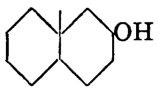
117. *Fused Carbon Rings. Part XIV. Synthesis of Dicyclic Compounds with an Angular Methyl Group from Substances containing a* n-*Pentenyl Side Chain.*

By G. H. Elliott and R. P. Linstead.

The general object was a model synthesis of the 8-methyl-1-hydrindanone type of structure, met with in many sexual hormones. An earlier synthetic method, involving the ring closure of butenyl side chains containing a terminal double bond, gave β- and not α-ketones. Analogous experiments have now been carried out with compounds containing pentenyl side chains. A new synthesis of 8-methyl-1-hydrindanone is described, and a connection has been established between 9-methyl-1-decalone and 9-methyl-2- and -3-decalones.

In previous papers it has been shown that various butenyl-*cyclo*hexanols and -*cyclo*hexenes can be cyclised to derivatives of decalin (J., 1936, 470, 476; 1937, 1136, 1140; compare following paper), the method being well adapted for the synthesis of compounds containing an angular methyl group, for example, of 9-methyl-2-decalol (I), and thence of 8-methyl-2-hydrindanone (II). One of the general objects of this series of investigations is the synthesis of sexual hormones which contain the isomeric 8-methyl-1-hydrindanone structure (III) and in the present paper we have explored the possibility of modifying the earlier synthetic method in order to obtain compounds of this type.

The use of compounds containing a Δ^{δ}-*n*-pentenyl side chain appeared promising for two reasons. 2-*Methyl*-1-Δ^{δ}-n-*pentenyl*cyclo*hexanol* (IV) might cyclise to yield 1 : 9-dimethyloctalin (either directly or through an alcohol). In this there seemed a reasonable possibility of the double bond approaching the 1-methyl group to yield at least a considerable proportion of the $\Delta^{1:2}$-form (V). Oxidation of this would then lead to 2-methyl*cyclo*hexane-2-carboxylic-1-propionic acid and thence to 8-methyl-1-hydrindanone (III).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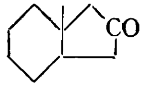
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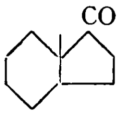
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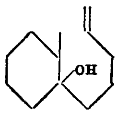
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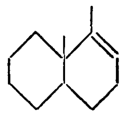
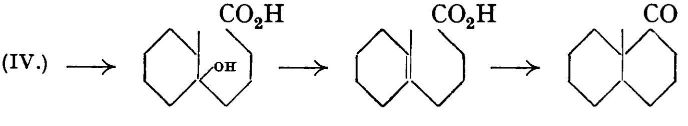

(V.)

The other possibility was that 2-methyl-1-Δ^{δ}-*n*-pentenyl*cyclo*hexanol (IV) could be oxidised to the hydroxy-acid (VI), which would yield γ-(2-methyl-Δ^{1}-*cyclo*hexenyl)butyric acid (VII) on dehydration. As this acid has been converted into 9-methyl-1-octalone and thence into 9-methyl-1-decalone (VIII) by Chuang, Tien, and Ma (*Ber.*, 1936, 69, 1494) and by Cook and Lawrence (J., 1937, 817), the synthetic possibilities were obvious.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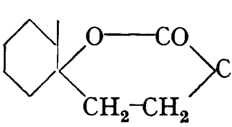

(IX.)

In practice, the first of these routes has so far proved of little value, but the second was successful.

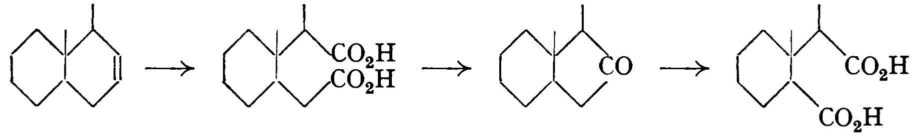
Oxidation of methylpentenyl*cyclo*hexanol (IV) with potassium permanganate, followed by distillation of the product with oxalic acid, yielded a mixture of the desired unsaturated acid (VII), and a smaller amount of the isomeric spiro-*lactone* (IX), which we suspect to be a mixture of isomerides. Linstead and Rydon (J., 1933, 580) showed that a δ-lactone of similar structure, containing a quaternary δ-carbon atom, could be converted (reversibly) into an isomeric γδ-unsaturated acid at the boiling point. When the *spiro*-lactone (IX) was heated to 200°, there was a small development of acidity, but it appears that either the equilibrium is far on the lactone side or else the mobility is very low. The lactone (IX) can, however, be converted into the unsaturated acid (VII) by esterification to the ester of (VI), dehydration, and hydrolysis.

