437. *Isomerisation Reactions. Part II.*

By G. M. Badger, W. Carruthers, and J. W. Cook.

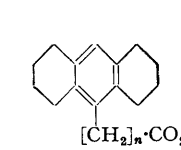
The structural requirements for the isomerisation of derivatives of *s*-octahydroanthracene by treatment with anhydrous hydrogen fluoride have been investigated. Compounds of type (I), in which $n = 2$ or 3, but not when $n = 1$, underwent simultaneous isomerisation and cyclisation in good yield. Compounds of type (III; R = H, alkyl, or CO_2H) were not isomerised; nor were compounds of type (IV; R = H or Me).

In the presence of aluminium chloride, in carbon disulphide solution, succinic anhydride and *s*-octahydroanthracene interacted to give β-(9-*s*-octahydrophenanthroyl)propionic acid. In tetrachloroethane, a mixture of the same acid and β-(9-s-*octahydroanthroyl*)*propionic acid* was obtained.

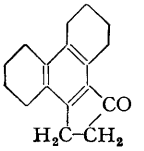
Cyclisation of β-(1 : 2 : 3 : 4-tetrahydro-9-phenanthryl)propionic acid (X) with hydrogen fluoride, with stannic chloride, or with aluminium chloride, gave the ketone (XII) and not the isomeric ketone (XI).

The discovery of a new type of reaction with anhydrous hydrogen fluoride, namely the isomerisation and cyclisation of *s*-octahydroanthranylpropionic acid (I*b*) to 1′-keto-9 : 10-*cyclo*penteno-*s*-octahydrophenanthrene (II) was reported by Badger, Carruthers, Cook, and Schoental (this vol., p. 169). Neither *s*-octahydroanthracene nor its 9-carboxylic acid underwent isomerisation under the same conditions, results which indicated that cyclisation may be an important part in the mechanism of the rearrangement. In this respect, therefore, the isomerisation appeared to differ from the somewhat analogous rearrangements long known to take place with aluminium chloride and sulphuric acid. Treatment of octahydroanthracene with aluminium chloride, for example, yields an equilibrium mixture of octahydroanthracene and octahydrophenanthrene (Schroeter, *Ber.*, 1924, **57**, 1990), and Schroeter and Götzky (*Ber.*, 1927, **60**, 2035) have effected the conversion of *s*-octahydroanthracene-9-sulphonic acid into *s*-octahydrophenanthrene-9-sulphonic acid by means of sulphuric acid. Nevertheless, the three types of reaction have many features in common, especially as it has now been found that isomerisation and cyclisation of the chloride of *s*-octahydroanthranylpropionic acid (I*b*) into the ketone (II) may also be achieved by the action of aluminium chloride under mild conditions.

Probably the closest analogy to the hydrogen fluoride transformations which we have studied is furnished by the displacement of alkyl groups by acyl groups by means of aluminium chloride (v. Auwers and Mauss, *Annalen*, 1928, **460**, 240; Hennion and McLeese, *J. Amer. Chem. Soc.*, 1942, **64**, 2421).



(I*a*, $n = 1$; I*b*, $n = 2$; I*c*, $n = 3$.)



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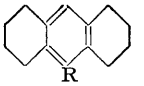

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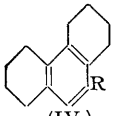

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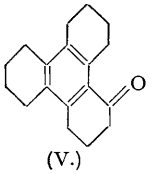

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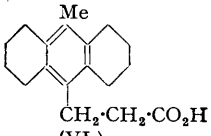


(VI.)

