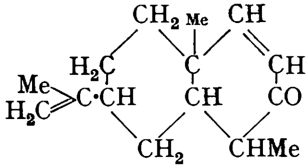
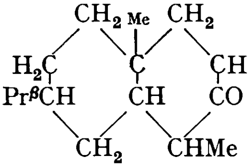
238. *Syntheses in the Sesquiterpene Series. Part III. A Synthesis of 1 : 10-Dimethyl-7-*iso*propyldecal-2-one.*

By A. E. Bradfield, E. R. Jones, and J. L. Simonsen.

It was shown recently (this vol., p. 667) that the sesquiterpene ketone α-cyperone was represented by (I) and that it gave on catalytic hydrogenation the decalone (II). We now record the synthesis of a ketone which we regard as structurally, although not stereochemically, identical with tetrahydro-α-cyperone (II).


(I.)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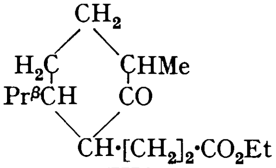
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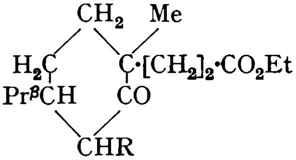
The condensation of *l*-tetrahydrocarvone with ethyl β-chloropropionate in the presence of sodamide can theoretically give a mixture of ethyl 1-methyl-4-*iso*propyl*cyclo*hexan-2-one-3-β-propionate (III) and ethyl 1-methyl-4-*iso*propyl*cyclo*hexan-2-one-1-β-propionate (IV; R = H). The latter, which in our experiments formed the main, if not the sole product of the condensation, was readily purified by condensation with ethyl oxalate, (IV; R = CO·CO_2Et), which was soluble in alkali, being obtained. Isolation of this ester through its sodium salt was found preferable to purification by distillation (compare Ruzicka, Koolhaas, and Wind, *Helv. Chim. Acta*, 1931, **14**, 1169).

Distillation of the ester (IV; R = CO·CO_2Et) after liberation from its sodium salt proceeded smoothly with the loss of carbon monoxide to give *ethyl 3-carbethoxy-1-methyl-4-*iso*propyl*cyclo*hexan-2-one-1-β-propionate* (IV; R = CO_2Et), from which, after hydrolysis with hydrochloric acid and re-esterification, the *ester* (IV; R = H) was obtained. The next stage in the synthesis consisted in the condensation of this ester with ethyl α-bromopropionate in the presence of zinc; it was anticipated that either the hydroxy-ester (V) or the related unsaturated ester would be formed. Condensation, in toluene solution, gave a product distilling with some decomposition over a wide range. An examination of the various fractions indicated that the reaction had proceeded abnormally and that ring closure had occurred. All the fractions reacted with 2 : 4-dinitrophenylhydrazine and gave with alcoholic ferric chloride a bluish-green coloration, the intensity of which increased with rise in boiling point. From the fraction boiling below 190°/11 mm. a scarlet 2 : *4-dinitrophenylhydrazone*, m. p. 187—189°, was prepared, which analysis showed to be derived from a ketone $C_{15}H_{24}O$. For this unsaturated ketone we suggest the structure (VI; R = H),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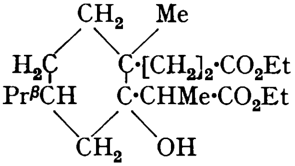
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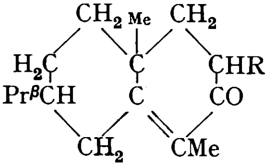
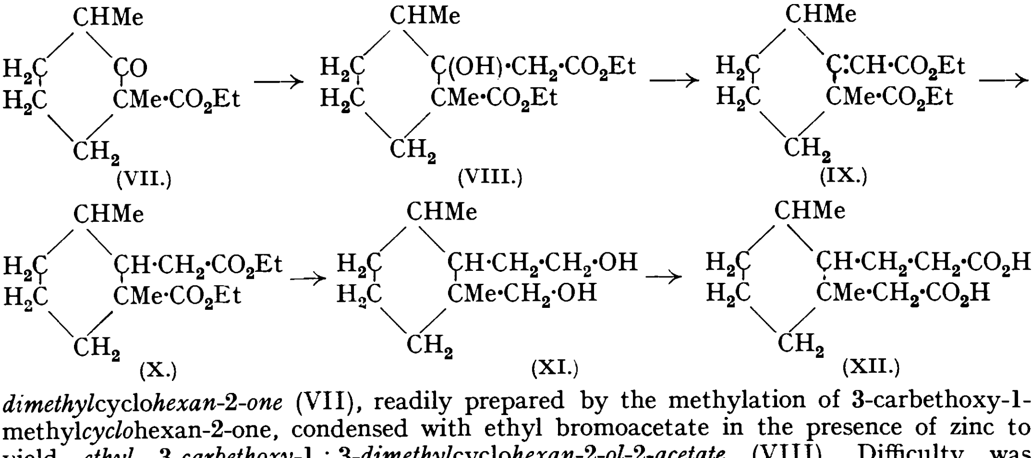

