193. *Indene Series. Part II. A Synthesis of 1 : 2 : 3 : 4 : 9 : 10-Hexahydro-2-keto*cyclo*pent*[a]*indene.*

By L. H. GROVES and G. A. SWAN.

The ketone (I) named in the title has been synthesised and converted into 1 : 2 : 3 : 8 : 9 : 10-hexahydro*cyclo*pent[*a*]indene (I; CH_2 instead of CO), but attempts to prepare *cyclo*pent[*a*]indene from it or related substances failed.

IN view of the low yield obtained in the syntheses of 1-keto-1 : 2 : 3 : 8-tetrahydro*cyclo*pent[*a*]-indene * described in Part I (preceding paper), the 2-ketohexhydro-derivative (I) has now been prepared (cf. the synthesis of *cis*-β-*bicyclo*octanone by Linstead and Meade, *J.*, 1934, 935).

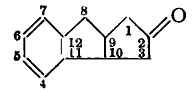
2-Bromoindan-1-one was condensed with ethyl sodiomalonate, to give ethyl 1-keto-2-indanylmalonate (III), which on hydrolysis and decarboxylation yielded the keto-acid (IV). The derived ethyl ester was subjected to the Reformatsky reaction with ethyl bromoacetate

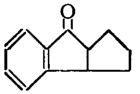
---

* See footnote, p. 863.

and then distilled: the product probably consisted of a mixture of the indene derivative (V) with the indane isomer containing an exocyclic double bond at position 1. A small amount of

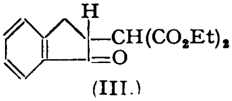
(I.)



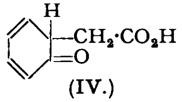


(II.)

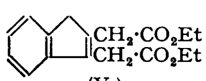
a lactone was also obtained, and this underwent hydrogenolysis in the presence of palladium charcoal to the half-ester (VI; R = H, R′ = Et) which on esterification gave ethyl indane-1 : 2-diacetate (VI; R = R′ = Et). The mixture of unsaturated esters was also hydrogenated



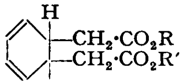
(III.)



(IV.)



(V.)



(VI.)

to this ester (VI; R = R′ = Et), which by Dieckmann cyclisation, followed by hydrolysis yielded 2-keto-1 : 2 : 3 : 8 : 9 : 10-hexahydro-2-keto*cyclo*pent[*a*]indene (I) in 64% yield. The ester (VI; R = R′ = Et) was also hydrolysed to the dibasic acid which on distillation with barium hydroxide at 330—365° gave the same ketone (I).

This ketone was reduced to the corresponding secondary alcohol by lithium aluminium hydride, and dehydration then yielded a liquid olefin, probably a mixture of 1 : 8 : 9 : 10- and 3 : 8 : 9 : 10-tetrahydro*cyclo*pent[*a*]indene. This was recovered unchanged after passage (in the vapour phase) over palladium–charcoal at 330°. Attempts were also made to dehydrogenate it in the liquid phase by palladium, sulphur, selenium, and chloranil, and also by bromination (with bromine or *N*-bromosuccinimide) followed by dehydrobromination (with pyridine, collidine, potassium acetate, etc.). In all cases, either the olefin was recovered unchanged, or black polymeric products resulted.

The ketone (I) was reduced by the Clemmensen method to 1 : 2 : 3 : 8 : 9 : 10-hexahydro*cyclo*pent[*a*]indene (I; CH_2 instead of CO). This hydrocarbon did not give a crystalline nitro-derivative, but the structure was confirmed by oxidation with chromic acid to ketone (II) (Baker and Leeds, *J.*, 1948, 974).

Diethyl indane-2-acetate-1-cyanoacetate was also synthesised, as it was hoped that it might provide an alternative route to the diester (VI; R = R′ = Et), but the yield was low.

The polymeric products resulting from attempts to prepare *cyclo*pent[*a*]indene may be due to its fulvene-like structure. As the introduction of a methyl group at position 8 might be expected to increase the stability of the fulvene structure somewhat (cf. Thiele, *Ber.*, 1900, **33**, 666), the synthesis of 8-methyl*cyclo*pent[*a*]indene was attempted. The ketone (II) was allowed to react with methylmagnesium iodide and the product, after dehydration, was treated first with *N*-bromosuccinimide, then with pyridine; but, as before, polymeric products resulted. The ketone (I) was similarly treated with phenylmagnesium bromide, but attempts to dehydrogenate the resulting olefin with palladium or selenium led to polymerisation.

