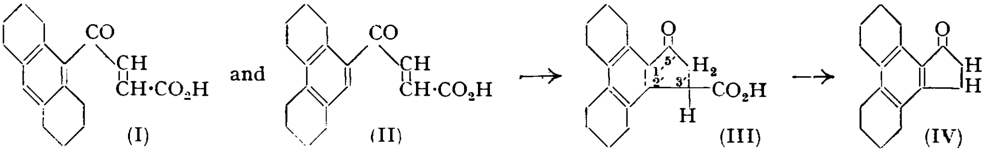
434. *Preparation and Isomerisation of Aromatic Ketones and Keto-acids.*

By G. Baddeley and R. Williamson.

The following changes have been effected through the agency of excess of aluminium chloride: β-(*s*-octahydro-9-anthroyl)- and β-(*s*-octahydro-9-phenanthroyl)-acrylic acids * to 1 : 2 : 3 : 4 : 5 : 6 : 7 : 8-octahydro-5′-keto-9 : 10-*cyclo*pentenophenanthrene-3′-carboxylic acid (I and II → III); 9-acetyl-*s*-octahydroanthracene to 7-acetyl-2-methyl-4 : 5-*cyclo*hexenoindane (VI) and 7-acetyl-3-methyl-4 : 5-*cyclo*hexenoindene (VII); 1-keto-*s*-dodecahydrotriphenylene * (IX) to 1 : 2 : 3 : 4 : 5 : 6 : 7 : 8-octahydro-1-keto-4′-methyl-9 : 10-*cyclo*pentenophenanthrene (X) and 1 : 2 : 3 : 4 : 5 : 6 : 7 : 8-octahydro-8-keto-3′-methyl-9 : 10-*cyclo*penta-1′ : 3′-dienophenanthrene (XI).

The 10-acetyl derivatives of *s*-octahydro-9-methyl- and 9-ethyl-*s*-octahydro-anthracene undergo intermolecular migration of acetyl or alkyl groups.

Succinoylation of *s*-octahydroanthracene * by the Friedel–Crafts method is reported to afford a mixture of β-(*s*-octahydro-9-anthroyl)- and β-(*s*-octahydro-9-phenanthroyl)-propionic acids (Badger, Carruthers, and Cook, *J.*, 1949, 2044); the latter is provided by isomerisation of the former (see Experimental), a process requiring the presence of undissolved aluminium chloride or the chloride in excess (*J.*, 1950, 944). This condition obtains almost invariably when powdered aluminium chloride is added to a mixture of the other two reactants or when the solvent is carbon disulphide, and can readily be avoided when methylene or ethylene chloride is the solvent (*J.*, 1952, 3289, 3605); thus only β-(*s*-octahydro-9-anthroyl)propionic acid is obtained when a solution of succinic anhydride in ethylene chloride is saturated with aluminium chloride and decanted into *s*-octahydroanthracene; reaction is complete in a few minutes. If, at this stage, aluminium chloride is added and the mixture is kept for several days, the corresponding phenanthroylpropionic acid is obtained.



Reaction of maleic anhydride with *s*-octahydro-anthracene and -phenanthrene in the absence of excess of aluminium chloride or undissolved chloride readily affords β-(*s*-octahydro-9-anthroyl)- and β-(*s*-octahydro-9-phenanthroyl)-acrylic acid (I and II) respectively; in

