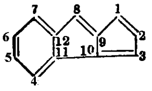
192. *Indene Series. Part I. A Synthesis of* 1 : 2 : 3 : 8-*Tetrahydro*-1-*keto*cyclo*pent*[a]*indene*.

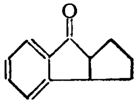
By G. R. Clemo, L. H. Groves, L. Munday, and G. A. Swan.

The ketone named in the title has been prepared by the cyclisation of β-3-indenylpropionic acid (V), obtained (*a*) by a Stobbe condensation with indan-1-one and (*b*) by the malonic ester synthesis from 3-bromomethylindene (X; X = Br). The ketone has been converted into the hexahydro-compound (II), but attempts to prepare *cyclo*pent[*a*]indene have been unsuccessful.

The work described in this and the following papers had, as its main object, the synthesis of the unknown hydrocarbon *cyclo*pent[*a*]indene (I).* Until recently, no simple derivative of (I) was known. However, Baker and Leeds (*J*., 1948, 974) have described the preparation of the ketone (II), and work begun in this laboratory in 1947 led to the synthesis of the ketone (III) and later of other derivatives.



(I.)



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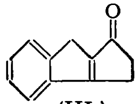
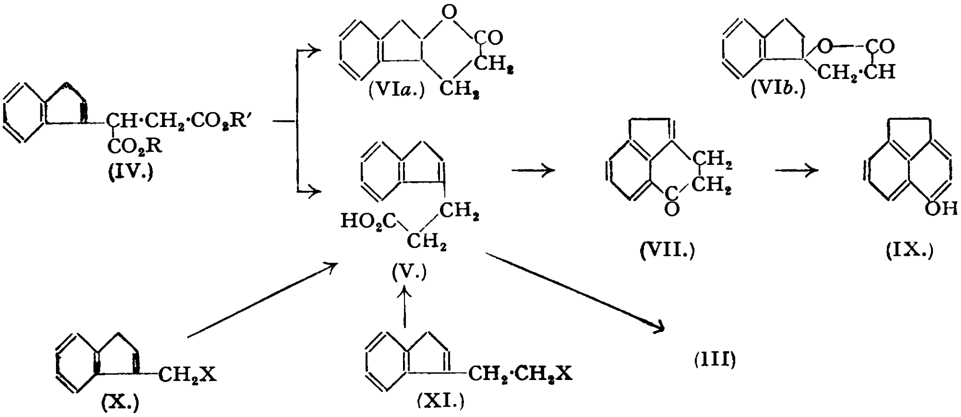


(III.)

Indan-1-one was condensed with ethyl succinate in a modified Stobbe condensation (Johnson, Johnson, and Petersen, *J. Amer. Chem. Soc.*, 1945, **67**, 1360), yielding a half ester which could not be crystallised and probably consisted of a mixture of (IV; R = Et, R′ = H) with the corresponding αβ-unsaturated ester, in which the possibility of geometrical isomerism arises. The crude product was therefore treated with diazomethane, giving (IV; R = Et, R′ = Me) (possibly accompanied by isomers) which was hydrolysed with hydrochloric acid to β-3-indenylpropionic acid (V) accompanied by the lactone (VI*a* or *b*). The acid appeared to be free from the isomer with an exocyclic double bond, for ozonolysis gave an uncrystallisable acid and no indan-1-one could be obtained. Attempts to hydrolyse the crude Stobbe condensation product without methylation gave unsatisfactory results.



The yield of the acid (V) was low, so other methods of preparation were investigated. By the action of phosphorus tribromide, 3-hydroxymethylindene was converted into the corresponding bromide (X; X = Br), which was condensed with ethyl sodiomalonate, then hydrolysed, and decarboxylated, to yield the acid (V).

