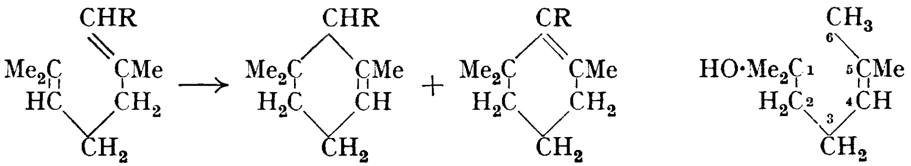
112. *Fused Carbon Rings. Part VII. The Preparation of Cyclic Hydrocarbons from Unsaturated Tertiary Alcohols. The Synthesis of* cis-*9-Methyl-octalin and -decalin, and a Proof of the Presence of the Angular Methyl Group.*

By D. C. HIBBIT and R. P. LINSTEAD.

THE main object of this work was to devise a method for the synthesis of polycyclic compounds containing an angular methyl group. This was intended to serve as a model for subsequent attempts at the preparation of substances of the type of sterols, sex-hormones, and the eudesmol group of sesquiterpenes. Much of the evidence for the existence of the angular group in these natural products is indirect, depending on the fact that it is eliminated during dehydrogenation. With a view to increasing the control over this method it was hoped during this work to prove the presence of the angular methyl group in suitable compounds *by methods independent of their synthesis* and then to examine their behaviour on dehydrogenation.

The synthetic method which we have studied is connected with the work of Tiemann and Semmler on the cyclisation of geraniolene and its derivatives. These chemists showed that dienes of type (I) are cyclised in good yield to the isomeric monocyclic compounds (II) and (III), containing one double bond, by treatment with sulphuric acid (see particularly *Ber.*, 1893, **26**, 2717; 1900, **33**, 3711).

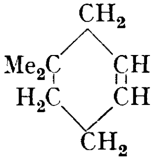


(I.) (II.) (III.) (IV.)

This reaction appears to be independent of the nature of the group R, and has been observed *inter alia* when R is H (geraniolene), Me (dihydromyrcene), $CH_2\cdot OAc$ (geranyl acetate), and CO_2H (geranic acid). The proportions of the forms (II) and (III) in the products vary with the nature of R and the conditions of cyclisation, but the α-form (II) generally predominates. Allied to these cyclisations is one by which Harries and Weil (*Ber.*, 1904, **37**, 848) prepared α-*cyclo*geraniolene (II, R = H) in good yield by the action of phosphoric acid on the dimethylheptenol (IV).

It appeared that such a *cyclo*-dehydration might have general synthetic possibilities and we accordingly examined a number of alcohols of allied structure with a view to finding what features were necessary for the reaction. The *gem*-dimethyl group at C_1 was retained for obvious reasons, the methyl group at C_5 was removed, and the length of the chain and the position of the double bonds were varied. The required unsaturated alcohols (V—VIII) were prepared by the action of methylmagnesium iodide on the esters of the appropriate pentenoic or hexenoic acids. All of these were available in a state of purity and the positions of the double bond were known with certainty (Linstead and Rydon, J., 1934, 1998; Letch and Linstead, *ibid.*, p. 1994; Boxer and Linstead, J., 1931, 740).

(V.) $CMe_2(OH)\cdot CH_2\cdot CH_2\cdot CH{:}CH_2$
(VI.) $CMe_2(OH)\cdot CH_2\cdot CH{:}CH\cdot CH_2Me$
(VII.) $CMe_2(OH)\cdot CH_2\cdot CH_2\cdot CH{:}CHMe$
(VIII.) $CMe_2(OH)\cdot CH_2\cdot CH_2\cdot CH_2\cdot CH{:}CH_2$ ⟶
(X.) $CMe_2(OH)\cdot CH_2\cdot CH_2\cdot CH_2\cdot CHMe\cdot OH$



(IX.)

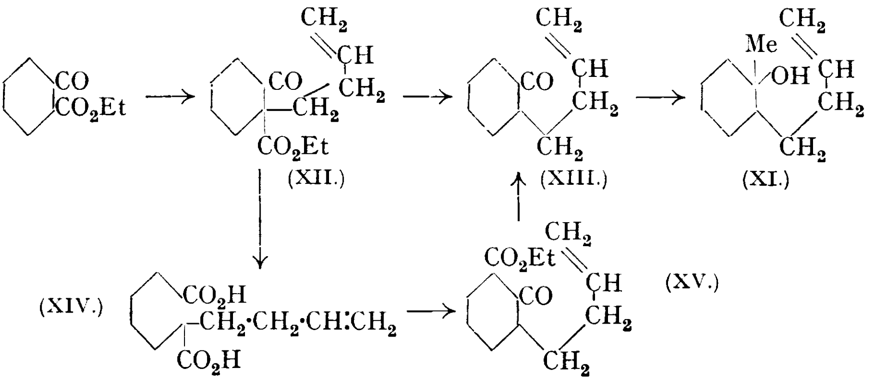
Treatment of the alcohols (V), (VI), and (VII) with phosphoric acid yielded the corresponding open-chain dienes or their polymerides, and no cyclisation could be detected. Dimethyl-Δ^3-butenylcarbinol (V) also gave no cyclic hydrocarbon on treatment with sulphuric acid.

