134. *Fused Carbon Rings. Part XVIII. Further Investigations of Model Substances of the Sexual Hormone Type.*

By V. C. E. Burnop and R. P. Linstead.

New synthetic routes to 8-methyl-1-hydrindanone have been investigated. The oxidation of 9-methyloctalin, obtained by dehydrating 9-methyl-2-decalol, has been re-examined. Its reaction with permanganate corresponds entirely with the oxidation of a $\Delta^{2:3}$-double bond. Its ozonolysis leads to products corresponding with both $\Delta^{2:3}$- and $\Delta^{1:2}$-double bonds. Its oxidation by lead tetra-acetate, selenium dioxide and oxygen in the presence of iron phthalocyanine gives products corresponding with a $\Delta^{1:2}$-double bond. These results are discussed. 8-Methyl-2-hydrindanone has been converted into 8-methyl-1-hydrindanone by a method paralleling in its last stage the conversion of oestriol into oestrone.

The oxidation of *trans*-$\Delta^{2:3}$-octalin by lead tetra-acetate has been examined.

8-Methyl-1-hydrindanone (I) is of interest as a model substance of the female hormone type. The earlier methods for its synthesis were recently improved by Elliott and Linstead (J., 1938, 660). When, however, this procedure was applied to the actual synthesis of sexual hormones, various difficulties were encountered, an account of which is given in the following paper. We therefore made an examination of alternative methods for the synthesis of the model structure.

By the " butenyl " method of Linstead, Millidge, and Walpole (J., 1937, 1140) dicyclic compounds containing an angular methyl group can easily be made in two stages from monocyclic ketones. This method, however, does not at first sight appear satisfactory for the synthesis of the sexual hormone model. It leads to β-alcohols; for example, 9-methyl-2-decalol (II) is obtained from 2-methyl-1-Δ^{γ}-butenyl*cyclo*hexanol (III). (II) on oxidation gives 1-methyl*cyclo*hexane-1 : 2-diacetic acid (IV) and thence 8-methyl-2-hydrindanone (V) with the carbonyl group in the wrong position. Moreover the 9-methyloctalin formed by the dehydration of (II) yields the same acid (IV) on oxidation and therefore contains the Δ^2-isomeride (VI).

It was decided : (1) To examine more carefully whether the Δ^1-isomeride (VII), which would be a source of the desired 8-methyl-1-hydrindanone, was not present in the olefin. (2) To examine the possibility of oxidising the Δ^2-olefin with reagents which are known to attack methylene groups next to a double bond. This would lead to either 9-methyl-1-octalone or -4-octalone. The former could be degraded to 8-methyl-1-hydrindanone; the latter would have many interesting synthetic possibilities. (3) To examine the possibility of converting 8-methyl-2-hydrindanone into the 1-isomeride.

The starting substance in this work, 9-methyl-2-decalol,* has so far only been prepared from 2-methyl-1-butenyl*cyclo*hexanol (III). To unite this method with earlier work we have now prepared the alcohol from the isomeric 1-methyl-2-Δ^{γ}-butenyl*cyclo*hexanol (VIII)

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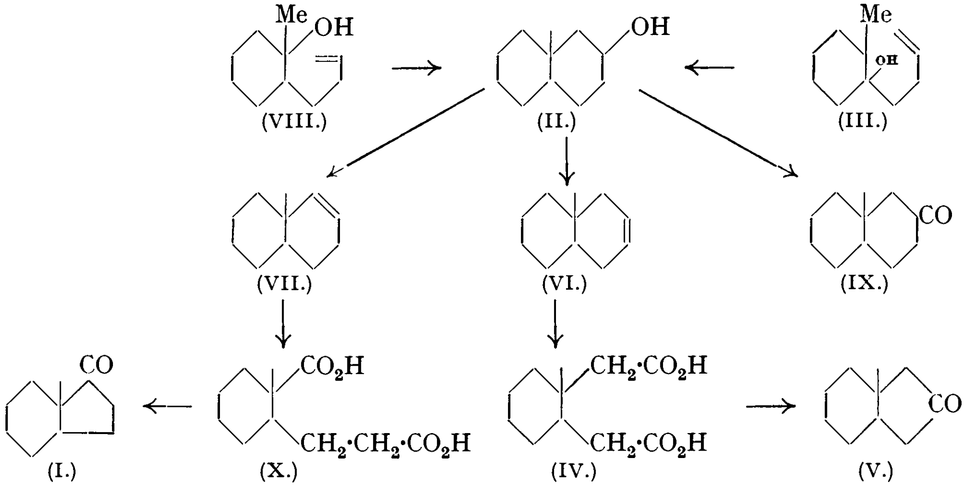
* All the substances described in the paper belong to the same stereochemical series, believed to be *cis* (Linstead, Millidge, and Walpole, *loc. cit.*).

of Hibbit and Linstead (J., 1936, 470) by the action of sulphuric acid and a mixture of acetic acid and anhydride. The product was a mixture of epimers which on oxidation with chromic acid gave 9-methyl-2-decalone (IX) (Linstead, Millidge, and Walpole, *loc. cit.*).



