## 645. *Perhydroindanes. Part III.** cis-*Hexahydroindane*-1-*carboxylic Acid.*

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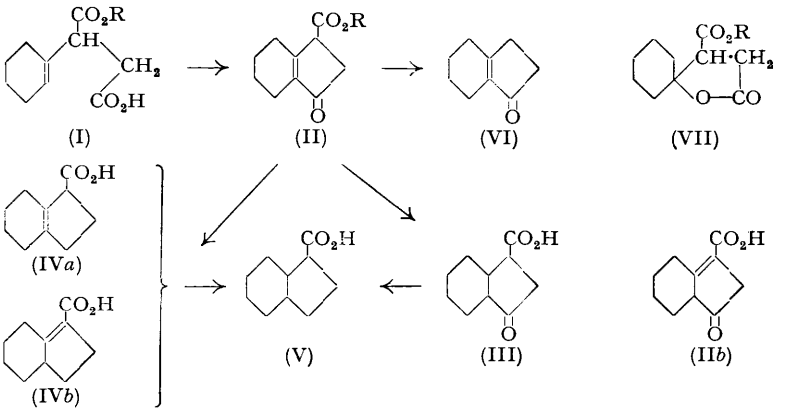
Towards a general synthesis of hexahydroindane-1-carboxylic acids, ring closure of the half ester of *cyclo*hexenylsuccinic acid has been examined. Ethyl 4 : 5 : 6 : 7-tetrahydro-3-oxoindane-1-carboxylate (II) thus formed has been reduced to *cis*-hexahydroindane-1-carboxylic acid. With hydrazoic acid this has been converted into the known *cis*-1-aminohexahydroindane.

THREE methods have previously been described which could conceivably be used for the synthesis of hexahydroindane-1-carboxylic acids from suitably substituted *cyclo*hexanes. First, ethyl hexahydro-2-oxoindane-1-carboxylate has been obtained by a Dieckmann reaction on ethyl *cyclo*hexane-1 : 2-diacetate (Hückel and Friederich, *Annalen*, 1927, **451**, 132). Secondly, the corresponding 3-oxo-derivative has similarly been made from ethyl 2-ethoxycarbonyl*cyclo*hexylsuccinate (Chatterjee, *J. Indian Chem. Soc.*, 1937, **14**, 419). Thirdly, ring closure of ethyl hydrogen *cyclo*hexenylsuccinate has been described by Johnson, Davis, Hunt, and Stork (*J. Amer. Chem. Soc.*, 1948, **70**, 3021). In all cases, however, the intermediate keto-esters were utilised for final compounds other than the acid required in the present instance. It was decided to investigate the last-named method further, since a large variety of such *cyclo*hexenylsuccinic acids were potentially available

* Part II, preceding paper.

in a single step from the corresponding *cyclo*hexanones by the Stobbe condensation. Reduction of the resulting keto-esters was expected to furnish the hydroindane-1-carboxylic acids.




*cyclo*Hexanone was condensed in presence of potassium *tert.*-butoxide with diethyl succinate (Johnson *et al.*, *loc. cit.*), but the product required extensive fractionation before satisfactory analytical figures could be obtained. When dimethyl succinate was used an unsaturated acid, m. p. 73—74°, was readily obtained. Its constitution as β-*cyclo*hex-1-enyl-β-methoxycarbonylpropionic acid (I; R = Me) follows from the following observations : (*a*) absorption of one mol. of hydrogen to yield, after hydrolysis, *cyclo*hexylsuccinic acid, (*b*) formation of *cyclo*hex-1-enylsuccinic acid on treatment with barium hydroxide, (*c*) absence of *cyclo*hexanone on permanganate oxidation, and (*d*) absence of light absorption at *ca.* 210 mμ in ethanol, a characteristic of the corresponding *cyclo*hexylidene compound.