Dimethyl-Δ^4*-pentenylcarbinol* (VIII), on the other hand, gave 1 : 1-dimethyl-Δ^3-*cyclo*hexene (IX) in good yield when treated with phosphoric acid.

The negative results obtained with (V), (VI), and (VII) show that there is no tendency to form a *cyclo*pentene ring under these conditions (contrast the work of Bogert and Davidson in the aromatic series; see p. 477). It is interesting that (VII) fails to yield a *cyclo*hexene, whereas its 5-methyl derivative (IV) does so readily. A reasonable explanation is that the 5-methyl group exercises its usual ability to promote the addition of acid to the double bond. The additive compound so formed then decomposes to give the olefinic alcohol with the terminal double bond (corresponding to VIII), which subsequently cyclises. It appears improbable that dihydric alcohols (such as X) intervene in these cyclisations (IV ⟶ II, VIII ⟶ IX), as, if this were true, it would be expected that the cyclisation of (VII) would be possible. The possible intervention of dienes is discussed in the next paper.

The structure of (IX) follows from its physical properties, from its reactions with one molecular proportion of bromine and of hydrogen, and from its oxidation to ββ-dimethyladipic acid. This fixes the position of the double bond, which corresponds to that of α-*cyclo*geraniolene. Catalytic hydrogenation yielded 1 : 1-dimethyl*cyclo*hexane. The physical constants of both (IX) and its reduction product agreed substantially with those recorded in the literature.

From these results it was anticipated that 1-*methyl*-2-$\Delta^{3'}$-*butenyl*cyclo*hexanol* (XI) would cyclise readily to a 9-methyloctalin. This alcohol was synthesised by the method given below, which establishes the structure:



Condensation of Δ^3-butenyl bromide and ethyl sodio*cyclo*hexanone-2-carboxylate in toluene yielded 2-$\Delta^{3'}$-*butenyl*cyclo*hexanone-2-carboxylate* (XII), which when hydrolysed by baryta gave mainly 2-$\Delta^{3'}$-*butenyl*cyclo*hexanone* (XIII). It is common for hydrolyses of this type to yield principally the corresponding pimelic acid (cf. Kon, J., 1933, 1081); but ring fission was subsidiary in the present instance. The crude acid which it yielded was purified through the ester, and the *ethyl* 1-$\Delta^{3'}$-*butenylpimelate* converted by the Dieckmann process into *ethyl* 2-$\Delta^{3'}$-*butenyl*cyclo*hexanone*-6-*carboxylate* (XV). On hydrolysis, this yielded 2-butenyl*cyclo*hexanone, identical with that prepared by the direct hydrolysis of (XII), together with a little 1-$\Delta^{3'}$-*butenylpimelic acid* (XIV). 2-$\Delta^{3'}$-Butenyl*cyclo*hexanone smoothly yielded 1-*methyl*-2-$\Delta^{3'}$-*butenyl*cyclo*hexanol* with methylmagnesium iodide.

Preliminary experiments on the preparation of this alcohol from butenylmagnesium bromide and 1-methyl*cyclo*hexene oxide or 2-chloro-1-methyl*cyclo*hexanol yielded rather poor yields of material of doubtful homogeneity and the method was not pursued. It is possible that some rearrangement of the carbon skeleton occurred (cf. Cook, Hewett, and Lawrence, this vol., p. 71).

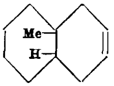
1-Methyl-2-$\Delta^{3'}$-butenyl*cyclo*hexanol gave a methyloctalin in good yield when dehydrated with phosphoric acid. The reaction required a rather higher temperature than that used in the preparation of dimethyl*cyclo*hexene (130° against 95°). From the evidence given below, the product is mainly cis-9-*methyl*-Δ^2-*octalin* (XVI). The position of the double bond is taken by analogy with dimethyl*cyclo*hexene and *cyclo*geraniolene. Oxidation yielded derivatives corresponding to the 9-position of the methyl group. Owing to the occurrence of more fundamental oxidation these were isolated in only 36% yield : hence we cannot exclude the possibility that some 8-methyloctalin, formed by an indirect process of dehydration and cyclisation, was present. For the sake of simplicity we shall for the present assume that the hydrocarbon is entirely the 9-methyl derivative. The dehydrogenation of the hydrocarbon and its reduction product is being studied.