It was next confirmed that the olefin obtained by dehydrating 9-methyl-2-decalol yielded the diacetic acid (IV) on oxidation with alkaline permanganate. No other acid could be isolated from the product (apart from oxalic acid), and when the crude oxidation product was heated with baryta it gave a ketone which yielded the almost pure semicarbazone of 8-methyl-2-hydrindanone. A method is described below by which the 1-ketone can be isolated from a mixture of the isomerides (I and V), but when this was applied in the present case, the derivative of the 1-ketone could not be detected. As far as permanganate oxidation is concerned, the olefin behaves as if it is entirely the Δ^2-isomeride, and the yield of diacetic acid indicates that it contains at least 50% of this form.

Ozonolysis, however, showed the presence of some of the Δ^1-isomeride. The methyl-octalin was ozonised both in chloroform at 0° and in ethyl acetate at − 75°, and the ozonide hydrolysed and further oxidised with alkaline hydrogen peroxide. The acidic product was proved to contain both the diacetic acid (IV) and the carboxy-propionic acid (X) by two methods. Esterification with boiling methyl-alcoholic sulphuric acid yielded an easily separable mixture of the methyl ester of the diacetic acid and the methyl hydrogen ester of its isomeride (X). The former was identified by hydrolysis to the acid, m. p. 190°, the latter by hydrolysis, followed by pyrolysis to 8-methyl-1-hydrindanone.* In the second method the mixture of acids was pyrolysed in the presence of baryta. The ketonic product was treated in the cold with semicarbazide acetate until no more derivative separated. The solution was then heated, a second semicarbazone separating. The derivative which was formed at room temperature readily yielded the semicarbazone of the 2-ketone (V) on crystallisation, whereas that which was formed on heating gave the semicarbazone of the 1-ketone (I). The difference in reactivity of the two ketones, the one with a free, the other with a hindered carbonyl group, had been observed by Linstead, Millidge, and Walpole (*loc. cit.*). The yields obtained were 40% of the diacetic acid and 12% of the

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* At the time this work was done it was believed that cis-1-*methyl*cyclo*hexane*-1-*carboxylic*-2-β-*propionic acid* was an uncrystallisable gum (cf. Robinson and Walker, J., 1937, 61, 1160; Kon, Linstead, and Simons, *ibid.*, p. 814). Dr. G. H. Elliott has recently obtained this acid as a crystalline solid. The gummy acid, made by the oxidation of 9-methyl-1-decalol (Elliott and Linstead, *loc. cit.*), solidified after standing in contact with water. Crystallisation proved difficult. It was carried out first from acetone–dilute acetic acid and finally from aqueous acetone. The acid forms large colourless rhombs, m. p. 108—109° (Found: C, 61·7, 61·8; H, 8·4, 8·2. $C_{11}H_{18}O_4$ requires C, 61·7; H, 8·45%). On pyrolysis the crystalline acid yields 8-methyl-1-hydrindanone (semicarbazone, m. p. 223°) identical with that previously obtained from the crude acid.—R. P. L.

carboxy-propionic acid. The overall yields of ketones were 16% of the 2-ketone and 8% of the 1-ketone. Very similar results were obtained from the ozonisation of 9-methyloctalin prepared as a by-product in the cyclisation (III) ⟶ (II).

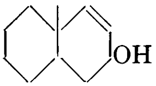
As the yield of 1-ketone left much to be desired, we next examined the oxidation of the mixture of olefins by lead tetra-acetate, selenium dioxide, and by oxygen in the presence of iron phthalocyanine (A. H. Cook, J., 1938, 1774).

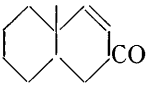
9-Methyloctalin was oxidised readily by lead tetra-acetate to the acetate of an unsaturated alcohol. Unexpectedly, this proved to be mainly *9-methyl-*Δ^1*-3-octalol* (XI). It was catalytically hydrogenated to *9-methyl-3-decalol*, which on oxidation with chromic acid yielded 9-methyl-3-decalone, m. p. 47°, identical with the ketone of duFeu, McQuillin, and Robinson (J., 1937, 53). No definite isomerides could be isolated, although a little liquid ketone was obtained. This yielded 1-methyl*cyclo*hexane-1 : 2-diacetic acid on oxidation with nitric acid, and hence contained the 3 (or perhaps 2)-ketone. As the parent olefin was known to be a mixture, some oxidations were carried out in stages, the first-formed acetate being separated and the recovered hydrocarbon reoxidised. The acetates so obtained, however, were almost identical in properties.