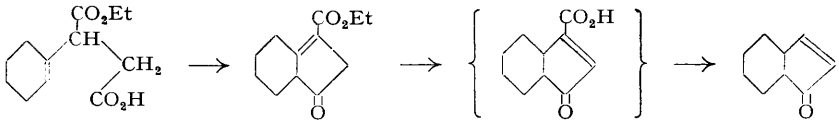
A similar product, m. p. 73·5—74·5°, has been described by Robinson and Seijo (*J.*, 1941, 582) as resulting from the condensation of *cyclo*hexanone and dimethyl succinate in presence of sodium methoxide, the constitution assigned by them being that of a methyl paraconate (VII; R = Me). Repetition of their work yielded no crystalline fraction insoluble in bicarbonate : it is here that any methyl paraconate would be found. From the fraction soluble in bicarbonate, a product, m. p. 73—74°, resulted, identical with that obtained when potassium *tert.*-butoxide was used. This compound, moreover, gave a large depression of the melting point on admixture with an authentic specimen of (VII), and it seems probable that the material obtained by Robinson and Seijo was (I; R = Me). Although initial ring-closure experiments were carried out on this methyl hydrogen ester, it was subsequently found equally satisfactory to utilise the once distilled crude oil which resulted when diethyl succinate was used, since distillation after ring closure sufficed for purification.

The action of various cyclising agents on these half esters is shown in the accompanying Table. The main product was a viscous oil previously assigned the structure (II*b*; R = Me or Et) (Johnson *et al.*, *loc. cit.*). The light absorption of this unsaturated keto-ester and related compounds, however, suggested that it was ethyl 4 : 5 : 6 : 7-tetrahydro-3-oxoindane-1-carboxylate (II). This was supported by its chemical properties. Careful

| Substance | Reagent | Products | Yield (%) | Substance | Reagent | Products | Yield (%) |
|---|---|---|---|---|---|---|---|
| I; R = Me | $ZnCl_2$–$Ac_2O$ | II; R = Me | 56—60 | Acid chloride of (I; R = Et) | $SnCl_4$ | II; R = Et | 36 |
| I; R = Et | $ZnCl_2$–$Ac_2O$ | II; R = Et | 55 | | | | |
| I; R = Et | $F{\cdot}SO_3H$ (room temp.)* | II; R = Et | 60 | Oily fraction (II; R = Me ?) | $ZnCl_2$–$Ac_2O$ | II; R = Me | 20 |
| | | VII; R = H | 20 | | | | |
| I; R = Et | $F{\cdot}SO_3H$ (100°) | II; R = H | 30 | | | | |
| | | II; R = Et | 25 | | | | |
| | | VI | 5 | | | | |

* Wilson Baker, Coates, and Glockling, *J.*, 1951, 1376.

hydrolysis of (II; R = Et) with barium hydroxide gave an acid, presumably (II; R = H), which on treatment with Brady's reagent yielded the dinitrophenylhydrazone of the starting keto-ester (for similar esterifications of keto-acids, cf. Ansell and Hey, *J.*, 1950, 2874). The acid was unstable, readily losing carbon dioxide at room temperature under a slight vacuum—behaviour identical with that of the acid fraction (II; R = H) isolated



from the fluorosulphonic acid ring closure (Table) and intelligible on the basis of formula (II) which is the vinylogue of a β-keto-acid. A possible alternative course shown above has already been demonstrated in the equilenin series (Johnson, Gutsche, Hirschmann, and Stromberg, *J. Amer. Chem. Soc.*, 1951, **73**, 322). It is ruled out in the present instance since the decarboxylation product of the acid fraction yielded only 4 : 5 : 6 : 7-tetrahydroindanone (VI) and none of the $\Delta^2$-isomer.

| | Ketone * | | 2 : 4-Dinitrophenylhydrazone † | | Semicarbazone * | |
|---|---|---|---|---|---|---|
| | $\lambda_{max.}$ (Å.) | *E* | $\lambda_{max.}$ (Å.) | *E* | $\lambda_{max.}$ (Å.) | *E* |
| (II; R = Me, Et) | 2375 | 10,000 | 3880 | 30,000 | 2670 | 25,500 |
| (III) ..... | 2880 | 21 | 3650 | 24,600 | 2300 | 12,500 |

* In ethanol. † In chloroform.