(VI.)

but we have not isolated it in a pure state or determined the position of the ethylenic linkage.

Before it was realised that ring closure with the loss of a carbethoxy-group in a part of the condensation product had already occurred, an attempt was made to hydrogenate the total distillate. This proceeded very slowly and incompletely and on redistillation a low-boiling fraction (up to 175°/10 mm.) was obtained. This fraction, after digestion with methyl-alcoholic potassium hydroxide solution to remove any ester present, gave an oil, b. p. 165—170°/16 mm., from which a 2 : 4-dinitrophenylhydrazone, identical with that referred to above, was prepared. Since this oil consisted, therefore, essentially of an unsaturated ketone, it was catalytically hydrogenated; the product, b. p. 146—155°/11 mm., partly crystallised. The solid crystallised from methyl alcohol in well-formed prisms, m. p. 102—103°. The *decalone*, which was dextrorotatory in chloroform solution, was characterised by the preparation of the *semicarbazone*, m. p. 210°, and the 2 : 4-*dinitrophenylhydrazone*, m. p. 221—223°. In view of the somewhat abnormal manner in which ring closure had occurred, we have confirmed the fact that this ketone is 1 : 10-*dimethyl*-7-iso*propyldecal*-2-*one* (II) by converting it into 1 : 2-dimethyl-7-*iso*propylnaphthalene, the picrate, m. p. 91·5—93°, and the *s*-trinitrobenzene derivative, m. p. 108—110°, of which were identical with those described previously (this vol., p. 670). We believe this to be the first synthetic ketone of the eudalene type, *i.e.*, with an angle methyl group, having a structure identical with that of a hydrogenated, naturally occurring sesquiterpene ketone.

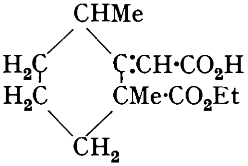
Preliminary experiments have been made with the object of hydrolysing the keto-ester (VI ; $R = CO_2Et$), which the ferric chloride reaction suggested was present in the higher-boiling fractions of the condensation product, with the object of preparing further quantities of the unsaturated ketone. These have so far proved unsuccessful, but further experiments will be instituted when material is available. It is anticipated that the further study of this ketone and of the related saturated ketone will throw light on the stereochemical configurations of α-cyperone and tetrahydro-α-cyperone. We intend also to extend these experiments by replacing tetrahydrocarvone by dihydrocarvone, from which we hope to prepare selinene and hydroxyeremophilone.

Prior to the inception of these experiments we undertook the preparation of 3-*hydroxymethyl*-2-β-*hydroxyethyl*-1 : 3-*dimethyl*cyclo*hexane* (XI) with a view to its conversion into the dicarboxylic acid (XII) *via* the dibromide and dinitrile. Unfortunately the replacement of the hydroxy-groups by bromine could not be effected. The preparation of the glycol was carried out in accordance with the scheme given above. 3-*Carbethoxy*-1 : 3-*dimethyl*cyclo*hexan*-2-*one* (VII), readily prepared by the methylation of 3-carbethoxy-1-methyl*cyclo*hexan-2-one, condensed with ethyl bromoacetate in the presence of zinc to yield *ethyl* 3-*carbethoxy*-1 : 3-*dimethyl*cyclo*hexan*-2-*ol*-2-*acetate* (VIII). Difficulty was experienced in the dehydration of the hydroxy-ester to the unsaturated ester, which could only be carried out by the Darzens process. Unfortunately the unsaturated ester so obtained, which may be regarded as *ethyl* 3-*carbethoxy*-1 : 3-*dimethyl*cyclo*hexylidene*-2-*acetate* (IX), although the position of the ethylenic linkage was not determined, contained


