180. *Fused Carbon Rings. Part XVI. The Stereoisomerism of the Perhydrophenanthrenes: Preliminary Investigations.*

By R. P. Linstead and A. L. Walpole.

The stereochemistry of the perhydrophenanthrenes is outlined and its importance in relationship to that of the sterol group is indicated.

The gross structure of three isomeric forms of 9-ketododecahydrophenanthrene, m. p. 39°, 94°, and 88°, has been proved. The first two of these ketones are identical, apart from the position of the double bond. In one this is in the 8 : 14-, and in the other in the 13 : 14-position. The third unsaturated ketone, m. p. 88°, is probably a *trans*^{13}-Δ^{10}-form.

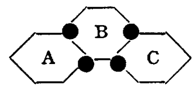
The first two unsaturated ketones both yield the same two fully reduced 9-keto-perhydrophenanthrenes, which are *cis*^{13}- and *trans*^{13}-forms, and otherwise identical in configuration. The third unsaturated ketone gives a distinct *trans*^{13}-9-ketoperhydrophenanthrene.

Various hydrocarbons and alcohols of the group are described, including a solid perhydrophenanthrene. A preliminary discussion is given of the configuration of the various substances.

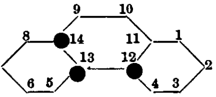
Since the appearance of the papers of Windaus (*Annalen*, 1926, **447**, 233), Bernal (*Nature*, 1932, **129**, 277, 721; *Chem. and Ind.*, 1932, **51**, 466), and Ruzicka (*Helv. Chim. Acta*, 1933, **16**, 216, 327) the importance of the stereochemical configurations of the compounds of the sterol group has been generally recognised. It therefore becomes of considerable interest to investigate the stereochemistry of the fundamental ring structures underlying this group of compounds—how the various stereoisomerides can be made and interconverted, how their properties are affected by their configuration, and what are their relative stabilities. The problem is very complex; even in the relatively simple molecule of aetiocholane there are six asymmetric carbon atoms, situated at the points of fusion of the rings. We have therefore made a preliminary attack on the problem by an examination of the perhydrophenanthrene system, which bridges the gap between the steroids and the decalins.

There are four asymmetric carbon atoms in perhydrophenanthrene. If we neglect any possible complications due to the persistence of labile ring structures and use a classical stereochemical basis, the molecule can be seen to exist in six inactive forms, of which four are racemic and two *meso-*. All will be multiplanar and, on a purely tetrahedal basis, all will be strainless. Actually it is to be anticipated that there will be definite differences of stability, due to the operation of other factors, such as the repulsion of adjacent groups.

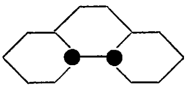
In terms of the convention proposed in 1937 (Linstead, *Chem. and Ind.*, **56**, 510) and adopted by Ruzicka (*Helv. Chim. Acta*, 1938, **21**, 498) they are represented as follows :



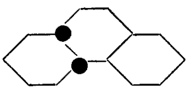
(I.) *cis-syn-cis* (*meso*).



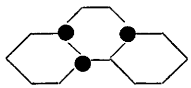
(II.) *cis-syn-trans* (rac.).



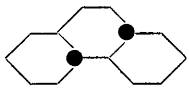
(III.) *trans-syn-trans* (*meso*).



(IV.) *cis-anti-cis* (rac.).



(V.) *cis-anti-trans* (rac.).

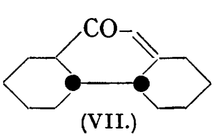


(VI.) *trans-anti-trans* (rac.).

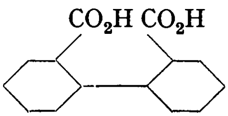
[The hexagons represent fully reduced *cyclo*hexane rings. The black dots indicate hydrogen atoms above the general plane of the molecule. The maximum number of dots is always used, as otherwise the *cis-syn-cis* structure would be unmarked and it would not be clear if a particular configuration were intended. A dot is always placed on C_{13}. As an example of the naming of a complicated structure on this basis, the unsaturated ketone (VII) is completely described as *syn-trans*-9-keto-Δ^{10}-dodecahydrophenanthrene.]

If ring B is opened by oxidation of suitable derivatives of perhydrophenanthrene, perhydrodiphenic acids (VIII) are produced. These are of particular interest in connection with the application of the Blanc rule to the determination of structure in the steroid group. For convenience in reference, our results in the field of the perhydrodiphenic acids are considered separately in the following paper.

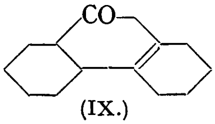
Our first object, therefore, was to prepare stereochemically homogeneous hydrophenanthrene derivatives substituted on carbon 9. One convenient method of approach was provided by the work of Marvel and his collaborators (*J. Amer. Chem. Soc.*, 1936, **58**, 972; 1937, **59**, 2666), who cyclised di-Δ^1-*cyclo*hexenylacetylene with formic acid to two isomeric ketones, $C_{14}H_{20}O$, one a solid and the other a liquid. The liquid isomeride was held to be *trans*-9-ketododecahydrophenanthrene (IX). The most important evidence was that it was reduced by the Clemmensen method to an unsaturated hydrocarbon, which on treatment with selenium yielded a product almost identical in properties with *trans*-*as*-octahydrophenanthrene. No solid derivatives, however, were obtained.



