76. *Hydroanthracenes and Hydrophenanthrenes. Part II.**

By J. W. Cook, (Miss) N. A. McGinnis, and Stotherd Mitchell.

cis-as-Octahydrophenanthrene has been isomerised by aluminium chloride to the *trans*-isomeride. Under more drastic conditions tetralin and perhydroanthracene are among the products. *trans-as*-Octahydroanthracene and a number of its derivatives have been prepared and their configurations established. Two of the five theoretically possible perhydroanthracenes have been described hitherto. A third has now been obtained. Configurations have been assigned to these three perhydroanthracenes, and evidence is given in support of the suggested configurations.

A dibenz*cyclo*octanone has been synthesised, but the small yield precluded an attempt to convert this into a derivative of *cyclo*octatetraene. 1 : 2 : 3 : 4 : 7 : 8 : 9 : 10-Octahydro-5 : 6-benzazulene has also been synthesised, but was found to resist dehydrogenation to 5 : 6-benzazulene.

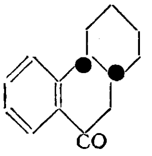
The heterogeneity of the saturated hydrocarbons formed by dehydration of 1-β-phenylethyl*cyclo*hexanol or by isomerisation of 1-β-phenylethyl-Δ^1-*cyclo*hexene (Bogert, *Science*, 1933, **77**, 289; Perlman, Davidson, and Bogert, *J. Org. Chem.*, 1936, **1**, 288; Cook and Hewett, J., 1933, 1098) was demonstrated (*a*) by fractional distillation into two fractions having different physical constants and giving different acetyl derivatives in the Friedel–Crafts reaction (van de Kamp and Mosettig, *J. Amer. Chem. Soc.*, 1936, **58**, 1063), and (*b*) by oxidation to ketones which could be separated by fractional crystallisation of their oximes (Cook, Hewett, and Lawrence, J., 1936, 71; Cook, Hewett, and Robinson, J., 1939, 168; Levitz, Perlman, and Bogert, *Science*, 1939, **90**, 114; *J. Org. Chem.*, 1941, **6**, 105). By the latter procedure Cook *et al.* obtained (i) the oxime, m. p. 124°, of *cis*-9-keto-*as*-octahydrophenanthrene (I),† which was the major product, (ii) the oxime, m. p. 176°, of *trans*-9-keto-*as*-octahydrophenanthrene (II), and (iii) an oxime, m. p. 187°, which was assumed to be derived from

---

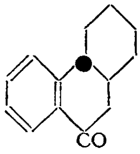
* The paper of Cook, Hewett, and Robinson (J., 1939, 168) is regarded as Part I of this series.

† Black dots in the formulæ denote hydrogen atoms above the general plane of the molecule, as in the convention proposed by Linstead (*Chem. and Ind.*, 1937, **56**, 510).

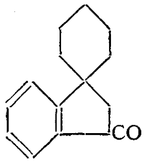
the spirocyclic ketone (III). The structures of (I) and (II) were shown by synthesis; their configurations were inferred from the physical constants of the hydrocarbons which they yielded on reduction.



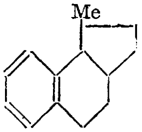
(I.)



(II.)



(III.)



(IV.)

Bogert *et al.* likewise obtained the oxime of the *cis*-ketone (I) and the oxime, m. p. 187°, but did not succeed in isolating the oxime, m. p. 176°, of the *trans*-ketone. Instead, they isolated an oxime, m. p. 137°, which they showed by synthesis to be derived from the spirocyclic ketone (III).* Hence the ketone which yields the oxime, m. p. 187°, must have some other structure, and the elucidation of this was one of the objectives of the present work. This, however, has not been attained.

A possible, but unlikely, interpretation was that the ketone giving the oxime, m. p. 187°, was formed by oxidation of uncyclised 1-β-phenylethyl-Δ^1-*cyclo*hexene present in the hydrocarbon mixture. Oxidation experiments carried out here with this unsaturated hydrocarbon by Mr. R. B. Crane gave a ketone mixture from which the oxime in question could not be isolated. Another possibility was that octahydrophenanthrene had been partly isomerised, under conditions of its formation, to a compound of type (IV), as in the isomerisation by aluminium chloride at elevated temperatures of *cyclo*hexane to methyl*cyclo*pentane (Zelinsky and Turowa-Pollak, *Ber.*, 1932, **65**, 1171; Nenitzescu and Cantuniari, *ibid.*, 1933, **66**, 1097) or of decahydronaphthalene to dimethyl*bicyclo*octane (Zelinsky and Turowa-Pollak, *Ber.*, 1925, **58**, 1292; Jones and Linstead, J., 1936, 616). On this hypothesis, treatment of the crude *as*-octahydrophenanthrene with aluminium chloride under conditions more drastic than those used in its preparation might be expected to increase the amount of hydrocarbon yielding the desired ketone on oxidation. This would facilitate a study of the structure by degradation methods.

The crude *as*-octahydrophenanthrene was, in fact, isomerised by aluminium chloride at temperatures from 20° to 50°; oxidation of the resulting hydrocarbon mixtures gave ketone mixtures very rich in *trans*-9-keto-*as*-octahydrophenanthrene (II), which was readily isolated in the crystalline state. The original hydrocarbon mixture gave very little of this ketone. The desired oxime of m. p. 187° could not be isolated after oximation of the material from the mother-liquors of this *trans*-ketone formed by isomerisation and oxidation. The action of aluminium chloride was thus essentially a conversion of *cis*-*as*-octahydrophenanthrene into its *trans*-isomeride, a reaction analogous to the transformation of *cis*-decalin into *trans*-decalin by aluminium chloride at room temperature (Zelinsky and Turowa-Pollak, *Ber.*, 1932, **65**, 1299).

At higher temperatures aluminium chloride produced more deep-seated changes. From the complex mixture formed at 125—130° were isolated tetralin, a perhydroanthracene (XIII), m. p. 89—90°, and a *hydrocarbon*, m. p. 204°, which appeared to be isomeric with this. The same products were obtained when *trans*-*as*-octahydroanthracene (VII) was treated with aluminium chloride under the same conditions. The formation of tetralin is evidently due to "cracking" by aluminium chloride. Possibly tetralin is an intermediate in the conversion of the tricyclic hydrocarbons into perhydroanthracene, for Schroeter (*Ber.*, 1924, **57**, 1990), who studied the complex reactions which occur when tetralin is treated with aluminium chloride at 50—70°, isolated from the products a hydrocarbon, m. p. 93°, which he suggested was one of the possible stereoisomeric perhydroanthracenes.