(VII.) (VIII.) (IX.)
(X.) (XI.) (XII.)

impurities which made catalytic hydrogenation to (X) impossible. It was only after it had been kept in contact with aluminium amalgam in ethereal solution for some days that the pure ester could be isolated. This was then hydrogenated at 3 atmospheres pressure with a platinic oxide catalyst to *ethyl* 3-*carbethoxy*-1 : 3-*dimethyl*cyclo*hexan*-2-*acetate* (X), from which, by reduction with sodium and alcohol, the glycol (XI) was obtained. The glycol showed a marked tendency to lose water with the formation of unsaturated substances and it is for this reason probably that all attempts to convert it, or its *diacetate*, into the dibromide failed.

During the experiments which were made to purify the ester (IX), it was hydrolysed with ethyl-alcoholic potassium hydroxide solution; in addition to the *dibasic acid*, m. p. 148—150°, a *hydrogen ester*, m. p. 120—121°, most probably (XIII), was then obtained. On re-esterification with alcohol and sulphuric acid of the liquid hydrolysis products, a mixture resulted, from which by hydrolysis of the appropriate fractions (see p. 1142) two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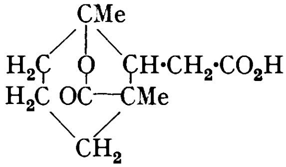
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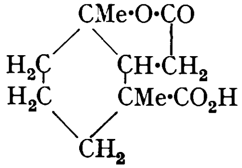
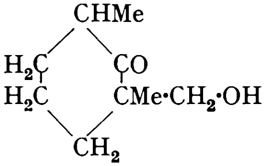
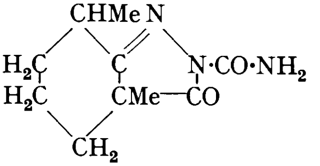

(XV.)

lactonic acids, $C_{11}H_{16}O_4$, were separated; *lactone* (*A*) had m. p. 194—195°, and *lactone* (*B*), m. p. 128—129°. As was anticipated, both these lactones were stable to potassium permanganate in alkaline solution. Their structures were not determined, but they are probably the two lactones (XIV) and (XV).

Since at one time it appeared probable that the keto-alcohol (XVI) would be of value for synthetic purposes, we prepared the *semicarbazone* of 3-carbethoxy-1 : 3-dimethyl-*cyclo*hexan-2-one, from which the alcohol would be obtainable by the method of Asahina and Ishidate (*Ber.*, 1934, **67**, 1202). The yield of the semicarbazone was, however, extremely poor, the main product of the reaction being a crystalline substance, probably 2-*carbamyl*-3-*keto*-7 : 9-*dimethyl*-3 : 4 : 5 : 6 : 7 : 9-*hexahydroindazole* (XVII).

(XVI.)




(XVII.)

In conclusion we may refer to two products which were isolated during the preparation of 3-carbethoxy-1-methyl*cyclo*hexan-2-one by the condensation of ethyl oxalate and 1-methyl*cyclo*hexan-2-one. After the carbethoxy-ketone had distilled, a fraction, b. p. 170—178°/12 mm., was obtained which rapidly solidified and after recrystallisation from methyl alcohol had m. p. 139—140°. Analysis showed this substance to have the composition $C_9H_{10}O_3$, and it is identical probably with the product, m. p. 141°, described by Kötz, Blendermann, and Meyer (*Ber.*,1912, **45**, 3704) which they suggest may be 6-methyl-3 : 4 : 5 : 8-tetrahydrocoumaran-1 : 2-dione. During the recovery of 1-methyl*cyclo*hexan-2-one from the higher-boiling products by hydrolysis with alkali an oil was separated which was 2-*methyl*cyclo*hexyl* 1-*methyl*cyclo*hexan*-2-*one*-3-*carboxylate*, since it gave on hydrolysis 1-methyl*cyclo*hexan-2-one and 1-methyl*cyclo*hexan-2-ol.