3-2′-Hydroxyethylindene (XI; X = OH) was prepared from 3-indenylmagnesium bromide and ethylene oxide. Conversion into the corresponding bromide and cyanide, followed by

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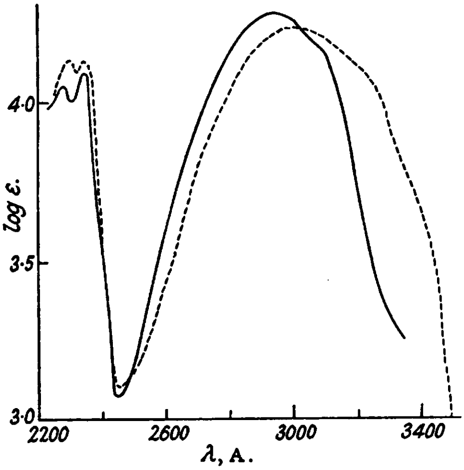
* This name and the numbering as in (I), except for the additional numbers (9—12) are those of the Ring Index and not those used in *J*., 1948, 974.

alkaline hydrolysis, gave (V) in low yield. Hydrolysis of the product of the reaction between indan-1-one, ethyl β-bromopropionate, and magnesium also afforded (V) in very low yield. Unsuccessful attempts were made to synthesise this acid by condensing ethyl β-bromopropionate with (*a*) the sodio-derivative of indene, (*b*) ethyl sodio-2-ketoindane-1-carboxylate, and (*c*) ethyl sodioindene-3-carboxylate (a convenient synthesis of this ester was found in the reaction between the sodio-derivative of indene and ethyl carbonate).

The acid (V) could not be cyclised by zinc chloride–acetic anhydride (Johnson *et al.*, *loc. cit.*). The action of concentrated phosphoric acid or anhydrous hydrogen fluoride gave no recognisable products, but that of concentrated sulphuric acid afforded a product, in yield too small to allow of purification, insoluble in sodium hydrogen carbonate but soluble in sodium hydroxide solution. The melting point of this impure material was *ca.* 110—130°, compared with 126° for 5-hydroxyacenaphthene (IX), which might be formed by cyclisation of (V) to (VII) followed by isomerisation. However, the action of stannic chloride on the acid chloride of (V) yielded 1 : 2 : 3 : 8-tetrahydro-1-keto*cyclo*pent[*a*]indene (III) in 55% yield. That the structure of this ketone is (III) rather than (VII) is indicated by the following facts: (1) The formation of a red 2 : 4-dinitrophenylhydrazone suggests an αβ-unsaturated ketone. The absorption spectrum of this derivative closely resembles that of ethyl styryl ketone (cf. Braude and Jones, *J.*, 1945, 498). (2) The ketone (VII) would be expected to be readily isomerised to (IX). After being heated with 50% sulphuric acid, the ketone was recovered unchanged. (3) The ultra-violet absorption spectrum of the ketone (see figure) closely resembles that of 1 : 2 : 3 : 4 : 9 : 10-hexahydro-1-ketophenanthrene (Wilds, Beck, Close, Djerassi, Johnson, Johnson, and Shunk, *J. Amer. Chem. Soc.*, 1947, **69**, 1985).



——— 1 : 2 : 3 : 8-*Tetrahydro*-1-*keto*cyclo*pent*[a]*indene.*
– – – – 1 : 2 : 3 : 4 : 9 : 10-*Hexahydro*-1-*ketophenanthrene.*
(*In ethanol.*)

The results obtained by Ponndorf–Meerwein, lithium aluminium hydride, Clemmensen, or Wolff–Kishner reduction of (III) were not encouraging. The substance absorbed two moles of hydrogen in the presence of either Adams's catalyst or palladium–charcoal; but the product was not homogeneous, probably consisting of a mixture of stereoisomers, and attempts to dehydrogenate either it or the ketone yielded no crystalline products. The crude hydrogenation product was therefore dehydrated with phosphoric oxide, the resulting olefin hydrogenated in the presence of palladium–charcoal, and the product (II; CH_2 instead of CO) oxidised by chromic acid to a ketone, the semicarbazone and 2 : 4-dinitrophenylhydrazone of which agreed in properties with those of (II); no depression of melting point occurred on admixture with corresponding specimens prepared by Baker and Leeds's method (*loc. cit.*).