EXPERIMENTAL.

(All m. p.s are uncorrected.)

Ethyl 1-*Keto*-2-*indanylmalonate* (III).—Indan-1-one (19 g.) in dry ether (150 ml.) was treated dropwise at 10° with bromine (22·9 g.), the solution being stirred briskly, and each drop of bromine was allowed to be decolorised before the next drop was added. The mixture was then stirred at room temperature so that any precipitate formed was dissolved, then poured on ice, the ethereal layer separated, washed with sodium carbonate solution, and dried (Na_2SO_4), and the ether removed by distillation, leaving crude 2-bromoindan-1-one. A solution of this in dry benzene (20 ml.) was added slowly, with external cooling, to a suspension of ethyl sodiomalonate [prepared from ethyl malonate (25 g.) and powdered sodium (2·31 g.) in dry benzene (70 ml.)]. The mixture was heated under reflux on the water-bath for 18 hours, cooled, and diluted with water, and the benzene layer separated, washed with water, dried (Na_2SO_4), and distilled, giving the crude *ester* (26·4 g.), b. p. 188—210°/2 mm. Redistillation afforded a pale yellow oil, b. p. 190—193°/2 mm. (Found: C, 66·05; H, 6·5. $C_{16}H_{18}O_5$ requires C, 66·1; H, 6·2%).

1-*Keto*-2-*indanylmalonic Acid*.—The crude ester (III) (27·8 g.), potassium hydroxide (28 g.), and alcohol (120 ml.) were heated under reflux for 1 hour, the bulk of the alcohol removed (reduced pressure), and water (100 ml.) added. The dark solution was filtered, extracted three times with ether, boiled, cooled in ice, and acidified (dilute hydrochloric acid). A small amount of precipitated tar was filtered off, the filtrate was extracted with ether, the extracts were dried (Na_2SO_4), and the ether was removed by distillation, the *acid* remaining as an oil, which set to a colourless solid (20·9 g.), m. p. 164—165° (decomp.) (Found: C, 61·2; H, 4·7. $C_{12}H_{10}O_5$ requires C, 61·55; H, 4·3%).

1-*Keto-2-indanylacetic Acid.*—The foregoing acid was quantitatively decarboxylated at 170° (oil-bath) (until gas evolution ceased). The *acetic acid* crystallised, on cooling, to a light brown solid, m. p. 143—146°, and separated from dilute methanol as almost colourless needles, m. p. 147—148° (Found: C, 69·25; H, 5·5. $C_{11}H_{10}O_3$ requires C, 69·45; H, 5·25%).

Absolute ethanol (60 ml.), containing the acid (15·6 g.), was saturated at 0° with dry hydrogen chloride, and heated under reflux for 5 hours. The bulk of the ethanol was removed by distillation, and the mixture diluted with water and extracted with ether. The extract was washed with sodium hydrogen carbonate solution, dried (Na_2SO_4), and distilled, giving the *ethyl* ester (16·2 g.) as a pale yellow oil, b. p. 155°/2 mm., which on cooling formed pale yellow crystals, m. p. 39—41° (Found: C, 71·2; H, 6·65. $C_{13}H_{14}O_3$ requires C, 71·55; H, 6·4%). Acidification of the sodium hydrogen carbonate extract gave unchanged acid (1·0 g.).

Reformatsky Reaction between Ethyl Bromoacetate and Ethyl 1-*Keto*-2-*indanylacetate.*—(*a*) The keto-ester (10 g.), ethyl bromoacetate (8·45 g.), zinc wool (5·9 g.), dry benzene (40 ml.), and a particle of iodine were heated on the water-bath until a vigorous reaction started, then removed from the water-bath until this had subsided, and finally heated under reflux for 10 minutes. The mixture was cooled, poured into ice-cold 10% sulphuric acid, and the benzene layer was washed with water and then with sodium carbonate solution, dried (Na_2SO_4), and distilled. The pale yellow oil of boiling range 185—210°/3 mm. (9·1 g.) was a mixture of the olefinic ester (V) and its isomer.