EXPERIMENTAL.

Condensation of 1-*Tetrahydrocarvone with Ethyl* β-*Chloropropionate. Ethyl* 1-*Methyl*-4-iso-*propyl*cyclo*hexan*-2-*one*-1-β-*propionate* (IV; R = H).—A mixture of *l*-tetrahydrocarvone (61·6 g.) and sodamide (16 g.) in ether (800 c.c.) was heated under reflux for 5 hours, hydrogen being passed to remove the ammonia liberated. It was then cooled in ice, and ethyl β-chloropropionate (54·8 g.) added with shaking during 15 minutes, sodium chloride separating. The whole was heated for 5 hours, ice added, and the ether separated, dried, and evaporated. Distillation of the residual oil at 14 mm. gave (i) tetrahydrocarvone (18 g.) and two fractions, (ii) b. p. 172—182° (38 g.), and (iii) b. p. 182—240° (12 g.). Hydrolysis of (ii) gave a liquid acid, from which the *semicarbazone*, m. p. 180—181°, was prepared in good yield. This crystallised from methyl alcohol in prisms, m. p. 186—187° (Found : C, 59·4; H, 8·6. $C_{14}H_{25}O_3N_3$ requires C, 59·4; H, 8·8%). As is shown later, this is the semicarbazone of the acid corresponding to (IV; R = H).

No improvement in the yield of the keto-esters was observed when ethyl β-iodopropionate was used in place of the chloro-ester.

To a solution of sodium (5·1 g.) in alcohol (120 c.c.) cooled in salt–ice, a similarly cooled solution of the keto-ester (fraction ii) (57 g.) and ethyl oxalate (45 g.) was added. On being allowed to warm gradually to room temperature (15 hours) a reddish-brown solution resulted, which was poured on ice. The ethereal layer (A) was separated, the alkaline solution acidified with dilute sulphuric acid, and the resulting yellow oil dissolved in ether. The residual oil, remaining after removal of the ether from the dried solution, readily lost carbon monoxide on being heated for 45 minutes at 160—190° and then had b. p. 180—195°/4 mm. (21·6 g.). From the neutral product (A) of the condensation a further quantity (3·8 g.) of the higher-boiling fraction was obtained and the recovered material was re-treated with ethyl oxalate. [This recovered material (58 g.) from several experiments gave ester (30 g.), b. p. 180—195°/4 mm.] *Ethyl 3-carbethoxy-1-methyl-4-*iso*propyl*cyclo*hexan-2-one-1-β-propionate* (IV ; R = CO_2Et), b. p. 186—189°/4 mm., $n_D^{25°}$ 1·4637, $[\alpha]_{5461}$ − 82° (in chloroform, *c* 2·4), was a colourless viscid oil giving with alcoholic ferric chloride a brownish-violet colour (Found : C, 66·5; H, 9·3. $C_{18}H_{30}O_5$ requires C, 66·2; H, 9·2%). The *semicarbazone* crystallised from alcohol in soft needles, m. p. 155° (Found : C, 59·4; H, 8·4. $C_{19}H_{33}O_5N_3$ requires C, 59·5; H, 8·6%).

Hydrolysis of the ester (40 g.) was conveniently effected by digestion with hydrochloric acid (170 c.c.) for 14 hours. The acid (29 g.) was esterified with alcohol (290 c.c.) and sulphuric acid (52 g.) by heating for 20 hours; *ethyl 1-methyl-4-*iso*propyl*cyclo*hexan-2-one-1-β-propionate* (25·7 g.), isolated in the usual manner, had b. p. 174°/11 mm., $d_{25°}^{25°}$ 0·9900, $n_D^{25°}$ 1·4641, $[\alpha]_{5461}$ − 112° (in chloroform, *c* 2·6), $[R_L]_D$ 70·83 (calc., 70·82) (Found : C, 70·6; H, 10·4. $C_{15}H_{26}O_3$ requires C, 70·9; H, 10·2%). The acid prepared by hydrolysis of the ester was an oil yielding a semicarbazone identical with that prepared from the crude acid (see above).

