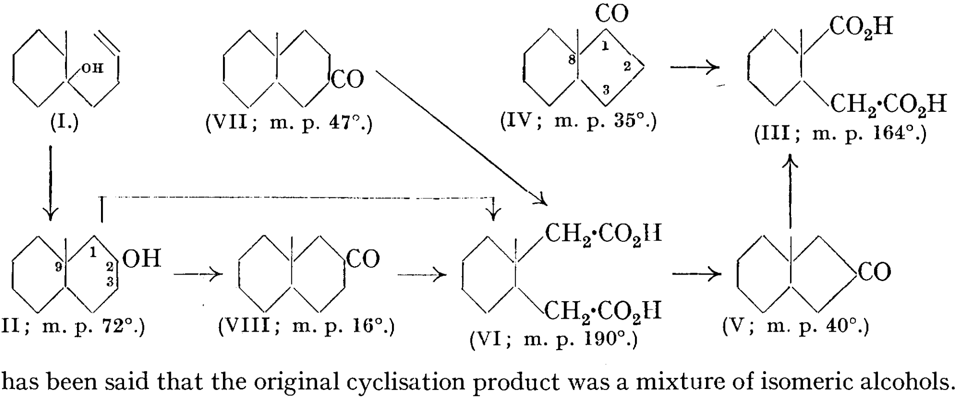
240. *Fused Carbon Rings. Part XIII. Synthesis of Derivatives of Decalin containing an Angular Methyl Group.*

By R. P. Linstead, A. F. Millidge, and A. L. Walpole.

This paper is concerned with the preparation of pure hydronaphthalenes containing an angular methyl group, for use as control substances in investigations of dehydrogenation. Syntheses of 9-methyl-octalin and -decalin have already been described (J., 1936, 470, *et seq.*), and the position of the methyl group proved by degradation. Nevertheless these substances were not satisfactory as reference compounds, because, although they contained a considerable amount of material of the desired structure, the presence of isomeric impurity could not be excluded. For the same reason the *trans*-9-methyldecalin of Ruzicka, Koolhaas, and Wind (*Helv. Chim. Acta*, 1931, **14**, 1154) did not appear to be a suitable reference compound. We now report the preparation of homogeneous compounds of the desired type.

It was shown in the preceding paper that 1-Δ^{γ}-butenyl*cyclo*hexanol yielded *cis*-β-decalyl acetate, and thence *cis*-β-decalol, when treated with a mixture of acetic and sulphuric acids and acetic anhydride. The same treatment of 2-methyl-1-Δ^{γ}-butenyl*cyclo*hexanol (I) yielded a mixture of methyldecalols. The yield was considerably better than in the unsubstituted series, the methyl group, as usual, assisting ring-closure. From the mixture a 9-methyl-2-decalol (II), m. p. 72°, was separated. The structure was proved as follows: On oxidation with nitric acid it gave a dibasic acid, $C_{11}H_{18}O_4$, m. p. 190°, in good yield. Distillation of this with a little baryta gave a dicyclic ketone, $C_{10}H_{16}O$, m. p. 40°, which formed a semicarbazone, m. p. 220°. Oxidation of this ketone yielded 1-methyl*cyclo*hexane-1-carboxylic-2-acetic acid (III), m. p. 164°, identical with synthetic material (Linstead and Millidge, J., 1936, 478; Chuang, Tien, and Huang, *Ber.*, 1935, **68**, 864). The only ketones which could yield this acid on oxidation are 8-methyl-1-hydrindanone (IV) and 8-methyl-2-hydrindanone (V). One stereoisomeric form of the first of these has recently been synthesised and its structure is certain (Kon, Linstead, and Simons, this vol., p. 814). It also gives the 164°-acid on oxidation and therefore belongs to the same stereochemical series. It melts at 35° and its semicarbazone at 224°, but in spite of their similarity the two ketones are quite distinct (see experimental section). The new ketone, m. p. 40°, is therefore *8-methyl-2-hydrindanone* (V), and the parent acid 1-methyl*cyclo*hexane-1 : 2-diacetic acid (VI). It follows that the original methyldecalol has the hydroxyl group in the 2- or the 3-position,* which agrees with the fact that *cis*-β-decalol is formed by an analogous cyclisation.

