41. *Azulenes. Part II. Exploration of New Synthetic Routes.*

By J. W. Cook, R. Philip, and A. R. Somerville.

Naturally occurring hydroazulene derivatives have not yet been prepared synthetically, although the blue azulenes which they yield on dehydrogenation have been synthesised. In an endeavour to synthesise the optically inactive tetrahydride (VIII) which is formed by reduction of optically active β-vetivone, the hydrindanone derivative (IV) has been prepared by a simplified route and converted, in three stages, into the *dicarboxylic acid* (VII). Distillation of the thorium salt of this acid gave a product which may have been (VIII), but the amount was insufficient for characterisation.

By a five-stage process azulene (II) has been synthesised from suberone, which is readily prepared from *cyclo*hexanone. By a similar method 2 : 3-benz-1-suberone has been converted into 1-*keto*-4 : 5-*benz*-$\Delta^{4:9}$-*hexahydroazulene* (XIII), from which it is hoped to synthesise 4 : 5-benzazulene and some of its derivatives.

In Part I (*J.*, 1942, 559) Coats and Cook described a synthesis of 4 : 7-dimethyl-2-*iso*propylhydrindan-5-one (IV). This was converted in small yield into vetivazulene by ring-enlargement with diazomethane, followed by dehydrogenation with selenium. We have now examined the possibility of using the same ketone (IV) as an intermediate in the synthesis of tetrahydro-β-vetivone (VIII), an internally compensated optically inactive ketone which Pfau and Plattner (*Helv. Chim. Acta*, 1939, **22**, 640) obtained by reduction of the optically active natural sesquiterpene ketone, β-vetivone (compare *idem, ibid.*, 1940, **23**, 768). Circumstances caused interruption of our work a year ago, and we wish now to record our experiments in view of the use by Plattner and Studer (*ibid.*, 1946, **29**, 1432) of a somewhat similar series of reactions for the synthesis of 6-methylazulene (see also Šorm and Fajkoš, *Coll. Czech. Chem. Comm.*, 1947, **12**, 81; Šorm, *ibid.*, p. 251).

We have also been interested in devising a simple synthetic route to azulene derivatives to facilitate more detailed study of the chemistry of this interesting type of quasi-aromatic ring system. A way to this objective seemed to be provided by an adaptation of the work of Johnson and his collaborators (*J. Amer. Chem. Soc.*, 1945, **67**, 1357, 1360, 1366) who improved the Stobbe condensation of ethyl succinate with cyclic ketones, and showed how the condensation products could be transformed into condensed-ring *cyclo*pentane derivatives. We found that the product of condensation of suberone with ethyl succinate was readily converted into a dicyclic ketone (I) which was reduced in two stages to decahydroazulene, from which azulene (II) was obtained in small yield by dehydrogenation with selenium. In this work we have been largely anticipated by Plattner and Büchi (*Helv. Chim. Acta*, 1946, **29**, 1608) who prepared the dicyclic ketone (I) by the same method which we used, and converted it into 1-methylazulene. We therefore record our own experiments, insofar as they supplement those of the Swiss authors.

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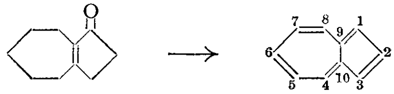
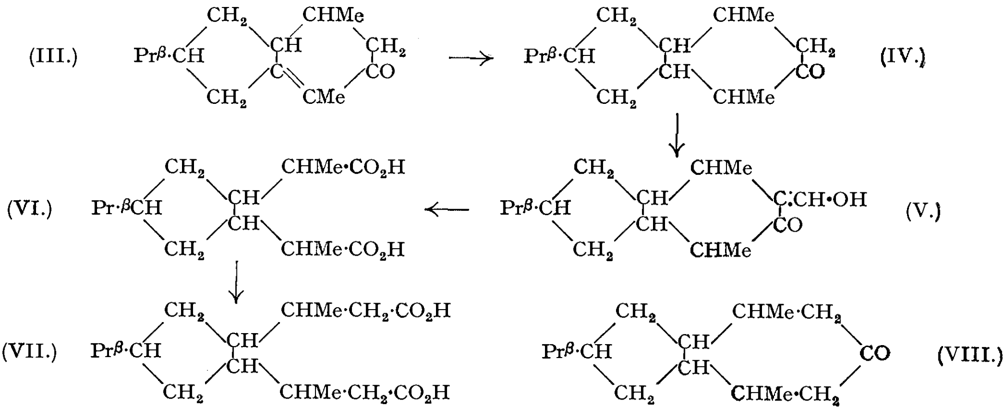


(II.)