When the olefin was treated with oxygen at 70° in the presence of a little ferrous phthalocyanine, it was oxidised to an unsaturated ketone. This was hydrogenated to 9-methyl-3-decalone, but its *semicarbazone* differed from that of the 9-methyl-$\Delta^{4:10}$-octalone of duFeu, McQuillin, and Robinson (*loc. cit.*). The new ketone therefore has the double bond in the Δ^1-position (XII). Oxidation of the olefin with selenium dioxide in acetic anhydride gave an unsaturated acetate, which was converted, through the corresponding alcohol, into the same ketone (XII).

The remarkable fact emerges that *all these oxidations involve an attack at* C_3, the double bond appearing in the Δ^1-position, in spite of the fact that the olefin contains a large amount of the Δ^2-isomeride.

(XI.)





(XII.)

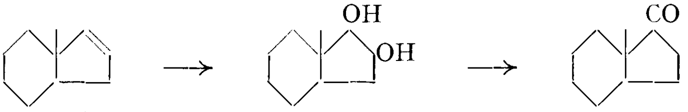
There are two possible explanations : (i) The Δ^2-olefin does not react with these reagents under the conditions of our experiments, because the α-carbon atoms are shielded in comparison with the β-carbon atom of the Δ^1-isomeride. (ii) The reagent attacks C_3 in both the Δ^1- and the Δ^2-olefin, and the reaction with the Δ^2-isomeride is accompanied or followed by a migration of the double bond.

The yields obtained in the various oxidations are tabulated below :

Reagent.	$KMnO_4$.	Ozone.	Lead tetra-acetate.	SeO_2.	O_2.
% Yield of product derived from Δ^1-olefin	0	12	46	17	17
,, ,, ,, ,, Δ^2-olefin	50	40	0	0	0

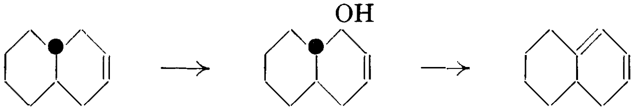
It will be seen that there is no actual overlapping of the yields. Hence the first explanation given above is able to account for the facts. Moreover, if the Δ^2-olefin were attacked at an unsaturated carbon atom, it is not easy to see why products corresponding to oxidation at C_2 should not be isolated. Some of the known facts concerning oxidations by selenium dioxide are also against the second explanation. Although attack at an unsaturated atom, followed by migration, could account for many of the oxidations reported in the literature, it could not account for all. We are therefore disposed to take the facts at their face value and to conclude that the olefin is a mixture of approximately equal portions of the two forms, and that the oxidations, both those which do and those which do not lead to fission of the ring, always proceed most readily with attack in the β-position. Whatever may be the mechanism of the observed oxidation, the absence of attack by lead tetra-acetate on the α-carbons of Δ^2-*cis*-9-methyloctalin remains puzzling. It is shown later in this paper that *trans*-Δ^2-octalin readily yields *trans*-Δ^2-1-octalol (XV) and thence, by reduction and oxidation, *trans*-α-decalone by an analogous series of changes. The configuration of the ring system may have some influence.

Conversion of the 2- *into the* 1-*Ketone.*—*cis*-8-Methyl-2-hydrindanone was reduced to the corresponding *alcohol* by the Verley–Ponndorf method. This was dehydrated to 8-methylhexahydroindene, which had the double bond in the Δ^1-position (XIII), from the fact that it yielded 1-methyl*cyclo*hexane-1-carboxylic-2-acetic acid on oxidation. Oxidation of the olefin with hydrogen peroxide in acetic acid gave the diacetate of 1 : 2-*dihydroxy*-8-*methylhydrindane* (XIV), the free diol being obtained on hydrolysis. When the diol was heated with potassium hydrogen sulphate at 200°, it yielded 8-methyl-1-hydrindanone. The last stage in this series of reactions is analogous to the conversion of oestriol into oestrone by Butenandt and Hildebrandt (*Z. physiol. Chem.*, 1931, **199**, 243).



(XIII.) (XIV.)