Attempts were also made to prepare a thioketal from (III), which might be expected to yield a hydrocarbon on treatment with Raney nickel. Mixtures of ethane- or toluene-ω-thiol and (III) rapidly developed a purple colour and fluorescence, which, on dilution with benzene, changed to green with a red fluorescence. The colour was discharged by water, but not by concentrated hydrochloric acid, and the ketone could be recovered unchanged. Similar results were obtained with the closely analogous 3 : 4-dihydro-3′-keto-1 : 2-*cyclo*pentenonaphthalene

(Johnson *et al.*, *loc. cit.*). However, with an open-chain analogue, ethyl styryl ketone, the reaction mixture developed only a pale pink colour, and use of ethanethiol in acetic acid containing a small amount of concentrated hydrochloric acid gave a monothio-compound;

$Et{\cdot}CO{\cdot}CH_2{\cdot}CHPh{\cdot}SEt$ (XII.) $(EtS)_2CEt{\cdot}CH{:}CHPh$ (XIII.) $(EtS)_2CEt{\cdot}CH_2{\cdot}CHPh{\cdot}SEt$ (XIV.)

this is probably (XII) as it possesses ketonic properties, although the 2 : 4-dinitrophenylhydrazone and semicarbazone were oils. Use of ethanethiol in the presence of anhydrous zinc chloride and sodium sulphate gave, as major product, a dithio-compound, probably (XIII) with a small amount of what may be the trithio-compound (XIV).

EXPERIMENTAL.

(All m. p.s are uncorrected.)

Methyl β-Carbethoxy-β-3-indenylpropionate (IV; R = Et, R′ = Me).—Potassium (4·4 g.) was dissolved in dry *tert.*-butyl alcohol (100 ml.), in a three-necked flask fitted with a tap-funnel, reflux condenser with a mercury seal, and a delivery tube which could be connected to either a water pump or a source of pure, dry nitrogen. The solution was cooled in ice, and ethyl succinate (29·0 g.) added. The apparatus was evacuated and filled with nitrogen several times and then the flask was heated in an oil-bath at 110—120°, with nitrogen passing through.

To the boiling solution indan-1-one (15·0 g.) in *tert.*-butyl alcohol (15 ml.) was added during 30 minutes. The solution was heated for a further 10 minutes, then cooled, acidified with 5N-hydrochloric acid (60 ml.), and the solvents removed (reduced pressure). The residue was extracted with ether (5 × 30 ml.), the extracts were filtered, and washed with water, and finally with 10% ammonia solution. The ammoniacal layer, after being washed with ether, was acidified, the precipitated oil was extracted with ether, the extract dried (Na_2SO_4), and the ether removed. The residue, a dark viscous oil (11·6 g.), was dissolved in dry ether (50 ml.), treated with a solution of diazomethane (5·0 g.) in ether (350 ml.) and kept overnight, the ether removed, and the residue distilled, giving (i) methyl ethyl succinate (2·0 g.), b. p. 90—95°/3 mm., 207—208°/750 mm., and (ii) the *indenyl* ester, a straw-coloured oil (4·1 g.), b. p. 208—210°/3 mm. (Found : C, 70·1; H, 6·85. $C_{16}H_{18}O_4$ requires C, 70·1; H, 6·6%). The neutral ethereal extract deposited, when kept, large light-brown needles of 2-indan-1′-ylideneindan-1-one (4·0 g.), m. p. 140—141·5° (lit., 142—143°) (Found : C, 87·9; H, 5·75. Calc. for $C_{18}H_{14}O$: C, 87·8; H, 5·7%); the mother-liquors therefrom were distilled, finally under reduced pressure to remove unchanged indan-1-one, and the residue triturated with light petroleum (b. p. 60—80°) and repeatedly recrystallised from toluene, giving a small amount of yellow solid, m. p. 244—247° [Found : C, 86·35; H, 5·3%; *M* (Rast), 286].