From its physical properties the hydrocarbon contained two rings and one double bond. It reacted with one molecular proportion of hydrogen over platinum. The properties of the 9-*methyldecalin* so obtained showed that it belonged to the *cis*-series (XVII). It differed from the synthetic *trans*-9-methyldecalin of Ruzicka, Koolhaas, and Wind (*Helv. Chim. Acta*, 1931, **14**, 1151) in the same way as *cis*-decalin differs from its *trans*-isomeride :

Substance.	B. p.	$d_{4^\circ}^{t^\circ}$.	$n_{4^\circ}^{t^\circ}$.	*t*.	$[R_L]_D$.	EM_D.
cis-Decalin (H.)	72°/12 mm.	0·898	1·4823	20°	43·88	−0·10
trans-Decalin (H.)	63/12 ,,	0·872	1·4713	20	44·26	+0·28
cis-9-Methyldecalin (H.L.)	82/11 ,,	0·8909	1·4813	16·1	48·63	+0·03
trans-9-Methyldecalin (R.K.W.)	70/12 ,,	0·8583	1·4631	20	48·82	+0·22
,, (H.L.)	70/11 ,,	0·8654	1·4697	17·6	49·03	+0·43

(H., Hückel; R.K.W., Ruzicka, Koolhaas, and Wind; H.L., present work.) These figures should be compared with the table given by Ruzicka, Koolhaas, and Wind (*loc. cit.*, p. 1174).

It has been shown by Zelinski and Turova-Pollak (*Ber.*, 1929, **62**, 1658; 1932, **65**, 1299) that *cis*-decalin is converted into the *trans*-isomeride by aluminium chloride at room temperature. We now find that the same reaction occurs with *cis*-9-methyldecalin; the product (XVIII) after careful purification had the properties shown in the last line of the table. The fall in the physical constants and the rise in molecular refractivity clearly show the change to the *trans*-series; the difference between our values for the molecular refractivity of *cis*- and *trans*-9-methyldecalin is 0·40, almost identical with that found by Hückel for the parent compounds. This change supports the *cis*-configuration for the primary product (XVI).



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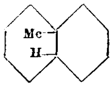

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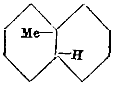
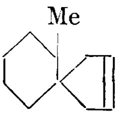


(XVIII.)

On oxidation with alkaline permanganate the hydrocarbon (XVI, $C_{11}H_{18}$) yielded a saturated monocyclic dibasic acid, $C_{11}H_{18}O_4$. This substance, m. p. 160—163°, contained a small amount of a persistent isomeric impurity which was isolated by fractional ketonisation (Barrett and Linstead, J., 1935, 436). When the crude acid was heated to 280° with a trace of baryta, it gave a good yield of a mixture of two saturated dicyclic ketones, $C_{10}H_{16}O$, the semicarbazones of which melted at 220° and 238°. The ketone giving the higher-melting semicarbazone was present only in small amount. The formation of ketone shows that the acids must be substituted adipic acids derived from a *cyclo*hexene ring and the original hydrocarbon must therefore be a methyloctalin and not a spiran such as (XIX). The remote possibility that the hydrocarbon contains a 7-membered ring is excluded by the results of oxidation of the ketone.



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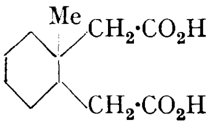

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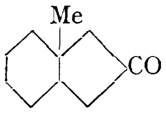
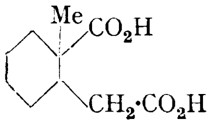
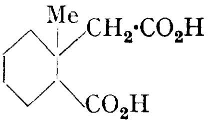


(XXI.)



(XXII.)



(XXIII.)

From the residue of the ketonisation a small amount of a pure acid, $C_{11}H_{18}O_4$, m .p. 195°, was recovered. When this was heated with baryta under rather more vigorous conditions, it gave the ketone forming the semicarbazone, m. p. 238°. We consider the acid of m. p. 160—163° to be nearly pure cis-1-*methyl*cyclo*hexane*-1 : 2-*diacetic* acid (XX) and that of m. p. 195° to be the trans-*isomeride,* which is cyclised a little less readily. The ketones with semicarbazones, m. p. 220° and 238°, are respectively the *cis*- and the *trans*-form of 8-*methyl-2-hydrindanone* (XXI). [The diacetic acid formula, corresponding to the Δ^2-position of the double bond, is not finally established. The alternative, which is much less probable, is that one or both of the acids $C_{11}H_{18}O_4$ is a 1-methyl*cyclo*hexane-1-carboxylic-2-propionic acid, in which case the corresponding ketone would be an 8-methyl-1-hydrindanone.]