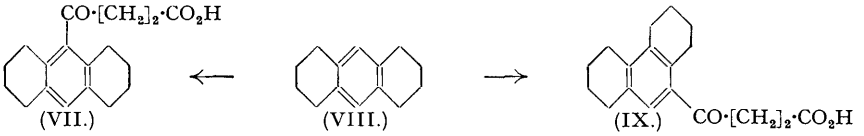
We have also extended our investigation on the effect of anhydrous hydrogen fluoride to several compounds related to octahydroanthranylpropionic acid, to provide some of the data necessary for an interpretation of the mechanism of the reaction. No isomerisation could be detected after treatment of 9-*methyl*- or 9-*ethyl*-s-*octahydroanthracene* or 9-s-*octahydroanthranylacetic acid* (I*a*) with hydrogen fluoride at room temperature; as previously recorded, neither the parent hydrocarbon nor its 9-carboxylic acid derivative was found to rearrange. Furthermore, *s*-octahydrophenanthrene and its 9-*methyl* derivative were unaffected, a result which excludes the possibility that there is an equilibrium, but displaced very much in the direction of the octahydroanthracene derivatives.

Isomerisation with simultaneous cyclisation has, however, been achieved with γ-(9-s-*octahydroanthranyl*)*butyric acid* (I*c*), 1-keto-*s*-dodecahydrotriphenylene (V) being isolated in excellent

yield. Moreover, Aitken, Badger, and Cook (future communication) have found that duryl-propionic acid also undergoes a similar reaction, although durene itself remains unaffected by hydrogen fluoride at room temperature. It therefore appears to be established that, at room temperature, the cyclisation is an essential factor in the rearrangement. This is in harmony with the findings of Calcott, Tinker, and Weinmayr (*J. Amer. Chem. Soc.*, 1939, **61**, 1010) that migration of alkyl groups attached to benzene rings does not occur in the presence of hydrogen fluoride at ordinary temperatures. It is noteworthy, however, that toluene may be prepared on a large scale by treatment of a mixture of xylene and benzene with hydrogen fluoride at high temperatures and pressures (U.S.P. 2,416,184).

It appeared to be of interest to attempt the isomerisation and cyclisation of β-(10-*methyl*-s-*octahydro*-9-*anthranyl*)*propionic acid* (VI), as such a rearrangement would necessarily involve the displacement of the methyl group. Treatment of this acid with hydrogen fluoride did indeed give rise to a neutral ketonic mixture, from which it was not found possible to isolate any pure constituent.

For the preparation of γ-(9-*s*-octahydroanthranyl)butyric acid (I*c*), we have used two methods. (I$_c$) was prepared, without difficulty, *via* γ-(9-s-*octahydroanthranyl*)*butyramide*, from the corresponding propionic acid (I*b*) by the Arndt–Eistert procedure. It has also been obtained by Clemmensen reduction of β-(9-s-*octahydroanthroyl*)*propionic acid*. In the preparation of this intermediate, we have observed another type of isomerisation. The product of the interaction of octahydroanthracene and succinic anhydride, in carbon disulphide, with aluminium chloride was not the expected octahydroanthroylpropionic acid (VII), but the corresponding derivative of octahydrophenanthrene (IX). Moreover, when the reaction was carried out in tetrachloroethane, at the same temperature, both products were isolated from the resulting mixture. This isomerisation is of interest as Arnold and Barnes (*J. Amer. Chem. Soc.*, 1944, **66**, 960) found that acetic anhydride reacts with octahydroanthracene in tetrachloroethane, with aluminium chloride, without isomerisation, to give 9-acetyl-*s*-octahydroanthracene. We have confirmed this result, and have also examined the reaction in carbon disulphide, under the same conditions, and with the same proportions of reactants, as led to isomerisation and condensation in the succinic anhydride experiment. In this case, however, no reaction occurred, and further investigation is desirable.