As methylpentenyl*cyclo*hexanol can be made in one stage from the Grignard compound of the readily available Δ^{δ}-pentenyl bromide, the acid (VII) is easily prepared by this route as a crystalline solid, m. p. 44°. The identity of our product with those of previous workers (*loc. cit.*) follows from the agreement in the m. p. of the *p*-bromophenacyl ester with that of Chuang, Tien, and Ma, and from the results of cyclisation. The 9-methyl-1-octalone and -decalone (VIII) obtained from the acid by Cook and Lawrence's method (J., 1935, 1637) agreed in properties with the products of previous workers, and the semicarbazone of the saturated ketone was identical with the derivative prepared by Kon, Linstead, and Simons (J., 1937, 814). The reduction of the intermediate chloromethyldecalone, obtained from the acid chloride of (VII), was attempted by treatment with aluminium chloride and *cyclo*hexane, following Nenitzescu and Cantuniari (*Annalen*, 1934, **510**, 269). We obtained, however, only a poor yield of an unsaturated *ketone*, isomeric with the 9-methyl-1-octalone obtained by the usual method. The method does not appear to be applicable to this type of polycyclic chloro-ketone (compare Robinson and Walker, J., 1937, 61; Cook and Lawrence, *loc. cit.*, 1937).

Reduction of 9-methyl-1-decalone with aluminium *iso*propoxide gave 9-methyl-1-decalol (probably an epimeric mixture) in excellent yield, and this on oxidation with nitric acid gave 2-methyl*cyclo*hexane-2-carboxylic-1-β-propionic acid. As in previous work (Kon, Linstead, and Simons, *loc. cit.*; Robinson and Walker, J., 1937, 1160), the acid could not be obtained crystalline, but on distillation with baryta yielded 8-methyl-1-hydrindanone (III). The ketone was identical with the synthetic product of Kon, Linstead, and Simons, and, like it, gave on oxidation the 2-methyl*cyclo*hexane-2-carboxylic-1-acetic acid, m. p. 164°, of Linstead and Millidge (J., 1936, 478). The carboxy-propionic acid (and thence the methylhydrindanone) was also obtained by direct oxidation of 9-methyl-1-decalone.

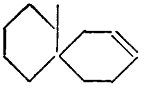
In previous work (Linstead, Millidge, and Walpole, J., 1937, 1140; Kon, Linstead, and Simons, *loc. cit.*) the following synthetic compounds containing an angular methyl group have been linked together by degradation: 9-methyl-2- and-3-decalones and 8-methyl-1- and -2-hydrindanones. To this list we can now add 9-methyl-1-decalone. These substances all have the same configuration, which, as has already been pointed out, is probably *cis*. This is supported by the physical properties of 9-methyl-1-decalone, which, it may be noted, was prepared by a process of reduction usually leading to a *cis*-configuration.