The light absorption (Table) of (II) and its semicarbazone confirms the presence of an αβ-unsaturated ketone grouping in this material and the values recorded agree with those of the corresponding derivatives of tetrahydroindanone (VI) (Part I, *J.*, 1951, 177; Hamlet, Henbest, and Jones, *J.*, 1951, 2652). The 2 : 4-dinitrophenylhydrazone is, however, anomalous: the main band at 2880 Å lies intermediately between those for the dinitrophenylhydrazones of the saturated hexahydroindanone (3670 Å) (Part II) or (III) (3650 Å) and the conjugated ketone (VI) (3950 Å). Such a value seems not inconsistent with structure (II*b*) where the double bond is conjugated with the ethoxycarbonyl grouping. The situation is similar to that with Hagemann's ester. Infra-red absorption measurements in $CS_2$ solution indicate that the ketone (VI) and the keto-ester (II) show a band at 1702 cm.$^{-1}$ assigned to the αβ-unsaturated keto-group, whilst, in addition, (II) possesses a band at 1735 cm.$^{-1}$ similar to that of *aetio*cholanic esters (1742—1737 cm.$^{-1}$) and assigned therefore to the ethoxycarbonyl group (Jones and Dobriner, *Vitamins and Hormones*, 1949, **7**, 293).

Clemmensen reduction of the unsaturated keto-ester (II; R = Me or Et) yielded an oily mixture of unsaturated acids, probably (IV*a* and *b*), which absorbed one mol. of hydrogen at Adams platinum oxide to give about 75% of a crystalline hexahydroindane-1-carboxylic acid (V), m. p. 88—92°. Several recrystallisations from light petroleum raised the m. p. to 95—96°. By dissolving the oily mixture of unsaturated acids in light petroleum and storage in the refrigerator for several months, a small amount of a crystalline tetrahydroindanecarboxylic acid (IV) was obtained (m. p. 126·5—127°) also produced by bromination of hexahydroindane-1-carboxylic acid followed by removal of the elements of hydrogen bromide. The presence of the double bond was confirmed by quantitative microhydrogenation. This substance showed maximum absorption at 2340 Å (*E* 12,000), a somewhat long wave-length for αβ-unsaturated acids which normally absorb at 2180 Å (Ungnade and Ortega, *J. Amer. Chem. Soc.*, 1951, **73**, 1564) even if allowance is made for strain. The nature of this by-product is obscure, and insufficient was available for further investigation. Its presence in the oily product from the Clemmensen reduction, however, made it impossible to detect absorption at 2180 Å typical of αβ-unsaturated acids.

In presence of palladium, the keto-ester (II; R = Et) yielded hexahydro-3-oxoindane-1-carboxylic acid (III) after hydrolysis. Although the m. p. of this substance and its semicarbazone do not agree with values previously reported (Chatterjee, *loc. cit.*), the light absorption of the ketone and its derivatives is identical with that of hexahydroindan-

1-one (Part II). Clemmensen reduction of (III) moreover yielded the same perhydro-acid (V) as before, the identity being confirmed as follows. Indene-1(3)-carboxylic acid was reduced with hydrogen at Adams platinum oxide. With acetic acid as solvent (Knowles, Kuck, and Elderfield, *J. Org. Chem.*, 1942, **7**, 377) uptake of hydrogen proceeded sluggishly but in ethyl alcohol occurred smoothly in two stages, first to give indane-1-carboxylic acid and then to saturate the benzene ring. In presence of a small amount of hydrogen chloride, simultaneous reduction and esterification took place and ethyl hexahydroindane-1-carboxylate was distilled directly from the reaction mixture. Hydrolysis yielded the free acid, identical with that synthesised as above.

