Perhydroindanes. Part IV. Some 1-Substituted Hexahydroindanes.*

By L. E. Coles, W. H. Linnell, David W. Mathieson, and A. S. Shoukri.

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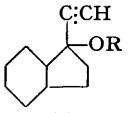
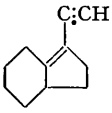
The action of formic acid on 1-ethynylhexahydroindan-1-ol (I; R = H) leads mainly to the non-conjugated ketone (III*a* or *b*). Several bicyclic analogues of cortical hormones, *e.g.*, (VIII) and (IX) have been synthesised.

The ready availability of hexahydroindanone and hence of 1-ethynylhexahydroindan-1-ol prompted investigation of the hydration of the triple bond under various conditions. It was hoped to synthesise thereby some bicyclic analogues of cortical hormones. The direct addition of water to an acetylenic alcohol of type (I; R = H) might be expected to lead to a pinacol rearrangement with the production of a decalol—this is well known in the steroid series (cf. Shoppee and Prins, *Helv. Chim. Acta*, 1943, **26**, 185, 201, 1004; Turner, *J. Amer. Chem. Soc.*, 1953, **75**, 3484). Under the conditions of the Rupe rearrangement, however, the initial step of dehydration to the conjugated vinyl acetylene is followed by addition of the elements of water to the triple bond (Hennion, Davis, and Maloney, *ibid.*, 1949, **71**, 2813): under such conditions rearrangement cannot occur and an αβ-unsaturated ketone results. Thus from ethynyl*cyclo*pentanol, 1-acetyl*cyclo*pentene is obtained (Heilbron, Jones, Toogood, and Weedon, *J.*, 1949, 1827). In one recorded case the action of formic acid on 17-ethynyltestosterone led to the corresponding Δ^{16}-compound by elimination of the elements of water (Inhoffen, Logemann, Hohlweg, and Serini, *Ber.*, 1938, **71**, 1024).

When the alcohol (I; R = H) was refluxed for 45 minutes with 90% formic acid, approximately 50% of a colourless oil was produced consisting mainly of 3-ethynyl-2 : 4 : 5 : 6 : 7 : 8-hexahydroindene (II) with a small amount of an unsaturated conjugated carbonyl component. For identification, the alcohol (I; R = H) was dehydrated with phosphorus oxychloride to give an unequivocal sample of the hydrocarbon (II). This



(I)



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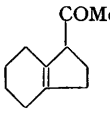
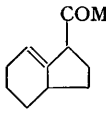
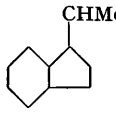


(III*a*)



(III*b*)



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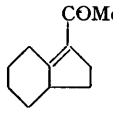


(V)

suggested formulation instead of the alternative with a 2 : 3-double bond, is discussed below. The product (II) was rather unstable and on distillation polymerised appreciably, which explains the low yields obtained. When the reflux period with formic acid was increased to 2½ hr., a carbonyl component was isolated as its semicarbazone in 16—20% yield. It was tentatively formulated as 1-acetyl-4 : 5 : 6 : 7(or 4 : 5 : 6 : 9)-tetrahydroindane (III) because of the analysis, uptake of 1 mol. of hydrogen on catalytic hydrogenation, and absence of evidence of conjugation in the ultra-violet absorption spectrum of the ketone and its semicarbazone. The arrangement of the carbon skeleton was confirmed by hydrogenation to the saturated ketone whence lithium aluminium hydride yielded the

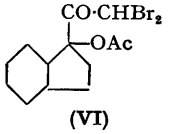
* Part III, *J.*, 1953, 3251.

secondary alcohol (IV). Ketone and alcohol proved identical with samples obtained by the following reactions, X·CO_2H ⟶ X·COMe ⟶ X·CHMe·OH (IV) (X = *cis*-hexahydro-1-indane residue).