The other method of attack—the cyclisation of methylpentenyl*cyclo*hexanol (IV)—gave a series of products, of which the structures are not fully established, but those given below appear the most probable. When treated with a mixture of acetic and sulphuric acids and acetic anhydride (Linstead, Millidge, and Walpole, *loc. cit.*), the alcohol (IV) gave the acetate of an isomeric dicyclic secondary *alcohol*, $C_{12}H_{22}O$ (? 1 : 9-dimethyl-2- or -3-decalol), together with a dicyclic olefin, $C_{12}H_{20}$, probably a 1 : 9-dimethyloctalin (*e.g.*, X). Oxidation of the dicyclic alcohol with chromic acid yielded the corresponding *ketone*, $C_{12}H_{20}O$ (? 1 : 9-dimethyl-2- or -3-decalone), and its dehydration gave an *olefin*, $C_{12}H_{20}$. Permanganate oxidation of the latter gave a dibasic *acid*, $C_{12}H_{20}O_4$, which was also obtained from the ketone by means of nitric acid. Attempted oxidation of the ketone with chromic and sulphuric acids yielded no keto-acid, such as might have been obtained from 1 : 9-dimethyl-2-decalone if Wallach and Franke's oxidation of 2-methyl*cyclo*hexanone had been paralleled (*Annalen*, 1903, **329**, 376). Pyrolysis of the acid $C_{12}H_{20}O_4$ with baryta readily yielded a *ketone*, $C_{11}H_{18}O$, which was in turn oxidised to an *acid*, $C_{11}H_{18}O_4$. These products could correspond with the oxidation of a 1 : 9-dimethyl-$\Delta^{2:3}$-octalin (X), thus :



(X.) (XI.) (XII.) (XIII.)

On the other hand, the possibility that the dicyclic substances mentioned above are wholly or partly *spiro*-compounds cannot be excluded. For example, the olefin might be (XIV), in which case the C_{11}-ketone would be (XV). We have proved that the C_{11}-acid is *not* 2-methyl*cyclo*hexane-1 : 1-diacetic acid (XVI) by direct comparison with authentic material, but there remains a possibility that it is an isomeric carboxy-propionic acid (XVII).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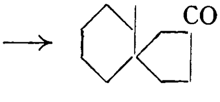

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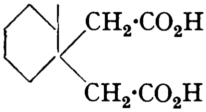

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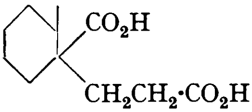

(XVII.)

The dicyclic olefin (X or XIV) evolved no hydrogen at the boiling point over an active platinum catalyst. This proves the presence of a quaternary carbon atom (Linstead, Millidge, Thomas, and Walpole, J., 1937, 1146), and excludes the presence of derivatives of 1 : 5-dimethyldecalin, formed by cyclisation of the pentenyl side chain away from the methyl group. At 335°, in the vapour phase over palladised asbestos, the olefin yielded a mixture of dimethylnaphthalenes. Dehydrogenation of the ketone $C_{12}H_{20}O$ over palladised charcoal gave a phenol, apparently a methylnaphthol, but in amount insufficient for identification. This evidence supports the decalin structure rather than the spiran, but we do not regard it as conclusive. As no evidence was obtained of the presence of olefin with the double bond in the desired $\Delta^{1:2}$-position (V) (which was the primary objective), the study of the substances obtained in these cyclisations has been temporarily discontinued in favour of more promising lines of attack.

While pentenyl bromide was under study, the opportunity was taken of confirming, from another angle, the synthesis of 1 : 1-dimethyl*cyclo*hexene from dimethyl-Δ^4-*n*-pentenylcarbinol (Hibbit and Linstead, J., 1936, 470). In the earlier work this carbinol was prepared from ethyl Δ^5-*n*-hexenoate and methylmagnesium iodide. We have now prepared it in excellent yield from the Grignard compound of Δ^4-*n*-pentenyl bromide and acetone. The product was cyclised by means of phosphoric acid to dimethyl*cyclo*hexene, and this was oxidised to ββ-dimethyladipic acid, in agreement with the earlier work.

EXPERIMENTAL.

The preparation of Δ^4-*n*-pentenyl bromide essentially followed that of Paul (*Bull. Soc. chim.*, 1935, 2, 745) and Gaubert, Linstead, and Rydon (J., 1937, 1971). In the preparation of Δ^4-*n*-pentenol by the action of sodium on tetrahydrofurfuryl chloride, better yields (90%, optimum 96%) were obtained by allowing the mixture to reflux with vigorous stirring overnight rather than for 1 hour.