We have also examined the action of lead tetra-acetate on *trans*-Δ^2-octalin. The reaction followed a course parallel to that observed by Criegee in the case of *cyclo*hexene (*Annalen*, 1930, **481**, 263). The main product was trans-Δ^2-1-*octalyl acetate* and the high-boiling fraction contained the diacetate of trans-*decalin*-2 : 3-*diol*. Hydrolysis of the octalyl acetate yielded trans-Δ^2-1-*octalol* (XV). The position of the alcohol group in this was proved by its reduction to *trans*-α-decalol, which was oxidised to *trans*-α-decalone, identified as the semicarbazone. *trans*-Δ^2-1-Octalol was dehydrated by means of potassium hydrogen sulphate to a *hexahydronaphthalene,* presumably with the double bonds 2 : 3- and 1 : 9- (XVI). This was catalytically hydrogenated to a mixture of *cis*- and *trans*-decalins, and formed an addition compound with maleic anhydride. When it was warmed to 160° with palladised charcoal, it underwent disproportionation to tetralin and a mixture of the two stereoisomeric decalins (cf. Linstead, Millidge, Thomas, and Walpole, J., 1937, 1146).



(XV.) (XVI.)

The diene (XVI) appears to be much less readily disproportioned than is *cyclo*hexadiene (Böeseken, *Rec. Trav. chim.*, 1918, **37**, 255).

EXPERIMENTAL.

35 G. of 1-methyl-2-Δ^γ-butenyl*cyclo*hexanol (VIII), b. p. 108—110°/19 mm. (Hibbit and Linstead, *loc. cit.*), were treated slowly with 160 c.c. of a reagent containing 10 vols. of glacial acetic acid, 1·5 vols. of acetic anhydride, and 1 vol. of concentrated sulphuric acid. (The alcohol imparts a purple colour to the reagent, even when only a trace is present.) After 4 days at room temperature the dark brown liquid was poured into water, extracted with ether, and freed from acids by washing with alkali. The residue from the removal of the ether was hydrolysed with 50 c.c. of 20% methyl-alcoholic potash, and the methyldecalol isolated by means of ether. Distillation yielded 3·5 g. of olefin, b. p. 82—88°/19 mm., followed by 18 g. (51%) of 9-methyl-2-decalol as an epimeric mixture, b. p. 135—138°/19 mm. Unlike the methyldecalol made from the isomeric alcohol (III), this failed to solidify. It was accordingly oxidised by means of chromic acid in acetic acid, to *cis*-9-methyl-3-decalone. Yield, 11 g.; b. p. 130—132°/20 mm. The semicarbazone melted at 209° after crystallisation from methanol, and the m. p. was not depressed by admixture with authentic material (m. p. 211°; Linstead, Millidge, and Walpole, *loc. cit.*).

The original preparative method (Linstead, Millidge, and Walpole, *loc. cit.*) is more convenient than that given above because 2-methyl-1-Δ^γ-butenyl*cyclo*hexanol (III) is more easily made than its isomeride. A number of experiments were made with the object of improving the yield of solid dicyclic alcohol. The results are in the table.

Preparation of *cis*-9-Methyl-2-decalol from 2-Methyl-1-Δ^{γ}-butenyl*cyclo*hexanol (III).

Composition of reagent.			Vols. of re-agent to 1 vol. of (III).	Temp.	Time (days).	% Yield of	
Vols. HOAc.	Vols. Ac_2O.	Vols. H_2SO_4.				alcohol.	hydro-carbon.
10	1·5	1	5	Room	3	53	17
10	1	1	5	,,	3	50—55	19—20
10	1	1	5	0°	3	50	18
10	1	1	5	60	1	44	13
10	2	1	5	Room	3	49	14
10	1	1	1	,,	7	15	40
10	0	1	1	,,	2	0	70

It will be seen that little change is caused by a fairly wide variation in conditions, provided that a large excess of acetic acid is present. The products of the first experiment were 9-methyloctalin, b. p. 88—90°/20 mm., and *cis*-9-methyl-2-decalol, b. p. 138—140°/20 mm., which gave a 35% yield of the pure solid form, m. p. 72°. The product of the last experiment was mainly uncyclised diene. For the preparation of 9-methyloctalin solid 9-methyl-2-decalol was dehydrated with an equal weight of potassium hydrogen sulphate. The product was redistilled over sodium. Yield, 80—90%; b. p. 74—76°/10 mm.

Oxidations.—(i) *Permanganate.* To a mixture of 6·0 g. of the olefin, 4·2 g. of anhydrous sodium carbonate, and 40 c.c. of water stirred at 0°, 100 c.c. of 0·5% potassium permanganate solution were added during 2 hours, followed by 250 c.c. of 1% permanganate solution during 5 hours, and finally by 800 c.c. of 2% permanganate solution during 24 hours. From the product 2·0 g. of unchanged hydrocarbon were isolated. This was reoxidised with 600 c.c. of 1% permanganate solution. The united material was filtered, evaporated to small bulk, acidified, and extracted with ether, first by hand, then in a continuous extractor. The hand extractions yielded 4·3 g. of solid acid, which on crystallisation from dilute acetic acid gave pure *cis*-1-methyl*cyclo*hexane-1 : 2-diacetic acid, m. p. 190°. The continuous extractions gave a pasty mass (1·3 g.), from which only oxalic acid could be isolated.