*Condensation of Ethyl 1-Methyl-4-*iso*propyl*cyclo*hexan-2-one-1-β-propionate with Ethyl α-Bromopropionate.*—A mixture of the keto-ester (22·8 g.), ethyl α-bromopropionate (21 g.), and zinc (8 g.) in toluene (150 c.c.) was heated in an oil-bath, a vigorous reaction taking place. After 15 hours the zinc compound was decomposed with dilute sulphuric acid, the toluene separated and dried, and the solvent removed under diminished pressure. On distillation of the residual oil the main fraction had b. p. below 185°/10 mm.; only a small fraction (5·7 g.) had b. p. 185—220°/10 mm.; considerable decomposition occurred. The lower-boiling fraction was treated again with ethyl α-bromopropionate and zinc and ultimately a product, b. p. 170—220°/11 mm., was obtained. From the first fraction, b. p. up to 190°/11 mm., $n_D^{17°}$ 1·4905 (Found: C, 75·0; H, 10·8%), a 2 : *4-dinitrophenylhydrazone* was prepared, which crystallised from alcohol–ethyl acetate in bright scarlet, woolly needles with a metallic reflex, m. p. 187—189° (Found : C, 63·1; H, 6·9. $C_{21}H_{28}O_4N_4$ requires C, 63·0; H, 7·0%). The constitution of the parent ketone is discussed on p. 1137.

The whole of the condensation product was combined, dissolved in alcohol, and shaken with hydrogen in the presence of palladium-norit under 3 atmospheres pressure. Reduction was slow and ceased completely after approximately 40% of the theoretical quantity of hydrogen had been absorbed. On distillation of the product under diminished pressure (10 mm.) two fractions were obtained, (*a*) up to 175° and (*b*) 175—220°, the latter giving an intense green ferric chloride coloration. The lower-boiling fraction (12 g.) was mixed with methyl-alcoholic potassium hydroxide solution (KOH, 5 g.) and heated on the water-bath for 1 hour. Addition of water caused the separation of an oil, which was collected in ether; evaporation of the dried solvent gave a ketone (7 g.), b. p. 165—170°/16 mm., giving a 2 : 4-dinitrophenylhydrazone, m. p. 187—189°, identical with that described above. Without further purification the ketone was reduced in alcoholic solution (palladium-norit catalyst) at the ordinary pressure, the absorption of hydrogen, which was rapid, being slightly below the theoretical amount. The saturated ketone, isolated in the usual manner, had b. p. 146—155°/11 mm., and was a colourless oil which rapidly crystallised on keeping. After addition of methyl alcohol the solid was collected and recrystallised from the same solvent, 1 : *10-dimethyl-7-*iso*propyldecal-2-one* (II) separating in well-formed prisms, m. p. 102—103°, $[\alpha]_{5461}$ + 22·2° (in chloroform, *c* 2·09) (Found : C, 81·3;

H, 11·6. $C_{15}H_{26}O$ requires C, 81·1; H, 11·7%). The *semicarbazone* crystallised from methyl alcohol, in which it was sparingly soluble, in prisms, m. p. 210° (Found: C, 69·2; H, 10·3. $C_{16}H_{29}ON_3$ requires C, 68·8; H, 10·2%), and the 2 : 4-*dinitrophenylhydrazone* from ethyl acetate in orange-yellow silky needles, m. p. 221—223° (some decomp.) (Found: N, 13·9. $C_{21}H_{30}O_4N_4$ requires N, 13·9%). Analysis of a fraction of the total distillate, b. p. 146—147°/11 mm., showed that it contained apparently a small quantity of a hydrocarbon (Found: C, 82·8; H, 12·2%).

Conversion of 1 : 10-*Dimethyl*-7-iso*propyldecal*-2-*one into* 1 : 2-*Dimethyl*-7-iso*propylnaphthalene*.—The product (3·4 g.), b. p. 130—160°/13 mm., of the action of methylmagnesium iodide on the ketone was dehydrogenated by heating with selenium (5 g.) at 300° for 30 hours. The oil obtained, b. p. 130—160°/14 mm., yielded a picrate, m. p. 91·5—93°, and *s*-trinitrobenzene derivative, m. p. 108—110°, both alone and in admixture with the corresponding derivatives prepared from synthetic 1 : 2-dimethyl-7-*iso*propylnaphthalene.