Mikhlina (*Uchenuie Zapinski*, 1934, **3**, 209; *Chem. Abstr.*, 1936, **30**, 8192) obtained perhydroanthracene, m. p. 90°, as one of the products of cracking with aluminium chloride of *s*-octahydroanthracene, and suggested a mechanism involving primary formation of tetralin and butadiene.

The hydrocarbon, m. p. 90°, which we obtained from *as*-octahydroanthracene and *as*-octahydrophenanthrene by treatment with aluminium chloride was identical with a specimen of one of the perhydroanthracenes obtained by catalytic hydrogenation of both *s*- and *as*-octahydroanthracenes (see below). It was not dehydrogenated by heating with palladium-black at 300° or selenium at 335°, in evacuated sealed tubes. The above-mentioned hydrocarbon, m. p. 204°, was likewise unaffected by these dehydrogenating agents under the same conditions. Our failure to dehydrogenate the perhydroanthracene is at variance with the results of Koller and Russ (*Monatsh.*, 1937, **70**, 54), who obtained anthracene when perhydroanthracene, m. p. 88°, was heated with selenium at 260—290° for 4 days in an evacuated sealed tube.

This sealed tube method of dehydrogenation, although convenient for small-scale work, seems less effective than the use of open vessels, for a dodecahydro-1 : 2-benzanthracene (V), when heated with selenium at 320—330° for 24 hours in an evacuated sealed tube, gave 5 : 6 : 7 : 8-tetrahydro-1 : 2-benzanthracene and not the

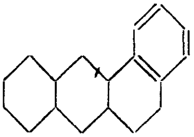
---

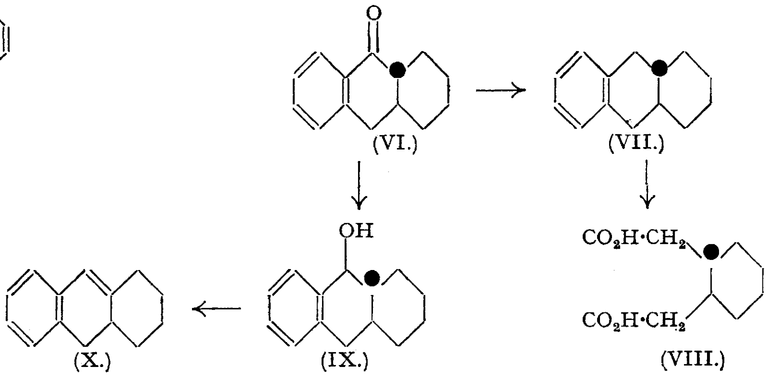
* Failure to isolate the oxime of m. p. 176° led Bogert to make the astonishing suggestion that the oxime of m. p. 187° was possibly derived from *trans*-keto-*as*-octahydrophenanthrene. This view ignored the synthesis of the *trans*-ketone giving the oxime of m. p. 176°, and also the depression of m. p. of this oxime when mixed with the oxime of m. p. 187° (J., 1936, 78). Further syntheses of the *trans*-ketone (II) have been recorded by Blumenfeld (*Ber.*, 1941, **74**, 524) and by Linstead, Whetstone, and Levine (*J. Amer. Chem. Soc.*, 1942, **64**, 2014).

fully aromatic 1 : 2-benzanthracene which is formed when the dehydrogenation is carried out in an open flask (Cook and Hewett, J., 1934, 375).

The configurations assigned by Cook, Hewett, and Robinson (*loc. cit.*) to the *as*-octahydrophenanthrenes were based on comparisons of their physical constants, and on the higher m. p.'s of the *trans*-ketone and its oxime. Attempts to verify the configuration of the relatively accessible *cis*-ketone (I) by degradation to *cis*-hexahydrohomophthalic acid had been unsuccessful. Hence we prepared a quantity of the *trans*-ketone (II) by our new method, with the object of degrading this to the easily crystallisable *trans*-hexahydrohomophthalic acid. This project was rendered unnecessary by the appearance of a paper by Linstead, Davis, and Whetstone (*J. Amer. Chem. Soc.*, 1942, **64**, 2009), who gave a rigid chemical proof of the configurations which we had assigned to the ketones (I) and (II). Another objective of our work was the preparation of stereochemically homogeneous perhydrophenanthrenes of known configuration, and experiments to this end are in progress with the *trans*-ketone (II).

A study of the stereochemical relationships of hydroanthracenes has also been commenced. Cook, Hewett, and Lawrence (*loc. cit.*) described a synthesis of the two stereoisomeric 9-keto-*as*-octahydroanthracenes, and suggested the *trans*-configuration (VI) for the readily available higher-melting isomeride (m. p. 109°). Proof of this has now been obtained. By Clemmensen reduction the ketone was converted into trans-as-***octahydroanthracene*** (VII). Sulphonation, followed by fusion with potash, converted this hydrocarbon into a ***hydroxy***-derivative, which was oxidised by alkaline permanganate to *trans-cyclo*hexane-1 : 2-diacetic acid (VIII).


(V.)



Catalytic hydrogenation of *trans*-9-keto-*as*-octahydroanthracene over Adams's platinum catalyst gave a mixture from which were isolated *trans-as*-octahydroanthracene (VII) and its 9-*hydroxy*-derivative (IX), in which the configuration of the hydroxyl group is unknown. Dehydration of the carbinol gave ***hexahydroanthracene*** (probably X), from which it was hoped to obtain *cis-as*-octahydroanthracene by catalytic hydrogenation. Hydrogenation rapidly took place over a platinum catalyst, but the product was mostly liquid and the isolation of a pure stereoisomeride was not feasible.