3-Indenylsuccinic Acid.—The ethyl methyl ester (0·3 g.) was heated under reflux with sodium hydroxide solution (10%; 10 ml.) for 6 hours in an atmosphere of nitrogen. The solution was cooled, washed with ether, boiled, cooled, and acidified. The precipitated brown gum soon crystallised. Recrystallisation from dilute ethanol (charcoal) gave the cream-coloured *acid*, m. p. 176·5—180° (Found : C, 67·55; H, 5·7. $C_{13}H_{12}O_4$ requires C, 67·25; H, 5·2%).

β-3-Indenylpropionic Acid.—The ethyl methyl ester (IV; R = Et, R′ = Me) (5·1 g.) was heated under reflux with acetic acid (70 ml.), water (30 ml.), and concentrated hydrochloric acid (25 ml.), in an atmosphere of nitrogen for 5 hours. The mixture was evaporated to dryness under reduced pressure and the residue extracted with ether. The extract was washed with water and then with sodium hydrogen carbonate solution. Acidification of the latter gave the *propionic acid* (1·6 g.), separating from aqueous methanol as cream-coloured needles, m. p. 120·5—121·5° (Found : C, 76·9; H, 6·7. $C_{12}H_{12}O_2$ requires C, 76·6; H, 6·4%).

The Lactone (VI*a* or VI*b*).—The neutral ethereal extract from the above experiment was dried (Na_2SO_4) and the ether was removed. A colourless oil remained which crystallised when scratched. Recrystallisation from benzene–light petroleum afforded the *lactone* (0·5 g.) as colourless plates, m. p. 125° (Found : C, 76·0; H, 6·6. $C_{12}H_{12}O_2$ requires C, 76·6; H, 6·4%). On hydrolysis with 10% sodium hydroxide solution (15 ml.) for 1 hour on the water-bath, in an atmosphere of nitrogen, this gave an almost theoretical yield of the acid (V).

Methyl β-Carboxy-β-3-indenylpropionate (IV; R = H, R′ = Me).—Partial hydrolysis of the ethyl methyl ester (IV), *i.e.*, for only 2 hours under reflux gave the *methyl carboxy*-ester (IV; R = H, R′ = Me). It was separated from the crude acid (V) by virtue of its relative insolubility in ether. Recrystallisation from dilute methanol gave light-brown prisms, m. p. 140—141° (Found : C, 67·9; H, 5·6. $C_{14}H_{14}O_4$ requires C, 68·3; H, 5·7%).

1 : 2 : 3 : 8-*Tetrahydro-1-keto*cyclo*pent*[a]*indene* (III).—A solution of β-3-indenylpropionic acid (0·2 g.) and phosphorus pentachloride (0·25 g.) in dry benzene (20 ml.) was kept at room temperature for 3 hours, cooled in ice, and treated with stannic chloride (0·8 g.) in benzene (10 ml.), a deep cherry-red solid being deposited immediately. The mixture was kept at room temperature for 2 days, and the complex then decomposed with ice and dilute hydrochloric acid. The aqueous layer was extracted with ether, the ether and benzene layers were combined, washed with dilute hydrochloric acid, water, 10% sodium hydroxide solution, and dried (Na_2SO_4), and the solvents were removed. Recrystallisation from light petroleum (b. p. 60—80°) gave the *ketone* as pale brown needles, m. p. 137—139° (0·1 g.) (Found : C, 84·6; H, 5·85. $C_{12}H_{10}O$ requires C, 84·7; H, 5·9%). Light absorption in ethanol: $\lambda_{max.}$ 2940, 2350, and 2290 A.; log $\varepsilon_{max.}$ = 4·28, 4·10, and 4·05 respectively; $\lambda_{min.}$ 2470 A.; log $\varepsilon_{min.}$ = 3·07.