(*b*) When the time of heating was increased to 45 minutes, two fractions were obtained: (i) a colourless oil (7·9 g.), b. p. 185—210°/3 mm., redistillation of which afforded the analytically pure mixture of olefinic esters, b. p. 188—190°/3 mm. (Found: C, 70·65; H, 7·05. Calc. for $C_{17}H_{20}O_4$: C, 70·8; H, 6·95%); and (ii) a viscous yellow *lactone* (1·3 g.), b. p. 228—230°/3 mm., which solidified on cooling and separated from benzene–light petroleum (b. p. 60—80°) as colourless silky needles, m. p. 86° (Found: C, 68·8; H, 6·05. $C_{15}H_{16}O_4$ requires C, 69·2; H, 6·15%).

Diethyl Indane-1 : 2-*diacetate* (VI; R = R′ = Et).—(*a*) The product from the Reformatsky reaction (*a*) or [*b*(i)] above (36 g.) in absolute ethanol (120 ml.) was hydrogenated at atmospheric temperature and pressure (10 hours) in presence of 10% palladium–charcoal (4 g.). After removal of the catalyst, the solution was saturated at 0° with dry hydrogen chloride and heated under reflux for 6 hours. The bulk of the ethanol was removed, and the mixture was diluted with water and extracted with ether. The extracts were washed several times with sodium carbonate solution, dried (Na_2SO_4), and distilled, giving the saturated *diester* (32 g.) as a colourless oil, b. p. 185—195°/3 mm. Redistillation gave the pure ester, b. p. 188°/3 mm. (Found: C, 70·3; H, 7·4. $C_{17}H_{22}O_4$ requires C, 70·35; H, 7·6%).

(*b*) Hydrogenation of the lactone (4·3 g.) in ethanol with palladium–charcoal, followed by esterification, yielded the diester (3·0 g.), b. p. 188°/3 mm.

Indane-1 : 2-*diacetic Acid* (VI; R = R′ = H).—The above ester (1 g.) was heated under reflux for 2 hours with potassium hydroxide (1 g.) in ethanol (5 ml.). The mixture was diluted with water, washed with ether, boiled, cooled, and acidified with dilute hydrochloric acid, precipitating the *acid* (0·7 g.), which after two recrystallisations from hot water had m. p. 146°, forming colourless prisms (Found: C, 66·35; H, 5·75. $C_{13}H_{14}O_4$ requires C, 66·65; H, 6·0%).

1 : 2 : 3 : 8 : 9 : 10-*Hexahydro*-2-*keto*cyclo*pent*[a]*indene* (I).—(*a*) A mixture of the diester (VI; R = R′ = Et) (2·7 g.), benzene (5 ml.), and sodium ethoxide (from sodium, 0·25 g.) was heated (water-bath) for 7 hours, cooled, acidified with concentrated hydrochloric acid (40 ml.), and then heated (water-bath) for a further 12 hours. It was cooled, diluted with water, and extracted with ether, and the extract washed with dilute sodium hydroxide solution, dried (Na_2SO_4), and distilled, affording the *ketone* as a pale yellow oil (1·0 g.), b. p. 135—140°/3 mm. This was purified by heating its semicarbazone with a 50% solution of oxalic acid in water under reflux for 3 hours; it then formed an almost colourless oil, b. p. 131°/2 mm. (Found: C, 83·55; H, 7·4. $C_{12}H_{12}O$ requires C, 83·7; H, 7·0%).

The *semicarbazone* separated as colourless needles (from dilute ethanol), m. p. 200—201° (Found: C, 68·2; H, 6·3. $C_{13}H_{15}ON_3$ requires C, 68·15; H, 6·55%). The 2 : 4-*dinitrophenylhydrazone* separated as orange needles (from ethanol), m. p. 174° (Found: C, 61·5; H, 4·2. $C_{18}H_{16}O_4N_4$ requires C, 61·4; H, 4·55%).

(*b*) A mixture of the acid (VI; R = R′ = H) (0·44 g.) and barium hydroxide (0·09 g.) was heated at 330—365° for 20 minutes. The distillate was extracted with ether and dried (Na_2SO_4) and the ether removed. The residue was distilled under reduced pressure, giving the ketone as a pale yellow oil (0·14 g.), b. p. (bath-temp.) 155—160°/3 mm. The semicarbazone was formed in quantitative yield, m. p. 200° not depressed on admixture with the semicarbazone of the ketone formed as in (*a*).