On oxidation with chromic acid the methyldecalol, m. p. 72°, yielded a 9-methyldecalone, which, after regeneration from the semicarbazone, melted at 18°. du Feu, McQuillin, and Robinson (this vol., p. 53) have described the preparation of an isomeric ketone, m. p. 47°, which there was good reason to believe was a 9-methyldecalone, and if so was certainly 9-methyl-3-decalone (VII). Through the kindness of Professor Robinson and Mr. McQuillin we have examined this substance. It differs from our ketone, but on oxidation yields the same 1-methyl*cyclo*hexane-1 : 2-diacetic acid (VI), also obtained by oxidation of our alcohol. Hence: (i) du Feu, McQuillin, and Robinson's structure for their ketone and their interpretation of their elegant synthetic method are confirmed; (ii) both sets of compounds belong to the same stereochemical series, the configuration of which we discuss below; (iii) our ketone by exclusion is 9-methyl-2-decalone (VIII). The relationships are summarised in the scheme:



(I.) (VII; m. p. 47°.) (IV; m. p. 35°.) (III; m. p. 164°.)

(II; m. p. 72°.) (VIII; m. p. 16°.) (VI; m. p. 190°.) (V; m. p. 40°.)

It has been said that the original cyclisation product was a mixture of isomeric alcohols. When the form of m. p. 72° was removed and the residue oxidised with chromic acid, the same ketone (VIII) was formed. Oxidation of the impure alcohol with nitric acid yielded the same acid (VI), but in this case it was possible to isolate a small quantity of an isomeride, m. p. 164°, a higher homologue of (III) (which has the same m. p.) and identical with the

---

* For convenience the carbon atom of octalins and decalins which carries the angular methyl group is referred to as C_9 throughout the introductions of this and the following paper.

acid obtained by Hibbit, Linstead, and Millidge (J., 1936, 478). It follows that the alcohol obtained by cyclisation is essentially a mixture of epimerides belonging to the same stereochemical series with respect to the locking of the rings (which we believe to be *cis*). The second C_{11} acid, m. p. 164°, is probably the stereoisomeride of (VI). It certainly belongs to the other stereoisomeric series (probably *trans*), for it has been degraded (*loc. cit.*) to the stereoisomeride of (III).

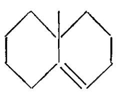
Reduction of pure 9-methyl-2-decalone (VIII) by the Clemmensen method yielded 9-methyldecalin, and dehydration of the solid alcohol (II) gave 9-methyloctalin. The oxygenated carbon atom is separated from the quaternary carbon atom (C_9) and there is therefore no possibility of a molecular rearrangement. On this account, and because the two hydrocarbons have been made from homogeneous solids, we have taken them as reference compounds for dehydrogenation experiments (see following paper). It is, of course, to be expected that the 9-methyloctalin will be a mixture of isomerides containing the double bond in different positions. On oxidation it yielded the diacetic acid (VI), which showed that it contained the Δ^2-form, and indicated that no molecular rearrangement had occurred during dehydration.

Configuration. The connection with the key-acid (III) shows that the compounds illustrated in the scheme all belong to the same stereochemical series. There is now strong (but not conclusive) evidence that they have the *cis*-configuration. This corrects an earlier suggestion (Linstead and Millidge, J., 1936, 480) that the 164°-acid (III) was the *trans*-acid, which was based on an unsatisfactory analogy. The new evidence comes first from the physical properties of pure 9-methyldecalin, 9-methyl-2-decalone, 8-*methylhydrindane* (made by reducing the ketone V) and 9-methyloctalin, the results from the last-named being less conclusive owing to the possibility of double-bond isomerism. All these have high densities and refractive indices and normal molecular refractivities; *e.g.*, the values for 9-methyldecalin and 9-methyl-2-decalone in round figures corrected to 20° are:

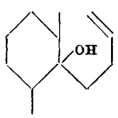
	$n_D^{20°}$.	$d_{4°}^{20°}$.	Exaltation in $[R_L]_D$.
9-Methyldecalin	1·481	0·892	−0·15
9-Methyl-2-decalone	1·492	0·989	+0·04

Related *trans*-ortho-dicyclic substances have exaltations of 0·3—0·4 of a unit. Furthermore the actual values for *n* and *d* for the 9-methyldecalin correspond well with those expected (cf. Ruzicka, Koolhaas, and Wind, *loc. cit.*; Hibbit and Linstead, J., 1936, 472). It is particularly interesting that the various *cis*-alkyldecalins derived from sesquiterpenes all have almost identical values for $d_{4°}^{20°}$ and $n_D^{20°}$ of about 0·89 and 1·48 respectively. The values for the ketone also fall into line well with those of *cis*-β-decalone, allowance being made for the usual fall in physical constants due to the methyl group. Secondly, the parent alcohol (II) is formed by a reaction which, in the case of the lower homologue, gives an undoubtedly *cis*-product (preceding paper).

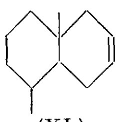
In the light of these results, it is clear that the methyloctalins obtained by direct cyclisation of methylbutenyl*cyclo*hexanols (Parts VII and VIII) were mixtures of isomerides, as was foreshadowed in the earlier work. The final oxidation product in both cases was mainly the 1-methyl*cyclo*hexane-1-carboxylic-2-acetic acid, m. p. 174°, stereoisomeric with (III). Hence the liquid, unregenerated, methylhydrindanone from which it had been obtained was a mixture containing *trans*-8-methyl-2-hydrindanone. The physical properties, however, indicate the presence of *cis*-material, and the 164°-acid was isolated from one oxidation (Part VIII). The parent methyloctalin must therefore have contained some of the *trans*-9-methyl isomeride. It is possible that the high physical constants indicate the presence of the $\Delta^{4:10}$-isomeride (IX). The double bond would be labile under the conditions of cyclisation (see preceding paper) and it might well migrate to the $\Delta^{4:10}$-position. A reversible migration of this kind would account for the formation of *trans*-octalins from primarily formed *cis*-isomerides. The presence of (IX) would account for the formation of a 9-methyldecalin, essentially *cis*-, on reduction, for there is evidence that bridge-head double bonds are reduced catalytically in this sense. The possible presence of derivatives of 1-methyldecalin is discussed in the next paper in the light of the results of dehydrogenation. The general conclusion is that, although the earlier methods of cyclisation give good yields of dicyclic material, at least partly of the angular methyl type, they are not suitable for the preparation of homogeneous compounds.



(IX.)



(X.)



(XI.)

As a preliminary exploration of the synthesis of substances more closely related to sesquiterpenes by cyclisation of butenyl compounds, we have examined the dehydration of 2 : 6-*dimethyl*-Δ^γ-*butenyl*cyclo*hexanol* (X). In this compound there seems to be no possibility of ring closure other than in the sense indicated (X $\longrightarrow$ XI), molecular rearrangement being most improbable. With a mixture of phosphoric acid and anhydride the alcohol (X) yielded 4 : 9-*dimethyloctalin* (XI, position of double bond uncertain), which was hydrogenated to 4 : 9-dimethyldecalin. The physical properties of this (b. p. 84°/10 mm., $d_{4^\circ}^{20^\circ}$ 0·881, $n_D^{20^\circ}$ 1·477, $\Sigma[R_L]_D + 0{\cdot}01$) were fairly close to those of the *cis*-4 : 9-dimethyldecalin (b. p. 85°/12 mm., $d_{4^\circ}^{20^\circ}$ 0·890, $n_D^{20^\circ}$ 1·481, $\Sigma[R_L]_D - 0{\cdot}04$) obtained by Ruzicka, Koolhaas, and Wind from eudesmol (*Helv. Chim. Acta*, 1931, **14**, 1175). The indications are that the synthetic material contains some *trans*-material, probably formed through an intermediate of type (IX). The synthesis of the exact saturated compound formed from the natural products will clearly be complicated by the presence of three asymmetric centres.