The mixture of ketones (mainly *cis*-) on oxidation with nitric acid gave a mixture of dibasic acids, $C_{10}H_{16}O_4$, m. p.'s 175° and 162—164°, the latter present in small amount. The structures of both these acids have been proved by their synthesis (see Part IX, this vol., p. 480, where the evidence for their configuration is discussed). The acid of m. p. 175° is cis-1-*methyl*cyclo*hexane-1-carboxylic-2-acetic acid* (XXII); the other is the *trans*-isomeride. Owing to the presence of the methyl group attached to the carbon atom carrying the carboxyl group, which prevents enolisation, these acids cannot be interconverted. The identity of the acids obtained by degradation and by synthesis proves conclusively the presence of the angular methyl group in the ketone and the parent methyloctalin. The ketone (XXI) is not oxidised to the isomeric acid (XXIII), both forms of which have been synthesised. The relationship of our acids with those recently described by Clemo and Chuang and their collaborators is discussed in Part IX (*loc. cit.*).

A preliminary account of this work appeared in March, 1935 (*Chem. and Ind.*, 1935, **54**, 315). Cohen, Cook, and Hewett have described some related experiments on 2-methyl-1-$\Delta^{3'}$-butenyl-3 : 4-dihydrophenanthrene (J., 1935, 1633; cf. Cook, *Chem. and Ind.*, *loc. cit.*). This was not cyclised by formic acid, but—from the evidence of dehydrogenation—yielded a tetracyclic substance with sulphuric acid in acetic acid. We had independently studied the simplest cyclisation of this type, namely, that of 2-methyl-1-butenyl*cyclo*hexanol (see following paper).

EXPERIMENTAL.

(1) *Preparation of Acyclic Alcohols.*—(*a*) Allylacetic acid, m. p. − 23° (Linstead and Rydon, *loc. cit.*), was converted into dimethyl-Δ^3-butenylcarbinol (V) by the method of Perkin and Pickles (J., 1905, **87**, 657). Yield 82%, b. p. 142—143°, m. p. − 22° to − 23° (corr.).

(*b*) The preparation of Δ^3-butenol from allyl bromide (Linstead and Rydon, J., 1934, 1998) gave an average yield of 42% of material of b. p. 112—116° on a 3 g.-molecular scale. The alcohol was converted through Δ^3-butenylmalonic acid, m. p. 92°, into Δ^5-*n*-hexenoic acid and its ethyl ester, b. p. 68—70°/23 mm., by the methods described in the last reference. 90 G. of ethyl Δ^5-*n*-hexenoate were added in portions to the Grignard reagent prepared from 385 g. of methyl iodide and 62 g. of magnesium in 1200 c.c. of dry ether; a gentle reaction ensued. After 12 hours, the product was decomposed with ice and dilute sulphuric acid, the ethereal layer washed with sodium sulphite solution, the ether removed, and the residue freed from unchanged ester by boiling with a little methyl-alcoholic potash for 4 hours. The neutral material, isolated in the usual way, yielded 77 g. (89%) of *dimethyl-*Δ^4*-pentenylcarbinol* (VIII) as a strong-smelling oil, b. p. 65—66°/15 mm., liquid at − 74°, $n_D^{16\cdot7°}$ 1·4393, $d_{4°}^{16\cdot7°}$ 0·8393, $[R_L]_D$ 40·18 (calc. 40·20) (Found: C, 74·7; H, 12·5. $C_8H_{16}O$ requires C, 74·9; H, 12·6%). 1 G. was left for 16 hours in a sealed tube with 0·93 g. of phenyl *iso*cyanate. The *phenylurethane* so obtained formed delicate needles from methyl alcohol, m. p. 67—68° (Found: C, 72·4; H, 8·5. $C_{15}H_{21}O_2N$ requires C, 72·8; H, 8·6%). The 3 : 5-dinitrobenzoate could not be obtained solid.

(*c*) Ethyl Δ^4-*n*-hexenoate, b. p. 68°/19 mm., was prepared from dihydrosorbic acid by the method of Letch and Linstead (*loc. cit.*; yield, 20 g. from 74 g.). From it *dimethyl-*Δ^3*-pentenylcarbinol* (VII) was prepared by the method described above for the Δ^4-isomeride. Yield 91%, b. p. 70°/17 mm., $n_D^{15\cdot2°}$ 1·4429, $d_{4°}^{15\cdot2°}$ 0·8397, $[R_L]_D$ 40·45 (calc., 40·20) (Found: C, 74·9; H, 12·6%). The *phenylurethane* melted at 89° (Found: C, 73·3; H, 8·3%). On oxidation of the carbinol with ice-cold alkaline permanganate, acetone (2 : 4-dinitrophenylhydrazone, m. p. 125—128°) and acetic acid (*p*-bromophenacyl ester, m. p. 87°) were formed. This confirms the penultimate position of the double bond.