(VII.)



(VIII.)



(IX.)

We have reinvestigated the Marvel cyclisation. The product was separated into two isomeric ketones, both crystalline solids, m. p. 39° and 94°, the latter being identical with Marvel's. On reduction by the Clemmensen method both yielded dodecahydrophenanthrenes. These hydrocarbons on dehydrogenation in the vapour phase over palladised charcoal (Linstead, Millidge, Thomas, and Walpole, J., 1937, 1146) both yielded phenanthrene. This proves the correctness of Marvel's view that the ketones are hydrophenanthrene derivatives.

The positions of the double bonds and of the keto-groups have been found as follows: The lower-melting ketone slowly absorbed one molecular proportion of hydrogen over palladised charcoal. The main product was a crystalline *9-ketoperhydrophenanthrene*, m. p. 51°, which formed an *oxime*, m. p. 164°. This condensed with methylmagnesium iodide to yield a tertiary alcohol, which on dehydration, and subsequent dehydrogenation over palladised charcoal in the vapour phase, gave a product from which 9-methylphenanthrene was isolated as the picrate.

The isomeric unsaturated ketone, m. p. 94°, rapidly absorbed one mol. of hydrogen over palladised charcoal, to yield mainly the same saturated ketone, m. p. 51°. Both the unsaturated ketones, therefore, contain a 9-keto-group.

Both the unsaturated ketones reacted very slowly with iodine chloride in chloroform–

alcohol, which indicated that the double bonds were in the αβ-position (Linstead and May, J., 1927, 2578). The reaction with the ketone of m. p. 94° was faster than that with the isomeride, which showed scarcely any reaction after 48 hours. The αβ-positions of the double bonds were proved by measurements of the ultra-violet absorption spectra. These were kindly carried out by Dr. R. K. Callow of the National Institute for Medical Research. The results are summarised in the following table, which also contains for comparison the values for some ketones both with and without conjugated double bonds.

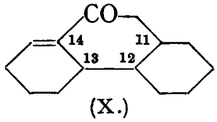
TABLE I.

	Maximum of main band.	
Ketone.	λ A.	log ε.
9-Ketododecahydrophenanthrene, m. p. 39°	2410	4·09
,, ,, 94°	2470	3·95
Mesityl oxide (αβ-double bond)	2350	4·14 [1]
Cholestenone ,, ...	2430	4·30 [2]
Eremophilone ,, ...	2430	3·90 [3]
Cyperone ,, ...	2510	4·28 [3]
Pulegone ,, ...	2450	3·71 [4]
Methylheptenone (no conjugation)	2780	1·72 [3]
Acetone ,, ...	2750	1·23 [3]

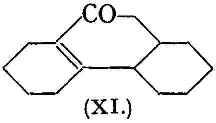
[1] Morton, J., 1926, 719. [2] Heilbron, Morton, and Sexton, J., 1928, 47. [3] Gillam, J., 1936, 676. [4] Lowry, Simpson, and Allsopp, *Proc. Roy. Soc.*, 1937, *A*, **163**, 483.

These results correct the view of Marvel that his liquid ketone (which clearly consisted mainly of the isomeride of m. p. 39°) had the double bond in the βγ-position (IX).

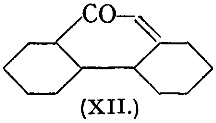
Both unsaturated ketones must have the same configuration of the locking of the rings, in so far as this is already determined, because they give the same saturated ketone. Hence they cannot be stereoisomeric modifications of the same unsaturated ketone, for example, (X), with *cis*- and *trans*-fusion respectively at C_{11}—C_{12}. The isomerism must depend upon the position of the double bond, and, since this is αβ- in both, the ketones must have two of the three structures shown below :



(X.)



(XI.)



(XII.)

A decision on this point was reached by a further study of the hydrogenation products. In each case an identical second saturated ketone was isolated in the form of its oxime, m. p. 186°. The two hydrogenation products were thus similar in all respects. Now, if one of the unsaturated ketones were (XII), the two saturated ketones obtained from it by reduction must have different configurations at C_{11}. On the other hand, the two saturated ketones from (X) would have the same configuration at C_{11}, and the same is true of (XI). Hence the two unsaturated ketones must be (X) and (XI) with the identical configurations at C_{11} and C_{12}. As to which is which, we incline to the view that the isomeride of m. p. 39° is (XI) on the following evidence, which is by no means conclusive : (i) The bridge position for a double bond is stable in hydronaphthalenes, *e.g.*, octalins tend to isomerise into the $\Delta^{9:10}$-form in the presence of acidic reagents (Hückel and Naab, *Annalen*, 1933, **502**, 136; Linstead, Wang, and Williams, J., 1937, 1136). It seems probable that the ketone of m. p. 39°, formed in preponderating amount in an acid medium, will have this stable position of the double bond. (ii) $\Delta^{9:10}$-Octalin is not as easily hydrogenated as its isomerides (Hückel, Danneel, Gercke, and Schwartz, *Annalen*, 1929, **474**, 144). The ketone of m. p. 39° is hydrogenated much more slowly than its isomeride under comparable conditions.