By the principle of one-sided addition of hydrogen (Linstead, Doering, Davis, and Whetstone, *J. Amer. Chem. Soc.*, 1942, **64**, 1985; Linstead and Whetstone, *J.*, 1950, 1431), hydrogenation of the indane nucleus under such conditions should yield a *cis*-perhydro-material. The concept of catalyst hindrance suggests that the carboxyl group would be *trans* to the hydrogen atom at $C_{(8)}$. Such conclusions are likewise reached by consideration of (IV). Thus, as with isolated double bonds, the catalytic addition of hydrogen to C:C $\alpha\beta$ to a carbonyl function proceeds mainly in *cis*-fashion (cf., *inter al.*, Weidlich and Meyer-Delius, *Ber.*, 1941, **74**, 1195, 1213) and in the present case involving (IV*a* or *b*) would occur so as to produce from such relatively planar unsaturated structures that form of lowest energy, a *cis*-hydroindane. Under such conditions of addition the carboxyl group is of necessity *trans* to the 8-hydrogenation.

These predictions have been partly confirmed by the degradation of hexahydroindane-1-carboxylic acid, with sodium azide, to *cis*-1-aminohexahydroindane. The benzoyl derivative had the melting point recorded by Hückel, Sachs, Yantschulewitsch, and Nerdel (*Annalen*, 1935, **518**, 155).

## Experimental

β-cyclo*Hex*-1-*enyl*-β-*methoxycarbonylpropionic Acid* (I).—To a solution of potassium *tert.*-butoxide (from potassium, 42 g., and dry *tert.*-butanol, 900 ml.) were added *cyclo*hexanone (117 g.) and dimethyl succinate (146 g.), the mixture being refluxed under nitrogen for 20 min. and then cooled in ice. Concentrated hydrochloric acid (150 ml.) in ice-water (150 ml.) was slowly added so that the temperature did not exceed 20°. Excess of *tert.*-butanol was removed on the steam-bath *in vacuo* and the residue extracted with ether. The acid fraction was isolated in the usual way with 10% aqueous sodium carbonate. There resulted a viscous residue, b. p. 138—140°/0·3 mm. (118 g., 81%). After a few days at room temperature this solidified and was crystallised from light petroleum (b. p. 60—80°). The total solid (A) weighed 60 g. (m. p. 69—72°). A specimen recrystallised several times from light petroleum (b. p. 60—80°) had m. p. 73—74° [Found : C, 62·3; H, 7·6%; equiv., 211; microhydrogenation (Pd–EtOH) 1·0 C:C. $C_{11}H_{16}O_4$ requires C, 62·3; H, 7·6%; equiv., 212]. From the mother-liquors on removal of solvent there resulted a viscous oil (B), b. p. 115—130°/0·1 mm. (45 g.), from which no crystalline material could be isolated.

Fraction (A) was hydrogenated at palladium–charcoal in ethanol, and the product was refluxed for 30 min. with 3N-sodium hydroxide, whereafter acidification yielded *cyclo*hexylsuccinic acid crystallising from water in colourless needles, m. p. 145—146° (Johnson *et al.*, *loc. cit.*, cite m. p. 145—146°).

Fraction (B) on microhydrogenation revealed the presence of 1·1 double bond. Hydrolysis of the resulting material yielded *cyclo*hexylsuccinic acid, m. p. 143—145°.

With barium hydroxide at room temperature fraction (B) yielded a mixture of acids from which *cyclo*hexylidenesuccinic acid, m. p. 193° (decomp.), was isolated by crystallisation from water (Johnson *et al.*, *loc. cit.*, cite m. p. 179—180°) (Found : C, 60·9; H, 7·3. Calc. for $C_{10}H_{14}O_4$ : C, 60·6; H, 7·5%). This acid absorbed 1 mol. of hydrogen in presence of 10% palladised carbon, to yield *cyclo*hexylsuccinic acid, m. p. 144—145°.

Potassium permanganate (3·19 g.) in water (180 ml.) was added during 2½ hr. with stirring at 0° to fraction (B) (2·2 g.) in a solution of sodium carbonate (2·13 g.) in water (10 ml.). Steam-distillation of the mixture into a solution of 2 : 4-dinitrophenylhydrazine yielded *cyclo*hexanone 2 : 4-dinitrophenylhydrazone (0·63 g.), m. p. and mixed m. p. 159—160°.

Similar treatment of the crystalline fraction (A) yielded no *cyclo*hexanone. Fraction (A) is thus β-cyclo*hex*-1-*enyl*-β-*methoxycarbonylpropionic acid*, whilst fraction (B) appears to contain in addition some of the *cyclo*hexylidene analogue [cf. ring closure experiment (d) below].