1 : 2 : 3 : 8 : 9 : 10-*Hexahydro*-2-*hydroxy*cyclo*pent*[a]*indene.*—The ketone (I) (2·65 g.) in absolute ether (22 ml.) was added dropwise to a solution of lithium aluminium hydride (0·3 g.) in ether (35 ml.). After the reaction had subsided, the mixture was kept at room temperature for 15 minutes and finally heated under reflux for 15 minutes. Water was added cautiously, the mixture acidified with dilute sulphuric acid, and the ethereal layer separated, dried (Na_2SO_4), and distilled, giving the *alcohol* as a colourless oil (2·35 g.), b. p. 144—146°/3 mm. (Found: C, 82·4; H, 8·0. $C_{12}H_{14}O$ requires C, 82·75; H, 8·05%).

Dehydration. The alcohol (2·35 g.) and phosphoric oxide (3 g.) in dry benzene (16 ml.) were heated under reflux for 2½ hours, cooled, and treated with water, and the benzene layer was separated. The aqueous layer was extracted several times with ether. The combined organic extracts were washed with sodium carbonate solution, dried (Na_2SO_4), and fractionated. The olefinic mixture was obtained as a colourless mobile oil (1·62 g.), b. p. 115°/15 mm. (Found: C, 92·1; H, 8·0. Calc. for $C_{12}H_{12}$: C, 92·3; H, 7·7%).

1 : 2 : 3 : 8 : 9 : 10-*Hexahydro*cyclo*pent*[a]*indene*.—Amalgamated zinc (4·0 g.), the ketone (I) (1·0 g.), and 1 : 1 hydrochloric acid (4 ml.) were heated under reflux for 24 hours; 1 ml. of concentrated hydrochloric acid was added each 6 hours. The mixture was cooled, diluted with water, and extracted with ether. The extract was dried (Na_2SO_4) and distilled, affording the *hydrocarbon* (0·65 g.) as a colourless mobile oil, b. p. 118—120°/20 mm. (Found: C, 91·4; H, 9·0. $C_{12}H_{14}$ requires C, 91·15; H, 8·85%).

1 : 2 : 3 : 8 : 9 : 10-*Hexahydro*-8-*keto*cyclo*pent*[a]*indene* (II).—The above hydrocarbon (2·9 g.) in acetic acid (5 ml.) was added slowly to chromium trioxide (3·6 g.) in 80% acetic acid (15 ml.). The mixture was left for 1 week at room temperature. *iso*Propyl alcohol was added, the solvents were removed (reduced pressure), the residue was treated with water, and the mixture extracted with ether. The extract was washed with sodium hydrogen carbonate solution, dried (Na_2SO_4), and distilled, giving unchanged hydrocarbon (0·9 g.), b. p. 115—116°/15 mm., and the ketone (1·0 g.) as an almost colourless oil, b. p. 150—153°/15 mm. The 2 : 4-dinitrophenylhydrazone was obtained as scarlet needles (from acetic acid), m. p. 216—217° (not depressed on admixture with an authentic sample) and the semicarbazone as colourless plates (from ethanol), m. p. 240—242° (decomp.) (not depressed on admixture with an authentic sample).

*Attempted Dehydrogenation of Tetrahydro*cyclo*pent*[a]*indene*.—The olefin (0·6 g.) was allowed to pass through the apparatus described by Nunn and Rapson (*J.*, 1949, 825) during 1 hour at 330°. 0·4 G. was recovered unchanged.

Grignard Reaction between (I) *and Phenylmagnesium Bromide*.—(a) 1 : 8 : 9 : 10(? 3 : 8 : 9 : 10)-*Tetrahydro*-2-*phenyl*cyclo*pent*[a]*indene*. The ketone (I) (0·3 g.) in ether (7 ml.) was added to a stirred and cooled Grignard solution prepared from magnesium (0·15 g.) and bromobenzene (0·91 g.). The mixture was heated under reflux for ½ hour and kept overnight at room temperature. Water and then dilute hydrochloric acid were added and the mixture was extracted with ether, and the extracts were dried (Na_2SO_4) and distilled, giving a pale yellow oil (0·24 g.), b. p. (bath-temp.) 180—200°/2 mm., which later solidified. Recrystallisation from methanol afforded the *tetrahydro*-2-*phenyl* compound as colourless stubby prisms, m. p. 117·5—118° (Found: C, 92·8; H, 7·15. $C_{18}H_{16}$ requires C, 93·1; H, 6·9%).