Preparation and Cyclisation of 1 : 1-*Dimethyl*-Δ^4-n-*pentenylcarbinol*.—A mixture of 72 g. of pentenyl bromide and 250 c.c. of ether was added to 12 g. of magnesium and 100 c.c. of ether, and, after the completion of the reaction, 29 g. of dry acetone in 150 c.c. of ether were added during 1 hour. After an hour's refluxing, the product was decomposed as usual and dried with potassium carbonate. The carbinol (48 g., 80%) had b. p. 61—66°/13 mm., $d_{4°}^{14·3°}$ 0·8346, $n_D^{14·3°}$ 1·4387, $[R_L]_D$ 40·36 (calc. for $|_{1}^{=}$, 40·31) (Found : C, 75·1; H, 12·6. Calc. : C, 74·9; H, 12·6%). The carbinol (17 g.) was cyclised under Hibbit and Linstead's conditions (*loc. cit.*) with 84 c.c. of phosphoric acid, the mixture finally being heated at 135—140° for 1·5 hours. The dimethyl*cyclo*hexene (55% yield, after redistillation over potassium) had b. p. 119—124°/752 mm., $d_{4°}^{16·2°}$ 0·8043, $n_D^{16·2°}$ 1·4474, $[R_L]_D$ 36·60 (calc. for $|_{1}^{=}$, 36·48). On oxidation with potassium permanganate it yielded ββ-dimethyladipic acid, m. p. and mixed m. p. 88°.

2-*Methyl*-1-Δ^δ-n-*pentenyl*cyclo*hexanol* (IV).—A mixture of 290 g. of pentenyl bromide and 400 c.c. of ether was added to a stirred mixture of 47 g. of activated magnesium and 400 c.c. of ether at such a rate that the solution boiled gently without external heating. The final mixture was refluxed for 40 minutes, treated slowly with 220 g. of 2-methyl*cyclo*hexanone in 400 c.c. of ether, and again refluxed for 40 minutes. The ethereal solution was decomposed with ice and aqueous ammonium chloride, and finally with dilute hydrochloric acid. The product was washed with water and aqueous sodium thiosulphate, dried with potassium carbonate, and isolated by distillation. 2-*Methyl*-1-Δ^δ-n-*pentenyl*cyclo*hexanol* has b. p. 122—124°/13 mm., $d_{4°}^{16·1°}$ 0·9164, $n_D^{16·1°}$ 1·4789, $[R_L]_D$ 56·56 (calc. for $|_{1}^{=}$, 56·48) (Found : C, 78·8; H, 12·1. $C_{12}H_{22}O$ requires C, 79·0; H, 12·2%). Yields of 57—68% were obtained, the best yields coming from bromide which had stood for some time over calcium chloride.

A mixture of 35 g. of this alcohol, 23 g. of sodium carbonate (anhydrous), and a little water was stirred at 0° and a total quantity of 2850 c.c. of 3% aqueous potassium permanganate was added in drops. The rate of addition was 5 c.c./min. for the first 2 hours, and subsequently 10 c.c./min. After standing overnight, the colourless supernatant liquid was decanted, the manganese mud washed with boiling water, and the combined aqueous solution evaporated to 200 c.c., acidified, and extracted with ether. The extract was dried thoroughly with sodium sulphate. Notwithstanding this, water separated when the ether had been removed and the residue was at 90°. Clearly this was due to a dehydration of the tertiary alcohol group catalysed by the acids formed in the oxidation. The products from the oxidation of 230 g. of alcohol were united, treated with 30 g. of anhydrous oxalic acid, and distilled at 7 mm. After a considerable and troublesome elimination of water, the residue distilled over as follows: (1) 145—151°, 43 g.; (2) 151—158°, 32 g.; (3) 158°, 15 g.; (4) 158—166°, 38 g.; (5) 166—175°, 4 g. Total 132 g. All the fractions were treated overnight with aqueous sodium bicarbonate and extracted with ether. The aqueous solution was acidified, and the organic acid isolated by means of ether and distilled. 67 G. of γ-(2-methyl-Δ^1-*cyclo*hexenyl)butyric acid (VII) were so obtained, boiling at 166—167°/10 mm. and rapidly solidifying. The acid was very soluble in organic media, but crystallised from light petroleum (b. p. 40—60°) in thin waxy plates, m. p. 44°. Chuang, Tien, and Ma describe the acid as forming colourless needles, but give no m. p. (Found: C, 72·7; H, 10·0; equiv., 183·8. Calc.: C, 72·5; H, 10·0%; equiv., 182·2). The *p*-bromophenacyl ester formed glistening plates, m. p. 64° (Chuang *et al.* give 65—66°).