The united acidic product was distilled with 0·3 g. of baryta up to 320°. The ketone formed was redistilled (b. p. 95—100°/10 mm., 1·0 g.) and converted into semicarbazone. 1·3 G. of this were formed in the cold, which after one crystallisation had m. p. 219° alone or in admixture with the authentic semicarbazone of 8-methyl-2-hydrindanone, m. p. 220° (Linstead, Millidge, and Walpole, *loc. cit.*). No further semicarbazone was formed on warming the filtrate.

(ii) *Ozonolysis.* (*a*) A solution of 12·3 g. of the olefin in 10 vols. of purified ethyl acetate was ozonised at − 73° to − 76°. When the issuing gas contained ozone, the solvent was removed, and the ozonide boiled with 4 vols. of water for 2 hours. The cooled product was treated with the theoretical amount of concentrated aqueous sodium hydroxide, followed by Merck's perhydrol (1·5 vols.). The mixture was warmed on the steam-bath until evolution of oxygen had ceased and freed from neutral material by means of ether. The alkaline solution was acidified and extracted with ether, and the extract dried and evaporated. The acid (10·5 g. of semi-solid) was distilled to 320° with 0·5 g. of baryta. The product was washed with alkali and dried. 3·0 G. of ketone were obtained, b. p. 94—100°/10 mm. This was dissolved in a little methanol and treated with a solution of 2·7 g. of semicarbazide hydrochloride and 3·0 g. of sodium acetate in water. 1·5 G. of *cis*-8-methyl-2-hydrindanone semicarbazone were formed in the cold, m. p. 210—212° (crude), 218—219° after crystallisation from methanol. When the filtrate was boiled for a few minutes, 0·79 g. of a semicarbazone separated. This melted at 210—212° (crude) and at 223—224° after two crystallisations from methanol, and was identified as the derivative of *cis*-8-methyl-1-hydrindanone by a mixed m. p. determination with authentic material, m. p. 224° (Elliott and Linstead, *loc. cit.*).

(*b*) 5·0 G. of 9-methyloctalin, formed as a by-product in the preparation of *cis*-9-methyl-2-decalol, were ozonised at 0° in 50 c.c. of chloroform. The product, treated in exactly the same way as under (*a*) above, yielded 900 mg. of ketone, b. p. 98—101°/15 mm. The properties of the semicarbazones formed by this material are tabulated below :

	M. p. (crude).	M. p. (after crystallisation).	Mixed m. p.	
			With 2-semicarbazone (m. p. 220°).	With 1-semicarbazone (m. p. 224°).
2-Semicarbazone, formed in the cold ...	212—214°	218°	218—220°	198—205°
1-Semicarbazone, formed in the hot......	214—215	224	below 200	224

(*c*) Another sample (8·6 g.) of the same olefin was ozonised as before to yield 9·0 g. of a mixture of acids. This was refluxed with 200 c.c. of 5% (vol.) methanolic sulphuric acid for 2 hours. The product was separated into neutral and acid fractions by means of sodium carbonate. Hydrolysis of the neutral product gave 5·0 g. of solid acid, yielding *cis*-1-methyl*cyclo*hexane-1 : 2-diacetic acid (IV), m. p. 190°, on crystallisation. The acidic fraction after hydrolysis gave the carboxy-propionic acid (X) as a hard glass (1·4 g.) [see footnote to p. 721]. When this was distilled with baryta, it gave 0·6 g. of *cis*-8-methyl-1-hydrindanone, b. p. 103—105°/15 mm. The semicarbazone, formed in the hot, was identified by m. p. (223°) and mixed m. p.

(iii) *Lead tetra-acetate.* (*a*) 18·6 G. of *cis*-9-methyloctalin (prepared by dehydration of 9-methyl-2-decalol) were stirred for 1½ hours at 70° with 70 g. of lead tetra-acetate and 85 c.c. of acetic acid. The product was cooled, poured into ice-water, and extracted with ether. The extract was washed with ice-cold alkali, dried, and freed from solvent. Distillation yielded 13·7 g. of recovered hydrocarbon (b. p. 78°/12 mm.) and 3·0 g. of octalyl acetate. Reoxidation of the recovered hydrocarbon raised the yield of acetate to 7·0 g. (27%). Hydrolysis of the total acetate with 12 c.c. of 20% methyl-alcoholic potash gave 5·4 g. of cis-9-*methyl*-Δ^1-3-*octalol* (XI) as a viscous liquid, b. p. 125—130°/12 mm., $n_D^{14\cdot8^\circ}$ 1·5137, $d_{4^\circ}^{14\cdot8^\circ}$ 1·0102, $[R_L]_D$ 49·69 (Calc. for $C_{11}H_{18}O\,|\overline{1}$, 49·65) (Found : C, 79·4; H, 10·6. $C_{11}H_{18}O$ requires C, 79·4; H, 10·9%).