Two perhydroanthracenes (tetradecahydroanthracenes) have been described in the literature. One of these, obtained by hydrogenation of anthracene or *s*-octahydroanthracene (XVI) over nickel catalysts at high temperatures, or by reduction with hydriodic acid and phosphorus, has m. p. 89—90° (figures varying between 88° and 93° have been given) (Lucas, *Ber.*, 1888, **21**, 2510; Godchot, *Compt. rend.*, 1907, **141**, 1028; Ipatiew, Jakowlew, and Rakitin, *Ber.*, 1908, **41**, 996; Fries and Schilling, *Ber.*, 1932, **65**, 1494). The other has m. p. 61° (Fries and Schilling, *loc. cit.*; Kagehira, *Bull. Chem. Soc. Japan*, 1931, **6**, 241; Brown, Durand, and Marvel, *J. Amer. Chem. Soc.*, 1936, **58**, 1594), and is formed by hydrogenation at the ordinary temperature over Adams's catalyst. However, Kagehira's product was isolated from a mixture formed by hydrogenation under pressure with nickel at 200°. The formation of this isomeride under such conditions is anomalous, but it is significant that Kagehira's hydrogenation of naphthalene under the same conditions gave a mixture of decalins which contained 90% of the *cis*-isomeride. The perhydroanthracene obtained by Prokopetz and Khadzhinov (*Khim. Tverdogo Topliva*, 1935, **6**, 347), using a molybdenum sulphide catalyst, was apparently a liquid mixture of isomerides. Hitherto, no attempt has been made to determine the configurations of the solid perhydroanthracenes, although du Feu, McQuillin, and Robinson (J., 1937, 53) have described a keto-dodecahydroanthracene (XVII), the configuration of which is partly known from its method of synthesis.

If we assume the absence of isomerism based on different multiplanar forms of the *cyclo*hexane ring (this assumption seems justified by a very large body of evidence), then there are five possible optically inactive forms of perhydroanthracene. In two of these (XI and XII) the rings are locked, in pairs, by *cis*-valency bonds; in two others (XIII and XIV) there is *trans*-locking of the rings; and in the fifth (XV), one ring fusion takes place by *cis*-valencies and the other by *trans*-valencies. We have prepared the two known perhydroanthracenes and also a third stereoisomeride, and have studied their inter-relationships and their physical constants.

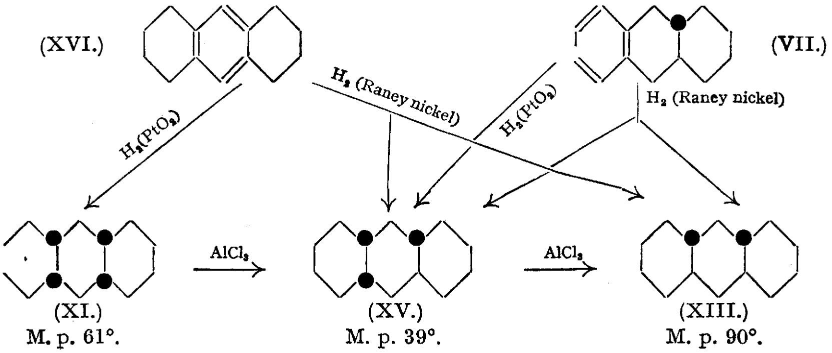
Hydrogenation over platinum catalysts in acetic acid solution usually leads almost exclusively to *cis*-compounds, and in accordance with the considerations advanced by Linstead, Doering, Davis, Levine, and

Whetstone (*J. Amer. Chem. Soc.*, 1942, **64**, 1985) we suggest that the perhydroanthracene, m. p. 61°, is formed by addition of all the hydrogen atoms to the same side of the plane of the molecule of *s*-octahydroanthracene, and has the completely *cis*-configuration (formula XI). A space model of this configuration shows a flat molecule in which all the carbon atoms lie in two parallel planes, which are close to one another. The model shows three strainless "boat" forms of the *cyclo*hexane ring, fused as in (XI*a*). The isomeride, of m. p. 90°, formed by high-temperature hydrogenation and also by the action of aluminium chloride on tetralin, *as*-octahydroanthracene and *as*-octahydrophenanthrene, is undoubtedly one in which there are *trans*-linkages of the rings, and from considerations of molecular symmetry we suggest that the configuration is that represented by (XIII), although (XIV) is not excluded. Models show that (XIII), but not (XIV), corresponds with a flat molecule, with three strainless "chair" forms of the *cyclo*hexane ring, as in (XIII*a*).

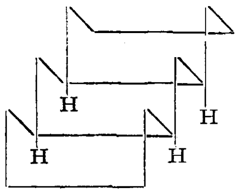
Hydrogenation of *trans*-*as*-octahydroanthracene (VII) with platinum in acetic acid gave the new ***perhydroanthracene***, m. p. 39°, and on Linstead's theory of one-sided addition of hydrogen this must have the configuration (XV). Fries and Schilling (*loc. cit.*) obtained the perhydride, m. p. 93°, by hydrogenation of anthracene in *cyclo*hexane solution with a nickel catalyst at 240°. They also claimed a 90% yield of the same product in the rapid hydrogenation of anthracene without a solvent at 90—110°. Using Raney nickel, we isolated only a 25% yield of this perhydride, m. p. 89—90°, when *s*-octahydroanthracene (XVI) was hydrogenated in *cyclo*hexane solution at 200°. From the more soluble products we also isolated, in 20% yield, the new perhydroanthracene (XV). Raney nickel is a very active catalyst, and it may well be that much of the hydrogenation took place at lower temperatures than that finally attained. Such conditions would favour *cis*-addition of hydrogen. The formation of these same two perhydrides by hydrogenation of *trans*-*as*-octahydroanthracene (VII) with Raney nickel demonstrates at least one *trans*-locking of rings in each of them. Waterman and his collaborators (*Rec. Trav. chim.*, 1934, **53**, 821; 1939, **58**, 83) have obtained evidence that *cis* ⟶ *trans* changes can be brought about in fully hydrogenated naphthalene and anthracene by prolonged heating under pressure with nickel and hydrogen at 260—300°, but it is very unlikely that such changes would occur under the milder conditions used in our hydrogenation experiments with Raney nickel.

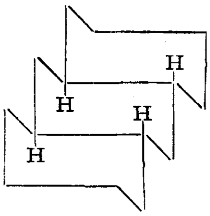
When the perhydroanthracene (XI), m. p. 61°, was heated with aluminium chloride at 100° for 7 hours, it was transformed into a mobile liquid which had not crystallised after several months. If, however, the reaction was carried out at room temperature in hexane solution, there was obtained a solid mixture from which the perhydride (XV) was isolated. The latter compound was further isomerised by aluminium chloride in hexane solution, and there was isolated, in small yield, the perhydride of m. p. 90° (XIII).