It was hoped to obtain confirmatory evidence from a study of the olefins obtained by Clemmensen reduction. The olefin from a ketone of formula (XI) would (in the absence of secondary reactions) contain a double bond between quaternary carbon atoms and give a blue nitrosochloride of the Thiele type. Experiment showed that the olefins obtained from ***both*** unsaturated ketones gave the same blue ***nitrosochloride***, m. p. 191°. Hence double bond migration must have accompanied the reduction of at least one of the ketones, so that the olefin from each ketone contained some proportion of a bridge—doubly bonded form, either $\Delta^{13:14}$ or $\Delta^{12:13}$. The reaction has therefore no diagnostic value. Durland and Adkins (*J. Amer. Chem. Soc.*, 1938, **60**, 1501) also have observed an apparent easy migration of the double bond in a dodecahydrophenanthrene.

There remains the question of configuration. The saturated ketone, m. p. 51°, was practically unchanged when heated alone, with sodium *tert.*-amyloxide, or with sodamide in benzene. The liquid *isomeride*, regenerated from the oxime, m. p. 186°, when heated at 280° for an hour, was largely converted into the solid of m. p. 51°. Since both ketones are obtained by the reduction of a 9-ketododecahydrophenanthrene with a double bond in the 8 : 14-position (X), they can differ only in the configuration at C_{14}. By analogy with the behaviour of the α-decalones, where the *cis*-form yields the *trans*- on distillation at atmospheric pressure (Hückel) the thermostable saturated ketone, m. p. 51°, is provisionally given the *trans*-arrangement, and the liquid isomeride (oxime, m. p. 186°), the *cis*-. The configuration of the rest of the molecule is the same in the two ketones. Although there are some indications of what this may be, it cannot profitably be discussed on the present rather indefinite evidence. The preferential formation of *trans*-ketone from the $\Delta^{13:14}$-ketone (XI) falls into line with the hydrogenation of $\Delta^{9:10}$-α-octalone to, mainly, the *trans*-α-decalone (Hückel and co-workers, *Annalen*, 1933, **502**, 114, 155).

Another line of attack was provided by the work of Rapson and Robinson (J., 1935, 1285), who obtained a crystalline ketododecahydrophenanthrene, m. p. 89°, and assigned to it the structure (XII) from the method of preparation. The substance is quite distinct from the isomeride, m. p. 94°, of Marvel. The gross structure is conclusively proved by its conversion into an independently synthesised perhydrodiphenic acid (following paper). The ultra-violet absorption spectrum, for which again we are indebted to Dr. R. K. Callow, shows a strong band at 2380 A., log $\varepsilon_{\max.}$ 4·14, corresponding to an αβ-double bond. The unsaturated ketone is rapidly hydrogenated in the presence of palladised charcoal, one mol. of hydrogen being taken up. It reacts very slowly with iodine chloride, but not so slowly as the isomeride of m. p. 39°. The position of the double bond assigned by Rapson and Robinson is supported by these facts, which are consistent with an αβ-double bond not situated between quaternary carbon atoms. The hydrogenation product was a homogeneous 9-ketoperhydrophenanthrene, m. p. 49°, forming an oxime, m. p. 227—228°, these substances being quite distinct from the isomerides already described. Three of the six possible forms of the perhydrophenanthrene ring have therefore been obtained.

TABLE II.

Perhydrophenanthrenes.

Preparation.	B. p./mm.	$d^{t^\circ}_{4^\circ}$.	$n^{t^\circ}_{D}$.	$[R_L]_D$.	*t*.
From ketone, m. p. 51°	140°/18	0·9365	1·4981	60·17	18·5°
,, ,, ,, 49°	141/18·5	0·9302	1·4978	60·54	19·0
Hydrogenation of dodecahydrophenanthrene [1]	86—89/2	0·9447	1·5011	59·93	20
,, of phenanthrene [1]	90—93/2·5	0·9385	1·4994	60·17	20
	93—96/2·5	0·9437	1·5019	60·10	20
,, ,, [2]	135/13	—	1·5003	—	25
By-product in hydrogenation [3]	135/13·14	—	1·5152	—	10·2

$[R_L]_D$, calc. for $C_{14}H_{24}$, 60·25.

[1] Marvel and co-workers, *loc. cit.* [2] Durland and Adkins, *J. Amer. Chem. Soc.*, 1937, **59**, 135; 1938, **60**, 1501. [3] Cook, Hewett, and Robinson, J., 1939, 175.