Treatment of the synthetic 4 : 9-dimethyldecalin with aluminium chloride (cf. Zelinski and Turova-Pollak, *Ber.*, 1929, **62**, 1658; 1932, **65**, 1299) led to a fall in the physical constants, corresponding to a change to the *trans*-configuration. The dehydrogenation of 4 : 9-dimethyl-octalin and -decalin is described in the following paper.

EXPERIMENTAL.

[The configurations assigned to the compounds below are provisional, see p. **1142**.]

The reagent used for cyclisation was a mixture of 10 parts of glacial acetic acid, 1 part of acetic anhydride, and 1 part of concentrated sulphuric acid (by vol.). 2-Methyl-1-Δ^γ-butenyl-*cyclo*hexanol (Hibbit, Linstead, and Millidge, *loc. cit.*) was cooled in ice, and 5 vols. of this reagent added slowly with stirring. The mixture became purple and turbid, a colourless layer (probably an intermediate hydrocarbon) separated slowly and then redissolved in the reagent, which finally became deep red brown. After 4 days at room temperature, the mixture was poured into water and extracted with ether, the extract washed with ice-cold alkali, and the ether removed. The residue of acetate was refluxed for 2 hours with an excess of 20% methyl-alcoholic potash, and the methyldecalol isolated by means of ether. Distillation yielded a low-boiling fraction containing a mixture of hydrocarbon and alcohol, followed by a main fraction, b. p. 127—131°/10 mm., which on refractionation gave the methyldecalol, b. p. 128—130°/10 mm., 141°/21 mm., in an average yield of 55%. This soon deposited a large amount of solid, which after repeated crystallisation from light petroleum, yielded cis-9-*methyl*-2-*decalol* (II), m. p. 72°, as clumps of needles, almost odourless and very soluble in organic media (Found : C, 78·0; H, 11·7. $C_{11}H_{20}O$ requires C, 78·5; H, 12·0%). 170 G. of the refractionated alcohol (A) gave 40 g. of this pure solid (B), 50 g. of impure solid (C), and a residual liquid (D) which had a camphoraceous odour.

The pure decalol (B) (900 mg.) in 10 c.c. of glacial acetic acid was oxidised with 500 mg. of chromium trioxide dissolved in the minimum quantity of water. After ½ hour at room temperature the excess of reagent was destroyed by warm ethyl alcohol, and the ketone isolated by distillation in steam and extraction with light petroleum. The residue from the removal of the solvent was converted into semicarbazone, which was crystallised from methanol to constant m. p. 760 Mg. were obtained, m. p. 211—212° (bath initially at 200°), together with 160 mg. melting a little lower. 7·6 G. of refractionated methyldecalol (A) were similarly oxidised and yielded 6·1 g. of distilled ketone, b. p. 132—134°/21 mm., which gave the same semicarbazone. 46 G. of the impure solid (C) similarly gave 35 g. of this *semicarbazone*, m. p. 210—212° (Found : C, 64·9; H, 9·6. $C_{12}H_{21}ON_3$ requires C, 64·5; H, 9·5%). Regeneration from the semicarbazone (35 g.) yielded 24·4 g. of pure cis-9-*methyl*-2-*decalone* (VIII), which was isolated by distillation in steam, and had b. p. 122—123°/14 mm., m. p. 17—18°, $n_D^{16°}$ 1·4937, $d_{4°}^{16°}$ 0·9938; $[R_L]_D$ 48·64 (calc., 48·61) (Found : C, 79·8; H, 10·9. $C_{11}H_{18}O$ requires C, 79·4; H, 10·95%). The ketone obtained by oxidation of the crude decalol had physical properties almost identical with the above ($[R_L]_D$ 48·65). Hence there was little *trans*-impurity.