(*d*) Ethyl Δ^3-*n*-hexenoate, b. p. 74°/27 mm., prepared from butaldehyde by the method of Boxer and Linstead (*loc. cit.*), was converted into *dimethyl-*Δ^2*-pentenylcarbinol* (VI) in the same way. Yield 83%, b. p. 63—64°/20 mm., m. p. − 27° to − 28° (corr.), $n_D^{14\cdot4°}$ 1·4407, $d_{4°}^{14\cdot4°}$ 0·8424, $[R_L]_D$ 40·15 (calc., 40·20) (Found: C, 74·7; H, 12·55%).

(2) *Dehydrations.*—(*a*) On dehydration with potassium hydrogen sulphate, dimethyl-Δ^3-

butenylcarbinol yielded allyl*iso*propenylmethane, b. p. 90—93°; nitrosochloride, m. p. 75° (cf. Perkin and Pickles, *loc. cit.*). When the carbinol (8 g.) was shaken with 36 c.c. of syrupy phosphoric acid (*d* 1·75), no heat was developed. The mixture was heated under reflux at 160° for ½ hour, and the upper layer then distilled off in a stream of carbon dioxide. The hydrocarbon in the distillate was extracted with a little ether, washed with sodium carbonate solution, and dried over calcium chloride. Distillation gave 2·5 g. of a product boiling indefinitely between 60° and 200°, which smelt of diene but was mainly polymeric. A similar product was obtained when the carbinol was shaken with 5 vols. of ice-cold sulphuric acid (60% by vol.). No fraction corresponding to a dimethyl*cyclo*pentene could be isolated in either case.

(*b*) 5 G. of dimethyl-Δ^4-pentenylcarbinol were shaken with 24 c.c. of syrupy phosphoric acid. The temperature rose to 50°; dehydration was completed by heating the mixture on the steam-bath for an hour. The acid layer assumed a reddish-brown colour, which subsequently spread to the upper layer and deepened. The product was isolated as before, 3·5 g. (81%) of 1 : 1-dimethyl-Δ^3-*cyclo*hexene, b. p. 128—129°/780 mm., being obtained. This was not quite pure after one redistillation over sodium (Found : C, 86·6; H, 12·8. Calc. for C_8H_{14} : C, 87·2; H, 12·8%). A preparation from 23 g. of the carbinol in which the mixture was heated at 160° for 1 hour gave 67% of product, b.p. 120—130°, which after two fractionations over sodium yielded the pure hydrocarbon; this had a powerful, rather pleasant, odour, b. p. 120—122°/760 mm., $n_D^{16·6°}$ 1·4479, $d_{4°}^{16·6°}$ 0·8092, $[R_L]_D$ 36·47 (calc. 1$|^{=}$ 36·48) (Found : C, 87·3; H, 12·6%). von Auwers and Lange (*Annalen*, 1915, **409**, 166) found b. p. 121°/750 mm., $n_D^{20°}$ 1·4456, $d_{4°}^{20°}$ 0·804. If the phosphoric acid was freshly dehydrated at 220° before use, only a poor yield of cyclic hydrocarbon was obtained together with a considerable quantity of polymeride. By the method of Rosenmund and Kuhnhenn (*Z. Unters. Nahr. Genussm.*, 1923, **46**, 154) the pure hydrocarbon added 159·8, 159·3 g. of bromine per mol. (calc. for one double bond, 159·8).

5·7 G. of 1 : 1-dimethyl-Δ^3-*cyclo*hexene were shaken with 1650 c.c. of aqueous ice-cold 2% potassium permanganate containing 5·5 g. of sodium carbonate. After 6 hours the unchanged hydrocarbon was removed in steam, the solution filtered, and the filtrate and washings evaporated to small bulk. The residue was acidified and extracted continuously with ether for 24 hours. The residue obtained by removal of the ether from the extract was purified through sodium bicarbonate in the usual manner and yielded a viscous oil, which crystallised in needles (2·8 g.) on standing in a vacuum; m. p. after crystallisation from water, and mixed m. p. with authentic ββ-dimethyladipic acid, 88° (Found : C, 55·35; H, 8·2. Calc. for $C_8H_{14}O_4$: C, 55·2; H, 8·1%).

1·34 G. of 1 : 1-dimethyl-Δ^3-*cyclo*hexene were hydrogenated without a solvent, Adams's catalyst being used; 267 c.c. of hydrogen, corresponding to 98% hydrogenation, were absorbed. After distillation over sodium, 0·95 g. of 1 : 1-dimethyl*cyclo*hexane, b. p. 120°, were obtained, $n_D^{17·6°}$ 1·4351, $d_{4°}^{17·6°}$ 0·7890, $[R_L]_D$ 37·08 (calc., 36·9) (Found : C, 84·9; H, 14·1. Calc. for C_8H_{16} : C, 85·6; H, 14·4%). The physical constants are very slightly higher than those in the literature (*e.g.*, v. Auwers and Lange, *loc. cit.*), possibly owing to the presence of a trace of unsaturated hydrocarbon.