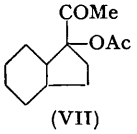
The conjugated ketone (V) was smoothly obtained by addition of aniline to the acetylene (II) in presence of mercuric chloride, followed by hydrolysis of the anil (cf. Stavely, *J. Amer. Chem. Soc.*, 1941, **62**, 3127). Reduction again gave *cis*-1-acetylhexahydroindane. The position of maximum light absorption for the unsaturated ketone (253 mμ) is in agreement with structure (V) : the observed bathochromic shift of 15 mμ between 1-acetyl*cyclo*hexene ($\lambda_{max.}$ 232 mμ) and 1-acetyl-2-methyl*cyclo*hexene ($\lambda_{max.}$ 247 mμ) (Heilbron, Jones, Toogood, and Weedon, *loc. cit.*; Braude, Jones, Koch, Richardson, Sondheimer, and Toogood, *J.*, 1949, 1890) is the same as that observed on comparing (V) with the nearest analogue, 1-acetyl*cyclo*pentene ($\lambda_{max.}$ 239 mμ). Similar conclusions as to the position of the double bond in the hydrocarbon (II) are reached by comparing its spectrum ($\lambda_{max.}$ 234 mμ) with that of 1-ethynyl*cyclo*pentene (227 mμ). The observed bathochromic shift is in agreement with that noted on passing from 1-ethynyl*cyclo*hexene ($\lambda_{max.}$ 223 mμ) to 1-ethynyl-2-methyl*cyclo*hexene ($\lambda_{max.}$ 229 mμ) (Milas, McDonald, and Black, *J. Amer. Chem. Soc.*, 1948, **70**, 1831). Since structures (II) and (V) are thus indicated, it follows that (III*a* or *b*) is the most probable structures for the non-conjugated ketone isolated from the Rupe rearrangement. The conjugated and the non-conjugated ketones (V) and (III) provided an interesting comparison in rates of hydrogenation. Under identical conditions with a palladium catalyst in ethanol, that of (V) was ten times more rapid than that of (III). Whether this is an effect of conjugation as in (V), or of steric hindrance about the double bond and therefore indicating (III*a*) rather than (III*b*) for the non-conjugated ketone, is not known. The suggested sequence of the steps during treatment with formic acid, *viz.*, (I) ⟶ (II) ⟶ (V) ⟶ (III) is in line with previous observations. Thus the initial step in a Rupe rearrangement has been shown to be dehydration to produce a conjugated vinylacetylene (Hennion, Davis, and Maloney, *loc. cit.*). The position of equilibrium for the unsaturated ketones Me·CH_2·CMe:CMe·COMe and Me·CH:CMe·CHMe·COMe has been shown to be 83% in favour of the βγ-isomer (Kon, Abbott, and Satchell, *J.*, 1928, 2514). These are structurally analogous to the present case. It has been reported moreover (Takeshima, *J. Amer. Chem. Soc.*, 1953, **75**, 330) that rearrangement of 3 : 4-dimethylhex-1-yn-3-ol with formic acid gives mainly the βγ-isomer, in agreement with the observed position of equilibrium.

Even samples of non-conjugated ketone (III) purified *via* the semicarbazone showed slight absorption at 250 mμ indicative of an amount of contamination by the αβ-isomer estimated to be about 18% : in conformity there was residual absorption at 260—265 mμ by the semicarbazone.

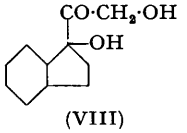
With the failure of these reactions to furnish an easy route to the required cortical analogues, ethynylhexahydroindanol was converted into its acetate (I; R = Ac) and Reichstein's method (*Helv. Chim. Acta*, 1947, **30**, 1616) was adopted. Treatment with *N*-bromoacetamide gave the ωω-dibromo-ketone (VI), which was smoothly debrominated with zinc dust in glacial acetic acid to the ketone (VII). Alternatively, direct addition of aniline to the acetate (I; R = Ac) followed by hydrolysis again gave (VII). This was converted into 1-acetoxy-1-ω-bromoacetylhexahydroindane, and on treatment of this with sodium hydroxide in methanol the bromine atom was replaced by hydroxyl and the ester group was hydrolysed : 1-glycollylhexahydroindan-1-ol (VIII) resulted.