β-Ethoxycarbonyl-β-*cyclo*hex-1-enylpropionic acid was synthesised as described by Johnson *et al.* (*loc. cit.*).

*Ring-closure Experiments.*—(a) *Zinc chloride–acetic anhydride.* The half ester (I; R = Me) (42 g.) in freshly distilled acetic anhydride (300 ml.) was refluxed (under nitrogen) with acetic acid (300 ml.) containing fused zinc chloride (6 g.) for 4½ hr. Excess of anhydride and acid were removed *in vacuo* and the residue poured into water which was then made alkaline with sodium carbonate. A dried ethereal extract on evaporation gave *methyl* 4 : 5 : 6 : 7-*tetrahydro*-3-*oxoindane*-1-*carboxylate* (II; R = Me) (22 g.), b. p. 112—115°/0·2 mm., $n_D^{21}$ 1·5056 (Found: C, 68·3; H, 7·1. $C_{11}H_{14}O_3$ requires C, 68·1; H, 7·2%). The 2 : 4-*dinitrophenylhydrazone*, m. p. 195—196°, crystallised from xylene in orange plates (Found: C, 54·9; H, 4·8; N, 15·0. $C_{17}H_{18}O_6N_4$ requires C, 54·6; H, 4·8; N, 15·0%). The *semicarbazone* crystallised from methanol in colourless needles, m. p. 210—210·5° (Found: C, 57·5; H, 6·9; N, 16·7. $C_{12}H_{17}O_3N_3$ requires C, 57·4; H, 6·8; N, 16·7%).

β-Ethoxycarbonyl-β-*cyclo*hex-1-enylpropionic acid (I; R = Et) under similar conditions gave a 55% yield of *ethyl* 4 : 5 : 6 : 7-*tetrahydro*-3-*oxoindane*-1-*carboxylate* (II; R = Et), a light yellow oil, b. p. 104—110°/0·1 mm., $n_D^{20}$ 1·5028 (Found: C, 69·5; H, 7·4. $C_{12}H_{16}O_3$ requires C, 69·2; H, 7·7%). The 2 : 4-*dinitrophenylhydrazone* crystallised from acetic acid in orange plates, m. p. 171—172° (Found: C, 55·4; H, 5·2; N, 14·6. $C_{18}H_{20}O_6N_4$ requires C, 55·6; H, 5·2; N, 14·3%). The *semicarbazone* crystallised in colourless needles (from methanol), m. p. 192—193° (Found: C, 58·9; H, 7·2; N, 16·0. $C_{13}H_{19}O_3N_3$ requires C, 58·9; H, 7·2; N, 15·9%). The alkaline mother-liquors on acidification yielded an unsaturated acid crystallising from water in colourless needles, m. p. 144—147° (Found: equiv., 99) (Johnson *et al.*, *loc. cit.*, cite m. p. 145—146° for *cyclo*hex-1-enylsuccinic acid).

Fraction B (p. 3254) (12 g.) was treated as described above with acetic anhydride (100 ml.) and zinc chloride (2 g.) in acetic acid (100 ml.). There resulted a neutral fraction (2·2 g., 20%), b. p. 125—127°/0·6 mm., $n_D^{20}$ 1·5070, which readily gave the 2 : 4-dinitrophenylhydrazone and semicarbazone of the keto-ester (II; R = Me).

(b) *Fluorosulphonic acid.* (i) Freshly distilled fluorosulphonic acid (40 ml.) was added with stirring to the half ethyl ester (I; R = Et) (22 g.) at 0—5° (ice-bath). After 6 hr. at room temperature the mixture was poured on ice, then separated into acid and neutral fractions with 10% sodium carbonate solution. From the neutral product (II; R = Et) (13·4 g.), b. p. 107—110°/0·1 mm., a 2 : 4-dinitrophenylhydrazone, m. p. 171—172°, was obtained giving no depression with a specimen isolated as in (a) above. The acid fraction (4·8 g.) was extracted with successive (100 ml.) portions of benzene, to yield colourless needles (2·25 g.), m. p. 176—180° (recrystallised from water: m. p. 186—187°). This did not depress the m. p. of the paraconic acid (VII; R = H) synthesised by Johnson, Davis, Hunt, and Stork's method.