Fractional distillation of the non-acidic fraction yielded 31 g. of the spiro-*lactone* of γ-(1-*hydroxy*-2-*methyl*cyclo*hexyl*)*butyric acid* (IX), an oil with a lactonic odour, b. p. 145—155°/10 mm., and 20 g. more of the same unsaturated acid. The total direct yield of acid (VII) from tertiary alcohol was therefore 38%. The occurrence of acid in the lactone fraction was probably due to an isomeric change of a labile lactone on distillation. After redistillation, the lactone had b. p. 135°/1·5 mm. and was free of acid (Found: C, 72·3; H, 10·0. $C_{11}H_{18}O_2$ requires C, 72·5; H, 10·0%). The equivalent weight, determined by refluxing with excess of baryta and back-titration (Linstead, J., 1932, 115), was 185·0 (calc. 182·2). The stable lactone so obtained developed only 5% of acidity after 5 hours at 190°; at 230—240° decomposition occurred.

The structure of the lactone was proved by its conversion into the acid (VII) as follows: 31 G. of the lactone were refluxed for 5 hours with 100 c.c. of 10% alcoholic sulphuric acid. The product was poured into water and extracted with ether; the extract was washed with calcium chloride solution, dried, and freed from solvent. A solution of the hydroxy-ester so obtained (37 g.) in 250 c.c. of dry ether and 26 g. of pyridine (2 mols.) was treated at 0° with 24 g. of thionyl chloride (1·25 mols.) in drops. The product was filtered off, freed from solvent, and distilled. The ester so obtained (26 g., b. p. 124—126°/12 mm.) on hydrolysis with cold aqueous-alcoholic caustic potash yielded 10 g. of the solid acid (VII), b. p. 156—159°/5 mm., together with 10 g. of lactone. Dehydration of the hydroxy-ester with anhydrous oxalic acid was less successful.

γ-(2-Methyl-Δ^1-*cyclo*hexenyl)butyric acid (84 g.) was cyclised following Cook and Lawrence (*loc. cit.*). The intermediate chloro-ketone boiled at 130°/10 mm. and failed to give a satisfactory semicarbazone. It was dehalogenated as usual with dimethylaniline at 200°. The yield of 9-methyl-1-octalone, b. p. 108—111°/12 mm., was 47 g. (61%). The semicarbazone formed rather slowly at 30°; it crystallised in flattened needles, m. p. 228—229° (Chuang, 225—226°; Cook and Lawrence, 222—223°). Hydrogenation of the unsaturated ketone in pure acetic acid over Adams's platinum took only 1 hour and the temperature rose to 70°. The 9-methyl-1-decalone (probably *cis*-) so obtained boiled at 120—122°/20 mm. (46 g.). The semicarbazone, which formed slowly at 30°, rapidly on warming, had m. p. 210—216° (crude), 224° after crystallisation, not depressed by the semicarbazone of Kon, Linstead, and Simons (*loc. cit.*). The regenerated ketone, an oil with a camphoraceous odour, had b. p. 106°/9 mm., m. p. + 2°. The following physical properties accord well with those of Cook and Lawrence: $d_{4^\circ}^{16\cdot2^\circ}$ 0·9958, $n_D^{16\cdot2^\circ}$ 1·4926, $[R_L]_D$ 48·45 (calc., 48·61).

9-Methyl-1-decalone was reduced almost quantitatively by the Ponndorf–Verley method as follows: The ketone (44 g.) was heated with 10 g. of aluminium *iso*propoxide and 100 g. of *iso*propyl alcohol, at such a rate that about 20 c.c. of a mixture of acetone and *iso*propyl alcohol distilled in an hour. At the end of each hour, 20 g. of *iso*propyl alcohol were added, and after 8 hours a further 10 g. of aluminium *iso*propoxide. The process was continued for, in all, 12 hours. The mixture was cooled and decomposed with ice, and the product distilled in steam.

