrotoluene complex, m. p. 75—76°.

β-4′-*Methoxy*-1′-*naphthylethyl*cyclo*pentene*.—12 G. of *cyclo*pentene oxide in ether were gradually added with constant stirring to an ice-cold Grignard reagent prepared from 25 g. of β-4-methoxy-1-naphthylethyl bromide exactly as described on p. 188; the mixture was then warmed under reflux for an hour. On distillation of the ether a sudden vigorous reaction took place and the contents of the flask swelled and became solid. The products were isolated in the usual way and the portion boiling above 190°/1 mm. was redistilled; 6 g., boiling at 150—160°/0·02 mm., consisted largely of the unsaturated *methoxy-hydrocarbon* (VII), though it doubtless contained some of the carbinol originally formed (Found: C, 84·1, 83·8; H, 7·9, 7·8. $C_{18}H_{20}O$ requires C, 85·6; H, 8·0%. $C_{18}H_{22}O_2$ requires C, 80·0; H, 8·2%). The methoxy-hydrocarbon formed a *s*-trinitrobenzene *complex*, orange needles, m. p. 107—108° (Found: C, 61·8; H, 4·9. $C_{24}H_{23}O_7N_3$ requires C, 61·9; H, 5·0%). There was also a fraction, b. p. 220—240°/0·02 mm., which doubtless consisted of αδ-*di*-(4-*methoxy*-1-*naphthyl*)*butane*, prisms, m. p. 124°, from alcohol–benzene (Found: C, 84·3; H, 7·0. $C_{26}H_{26}O_2$ requires C, 84·3; H, 7·1%); it was characterised by a picrate, red needles, m. p. 173°, a *s*-trinitrobenzene complex, orange-red needles, m. p. 189—190°, and a trinitrotoluene complex, yellow needles, m. p. 140°. The fraction of lowest b. p., 97—140°/1 mm., probably contained 4-methoxy-1-ethylnaphthalene, forming a reddish picrate, m. p. 126°, and an orange *s*-trinitrobenzene complex, m. p. 162°.

9-*Methoxy*-3 : 4-*dihydro*-1 : 2-cyclo*pentanophenanthrene*.—5 G. of the crude methoxy-hydrocarbon described above were heated with 10 g. of phosphoric oxide at 130—140° for 30 minutes, and the product isolated by addition of ice and ether. The yellow oil obtained had b. p. 185—186°/0·8 mm. (Found: C, 85·3; H, 7·9. $C_{18}H_{20}O$ requires C, 85·6; H, 8·0%) and formed a *s*-trinitrobenzene *complex*, orange needles, m. p. 166° (Found: C, 61·9; H, 5·0. $C_{24}H_{23}O_7N_3$ requires C, 61·9; H, 5·0%). On dehydrogenation with selenium at 340—345° a small amount of *cyclo*pentenophenanthrene was formed.

2-*Methyl*-1-β-4′-*methoxy*-1′-*naphthylethyl*cyclo*pentanol* (VIII).—29 G. of 2-methyl*cyclo*pentanone in 50 c.c. of ether were slowly added to a well-stirred, ice-cold Grignard reagent prepared from 59 g. of β-4-methoxy-1-naphthylethyl bromide, and the mixture warmed under reflux for 3 hours. On working up as before, 19 g. of a fraction, b. p. 185—190°/0·1 mm., were obtained, consisting of the desired *carbinol* (Found: C, 80·0; H, 8·4. $C_{19}H_{24}O_2$ requires C, 80·2; H, 8·3%). There was also a low fraction, b. p. 141—145°/0·1 mm. after redistillation (Found: C, 78·8, 79·1; H, 9·1, 8·8%), forming a red picrate, m. p. 112—113°, and a *s*-trinitrobenzene complex, m. p. 129—130°, which was not further investigated. The high fraction consisted of the dinaphthylbutane derivative already described.