The *semicarbazone* separated from acetic acid as yellow needles, m. p. 253—254° (decomp.) (Found :

C, 68·4; H, 5·55. $C_{13}H_{13}ON_3$ requires C, 68·7; H, 5·75%). The 2 : 4-*dinitrophenylhydrazone* formed clusters of red needles, m. p. 257—257·5° (decomp.) (from acetic acid) (Found : C, 62·0; H, 4·3. $C_{18}H_{14}O_4N_4$ requires C, 61·7; H, 4·0%). Light absorption in chloroform : $\lambda_{max.}$ 4040 and 3150 A.; log $\varepsilon_{max.}$ = 4·47 and 4·07; $\lambda_{min.}$ 3360 and 2925 A.; log $\varepsilon_{min.}$ = 3·96 and 3·90. Light absorption of ethyl styryl ketone 2 : 4-dinitrophenylhydrazone in chloroform : $\lambda_{max.}$ 3920 and 3050 A.; log $\varepsilon_{max.}$ = 4·43 and 4·17; $\lambda_{min.}$ 3270 and 2850 A.; log $\varepsilon_{min.}$ = 3·97 and 4·05.

Ozonolysis of β-3-Indenylpropionic Acid.—A solution of the acid (0·2 g.) in dry pure ethyl acetate (25 ml.) was ozonised for 1½ hours. After removal of the excess of ozone by evacuation, the mixture was hydrogenated in the presence of palladium–charcoal at atmospheric pressure and temperature. The catalyst was filtered off, the filtrate evaporated (reduced pressure), and the residue dissolved in ether and extracted with sodium hydrogen carbonate solution. The neutral ethereal solution, on evaporation gave a negligible residue, while the sodium hydrogen carbonate extract on acidification yielded a gummy acid.

Reaction between Ethyl Styryl Ketone and Ethanethiol.—(*a*) A solution of the ketone (6·5 g.), ethanethiol (13 g.), and concentrated hydrochloric acid (0·5 ml.) in acetic acid (60 ml.) was kept at room temperature for 3 days and then distilled, giving 5-*ethylthio*-5-*phenylpentan*-3-*one* (XII) (7 g.) as a colourless oil, b. p. 143—147°/3 mm. During 24 hours at 0° this formed colourless thick needles, m. p. 33—34° (Found : C, 70·45; H, 8·0; S, 15·0. $C_{13}H_{18}OS$ requires C, 70·25; H, 8·1; S, 14·4%).

(*b*) A mixture of the ketone (2·1 g.), freshly fused zinc chloride (2·5 g.), and anhydrous sodium sulphate (2·5 g.) was cooled in ice, treated slowly with ethanethiol (4·0 g.), and kept at room temperature for 4 days during which a deep red colour developed. Water was added, the mixture extracted with chloroform, the extract dried (Na_2SO_4), and the solvent removed. Light petroleum (b. p. 40—60°) was added to the residue, a white solid (0·15 g.) of indeterminate m. p. (60—65°), containing sulphur was filtered off, the filtrate evaporated, and the residue distilled. 3 : 3-*Diethylthio*-1-*phenylpent*-1-*ene* (XIII) (1·5 g.), b. p. 130—132°/3 mm., formed a colourless oil (Found : C, 68·1; H, 8·05; S, 25·3. $C_{15}H_{22}S_2$ requires C, 67·7; H, 8·25; S, 24·1%).

3-*Bromomethylindene.*—Phosphorus tribromide (7·7 g.) in dry benzene (50 ml.) was added slowly to a solution of 3-hydroxymethylindene (10 g.) (Grignard and Courtot, *Compt. rend.*, 1915, **160**, 501; *Ann. Chim.* 1915, [ix], **4**, 95) in benzene (50 ml.). The mixture was kept overnight at room temperature, then treated with ice, the benzene layer washed with sodium carbonate solution and dried (Na_2SO_4), the benzene removed under reduced pressure at 35—40°, and the residue distilled, not more than 4 g. at a time, giving unchanged 3-hydroxymethylindene (1·0 g.), b. p. 100—125°/2 mm., and the required *bromide* (4·1 g.), b. p. 125—135°/2 mm., a yellow unstable lachrymatory oil (Found : Br, 38·2. $C_{10}H_9Br$ requires Br, 38·3%). This compound is unstable to heat but, unless distilled, it was unsatisfactory for the next stage of our work.