The distillate (2 l.) was extracted with ether, and the extract dried with sodium sulphate and freed from solvent under a column. The residue yielded 40 g. of 9-*methyl*-1-*decalol* (probably *cis*-), b. p. 134—135°/20 mm. (Found : C, 78·3; H, 12·1. $C_{11}H_{20}O$ requires C, 78·5; H, 12·0%).

8-*Methyl*-1-*hydrindanone* (III).—A solution of 9-methyl-1-decalone (16 g.) in acetic anhydride (10 c.c.) was added in drops to 50 c.c. of concentrated nitric acid, previously heated nearly to boiling, at such a rate that the acid was kept gently boiling. Finally the mixture was boiled for 2 minutes, diluted with 20 c.c. of water, and boiled for a further 20 minutes. The product was evaporated over caustic potash in a vacuum desiccator. The acid fraction (12 g.) was separated by means of sodium bicarbonate. The neutral product (7 g.) was used for further oxidations. The gummy 2-methyl*cyclo*hexane-2-carboxylic-1-β-propionic acid would not solidify even after distillation under reduced pressure (cf. Kon, Linstead, and Simons; and Robinson and Walker, *locc. cit.*). 12 G. of the crude acid were heated with 1 g. of baryta to 270—290°, finally to 320°. The distillate was extracted with light petroleum (b. p. 50°), and the extract washed with aqueous sodium hydroxide, dried, and evaporated. The residue was treated with 12 g. of semicarbazide hydrochloride, 10 g. of sodium acetate, and sufficient methanol. The semicarbazone was not formed at 25°, but separated readily on the steam-bath, in agreement with Linstead, Millidge, and Walpole (*loc. cit.*). The yield of pure, twice crystallised semicarbazone, m. p. 223°, was 3·8 g. From this, 2·0 g. of 8-methyl-1-hydrindanone (probably *cis*-), b. p. 95—96°/12 mm., m. p. 34°, were regenerated. The ketone and the semicarbazone did not depress the m. p.'s of the corresponding products of Kon, Linstead, and Simons.

9-Methyl-1-decalol (20 g.) was added in small quantities to 50 c.c. of concentrated nitric acid, the vigour of the reaction being controlled by cooling in ice. The product was warmed on the steam-bath for 5 minutes, kept for 2 hours, and worked up as above. The acid, which did not solidify, was converted into 8-methyl-1-hydrindanone as before. The yields were 8 g. of non-acidic material and 18 g. of acid, which gave 4·8 g. of distilled solid ketone and 2 g. of uncyclised acid.

The 8-methyl-1-hydrindanone on oxidation with nitric acid in acetic anhydride yielded an acid, m. p. (crude) 152—154°, and 165° after crystallisation. A mixed m. p. with the 2-methyl*cyclo*hexane-2-carboxylic-1-acetic acid, m. p. 164°, of Linstead and Millidge (*loc. cit.*) showed no depression.

6 G. of the 10-chloro-9-methyl-1-decalone obtained above were stirred under reflux in a bath at 95° for 3 hours with 5·2 g. of resublimed aluminium chloride and 30 c.c. of sodium-dried *cyclo*hexane, moisture being excluded (cf. Nenitzescu and Cantuniari, *loc. cit.*). The product was cooled and poured on ice and dilute acid, and the ketonic material, isolated by means of light petroleum, was distilled. The fractions boiling above 102°/13 mm. gave a little *semicarbazone* of a 9-*methyl*-1-*octalone* which, after crystallisation from methanol, melted at 228° but greatly depressed the m. p.'s of the semicarbazone of 9-methyloctalone, obtained by means of dimethylaniline, and of that of 9-methyl-1-decalone (Found : C, 65·2, 65·3; H, 8·5, 8·6. $C_{12}H_{19}ON_3$ requires C, 65·1; H, 8·7%). Presumably this corresponds with a different position of the double bond.