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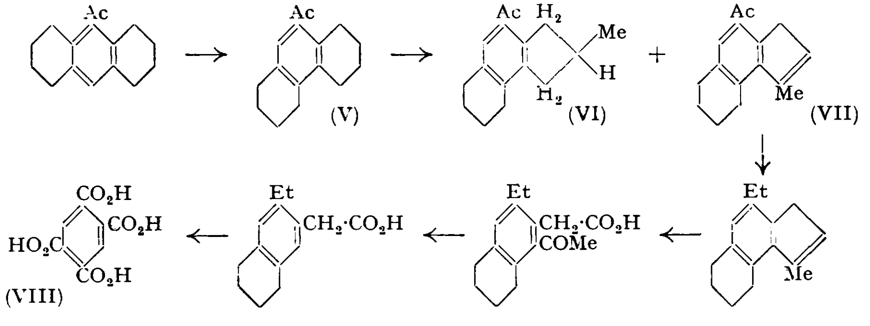
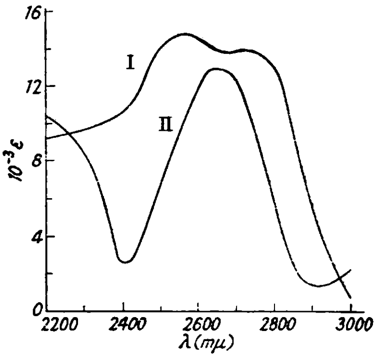
* In this paper *s*-octahydro and *s*-dodecahydro are used when the central ring is aromatic.

each instance excess of reagent effects isomerisation with formation of 1 : 2 : 3 : 4 : 5 : 6 : 7 : 8-octahydro-5′-keto-9 : 10-*cyclo*pentenophenanthrene-3′-carboxylic acid (III). This acid is obtained in 90% yield when each of the acrylic acids is fused with excess of aluminium chloride at 100°, and in 50% yield when concentrated sulphuric acid is used. It was identified by decarboxylation to (IV) which has been described by Badger, Carruthers, Cook, and Schoental (*J.*, 1949, 169). Cyclisation of β-aroylacrylic acids was reported first by Lambert and Martin (*Bull. Soc. chim. Belg.*, 1952, **61**, 132) and one of us (G. B.) was unaware of this when submitting papers (*J.*, 1952, 3289, 3605).



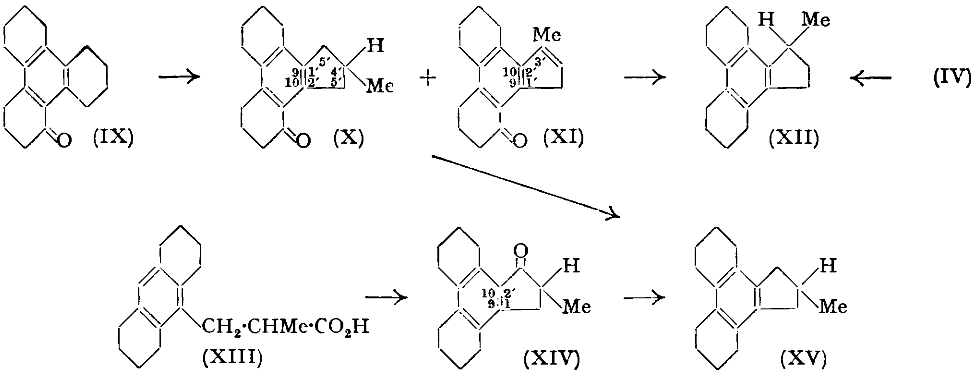
Acetylation of *s*-octahydro-anthracene and -phenanthrene, while affording the 9-acetyl derivatives when *excess* of aluminium chloride is absent, provides 7-acetyl-2-methyl-4 : 5-*cyclo*hexenoindane (VI) when the reaction mixtures are kept for several days in the presence of excess of reagent. This ring contraction, which is not a feature of reaction of these hydrocarbons with succinic or maleic anhydride, was observed previously on fusion with aluminium chloride at 100° (Baddeley and Pendleton, *J.*, 1952, 807), the indane being contaminated by an oil representing 25% of the product. The oil has now been examined and is probably a mixture of (VI) (3 parts) and 7-acetyl-3-methyl-4 : 5-*cyclo*hexenoindene (VII) (1 part) : it was reduced by the Clemmensen method to a hydrocarbon which was ozonised; the product, like the original oil and the hydrocarbon obtained from it by Clemmensen reduction, absorbed hydrogen (0·25 mol.) on catalytic hydrogenation; subsequent oxidation with alkaline hydrogen peroxide provided a keto-acid which was separated from saturated hydrocarbon; the keto-acid gave a positive iodoform test and was hydrolysed by syrupy phosphoric acid to acetic acid and an aromatic acid which afforded benzene-1 : 2 : 4 : 5-tetracarboxylic acid when oxidised by dilute nitric acid. These results are compatible with the formulation (VII ⟶ VIII). The hydrocarbon recovered after ozonolysis is 7-ethyl-2-methyl-4 : 5-*cyclo*hexenoindane and like an authentic sample, obtained by Clemmensen reduction of (VI), afforded 7-ethyl-2-methyl-4 : 5-benzindane on catalytic dehydrogenation.