3-*Carbethoxy*-1 : 3-*dimethyl*cyclo*hexan*-2-*one* (VII).—This *ester*, prepared in a yield of 80% in the usual manner from 3-carbethoxy-1-methyl*cyclo*hexan-2-one, had b. p. 115—116°/16 mm., $d_{25^\circ}^{25^\circ}$ 1·003, $n_D^{25^\circ}$ 1·4484 (Found: C, 66·4; H, 9·1. $C_{11}H_{18}O_3$ requires C, 66·7; H, 9·1%). The *semicarbazone*, obtained in 30% yield from the ester and alcoholic semicarbazide acetate, crystallised from alcohol in prisms, m. p. 181° (Found: C, 56·3; H, 8·4. $C_{12}H_{21}O_3N_3$ requires C, 56·4; H, 8·2%). Addition of ammonium sulphate to the water–alcohol solution from which the semicarbazone had been separated precipitated 2-*carbamyl*-3-*keto*-7 : 9-*dimethyl*-3 : 4 : 5 : 6 : 7 : 9-*hexahydroindazole* (XVII), which after crystallisation from alcohol had m. p. 144—147° (Found: C, 57·2; H, 7·1. $C_{10}H_{15}O_2N_3$ requires C, 57·4; H, 7·2%).

Ethyl 3-*Carbethoxy*-1 : 3-*dimethyl*cyclo*hexan*-2-*ol*-2-*acetate* (VIII).—A mixture of 3-carbethoxy-1 : 3-dimethyl*cyclo*hexan-2-one (32 g.), ethyl bromoacetate (33 g.), and zinc (15 g.) was heated in benzene (100 c.c.), the reaction being as a rule complete in 3 hours. The cooled solution was washed twice with dilute sulphuric acid, diluted with an equal volume of ether, and washed repeatedly with dilute sodium carbonate solution. This procedure was essential, as otherwise considerable decomposition occurred on distillation. After removal of the solvents fractionation of the residual oil gave the *hydroxy-ester* (15 g.), b. p. 150—176°/15 mm., which after further distillation had b. p. 172—173°/17 mm., $d_{25^\circ}^{25^\circ}$ 1·074, $n_D^{25^\circ}$ 1·4712. The ester was a somewhat viscid oil having a faint bluish fluorescence (Found: C, 62·6; H, 9·0. $C_{15}H_{26}O_5$ requires C, 62·9; H, 9·1%).

Ethyl 3-*Carbethoxy*-1 : 3-*dimethyl*cyclo*hexylidene*-2-*acetate* (IX) (?).—To a cooled (salt–ice) and mechanically stirred mixture of the hydroxy-ester (50 g.) and pyridine (32 g.) in dry ether (300 c.c.), freshly distilled thionyl chloride (21 g.) was added during 1½ hours. The stirring was continued for a further hour, and the mixture then kept at room temperature over-night. After addition of ice, the ethereal solution was separated, washed with dilute hydrochloric acid and sodium carbonate solution, and dried, and the solvent evaporated. The residual oil distilled mainly at 163—176°/20 mm. (41 g.) and on refractionation the unsaturated ester had b. p. 166—169°/20 mm. The ester, which contained volatile sulphur compounds, could not be purified by distillation (Found: C, 66·0; H, 8·9%). To prepare the pure ester, the product (45 g.) in moist ether (1 l.) was added to freshly prepared aluminium amalgam (100 g.) and kept in the cold for 6 days, water being added from time to time. After filtration the sludge was washed repeatedly with ether, and the combined filtrates dried and evaporated; the pure unsaturated *ester*, b. p. 159°/13 mm., $n_D^{25^\circ}$ 1·4696, was then obtained as a colourless, pleasant-smelling oil (Found: C, 67·1; H, 9·1. $C_{15}H_{24}O_4$ requires C, 67·1; H, 8·9%).