The new ketone was stable to heat and alkaline reagents. We therefore tentatively assign a *trans*-configuration to the ring-fusion adjacent to the keto-group.*

Perhydrophenanthrenes.—The two readily available and stereochemically homogeneous ketoperhydrophenanthrenes, m. p. 51° and 49°, were reduced by Clemmensen's method to the corresponding perhydrophenanthrenes. These were freed from oxygenated impurities and then had the physical constants shown in Table II. The constants of a number of previous preparations of perhydrophenanthrene are added for comparison.

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* All three perhydro-ketones are stable under the conditions of regeneration from their derivatives.

The products of the direct reduction of phenanthrene are appreciably denser and have higher refractive indices than those made in the present work. This indicates that they contain a higher proportion of *cis*-material. The product of Cook, Hewett, and Robinson, which contains at least one *cis*-fusion, has a noticeably higher refractivity.

The hydrocarbon from the ketone of m. p. 49° solidified in ice to a crystalline solid, m. p. 10°. We take this to be the first perhydrophenanthrene of undoubted stereochemical homogeneity. None of the other hydrocarbons mentioned above was obtained solid. Liebermann and Spiegel (*Ber.*, 1889, **22**, 779) reported the preparation of a perhydrophenanthrene by the reduction of phenanthrene with phosphorus and hydrogen iodide. Their product had b. p. 270—275°, $d_{20^\circ}^{20^\circ}$ 0·933, m. p. —3°, and gave satisfactory analytical figures. This work, however, could not be confirmed by Schmidt and Mezger (*Ber.*, 1907, **40**, 4240) and Ipatiev and co-workers (*Ber.*, 1908, **41**, 1000).

Miscellaneous.—Various attempts were made to bring about isomeric change (stereochemical inversion and/or double bond migration) in all three unsaturated ketones. In all cases, the ketones of m. p. 39° and 88° were recovered unchanged, but that of m. p. 94° yielded high-boiling auto-condensation products.

The reduction of the unsaturated ketones by means of sodium and alcohol was also examined in the hope that additional isomeric forms of the saturated ring system might result. In this way saturated alcohols were formed, but these on oxidation yielded only the known saturated ketones, m. p. 51° and 49°. The fact that saturated alcohols were produced from all three unsaturated ketones provides further support for the αβ-position of the double bonds.

The relationship between these tricyclic substances and the perhydrodiphenic acids is discussed in the following paper.

EXPERIMENTAL.

1. *Unsaturated Ketones.*

In the routine preparation of di-Δ^1-*cyclo*hexenylacetylene from di-1-hydroxy*cyclo*hexylacetylene, the use of 40% sulphuric acid was found preferable to that of potassium hydrogen sulphate (compare Pinkney, Nesty, Wiley, and Marvel, *J. Amer. Chem. Soc.*, 1936, **58**, 972). The average yield was 86%. The acetylene (90 g.) was cyclised with formic acid, following Marvel and co-workers. The crude ketonic product (68 g.), b. p. 148—154°/5 mm., was refractionated, and the fractions of b. p. 149—153°/5 mm. frozen in ice and salt. The solid yielded, on fractional crystallisation from light petroleum, 9-ketododecahydrophenanthrene (X or XI), m. p. 93—94° (3·8 g.) (Found : C, 82·2; H, 9·9. Calc. for $C_{14}H_{20}O$: C, 82·3; H, 9·9%), together with 21 g. of a second solid, melting indefinitely at about 28°. Repeated crystallisation of this raised the m. p. to 33—34°, but the process was wasteful. A better separation is through the oxime. The ketone of m. p. 93° readily yielded an *oxime* (2 hours at 80°), which formed long needles from methanol, m. p. 157—158° (Found : C, 76·4; H, 9·6. $C_{14}H_{21}ON$ requires C, 76·65; H, 9·7%). The ketone of m. p. 33—34° yielded an *oxime* in almost quantitative yield, which formed brilliant massive polyhedra from alcohol, m. p. 183—184° (Found : C, 76·6; H, 9·6%). These and the other oximes described in this paper were prepared from hydroxylamine hydrochloride, sodium acetate, and the ketone in aqueous alcohol, following Hückel and Sachs (*Annalen*, 1932, **498**, 176), and not in alkaline solution. The residual liquid ketone from the original fraction of b. p. 149—153°/5 mm. yielded the same oxime, m. p. and mixed m. p. 183°, and this was also given by the solid of m. p. *ca.* 29°.

The following semicarbazones were obtained, but they were less convenient than the oximes; from the 93° ketone, irregular polyhedra from methanol, m. p. 232°; from the 33° ketone and from the liquid, crystals similar in appearance, m. p. 227—228°. A mixture of the two semicarbazones melted at 216°.