1-Keto-*s*-dodecahydrotriphenylene (IX) also affords two products when fused with aluminium chloride at 100°. Chromatography on alumina gave a ketone $C_{18}H_{22}O$, as the more mobile component. This afforded 1 : 2 : 3 : 4 : 5 : 6 : 7 : 8-octahydro-4′-methyl-9 : 10-*cyclo*pentenophenanthrene (XV) when reduced by the Clemmensen method and is 1 : 2 : 3 : 4 : 5 : 6 : 7 : 8-octahydro-1-keto-4′-methyl-9 : 10-*cyclo*pentenophenanthrene (X). Its ultra-violet absorption spectrum (see Figure, curve II) is similar to that of acetophenone. The other component is a ketone $C_{18}H_{20}O$, and is probably 1 : 2 : 3 : 4 : 5 : 6 : 7 : 8-octahydro-8-keto-3′-methyl-9 : 10-*cyclo*penta-1′ : 3′-dienophenanthrene (XI) for the following reasons: (i) Catalytic hydrogenation provided a dihydro-derivative which gave 1 : 2 : 3 : 4 : 5 : 6 : 7 : 8-octahydro-3′-methyl-9 : 10-*cyclo*pentenophenanthrene (XII) by Clemmensen reduction.

(ii) Its ultra-violet absorption spectrum has a broad band (see Figure, curve I), probably formed by overlap of two bands, and is compatible with conjugation of a carbonyl group and an ethylenic linkage with a benzene ring but not with one another. (iii) The change (IX ⟶ X + XI) is analogous to (V ⟶ VI + VII).

Authentic samples of (XII) and (XV) were needed for comparison; the former was prepared from (IV) by standard procedure and the latter as follows : Interaction of 9-chloromethyl-*s*-octahydroanthracene and sodiomethylmalonic ester and subsequent hydrolysis and decarboxylation at 200° gave α-methyl-β-(9-*s*-octahydroanthryl)propionic acid (XIII), which was isomerised and cyclised to 1 : 2 : 3 : 4 : 5 : 6 : 7 : 8-octahydro-3′-keto-4′-methyl-9 : 10-*cyclo*pentenophenanthrene (XIV) by the action of anhydrous hydrogen fluoride (see Badger, Carruthers, Cook, and Schoental, *J.*, 1949, 169); this ketone gave (XV) on Clemmensen reduction.



The 10-acetyl derivatives of *s*-octahydro-9-methyl- and 9-ethyl-*s*-octahydro-anthracene did not afford derivatives of hydrindacene on fusion with aluminium chloride; instead, intermolecular migration of acetyl and/or alkyl groups occurred. The former gave a mixture containing the 9-methyl derivatives of *s*-octahydroanthracene and *s*-octahydrophenanthrene, and the latter, a mixture containing 9-ethyl- and 9-acetyl-*s*-octahydrophenanthrene.

The mechanisms of the reactions effected by aluminium chloride will be discussed in a further communication.