Ethyl α-Carbethoxy-β-3-indenylpropionate.—To a solution of sodium (0·3 g.) in absolute ethanol (10 ml.) were added first ethyl malonate (2·2 g.), then a solution of 3-bromomethylindene (2·8 g.) in ethanol (10 ml.). The mixture was heated at 50° for 6 hours and then on the water-bath for a further 12 hours, the bulk of the ethanol removed by distillation, and the residue treated with water. The mixture was extracted with ether, and the extracts were washed (water), dried ($CaCl_2$), and distilled, finally under reduced pressure, affording the *ester* as a straw-coloured oil (2·95 g.), b. p. 164—166°/2 mm. (Found : C, 71·1; H, 7·4. $C_{17}H_{20}O_4$ requires C, 70·8; H, 6·95%).

This ester (3·45 g.) was heated under reflux for 1 hour with a solution of potassium hydroxide (4 g.) in ethanol (15 ml.), and the bulk of the ethanol then removed by distillation. The residue was dissolved in water, and the solution extracted with ether, boiled, and acidified with dilute hydrochloric acid, the *acid* (2·7 g.) separating as light brown crystals, m. p. 181—182° (decomp.) (Found : C, 67·1; H, 5·5. $C_{13}H_{12}O_4$ requires C, 66·95; H, 5·55%).

β-3-Indenylpropionic Acid.—The foregoing acid (4·9 g.) was heated at 185° (oil-bath) for 3—4 minutes until evolution of carbon dioxide ceased. The cooled residue, recrystallised twice from aqueous methanol, had m. p. 118—120° (3·3 g.).

3-2′-*Hydroxyethylindene.*—A suspension of 3-indenylmagnesium bromide in ether (30 ml.), prepared from indene (10 g.) (Grignard, *Compt. rend.*, 1911, **152**, 273), was cooled in ice, and ethylene oxide (5 g.) in ether (10 ml.) was added dropwise. When the vigorous reaction had subsided, the ether was removed by distillation and the residue heated at 100° for 1 hour, cooled, and decomposed with ice and dilute hydrochloric acid; the organic layer was separated and the aqueous portion extracted with ether. The combined organic extracts were washed with sodium carbonate solution, then dried (Na_2SO_4), the ether removed by distillation, and the residue fractionated under reduced pressure, giving unchanged indene (5 g.), b. p. 80—90°/15 mm., and the *alcohol*, a pale yellow oil (3·7 g.), b. p. 168—170°/15 mm. (Found : C, 82·55; H, 7·4. $C_{11}H_{12}O$ requires C, 82·5; H, 7·5%).

3-2′-*Bromoethylindene.*—The above alcohol (1·0 g.), phosphorus tribromide (0·77 g.), and benzene (10 ml.) were heated at 50° for 8 hours and then kept overnight at room temperature. The mixture was decomposed with water, the benzene layer washed with sodium carbonate solution and dried (Na_2SO_4), and the benzene removed at 35—40°. The residue was distilled, affording a yellow *bromide* (0·55 g.), b. p. 117—120°/3 mm. (Found : C, 59·4; H, 5·3; Br, 35·8. $C_{11}H_{11}Br$ requires C, 59·2; H, 4·95; Br, 35·85%).

β-3-Indenylpropionic Acid.—The above bromide (1·55 g.) in ether–ethanol (2 : 5) was added to sodium cyanide (0·5 g.) in water (0·6 ml.). The mixture was left at room temperature overnight and then heated on the water-bath for 4 hours, treated with water, and extracted with ether. The extracts were dried (Na_2SO_4), the ether was removed, and the residue distilled, giving a pale yellow oil, b. p. 120°/3 mm. (0·6 g.). This cyanide in 15% aqueous-ethanolic sodium hydroxide (0·75 g.) was heated under reflux for 5 hours on the water-bath. Most of the ethanol was removed, and the solution diluted with water, washed with ether, boiled with charcoal, filtered, cooled, and acidified (dilute hydrochloric acid). The product (V) (0·1 g.), after recrystallisation from dilute methanol, had m. p. 119—121°, not depressed by admixture with a specimen prepared as above.