These relationships are illustrated by the following scheme:



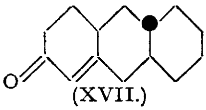
(XI*a*.)



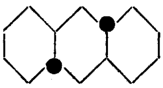


(XIII*a*.)

(XII.)



(XVII.)



(XIV.)

The following table of physical constants of the three perhydroanthracenes gives values which are in harmony with the proposed configurations. The compound with a complete *cis*-configuration (XI) has the highest b. p., density and refractive index, but the smallest molecular refraction; the compound which is mostly *trans* (XIII or XIV) has the lowest b. p., density and refractive index, and the largest molecular refraction.

	B. p. at 743·5 mm.	$n_D^{100°}$.‡	$d_{4°}^{100°}$.	$[R_L]_D$.
Perhydroanthracene, m. p. 62°	282—283°	1·4810	0·9021	60·64
* ,, m. p. 32°	274—275	1·4700	0·8788	61·02
† ,, m. p. 90°	272—273	1·4637	0·8647	61·30

* The purified specimen, m. p. 39—40°, was not available in sufficient quantity for physical measurements, so the values given for this isomeride are approximate.

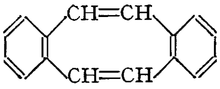
† Waterman, Leendertse, and Cranedonk (*Rec. Trav. chim.*, 1939, **58**, 83) give $n_D^{95°}$ 1·4640 and $d_{4°}^{95°}$ 0·8729 for the perhydride, m. p. 88—89°.

‡ For determining the refractive indices at 100° we used a spectrometer and a hollow brass prism with two glass windows cemented in position. The prism was inserted in an electrically heated steel cylinder, in the side of which holes were drilled at the appropriate angles to permit the passage of the light (from a sodium lamp). After the molten substance had been introduced, the apparatus was heated to 105°, and the readings of the angle of minimum deviation (for λ = 5893 A.) were taken at this and intermediate temperatures as it cooled to 95°. The prism angle was next measured, and the refractive index calculated for each temperature. Its value at 100° was then obtained graphically.

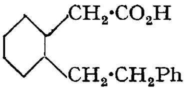
Dehydrogenation experiments also gave results which are consistent with the configurations suggested for the perhydroanthracenes melting at 61° and 90°. The latter (*trans-trans*) isomeride was completely resistant to selenium dehydrogenation under conditions which led to the formation of anthracene in the case of the former (*cis-cis*) isomeride.

Concurrently with the above studies, which are being continued, preliminary experiments have been carried out in connexion with two other projects :

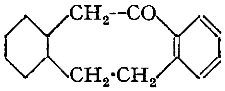
(i) Interest in *cyclo*octatetraene has been revived by the suggestion of Hurd and Drake (*J. Amer. Chem. Soc.*, **1939**, **61**, **1943**) that the hydrocarbon formerly believed to be this was styrene, and several attempts to prepare the true *cyclo*octatetraene or one of its derivatives have been recorded. Tetrabenz*cyclo*octatetraene has been described recently (Rapson, Shuttleworth, and van Niekerk, J., 1943, 326). As a stage in a possible synthesis of a dibenz*cyclo*octatetraene (XVIII) we have condensed 2-β-phenylethyl*cyclo*hexanone with ethyl bromoacetate and zinc. Dehydration of the resulting hydroxy-ester, followed by hydrogenation and hydrolysis, gave 2-β-phenylethyl*cyclo*hexylacetic acid (XIX) (characterised as its p-*phenylphenacyl* ester). Attempts to cyclise the crude acid gave the desired ketone (XX) in very unsatisfactory yield, and also a *lactone* (XXI) which was evidently formed by isomerisation of the unsaturated acid which had resisted hydrogenation.



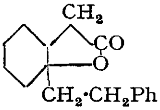
(XVIII.)



(XIX.)

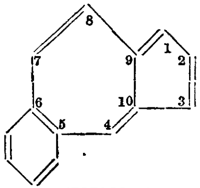


(XX.)

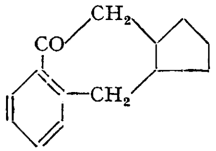


(XXI.)

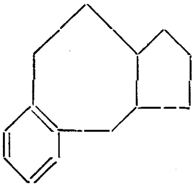
(ii) Azulenes, containing a closed system of 5 conjugated double bonds in the *bicyclo*[0 : 3 : 5]decane ring system, are often readily obtained by dehydrogenation of less highly unsaturated compounds, and a detailed study of their chemical behaviour would be of interest. 2-Benzyl*cyclo*pentylacetic acid was converted, through its chloride, into the *ketone* (XXIII), from which it was hoped to obtain 5 : 6-benzazulene (XXII). This could not be accomplished. When the *carbinol* corresponding to (XXIII) was heated with selenium, it was largely converted into resin, probably by polymerisation of its dehydration product. The saturated *hydrocarbon* (XXIV) was surprisingly resistant to dehydrogenation with selenium or palladium-black, although in one experiment with palladium the development of a feeble reddish-violet colour in the product suggested the formation of a small amount of the azulene.



(XXII.)*



(XXIII.)



(XXIV.)

* The azulene numbering is that used by Susz, St. Pfau, and Plattner (*Helv. Chim. Acta*, 1937, **20**, 469).

EXPERIMENTAL.

(M. p.'s are corrected.)

Action of Aluminium Chloride on Crude as-*Octahydrophenanthrene*.—The material used was the mixture of saturated hydrocarbons obtained by cyclisation of 1-β-phenylethyl-Δ^1-*cyclo*hexene in carbon disulphide solution with aluminium chloride at room temperature (Cook and Hewett, J., 1933, 1098). A series of experiments was carried out on the isomerisation of this material by aluminium chloride, without a solvent. The yield of *trans-as*-octahydrophenanthrene was variable, being influenced apparently by the quality of the aluminium chloride and the extent of stirring as well as by the temperature. In all cases, after oxidation and distillation, the ketonic fraction readily crystallised. This had never been observed in the many oxidations previously carried out on material which had not been submitted to the action of aluminium chloride in the absence of solvent. The following are accounts of four of the experiments :