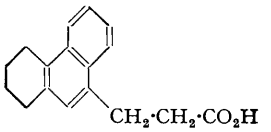
9-Ethyl-*s*-octahydroanthracene (III; R = Et) was prepared from the 9-acetyl compound by Clemmensen reduction, and its structure was confirmed by its dehydrogenation to 9-ethylanthracene. 9-Chloromethyl-*s*-octahydroanthracene was used to prepare the 9-methyl-*s*-octahydroanthracene (Badger *et al.*, *loc. cit.*) and also for the preparation of 9-*cyanomethyl*-s-*octahydroanthracene*, from which 9-*s*-octahydroanthranylacetic acid (I*a*) was obtained by hydrolysis. Chloromethylation of 9-methyl-*s*-octahydroanthracene gave 9-*methyl*-10-*chloromethyl*-s-*octahydroanthracene*, which was condensed with ethyl malonate, the product being hydrolysed and decarboxylated to give β-(10-methyl-*s*-octahydro-9-anthranyl)propionic acid (VI).

Chloromethylation of *s*-octahydrophenanthrene gave 9-*chloromethyl*-s-*octahydrophenanthrene*, together with a little 9 : 10-*bischloromethyl*-s-*octahydrophenanthrene*. Reduction with hydrogen and palladium gave 9-methyl- and 9 : 10-*dimethyl*-s-*octahydrophenanthrene*, respectively.

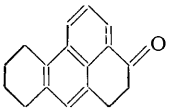
Experiments on the cyclisation of β-(1 : 2 : 3 : 4-tetrahydro-9-phenanthryl)propionic acid (X) (Bachmann and Cronyn, *J. Org. Chem.*, 1943, **8**, 456) have also been carried out. This acid, for which the structure was established by the American workers, might conceivably cyclise to give either (XI) or (XII). The acid can be regarded as a naphthalene derivative, analogous to a β-1-naphthylpropionic acid having two alkyl substituents. The cyclisation of naphthylpropionic acid can theoretically take place in either the 2- or the 8-position, but, in fact, it is known to take place almost exclusively in the 8-position, although a small proportion of the isomeric product is also formed (Fieser and Gates, *J. Amer. Chem. Soc.*, 1940, **62**, 2335). Again, Buu-Hoï and Cagniant (*Rev. Sci.*, 1941, **79**, 644) showed that treatment of β-(4-methyl-1-naphthyl)propionyl chloride with aluminium chloride gave 6-methylperinaphthan-1-one,* none

* Buu-Hoï and Cagniant numbered this compound 3-methylperinaphthan-7-one. For numbering used here see this vol., p. 1768.

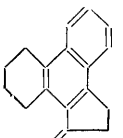
of the alternative product being isolated. The formation of this product involves cyclisation into the 8-position of the naphthalene system.



(X.)



(XI.)



(XII.)

These, and other known examples, illustrate the readiness with which cyclisation of β-1-naphthylpropionic acids takes place in the 8-position. This orientation is favoured both by the well-known preference for the formation of six-membered rather than five-membered rings in intramolecular acylations, and by the tendency for cyclisation to take place in the most reactive centre available. It was therefore expected that tetrahydrophenanthrenepropionic acid (X) would cyclise to give the ketone (XI) rather than the alternative ketone (XII). In fact, however it has been found that the opposite is the case, for cyclisation with hydrogen fluoride, with stannic chloride, or with aluminium chloride all resulted in the formation of the ketone (XII) in satisfactory yield. The structure of this compound was proved by its reduction to 9 : 10-cyclo*penteno*-1 : 2 : 3 : 4-*tetrahydrophenanthrene*, which on dehydrogenation gave the known 9 : 10-*cyclo*pentenophenanthrene.

It may be that the tetramethylene ring activates the 10-position to such an extent that cyclisation into this position, with formation of a five-membered ring, is preferred.

Experimental.

Isomerisation and Cyclisation of Octahydroanthranylpropionic Acid (Ib) *by the Friedel–Crafts Method.*—β-(9-*s*-Octahydroanthranyl)propionic acid (1 g.) was converted into the chloride, which was then treated with aluminium chloride, in nitrobenzene, exactly as described for octahydrophenanthrylpropionic acid by Badger, Carruthers, Cook, and Schoental (*loc. cit.*). The product was worked up in the usual way. Crystallisation from ethanol gave 1′-keto-9 : 10-*cyclo*penteno-*s*-octahydrophenanthrene as colourless needles, m. p. 193—195°, not depressed by an authentic specimen prepared from β-(9-*s*-octahydrophenanthryl)propionic acid by the Friedel–Crafts method.