Coats and Cook (*loc. cit.*) obtained 4 : 7-dimethyl-2-*iso*propylhydrindan-5-one (IV) by hydrogenation of the crude unsaturated ketone (III) which we have now characterised by the preparation of its *oxime* and *semicarbazone*. An important intermediate in this synthesis was *p*-*iso*propylphenol which was prepared from benzene by a laborious series of reactions. We have simplified the preparation of this phenol by modifying the method of von Braun (*Annalen*, 1929, **472**, 67; cf. U.S.PP. 1,788,847, 1,782,621; D.R.-PP. 467,640, 510,442), who found that both *p*-*iso*propylphenol and 4-*iso*propyl*cyclo*hexanol could be obtained by hydrogenolysis of the 2 : 2-di-(*p*-hydroxyphenyl)propane which arises from the condensation of phenol with acetone. In our experience copper chromite at 220—230° proved to be the most satisfactory catalyst for hydrogenolysis, by which *p*-*iso*propylphenol was obtained in 35% yield. This was then hydrogenated by Raney nickel to 4-*iso*propyl*cyclo*hexanol, from which the ketone (IV) was obtained by the procedure of Coats and Cook.

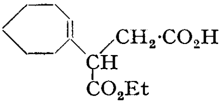
In conformity with the findings of these authors, the unsaturated ketone (III) was hydrogenated by palladium-black at room temperature to give a stereoisomeric mixture of saturated ketones from which a pure constituent giving a semicarbazone, m. p. 204°, was readily and consistently isolated in relatively small yield. Hydrogenation was very slow, and in order to accelerate the reaction the main batch of unsaturated ketone was treated with hydrogen under pressure at 50° in presence of palladised strontium carbonate. This modification of the conditions had a profound influence on the composition of the resulting mixture. The semicarbazone of m. p. 204° was not isolated; there was obtained instead a semicarbazone mixture from which was isolated by recrystallisation only a small amount of well crystallised, apparently homogeneous material, m. p. 175°. The same *semicarbazone*, in an impure state (m. p. 168°), had been obtained by Coats and Cook by the action of diazomethane on the ketone which forms the



semicarbazone, m. p. 204°. The two ketones corresponding with these semicarbazones are clearly stereoisomeric, and it was the failure to obtain a satisfactory quantity of stereochemically homogeneous ketone (IV) which has frustrated the complete attainment of the objective of this work, namely, synthesis of a compound of the structure (VIII).

A possible method of ring-enlargement of the six-membered ring in (IV) was the action of nitrous acid on the amine which should be obtainable by reduction of the cyanohydrin of (IV). On account of the structural ambiguity of the perhydroazulene derivative which should be formed this method was not adopted, but such a method has in fact been used as a synthetic route to azulene derivatives (compare Arnold, *Ber.*, 1943, **76**, 777). After some exploratory experiments in regard to other methods, it was decided to convert the ketone (IV) into the dicarboxylic acid (VI), through the hydroxymethylene-ketone (V). The ketone (IV*a*), regenerated from the semicarbazone, m. p. 204°, reacted with sodium and ethyl formate to give a golden-yellow, acid, liquid hydroxymethylene ketone (V), together with a colourless neutral crystalline *isomeride*, m. p. 70°, which appeared to be the tautomeric formyl ketone. This colourless solid gave an intense violet colour with ferric chloride but formed a *disemicarbazone*. The same neutral product, together with a liquid hydroxymethylene compound, was obtained by analogous treatment of the ketone (IV*b*) regenerated from the semicarbazone, m. p. 175°. Permanganate oxidation of the hydroxymethylene ketone (V), obtained from the ketone (IV*a*), gave 1-iso*propyl*cyclo*pentane*-3 : 4-*bis*-(α-*propionic acid*) (VI), m. p. 154—156°. A satisfactory product could not be obtained by similar oxidation of the hydroxymethylene derivative of the isomeric ketone (IV*b*).