EXPERIMENTAL

Materials.—Hydrocarbons. (i) *s*-Octahydro-9-methylanthracene was obtained by catalytic reduction of the 9-chloromethyl derivative (Badger, Carruthers, and Cook, *loc. cit.*). During chloromethylation of *s*-octahydroanthracene by paraformaldehyde and hydrogen chloride in glacial acetic acid, sufficient solvent to prevent separation of an oil must be used, otherwise considerable quantities of the 9 : 10-bischloromethyl derivative are obtained.

(ii) 9-Ethyl-*s*-octahydroanthracene was obtained from the 9-acetyl derivative by a three-stage process : The ketone (23 g.) was reduced by lithium aluminium hydride (1·2 g.) in ethereal solution to *s-octahydro-*9-1′-*hydroxyethylanthracene* (19 g.), b. p. 170°/0·25 mm., plates (from ethanol), m. p. 104° (Found : C, 83·7; H, 10·0. $C_{16}H_{22}O$ requires C, 83·5; H, 9·7%), and afforded the 9-vinyl derivative (18 g.), b. p. 154°/0·5 mm. (Found : C, 90·5; H, 9·1. $C_{16}H_{20}$ requires C, 90·6; H, 9·4%), when distilled from a trace of sulphuric acid. Catalytic hydrogenation then provided the required hydrocarbon.

(iii) Finely powdered *s*-octahydro-1′-keto-9 : 10-*cyclo*pentenophenanthrene (2 g.) was gradually added to a stirred solution of magnesium (0·3 g.) in methyl iodide (1·5 g.) and ether (50 c.c.); the mixture was kept overnight and, when decomposed with ammonium chloride solution, afforded the tertiary *alcohol*; this crystallised from ethanol in plates, m. p. 135—137° (Found : C, 84·1; H, 9·8. $C_{18}H_{24}O$ requires C, 84·4; H, 9·4%). It was dissolved in a minimum of benzene and vigorously stirred with formic acid (90%; 10 c.c.) for 4 hr. After addition of water, the benzene layer was separated and washed with water; removal of solvent provided a residue which was hydrogenated in ethanol over Raney nickel. The resultant

1 : 2 : 3 : 4 : 5 : 6 : 7 : *8-octahydro-3′-methyl-9* : 10-cyclo*pentenophenanthrene* (XII) crystallised from aqueous acetic acid in needles, m. p. 115° (Found : C, 89·6; H, 9·9. $C_{18}H_{24}$ requires C, 90·0; H, 10·0%).

(iv) 9-Chloromethyl-*s*-octahydroanthracene (23 g.) was added to a solution of sodium (2·3 g.) in methylmalonic ester (17·4 g.) and toluene (75 c.c.); the mixture was kept overnight and was then refluxed for 7 hr. After addition of water, the organic layer was separated, toluene was removed by distillation, and the residue was refluxed for 4 hr. with 30% sodium hydroxide solution. Insoluble material was extracted by chloroform, and the aqueous solution was acidified; the precipitated dicarboxylic acid (m. p. 190°) was decarboxylated at 200° and the product recrystallised from aqueous acetic acid (charcoal); *α-methyl-β-(*s*-octahydro-9-anthryl)-propionic acid* (15 g.) separated in needles, m. p. 151—152° (Found : C, 79·2; H, 8·7%; equiv., 280. $C_{18}H_{14}O_2$ requires C, 79·5; H, 8·8%; equiv., 272). This acid (10 g.) in anhydrous hydrofluoric acid (120 c.c.) was set aside for 60 hr. and afforded 1 : 2 : 3 : 4 : 5 : 6 : 7 : *8-octahydro-3′-keto-4′-methyl-9* : 10-cyclo*pentenophenanthrene* (XIV) (5 g.), needles (from aqueous acetic acid), m. p. 158—160° (Found : C, 85·0; H, 8·6. $C_{18}H_{22}O$ requires C, 85·0; H, 8·7%). This ketone (3 g.) was reduced by the Clemmensen method to 1 : 2 : 3 : 4 : 5 : 6 : 7 : *8-octahydro-4′-methyl-9* : 10-cyclo*pentenophenanthrene* (XV) (2·8 g.), needles (from aqueous acetic acid), m. p. 135° (Found : C, 89·6; H, 9·7. $C_{18}H_{24}$ requires C, 90·0; H, 10·0%).