(ii) Fluorosulphonic acid (20 ml.) was added as above to the half ester (I; R = Et) (11 g.), and the whole then warmed on the steam-bath for 40 min. After working up in the usual way there was obtained a neutral fraction (3·6 g.) which gave 4 : 5 : 6 : 7-tetrahydroindanone, b. p. 80—82°/0·2 mm. (0·3 g.), and the keto-ester (II; R = Et), b. p. 114—116°/0·2 mm. (3 g.). Both were identified as their 2 : 4-dinitrophenylhydrazones. The acid fraction (II; R = H) (3·5 g.) proved to be a dark brown oil which gave the 2 : 4-dinitrophenylhydrazone, m. p. 195—196° (from methanol) of (II; R = Me), and the corresponding derivative, m. p. 171—172° (from ethanol) (II; R = Et).

The acid fraction (1·4 g.) was decarboxylated by warming it gently under reduced pressure. When evolution of gas was complete the residue was distilled, to give a colourless oil (0·26 g.), b. p. 80—85°/0·5 mm. The 2 : 4-dinitrophenylhydrazone crystallised in dark red needles, m. p. 239°, from ethanol. The semicarbazone crystallised in pale yellow needles, m. p. 244—245° (placed in bath at 237°), from dilute acetic acid. Neither derivative gave a depressed m. p. on admixture with the corresponding derivative of 4 : 5 : 6 : 7-tetrahydroindanone (Mathieson, *J.*, 1951, 177).

(c) *Acid chloride–stannic chloride ring closure* [with Dr. E. I. HAIBA]. Thionyl chloride (13 ml.) was added dropwise with stirring at 0° to a mixture of the half ester (I; R = Et) (20 g.) and pyridine (9 g.) in dry ether (140 ml.). The whole was then kept at room temperature for 3 hr. Precipitation of pyridine hydrochloride was completed by the addition of a further quantity of ethereal hydrogen chloride, and the precipitate was filtered off. Evaporation yielded the acid chloride of (I; R = Et) as a colourless viscous oil, b. p. 124—128°/2 mm. (13 g.). This was then added at −7° to −10° to ethylene dichloride (18 ml.) and stannic chloride (15 g.), and after 1 hr. the mixture was allowed to attain room temperature during 10 hr. Ice was then added. Ether-extraction gave a dark brown oil which was refluxed in

collidine (20 g.) for 3 hr. under nitrogen. After acidification with dilute hydrochloric acid the keto-ester was extracted with ether; it had b. p. 114—116°/0·3 mm., $n_D^{20}$ 1·5070 (6·5 g.).

Ethyl 4 : 5 : 6 : 7-tetrahydro-3-oxoindane-1-carboxylate (1·6 g.) in ethanol (10 ml.) was shaken for 14 hr. with barium hydroxide (1·3 g.) in water (50 ml.). The precipitated barium salts were filtered off, suspended in water at 0°, and covered with ether. Dilute hydrochloric acid was then added dropwise with vigorous shaking. From the dried ethereal layer a light brown gum (90 mg.) was obtained which gave the dinitrophenylhydrazone, m. p. 169—171°, of (II; R = Et) on treatment with Brady's reagent in ethanol. When the flask containing the above gum was gently evacuated at 20° vigorous evolution of carbon dioxide occurred. Treatment of the residue with Brady's reagent in ethanol yielded the tetrahydroindanone 2 : 4-dinitrophenylhydrazone (143 mg.), m. p. 239—242°.

*Hexahydro-3-oxoindane-1-carboxylic Acid* (III).—The keto-ester (II; R = Et) (1 g.) in ethanol (10 ml.) was shaken with hydrogen in presence of 5% palladised strontium carbonate (1 g.), 120 ml. being absorbed in 18 hr. Evaporation of the solvent gave a viscous gum, hydrolysed by 20% sodium hydroxide to a keto-acid (600 mg.), m. p. 149—150° (from benzene–light petroleum) (Chatterjee, *loc. cit.*, cites m. p. 136°) (Found: C, 66·4; H, 7·9. Calc. for $C_{10}H_{14}O_3$: C, 66·0; H, 7·7%).