(*a*) A mixture of crude *as*-octahydrophenanthrene (27 g.) and aluminium chloride (9 g.) was heated at 50—70°, for 15 hours, without stirring. The product, after cooling, was poured on ice and hydrochloric acid. When decomposition of the black viscous mass was complete, the mixture was distilled in steam, and the steam-volatile oil was extracted with ether. The oil (16·5 g.) recovered from the extract was dissolved in purified acetic acid (160 c.c.) and treated slowly with a solution of chromic acid (18·3 g.) in 80% acetic acid (36 c.c.). After being kept at room temperature for 6 days, the green solution was poured into water (1·5 l.), extracted with ether, and the extract washed with sodium carbonate solution, dried, and distilled at 0·2 mm. The first fraction, b. p. 110°, was mostly hydrocarbon; the higher fraction (5·7 g.), b. p. 110—140°, slowly solidified. Crystallisation from alcohol gave *trans*-9-keto-*as*-octahydrophenanthrene (II), m. p. 95—96°, which formed an oxime, m. p. 176—177° (Cook, Hewett, and Lawrence, *loc. cit.*). The m. p. of the oxime was depressed to 147—156° by admixture with the oxime, m. p. 187°, of undetermined constitution.

(*b*) The crude *as*-octahydrophenanthrene (10 g.) was kept at room temperature for 26 hours with aluminium chloride (3·4 g.). During the first 7 hours and the last 4 hours the mixture was stirred. The product was worked up as described under (*a*) and gave, after oxidation, 1·5 g. of the *trans*-ketone (II).

(*c*) A mixture of crude *as*-octahydrophenanthrene (75 g.) and aluminium chloride (25 g.) was stirred at 60—70° for 14 hours. Much more extensive change took place than in experiment (*a*). The steam-volatile oil subsequently obtained had an odour of tetralin (see *d*, below); the less volatile portions solidified partly in the receiver. This material, triturated with a little ether, gave a solid which, after crystallisation from benzene, had m. p. 201° and was identical with the hydrocarbon obtained as described under (*d*). The total steam-volatile product amounted to only 13·5 g., and this gave very little crystalline ketone.

(*d*) A mixture of crude *as*-octahydrophenanthrene (25 g.) and aluminium chloride (8 g.) was heated at 125—130° for 24 hours. The cooled mass was decomposed with dilute hydrochloric acid, with addition of a little carbon disulphide. The product was then distilled in steam. The last portions of the steam distillate passed over very slowly and partly solidified. A solution of this fraction in hot alcohol deposited a white solid (0·25 g.), which crystallised from benzene in colourless leaflets, m. p. 203—204° (Found: C, 87·3, 87·4; H, 12·75, 12·7. $C_{19}H_{24}$ requires C, 87·4; H, 12·6%). This *hydrocarbon* (1 part) was recovered unchanged after heating in an evacuated sealed tube with palladium-black (0·5 part) at 300° for 4½ hours or with selenium (2·5 parts) at 310—325° for 24 hours. The alcoholic liquors from which this compound had been isolated were combined with the remainder of the steam-volatile products, and the whole was distilled at 15 mm. The first fraction (3 g.), b. p. to 120°, was redistilled at atmospheric pressure; it boiled mostly at 205—210°, had a strong odour of tetralin, and was dehydrogenated to naphthalene by refluxing with sulphur. The second fraction (1·5 g.), b. p. 120—150°/15 mm., and the third fraction (3 g.), b. p. 150—170°/15 mm., both crystallised in part, and the solid was isolated by cooling solutions of the distillates in hot alcohol. Both fractions gave perhydroanthracene, in colourless leaflets, m. p. 89—90° (from methyl alcohol) (Found: C, 87·35; H, 12·65. Calc. for $C_{14}H_{24}$: C, 87·4; H, 12·6%). The m. p. was not depressed by the perhydroanthracene, m. p. 89—90°, obtained by hydrogenation of *s*-octahydroanthracene. This perhydride was recovered unchanged after attempted dehydrogenation with palladium-black and selenium, under the conditions described above for the hydrocarbon of m. p. 204°. Further quantities of the latter hydrocarbon were obtained from the residue in the flask from the vacuum distillation, and also (0·3 g.) from a distillation at 1 mm. of the portion of the reaction product which did not distil in steam. This hydrocarbon, m. p. 204°, sublimed at 120°/0·1 mm.

Dehydrogenation of Dodecahydro-1 : 2-*benzanthracene* (V).—A mixture of the hydrocarbon (100 mg.), m. p. 71°, and selenium (200 mg.) was heated at 320—340° for 24 hours in an evacuated sealed tube. An alcoholic extract of the product gave, with picric acid, orange needles, m. p. 155°, consisting of the picrate of 5 : 6 : 7 : 8-tetrahydro-1 : 2-benzanthracene (Cook and Hewett, J., 1934, 375). This was the main product.

trans-as-*Octahydroanthracene and its Derivatives*.—*trans*-Hexahydroanthrone (VI) was obtained by addition of *trans*-2-benzylhexahydrobenzoic acid (108 g.) to concentrated sulphuric acid (500 c.c.). The solid dissolved rapidly, and the clear solution was poured into ice-water. The precipitate was collected and crystallised from alcohol, giving *trans*-hexahydroanthrone (70 g.), m. p. 109—110° (Cook, Hewett, and Lawrence, J., 1936, 79). Nitration of this ketone (1 part) by addition of potassium nitrate (1 mol.) to a well-cooled solution of the ketone in concentrated sulphuric acid (5 parts) gave a *nitro-ketone*, which crystallised from alcohol in colourless leaflets, m. p. 130·5—131·5° (Found: C, 68·6; H, 6·0. $C_{14}H_{15}O_3N$ requires C, 68·5; H, 5·7%).* By hydrogenation in acetone solution over palladium-black this nitro-ketone was reduced to the corresponding *amino-ketone*, which formed colourless needles (from benzene), m. p. 165—166° (Found: C, 78·2; H, 8·1. $C_{14}H_{17}ON$ requires C, 78·0; H, 8·0%).

For reduction to the hydrocarbon, *trans*-hexahydroanthrone (VI) (40 g.) was suspended in concentrated hydrochloric acid (140 c.c.), water (60 c.c.), and toluene (80 c.c.), and the whole boiled under reflux for 36 hours with amalgamated zinc (80 g.). The resulting mixture was distilled in steam. After removal of the toluene the trans-as-*octahydroanthracene* (VII) distilled slowly in steam. It crystallised from alcohol in colourless prisms (30 g.), m. p. 63—64° (Found: C, 90·5; H, 9·5. $C_{14}H_{18}$ requires C, 90·3; H, 9·7%). The residue non-volatile in steam was a white solid which crystallised from benzene in colourless needles, m. p. 245—250°. This was presumably a *hexadecahydro*-9 : 9′-*dianthryl* (Found: C, 91·2; H, 9·1. $C_{28}H_{34}$ requires C, 90·75; H, 9·25%).