700 Mg. of pure 9-methyl-2-decalol (B) were added slowly to 5 c.c. of concentrated nitric acid, the temperature being kept below 30°. After 2 hours 5 c.c. of water were added, the product cooled in ice, and the solid acid filtered off and crystallised twice from dilute acetic acid (charcoal). cis-1-*Methyl*cyclo*hexane*-1 : 2-*diacetic acid* (VI) (520 mg.) had m. p. 189—190° (Found : C, 61·9; H, 8·5. $C_{11}H_{18}O_4$ requires C, 61·7; H, 8·45%). Similar oxidation of 21·8 g. of liquid decalol (D) yielded a crude acid, which was separated by fractional crystallisation into the above acid (7·8 g.), m. p. 189—190° [Found : equiv. (dibasic), 107·1. Calc., 107·1], and 1 g. of an acid, m. p. 163—165°. The m. p. of the latter was not depressed by the acid of Hibbit, Linstead, and Millidge (*loc. cit.*), which was described as the *cis*-diacetic acid but now appears to be probably the *trans*-isomeride. The *cis*-acid, m. p. 189—190°, depressed the m. p. of the isomeric acid, m. p. 194°, isolated in small amount by Hibbit and Linstead (*loc. cit.*, p. 476). It appears probable that the latter acid is an oxidation product of 1-methyloctalin, *e.g.*, a 3-methyl*cyclo*hexane-1 : 2-diacetic acid.

800 Mg. of regenerated 9-methyl-2-decalone were added in drops to 10 c.c. of boiling concentrated nitric acid under reflux. After a few minutes 4 c.c. of water were added, the boiling continued for 30 minutes, and the product diluted and evaporated to dryness over potash in a vacuum desiccator. The residual solid after crystallisation from dilute acetic acid (charcoal) yielded *cis*-1-methyl*cyclo*hexane-1 : 2-diacetic acid (250 mg.), m. p. and mixed m. p. 189—190°. Repetition failed to improve this yield and it seems generally true that dicyclic ketones give worse yields than the corresponding alcohols on oxidation with nitric acid.

450 Mg. of the 10-methyl-2-decalone (9-methyl-3-decalone, VII) of du Feu, McQuillin, and Robinson (*loc. cit.*), on oxidation in the same way, yielded 160 mg. of *cis*-1-methyl*cyclo*hexane-1 : 2-diacetic acid (m. p. and mixed m. p. 189—190°) together with a lower-melting acid in an amount insufficient for identification.

7·3 G. of the diacetic acid, m. p. 189—190°, were ketonised with 5% of baryta at 280—330°. The ketone distilled over and partly solidified; it was extracted with light petroleum, the extract washed with alkali, and the cis-8-*methyl*-2-*hydrindanone* (V) isolated, finally by distillation. It had b. p. 105°/14 mm. and at once solidified to a camphor-like mass (3·6 g.), m. p. 39—40° (Found : C, 78·5; H, 10·5. $C_{10}H_{16}O$ requires C, 78·9; H, 10·6%). The *semicarbazone* melted at 220° (Found : C, 63·3; H, 8·6. $C_{11}H_{19}ON_3$ requires C, 63·1; H, 9·2%). The alkaline washings and residual barium salt from the cyclisation regenerated the original acid (m. p. and mixed m. p.). On oxidation with boiling nitric acid by the method described above for 9-methyl-2-decalone, 2 g. of 8-methyl-2-hydrindanone yielded 1·5 g. of a crude acid, m. p. about 150°. After crystallisation this melted at 163—164° and did not depress the m. p. of the *cis*-1-methyl*cyclo*hexane-1-carboxylic-2-acetic acid of Linstead and Millidge (*loc. cit.*) but depressed the m. p. of the stereoisomeric acid, m. p. 174° (*ibid.*) to 140° (Found : C, 59·7; H, 8·0. Calc. for $C_{10}H_{16}O_4$: C, 60·0; H, 8·1%). The differences between this *cis*-8-methyl-2-hydrindanone and the 8-methyl-1-hydrindanone (IV) (now seen to be *cis*-) of Kon, Linstead, and Simons (*loc. cit.*) are summarised below :