9-*Methoxy*-1-*methyl*-3 : 4-*dihydro*-1 : 2-cyclo*pentanophenanthrene*.—The cyclisation of the carbinol, carried out as described above, gave the *methoxy-hydrocarbon* in good yield, as a very viscous, yellow oil, b. p. 165—170°/0·1 mm. after distillation over sodium (Found: C, 85·4; H, 8·4. $C_{19}H_{22}O$ requires C, 85·6; H, 8·3%); the picrate formed red needles, m. p. 138°, and the *s*-trinitrobenzene complex, orange needles, m. p. 149°.

Dehydrogenation. 10 G. of the methoxy-hydrocarbon were heated with 8·7 g. of selenium powder for 20 hours to 340—345° (bath temperature); some 2 g. of dehydrogenation product were obtained and identified as 1 : 2-*cyclo*pentenophenanthrene by analysis (Found: C, 93·2; H, 6·6. Calc.: C, 93·5; H, 6·5%) and by the preparation of derivatives. Another attempt under similar conditions gave material containing some oxygen. When the experiment was repeated, 12 g. of selenium being used and the bath temperature kept at 280—290° for 21 hours, 5 g. of almost colourless solid were obtained after distillation in a high vacuum, consisting of the desired 9-*methoxy*-1 : 2-cyclo*pentenophenanthrene* (IX), crystallising in plates from petroleum and in needles from alcohol, m. p. 129° (Found: C, 86·8; H, 6·6. $C_{18}H_{16}O$ requires C, 87·1; H, 6·4%). The *picrate* formed reddish needles, m. p. 124° (Found: C, 60·4, 60·1, 60·4; H, 5·1, 4·7, 4·9.* $C_{24}H_{19}O_8N_3$ requires C, 60·4; H, 4·0%); the *s*-trinitrobenzene *complex*, orange needles, m. p. 132° (Found: C, 62·4, 62·3; H, 5·0, 4·8. $C_{24}H_{19}O_7N_3$ requires C, 62·5; H, 4·1%), the trinitrotoluene *complex*, deep yellow needles, m. p. 105—106° (Found: C, 62·9, 63·2, 63·4; H, 5·3, 5·5, 5·4. $C_{25}H_{21}O_7N_3$ requires C, 63·1; H, 4·5%), and the styphnate, yellow needles, m. p. 122°. The m. p.'s of all these derivatives were considerably depressed on admixture of the relevant derivatives of *cyclo*pentenophenanthrene.

2 : 5-*Dimethyl*-1-β-4′-*methoxy*-1′-*naphthylethyl*cyclo*pentanol* was obtained in the same way as the lower homologue, 2 : 5-dimethyl*cyclo*pentanone being used; the yield was even better; b. p. 195—200°/0·2 mm. (Found: C, 80·8; H, 8·7. $C_{20}H_{26}O_2$ requires C, 80·5; H, 8·7%).

9-*Methoxy*-1 : 3′-*dimethyl*-3 : 4-*dihydro*-1 : 2-cyclo*pentanophenanthrene*.—On dehydration of the above alcohol a good yield of the *methoxy-hydrocarbon* was obtained as a yellow oil, b. p. 180—183°/0·3 mm. (Found: C, 85·4; H, 8·7. $C_{20}H_{24}O$ requires C, 85·6; H, 8·6%), giving a *picrate*, red needles, m. p. 119—120° (Found: C, 61·1; H, 5·3. $C_{26}H_{27}O_8N_3$ requires C, 61·3; H, 5·3%), a *s*-trinitrobenzene *complex*, dark orange needles, m. p. 140—141° (Found: C, 63·0; H, 5·5. $C_{26}H_{27}O_7N_3$ requires C, 63·3; H, 5·5%), and a trinitrotoluene complex, yellow needles, m. p. 88°.