The methyloctalol was catalytically hydrogenated in alcohol over Adams's catalyst, 96% of the theoretical quantity of hydrogen being taken up. cis-9-*Methyl*-3-*decalol* was a viscous liquid, b. p. 130—132°/12 mm., $n_D^{13\cdot9^\circ}$ 1·5041, $d_{4^\circ}^{13\cdot9^\circ}$ 0·9993, $[R_L]_D$ 49·87 (Calc., 50·12) (Found : C, 78·6; H, 10·7. $C_{11}H_{20}O$ requires C, 78·6; H, 11·75%). The alcohol (4·9 g.) was oxidised in the usual way with 2·5 g. of chromic acid in 50 c.c. of acetic acid. The product was poured into water, extracted by means of light petroleum, and washed with alkali. Distillation yielded 3·4 g. of *cis*-9-methyl-3-decalone, b. p. 118—120°/12 mm. The semicarbazone melted at 193° after one crystallisation from ethanol. The mixed m. p.'s with the three authentic *cis*-9-methyldecalone semicarbazones were :

With *cis*-9-methyl-1-decalone semicarbazone (m. p. 224°) : below 180°.
With *cis*-9-methyl-2-decalone semicarbazone (m. p. 210°) : 183—185°.
With *cis*-9-methyl-3-decalone semicarbazone (m. p. 200°) : 194—199°.

The semicarbazone was hydrolysed back to the ketone without further purification. The ketone solidified after distillation and melted at 47°, alone or in admixture with authentic *cis*-9-methyl-3-decalone (duFeu, McQuillin, and Robinson, *loc. cit.*).

In another series of oxidations the product was reoxidised with lead tetra-acetate twice, with the results shown below :

	Initial hydrocarbon, g.	Acetate obtained, g.	Hydrocarbon recovered, g.
1st Oxidation	19·5	7·8	8·2
2nd ,, ...	8·2	3·5	3·1
3rd ,, ...	3·1	1·2	1·2

The total yield of acetate was 46%. The acetates formed in the first and in the subsequent oxidations were worked up separately by the process described above. Both gave *cis*-9-methyl-3-decalone (m. p. 47°) as the final product.

A certain amount of liquid ketone was obtained after the separation of the solid 9-methyl-3-decalone from these products. This was examined carefully to see if any of the 1-ketone or the so far unknown 4-ketone could be obtained from it. It yielded an impure semicarbazone, the m. p. of which was raised by admixture with the derivative of the 3-ketone. No second isomeride could be isolated. The regenerated ketone yielded *cis*-1-methyl*cyclo*hexane-1 : 2-diacetic acid on oxidation with nitric acid in the usual manner.

(iv) *Catalytic oxidation* (cf. Cook, *loc. cit.*). 20 G. of methyloctalin were heated at 70° with 40 mg. of ferrous phthalocyanine (Barrett, Dent, and Linstead, J., 1936, 1735) and a slow stream of oxygen was passed for 5 days. The pigment turned brown in the course of a few hours. The viscous product was taken up in ether and washed with sodium bicarbonate and acid ferrous sulphate solutions. It was dried and distilled, giving 5·0 g. of recovered hydrocarbon and 5·5 g. of liquid, b. p. 128—138°/16 mm. The high fraction gave an oily semicarbazone which solidified when rubbed with light petroleum. The yield of solid was 4·0 g. After crystallisation from methanol, the *semicarbazone* of cis-9-*methyl*-Δ^1-3-*octalone* (XII) was obtained in prisms, m. p. 202—203° (Found : C, 64·9; H, 8·6. $C_{12}H_{19}ON_3$ requires C, 65·1; H, 8·7%). The m. p. was depressed by admixture with the semicarbazone of the isomeric $\Delta^{4:10}$-ketone (duFeu, McQuillin, and Robinson, *loc. cit.*). The regenerated ketone boiled at 130°/16 mm. Catalytic hydrogenation in alcohol over palladised asbestos gave 2·5 g. of *cis*-9-methyl-3-decalone,

b. p. 124°/15 mm., m. p. 47°; semicarbazone, m. p. 200—201°. These m. p.'s were not depressed by admixture with the corresponding authentic materials.