By the Arndt–Eistert method adipic acid has been converted into suberic acid and sebacic acid into decane-1 : 10-dicarboxylic acid (Walker, *J.*, 1940, 1304). When the dicarboxylic acid (VI) was submitted to this technique it was smoothly converted into 1-iso*propyl*cyclo*pentane*-3 : 4-*bis*-(β-*butyric acid*) (VII). By distillation of the thorium salt of this homologous acid there was formed a pleasant-smelling liquid, which gave a red precipitate with 2 : 4-dinitrophenylhydrazine. This liquid may have been the desired ketone (VIII), but the amount of material available was insufficient for characterisation.



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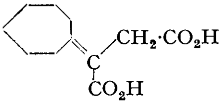

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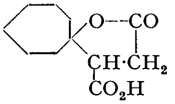
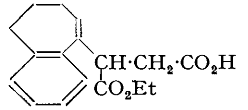
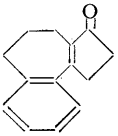


(XI.)

(XII.)





(XIII.)

Condensation of suberone with ethyl succinate by means of potassium *tert.*-butoxide gave *cyclo*heptenylsuccinic acid monoethyl ester (IX), the properties of which agreed with the description given by Plattner and Büchi (*loc. cit.*). When this was treated with zinc chloride and acetic anhydride in acetic acid there were obtained, not only the dicyclic ketone (I) but also, in much larger amount, a mixture of isomeric acids which was separated by fractional crystallisation into an unsaturated dicarboxylic acid, m. p. 171° [probably *cyclo*heptylidenesuccinic acid (X), for which, however, Plattner and Büchi give m. p. 160—163°], and a *lactonic acid* (presumably XI), m. p. 184—186°.

The dicyclic ketone (I) was treated with phenylmagnesium bromide, and the crude product heated with selenium. Although this yielded a material with a blue-green colour, a crystalline complex with *s*-trinitrobenzene could not be isolated. It does not follow that a phenylazulene was not formed, as Plattner, Sandrin, and Wyss (*Helv. Chim. Acta*, 1946, **29**, 1604) found that 1-phenylazulene easily isomerises to 2-phenylazulene which does not give a picrate or a trinitrobenzene complex.

Preliminary work has also been carried out on the synthesis of 4 : 5-benzazulene, which represents a type of hydrocarbon as yet unknown. Benzsuberone, obtained by an improved method, was condensed with ethyl succinate to give the *mono-ester* (XII), and this was cyclised to the tricyclic *ketone* (XIII), the reduction of which is being studied.

EXPERIMENTAL.

p-iso*Propylphenol*.—2 : 2-Di-(*p*-hydroxyphenyl)propane was prepared from phenol, acetone, and fuming hydrochloric acid as described by Zincke (*Annalen*, 1905, **343**, 85). This method was found superior to that of von Braun (*loc. cit.*). For hydrogenolysis, a mixture of the crude diphenol (380 g.) and the copper chromite catalyst (*Org. Synth.*, Coll. Vol. II, 142) (38 g.) was agitated with hydrogen for 5 hours in a stainless-steel autoclave heated at 220—230°, The initial pressure was 180 atm., and during the course of the reaction some 70 l. of hydrogen were absorbed. The viscous product was distilled into two fractions : (i) b. p. 88—100°/15 mm. (130 g.), (ii) b. p. 100—125°/15 mm. (100 g.). Fraction (ii) crystallised and gave colourless needles, m. p. 62—63°, of *p*-*iso*propylphenol. This was hydrogenated over Raney nickel as described by Coats and Cook (*loc. cit.*) and gave a mixture of stereoisomeric 4-*iso*propyl*cyclo*hexanols, the heterogeneous nature of which was shown by conversion into a mixture of acid phthalates, m. p. 90—98°. 1 Kg. of *iso*propyl*cyclo*hexanol was prepared in this way.