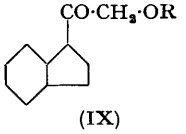
(VI)



(VII)



(VIII)



(IX)

A similar series of reactions on *cis*-1-ethynylhexahydro-8-methylindanol gave the 8-methyl analogue of (VII). Finally for the purposes of biological comparison some related substances were synthesised. The counterpart of (VII) in the decalin series was obtained from *trans*-1-ethynyldecalol. In contrast to the indane compound, 1-acetoxy-1-

ethynyldecalin was easily separated into a crystalline solid and a viscous oil: each was carried separately through the same reactions, to give two 1-acetoxy-1-acetyldecalins, probably isomeric about $C_{(1)}$.

Finally *cis*-hexahydroindane-1-carboxylic acid was converted *via* the diazo-ketone into *cis*-1-ω-acetoxyacetyl- and *cis*-1-glycollylhexahydroindane (IX; R = H and Ac respectively).

Through the courtesy of Dr. A. E. Kellie of the Courtauld Institute of Biochemistry and Dr. R. N. Jones of the National Research Council of Canada, the structurally significant infra-red bands in the annexed Table are recorded. Bands around 1405 cm.$^{-1}$ due to

Substance	Absorption max. (cm.$^{-1}$)	Assignment
1-Acetylhexahydroindane (IX; R = H)	1708 *	Carbonyl
	1353	Acetyl-methyl
(IX; R = Ac)	1753,* 1728, 1705	Carbonyl
	1370	Acetate methyl
(VII)	1732,† 1711	Carbonyl
	1372	Acetate-methyl
	1355	Acetyl-methyl
8-Me homologue of (VII)	1732,† 1711	Carbonyl
	1385	Angular methyl (infl.)
	1372	Acetate-methyl
	1356	Acetyl-methyl
1-Acetoxy-1-ethylhexahydroindane (VIII)	1727 ‡	Carbonyl
	1380	Side-chain methyl
	1367	Acetate-methyl
	3570,† 3430	Hydroxyl
	1710	Carbonyl
	1405	Side-chain methylene
1-Acetoxy-1-acetyldecalin liquid	1732,‡ 1710	Carbonyl
	1372	Acetate-methyl
	1355	Acetyl-methyl
1-Acetoxy-1-acetyldecalin solid	1740,† 1716	Carbonyl
	1370	Acetate-methyl
	1355	Acetyl-methyl

Solvents: * CS_2; † $CHCl_3$; ‡ CCl_4.

unperturbed methylene groups were given by all the compounds. Dr. R. N. Jones reports: "By and large the agreement with true steroids is excellent. Not only do we recognise the same characteristic carbonyl frequencies but also the angular-methyl band at 1380—1385, the acetyl-methyl group at 1350—1355, the acetate-methyl at 1370 and the acetoxymethyl-methylene band at 1410—1415 cm.$^{-1}$."

Experimental

Quantitative hydrogenations were on a micro-scale with PtO_2.

1-Ethynylhexahydroindan-1-ol (I; R = H).—Hexahydroindanone (Mathieson, *J.*, 1953, 3248) (10·6 g.) in dry benzene (200 ml.) was added to a solution from potassium (20 g.) in *tert.*-amyl alcohol (260 ml.). This was added dropwise with stirring during 20 min. to dry ether (500 ml.) through which acetylene had been bubbling for 1 hr. Stirring and passage of acetylene was continued for 7 hr. A saturated solution of ammonium chloride (150 ml.) was then added followed by concentrated hydrochloric acid to acidity to Congo-red. Ether-extraction gave the *acetylene* as a colourless oil (10 g.), b. p. 73°/1 mm., n_D^{18} 1·5042 (Found: C, 80·0; H, 9·7; absorbed 2·0 H_2. $C_{11}H_{16}O$ requires C, 80·4; H, 9·8%). The 3:5-*dinitrobenzoate* crystallised from aqueous ethanol in needles, m. p. 114—115° (Found: C, 60·0; H, 4·8; N, 8·1. $C_{18}H_{18}O_6N_2$ requires C, 60·3; H, 5·0; N, 7·8%).