The oxime of m. p. 183° (11·1 g.) was boiled under reflux for 6 hours with 100 c.c. of 5% sulphuric acid (mechanical stirring). The ketone formed was not appreciably volatile in steam. It was extracted with purified light petroleum, and the extract washed with concentrated hydrochloric acid, aqueous sodium carbonate, and water. The solution, dried and freed from solvent, yielded 9-*ketododecahydrophenanthrene* (X or XI) in 70% yield, b. p. 146—147°/5 mm. (Found : C, 82·3; H, 9·8. $C_{14}H_{20}O$ requires C, 82·3; H, 9·9%). It solidified completely on cooling, melted at 38—39°, and re-formed the oxime, m. p. 184°. A mixture with the original solid ketone, m. p. 34°, melted at 36—37°. No isomeric change had therefore accompanied the regeneration from the oxime. The hydrochloric acid washings yielded some unchanged oxime.

In a later preparation, the distilled product (72 g.) after removal of the ketone of m. p. 94°, yielded 60 g. of recrystallised oxime (m. p. 183—184°), which gave 42 g. of regenerated ketone, m. p. 38—39°.

A number of preparations of the ketone of Rapson and Robinson (*loc. cit.*) were performed, the best conditions being as follows : Sodio*cyclo*hexanone, from 23 g. of sodamide and 58 g. of *cyclo*hexanone in anhydrous ether (1·5 l.), was cooled in ice and treated with 72 g. of acetyl*cyclo*hexene in 250 c.c. of ether (stirring). The mixture was stirred at room temperature for 6 hours and for 2 hours on the steam-bath, and was decomposed with ice and ammonium chloride. The product, isolated in the usual way, yielded a main fraction (65 g.), b. p. 158—162°/3 mm., which gave 38 g. of the pure crystalline 9-ketododecahydrophenanthrene (XII), m. p. 87—88°. The oxime melted at 202°.

The addition to the three ketones of iodine chloride (Hübl reagent) was examined under the conditions of Linstead and May (*loc. cit.*) with the following results : 39° Ketone : in 2·5 hours, 0%; in 46 hours, 1·9%. 94° Ketone : in 2·5 hours, 3%; in 46 hours, 74·5%. 88° Ketone : in 8 hours, 10·5%; in 50 hours, 56%.

Attempted Isomerisations.—9-Ketododecahydrophenanthrene, m. p. 39°, was recovered as essentially unchanged solid (m. p. and mixed m. p.) after being (i) heated under nitrogen for 2 hours at 200°, (ii) heated with 10% of piperidine under nitrogen for 2 hours at 100°, and at 200°, (iii) kept at room temperature for 48 hours with N-sodium *tert.*-amyloxide (20 c.c. to 1 g. of ketone), (iv) heated for 2 hours at 100° with N-sodium *tert.*-amyloxide.

Under the same conditions, the isomeric ketone, m. p. 88°, was also recovered unchanged. In the experiments with sodium amyloxide a trace of a liquid appeared to be formed.

The third isomeride, m. p. 94°, both when heated alone and when treated with sodium amyloxide, yielded a viscous gum.

2. *Saturated Ketones.*

(*a*) A solution of pure regenerated 9-ketododecahydrophenanthrene (17 g.), m. p. 39°, in alcohol (250 c.c.) was shaken with 0·5 g. of palladised charcoal under hydrogen. Absorption ceased after 48 hours, 2050 c.c. (*N.T.P.*) having been absorbed (calc. for one double bond, 1870 c.c.). The product from the reduction of 32 g. of unsaturated ketone yielded 5 g. of low-boiling material and 26 g. of a fraction, b. p. 127—130°/2 mm., which partly solidified in ice. The solid (m. p. 46—48°) was collected on an ice-cold sintered glass filter and repeatedly crystallised from light petroleum to constant m. p. (11·4 g.). 9-*Ketoperhydrophenanthrene* (form 1) formed flattened rhombs, m. p. 51° (Found : C, 81·4; H, 10·6. $C_{14}H_{22}O$ requires C, 81·5; H, 10·8%). It yielded a semicarbazone in the cold, which formed small plates from methanol, m. p. 187°. The *oxime*, prepared in boiling alcoholic solution, crystallised from much methanol in flattened rhombs, m. p. 163—164° (Found : C, 76·2; H, 10·2. $C_{14}H_{23}ON$ requires C, 76·0; H, 10·5%).

The material (total weight, 13·1 g.), recovered from the various filtrates obtained in the purification of the solid ketone, was converted into semicarbazone, m. p. 170—180°, after washing with water and light petroleum. Tedious fractional crystallisation from methanol yielded a product (2·3 g.), m. p. 182—183°, depressed by the isomeric semicarbazone, m. p. 187°. The semicarbazone of m. p. 182—183° was converted by means of oxalic acid into 9-ketoperhydrophenanthrene (1·4 g.) (form 2), b. p. 128°/2 mm., which failed to solidify. Its *oxime*, m. p. 184—185°, formed flattened needles from methanol (Found : C, 76·1; H, 10·2. $C_{14}H_{23}ON$ requires C, 76·0; H, 10·5%), and depressed the m. p.'s of the oximes of the parent unsaturated ketone and of the saturated ketone, m. p. 51°.