5-*Keto*-4 : 7-*dimethyl*-2-iso*propyl*-$\Delta^{4(9)}$-*tetrahydroindane* (III).—Very slow addition of the mixture of *iso*propyl*cyclo*hexanols to 50% nitric acid catalysed by ammonium vanadate (Coats and Cook, *loc. cit.*) gave *β*-*iso*propyladipic acid (80% yield), which crystallised when the reaction mixture was cooled in a refrigerator. This was esterified, the ester submitted to the Dieckmann reaction, and the product condensed with hex-2-en-4-one, all as described by Coats and Cook. In the preparation of hexenone from allyl bromide and propionitrile the best results were obtained by using zinc powder freshly prepared by milling pure zinc rods. A trace of pyridine was used to initiate the reaction. The dicyclic keto-ester formed by this series of reactions was decarbethoxylated with boiling aqueous potassium hydroxide. The resulting ketone (III) reacted with semicarbazide hydrochloride and potassium acetate in aqueous alcohol to give a *semicarbazone*, which crystallised from aqueous ethanol in colourless needles, m. p. 208—210° (Found : C, 68·5; H, 9·3; N, 16·1. $C_{15}H_{25}ON_3$ requires C, 68·4; H, 9·5; N, 16·0%). The *oxime*, obtained from the crude ketone by treatment with hydroxylamine hydrochloride in boiling pyridine solution, formed clusters of small colourless needles (from ethanol), m. p. 172·5—173·5° (Found : C, 76·2; H, 10·2; N, 6·45. $C_{14}H_{23}ON$ requires C, 76·0; H, 10·4; N, 6·3%).

The distilled ketone (b. p. 88°/0·15 mm.), obtained by steam distillation of the pure semicarbazone with oxalic acid, was hydrogenated in ethanolic solution by means of palladium-black. In spite of the homogeneity of the unsaturated ketone (III), the hydrogenation product was a mixture of stereoisomerides (IV), for the semicarbazone prepared from it had m. p. *ca.* 170°, raised to 201° by 3 recrystallisations from ethanol. The purified semicarbazone was identical with the compound similarly prepared by Coats and Cook from the crude unsaturated ketone. By fractional crystallisation of the material from the liquors of the semicarbazone, there was obtained a fraction, m. p. 156—164° depressed to 150° by admixture with the semicarbazone, m. p. 201°. It is, of course, possible for 4 stereoisomerides to arise by hydrogenation of the ethylenic bond in (III). As the use of the pure unsaturated ketone offered no advantage over that of the crude material, the latter was used in subsequent work.

When working with a larger batch, a solution of the unsaturated ketone (III) (50 g.) in ethanol (500 c.c.) was agitated for 6 hours with hydrogen and palladised strontium carbonate (20 g.) at 50° and 110 atm. The filtered solution gave a resinous mixture of semicarbazones from which was eventually obtained by fractional crystallisation from ethanol a crystalline semicarbazone, m. p. 162—164° (8 g.), not depressed by admixture with the semicarbazone, m. p. 167—168°, obtained by Coats and Cook from the ketone recovered from the action of diazomethane on the saturated ketone (IV*a*) which gives a semicarbazone, m. p. 204°. Further crystallisation from ethanol gave colourless leaflets of the *semicarbazone*, m. p. 175—176° (Found: C, 67·7; H, 10·4. $C_{15}H_{27}ON_3$ requires C, 67·9; H, 10·2%). The *ketone* (IV*b*) recovered from this by steam distillation with 20% sulphuric acid was distilled in an air-bath at 85°/0·3 mm. and formed a colourless liquid (Found : C, 80·8; H, 11·4. $C_{14}H_{24}O$ requires C, 80·8; H, 11·5%), which reacted with semicarbazide to form the semicarbazone from which it was obtained.

Oxidation of the mixed ketones (IV) with hydrogen peroxide and vanadium pentoxide (Treibs, *Ber.*, 1939, **72**, 1194) gave no useful result. Oxidation of the pure ketone (IV*a*) (1 g.) with amyl nitrite (0·6 g.) and concentrated hydrochloric acid (0·5 c.c.) for 9 hours gave the keto-acid, m.p. 71—72°, obtained by Coats and Cook by oxidation of the same ketone with chromic acid (the earlier sample had m. p. 64—65°). (Found : C, 69·9; H, 10·0. Calc. for $C_{14}H_{24}O_3$: C, 69·9; H, 10·1%).