The acetylenic alcohol (8·5 g.) in dry pyridine (25 ml.) was refluxed with acetic anhydride (25 ml.) for 15 hr. Pouring on ice and ether-extraction gave the *acetate* (I; R = Ac) (8 g.), b. p. 80°/3 mm., n_D^{18} 1·4860 (Found: C, 75·8; H, 8·9. $C_{13}H_{18}O_2$ requires C, 75·8; H, 8·7%). This ester absorbed 2 mols. of hydrogen in ethyl acetate at Adams's platinum oxide to give *1-acetoxy-1-ethylhexahydroindane*, b. p. 94—96°/3 mm., n_D^{22} 1·4700 (Found: C, 74·5; H, 10·7. $C_{13}H_{22}O_2$ requires C, 74·3; H, 10·5%).

Rupe Rearrangement of the Alcohol (I; R = H).—(*a*) 1-Ethynylhexahydroindanol (5 g.) was refluxed for 50 min. under nitrogen with 90% formic acid (30 ml.). After neutralisation with sodium hydroxide, ether-extraction gave a colourless oil (2·44 g.) which was fractionated, with the results tabulated.

B. p./1·5 mm.	Yield (mg.)	Micro-hydrogen (H_2, mols.)	$\lambda_{max.}$ (mμ)	$\varepsilon_{max.}$	Reaction with $AgNO_3$	Semi-carbazone	Iodoform test
52—55°	434	2·0	233	3950	Ppt.	—	—
55—65	240	1·5	234	4600	Ppt.	—	—
65—70	414	0·8	237	2600	Faint ppt.	+	—
70	546	0·65	243	2300	No ppt.	+	+

(*b*) 1-Ethynylhexahydroindanol (10·3 g.) with boiling 90% formic acid for 2½ hr. gave a colourless oil (2·3 g.), b. p. 79—89°/8 mm. Based on semicarbazone formed the yield is 16—20%. The *semicarbazone* crystallised in colourless plates from 50% ethanol and after five recrystallisations had m. p. 139—141° (Found: C, 65·2; H, 8·8; N, 19·1. $C_{12}H_{19}ON_3$ requires C, 65·2; H, 8·6; N, 19·0%), $\lambda_{max.}$ 228 mμ (ε 17,380). Decomposition of a sample of semicarbazone, m. p. 128—138° ($\lambda_{max.}$ 230 mμ, ε 15,330) with sulphuric acid gave the *acetylindane* (III), b. p. 91°/10 mm., n_D^{21} 1·5080 (Found: C, 80·9; H, 9·9; absorbed 0·9 H_2. $C_{11}H_{16}O$ requires C, 80·4; H, 9·8%). That no rearrangement had occurred during decomposition of the semicarbazone was shown by re-formation of the semicarbazone, m. p. 128—138°. The brick red 2 : 4-*dinitrophenylhydrazone* was unstable on recrystallisation; a crude sample had m. p. 140—142° (Found: N, 16·2. $C_{17}H_{20}O_4N_4$ requires N, 16·3%).

Hydrogenation (palladium in ethanol) of the ketone gave 1-acetylhexahydroindane which after reduction with lithium aluminium hydride in ether gave the alcohol (IV), identified as 3 : 5-dinitrobenzoate (see below).