(v) Reduction of 7-acetyl-2-methyl-4 : 5-*cyclo*hexenoindane (Baddeley and Pendleton, *loc. cit.*) by the Clemmensen method provided the 7-ethyl-2-methyl derivative which gave 7-ethyl-2-methyl-4 : 5-benzindane by dehydrogenation; the *picrate* crystallised from ethanol in brick-red needles, m. p. 120—121° (Found : C, 60·5; H, 5·0; N, 10·0. $C_{22}H_{21}O_7N_3$ requires C, 60·2; H, 4·8; N, 9·6%).

Ketones. Acetyl chloride (1·1 mols.) was added to a suspension of aluminium chloride (1·3 mols.) in methylene or ethylene chloride, and the solution was slowly decanted from undissolved aluminium chloride into a solution of aromatic hydrocarbon (1 mol.) in methylene or ethylene chloride. Reaction was complete after a few minutes and the product was worked up in the usual way. 9-Acetyl-*s*-octahydroanthracene crystallised from methanol in large needles, m. p. 71° (Arnold and Barnes, *J. Amer. Chem. Soc.*, 1944, **66**, 963). *10-Acetyl-*s*-octahydro-9-methylanthracene* crystallised from ethanol in needles, m. p. 124° (Found : C, 84·3; H, 8·9. $C_{17}H_{22}O$ requires C, 84·3; H, 9·1%), and *10-acetyl-9-ethyl-*s*-octahydroanthracene*, b. p. 166°/0·2 mm., in needles, m. p. 136° (Found : C, 83·9; H, 9·6. $C_{18}H_{24}O$ requires C, 84·4; H, 9·4%). *s*-Dodecahydro-1-ketotriphenylene (IX), m. p. 221°, was obtained by the action of anhydrous hydrofluoric acid on γ-(*s*-octahydro-9-phenanthryl)butyric acid (Badger, Carruthers, and Cook, *loc. cit.*).

Succinic Anhydride and s*-Octahydroanthracene in Ethylene Chloride.*—(i) A mixture of the anhydride (12 g., 1·2 mols.) and aluminium chloride (30 g., 2·2 mols.) in solvent (100 c.c.) was stirred for 15 min. and the solution was decanted from undissolved chloride into a solution of the hydrocarbon (18·6 g.) in solvent (100 c.c.). After 10 min., the mixture was decomposed with ice and hydrochloric acid and afforded β-(*s*-octahydro-9-anthroyl)propionic acid (15 g.), m. p. and mixed m. p. 214°, as the only product which was not volatile in steam.

(ii) When aluminium chloride (45 g., 3 mols.) was used and the mixture kept for 3 days at 18°, β-(*s*-octahydro-9-phenanthroyl)propionic acid (18 g.), m. p. and mixed m. p. 148°, was obtained.

(iii) A mixture of β-(*s*-octahydro-9-anthroyl)propionic acid (5·7 g.) and aluminium chloride (10 g., 4 mols.) in solvent (50 c.c.) was kept for 2 days at 18° and afforded β-(*s*-octahydro-9-phenanthroyl)propionic acid (4 g.). This acid (17 g.) was obtained from a mixture of succinic anhydride (10 g.), aluminium chloride (30 g.), *s*-octahydrophenanthrene (16 g.), and solvent (200 c.c.) which had been kept for 10 min.