4 : 7-*Dimethyl*-6-*hydroxymethylene*-2-iso*propylhydrindan*-5-*one* (V).—(*a*) Ethyl formate (5·5 c.c.) was added to a suspension of atomised sodium (1 g.) in the pure ketone (IV*a*) (1 g.) and anhydrous ether (25 c.c.). A vigorous reaction ensued and the colour became yellow and then red. After 24 hours at room temperature, the mixture was poured into ice-water (300 c.c.) and extracted with ether. A white solid which separated at the interface was collected and added to a further quantity obtained by distillation of the ethereal extract. This compound, probably 6-*formyl*-4 : 7-*dimethyl*-2-iso*propylhydrindan*-5-*one*, crystallised from acetic acid in colourless rhombic plates, m. p. 69—70° (Found : C, 76·7; H, 9·8. $C_{15}H_{24}O_2$ requires C, 76·3; H, 10·2%). It gave an intense violet colour with ferric chloride, and formed a *disemicarbazone*, m. p. 206—208° (Found : C, 58·4; H, 8·5. $C_{17}H_{30}O_2N_6$ requires C, 58·3; H, 8·6%). The alkaline solution containing the hydroxymethylene-ketone was acidified with hydrochloric acid and then extracted with ether. Distillation of the dried extract gave a golden-yellow viscous liquid (0·6 g.), b. p. 98—105°/0·2 mm. (bath temp.). This hydroxymethylene-ketone (V*a*) gave an intense violet colour with ferric chloride.

(*b*) A similar experiment with the stereoisomeric ketone (IV*b*) gave the corresponding yellow viscous hydroxymethylene-ketone (V*b*) and also a small amount of the solid formyl compound, m. p. 69—70°, described under (*a*).

It was found disadvantageous to carry out these condensations with large batches of ketone.

1-iso*Propyl*cyclo*pentane*-3 : 4-*bis*-(*α*-*propionic Acid*).—(*a*) A solution of the hydroxymethylene ketone (V*a*) (0·5 g.) in 10% sodium hydroxide (1·5 c.c.) was treated dropwise at 0° with an ice-cold solution of potassium permanganate (1 g. in 38 c.c.). After several hours at 0° the permanganate was completely reduced and the filtered solution was acidified and extracted with ether. The dried ethereal extract was evaporated and gave a gum which partly crystallised in a vacuum desiccator. The residual oil was removed by extraction with hexane and the undissolved solid was crystallised from water and then hexane. The *dipropionic acid* (VI) formed colourless cubes (0·2 g.), m. p. 154—156° (Found : C, 65·6; H, 9·0. $C_{14}H_{24}O_4$ requires C, 65·6; H, 9·4%). The *di*-p-*phenylphenacyl* ester formed tufts of colourless needles (from ethanol), m. p. 153—153·5° (Found : C, 78·0; H, 7·05. $C_{42}H_{44}O_6$ requires C, 78·2; H, 6·8%).

(*b*) Similar oxidation of the isomeric hydroxymethylene-ketone (V*b*) gave a resinous acid which could not be crystallised. Its *p*-phenylphenacyl ester was obtained as colourless microscopic needles, m. p. 132—146°, very slightly depressed by admixture with the isomeric ester described under (*a*).

1-iso*Propyl*cyclo*pentane*-3 : 4-*bis*-(*β-butyric Acid*).—The acid (VI), m. p. 154°(0·75 g.), was added to thionyl chloride (2 c.c.) at 0°, and the mixture kept for 20 hours. The excess of thionyl chloride was distilled under reduced pressure, and this process was twice repeated after addition, first of ether and then of benzene. A solution of the residual viscous liquid in ether (12 c.c.) was added dropwise at 0° to ethereal diazomethane (from 9 g. of nitrosomethylurea). After being kept overnight the solution was concentrated under diminished pressure and the lemon-yellow solid (0·3 g.) which separated was collected. This *αα′-bisdiazoacetyl*-3 : 4-*diethyl*-1-iso*propyl*cyclo*pentane* crystallised from hexane in yellowish microscopic needles, m. p. 111—111·5° (Found : C, 63·8; H, 7·7. $C_{16}H_{24}O_2N_4$ requires C, 63·2; H, 7·9%).