Condensation of s-*Octahydroanthracene with Succinic Anhydride.*—(a) *In carbon disulphide.* Powdered aluminium chloride (18·4 g.) was added gradually, during ½ hour, to an ice-cold suspension of *s*-octahydroanthracene (VIII) (12·4 g.) and succinic anhydride (8 g.) in carbon disulphide (132 c.c.). After 4 hours in an ice-bath the mixture was left overnight at room temperature, and then warmed to 45° for 15 minutes. Carbon disulphide was decanted from the cooled mixture and the residual gummy complex decomposed with ice and hydrochloric acid. After extraction with dilute sodium carbonate the crude acidic product (14 g.) was reprecipitated, and recrystallised from acetic acid and then ethanol. β-(9-*s*-Octahydrophenanthroyl)propionic acid (IX) (9·8 g.) was obtained as colourless glistening needles, m. p. 143—144°, alone or mixed with an authentic specimen prepared from *s*-octahydrophenanthrene and succinic anhydride (Van de Kamp, Burger, and Mosettig, *J. Amer. Chem. Soc.*, 1938, **60**, 1321). The same acid was obtained when the reaction was carried out with omission of the short period of heating. Reduction of this keto-acid (8·5 g.) by heating it under reflux for 24 hours with amalgamated zinc (30 g.), concentrated hydrochloric acid (100 c.c.), acetic acid (20 c.c.), and toluene (30 c.c.) gave γ-(9-*s*-octahydrophenanthryl)butyric acid, b. p. 240°/2 mm. (6 g.), m. p. 128—129°, from ethanol (lit., m. p. 128—129°). Cyclisation of this acid (1·5 g.) with anhydrous hydrogen fluoride gave 1-keto-*s*-dodecahydrotriphenylene (1·42 g.), which crystallised from alcohol in long colourless needles, m. p. 222° (lit., m. p. 222—222·5°).

(b) *In tetrachloroethane.* *s*-Octahydroanthracene (VIII) (3·1 g.) was added to a well-stirred suspension of powdered aluminium chloride (10 g.) in dry tetrachloroethane (30 c.c.). After cooling in a freezing mixture, a slurry of succinic anhydride (3·7 g.) in tetrachloroethane (50 c.c.) was added. The mixture was stirred, with cooling, for several hours, and then left overnight. After decomposition with ice and hydrochloric acid, and removal of the solvent in steam, the crude product was extracted with boiling dilute sodium carbonate, and the acid reprecipitated. Recrystallisation from acetic acid gave *β-(9-s-octahydroanthroyl)propionic acid* (VII) (2·5 g.) which, after further recrystallisation from acetic acid and from ethanol, formed colourless prismatic needles, m. p. 210° (Found: C, 75·6; H, 7·8. $C_{18}H_{22}O_3$ requires C, 75·5; H, 7·7%). Addition of water to the mother-liquors of the initial crystallisation gave, after standing overnight, β-(9-*s*-octahydrophenanthroyl)propionic acid (1·4 g.), m. p. 143—144° alone or mixed with an authentic specimen prepared as described in (a).

γ-(9-s-Octahydroanthranyl)butyric Acid (Ic).—(a) *Arndt–Eistert method.* A mixture of octahydroanthranylpropionic acid (2·2 g.; Badger, Carruthers, Cook, and Schoental, *loc. cit.*), thionyl chloride (2·5 c.c.), and a few drops of pyridine in dry benzene (6 c.c.) was warmed at 50—60° for 2 hours. The crystalline solid obtained on removal of the excess of thionyl chloride and benzene *in vacuo* was dissolved in dry benzene (10 c.c.) and slowly added to a stirred, ice-cold solution of diazomethane (from 7 g. of nitrosomethylurea) in ether (150 c.c.). After some hours, the ether and excess of diazomethane were allowed to evaporate at room temperature. The yellow crystalline diazo-ketone so obtained, dissolved in dioxan (15 c.c.), was added to a 20% solution of ammonia (15 c.c.) and 10% aqueous silver nitrate (3 c.c.), and the mixture heated on the steam-bath for 2½ hours. The dark mixture was diluted with