Maleic Anhydride and s*-Octahydroanthracene in Ethylene Chloride.*—(i) A mixture of the anhydride (2·5 g., 1 mol.) and aluminium chloride (10 g., 2·5 mols.) in solvent (50 c.c.) was stirred for 15 min. and the clear solution was decanted into the hydrocarbon (4·7 g.) in solvent (50 c.c.). After several min. the mixture was decomposed in the usual way and afforded *2-(*s*-octahydro-9-anthroyl)acrylic acid* (I) (6·5 g.) as bright yellow needles, m. p. 208° (from glacial acetic acid) (Found : C, 75·6; H, 7·0%; equiv., 287. $C_{18}H_{20}O_3$ requires C, 76·0; H, 7·0%; equiv., 284). It afforded the corresponding propionic acid on hydrogenation.

When subjected to the above process, *s*-octahydrophenanthrene (4·7 g.) afforded *2-(*s*-octahydro-9-phenanthroyl)acrylic acid* (II) (6 g.) which crystallised from glacial acetic acid in yellow needles, m. p. 175—177° (Found : C, 76·4; H, 7·2%), and provided the corresponding propionic acid on hydrogenation.

(ii) When excess of aluminium chloride was used in the above reactions and the mixtures kept for several days, *s*-octahydro-anthracene and -phenanthrene afforded the same acid, m. p. 237° (decomp.) [*methyl* ester, m. p. and mixed m. p. 138° (Found : C, 76·8; H, 7·6. $C_{19}H_{22}O_3$ requires C, 76·5; H, 7·4%)]. This acid 1 : 2 : 3 : 4 : 5 : 6 : 7 : 8-octahydro-5′-keto-9 : 10-*cyclo*pentenophenanthrene-3′-carboxylic acid (III) was obtained in 90% yield when the above acrylic acids were added to aluminium chloride–sodium chloride at 100° and in 50% yield by the action of sulphuric acid at 100°. The acid (9·7 g.) was decarboxylated by copper chromite (2 g.) in quinoline (40 c.c.) at 200°; the product provided colourless needles (6 g.), m. p. 196° when sublimed at 190°/0·1 mm. and these formed a 2 : 4-dinitrophenylhydrazone, m. p. 295° (Badger, Carruthers, and Cook, *loc. cit.*, record the m. p. of 1 : 2 : 3 : 4 : 5 : 6 : 7 : 8-octahydro-3′-keto*cyclo*pentenophenanthrene and of its 2 : 4-dinitrophenylhydrazone as 197—198° and 298° respectively). Clemmensen reduction of this ketone gave 1 : 2 : 3 : 4 : 5 : 6 : 7 : 8-*octahydro*-9 : 10-cyclo*pentenophenanthrene* which crystallised from ethanol in colourless needles, m. p. 153° (Found : C, 89·7; H, 9·9. $C_{17}H_{22}$ requires C, 90·2; H, 9·8%).

Acetyl Chloride and s-*Octahydroanthracene in Ethylene Chloride.*—(i) A solution obtained from acetyl chloride (8·5 g.) and aluminium chloride (18 g.) in solvent (100 c.c.) was decanted from undissolved aluminium chloride into a solution of the hydrocarbon (18·6 g.) in solvent (100 c.c.); the mixture was decomposed after 5 min. at room temperature and afforded 9-acetyl-*s*-octahydroanthracene (17 g.), b. p. 175°/0·7 mm., m. p. and mixed m. p. 72°.

(ii) The reaction mixture was prepared as in the previous experiment, and excess of aluminium chloride (14 g., 1 mol.) was then added. After 2 days, at room temperature, decomposition afforded 7-acetyl-2-methyl-4 : 5-*cyclo*hexenoindane (VI) (17 g.), b. p. 148°/0·1 mm., m. p. and mixed m. p. 98°.