A solution of this bisdiazo-ketone (0·3 g.) in dioxan (20 c.c.) was heated on the water-bath and treated with 20% aqueous ammonia (1·5 c.c.) and 10% silver nitrate solution (0·3 c.c.). After being heated for 1½ hours the solution was filtered, and the filtrate concentrated to 10 c.c. and again filtered. Evaporation to dryness gave a gum which solidified when rubbed with hexane. This product, presumably a diamide, was hydrolysed by boiling with methanolic potassium hydroxide (0·4 g. in 6 c.c.) until ammonia was no longer liberated (several hours). The acid (0·12 g.) recovered after concentration and acidification was twice recrystallised from aqueous acetic acid. 1-iso*Propyl*cyclo*pentane*-3 : 4-*bis*-(*β-butyric acid*) (VII) formed somewhat discoloured fine needles, m. p. 172—173° (Found : C, 68·1; H, 10·2. $C_{16}H_{28}O_4$ requires, C, 67·6; H, 9·9%).

γ-iso*Propylsuberic Acid*.—This was prepared from *β*-*iso*propyladipic acid in order to gain experience of the Arndt–Eistert reaction with this type of compound. The *iso*propyladipic acid was converted into its chloride and this treated with diazomethane, to give the bis-diazoacetyl compound, which could not be crystallised. It was treated with ammonia and silver nitrate in aqueous dioxan, and the resulting crude amide was hydrolysed with aqueous potash, all these operations being carried out essentially as in the example described above. *γ*-iso*Propylsuberic acid* crystallised from hexane in colourless needles, m. p. 69·5—71° (Found : C, 60·9; H, 9·0. $C_{11}H_{20}O_4$ requires C, 61·1; H, 9·25%). By heating its thorium salt at 300—350° under reduced pressure there was formed a mobile liquid distillate having an odour of violets. It gave a semicarbazone, but with the small quantity of material available this could not be obtained analytically pure.

α-(2-*Keto*-4-iso*propyl*cyclo*pentyl*)*propionic Acid*.—This was prepared in connection with an alternative scheme for the synthesis of the dicarboxylic acid (VI), but in view of the small yield obtained the scheme was not pursued further. Ethyl 4-*iso*propyl*cyclo*pentanone-2-carboxylate (Coats and Cook, *loc. cit.*) (10 g.) was added to a suspension of powdered sodium (1·2 g.) in benzene (40 c.c.) and the mixture was heated under reflux for 2 hours. To the cooled suspension of sodio-compound thus formed was added ethyl α-bromopropionate (10 g.). The mixture was heated on the steam-bath for 6 hours, cooled, poured into water, and extracted with ether; the benzene–ether layer was dried (Na_2SO_4) and distilled. The principal fraction (8·8 g.) formed a colourless liquid, b. p. 140—180°/10 mm. This crude keto-ester was hydrolysed by boiling its suspension in concentrated hydrochloric acid (60 c.c.) for 6 hours. The crude acidic product formed a resin which solidified when treated with light petroleum. After three recrystallisations from hexane *α*-(2-*keto*-4-iso*propyl*cyclo*pentyl*)*propionic acid* formed small colourless needles, m. p. 109—110° (Found : C, 66·6; H, 9·3. $C_{11}H_{18}O_3$ requires C, 66·7; H, 9·1%). The ethyl ester, b. p. 145—150°/15 mm., prepared from the crude acid, gave a *semicarbazone* which crystallised from aqueous methanol in long flat needles, m. p. 164—166·5° (Found : C, 59·6; H, 8·8; N, 14·8. $C_{14}H_{25}O_3N_3$ requires C, 59·3; H, 8·9; N, 14·8%).

Cyclisation of Monoethyl Ester of cyclo*Heptenylsuccinic Acid* (IX).—The crude ester was obtained in 80% yield by condensation of suberone with ethyl succinate, using essentially the conditions described by Plattner and Büchi (*loc. cit.*). Our purified material had m. p. 68—70° (Found : C, 65·1; H, 8·2. Calc. for $C_{13}H_{20}O_4$: C, 65·0; H, 8·4%). Plattner and Büchi give m. p. 68·5—69°. A solution of the crude half-ester (13·6 g.) in acetic anhydride (155 c.c.) and acetic acid (80 c.c.) containing fused zinc chloride (20 mg. per c.c.) was boiled under reflux for 3½ hours, during which a slow stream of nitrogen was passed into the reaction flask. Water (155 c.c.) and concentrated hydrochloric acid (60 c.c.) were then added and boiling continued for ¾ hour, to hydrolyse the intermediate keto-ester. The solvents were distilled off under reduced pressure, and the residue heated on the steam-bath for ½ hour with 5% potassium hydroxide solution (200 c.c.). Extraction with ether then removed the dicyclic ketone (I), which, after purification through the semicarbazone, m. p. 235—236° (Plattner and Büchi give m. p. 238°), formed a colourless liquid, b. p. 58—60°/0·1 mm.; $n_D^{11·5°}$ 1·5275 (Found : C, 79·9; H, 9·2. Calc. for $C_{10}H_{14}O$: C, 80·0; H, 9·4%) (25% yield).