3-*Ethynyl*-2 : 4 : 5 : 6 : 7 : 8-*hexahydroindene* (II).—Phosphorus oxychloride (6 ml.) in dry pyridine (5 ml.) was added dropwise to the alcohol (I; R = H) (6·6 g.) in pyridine (12 ml.) at such a rate that gentle reflux was maintained. After 1 hr. at 100° the dark mixture was poured on ice. Extraction with light petroleum (b. p. 40—60°) gave the *hydrocarbon* (3·8 g.), b. p. 75°/12 mm., n_D^{25} 1·5205 (Found: C, 88·9; H, 9·7; absorbed 2·6 H_2. $C_{11}H_{14}$ requires C, 90·4; H, 9·7%), $\lambda_{max.}$ 234 mμ (ε 12,790). This material polymerised fairly rapidly at room temperature. It failed to form an adduct with maleic anhydride or benzoquinone in refluxing benzene.

3-*Acetyl*-2 : 4 : 5 : 6 : 7 : 8-*hexahydroindene* (V).—The hydrocarbon (II) (3·2 g.) in benzene (250 ml.) was added to a solution of mercuric chloride (12·9 g.) in water (13 ml.) and aniline (2·3 g.) in benzene (350 ml.). The mixture was stirred at 60° for 18 hr. Hydrochloric acid (36% w/w) (2·43 ml.) was added and the whole was saturated with hydrogen sulphide. After filtration and washing of the precipitate with benzene the combined benzene layers yielded the *ketone* (2·1 g.), b. p. 117—119°/12 mm. A sample purified *via* the semicarbazone had b. p. 101—102°/8 mm., n_D^{20} 1·5110 (Found: C, 80·3; H, 9·7. $C_{11}H_{16}O$ requires C, 80·4; H, 9·8%), $\lambda_{max.}$ 253 mμ (ε 8000), $\lambda_{max.}$ (in CS_2) 1670 cm.$^{-1}$. The *semicarbazone* crystallised in colourless needles (from ethanol), m. p. 211—212° (Found: C, 65·6; H, 8·4; N, 19·3. $C_{12}H_{19}ON_3$ requires C, 65·2; H, 8·6; N, 19·0%), $\lambda_{max.}$ 268 mμ (ε 20,000). The 2 : 4-dinitrophenylhydrazone proved to be unstable. Catalytic hydrogenation of this ketone at a palladium–barium sulphate catalyst led to the absorption of 1·84 atoms of hydrogen per mole; the 2 : 4-dinitrophenylhydrazone of the resultant 1-acetylhexahydroindane had m. p. 97—98°, identical with a specimen described below.

cis-1-*Acetylhexahydroindane*.—Cadmium chloride (20 g.) was added to the Grignard reagent from magnesium (4·8 g.) and sufficient methyl bromide to react with all the magnesium. To this dimethylcadmium, *cis*-hexahydroindan-1-carbonyl chloride (18·6 g.) in dry ether (60 ml.) was added dropwise with stirring and the whole was refluxed for 4 hr. After a further 24 hr. at room temperature the mixture was poured on ice, sufficient dilute sulphuric acid being used to dissolve the cadmium salts. Ether-extraction gave an almost colourless oil which was warmed with 10% potassium hydroxide solution for 3 hr., to cleave any ester formed. Ether-extraction of the alkaline residue gave the *acetyl* compound (11·2 g.), b. p. 122°/15 mm., n_D^{20} 1·4808 (Found: C, 79·3; H, 10·9. $C_{11}H_{18}O$ requires C, 79·5; H, 10·8%). The 2 : 4-*dinitrophenylhydrazone* crystallised from ethanol in orange-yellow plates, m. p. 97—98° (Found: C, 58·8; H, 6·7; N, 16·1. $C_{17}H_{22}O_4N_4$ requires C, 59·0; H, 6·4; N, 16·2%). The *semicarbazone* crystallised from ethanol in colourless needles, m. p. 187—188° (Found: C, 64·4; H, 9·5; N, 18·5. $C_{12}H_{21}ON_3$ requires C, 64·6; H, 9·4; N, 18·8%).