(v) *Selenium dioxide.* 10 G. of the hydrocarbon, 10 c.c. of acetic anhydride, and 4 g. of selenium dioxide were heated at 60° for 5 hours and then at 100° for 3 hours. The anhydride was removed under reduced pressure, and the residue fractionated. 5·6 G. of hydrocarbon were recovered, and a second fraction, b. p. 110—115°/13 mm., obtained (2·0 g., 17%). This was hydrolysed with 8 c.c. of 20% alcoholic potash for 2 hours, and yielded 0·9 g. of an alcohol, b. p. 120—130°/16 mm. This was cautiously oxidised with 0·4 g. of chromic acid, and the ketonic product converted into semicarbazone. Yield, 0·6 g.; m. p. 203—204°. The semicarbazone was identified as that of *cis*-9-methyl-Δ^1-3-octalone by a mixed m. p. determination.

Conversion of 8-Methyl-2-hydrindanone into 8-Methyl-1-hydrindanone.—9·0 G. of *cis*-8-methyl-2-hydrindanone, m. p. 40° (Linstead, Millidge, and Walpole, *loc. cit.*), were added to 40 c.c. of a 3N-solution of aluminium *iso*propoxide in *iso*propyl alcohol. The solvent was slowly distilled through a good column, the loss being replaced by fresh *iso*propyl alcohol. After 50 c.c. of distillate had been collected (6 hours), tests with 2 : 4-dinitrophenylhydrazine showed that no more acetone was being given off. The residue, decomposed by acid, yielded 7·3 g. (87%) of cis-8-*methyl-2-hydrindanol* (presumably an epimeric mixture) as an oil, b. p. 120—122°/21 mm., $n_D^{16^\circ}$ 1·4923, $d_{4^\circ}^{16^\circ}$ 0·9865, $[R_L]_D$ 45·37 (calc., 45·51) (Found : C, 77·5; H, 11·5. $C_{10}H_{18}O$ requires C, 77·9; H, 11·75%). The alcohol (7·0 g.) was dehydrated in the usual way with an equal weight of powdered potassium hydrogen sulphate. After two distillations, the second over potassium, the *cis*-8-methylhexahydroindene (XIII) boiled at 61—62°/19 mm., $n_D^{19\cdot8^\circ}$ 1·4742, $d_{4^\circ}^{19\cdot8^\circ}$ 0·8820; $[R_L]_D$ 43·35 (calc. for $C_{10}H_{16}$, $|\overline{1}$, 43·46). Yield, 3·7 g.

The olefin resisted the action of ozone in ethyl acetate, but oxidation by 3% aqueous permanganate yielded *cis*-1-methyl*cyclo*hexane-1-carboxylic-2-acetic acid, m. p. 162° alone and 163° in admixture with authentic material, m. p. 164° (Linstead and Millidge, J., 1936, 478).

A mixture of 2·8 g. of 8-methylhexahydroindene, 40 c.c. of glacial acetic acid, and 10 c.c. of Merck's perhydrol was kept at room temperature for 4 days. The product was isolated by means of ether and hydrolysed with 20% methyl-alcoholic potash. The neutral product, again isolated with ether, distilled at 170—172°/18 mm. (1·7 g.). cis-8-*Methylhydrindan*-1 : 2-*diol* (XIV), so obtained, set to a glass (Found : C, 70·6; H, 10·8. $C_{10}H_{18}O_2$ requires C, 70·6; H, 10·6%). 1·2 G. of the diol were heated to 200° with an equal weight of powdered potassium hydrogen sulphate. The product was cooled, and distilled in steam after the addition of dilute alkali solution. From the distillate, ether extracted a camphoraceous oil, b. p. 103—105°/19 mm. (0·4 g.). This yielded a semicarbazone when warmed with semicarbazide acetate. The derivative melted at 220—221° after two crystallisations from methanol, at 222—223° in admixture with the semicarbazone of 8-methyl-1-hydrindanone, and at about 200° in admixture with that of 8-methyl-2-hydrindanone.

Action of Lead Tetra-acetate on trans-Δ^2-*Octalin.*—The Δ^2-octalin was obtained by dehydration of *trans*-2-decalol (m. p. 75°) with potassium hydrogen sulphate. It had b. p. 186—188°/756 mm., $n_D^{16\cdot5^\circ}$ 1·4890, $d_{4^\circ}^{16\cdot5^\circ}$ 0·9007, $[R_L]_D$ 43·58 (cf. Hückel and Friedrich, *Annalen*, 1927, **451**, 147).

40 G. of *trans*-Δ^2-octalin, 160 g. of lead tetra-acetate, and 200 c.c. of glacial acetic acid were stirred together for 3 hours at 70°. The mixture was worked up as described above for the analogous oxidation of 9-methyloctalin. The product gave 13·4 g. (34%) of unchanged hydrocarbon and 12·6 g. (22%) of trans-Δ^2-*octalyl acetate*, b. p. 131°/12 mm., $n_D^{15\cdot8^\circ}$ 1·4860, $d_{4^\circ}^{15\cdot8^\circ}$ 1·0162, $[R_L]_D$ 54·84 (calc., 54·42) (Found : C, 74·4; H, 9·1. $C_{12}H_{18}O_2$ requires C, 74·4; H, 9·3%). There was also a high fraction of indefinite b. p., containing the 2 : 3-diacetate (16 g.).