Cyclisation of 2-*Methyl*-1-Δ^{δ}-n-*pentenyl*cyclo*hexanol* (IV).—70 G. of the alcohol (IV) were added to a stirred, ice-cooled mixture of 210 c.c. of glacial acetic acid, 30 c.c. of acetic anhydride, and 12 c.c. of concentrated sulphuric acid. The mixture turned dark red and remained clear, but after the addition of a further 11 c.c. of concentrated sulphuric acid, it soon became dark brown and turbid, and separated into two clear layers. The colourless upper layer almost disappeared after 12 hours' standing. After 80 hours, the product from two such cyclisations was poured into 1200 c.c. of ice-water, well shaken, and extracted with ether. The extract was washed with alkali and dried over anhydrous potassium carbonate. The solvent was removed, and the residue hydrolysed (3 hours' boiling with 50 g. of caustic potash in 250 c.c. of methanol). The neutral product was fractionated into 29 g. of hydrocarbon, b. p. 98—103°/12 mm. (25%), and 65 g. of alcohol, b. p. 143—147°/12 mm. (46%).

The hydrocarbon (? 1 : 9-dimethyloctalin ; X) had $d_{4^\circ}^{16\cdot7^\circ}$ 0·9121, $n_{D}^{16\cdot7^\circ}$ 1·4975, $[R_L]_D$ 52·63, (calc. for $|^{=}_{1}$, 52·75). The *alcohol* (? 1 : 9-dimethyl-2- or-3-decalol) had b. p. 152°/17 mm., $d_{4^\circ}^{14\cdot8^\circ}$ 1·0028, $n_{D}^{14\cdot8^\circ}$ 1·5074, $[R_L]_D$ 54·01 (calc., 54·75) (Found : C, 78·9 ; H, 12·1. $C_{12}H_{22}O$ requires C, 79·0 ; H, 12·2%). It failed to solidify at − 20°.

A solution of 40 g. of the alcohol in 120 c.c. of acetic acid was treated with 15 g. of chromic acid dissolved in the minimum amount of water, and the oxidation completed in the usual manner. The ketone, isolated by extraction with light petroleum, boiled at 140—142°/14 mm. (32 g., 81%). The sparingly soluble *semicarbazone* melted crude at 216° and at 223° after three crystallisations from methanol (Found: C, 65·2; H, 9·7. $C_{13}H_{23}ON_3$ requires C, 65·7; H, 9·8%). The pure *ketone* (? 1 : 9-dimethyl-2- or-3-decalone) regenerated from the semicarbazone had b. p. 138·5°/13 mm., $d_{4°}^{16·6°}$ 0·9910, $n_D^{16·6°}$ 1·4966, $[R_L]_D$ 53·16 (calc., 53·23) (Found: C, 79·6; H, 11·1. $C_{12}H_{20}O$ requires C, 79·9; H, 11·2%).

The alcohol (25 g.) was heated for 90 minutes with an equal weight of potassium bisulphate at 180°. Extraction of the product with ether yielded an *olefin*, $C_{12}H_{20}$ (? 1 : 9-dimethyl-Δ^2-octalin; X), which was purified by heating with potassium at 170° and distillation at 95—99°/10 mm. Yield, 70%. The product had $d_{4°}^{16·4°}$ 0·9153, $n_D^{16·4°}$ 1·4974, $[R_L]_D$ 52·52 (calc. for $|^{=}_{1}$, 52·75), physical properties very close to those of the olefin obtained as a by-product in the cyclisation (Found: C, 87·5; H, 12·4. $C_{12}H_{20}$ requires C, 87·7; H, 12·3%). A similar product was obtained in 51% yield by dehydrating with oxalic acid. A solid nitrosochloride could not be obtained.