(*c*) Dimethyl-Δ^3-pentenylcarbinol on treatment with phosphoric acid gave a hydrocarbon, b. p. 76—180°, smelling of diene, from which no definite substance could be isolated. Dimethyl-Δ^2-pentenylcarbinol gave the corresponding diene, partly polymerised, on treatment both with anhydrous potassium sulphate and with phosphoric acid. This was not further investigated.

(3) 9-*Methyloctalin.*—*cyclo*Hexanone-2-carboxylic ester (240 g., 15% excess) was added to 27·2 g. (1 mol.) of " molecular " sodium in 1400 c.c. of sodium-dry toluene, and the formation of sodio-compound completed by an hour's heating at 130°. The cooled product was treated with 160 g. (1 mol.) of Δ^3-butenyl bromide, and the mixture heated under reflux at 130° for 63 hours. The product was decomposed with ice and acid and extracted with ether, the extract washed with sodium bicarbonate solution and water, dried, and evaporated; fractionation of the residue gave a 70% yield of *ethyl* 2-$\Delta^{3'}$-*butenyl*cyclo*hexanone-2-carboxylate* (XII), b. p. 134—143°/11 mm., and 156—158°/25 mm. on refractionation (Found : C, 69·2; H, 9·0. $C_{13}H_{20}O_3$ requires C, 69·6; H, 9·0%). No condensation product was obtained in boiling light petroleum (b. p. 60—80°), and the yield was only 30% in toluene at 130° after 20 hours. 13 G. of ethyl butenyl*cyclo*hexanonecarboxylate were refluxed with a solution of 26 g. of baryta in 4 vols. of water for 14 hours. The cold product was acidified and extracted with ether, and the extract washed thoroughly with sodium bicarbonate solution. The neutral product gave 4·6 g. (63%) of 2-$\Delta^{3'}$-*butenyl*cyclo*hexanone* (XIII), b. p. 110—112°/23 mm. This yielded 6 g. of a *semicarbazone*, m. p. 125°, which crystallised from dilute alcohol in lustrous plates, m. p. 127° (Found : C, 63·1; H, 9·1. $C_{11}H_{19}ON_3$ requires C, 63·2; H, 9·2%). From this, the ketone was regener-

ated by Kon's method (J., 1930, 1616) in 67% yield; b. p. 112—114°/28 mm. (Found: C, 78·8; H, 10·4. $C_{10}H_{16}O$ requires C, 78·95; H, 10·5%). On a larger scale 183 g. of the keto-ester yielded 78 g. of crude or 67 g. (45%) of pure ketone (b. p. 97—100°/15 mm.), together with 78 g. of acidic material. Acid hydrolysis of 2-butenyl*cyclo*hexanonecarboxylic ester was unsatisfactory.

Direct ketonisation of the acidic by-product with baryta was unsatisfactory. 40 G. were esterified in the cold with alcoholic sulphuric acid and the product, isolated in the usual way, was fractionated into ethyl pimelate, b. p. 136°/9 mm., and 26 g. of *ethyl* 1-$\Delta^{3'}$-*butenylpimelate*, b. p. 156—160°/9 mm. Refractionation gave 21 g., b. p. 161—162°/11 mm. (Found: C, 66·35; H, 9·6. $C_{15}H_{26}O_4$ requires C, 66·7; H, 9·6%). The ester was refluxed for 18 hours with 1·95 g. of sodium in 100 c.c. of light petroleum (b. p. 40—60°), and the product worked up. After two fractionations, 10 g. of *ethyl* 2-$\Delta^{3'}$-*butenyl*cyclo*hexanone*-6-*carboxylate* (XV), b. p. 146—148°/11 mm., were isolated (Found: C, 69·2; H, 9·0. $C_{13}H_{20}O_3$ requires C, 69·6; H, 9·0%). Hydrolysis of this with baryta gave a 67% yield of 2-$\Delta^{3'}$-butenyl*cyclo*hexanone, b. p. 95—97°/11 mm., identical with that already prepared (semicarbazone, m.p. and mixed m. p. 126°). The bicarbonate washings of the last hydrolysis gave on acidification and ether extraction an oily acid which slowly crystallised. 1-$\Delta^{3'}$-*Butenylpimelic acid* (XIV) crystallised from ether in slender needles, or very slowly from water in transparent cubes, m. p. 39° [Found: C, 61·9; H, 8·3; equiv., 108. $C_{11}H_{18}O_4$ requires C, 61·6; H, 8·5%; equiv. (dibasic), 107].