Hydrolysis of the octalyl acetate with a small excess of alcoholic potash yielded trans-Δ^2-1-*octalol* (XV) as a viscous liquid, b. p. 133—134°/16 mm., $n_D^{16\cdot3^\circ}$ 1·5854, $d_{4^\circ}^{16\cdot3^\circ}$ 1·0038, $[R_L]_D$ 45·19 (calc. for $C_{10}H_{16}O$ $|\overline{1}$, 44·93) (Found : C, 78·7; H, 10·5. $C_{10}H_{16}O$ requires C, 78·9; H, 10·6%). Hydrolysis of the high fraction yielded a neutral liquid which deposited 1 g. of solid. This crystallised from alcohol in small plates of trans-*decalin*-2 : 3-*diol*, m. p. 140° (Found : C, 69·8; H, 10·6. $C_{10}H_{18}O_2$ requires C, 70·0; H, 10·6%).

When reduced in alcoholic solution over Adams's catalyst, *trans*-Δ^2-1-octalol (6·0 g.) took up 93% of the theoretical amount of hydrogen and gave *trans*-α-decalol in nearly theoretical amount as a viscous oil, b. p. 112—115°/10 mm. This was oxidised with chromic and acetic acids to α-decalone (4·8 g.), b. p. 102—104°/11 mm. This was solid in ice but liquefied at room temperature and was not quite pure *trans*-α-decalone (m. p. 33°). However, it readily gave the semicarbazone of this ketone, m. p. and mixed m. p. 229° (compare Hückel and Brinkmann, *Annalen*, 1925, **441**, 21).

trans-Δ^2-1-Octalol (9·5 g.) was dehydrated with potassium hydrogen sulphate, giving 5·0 g. (60%) of a *hexahydronaphthalene* (XVI). This diene, after distillation over sodium, had b. p. 82°/17 mm., $n_{\mathrm{D}}^{19\cdot0^\circ}$ 1·5185, $d_{4^\circ}^{19\cdot0^\circ}$ 0·9369, $[R_L]_{\mathrm{D}}$ 43·32 (calc. for $C_{10}H_{14}|\overline{2}$, 43·06) (Found: C, 88·9; H, 10·35. $C_{10}H_{14}$ requires C, 89·5; H, 10·5%). A diene with almost identical physical properties was obtained by dehydrating the unsaturated alcohol with alcoholic hydrogen chloride.

Over Adams's catalyst 0·557 g. of the diene in 10 c.c. of alcohol took up 186 c.c. of hydrogen (N.T.P.), corresponding to the saturation of two double bonds. The decalin so obtained, after distillation over sodium, had $n_{\mathrm{D}}^{20\cdot1^\circ}$ 1·4819, $d_{4^\circ}^{20\cdot1^\circ}$ 0·8890, and was therefore mainly the *cis*-isomeride, as expected.

2·7 G. of the diene were heated with 0·2 g. of 30% palladised charcoal for 24 hours at 160°. The product was filtered, and shaken with 1·9 c.c. of 100% sulphuric acid for 2 hours at 100°. 10 C.c. of saturated brine were then added, which precipitated 3·0 g. of sodium tetralin-β-sulphonate. This was identified by conversion into the β-sulphonanilide. Yield, 1·6 g.; m. p. 151—152° (cf. Linstead, Millidge, Thomas, and Walpole, *loc. cit.*). From control experiments 3·0 g. of the sodium salt correspond with *ca.* 1·9 g. of tetralin. The saturated hydrocarbon, unattacked by sulphuric acid, was distilled over potassium (0·7 g.). It had $n_{\mathrm{D}}^{20\cdot7^\circ}$ 1·4788, $d_{4^\circ}^{20\cdot7^\circ}$ 0·8853 and was therefore a mixture of *cis*- and *trans*-decalins. From the relative quantities of tetralin and decalin obtained, a little direct loss of hydrogen had occurred, which is not surprising at the comparatively high temperature. The diene, unlike *cyclo*hexadiene, was unaffected by the same catalyst at room temperature.

When the diene was heated with maleic anhydride in benzene at 100°, it yielded a glass, which was converted into a white powder by the addition of ether. Addition of light petroleum to an acetone solution precipitated the adduct as an amorphous solid, m. p. 275° (decomp.). The adduct was soluble in alkali and reprecipitated by acid.

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