16 G. of the olefin (potassium bisulphate product) were shaken overnight with 6 g. of sodium carbonate and 1200 c.c. of 3% aqueous potassium permanganate. The product, worked up in the usual manner, yielded an acid which failed to solidify. It was esterified by means of ethereal diazomethane, and the main fraction of the ester (b. p. 130—140°/0·2 mm.) was hydrolysed with hydrochloric acid. The gum so obtained eventually solidified and the *acid* (? 1-methyl*cyclo*hexane-1-α-propionic-2-acetic acid; XI), melted at 156° after several crystallisations from water, in which it was not very soluble (Found: C, 63·1; H, 8·7. $C_{12}H_{20}O_4$ requires C, 63·1; H, 8·9%). The same acid was obtained by oxidising the ketone $C_{12}H_{20}O$ with boiling concentrated nitric acid. When the ketone (6·2 g.) was treated with chromium trioxide (4·6 g.), concentrated sulphuric acid (5 c.c.), and water (30 c.c.), there was little reaction, and no ketonic acid could be isolated from the product.

The dibasic acid $C_{12}H_{20}O_4$ (12 g. of crude gum), mixed with 0·2 g. of baryta, was converted into ketone in the manner already described for the preparation of 8-methyl-1-hydrindanone. 6 G. of crude *semicarbazone* were obtained, which after three crystallisations from methanol melted at 214·5° (Found: C, 64·35; H, 9·2. $C_{12}H_{21}ON_3$ requires C, 64·5; H, 9·5%). Ketonisation of the pure acid, m. p. 156°, gave the same compound. Regeneration from 3·2 g. of the pure semicarbazone yielded 2·0 g. of a *ketone*, $C_{11}H_{18}O$ (? 1 : 8-dimethyl-2-hydrindanone; XII), with b. p. 114°/9 mm., $d_{4°}^{16·8°}$ 0·9862, $n_D^{16·8°}$ 1·4896, $[R_L]_D$ 48·67 (calc., 48·61) (Found: C, 80·2; H, 11·0. $C_{11}H_{18}O$ requires C, 80·4; H, 11·05%).

Oxidation of the ketone with boiling nitric acid yielded an acid oil which rapidly solidified. After two crystallisations from water, white crystals of an *acid* (? 1-methyl*cyclo*hexane-1-α-propionic-2-carboxylic acid; XIII) were obtained, m. p. 144° (Found: C, 62·0; H, 8·3. $C_{11}H_{18}O_4$ requires C, 61·6; H, 8·5%). The m. p. was depressed by 2-methyl*cyclo*hexane-1 : 1-diacetic acid, m. p. 148° (Kon and Thorpe, J., 1919, **115**, 694).

Dehydrogenation.—(1) The olefin (1 g.) was refluxed vigorously for 3 hours in a stream of carbon dioxide over palladised charcoal. The total quantity of hydrogen evolved was less than 10 c.c., all of which came over in the first 10 minutes. The activity of the catalyst was checked against tetralin. (2) The olefin (1·2 g.) was passed over palladised asbestos, maintained at 335°, during 4 hours; 200 c.c. of gas were evolved. The product was swept out with hydrogen and converted directly into picrate with an excess of picric acid. The aromatic hydrocarbon (a liquid, 0·08 g.) was regenerated with ammonia and again converted into *picrate*. After crystallisation from methanol, this formed chrome-yellow needles, m. p. 134—135°, and gave the analysis of a dimethylnaphthalene picrate (Found: C, 56·05, 55·8; H, 4·0, 3·9. $C_{12}H_{12},C_6H_3O_7N_3$ requires C, 56·1; H, 3·9%). Admixture with the picrate of 1 : 5-dimethylnaphthalene (m. p. 137°) depressed the m. p. to 132—133°. It appears probable that the picrate is a mixture; the most likely components are the picrates of 1 : 8- and 1 : 2-dimethyl- and perhaps a little 1-methyl-naphthalene. (3) Dehydrogenation of the olefin with sulphur gave no picrate-forming material. (4) 6 G. of the ketone $C_{12}H_{20}O$ were refluxed with 0·6 g. of 30% palladised charcoal for 40 hours. The temperature fell from 260° to 220° and some water separated. A trace of phenol was separated from the product by means of caustic soda; this had m. p. 92—96°, gave a red-purple colour with ferric chloride, and formed a red picrate, m. p. 140—148°. The quantity was insufficient for complete purification, but these results are not inconsistent with the material being impure 1-methyl-2-naphthol. No picrate could be obtained from the neutral fraction.

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