Acidification of the alkaline solution from which the ketone had been extracted precipitated a mixture of acids (28·2 g. obtained from 57·5 g. of the half-ester) which was separated by fractional crystallisation from aqueous acetic acid into two components. One of these formed stout colourless needles, m. p. 171°, and rapidly reduced potassium permanganate solution (Found : C, 62·3; H, 7·2; equiv., by titration with alcoholic potash, 106·5. Calc. for $C_{11}H_{16}O_4$: C, 62·3; H, 7·6%; equiv., 106). This is regarded as *cyclo*heptylidenesuccinic acid (X), obtained by Plattner and Büchi by direct hydrolysis of the half-ester (IX). The second acid, which was stable to permanganate, formed small colourless plates, m. p. 184—186° (Found : C, 62·3; H, 7·4; equiv., by direct titration, 211; by solution in alkali and back-titration, 97. $C_{11}H_{16}O_4$ requires, C, 62·3; H, 7·6%; equiv., 212). These data support the view that the compound is the *lactonic acid* (XI). It was recovered unchanged from an attempt to convert it into the dicyclic ketone (I) by boiling acetic acid–acetic anhydride containing zinc chloride. Attempts to cyclise the unsaturated acid (X) by means of an internal Friedel–Crafts reaction or of the half-ester (IX) by treatment with anhydrous hydrogen fluoride also failed.

The work of Johnson *et al.* (*J. Amer. Chem. Soc.*, 1945, **67**, 2274) suggested that better results might be obtained by condensing ethyl succinate with α-cyanosuberone rather than suberone itself. By a similar reaction Johnson synthesised a condensed 5-membered ring in one operation. For the preparation of α-cyanosuberone (Ziegler *et al.*, *Annalen*, 1933, **504**, 117), hydroxymethylenesuberone (Wallach and Steindorff, *ibid.*, 1903, **329**, 128) was treated with hydroxylamine followed by sodium methoxide, as described by Johnson and Shelberg (*J. Amer. Chem. Soc.*, 1945, **67**, 1745) for a similar case. A by-product of the reaction was 3 : 4-cyclo*heptene*iso*oxazole*, which was extracted from the mother-liquors of the crude cyanosuberone by means of ethanolic mercuric chloride. The mercurichloride was decomposed with alkali, and the *iso*oxazole isolated by steam distillation. It formed a colourless liquid, b. p. 50—52°/0·2 mm. (Found : C, 69·5; H, 7·6; N, 10·0. $C_8H_{11}ON$ requires C, 70·1; H, 8·0; N, 10·2%). Condensation of α-cyanosuberone with ethyl succinate, in presence of potassium *tert.*-butoxide, gave no ketonic product.

Azulene.—Hydrogenation of 1-keto-$\Delta^{9:10}$-octahydroazulene (I) was effected in ethanolic solution by Adams's platinum catalyst or, more rapidly, by palladised strontium carbonate. The resulting 1-ketodecahydroazulene gave a homogeneous *semicarbazone*, m. p. 229—230° (decomp.) (Found : C, 63·3; H, 8·9; N, 20·0. $C_{11}H_{19}ON_3$ requires C, 63·2; H, 9·1; N, 20·1%). Reduction of the saturated ketone with amalgamated zinc and hydrochloric acid containing a little acetic acid gave, after 30 hours, a 60% yield of the saturated hydrocarbon, b. p. 192° (Plattner, Fürst, and Jirasek, *Helv. Chim. Acta*, 1946, **29**, 730, give b. p. 80°/11 mm.). This hydrocarbon was resistant to dehydrogenation which was, however, achieved by heating with selenium (2 parts) at 360° for 4 days in a long-necked flask with an internal condenser. In the later stages the temperature was raised to above 400°. The deep blue solution of the product in light petroleum was extracted with phosphoric acid (*d* 1·75), and the acid solution diluted and extracted with ether. On evaporation of the ether, azulene remained as a blue solid, and was purified through its *s*-trinitrobenzene complex (55 mg. from 1·1 g. of decahydroazulene), m. p. 165—167° (lit., 166·5—167·5°) (Found, N, 11·9. Calc. for $C_{16}H_{11}O_6N_3$: N, 12·3%). A solution of this complex in hexane was passed through a column of alumina, and gave blue crystals of azulene, micro-m. p. 85—89°.