In another series of experiments, the original reduction was performed in acetic acid solution with Adams's catalyst. There was no break in the absorption of hydrogen corresponding to 1 mol. After 5 days, 38 g. of unsaturated ketone (m. p. 39°) had absorbed 6 l. of hydrogen. Fractionation of the product and freezing of the various fractions yielded 8·6 g. of the solid saturated ketone, m. p. 51°. The liquid residues were converted into oxime (10·6 g.), which was fractionally crystallised from methanol. This process, although tedious and wasteful, led to the separation of three oximes : (i) that of the solid saturated ketone, m. p. 162—163° (3·5 g.), (ii) that of the liquid saturated ketone, m. p. 182—183° (1·8 g.), and (iii) by hand picking, a little of the oxime of the original unsaturated ketone, m. p. and mixed m. p. 180°. The appearance of unsaturated material in the product after the absorption of far more than the theoretical quantity of hydrogen for the saturation of the double bond shows that some further reduction, presumably of the carbonyl group, was occurring.

9-Ketoperhydrophenanthrene (form 1), m. p. 51°, was unchanged (m. p. and mixed m. p.) when it was heated at 250° in nitrogen for 1 hour. It was also practically unchanged by treatment with sodamide in boiling benzene (6 hours).

9-Ketoperhydrophenanthrene (form 2) was regenerated from the oxime, m. p. 184—185°, by refluxing with an excess of 5% sulphuric acid, and isolated by distillation in steam. It was unchanged in b. p. and failed to solidify in a freezing mixture. The ketone (1 g.) was heated in nitrogen at 280° for 1 hour; the product solidified when cooled in ice and partly liquefied at room temperature. The solid melted at 46—48° alone, and at 47—48° in admixture with 9-ketoperhydrophenanthrene (form 1), m. p. 51°. The liquid portion was converted into oxime, m. p. 145°. After crystallisation from methanol it melted at 159—161°, and at 160—162° in admixture with the oxime (m. p. 163—164°) of form 1. Form 2 is therefore very largely converted into its stable isomeride (form 1) under these conditions.

(*b*) 9·0 G. of 9-ketododecahydrophenanthrene, m. p. 94°, in 200 c.c. of alcohol were shaken with 0·5 g. of palladised charcoal (30% Pd) in hydrogen. Reduction was rapid, and ceased after 2 hours, 1040 c.c. (*N.T.P.*) having been absorbed (calc. for one double bond, 990 c.c.). The main fraction of the product boiled at 130—132°/4 mm. (7·6 g.) and solidified in ice. After 2 hours at −20° the liquid portion was filtered through a cooled filter. The solid melted at 47—48° in the crude state and at 51° after crystallisation from light petroleum. The identity with 9-ketoperhydrophenanthrene (form 1) was confirmed by mixed m. p. determinations of the ketones and the oximes. Yield of pure ketone, 4·3 g.

The various liquid portions of the reduction product were converted into oxime, which was triturated with petroleum and crystallised from methanol. After a series of fractional crystallisations there were isolated the oximes of the two forms of 9-ketoperhydrophenanthrene already mentioned, *viz.*, that of form 1, m. p. 161—162°, mixed m. p. 162—163° (0·3 g.), and that of form 2, m. p. 181—182°, mixed m. p. 182—183° (0·5 g.).

Catalytic hydrogenation of the unsaturated ketone, m. p. 94°, in acetic acid solution also yielded form 1 of the saturated ketone as the main product.

(*c*) 9-Ketododecahydrophenanthrene (3 g.), m. p. 88°, was rapidly hydrogenated in alcoholic solution (30 c.c.) over palladised charcoal (0·2 g.), 350 c.c. of hydrogen being absorbed in 1 hour (calc., 300 c.c.). The product (3 g.), when freed from solvent and catalyst, solidified, and on crystallisation from light petroleum gave 2·5 g. of 9-*ketoperhydrophenanthrene* (form 3) in plates, m. p. 47—48° (Found: C, 81·3; H, 10·45. $C_{14}H_{22}O$ requires C, 81·5; H, 10·8%). A mixture with the isomeric form 1 liquefied at room temperature. The oxime formed in the cold and was almost insoluble in methanol. It crystallised from ethyl alcohol in silky needles, m. p. 227—228°.

In a subsequent large-scale reduction, the semi-solid ketone, after the removal of pure form 3, was converted into oxime, which was fractionally crystallised. Only the oxime of form 3 could be isolated. Reduction of the unsaturated ketone, m. p. 88°, in acetic acid solution gave the same result.

The unsaturated ketone (form 3), m. p. 47—48°, was unaffected by treatment with sodamide in boiling benzene (m. p. and mixed m. p.).