dioxan (15 c.c.) and boiled with charcoal. After filtration and dilution with water, *γ*-(9-s-*octahydroanthranyl*)*butyramide* (1·7 g.) separated. It crystallised from benzene–light petroleum in soft white needles, m. p. 163—164° (Found: C, 79·9; H, 9·2; N, 5·3. $C_{18}H_{25}ON$ requires C, 79·7; H, 9·2; N, 5·2%). Hydrolysis of the amide (1·15 g.) by heating it under reflux for 12 hours with potassium hydroxide (5 g.) in ethanol (50 c.c.) gave *γ*-(9-s-*octahydroanthranyl*)*butyric acid* (1 g.), which crystallised from ethanol as fine colourless needles, m. p. 152° (Found: C, 79·5; H, 8·9. $C_{18}H_{24}O_2$ requires C, 79·4; H, 8·8%).

(b) *By reduction of octahydroanthroylpropionic acid.* A mixture of the acid (2·5 g.), amalgamated zinc (10 g.), concentrated hydrochloric acid (75 c.c.), acetic acid (10 c.c.), and toluene (15 c.c.) was heated under reflux for 24 hours. The product was isolated in the usual way, and after distillation at 185°/1 mm., it crystallised from acetic acid in colourless needles, m. p. 148—150°, alone or mixed with authentic octahydroanthranylbutyric acid prepared as described above.

Isomerisation and Cyclisation of Octahydroanthranylbutyric Acid.—This acid (0·5 g.) was treated with anhydrous hydrogen fluoride (*ca.* 20 c.c.) at room temperature for 12 hours. The product was dissolved in benzene and washed with caustic alkali. No acidic material was recovered from the alkaline extract. The neutral material obtained on removal of the benzene was recrystallised from ethanol. 1-Keto-*s*-dodecahydrotriphenylene (0·39 g.) was obtained as colourless needles, m. p. and mixed m. p. with an authentic specimen, 222° (lit., m. p. 222—222·5°).

9-*Acetyl*-s-*octahydroanthracene* (III; R = Ac).—The method of Arnold and Barnes (*J. Amer. Chem. Soc.*, 1944, **66**, 960), involving the interaction of acetic anhydride and *s*-octahydroanthracene with aluminium chloride in tetrachloroethane solution, was found to be satisfactory.

9-*Ethyl*-s-*octahydroanthracene* (III; R = Et).—9-Acetyl-*s*-octahydroanthracene (1·5 g.), amalgamated zinc (10 g.), toluene (10 c.c.), acetic acid (10 c.c.), and concentrated hydrochloric acid (50 c.c.) were heated under reflux for 24 hours. The cooled mixture was extracted with benzene, the benzene evaporated, and the product distilled. 9-*Ethyl*-s-*octahydroanthracene*, redistilled for analysis, b. p. 140° (air-bath temp.)/2 mm., was obtained as a colourless liquid (Found: C, 90·1; H, 9·9. $C_{16}H_{22}$ requires C, 89·7; H, 10·3%).

After dehydrogenation of a specimen (0·16 g.) with palladium-black at 300° for 30 minutes in an atmosphere of carbon dioxide, the product was dissolved in ethanol, and a small amount of a white solid, m. p. 210°, filtered off. This was identified as anthracene by comparison with an authentic specimen. The ethanolic filtrate was treated with picric acid, and the picrate recrystallised from ethanol. It formed red-yellow needles, m. p. 120° (lit., m. p. of 9-ethylanthracene picrate, 120°). Decomposition of the picrate on alumina gave 9-ethylanthracene as colourless needles, m. p. 63—64° (lit., m. p. 64°), from ethanol.