41 G. of 2-$\Delta^{3'}$-butenyl*cyclo*hexanone were added in drops to a solution of methylmagnesium iodide prepared from 7·1 g. of magnesium in 450 c.c. of dry ether; the reaction was fairly vigorous; after 12 hours, the product was decomposed with ice and a slight excess of acetic acid, and 1-*methyl*-2-$\Delta^{3'}$-*butenyl*cyclo*hexanol* (XI) isolated by means of ether in 91% yield, b. p. 97—102°/11 mm. Refractionation gave 39 g., b. p. 102—104°/13 mm., $n_D^{17·6°}$ 1·4814, $d_{4°}^{17·6°}$ 0·9252, $[R_L]_D$ 51·77 (calc., 51·86), which did not solidify at — 70° (Found: C, 78·4; H, 11·7. $C_{11}H_{20}O$ requires C, 78·5; H, 11·9%). It was essential to remove all traces of iodine from this alcohol before distillation, otherwise catalytic decomposition to the diene occurred.

When 15 g. of the alcohol were mixed with syrupy phosphoric acid (*d* 1·75; 4 vols.), the temperature rose to 40°. The mixture was heated for 30 minutes at 140°, cooled, diluted with an equal volume of water, and extracted with purified light petroleum (b. p. 40—60°). The extract was washed with aqueous soda and water and dried with calcium chloride. Fractional distillation over sodium yielded 12 g. (89%) of cis-9-*methyl*-Δ^2-*octalin* (XVI), b. p. 82°/14 mm., $n_D^{15·2°}$ 1·4943, $d_{4°}^{15·2°}$ 0·9085, $[R_L]_D$ 48·13 (calc. for 1 $\vDash$, 48·13) (Found: C, 87·9; H, 12·0. $C_{11}H_{18}$ requires C, 87·9; H, 12·1%). When the dehydration was carried out at 95° for 30 minutes, the yield was 54%. Reaction with bromine under Rosenmund and Kuhnhenn's conditions apparently led to bromination, for the results were high for one double bond (Found: bromine addition per g.-mol., 205; calc., 159·8).

6·3 G. of 9-methyloctalin were catalytically reduced over Adams's platinum oxide; the volume of hydrogen absorbed corresponded to that calculated for $C_{11}H_{18}$ with one double bond. The reduced hydrocarbon was shaken successively with warm 2% potassium permanganate solution and concentrated sulphuric acid to remove any trace of octalin and was distilled over sodium; 5 g. of cis-9-*methyldecalin* (XVII) were obtained with the physical properties given on p. 472 (Found: C, 86·5; H, 13·1. $C_{11}H_{20}$ requires C, 86·75; H, 13·25%). 2·6 G. of this material were kept for several days in contact with 1·04 g. ($\frac{1}{2}$ mol.) of aluminium chloride with exclusion of water. There was no apparent reaction. The product was washed with water, dried, and distilled. Yield of *trans*-9-methyldecalin (XVIII) 1·8 g., b. p. 75°/14 mm., $n_D^{17·6°}$ 1·4702, $d_{4°}^{17·6°}$ 0·8684, $[R_L]_D$ 48·91 (calc., 48·60). This hydrocarbon was treated with warm 2% potassium permanganate solution for 1 hour, refluxed over potassium for 6 hours, and distilled. The physical properties (p. 472) were only slightly changed (Found: C, 86·2; H, 13·2. Calc. for $C_{11}H_{20}$: C, 86·75; H, 13·25%).

Oxidation of cis-9-*Methyl*-Δ^2-*octalin*.—6 G. of the hydrocarbon were shaken mechanically with 20 g. (25% excess) of potassium permanganate in 3% solution and 4·2 g. of sodium carbonate. After 4 hours the solution was decolourised with sulphur dioxide, evaporated to small bulk, acidified, and extracted with ether (five hand extractions). Removal of the solvent from the extract left an oil, which rapidly solidified. After purification through sodium bicarbonate, 3·1 g. of solid acid were obtained, which were crystallised several times from boiling water, forming white opaque nodules, m. p. 160—163° [Found: C, 61·6; H, 8·3; equiv., 106·9. $C_{11}H_{18}O_4$ requires C, 61·7; H, 8·3%; equiv. (dibasic), 107·0]. This substance is mainly cis-1-*methyl*cyclo*hexane*-1 : 2-*diacetic acid* (XX).