Reduction of the Unsaturated Ketones with Sodium and Alcohol.—2 G. of sodium were added to a boiling solution of 9-ketododecahydrophenanthrene (3 g.), m. p. 39°, in absolute alcohol. When the sodium had dissolved, the solution was cooled and acidified, and the alcohol removed at 50°. The product, isolated by means of ether, boiled at 138—140°/2 mm. and set to a cheesy solid which could not be crystallised and appeared to be a mixture of saturated alcohol and saturated ketone (Found: C, 81·0; H, 11·0. Calc. for $C_{14}H_{24}O$: C, 80·7; H, 11·6%. Calc. for $C_{14}H_{22}O$: C, 81·5; H, 10·8%). When it was oxidised with chromic acid in acetic acid, it yielded a product which partly solidified after distillation. The solid was identified as 9-ketoperhydrophenanthrene (form 1) by m. p. and mixed m. p.

The preparation of a saturated alcohol corresponding to form 1 is described in the following paper.

The isomeric unsaturated ketone, m. p. 94°, gave a similar mixture on reduction with sodium and alcohol. Oxidation of the product with chromic acid yielded form 1 of the saturated ketone.

The third unsaturated ketone (3 g.), m. p. 88°, in 30 c.c. of boiling absolute alcohol was treated with 2 g. of sodium, followed by a further 10 c.c. of alcohol and 2 g. of sodium. The product had b. p. 135°/1·3 mm. (2·9 g.) and solidified on cooling. Crystallisation from light petroleum yielded 1·9 g. of 9-*hydroxyperhydrophenanthrene* in flattened prisms, m. p. 119°

(Found: C, 80·6; H, 11·5. $C_{14}H_{24}O$ requires C, 80·7; H, 11·6%). Oxidation of 1 g. of this with 0·4 g. of chromic acid yielded 0·8 g. of form 3 of 9-ketoperhydrophenanthrene, almost pure.

3. *Hydrocarbons.*

(*a*) 18 G. of 9-ketododecahydrophenanthrene, m. p. 38°, 120 g. of amalgamated zinc, and 50 c.c. of 5N-hydrochloric acid were boiled together for 48 hours, concentrated hydrochloric acid being added from time to time. The reduction product was isolated by means of ether after distillation in steam. It was dried, freed from solvent, heated with potassium for an hour at 210°, and distilled, 14·5 g. of *dodecahydrophenanthrene* being obtained, b. p. 116°/9 mm., having the physical properties given in Table III (Found: C, 88·3; H, 11·6. $C_{14}H_{22}$ requires C, 88·4; H, 11·6%). In acetic acid solution over Adams's catalyst it absorbed an amount of hydrogen corresponding to one double bond. 1 C.c. of the hydrocarbon was treated with 1 c.c. of freshly prepared amyl nitrite and 1 c.c. of dry ether. The mixture was treated at 0° with 1 c.c. of 10N-hydrochloric acid. Pale blue crystals separated in the ethereal layer after a time, m. p. (crude) 188—189°. The *nitrosochloride* separated from ether in pale blue, flattened needles, m. p. 191° (Found: Cl, 13·4. $C_{14}H_{22}ONCl$ requires Cl, 13·9%). No white nitrosochloride could be isolated.

The isomeric unsaturated ketone, m. p. 94°, was reduced in exactly the same way. The *dodecahydrophenanthrene* obtained (8·2 g. from 10 g. of ketone) boiled at 121—122°/12 mm. (Found: C, 88·1; H, 11·7%) and yielded the blue nitrosochloride, m. p. 191°, mentioned above. In spite of the formation of this common derivative the physical properties of the two unsaturated hydrocarbons show that they are different, or at least contain considerable proportions of different isomerides (see Table III).

TABLE III.

Physical Properties of Dodecahydrophenanthrenes, $C_{14}H_{22}\ |\overset{=}{1}$. $[R_L]_D$ *calc.,* 59·78.

Origin.	B. p./mm.	$n_D^{t°}$.	$d_{4°}^{t°}$.	*t*.	$[R_L]_D$.	Exaltn.
Reduction of ketone, m. p. 39° [1]	116°/9	1·5116	0·9641	19·5°	59·16	−0·62
,, ,, ,, 94° [1]	121/12	1·5106	0·9553	19·0	59·60	−0·18
,, of liquid ketone [2]	81/1·5	1·5102	0·9674	20·0	58·83	−0·95 (?)
,, of phenanthrene (P + HI) [3] ...	268/737	1·5119	0·964	20·0	59·19	−0·59
,, ,, (H_2 and Raney nickel) [4]	141/13	1·512	—	25·0	—	—

[1] Present work. [2] Marvel and co-workers, *loc. cit.* [3] Schmidt and Mezger, *loc. cit.* [4] Durland and Adkins, *J. Amer. Chem. Soc.*, 1938, **60**, 1501.