Treatment of 9-ethyl-*s*-octahydroanthracene with anhydrous hydrogen fluoride at room temperature for 15 hours gave an oil, which was dehydrogenated as above. Only 9-ethylanthracene could be detected in the product.

9-*Methyl*-s-*octahydroanthracene* (III; R = Me).—Methyloctahydroanthracene was prepared by reduction of the chloromethyl derivative as described by Badger, Carruthers, Cook, and Schoental (*loc. cit.*). As a further check on the homogeneity of the product obtained in the chloromethylation experiments, the following transformation were carried out. 9-*Acetoxymethyl*-s-*octahydroanthracene* (2·4 g.) was obtained when 9-chloromethyloctahydroanthracene (2·2 g.) and anhydrous potassium acetate (2·2 g.) were heated in boiling glacial acetic acid (100 c.c.) for 2 hours. It formed colourless, flat, glistening needles, m. p. 73°, from ethanol (Found: C, 78·9; H, 8·6. $C_{17}H_{22}O_2$ requires C, 79·1; H, 8·5%). Hydrolysis of the acetoxy-compound (1·5 g.) with alcoholic potassium hydroxide gave 9-*hydroxymethyl*-s-*octahydroanthracene* (1·2 g.) as colourless prismatic needles, m. p. 114°, from ethanol (Found: C, 83·5; H, 9·2. $C_{15}H_{20}O$ requires C, 83·3; H, 9·3%). Passage of hydrogen chloride through a solution of this compound in benzene (containing an equal weight of anhydrous calcium chloride) gave the 9-chloromethyl compound, identical with that obtained by direct chloromethylation of *s*-octahydroanthracene.

9-*Cyanomethyl*-s-*octahydroanthracene*.—A mixture of 9-chloromethyl-*s*-octahydroanthracene (1·2 g.) and potassium cyanide (3 g.) in ethanol (15 c.c.) and water (5 c.c.) was refluxed for 2½ hours. 9-*Cyanomethyl*-s-*octahydroanthracene* (1 g.) formed colourless lustrous plates, m. p. 108—109°, from ethanol (Found: C, 85·6; H, 8·3; N, 6·3. $C_{16}H_{19}N$ requires C, 85·3; H, 8·4; N, 6·2%).

9-s-*Octahydroanthranylacetic acid* (I*a*).—The above nitrile (0·9 g.) was heated at 150—160° for 10 hours in a mixture (50 c.c.) of equal volumes of water, acetic acid, and concentrated sulphuric acid. The *acid* (0·8 g.) formed colourless plates, m. p. 212—214° (decomp.) after sintering at 190° (Found: C, 78·6; H, 8·4. $C_{16}H_{20}O_2$ requires C, 78·7; H, 8·2%). It was recovered unchanged after treatment with anhydrous hydrogen fluoride at room temperature.

9-*Methyl*-10-*chloromethyl*-s-*octahydroanthracene*.—Hydrogen chloride was passed into a suspension of paraformaldehyde (1·2 g.) in glacial acetic acid (20 c.c.) until a clear solution was obtained. 9-Methyl-*s*-octahydroanthracene (6 g.) was added, and the passage of hydrogen chloride continued, the temperature being maintained at 60—70°. After 2 hours, the crystals (6·7 g.) were collected, washed with water, and recrystallised from benzene–light petroleum. 9-*Methyl*-10-*chloromethyl*-s-*octahydroanthracene* formed colourless plates, m. p. 143—144° (Found: C, 77·1; H, 8·1. $C_{16}H_{21}Cl$ requires C, 77·3; H, 8·45%).

Attempted recrystallisation of this compound from ethanol led to the formation of 9-*methyl*-10-*ethoxymethyl*-s-*octahydroanthracene*, which formed fluffy colourless needles, m. p. 73° (Found: C, 83·7; H, 9·8. $C_{18}H_{26}O$ requires C, 83·7; H, 10·1%).