Treatment of the keto-acid with Brady's reagent in methanol gave *methyl hexahydro-3-oxoindane-1-carboxylate 2 : 4-dinitrophenylhydrazone*, crystallising from ethyl acetate in yellow plates, m. p. 196—197° (Found: C, 54·2; H, 5·5; N, 14·7. $C_{17}H_{20}O_6N_4$ requires C, 54·3; H, 5·3; N, 14·9%). All keto-acids described in the present paper suffer such simultaneous esterification when treated with 2 : 4-dinitrophenylhydrazine in sulphuric acid–alcohol solution. The semicarbazone crystallised from *iso*propyl alcohol in colourless needles, m. p. 240—241° (decomp.) (Chatterjee, *loc. cit.*, cites 220°) (Found: C, 55·3; H, 7·3; N, 17·4. Calc. for $C_{11}H_{17}O_3N$: C, 55·2; H, 7·1; N, 17·6%).

*Tetrahydroindane-1-carboxylic Acid* (IV).—(i) Zinc wool (35 g.), amalgamated by being shaken for 30 min. with mercuric chloride (3 g.) in concentrated hydrochloric acid (3 ml.) and water (100 ml.), was covered with 50% hydrochloric acid (100 ml.) and to this was added the ester (II; R = Et) (12·5 g.) in acetic acid (40 ml.). The mixture was refluxed for 10 hr., with occasional additions of hydrochloric acid (5 ml.). From the cold diluted mixture all organic matter was removed by ether-extraction, and the residue left on evaporation freed from acetic acid on the steam-bath under reduced pressure. The brown oil was purified *via* the sodium salt, to give 8·8 g. of acid material. This partly solidified and the solid material (715 mg.) was separated by trituration with ether at −70°. It crystallised from benzene–ethanol in colourless needles, m. p. and mixed m. p. 185—186° [for the paraconic acid (VII; R = H) see Johnson *et al.*, *loc. cit.*]. The oil remaining was fractionated, to yield a colourless oil, b. p. 103—106°/0·1 mm., $n_D^{20}$ 1·5100 (4·7 g.), unsaturated to bromine in carbon tetrachloride and 1% potassium permanganate in acetone. It gave no ketonic reactions. A refractionated sample had b. p. 112—113°/1 mm., $n_D^{20}$ 1·5097 (Found: C, 72·5; H, 8·7%; equiv., 165. $C_{10}H_{14}O_2$ requires C, 72·3; H, 8·4%; equiv., 166). The above oil (1·5 g.) in light petroleum (b. p. 40—60°) (35 ml.) was allowed to remain in the refrigerator for several months. A colourless crystalline acid (120 mg.), m. p. 125—126°, was thus obtained, identical with a sample obtained below.

*Bromination of Hexahydroindane-1-carboxylic Acid.*—The acid (3 g.), bromine (1·2 ml.), and phosphorus trichloride (0·5 ml.) were heated together in a sealed tube on the steam-bath for 3 hr. The resulting dark brown gum was refluxed in collidine (8 ml.) under nitrogen for 3 hr. and then poured into hydrochloric acid. Ether-extraction gave an *acid* fraction (?IV) (400 mg.) as a brown gum which slowly solidified, crystallising from light petroleum (b. p. 40—60°) as colourless needles, m. p. 126·5—127° [Found: C, 72·1; H, 8·3%; microhydrogenation (Pt in EtOH), 1·0 C:C. $C_{10}H_{14}O_2$ requires C, 72·3; H, 8·4%].