Hydrolysis of Ethyl 3-*Carbethoxy*-1 : 3-*dimethyl*cyclo*hexylidene*-2-*acetate*.—The ester (12·2 g.) was heated for 6 hours with ethyl-alcoholic potassium hydroxide solution (potassium hydroxide, 12·2 g.; ethyl alcohol, 120 c.c.), a crystalline potassium salt separating. This was collected and dissolved in water and the solution was evaporated until free from alcohol and acidified. The gummy acid obtained partly solidified when triturated with formic acid and then crystallised from water in prisms, m. p. 148—150°, containing water of crystallisation, which was removed in a low vacuum at 100° [Found: C, 59·8; H, 7·7; (dried at 100°) C, 62·4; H, 7·6. $C_{11}H_{16}O_4,\frac{1}{2}H_2O$ requires C, 59·7; H, 7·7%. $C_{11}H_{16}O_4$ requires C, 62·3; H, 7·5%).

The alcoholic solution from which the crystalline potassium salt had been separated was freed from alcohol and acidified, a gum (4·6 g.) being obtained. This partly crystallised on keeping and after trituration with formic acid gave a crystalline solid (1·3 g.), m. p. 104—112°, raised to 120—121° by three crystallisations from formic acid, from which it separated in prisms. The *hydrogen ester* (XIII) (?) was unstable to potassium permanganate in alkaline solution (Found: C, 64·7; H, 8·4. $C_{13}H_{20}O_4$ requires C, 65·0; H, 8·3%).

Re-esterification of the liquid acids (34·3 g.), from a similar hydrolysis, with ethyl alcohol

(150 c.c.) and sulphuric acid (30 c.c.) gave an oil which distilled irregularly 170—198°/22 mm., analysis of the various fractions showing them to consist of a mixture of the unsaturated ester and a lactonic ester. Hydrolysis of the fraction, b. p. 187—195°/21 mm. (1·8 g.) (Found : (C, 64·0; H, 8·1%), with ethyl-alcoholic potassium hydroxide solution (potassium hydroxide, 1 g.; ethyl alcohol, 10 c.c.) gave an oil, which partly crystallised. The solid was collected and recrystallised from water, in which it was sparingly soluble, the *lactonic acid A* separating in thick prisms, which, after drying in a low vacuum, had m. p. 194—195° (Found : C, 62·2; H, 7·7; *M*, 212, 100. $C_{11}H_{16}O_4$ requires C, 62·3; H, 7·5%; *M*, 212, 106). The lactonic acid was stable to potassium permanganate in alkaline solution. The *lactonic ester*, prepared by esterification with ethyl alcohol and sulphuric acid, was an oil, b. p. 174—176°/11 mm., $n_D^{25°}$ 1·4700 (Found : C, 65·0; H, 8·5. $C_{13}H_{20}O_4$ requires C, 65·0; H, 8·3%).

When the oil from which the lactonic acid A had been removed was again digested with ethyl-alcoholic potassium hydroxide and the product isolated in the usual manner after acidification, an isomeric *lactonic acid B* was obtained, which crystallised from water in plates, m. p. 128—129° (Found : C, 62·1; H, 7·7%; *M*, 221, 112).

Ethyl 3-*Carbethoxy*-1 : 3-*dimethyl*cyclo*hexan*-2-*acetate* (X).—The unsaturated ester was slowly reduced in alcoholic solution, a platinum oxide catalyst being used under 3 atmospheres pressure. The saturated *ester*, which gave no colour with tetranitromethane, had b. p. 155°/12 mm., $d_{25°}^{25°}$ 1·025, $n_D^{25°}$ 1·4609 (Found : C, 66·8; H, 9·5. $C_{15}H_{26}O_4$ requires C, 66·7; H, 9·6%).

3-*Hydroxymethyl*-2-β-*hydroxyethyl*-1 : 3-*dimethyl*cyclo*hexane* (XI).—To sodium (36 g.) covered with dry xylene, ethyl 3-carbethoxy-1 : 3-dimethyl*cyclo*hexane-2-acetate (27 g.) in absolute alcohol (360 c.c.) was added. The reduction proceeded smoothly and cooling was unnecessary. When the initial reaction had subsided (20 minutes), the mixture was heated at 130° for ½ hour. Water (15 c.c.) was added, the solution heated for a further hour, and concentrated hydrochloric acid (170 c.c.) added slowly down the condenser to the cooled solution. The sodium chloride was removed, and potassium carbonate (200 g.) added. After remaining over-night, the solution was filtered, the carbonate well washed with alcohol, and the alcohol removed through a column. The residue, which contained some water, was dissolved in ether, and the solution dried and evaporated. On distillation the product (11·9 g.) separated into two fractions, (i) b. p. 130—150°/16 mm. (3·9 g.), (ii) b. p. 150—180°/15 mm. (6·6 g.). The higher-boiling fraction, which consisted of the slightly impure *glycol*, was an extremely viscid oil and was analysed without further purification (Found : C, 71·4; H, 11·0. $C_{11}H_{22}O_2$ requires C, 70·9; H, 11·8%). The lower-boiling fraction, which was unsaturated (percamphoric acid value, 10%), evidently consisted of an unsaturated *alcohol* (Found : C, 76·2; H, 11·5. $C_{11}H_{20}O$ requires C, 78·5; H, 11·9%).