	8-Methyl-1-hydrindanone.	8-Methyl-2-hydrindanone.
Physical properties	Camphor-like mass, m. p. 35°.	Camphor-like mass, m. p. 40°.
Smell	Very like that of camphor.	Similar, but weaker and more mentholic.
Semicarbazone	Not formed in cold, but rapidly on warming. Transparent flattened needles from methanol, m. p. 224°.	Formed almost instantaneously in cold. Shining leaflets from methanol, m. p. 220°.

A mixture of the two ketones melted indefinitely at 30°, and a mixture of the semicarbazones at 195—200°. The comparative difficulty of forming the semicarbazone of the α-ketone is probably due to steric hindrance by the adjoining alkyl group.

The methyl*cyclo*hexanecarboxylicacetic acid (m. p. 164°) is obtained in a purer form by the oxidation of the α-ketone than by that of the β-ketone, presumably because the former can only be oxidised (primarily) in one direction, whereas two routes are open for the latter. The semicarbazone of *cis*-8-methyl-2-hydrindanone depressed the m. p. of the semicarbazone, m. p. 220°, of Hibbit and Linstead (*loc. cit.*), which is probably the *trans*-isomeride.

12 G. of 9-methyl-2-decalone, regenerated from the pure semicarbazone, were boiled under

reflux with 140 g. of amalgamated zinc, 120 c.c. of acetic acid, and 60 c.c. of concentrated hydrochloric acid, in a slow stream of hydrogen chloride. After 7 hours at a bath temperature of 130°, the product was distilled in steam, and the distillate extracted with purified light petroleum. The extract was shaken with successive quantities of concentrated sulphuric acid until there was no more discoloration of the acid, then with water and dilute alkali. It was dried over calcium chloride, the solvent removed through a column, and the residue heated with potassium at 170° for ½ hour. cis-9-*Methyldecalin* was isolated by distillation; b. p. 79°/11 mm., $n_D^{12\cdot5°}$ 1·4844, $d_{4°}^{12\cdot5°}$ 0·8994; $[R_L]_D$ 48·45 (calc., 48·60). Yield: 8·9 g., 81% (Found: C, 86·8; H, 13·2. $C_{11}H_{20}$ requires C, 86·75; H, 13·25%). In solid carbon dioxide–ether it solidified to a camphor-like mass melting at about − 22°. By a similar treatment, 8-methyl-2-hydrindanone (7 g.) yielded 4·1 g. of cis-8-*methylhydrindane*, b. p. 56°/10·5 mm., $n_D^{13\cdot5°}$ 1·4699, $d_{4°}^{13\cdot5°}$ 0·8754, $[R_L]_D$ 44·02 (calc., 43·98) (Found: C, 86·6; H, 13·0. $C_{10}H_{18}$ requires C, 86·9; H, 13·1%). In solid carbon dioxide–ether it solidified to a camphor-like mass, m. p. 10—14°. The liquid is easily supercooled to − 10°.

Pure *cis*-9-methyldecalol was refluxed with an equal weight of anhydrous oxalic acid at 160° for 3 hours, and the residue distilled. The crude hydrocarbon, isolated by means of ether, was heated with sodium at 190° for ½ hour and then distilled over fresh sodium. Yield of cis-9-*methyloctalin*: 3·8 g. from 6 g. of alcohol. B. p. 78—80°/12 mm., $n_D^{16°}$ 1·4956, $d_{4°}^{16°}$ 0·9098, $[R_L]_D$ 48·16 (calc., $C_{11}H_{18}\,|\overline{=}_1$ 48·13) (Found: C, 88·1; H, 12·2. $C_{11}H_{18}$ requires C, 87·9; H, 12·1%). A second preparation had almost identical physical properties. 32 G. of the pure decalol were heated at 190—195° for 3 hours with powdered anhydrous potassium bisulphate. Water was added, and the product distilled in steam. *cis*-9-Methyloctalin was isolated as before, b. p. 78—80°/12 mm., $n_D^{16\cdot2°}$ 1·4916, $d_{4°}^{16\cdot2°}$ 0·9074, $[R_L]_D$ 47·96. The difference in the refractive index of this and the foregoing product shows that they are not exactly identical with respect to the position of the double bond. The last runnings of the steam distillation deposited unchanged 9-methyl-2-decalol, m. p. 72°.