*Hexahydroindane-1-carboxylic Acid.*—(i) The above oily acid (IV) (1·65 g.) was hydrogenated in glacial acetic acid (15 ml.) at Adams platinum oxide (140 mg.): 250 ml. hydrogen were absorbed in 90 min. Evaporation gave a gum (1·66 g.) which solidified to colourless needles, m. p. 81—90°. Recrystallised from light petroleum (b. p. 60—80°) there resulted colourless needles of hexahydroindane-1-carboxylic acid, m. p. 88—92° (1·3 g.). On repeated crystallisation a sample had m. p. 94—95° (Found: C, 71·5; H, 9·7%; equiv., 167. Calc. for $C_{10}H_{16}O_2$: C, 71·5; H, 9·5%; equiv., 168). The p-*toluidide* crystallised in colourless needles (from benzene), m. p. 189—190° (Found: C, 79·5; H, 9·2; N, 5·4. $C_{17}H_{23}ON$ requires C, 79·4; H, 9·0; N, 5·5%). The p-*bromophenacyl* ester crystallised from methanol in plates, m. p. 115° (Found: C, 59·2; H, 5·6; Br, 21·7. $C_{18}H_{21}O_3Br$ requires C, 59·2; H, 5·8; Br, 21·9%).

(ii) Hexahydro-3-oxoindane-1-carboxylic acid (1 g.), treated with amalgamated zinc (3 g.)

as described above, gave a colourless oil (200 mg.) which slowly solidified. Crystallised from light petroleum (b. p. 60—80°), colourless needles were obtained having m. p. 94—95°, alone or mixed with a sample from (i).

(iii) (cf. Knowles, Kuck, and Elderfield, *loc. cit.*). Indene-1(3)-carboxylic acid (5 g.) (Courtot, *Ann. Chim.*, 1915, **4**, 58, 82) in ethanol (75 ml.) was hydrogenated in presence of Adams platinum oxide (500 mg.) and 3 drops of concentrated hydrochloric acid. Uptake of 1 mol. occurred in 30 min., followed by a slower uptake (6 hr.) of a further 3 mols. Removal of solvent yielded a colourless oil which was dissolved in ether and washed with 5% sodium carbonate solution. The neutral fraction, *ethyl hexahydroindane-1-carboxylate* (5·2 g., 99%) had b. p. 106—108°/0·5 mm., $n_D^{17}$ 1·4782 (Found : C, 73·5; H, 10·4%; sap. equiv., 196. $C_{12}H_{20}O_2$ requires C, 73·4; H, 10·2%; sap. equiv., 196).

The ester (5 g.) was refluxed for 4 hr. with potassium hydroxide (4·4 g.) in water (45 ml.) and methanol (20 ml.). Precipitation of the acid with hydrochloric acid gave 4·2 g., crystallising from light petroleum (b. p. 60—80°) in colourless needles, m. p. 90—93°. The *p*-toluidide had m. p. 189—190° (from benzene). Mixed m. p.s of this acid and its toluidide with the corresponding substances synthesised from *cyclo*hexanone gave no depression.

When hydrochloric acid was omitted from the above catalytic reduction no ester was isolated and the product consisted solely of hexahydroindane-1-carboxylic acid. No difference in the rate of hydrogen uptake with or without the addition of hydrogen chloride was observed (cf. Brown, Durand, and Marvel, *J. Amer. Chem. Soc.*, 1936, **58**, 1594); the purity of the indenecarboxylic acid used, however, had a marked influence on the speed of reduction.

cis-1-*Aminohexahydroindane*.—Hexahydroindane-1-carboxylic acid (m. p. 94—95°) (0·88 g.) was dissolved in chloroform (25 ml.), and concentrated sulphuric acid (10 ml.) was added. With stirring, sodium azide (0·5 g.) was added gradually so that the temperature remained at 20—25°. After 30 min. at 50° the mixture was poured on to ice, and any non-basic fraction extracted with ether. The aqueous layer was made alkaline with sodium hydroxide and extracted with ether, to yield a base (0·7 g., 99% conversion). This amine (0·35 g.) was benzoylated (Schotten–Baumann), to give *cis*-1-benzamidohexahydroindane (0·42 g., 70%), crystallising from acetone in colourless needles, m. p. 183·5—184°. Hückel, Sachs, Yantschulewitsch, and Niederl (*loc. cit.*) cite m. p. 183—184°.

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