9-*Methoxy*-3′-*methyl*-1 : 2-cyclo*pentenophenanthrene*.—When 13·5 g. of the above compound were dehydrogenated at 280—290°, 11 g. of product, b. p. 185—190°/0·4 mm., were obtained; this was purified by chromatographic adsorption (compare Gamble, Kon, and Saunders, J., 1935, 644) and finally recrystallised from alcohol, forming needles, m. p. 111° (Found: C, 87·0; H, 6·9. $C_{19}H_{18}O$ requires C, 87·0; H, 6·9%). The *picrate* formed long red needles, m. p. 147° (Found: C, 61·2; H, 4·3. $C_{25}H_{21}O_8N_3$ requires C, 61·1; H, 4·3%), the *s*-trinitrobenzene complex, deep orange needles, m. p. 142°, and the trinitrotoluene complex, light orange needles, m. p. 104°.

β-5-*Methoxy*-1-*naphthylethyl Alcohol*.—In the preparation of 1-bromo-5-methoxynaphthalene (Fuson, *loc. cit.*) it was found convenient to reduce 1-bromo-5-nitronaphthalene by West's method (J., 1925, **127**, 494); the conversion of the resulting amine into the bromonaphthol was carried out by dissolving 570 g. in 4250 c.c. of acetic acid and adding 1130 c.c. of sulphuric acid mixed with 1130 c.c. of water with vigorous stirring. The resulting fine suspension of sulphate was diazotised at 5—10° with 221 g. of sodium nitrite in 870 c.c. of water, 30·5 g. of urea added, and the solution slowly run into a boiling solution of 1120 c.c. of sulphuric acid in 20 l. of water. The hot solution was filtered; 115 g. of almost pure bromonaphthol separated on cooling and were recrystallised from dilute alcohol. The preparation of the *alcohol* was carried out exactly as described on p. 188, but the yields were not so good (13 g. from 50 g. of bromide); the product, b. p. 185—190°/1·7 mm., solidified and then crystallised from petroleum (b. p. 40—50°) in plates, m. p. 53—54° (Found: C, 76·7; H, 7·2. $C_{13}H_{14}O_2$ requires C, 77·1; H, 7·0%). On one occasion a large excess of ethylene oxide was used in the preparation; the *product* boiling at the correct temperature crystallised from benzene–petroleum in needles, m. p. 128°, which appeared to have the composition $C_{13}H_{10}O_5$ (Found: C, 59·5; H, 4·1. Calc.: C, 59·5; H, 3·9%); it was not further investigated.

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* This and the two following compounds give unaccountably high values for hydrogen; they were repeatedly analysed by Dr. G. Weiler of Oxford and Dr. A. Schoeller of Berlin, whose results show a satisfactory agreement.

The *bromide*, prepared from the alcohol by means of phosphorus tribromide, had b. p. 180°/1·7 mm. (Found : Br, 29·9. $C_{13}H_{13}OBr$ requires Br, 30·1%) ; the yield from 38 g. of the alcohol was 32 g.

2-*Methyl*-1-(β-5′-*methoxy*-1′-*naphthylethyl*)cyclo*pentanol*.—This compound was prepared from the above bromide in exactly the same way as its isomeride (VIII) and the fraction, b. p. 190°—195°/0·1 mm., was comparable in yield with the corresponding fraction (Found : C, 80·8; H, 8·6. $C_{19}H_{24}O_2$ requires C, 80·3; H, 8·5%). The analysis figures suggest that the alcohol had undergone dehydration to a small extent; it gave a *s*-trinitrobenzene complex, m. p. 110—111°. The high fraction, b. p. 240—250°/0·1 mm., consisted of αδ-*di*-(5-*methoxy*-1-*naphthyl*)-*butane*, forming prisms, m. p. 176°, from benzene–alcohol (Found : C, 84·1; H, 7·2. $C_{26}H_{26}O_2$ requires C, 84·3; H, 7·1%); the picrate had m. p. 205°, the *s*-trinitrobenzene complex, m. p. 228°, and the trinitrotoluene complex, m. p. 146°.