The aqueous solution from the hand extractions was extracted continuously with ether for several days. The extract on removal of the ether left a gum, which deposited a few crystals of an acid very soluble in water. This crystallised by evaporation of its ethereal solution in beautiful needles, m. p. 103°, and was not oxalic acid. Insufficient was obtained for identification. 5 G. of the uncrystallisable gum from several oxidations were esterified in the usual way. Fractionation of the ethyl ester so obtained yielded (i) 1·3 g., b. p. 128°/12 mm., probably ethyl adipate (Found: C, 59·3; H, 8·7. Calc. for $C_{10}H_{18}O_4$: C, 59·4; H, 8·9%); (ii) 2·2 g., b. p. 158—170°/12 mm., from which 0·4 g. of ester, b. p. 158°/16 mm., was isolated. This appears to be mainly *ethyl* 1-*methyl*cyclo*hexane*-1 : 2-*dicarboxylate* (Found: C, 64·8; H, 8·9. $C_{13}H_{22}O_4$ requires C, 64·4; H, 9·1%); on hydrolysis it gave a mixture of acids, m. p. 138—171°. The higher fractions of (ii) yielded 0·6 g. of ester, b. p. 178°/18 mm., which was mainly the *homologue* of the foregoing ester, but yielded a mixture of acids on hydrolysis (Found: C, 65·1; H, 9·0. $C_{14}H_{24}O_4$ requires C, 65·6; H, 9·4%).

The crude *cis*-1-methyl*cyclo*hexane-1 : 2-diacetic acid, m. p. 160—163°, was heated with a crystal of baryta in a fused-salt bath to 280—285°; carbon dioxide and a ketone were then evolved. The distillate was washed with alkali, and the ketone converted into the *semicarbazone*, which formed readily in the cold. Yield 1·7 g., m. p. 221—223° (Found: C, 63·3; H, 8·8. $C_{11}H_{19}ON_3$ requires C, 63·1; H, 9·2%). Repeated crystallisation of this from alcohol gave a very small amount of a less soluble semicarbazone (probably *trans*-), m. p. 238°, and a more soluble isomeride (probably *cis*-), m. p. 220°. The residual barium salt from the ketonisation was boiled with a little dilute hydrochloric acid. The filtered solution on cooling deposited 0·1 g. of an acid, m. p. 188—194°, probably trans-1-*methyl*cyclo*hexane*-1 : 2-*diacetic acid*, which formed flattened needles from water, m. p. 194—196° (Found: C, 61·2; H, 8·4. $C_{11}H_{18}O_4$ requires C, 61·7; H, 8·3%). This, heated with baryta, gave a ketone which yielded a semicarbazone, m. p. 238—239° after one crystallisation from methyl alcohol, identical with that, m. p. 238°, described above.

The mixed semicarbazones from the ketonisation, m. p. 224—228°, were hydrolysed with oxalic acid, and the 9-*methyl-2-hydrindanone* distilled in steam and isolated by means of ether. Two separate regenerations gave the following results: yield 72, 76%; b. p. 109°/20 mm., 219°/760 mm.; $n_D^{17\cdot5^\circ}$ 1·4791, 1·4792; $d_{4^\circ}^{17\cdot5^\circ}$ 0·9811, 0·9798; $[R_L]_D$ 43·97, 44·05 (calc., 43·99) (Found: C, 79·3; H, 11·0. $C_{10}H_{16}O$ requires C, 78·95; H, 10·5%). The normal molecular refractivity agrees with the *cis*-configuration. The introduction of the 9-methyl group into 2-hydrindanone brings about a fall in the physical constants. The physical measurements given above were carried out on a supercooled sample: the ketone readily set to a glassy solid, which had a low but indefinite m. p. It had a pleasant, rather camphoraceous, odour.

0·5 G. of the regenerated ketone was slowly added to 0·6 c.c. of boiling concentrated nitric acid under reflux. After addition of 2 c.c. of water, the mixture was boiled for 30 minutes and left over caustic soda in a desiccator. Some solid separated rapidly and was removed. The mother-liquor deposited an oil on evaporation, which was taken up in water and again evaporated in a vacuum desiccator, more solid being formed. Total yield, 0·21 g.; m. p. 135—152° after one crystallisation from water [Found: equiv., 99·3. Calc. for $C_8H_{14}(CO_2H)_2$: equiv., 100]. Fractional crystallisation from water yielded a less soluble acid in prismatic needles, m. p. 173—175° alone or mixed with cis-1-*methyl*cyclo*hexane*-1-*carboxylic*-2-*acetic* acid (m. p. 175°; see p. 473) (Found: C, 60·2; H, 8·6. $C_{10}H_{16}O_4$ requires C, 60·0; H, 8·1%). The more soluble fractions yielded a very small quantity of prismatic crystals of the trans-*isomeride*, m. p. 162—164° alone or mixed with synthetic material (m. p. 163—164°; see p. 473). The m. p. was depressed by admixture with *cis*-1-methyl*cyclo*hexane-1 : 2-dicarboxylic acid (m. p. 160°). Oxidation of the ketone with potassium permanganate in acetone led to gross decomposition.

IMPERIAL COLLEGE, LONDON, S.W. 7.

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