δ-*Phenylvaleric Acid.*—This was obtained in 63% yield from cinnamaldehyde by the following procedure, which represents a vast improvement on the yields claimed by previous workers (compare Kadesch, *J. Amer. Chem. Soc.*, 1944, **66**, 1212) : Cinnamaldehyde (100 g.), malonic acid (80 g.), and quinoline (98 g.) were warmed together on the water-bath until a clear red solution was formed. Piperidine (2 c.c.) was then added, and the solution was cooled and kept in the dark for 10 days. The solid mass was treated with excess of sodium hydroxide solution, the quinoline was extracted with ether, and the alkaline solution was acidified. This precipitated cinnamylidenemalonic acid (153 g.), which was reduced in alkaline solution to γ-phenylpropylmalonic acid by means of a nickel–aluminium alloy (cf. Schwenck, Papa, Whitman, and Ginsberg, *J. Org. Chem.*, 1942, **7**, 587; 1944, **9**, 1, 175). For this purpose, Raney nickel alloy (135 g.) was added during 2 hours to a stirred, almost boiling, solution of crude cinnamylidenemalonic acid (137 g.) in sodium hydroxide (230 g. in 1500 c.c. of water). To minimise frothing, a little *sec.*-octyl alcohol was added. The mixture was stirred at 90° for another hour, filtered, and the filtrate slowly run into a hot solution of sulphuric acid (450 c.c. of concentrated acid in 1 l. of water). The main bulk of the precipitated oil was not purified, but was separated and then heated under reduced pressure at 140—180° for 2 hours, in order to decarboxylate the phenylpropylmalonic acid. The resulting δ-phenylvaleric acid (75·5 g.) required very little purification.

Cyclisation of this acid to 2 : 3-benzsuberone was effected in 90% yield by the excellent method of Plattner (*Helv. Chim. Acta*, 1944, **27**, 804), but no reaction occurred when the acid was treated with anhydrous hydrogen fluoride.

1-*Keto*-4 : 5-*benz*-$\Delta^{4:9}$-*hexahydroazulene* (XIII).—Benzsuberone (5 g.) was condensed with ethyl succinate (8·25 g.) by means of potassium *tert.*-butoxide (1·5 g. of potassium in 30 c.c. of *tert.*-butyl alcohol) as in the case of suberone. The crude half-ester (XII) gave crystals, m. p. 170—173°, by sublimation at 0·2 mm., but the analysis figures of these were not satisfactory. This half-ester (5·2 g.) was treated in the usual manner with acetic anhydride (52 c.c.) and acetic acid (26 c.c.), containing zinc chloride. In addition to acidic products which were not investigated, there was formed a neutral oil (1 g.) which was separated by distillation into (*a*) a fraction, b. p. 125—130°/0·4 mm., and (*b*) a residue which sublimed at 155—160°/0·4 mm. Fraction (*b*) crystallised from ethanol in colourless prisms, m. p. 199—201° (Found : C, 75·4; H, 6·0%). This material, which gave a 2 : 4-dinitrophenylhydrazone only on long standing, was not further examined. Fraction (*a*) was the desired *ketone* (XIII), and crystallised from methanol in long colourless needles, m. p. 60—62° (Found : C, 84·9; H, 7·0. $C_{14}H_{14}O$ requires C, 84·8; H, 7·1%); it gave a *semicarbazone*, which formed clusters of colourless needles (from ethanol), m. p. 236° (decomp.) after sintering (Found : C, 69·7; H, 6·5; N, 16·6. $C_{15}H_{17}ON_3$ requires C, 70·6; H, 6·7; N, 16·5%). Work on the conversion of this ketone into 4 : 5-benzazulene and its derivatives is being continued.

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