9-*Hydroxy*-trans-as-*octahydroanthracene* (IX).—A solution of *trans*-hexahydroanthrone (10 g.) in acetic acid (250 c.c.) was shaken with hydrogen and Adams's platinum oxide catalyst (0·3 g.). The absorption of hydrogen was rapid, and after 50 minutes corresponded with addition of 1 molecule. Hydrogenation was, however, continued for a further hour, by which time about 30% more hydrogen had been absorbed. After filtration from catalyst the solution was freed from solvent by evaporation on the water-bath, under reduced pressure. The residual liquid was dissolved in light petroleum, and the solution strongly cooled. The crystals which separated (5·5 g.) consisted of 9-*hydroxy*-trans-as-*octahydroanthracene* (IX), which crystallised from methyl alcohol in colourless leaflets, m. p. 136° (Found: C, 82·8; H, 8·9. $C_{14}H_{18}O$ requires C, 83·1; H, 9·0%). The material from the petroleum liquors was distilled at 11 mm., and gave a distillate which largely crystallised. The crystals were drained on a tile and recrystallised from methyl alcohol, pure *trans-as*-octahydroanthracene being obtained.

Hexahydroanthracene (X).—A mixture of the aforesaid carbinol (4·5 g.) and powdered potassium hydrogen sulphate (9 g.) was heated in a flask immersed in an oil-bath kept at 160—170°, the pressure being maintained at 11 mm. The solid distillate, recrystallised from methyl alcohol, formed colourless crystals (3·3 g.), m. p. 63—66° (Found: C, 91·0; H, 9·2. $C_{14}H_{16}$ requires C, 91·2; H, 8·8%). The m. p. of this *hexahydroanthracene* was not depressed by admixture with octahydroanthracene, but, unlike the latter, the hexahydro-compound gave an orange colour with alcoholic picric acid. In an attempt to prepare *cis-as*-octahydroanthracene this hexahydroanthracene (3 g.) was hydrogenated in acetic acid solution with platinum-black. The theoretical amount of hydrogen was absorbed in 3 hours, but a homogeneous product could not be isolated.

Sulphonation of trans-as-*Octahydroanthracene*.—The hydrocarbon (VII) (3 g.) was added to concentrated sulphuric acid (10 c.c.), and the mixture was slowly heated to 70°, with continuous stirring. After the hydrocarbon had melted solution was complete in 5 minutes; the yellow solution was then cooled and treated with water (20 c.c.). After cooling to 0° the solid which had separated was collected, dissolved in warm water, and the solution made slightly alkaline with

---

* The preparation of this and the two following compounds was carried out by Dr. R. W. Lapsley.

sodium hydroxide. The *sodium sulphonate* (4·5 g.) crystallised on cooling as glistening white plates which crumbled to a powder when dried. It was recrystallised from water and dried in a vacuum desiccator over phosphoric oxide (Found: Na, 7·2. $C_{14}H_{17}O_3SNa,2H_2O$ requires Na, 7·1%).

*ar-Hydroxy-*trans-as-*octahydroanthracene* was obtained by addition of this sodium sulphonate (4 g.) to stirred fused potassium hydroxide (20 g.) at 230—240°. The temperature was then raised to 280° and maintained there for 1½ hours. The cooled mass was extracted with water, the extract acidified, and the phenol extracted with ether. The crude phenol, obtained from the ethereal solution, was distilled from an air-bath at 120°/0·1 mm. and then crystallised from hexane (yield, 2 g.). This *phenol*, which was mostly insoluble in alkali, formed small colourless crystals, m. p. 104° (Found: C, 83·25; H, 8·85. $C_{14}H_{18}O$ requires C, 83·1; H, 9·0%).

For oxidation, the phenol (1 g.) was added to a solution of potassium permanganate (6·3 g.) in water (125 c.c.) and 6N-potassium hydroxide (10 c.c.). The suspension was kept, with occasional shaking, for 2 days, by which time the whole of the permanganate had been reduced. The filtered solution was acidified and extracted with ether. The extract was dried with sodium sulphate and evaporated. The residual gum partly crystallised on standing, and the crystals were drained and recrystallised twice from water. The resulting colourless crystals had m. p. 166—167°, not depressed by a specimen of *trans-cyclo*hexane-1 : 2-diacetic acid (VIII) prepared by oxidation of *trans*-β-decalol, m. p. 75° (Hückel, *Annalen*, 1925, **441**, 20). There was a considerable depression of the m. p. on admixture with a specimen of *cis-cyclo*hexane-1 : 2-diacetic acid prepared by oxidation of *cis*-β-decalone.

Action of Aluminium Chloride on trans-as-*Octahydroanthracene*.—A mixture of the hydrocarbon (10 g.) and powdered anhydrous aluminium chloride (3·5 g.) was heated in an oil-bath at 130° for 30 hours. The product, which had a strong odour of tetralin, was treated with dilute hydrochloric acid, a little carbon disulphide being added to facilitate decomposition of the aluminium chloride complex. The black tarry mass was distilled in steam. The latter portions of the steam distillate solidified, and crystallisation from alcohol and then benzene gave the hydrocarbon, m. p. 202°, which had been obtained by similar treatment of crude *as*-octahydrophenanthrene. This was the only pure product isolated.

Hydrogenation of trans-as-*Octahydroanthracene* (VII).—(a) *With platinum*. A solution of the hydrocarbon (5 g.) in acetic acid (250 c.c.) was shaken with hydrogen and platinum oxide (0·25 g.) until absorption ceased. The uptake of hydrogen corresponded with addition of 3 molecules of hydrogen. Most of the acetic acid was distilled, the last traces being removed from an ethereal solution of the residue by washing with alkali. The oil which remained after evaporation of the ether crystallised when cooled, and was recrystallised from methyl alcohol, giving 3 g. of material, m. p. 32—35°. After several recrystallisations from methyl alcohol this *perhydroanthracene* (XV) formed colourless needles, m. p. 39—40° (Found: C, 87·5; H, 12·55. $C_{14}H_{24}$ requires C, 87·4; H, 12·6%).