Hexahydro-1-1′-*hydroxyethylindane*.—1-Acetylhexahydroindane (1·78 g.) in dry ether (50 ml.) was added dropwise to a solution of lithium aluminium hydride (1·8 g.) in dry ether (75 ml.). When gas evolution had ceased water was carefully added to destroy excess of reagent, and the mixture was acidified. Ether-extraction yielded the *alcohol* (1·19 g.), b. p. 70—72°/0·1 mm., n_D^{25} 1·4897 (Found: C, 78·4; H, 12·2. $C_{11}H_{20}O$ requires C, 78·5; H, 12·0%). The α-*naphthylurethane* crystallised from light petroleum (b. p. 100—120°) in needles, m. p. 106·5—108° (Found: C, 78·3; H, 8·1; N, 4·3. $C_{22}H_{27}O_2N$ requires C, 78·3; H, 8·1; N, 4·2%). The 3 : 5-*dinitrobenzoate* crystallised in needles, m. p. 89—90·5°, from 90% ethanol (Found: C, 59·7; H, 6·1; N, 7·6. $C_{18}H_{22}O_6N_2$ requires C, 59·7; H, 6·1; N, 7·7%).

1-*Acetylhexahydroindan*-1-*yl Acetate* (VII).—(*a*) Mercuric chloride (18·2 g.) in water (140 ml.) was added to a solution of 1-ethynylhexahydroindan-1-yl acetate (7 g.) and aniline (3·2 g.) in

benzene (700 ml.), and the whole stirred at 60° for 24 hr. Concentrated hydrochloric acid (3 g.) was next added and the mixture was saturated with hydrogen sulphide. After filtration, the aqueous layer was extracted with benzene. The combined organic layers yielded the required *compound* (4 g.), which sublimed at 80°/10 mm. Crystallisation from light petroleum (b. p. 40—60°) gave colourless needles, m. p. 68° (Found: C, 69·7; H, 9·0; OAc, 21·8. $C_{13}H_{20}O_3$ requires C, 69·6; H, 9·0; OAc, 19·2%).

(*b*) 1-Ethynylhexahydroindanyl acetate (I; R = Ac) (2·8 g.) in *tert.*-butanol (35 ml.) was added to a solution of *N*-bromoacetamide (7 g.) and sodium acetate (7 g.) in water (35 ml.). Acetic acid (35 ml.) was then added dropwise with stirring. After 2 hr. a colourless precipitate resulted. The mixture was cooled to 0°, then filtered, 1-*acetoxy*-1-(ωω-*dibromacetyl*)*hexahydroindane* (VI) resulting (4·1 g.). This crystallised from light petroleum (b. p. 80—100°) in colourless needles, m. p. 92—93° (Found: C, 40·8; H, 4·7. $C_{13}H_{18}O_3Br_2$ requires C, 40·8; H, 4·7%). Bromine analyses were variable. This dibromo-ketone (3 g.) was shaken at 80° for 10 min. with zinc dust (12 g.) and sodium acetate trihydrate (12 g.) in acetic acid (150 ml.). The supernatant liquors were decanted from the residual zinc which was washed with ether. Evaporation of the combined solvents gave a residue (1·3 g.) which crystallised from light petroleum (b. p. 80—100°) at −50° in needles, m. p. 64—65°, identical with a sample synthesised as in (*a*) above.

1-*Glycolloylhexahydroindan*-1-*ol* (VIII).—The above compound (VII) (7·6 g.) was dissolved in glacial acetic acid (200 ml.) at 50° and to the solution was added bromine (6 g.) in acetic acid (100 ml.), followed by a few drops of hydrogen bromide in the same solvent. After 30 minutes' stirring the almost colourless solution was poured into water and the precipitate crystallised from light petroleum (b. p. 60—80°). 1-*Bromoacetylhexahydroindane*-1-*yl acetate* (8·16 g.) was thus obtained in colourless needles, m. p. 118—119° (Found: C, 51·2; H, 6·3; Br, 26·9. $C_{13}H_{19}O_3Br$ requires C, 51·5; H, 6·3; Br, 26·4%).