*Reaction between Indan-*1*-one and Ethyl β-Bromopropionate.*—A mixture of ethyl β-bromopropionate (6 g.), indan-1-one, (4·4 g.), magnesium shavings (0·8 g.), and toluene (4 ml.) was heated under reflux for 4 hours, cooled, filtered, and treated with ice and dilute sulphuric acid. The organic layer was separated, then dried (Na_2SO_4), and the solvent removed. The residue was boiled with a solution of potassium hydroxide (5 g.) in water (5 ml.) and ethanol (10 ml.) for 2 hours. The mixture was cooled, diluted with water, and washed with ether. The aqueous layer was acidified (dilute hydrochloric acid) and extracted with ether, the extracts were dried (Na_2SO_4), and the solvent removed, leaving a dark red oil (2·0 g.) which was distilled, giving the required acid (0·3 g.), b. p. (bath-temp.) 240°/2 mm., m. p. 118—120°, not depressed on admixture with (V) obtained as above.

*Ethyl Indene-*3*-carboxylate.*—To sodamide prepared from sodium (4·1 g.) in liquid ammonia (140 ml.) (Levine and Hauser, *J. Amer. Chem. Soc.*, 1944, **66**, 1768), indene (10 g.) in dry ether (40 ml.) was added during 15 minutes. The mixture was warmed on the water-bath, dry ether being added to maintain a constant volume. When all the ammonia had evaporated, ethyl carbonate (20 g.) was added slowly, the mixture was heated under reflux (water-bath) for 3½ hours, and poured on crushed ice (150 g.) and acetic acid (15 ml.). The ethereal layer was separated, washed three times with saturated sodium hydrogen carbonate solution, dried (Na_2SO_4), and distilled, first at atmospheric pressure to remove the excess of ethyl carbonate (8 g.) and then under reduced pressure, affording unchanged indene (4 g.), b. p. 75—85°/15 mm., and the required ester (6·2 g.), b. p. 155°/15 mm. Alkaline hydrolysis gave indene-3-carboxylic acid, m. p. 156—157° (not depressed on admixture with an authentic specimen).

1 : 2 : 3 : 8 : 9 : 10-*Hexahydro-*8*-keto*cyclo*pent*[a]*indene* (II).—The ketone (III) (1·45 g.), hydrogenated in glacial acetic acid at room temperature and atmospheric pressure over Adams's catalyst, absorbed 2 mols. of hydrogen. The crude product was dehydrated with phosphoric oxide (2·5 g.) in benzene (20 ml.) under reflux (2½ hours). The olefin, thus obtained as an almost colourless oil (0·51 g.), b. p. 120—125°/20 mm., was hydrogenated in ethanol in presence of palladium–charcoal, 1 mol. of hydrogen being absorbed. The crude product obtained by filtration and removal of the solvent was heated on the water-bath for 3 hours with sodium dichromate (1·5 g.) and acetic acid (5 ml.). The solvent was removed (reduced pressure), water added, and the mixture extracted with ether. The extract was dried (Na_2SO_4) and fractionated, giving unchanged 1 : 2 : 3 : 8 : 9 : 10-hexahydro*cyclo*pent[*a*]indene (0·2 g.), a colourless oil, b. p. (bath-temp.) 135—145°/15 mm., and the ketone (II) (0·15 g.), a colourless oil, b. p. (bath-temp.) 170—180°/15 mm.

The 2 : 4-dinitrophenylhydrazone of (II) separated from acetic acid as dark red needles, m. p. 215—216°, not depressed on admixture with an authentic specimen (lit., 216—217°) (Found : C, 61·15; H, 4·8. Calc. for $C_{18}H_{16}O_4N_4$: C, 61·4; H, 4·55%). The semicarbazone separated from ethanol as colourless plates, m. p. 242° (decomp.), not depressed on admixture with an authentic specimen [lit., 242° (decomp.)] (Found : C, 68·1; H, 6·6. Calc. for $C_{13}H_{15}ON_3$: C, 68·1; H, 6·55%).

The light-absorption data were determined by use of a Hilger Medium Quartz Spectrograph.

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