(b) *With Raney nickel*. A solution of *trans-as*-octahydroanthracene (5 g.) in *cyclo*hexane (35 c.c.) was heated in an autoclave, with stirring, with Raney nickel (2 g.) and hydrogen. The temperature was raised to 200° (during 2½ hours) and maintained at this point for 1½ hours. The maximum pressure was 150 atms. The product was freed from solvent and recrystallised from methyl alcohol, giving 2 g. of perhydroanthracene, m. p. 89—90°, not depressed by a specimen similarly prepared from *s*-octahydroanthracene (below). The most soluble fractions from the mother-liquors crystallised with difficulty; recrystallisation from methyl alcohol gave small plates (0·2 g.), m. p. 32—34°, alone or mixed with the product obtained as described under (a).

Hydrogenation of s-*Octahydroanthracene* (XVI).—(*a*) Hydrogenation with platinum oxide in acetic acid, as described by Fries and Schilling (*Ber.*, 1932, **65**, 1499), gave in satisfactory yield large elongated plates, m. p. 61·5—63°, in conformity with the results of the German workers. This perhydroanthracene is regarded as having the completely *cis*-configuration (XI).

(*b*) A stirred mixture of *s*-octahydroanthracene (100 g.), *cyclo*hexane (250 c.c.), and Raney nickel (25 g.) was heated slowly to 200° with hydrogen under pressure. The pressure attained was 155 atms. The temperature was maintained at 200° until the pressure was constant at 115 atms. The product obtained by removal of solvent from the filtered solution was recrystallised from methyl alcohol, and gave the sparingly soluble perhydroanthracene (25 g.), m. p. 89—90°, for which we suggest the configuration (XIII). The liquors were freed from solvent and gave an oil, which slowly crystallised in part at room temperature. The crystals were collected and drained, and recrystallised from methyl alcohol. The crystals thus obtained (20 g.) had m. p. 32—34°, not depressed by the perhydroanthracene formed by hydrogenation of *trans-as*-octahydroanthracene over a platinum catalyst.

Isomerisation of Perhydroanthracenes with Aluminium Chloride.—(*a*) Powdered anhydrous aluminium chloride (2 g.) was added to a solution of perhydroanthracene (2 g.), m. p. 61°, in hexane (5 c.c.), and the suspension was kept at room temperature for 7 days, with occasional shaking. The filtered solution was washed and freed from solvent, and the residue crystallised from methyl alcohol. The colourless plates (1·3 g.) had m. p. 33—35°, not appreciably changed by further crystallisation. The m. p. was not depressed by admixture with the perhydroanthracene formed by hydrogenation of *trans-as*-octahydroanthracene with Adams's catalyst. Crystallisation from methyl alcohol of a mixture of equal parts of the isomerides melting at 61° and 90° gave material of m. p. 40—60°.

(*b*) Anhydrous aluminium chloride (2 g.) was added to a solution of perhydroanthracene (2 g.), m. p. 34°, in hexane (5 c.c.), and the suspension kept at room temperature for 4 days with occasional shaking. Crystallisation of the product from methyl alcohol gave, in addition to unchanged material, a less soluble fraction (0·5 g.), m. p. 40—65°, which, after further crystallisation, had m. p. 89—90° (0·1 g.), and was identical with the perhydroanthracene of like m. p.

Action of Selenium on Perhydroanthracenes.—(*a*) A mixture of perhydroanthracene (1 g.), m. p. 89°, and selenium (1 g.) was heated in a metal bath at 305—315° for 30 hours. The hydrocarbon boiled briskly. The product was extracted with ether and recrystallised from methyl alcohol. It had m. p. 88—90°, and was completely unchanged perhydroanthracene.

(*b*) A similar experiment was carried out simultaneously, in the same bath, with a mixture of perhydroanthracene (0·5 g.), m. p. 61°, and selenium (0·5 g.). The crude brown product, crystallised from methyl alcohol, had m. p. 170—205°, and after sublimation in a vacuum, followed by crystallisation from benzene–alcohol, the m. p. was 214—216°, and was not depressed by pure anthracene.

Ethyl 2-β-*Phenylethyl*cyclo*hexanol*-1-*acetate*.—A solution of 2-β-phenylethyl*cyclo*hexanone (Kon, J., 1933, 1083) (14·2 g.) in dry benzene (30 c.c.) was added dropwise to a suspension of zinc turnings (5·7 g.) and ethyl bromoacetate (14 g.) in dry benzene (30 c.c.). The vigorous reaction which set in on warming was completed by boiling for 2 hours. The ice-cooled product was treated with dilute sulphuric acid (20 c.c. of concentrated acid were diluted). The benzene solution was then washed with dilute sulphuric acid, sodium carbonate solution, and water, dried over sodium sulphate, and distilled. The resulting colourless liquid (12 g.) had b. p. 168—171°/1 mm.

This hydroxy-ester was dehydrated by heating for an hour with potassium hydrogen sulphate (1·5 parts), and the unsaturated ester was hydrogenated in acetic acid solution, over palladium-black. Hydrolysis of the hydrogenated ester with boiling alcoholic alkali gave the crude 2-β-phenylethyl*cyclo*hexylacetic acid (XIX) as a viscous oil, b. p. 190—200°/1 mm. Its p-*phenylphenacyl* ester crystallised from alcohol in rosettes of colourless needles, m. p. 75—77° (Found: C, 81·5; H, 7·1. $C_{30}H_{32}O_3$ requires C, 81·8; H, 7·3%).

Cyclisation of 2-β-*Phenylethyl*cyclo*hexylacetic Acid* (XIX).—(*a*) Phosphorus pentachloride (3·5 g.) was added to a solution of the acid (3·5 g.) in dry benzene (30 c.c.) and the suspension was kept at room temperature with occasional shaking until a clear solution was formed (2 hours). The benzene and phosphorus oxychloride were removed by heating on the water-bath under diminished pressure, and a solution of the residual acid chloride in nitrobenzene (15 c.c.) was added to an ice-cooled solution of aluminium chloride (4·2 g.) in nitrobenzene (25 c.c.). After being kept at room temperature overnight, the reaction mixture was poured on ice and hydrochloric acid, and freed from nitrobenzene by steam distillation. The residue was extracted with ether, washed with sodium carbonate solution, and the dried solution distilled at 150°/0·2—0·4 mm. A small amount of yellow viscous oil was obtained. This, dissolved in alcohol and treated with Brady's reagent (10 c.c.), gave the 2 : 4-*dinitrophenylhydrazone* of the tricyclic ketone (XX), which crystallised from alcohol in clusters of long orange-red needles, m. p. 242—244° (Found : C, 65·2; H, 5·55; N, 13·8. $C_{22}H_{24}O_4N_4$ requires C, 64·7; H, 5·9; N, 13·7%).