The bromo-ketone (5 g.) in ether (20 ml.) was added to sodium hydroxide (1·5 g.) in 50% aqueous methanol (400 ml.). After 1 hr. at room temperature under nitrogen, the solution was made faintly acid to litmus with concentrated hydrochloric acid, then evaporated under reduced pressure to one-third of its volume. The residue was saturated with salt and extracted with ether, to give the *diol* (VIII) (1·2 g.), crystallising from light petroleum (b. p. 60—80°) in plates, m. p. 108° (Found: C, 66·7; H, 9·0. $C_{11}H_{18}O_3$ requires C, 66·7; H, 9·1%). This reduced Fehling's solution and gave a silver mirror with ammoniacal silver nitrate.

cis-*Hexahydro*-8-*methylindanone*.—This was synthesised essentially as described by Bachmann and Kushner (*J. Amer. Chem. Soc.*, 1943, **65**, 1963).

cis-1-*Ethynylhexahydro*-8-*methylindanol* was prepared, in the manner described above for 1-ethynylhexahydrindanol, from *cis*-hexahydro-8-methylindanone (7·5 g.). It was obtained as a colourless oil (2·7 g.), b. p. 104°/8 mm. (Found: C, 80·5; H, 10·0; absorbs 2·0 H_2. $C_{12}H_{18}O$ requires C, 80·9; H, 10·1%). Subsequent steps were identical with those described for the corresponding substances lacking the 8-methyl group.

cis-1-*Ethynylhexahydro*-8-*methylindanyl acetate* had b. p. 106°/9 mm. (Found: C, 76·5; H, 8·9. $C_{14}H_{20}O_2$ requires C, 76·4; H, 9·1%).

cis-1-*Acetoxy*-1-(ωω-*dibromoacetyl*)*hexahydro*-8-*methylindane* crystallised from light petroleum (b. p. 60—80°) in pale buff needles, m. p. 141° (Found: C, 42·1; H, 4·9. $C_{14}H_{20}O_3Br_2$ requires C, 42·4; H, 5·1%).

cis-1-*Acetylhexahydro*-8-*methylindan*-1-*yl acetate* crystallised from light petroleum (b. p. 40—60°) in needles, m. p. 52—53° (Found: C, 70·3; H, 9·1. $C_{14}H_{22}O_3$ requires C, 70·6; H, 9·2%). Under the usual conditions, neither this compound nor (VII) formed a 2:4-dinitrophenylhydrazone or semicarbazone.

trans-1-*Ethynyldecal*-1-*yl Acetate*.—*trans*-1-Ethynyldecal-1-ol (Dimroth, *Ber.*, 1938, **71**, 1333) (17 g.) with acetic anhydride in dry pyridine gave the acetate (18·5 g.), b. p. 96°/2 mm., n_D^{18} 1·4955. Crystallised from light petroleum (b. p. 40—60°; 40 ml.) at 0° an *isomer* (6·5 g.) was obtained which, recrystallised from the same solvent, had m. p. 79—80° (Found: C, 76·6; H, 9·3. $C_{14}H_{20}O_2$ requires C, 76·4; H, 9·1%). After removal of all crystalline material the residue, a viscous oil, had b. p. 127°/8 mm., n_D^{20} 1·4960 (10 g.) (Found: C, 76·4; H, 9·2%). These fractions are designated (sol.) and (liquid) respectively. The mixture of the two acetates absorbed four atoms of hydrogen per mole at PtO_2 in ethanol, yielding 1-*acetoxy*-1-*ethyldecalin*, b. p. 135°/15 mm., n_D^{22} 1·5751 (Found: C, 75·0; H, 10·5. $C_{14}H_{24}O_2$ requires C, 75·0; H, 10·7%). The undernoted compounds were obtained in the manner described above for the synthesis of the indane derivatives (VI) and (VII).