Aromatic Ketones and Aluminium Chloride.—(i) 10-*Acetyl*-s-*octahydro*-9-*methylanthracene.* This ketone (5 g.), aluminium chloride (8 g., 3 mols.), and sodium chloride (0·5 g.) were heated together at 100° for 3 hr. After decomposition with ice and hydrochloric acid, the product (4·4 g.), b. p. 135—200°/0·5 mm., was dissolved in light petroleum and extracted with sulphuric acid (90%). The petroleum retained aromatic hydrocarbon (1·0 g.) and this was dehydrogenated over palladised charcoal (5%) at 260°; the product was crystallised from ethanol and afforded colourless needles of 9-methylphenanthrene, m. p. and mixed m. p. 90° (Found : C, 93·3; H, 6·4. Calc. for $C_{15}H_{12}$: C, 93·7; H, 6·3%). The filtrate was fluorescent and addition of an ethanolic solution of picric acid precipitated 9-methylanthracene picrate in deep red needles (from benzene), m. p. and mixed m. p. 137° (Found : C, 59·6; H, 3·6; N, 9·9. Calc. for $C_{21}H_{15}O_7N_3$: C, 59·8; H, 3·6; N, 10·0%). Ketonic products, isolated by dilution of the acid extract, distilled over a wide range of temperature and were not investigated.

(ii) 10-*Acetyl*-9-*ethyl*-s-*octahydroanthracene.* This ketone (10 g.), aluminium chloride (15 g.), and sodium chloride (1·5 g.) were heated together at 100° for 3 hr. Recovered organic material afforded a pale yellow oil (6·5 g.), b. p. 140—180°/0·1 mm. Separation by sulphuric acid as in the previous experiment gave mainly ketonic material, b. p. 170—180°/0·1 mm., which was 9-acetyl-*s*-octahydrophenanthrene (V) since oxidation with selenium dioxide and then alkaline hydrogen peroxide (Arnold and Rondestvedt, *J. Amer. Chem. Soc.*, 1945, **67**, 1265) afforded *s*-octahydro-9-phenanthroic acid, m. p. and mixed m. p. 241°. The material which did not dissolve in sulphuric acid contained 9-ethyl-*s*-octahydrophenanthrene; when dehydrogenated with palladised charcoal at 260° it afforded 9-ethylphenanthrene which was identified by its picrate, m. p. and mixed m. p. 124° (Pschorr, *Ber.*, 1906, **39**, 3128) (Found : C, 60·1; H, 3·8. Calc. for $C_{22}H_{17}O_7N_3$: C, 60·7% H, 3·9%)

(iii) 9-*Acetyl*-s-*octahydroanthracene.* A mixture of this ketone (50 g.), aluminium chloride (76 g.), and sodium chloride (3 g.) was heated at 100° for 2 hr. Decomposition gave a semi-solid product (45 g.), b. p. 148°/0·12 mm., consisting of solid, 7-acetyl-2-methyl-4 : 5-*cyclo*hexenoindane (VI) (30 g.), m. p. and mixed m. p. 98°, and oil (15 g.). (Very little oil was formed when the ketone was isomerised in ethylene chloride at room temperature, but oil was gradually formed when 7-acetyl-2-methyl-4 : 5-*cyclo*hexenoindane was fused with excess of aluminium chloride at 100°.) The oil (Found : C, 84·5; H, 9·4. Calc. for $C_{16}H_{20}O$: C, 84·2; H, 8·8%) contained unsaturated material since it decolorised bromine in carbon tetrachloride and aqueous permanganate, and absorbed hydrogen (0·25 mol.) over palladised charcoal (5%). Oxidation by Arnold and Rondestvedt's method (*loc. cit.*) provided a mixture of carboxylic acids (Found: C, 78·2; H, 7·9%; equiv., 227. Calc. for $C_{15}H_{18}O_2$: C, 78·3; H, 7·8%; equiv., 230). Neither the oil nor the mixture of acids obtained from it could be separated into their components. The oil (15 g.) afforded hydrocarbon (11 g.), b. p. 130—135°/0·2 mm., on Clemmensen reduction; the hydrocarbon absorbed hydrogen (0·25 mol.) on catalytic hydrogenation. The hydrocarbon (10·0 g.) in ethyl acetate was subjected to a stream of ozonised oxygen for 2 hr.; the product, over palladised charcoal (30%), absorbed hydrogen (270 c.c.); this volume is compatible with the view that the hydrocarbon contains 25% of indene. After removal of solvent, the residue, in ethanol (10 c.c.), was treated with hydrogen peroxide (30%; 5 c.c.) and sodium hydroxide solution (10%) until there was no further reaction; after being heated at 80° for 30 min., the mixture was cooled, diluted with water, and extracted with ether. The ethereal layer contained 7-ethyl-2-methyl-4 : 5-*cyclo*hexenoindane, b. p. 135°/0·2 mm. A sample (1 g.) was dehydrogenated over palladised charcoal at 260° and afforded 7-ethyl-2-methyl-4 : 5-benzindane. Its picrate crystallised from ethanol in brick-red needles, m. p. and mixed m. p. 120—121° (Found : C, 60·5; H, 5·0; N, 10·0. Calc. for $C_{22}H_{21}O_7N_3$: C, 60·2; H, 4·8; N, 9·6%). On acidification, the aqueous layer provided a keto-acid which gave a ready iodoform reaction; it evolved acetic acid when heated with syrupy phosphoric acid at 180° and the residue, which was isolated by dilution with water and extraction with chloroform, afforded benzene-1 : 2 : 4 : 5-tetracarboxylic acid (tetramethyl ester, m. p. and mixed m. p. 124°) when heated with nitric acid (*d* 1·1) at 160° for 3 hr.