(*b*) A solution of the acid (XIX) (4 g.) in benzene (50 c.c.) was stirred with phosphorus pentachloride (4·2 g.), and to the clear solution of the resulting acid chloride was slowly added a solution of anhydrous stannic chloride (2·35 g.) in benzene (5 c.c.). Stirring was continued for 18 hours, and the product was treated with ice and hydrochloric acid. The benzene solution was washed with sodium carbonate solution, dried, and distilled. The crystalline distillate (1·4 g.), b. p. 160—170°/0·4 mm., was recrystallised from alcohol and had m. p. 67—68° (Found : C, 78·9; H, 8·5. $C_{16}H_{20}O_2$ requires C, 78·7; H, 8·2%). This substance had the properties of a *lactone* and is doubtless represented by the structure (XXI), the formation of which may be attributed to isomerisation of unsaturated acid which had resisted hydrogenation to (XIX).

A number of other cyclisation experiments were carried out, but the desired ketone (XX) was not obtained in satisfactory yield.

2-*Benzyl*cyclo*pentylacetic Acid*.—This acid was prepared from ethyl *cyclo*pentanone-2-carboxylate (Cornubert and Borrel, *Bull. Soc. chim.*, 1930, **47**, 301) by the 8-stage procedure of Duff and Ingold (J., 1934, 87). Hydrolysis of the intermediate ethyl α-benzyladipate was more satisfactorily effected by boiling alcoholic potash than by the acid hydrolysis method of Duff and Ingold.

1 : 2 : 3 : 4 : 7 : 8 : 9 : 10-*Octahydro*-5 : 6-*benz*-7-*azulone* (XXIII).—Phosphorus pentachloride (9·5 g.) was added to a stirred solution of 2-benzyl*cyclo*pentylacetic acid (9·5 g.) in benzene (110 c.c.). When a clear solution was obtained, the benzene and phosphorus oxychloride were removed by heating on the water-bath under reduced pressure. The residual chloride, dissolved in carbon disulphide (90 c.c.), was treated with powdered anhydrous aluminium chloride (6·6 g.). When the vigorous evolution of hydrogen chloride had subsided, the whole was heated on the water-bath for 8 hours. The aluminium chloride complex was decomposed with ice and hydrochloric acid, and the product was distilled in steam. After the carbon disulphide had been driven off, a white solid slowly collected in the steam distillate; more was extracted with ether from the aqueous distillate. This *octahydrobenzazulone* (XXIII) (6·4 g.) crystallised from methyl alcohol in colourless prisms, m. p. 56° (Found : C, 84·0; H, 7·9. $C_{14}H_{16}O$ requires C, 84·0; H, 8·0%). Its 2 : 4-*dinitrophenylhydrazone* formed small orange prisms (from ethyl acetate), m. p. 169—170° (Found : N, 14·7. $C_{20}H_{20}O_4N_4$ requires N, 14·7%).

1 : 2 : 3 : 4 : 7 : 8 : 9 : 10-*Octahydro*-5 : 6-*benz*-7-*azulol* was obtained in theoretical yield by reduction of the ketone (XXIII) with aluminium *iso*propoxide (compare Lund, *Ber.*, 1937, **70**, 1520). It crystallised from ligroin in a fine matte of colourless needles, m. p. 128—129° (Found : C, 83·2; H, 8·8. $C_{14}H_{18}O$ requires C, 83·2; H, 8·9%). An attempt to obtain benzazulene by heating this carbinol with selenium at 300° led to polymerisation, the product being mostly non-volatile in a high vacuum. When the carbinol (3·4 g.) was heated at 160° for an hour with potassium hydrogen sulphate (7 g.), it gave 1 : 2 : 3 : 4 : 9 : 10-hexahydrobenzazulene (2·7 g.), b. p. 130—135°/1 mm. The distillate solidified to a mass of crystals, m. p. 29—35°. Hydrogenation of this unsaturated hydrocarbon to *octahydrobenzazulene* (XXIV) was effected by palladium-black in alcoholic solution. The resulting oil crystallised in the refrigerator, giving fine needles, which after recrystallisation from alcohol had m. p. 29—30° (Found : C, 90·2; H, 9·7. $C_{14}H_{18}$ requires C, 90·3; H, 9·7%).

Attempted Dehydrogenation of 1 : 2 : 3 : 4 : 7 : 8 : 9 : 10-*Octahydrobenzazulene* (XXIV).—(*a*) A mixture of the hydrocarbon (1 g.) and selenium (1·7 g.) was heated in an atmosphere of carbon dioxide for 29 hours. The distilled product was a brownish liquid which gave no addition compound with *s*-trinitrobenzene.

(*b*) A mixture of the hydrocarbon (1 g.) and palladium-black (0·1 g.) was heated in an atmosphere of carbon dioxide, first at 250° for 3 hours and then at 300° for 4 hours. Distillation of the product gave a violet liquid (0·5 c.c.), b. p. 110—120°/1 mm., but the feeble intensity of colour suggested that the amount of azulene present was very small.

(*c*) The hydrocarbon (1 g.) was heated with palladium-black as described under (*b*), except that the evolved gas was collected over 50% potassium hydroxide solution. Only 16 c.c. of gas were collected after 3 hours' heating at 300°, showing the almost complete absence of dehydrogenation. The activity of the catalyst was subsequently demonstrated by the fact that it rapidly liberated the theoretical amount of hydrogen from *s*-octahydroanthracene at 300°

We express our thanks to the Carnegie Trust for the Universities of Scotland, for a grant for the purchase of a hydrogenation autoclave, and to Dr. E. de Barry Barnett for a gift of *s*-octahydroanthracene. We are also indebted to Dr. R. Wright for advice on the determination of densities of fused hydrocarbons.

UNIVERSITY OF GLASGOW. [*Received, January* 14*th*, 1944.]