1-*Acetoxy*-(ωω-*dibromoacetyl*)*decalin* (sol.) crystallised from light petroleum (b. p. 60—80°) in needles, m. p. 93° (Found: C, 43·0; H, 4·9. $C_{14}H_{20}O_3Br_2$ requires C, 42·4; H, 5·1%).

1-*Acetyldecal*-1-*yl acetate* (sol.) was obtained as a viscous colourless oil, b. p. 114°/3 mm., n_D^{18} 1·4862 (Found : C, 70·9; H, 9·2; OAc, 18·1. $C_{14}H_{22}O_3$ requires C, 70·6; H, 9·2; OAc, 18·1%). The 2 : 4-*dinitrophenylhydrazone* crystallised from ethanol in light yellow plates, m. p. 179—180° (Found : C, 57·6; H, 6·0; N, 13·3. $C_{20}H_{26}O_6N_4$ requires C, 57·5; H, 6·2; N, 13·4%).

1-Acetoxy-1-(ωω-dibromoacetyl)decalin (liq.) decomposed on attempted purification and the crude material was carried on to the next stage, giving 1-*acetyldecal*-1-*yl acetate* (liq.) as a colourless oil, b. p. 122°/3 mm., n_D^{18} 1·4910 (Found : C, 70·4; H, 9·2; OAc, 18·2. $C_{14}H_{22}O_3$ requires C, 70·6; H, 9·2; OAc, 18·1%).

cis-1-*Acetoxyacetylhexahydroindane* (IX; R = Ac).—*cis*-Hexahydroindane-1-carboxylic acid (Mathieson, *J.*, 1953, 325) (1·16 g.) was refluxed with thionyl chloride (3 ml.) in dry benzene (5 ml.). The acid chloride (1·2 g.), b. p. 115—116°/6 mm., in dry ether was added to ethereal diazomethane (from *N*-nitrosomethylurea, 3·5 g., in ether, 50 ml.). After 16 hr. at room temperature removal of ether gave the *diazo-ketone* which crystallised from light petroleum (b. p. 40—60°) in yellow needles, m. p. 70—71° (decomp.) (Found : N, 14·2. $C_{11}H_{16}ON_2$ requires N, 14·6%). The diazo-ketone (1·12 g.) was then warmed with glacial acetic acid (10 ml.) on the water-bath until evolution of nitrogen was complete (20 min.). Evaporation of the acetic acid under reduced pressure gave a residue which slowly solidified. This sublimed at 80°/0·05 mm. (1·11 g.). Crystallisation from light petroleum (b. p. 60—80°) gave needles, m. p. 60—62° (Knowles, Kuck, and Elderfield, *J. Org. Chem.*, 1942, **7**, 377, give m. p. 59—61°). The *semicarbazone* crystallised from ethanol in colourless needles, m. p. 171—172° (Found : C, 59·7; H, 8·3; N, 14·7. $C_{14}H_{23}O_3N_3$ requires C, 59·8; H, 8·2; N, 15·0%).

cis-1-*Hydroxyacetylhexahydroindane* (IX; R = H).—The diazo-ketone (from hexahydroindane-1-carboxylic acid, 5 g.) in dioxan (25 ml.) was warmed on the steam-bath for 30 min. with N-sulphuric acid (40 ml.). The mixture was diluted with water (200 ml.) and extracted with ether, to yield a light yellow oil, b. p. 90—95°/0·05 mm., which slowly solidified (2·65 g.). Crystallisation from light petroleum (b. p. 60—80°) gave the *ketol* as colourless needles, m. p. 99° (Found : C, 72·4; H, 9·9. $C_{11}H_{18}O_2$ requires C, 72·6; H, 9·9%).

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SCHOOL OF PHARMACY, UNIVERSITY OF LONDON,
17 BLOOMSBURY SQUARE, LONDON, W.C.1. [*Received, March 11th*, 1954.]