8-*Methoxy*-1-*methyl*-3 : 4-*dihydro*-1 : 2-cyclo*pentanophenanthrene*.—The dehydration of 22 g. of the carbinol as described on p. 189 gave 16 g. of the *methoxy-hydrocarbon*, b. p. 185°/0·3 mm. (Found : C, 85·3; H, 8·4. $C_{19}H_{22}O$ requires C, 85·6; H, 8·3%). This formed a picrate, red needles, m. p. 158°, and a *s*-trinitrobenzene complex, orange needles, m. p. 135°.

8-*Methoxy*-1 : 2-cyclo*pentenophenanthrene*.—The dehydrogenation of the above compound at 290° for 19 hours gave a good yield of product, which was purified twice by chromatographic adsorption and finally recrystallised from alcohol, forming long needles, m. p. 153° (Found : C, 86·9; H, 6·7. $C_{18}H_{16}O$ requires C, 87·1; H, 6·4%). The *picrate* formed reddish needles, m. p. 160° (Found : C, 60·3; H, 4·3. $C_{24}H_{19}O_8N_3$ requires C, 60·4; H, 4·0%), and the *s*-trinitrobenzene *complex*, light orange needles, m. p. 194° (Found : C, 62·4; H, 4·2. $C_{24}H_{19}O_7N_3$ requires C, 62·5; H, 4·1%).

β-5-*Methoxy*-1-*naphthylethylmalonic Acid*.—70 G. of ethyl malonate were gradually added to 7·1 g. of " molecular " potassium, suspended in xylene, and the reaction was completed by warming for an hour; 55 g. of β-5-methoxy-1-naphthylethyl bromide were then added and the mixture was heated in an oil-bath at 150° for 45 hours. The product was isolated by means of ether, freed from solvents, and distilled, 35 g. being collected between 205° and 210°/0·8 mm. A considerable lower-boiling fraction was also collected, which solidified and formed plates from methyl alcohol, m. p. 70—71°, apparently of the composition $C_{13}H_{12}O_7$ (Found : C, 55·8; H, 4·4. Calc. : C, 55·7; H, 4·3%); it has not been further investigated.

The ester was directly hydrolysed to the *acid* by warming it over-night with an excess of 30% aqueous sodium hydroxide and enough alcohol to give a homogeneous solution; a crystalline, sparingly soluble sodium salt soon began to separate. On acidification a theoretical yield of the acid was precipitated; this formed plates, m. p. 182° (decomp.), from ethyl acetate–petroleum (Found : C, 66·6; H, 5·6. $C_{16}H_{16}O_5$ requires C, 66·6; H, 5·6%).

γ-5-*Methoxy*-1-*naphthylbutyric Acid*.—The malonic acid (28 g.) was heated under reduced pressure above its m. p., the melt dissolved in 1 l. of 5% aqueous sodium hydroxide, and the solution extracted with ether and acidified. The *acid* was recrystallised from dilute alcohol (charcoal) and finally from ethyl acetate–petroleum (b. p. 80—100°), 17 g. of pure product, m. p. 143°, being obtained (Found : C, 73·7; H, 6·5. $C_{15}H_{16}O_3$ requires C, 73·7; H, 6·6%).

Cyclisation. (i) 5 G. of the acid were boiled for ¾ hour with 25 c.c. of chloroform and 6 c.c. of thionyl chloride, the solvent removed under reduced pressure, and the residue twice evaporated under reduced pressure with benzene to ensure the complete removal of the thionyl chloride. 25 C.c. of tetrachloroethane were added and 6 g. of finely powdered aluminium chloride were introduced in three portions into the ice-cold solution, which was then kept in ice for a further 16 hours. The product was worked up in the usual way, taken up in ether, freed from solvent, and distilled, a brown oil (1·9 g.) being obtained. When rubbed with methyl alcohol, this solidified; it then crystallised from dilute methyl alcohol (charcoal) in plates, m. p. 88—89° (Found : C, 79·4; H, 6·5. $C_{15}H_{14}O_2$ requires C, 79·6; H, 6·2%). This material did not form a semicarbazone, although the mother-liquors from its preparation gave a small amount of sparingly soluble precipitate, m. p. 224°, on treatment with semicarbazide acetate.