The chloromethyl compound, in acetone, was smoothly reduced with hydrogen and palladium-black to 9 : 10-dimethyl-*s*-octahydroanthracene, identical with a specimen prepared by Badger, Carruthers, Cook, and Schoental (*loc. cit.*).

β-(10-*Methyl*-s-*octahydro*-9-*anthranyl*)*propionic Acid* (VI).—A mixture of atomised sodium (1·1 g.), ethyl malonate (7·5 g.), and dry benzene (25 c.c.) was heated under reflux for 2 hours. 9-Methyl-10-chloromethyl-*s*-octahydroanthracene (5 g.) in dry benzene (35 c.c.) was added, and the refluxing continued for a further 8 hours. After removal of the benzene, the ester was hydrolysed by 3 hours' boiling with

potassium hydroxide (15 g.) in aqueous ethanol (1 : 1; 100 c.c.). After decarboxylation of the acidic product by heating at 240° for 15 minutes, *β-(10-methyl-s-octahydro-9-anthranyl)propionic acid* (3·2 g.) was obtained. It crystallised from acetic acid in long colourless needles, m. p. 206—208° after sintering (Found: C, 79·4; H, 8·7. $C_{18}H_{24}O_2$ requires C, 79·4; H, 8·8%).

Treatment of this acid with anhydrous hydrogen fluoride resulted in its conversion into a neutral ketonic, but gummy, product. Attempted distillation led to extensive decomposition, and chromatography gave no purification. It formed a solid oxime and dinitrophenylhydrazone, but neither product could be isolated in a pure condition.

9-Chloromethyl-s-octahydrophenanthrene (IV; R = CH_2Cl).—Hydrogen chloride was passed into a vigorously stirred mixture of *s*-octahydrophenanthrene (8 g.; Durland and Adkins, *J. Amer. Chem. Soc.*, 1937, **59**, 135), aqueous formaldehyde (8 c.c., 40%), concentrated hydrochloric acid (40 c.c.), and acetic acid (5 c.c.) at 70° for 5½ hours. The cooled mixture was extracted with benzene, and the extract was washed, dried, and distilled. After removal of some unchanged hydrocarbon, a colourless oil (5 g.) was collected at 170—180°/1·5 mm. Crystallisation from light petroleum gave *9-chloromethyl-s-octahydrophenanthrene* as clusters of colourless prismatic needles, m. p. 56° (Found: C, 76·8; H, 8·2. $C_{15}H_{19}Cl$ requires C, 76·8; H, 8·1%). The residue from the distillation was extracted with light petroleum and gave 9 : 10-*bischloromethyl-s-octahydrophenanthrene* (0·8 g.) as colourless needles, m. p. 160° from ethanol, in which solvent it is sparingly soluble (Found: C, 67·9; H, 6·9. $C_{16}H_{20}Cl_2$ requires C, 68·1; H, 7·1%).

9-Methyl-s-octahydrophenanthrene (IV; R = Me).—Reduction of chloromethyloctahydrophenanthrene, in acetone, with hydrogen and palladium proceeded smoothly to give *9-methyl-s-octahydrophenanthrene* as a colourless oil, b. p. 106—110° (air-bath temp.)/0·3 mm. (Found: C, 90·0; H, 9·9. $C_{15}H_{20}$ requires C, 90·0; H, 10·0%). Dehydrogenation with palladium-black at 280° for 3 hours gave 9-methylphenanthrene, identified by comparison with an authentic specimen. In the same way, reduction of the bischloromethyl derivative gave 9 : 10-*dimethyl-s-octahydrophenanthrene* as colourless glistening plates, m. p. 98°, from ethanol (Found: C, 89·75; H, 10·3. $C_{16}H_{22}$ requires C, 89·7; H, 10·3%).