(b) 1 : 2 : 3 : 8 : 9 : 10-*Hexahydro*-2-*hydroxy*-2-*phenyl*cyclo*pent*[a]*indene*. In an experiment on a larger scale (1·84 g. of ketone), a liquid *carbinol* (2·16 g.), b. p. 185°/2 mm., was obtained. It solidified on cooling, and recrystallisation from light petroleum (b. p. 40—60°) gave colourless crystals, m. p. 75·5—76·5° (Found: C, 85·9; H, 7·5. $C_{18}H_{18}O$ requires C, 86·4; H, 7·2%).

The carbinol (1·6 g.) was dehydrated with phosphoric oxide (1·38 g.) in benzene (20 ml.) by heating the mixture under reflux for 3 hours. The olefin (1·2 g.), m. p. 115—117°, was obtained.

2-*Indanylacetic Acid*.—1-Keto-2-indanylacetic acid (1·0 g.), amalgamated zinc (4·0 g.), concentrated hydrochloric acid (6 ml.), and toluene (2 ml.) were heated under reflux for 24 hours, concentrated hydrochloric acid (1 ml.) being added after each 6 hours. The cooled mixture was diluted with water and extracted with ether, the extracts were dried (Na_2SO_4), and the solvent was removed, leaving the crude *acid* (0·7 g.) as light brown crystals, m.p. 84—86°. After being twice recrystallised from dilute methanol it afforded fine colourless needles, m. p. 91—92° (Found: C, 74·7; H, 7·0. $C_{11}H_{12}O_2$ requires C, 75·0; H, 6·8%).

Diethyl Indane-2-*acetate*-1-*cyanoacetate*.—The keto-ester (IV) (3·4 g.) and ethyl cyanoacetate (1·77 g.) were added to a solution of potassium (0·64 g.) in absolute ethanol (10 ml.), and the mixture was kept at room temperature for 1 week, diluted with water, acidified with dilute hydrochloric acid, and extracted with ether. The extract was washed with sodium carbonate solution, dried (Na_2SO_4), and distilled. Half of the original materials was recovered together with 0·8 g. of a light brown viscous oil, b. p. 195—205°/3 mm., which, on cooling, nearly all solidified; after recrystallisation from dilute ethanol the *product* formed colourless prisms, m. p. 105—106° (Found: C, 68·6; H, 6·2. $C_{18}H_{19}O_4N$ requires C, 69·0; H, 6·1%).

Reaction between 1 : 8 : 9 : 10(? 3 : 8 : 9 : 10)-*Tetrahydro*cyclo*pent*[a]*indene and* N-*Bromosuccinimide*.—The olefin (0·55 g.), *N*-bromosuccinimide (0·63 g.), dibenzoyl peroxide (5 mg.), and carbon tetrachloride (5 ml.) were heated under reflux for 1 hour, cooled, and filtered. To the filtrate was added *N*-bromosuccimide (0·63 g.) and dibenzoyl peroxide (5 mg.), and the mixture refluxed for a further ½ hour. It was then filtered, the filtrate washed with sodium hydrogen carbonate solution and dried (Na_2SO_4), and the solvent removed, leaving a dark non-crystalline viscous gum (1·1 g.), containing halogen. This was kept in dry pyridine (5 ml.) for a week at room temperature, depositing a black amorphous powder, which was filtered off. The solution was acidified with dilute hydrochloric acid and extracted with ether, the extract dried (Na_2SO_4), and the solvent removed, leaving a negligible residue.

Reaction between Methylmagnesium Iodide and (II).—To a Grignard solution from methyl iodide (4·5 g.; 300% excess) the ketone (1·9 g.) in dry ether (10 ml.) was added slowly. The mixture was heated (water-bath) for ½ hour, decomposed with ice and dilute hydrochloric acid, and extracted with ether, the ether extracts were washed with water, dried (Na_2SO_4), and distilled. The product (1·2 g.), b. p. 138—140°/18 mm., was heated under reflux for 2 hours with phosphoric oxide (1·5 g.) in benzene (15 ml.) and treated with water, and the benzene layer separated, dried (Na_2SO_4) and distilled, giving an *olefin* as a colourless oil, b. p. 138—140°/18 mm. (Found: C, 91·5; H, 8·35. $C_{13}H_{14}$ requires C, 91·75; H, 8·25%).

Thanks are offered to the Department of Scientific and Industrial Research for a maintenance grant (to L. H. G.), and to Professor G. R. Clemo, F.R.S., for his interest.

UNIVERSITY OF DURHAM, KING'S COLLEGE,
NEWCASTLE-ON-TYNE, 1.

[*Received, October* 21*st*, 1950.]