Dehydrogenations.—The unsaturated hydrocarbon obtained from the ketone of m. p. 39° was boiled for 24 hours with one-tenth of its weight of palladised charcoal. The product was considerably changed in physical properties (b. p. 95—98°/1·5 mm., $n_D^{16°}$ 1·5452, $d_{4°}^{16°}$ 0·9872). It failed to yield a picrate and the refractive index differs from those of the two forms of *as*-octahydrophenanthrene (Cook, Hewett, and Robinson, *loc. cit.*). 1·25 G. of the original hydrocarbon were passed over palladised charcoal (catalyst 1 of Linstead, Millidge, Thomas, and Walpole, *loc. cit.*) at 330° during 8 hours; the gas evolution (680 c.c.) corresponded to 75% dehydrogenation. When the tube was swept out with hydrogen at 330°, only a small quantity (0·2 g.) of a liquid collected in the receiver, but at 345—350° a solid sublimed from the catalyst. The solid (0·5 g.), m. p. 94—95°, was identified as phenanthrene by sublimation (m. p. and mixed m. p. 98°) and the formation of the picrate (m. p. and mixed m. p. 143°). A further quantity of phenanthrene picrate was obtained from the liquid dehydrogenation product.

The same procedure was applied to dodecahydrophenanthrene obtained from the ketone of m. p. 94°. 800 Mg. of this yielded 280 c.c. (50%) of gas when passed over palladium at 340° for 6 hours. The product was swept out at 340—350°, and yielded 200 mg. of solid phenanthrene, together with a liquid residue from which phenanthrene picrate was prepared.

(*b*) 9-Ketoperhydrophenanthrene (form 1) (2·8 g.), m. p. 51°, was boiled with 20 g. of amalgamated zinc, 20 c.c. of glacial acetic acid, and 10 c.c. of hydrochloric acid for 24 hours, a slow stream of hydrogen chloride being passed in. The product was extracted with purified light petroleum, washed with concentrated sulphuric acid until the extract was no longer coloured, then with alkali and with water. It was dried over calcium chloride, heated with potassium for an hour at 210°, and distilled. 2·73 G. boiled at 140—140·5°/18 mm. and had $n_D^{23·3°}$ 1·4974,

$d_{4°}^{23\cdot3°}$ 0·9340; $[R_L]_D$ 60·25. The product was still slightly unsaturated towards bromine in chloroform. It was therefore warmed on the steam-bath for 2 hours with 5 c.c. of concentrated sulphuric acid containing a little oleum. The *perhydrophenanthrene* was isolated as before, unchanged in b. p. An arbitrary middle fraction (1·5 g.) had $n_D^{18\cdot5°}$ 1·4981, $d_{4°}^{18\cdot5°}$ 0·9365, $[R_L]_D$ 60·17 (calc. for $C_{14}H_{24}$, 60·25) (Found : C, 87·5; H, 12·3. $C_{14}H_{24}$ requires C, 87·5; H, 12·5%). It did not solidify in solid carbon dioxide–ether.

9-Ketoperhydrophenanthrene (form 3), m. p. 48°, was similarly reduced, and the product purified in the same way. Before being heated with sulphuric acid, it had b. p. 140—140·5°/18 mm., $n_D^{23\cdot3°}$ 1·4966, $d_{4°}^{23\cdot3°}$ 0·9277, $[R_L]_D$ 60·58; and after such treatment $n_D^{19°}$ 1·4978, $d_{4°}^{19°}$ 0·9302, $[R_L]_D$ 60·54 (Found : C, 87·5; H, 12·4%). This form of *perhydrophenanthrene* solidified in a freezing mixture to a crystalline mass, m. p. 10°.

(*c*) A solution of 4 g. of 9-ketoperhydrophenanthrene (form 1), m. p. 51°, in 20 c.c. of ether was added with stirring to a Grignard reagent prepared from 4·3 g. of methyl iodide and 0·75 g. of magnesium. The mixture was refluxed overnight and worked up in the usual manner. On distillation under 2 mm. spontaneous dehydration occurred at a bath temperature of *ca.* 170°; the distillation was therefore repeated a number of times with a crystal of iodine under 40 mm. The product was finally heated with potassium (1 hour at 210°) and distilled over fresh potassium. The yield of 9-*methyldodecahydrophenanthrene*, b. p. 140°/15·5 mm., was 0·9 g. (Found : C, 88·4; H, 11·4. $C_{15}H_{24}$ requires C, 88·1; H, 11·9%). The hydrocarbon (1·23 g.) was dehydrogenated over palladised charcoal in the vapour phase at 330°. Yield of hydrogen, 320 c.c. (40%), in two passages. The product swept out at 360° did not solidify in a freezing mixture. The aromatic portion, separated by means of picric acid, melted indefinitely at 75° and depressed the m. p. of phenanthrene. It gave the picrate of 9-methylphenanthrene, orange needles, m. p. 148—149°, depressed to 143—144° by phenanthrene picrate (Found : C, 59·95; H, 3·95. Calc. for methylphenanthrene picrate : C, 59·8; H, 3·6%. Calc. for phenanthrene picrate : C, 58·95; H, 3·2%). Windaus, Jensen, and Schramme (*Ber.*, 1924, **57**, 1877) report that 9-methylphenanthrene melts at 91° and gives an orange picrate, m. p. 152—153°.

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