After treatment with anhydrous hydrogen fluoride, 9-methyl-*s*-octahydrophenanthrene was recovered unchanged, for dehydrogenation of the resulting oil gave only 9-methylphenanthrene.

Cyclisation of Tetrahydrophenanthrylpropionic Acid (X).—(a) *With hydrogen fluoride.* *β*-(1 : 2 : 3 : 4-Tetrahydro-9-phenanthryl)propionic acid (0·6 g.; Bachmann and Cronyn, *loc. cit.*) was treated with hydrogen fluoride at room temperature for 12 hours. The product, in benzene, was washed with dilute sodium carbonate, and the neutral material was isolated by removal of the benzene. Crystallisation from ethanol gave *3′-keto-9 : 10-cyclopenteno-1 : 2 : 3 : 4-tetrahydrophenanthrene* (XII) (0·4 g.) as soft colourless needles, m. p. 179° (Found: C, 86·5; H, 6·9. $C_{17}H_{16}O$ requires C, 86·4; H, 6·8%). When this experiment was repeated on a larger scale, some evidence for the presence of another neutral product, in very small quantity, was obtained. This substance could not, however, be obtained homogeneous.

(b) *With stannic chloride.* The propionic acid (0·5 g.), in dry benzene (10 c.c.), was treated with phosphorus pentachloride (0·4 g.). After an hour, the mixture was warmed on the steam-bath for a few minutes to complete the reaction. This solution of the acid chloride was cooled in ice, and an ice-cold solution of stannic chloride (1 c.c.) in dry benzene (10 c.c.) added. After standing for an hour, in an ice-bath, the dark red complex was decomposed with ice and hydrochloric acid. The benzene solution, after being washed with dilute sodium carbonate, was concentrated, and passed through a column of alumina. Only one product (0·3 g.) was isolated from the eluate, and this formed colourless needles, m. p. 177° (from alcohol) not depressed by admixture with product obtained as in (a).

(c) *With aluminium chloride.* A mixture of the propionic acid (0·5 g.) and thionyl chloride (2 c.c.) in ether was left at room temperature for 2 hours. Ether and excess of thionyl chloride were removed by warming under reduced pressure, and the resulting acid chloride, in nitrobenzene (5 c.c.), was added to an ice-cold mixture of aluminium chloride (1 g.) and nitrobenzene (5 c.c.). After 24 hours at room temperature, the product (0·25 g.) was isolated in the usual way. It formed colourless needles, m. p. 177—179°, from ethanol, and the m. p. was not depressed by admixture with a specimen obtained as above.

9 : 10-cyclo*Penteno*-1 : 2 : 3 : 4-*tetrahydrophenanthrene*.—The above keto*cyclo*pentenotetrahydrophenanthrene (0·7 g.) was heated under reflux with amalgamated zinc (7 g.), concentrated hydrochloric acid (40 c.c.), glacial acetic acid (10 c.c.), and toluene (10 c.c.) for 24 hours. The toluene layer was separated, and the product obtained from this was dissolved in benzene and passed through a column of alumina. A colourless band with a blue fluorescence in ultra-violet light was eluted, and the product obtained from it recrystallised from ethanol. 9 : 10-cyclo*Penteno*-1 : 2 : 3 : 4-*tetrahydrophenanthrene* (0·4 g.) formed colourless needles, m. p. 65—66° (Found: C, 91·9; H, 8·1. $C_{17}H_{18}$ requires C, 91·9; H, 8·1%).

Dehydrogenation of this substance (0·1 g.) with palladium-black (0·02 g.) at 290—300° in an atmosphere of carbon dioxide proceeded smoothly. After sublimation *in vacuo* and recrystallisation from ethanol, 9 : 10-*cyclo*pentenophenanthrene was obtained as long colourless needles, m. p. 149° (lit., m. p. 154°; 149—150°), not depressed on admixture with an authentic specimen of 9 : 10-*cyclo*pentenophenanthrene.

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