A suspension of 9-methyloctalin (2·1 g.), prepared by means of oxalic acid, in aqueous sodium carbonate was oxidised with 3% potassium permanganate solution and yielded 0·21 g. of 1-methyl*cyclo*hexane-1 : 2-diacetic acid, m. p. 189°. The hydrocarbon prepared by means of potassium bisulphate gave a better yield of the same acid (0·58 g. from 2·3 g.), which showed that it contained more of the Δ^2-form.

Derivatives of 4 : 9-*Dimethyldecalin*.—6-Methyl*cyclo*hexanone-2-carboxylic ester (Ruzicka, Koolhaas, and Wind, *Helv. Chim. Acta*, 1931, **14**, 1161) was methylated by means of methyl iodide and molecular sodium in petroleum (b. p. 60—80°). The methylated ester (80% yield, b. p. 108—112°/9 mm.) was hydrolysed with baryta in 86% yield to 2 : 6-dimethyl*cyclo*hexanone, b. p. 56°/9 mm. Condensation of 86 g. of this ketone with the Grignard compound from 90 g. of butenyl bromide in the usual way yielded 48 g. of 2 : 6-*dimethyl*-1-Δ^{γ}-*butenyl*cyclo*hexanol* (X), which boiled at 100—105°/10 mm. with a tendency to dehydration (Found: C, 79·3; H, 12·2. $C_{12}H_{22}O$ requires C, 79·0; H, 12·2%). 9 G. of the alcohol were treated with a mixture of phosphoric acid and phosphoric oxide in the manner used for the cyclisation of the lower homologue (Hibbit, Linstead, and Millidge, *loc. cit.*). Fractionation of the product over sodium yielded 5 g. of 1 : 10 (= 4 : 9)-*dimethyloctalin* (XI), b. p. 86—90°/10 mm., $n_D^{15°}$ 1·4924, $d_{4°}^{15°}$ 0·9020, $[R_L]_D$ 52·84 (calc., $C_{12}H_{20}\,|\overline{=}_1$ 52·75) (Found: C, 87·7; H, 12·7. $C_{12}H_{20}$ requires C, 87·7; H, 12·3%). This rapidly absorbed the theoretical quantity of hydrogen (for one double bond) in acetic acid solution over Adams's catalyst. The product, after removal of the solvent, was shaken with potassium permanganate until the latter was no longer decolorised and isolated by distillation over sodium. The 1 : 10 (4 : 9)-*dimethyldecalin* (mainly *cis*-) so obtained had b. p. 84—85°/10 mm., $n_D^{16°}$ 1·4787, $d_{4°}^{16°}$ 0·8847, $[R_L]_D$ 53·23 (calc., 53·22) (Found: C, 86·6; H, 13·15. $C_{12}H_{22}$ requires C, 86·65; H, 13·35%). A mixture of this hydrocarbon with an equal weight of aluminium chloride was left in a desiccator for 2 days, and the hydrocarbon recovered in the usual manner. After distillation over sodium, it had b. p. 76—78°/10 mm., $d_{4°}^{15°}$ 0·8544, $n_D^{15°}$ 1·4658, $[R_L]_D$ 53·83, corresponding with the conversion into the *trans*-form.

We thank the Chemical Society and the Royal Society for grants.

IMPERIAL COLLEGE OF SCIENCE AND TECHNOLOGY,
LONDON, S.W. 7.

[*Received, May 4th,* 1937.]