The glycol (6·8 g.) in acetic anhydride (40 c.c.) containing a trace of pyridine was boiled for 2 hours. The excess of anhydride was removed through a column, the residue dissolved in ether, the solution washed with sodium carbonate solution and dried, and the solvent evaporated. The *diacetate* was a pleasant-smelling oil, b. p. 136—137°/4 mm. (Found : C, 67·4; H, 9·2. $C_{15}H_{26}O_4$ requires C, 67·7; H, 9·6%). Hydrolysis of the diacetate with sodium hydroxide gave an oil which was not homogeneous, giving on distillation two fractions similar to those referred to above.

The original potassium carbonate extract from which these alcohols had been separated gave on acidification 3-*carboxy*-1 : 3-*dimethyl*cyclo*hexan*-2-*acetic acid* (7 g.), which after crystallisation from water had m. p. 185° (Found : C, 61·8; H, 8·6. $C_{11}H_{18}O_4$ requires C, 61·7; H, 8·6%).

6-*Methyl*-3 : 4 : 5 : 8-*tetrahydrocoumaran*-1 : 2-*dione*(?).—From the residues remaining after the distillation of 3-carbethoxy-1-methyl*cyclo*hexan-2-one an oil, b. p. 170—178°/12 mm., was obtained, which rapidly crystallised on cooling. It was freed from oil by trituration with ligroin (b. p. 40—60°) and then crystallised from dilute methyl alcohol in long needles, m. p. 139—140°. It was very readily oxidised on exposure to the air, giving a gum. For analysis it was dried in a low vacuum over phosphoric oxide (Found : C, 64·8; H, 6·1. Calc. : C, 65·1; H, 6·0%). With alcoholic ferric chloride it gave a violet coloration.

2-*Methyl*cyclo*hexyl* 1-*Methyl*cyclo*hexan*-2-*one*-3-*carboxylate*.—For the recovery of 1-methyl*cyclo*hexan-2-one from the by-products formed in its condensation with ethyl oxalate, the higher-boiling fractions were digested with aqueous potassium hydroxide for some hours, and the ketone removed in steam. The non-volatile residue, isolated with ether, distilled at 181—182°/19 mm. and gave with alcoholic ferric chloride a violet colour (Found : C, 71·1; H, 9·5. $C_{15}H_{24}O_3$ requires C, 71·4; H, 9·5%). The *semicarbazone* crystallised from methyl alcohol in needles, m. p. 152—153° (Found : C, 62·1; H, 8·7. $C_{16}H_{27}O_3N_3$ requires C, 62·1; H, 8·7%);

the 2 : 4-*dinitrophenylhydrazone* separated from the same solvent in orange-yellow needles, decomp. 109—110° (Found: C, 58·1; H, 6·6. $C_{21}H_{28}O_6N_4$ requires C, 58·3; H, 6·5%). Hydrolysis of the oil with methyl-alcoholic potassium hydroxide solution gave 1-methyl*cyclo*hexan-2-one (semicarbazone, m. p. 190°, and 2 : 4-dinitrophenylhydrazone, m. p. 134°, both alone and in admixture with authentic specimens) and 1-methyl*cyclo*hexan-2-ol (phenylurethane, m. p. and mixed m. p. 103—104°).

One of us (E. R. J.) is indebted to the University of Wales for a Fellowship. We have to thank also the Government Grants Committee of the Royal Society, the Chemical Society, and Imperial Chemical Industries, Ltd., for grants.

UNIVERSITY COLLEGE OF NORTH WALES, BANGOR. [*Received, May 25th,* 1936.]