The compound was converted into the free phenol by boiling 0·8 g. with 36 c.c. of acetic acid and 45 c.c. of hydrobromic acid (*d* 1·45) for 3 hours. The acetic acid was distilled off under reduced pressure, the solid product purified by reprecipitation from an alkaline solution and finally isolated by means of ether as a dark solid mass; this was sublimed at 135°/0·02 mm., giving a cream-coloured solid, which crystallised from chloroform–petroleum in small needles, m. p. 155°, and gave a bluish-violet colour with alcoholic ferric chloride; its composition appeared to be $C_{14}H_{14}O_3$ and it did not give the original methoxy-compound on methylation with methyl sulphate in alkaline solution (Found : C, 73·2; H, 6·6. Calc. : C, 73·1; H, 6·2%).

(ii) The acid was cyclised with stannic chloride exactly as described by Haworth and Sheldrick (J., **1934**, 867), and the product isolated in the same way. Some acid was recovered, and a 40% yield of neutral solid obtained. This was recrystallised from methyl alcohol with a little water, forming small needles, m. p. 137°, evidently consisting of 1-*keto*-8-*methoxy*-1 : 2 : 3 : 4-*tetrahydrophenanthrene* (V) (Found: C, 79·7; H, 6·4. $C_{15}H_{14}O_2$ requires C, 79·6; H, 6·2%); it formed a very sparingly soluble semicarbazone, m. p. 272°. The methoxy-ketone was demethylated as described above, the *hydroxy-ketone* being finally sublimed at 0·02 mm.; it formed small yellowish needles, m. p. 256°, from acetone–petroleum (b. p. 60—80°), and was reconverted into the methoxy-ketone, m. p. 137°, on methylation (Found: C, 79·4; H, 5·8. $C_{14}H_{12}O_2$ requires C, 79·3; H, 5·7%).

β-4-*Methoxy*-1-*naphthylethylmalonic Acid* [with C. Simons].—23 G. of β-4-methoxy-1-naphthylethyl bromide were warmed over-night with 27 g. of ethyl malonate and 2·2 g. of sodium in 40 c.c. of absolute alcohol; 21 g. of the new ester, b. p. 210°/3—5 mm., were isolated, and hydrolysed as described on p. 191, giving 18 g. of the *acid*, which was recrystallised from dilute alcohol and then from ethyl acetate–petroleum, forming stout prisms, m. p. 180° (decomp.) (Found: C, 66·5; H, 5·6. $C_{16}H_{16}O_5$ requires C, 66·6; H, 5·6%).

γ-4-*Methoxy*-1-*naphthylbutyric Acid*.—The decarboxylation of the malonic acid and the purification of the product were carried out as described on p. 191 and the *acid* was crystallised from dilute alcohol; m. p. 131° (Found: C, 73·9; H, 6·7. $C_{15}H_{16}O_3$ requires C, 73·7; H, 6·6%).

1-*Keto*-9-*methoxy*-1 : 2 : 3 : 4-*tetrahydrophenanthrene* (IV).—The cyclisation of the acid (12 g.) was carried out with aluminium chloride and gave 9·5 g. of oil, b. p. 224°/1·2 mm.; this slowly solidified and formed fine prisms, m. p. 98°, from dilute methyl alcohol (Found: C, 79·7; H, 6·3. $C_{15}H_{14}O_2$ requires C, 79·7; H, 6·2%).

1-*Keto*-9-*hydroxy*-1 : 2 : 3 : 4-*tetrahydrophenanthrene*.—The methoxy-ketone was demethylated as described on p. 191, giving a good yield of the *phenol*, which was purified by vacuum sublimation and recrystallisation from benzene–petroleum and formed small crystals, m. p. 260° (Found: C, 79·3; H, 5·6. $C_{14}H_{12}O_2$ requires C, 79·3; H, 5·7%); it gave a faint white precipitate with alcoholic ferric chloride.

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