(iv) s-*Dodecahydro*-1-*ketotriphenylene*. This ketone (5 g.), aluminium chloride (15 g.), and sodium chloride (5 g.) were fused together at 100° for 1 hr. After decomposition with ice and hydrochloric acid the product (3·8 g.), b. p. 210°/0·5 mm., gradually crystallised. Chromatography in light petroleum on activated grade " H " alumina provided two components : 1 : 2 : 3 : 4 : 5 : 6 : 7 : 8-*octahydro*-1-*keto*-4′-*methyl*-9 : 10-cyclo*pentenophenanthrene* (X), the more mobile, crystallised from ethanol in needles, m. p. 148—149° (Found : C, 85·1; H, 8·9. $C_{18}H_{22}O$ requires C, 85·05; H, 8·7%); 1 : 2 : 3 : 4 : 5 : 6 : 7 : 8-*octahydro*-8-*keto*-3′-*methyl*-9 : 10-cyclo*penta*-1′ : 3′-*dienophenanthrene* (XI), the other component, crystallised from ethanol in long needles, m. p. 116—117° (Found : C, 85·1; H, 7·9. $C_{18}H_{20}O$ requires C, 85·6; H, 7·9%). Reduction of (X) by the Clemmensen method provided 1 : 2 : 3 : 4 : 5 : 6 : 7 : 8-octahydro-4′-methyl-9 : 10-*cyclo*pentenophenanthrene, m. p. and mixed m. p. 135° (Found : C, 89·6; H, 9·7. Calc. for $C_{18}H_{24}$: C, 90·0; H, 10·0%) after recrystallisation from aqueous acetic acid. The compound (XI) decolorised bromine in carbon tetrachloride and aqueous permanganate and absorbed hydrogen (1 mol.) over Raney nickel; the cyclo*penteno*-derivative crystallised from ethanol in needles, m. p. 145° (Found : C, 85·4; H, 8·9. $C_{18}H_{22}O$ requires C, 85·0; H, 8·7%), readily formed a 2 : 4-dinitrophenylhydrazone, depressed the m. p. of (X) on admixture, and afforded 1 : 2 : 3 : 4 : 5 : 6 : 7 : 8-octahydro-3′-methyl-9 : 10-*cyclo*pentenophenanthrene, m. p. and mixed m. p. 115° (Found : C, 89·5; H, 9·9. Calc. for $C_{18}H_{24}$: C, 90·0; H, 10·0%), on Clemmensen reduction.

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