171. *Attempts to Prepare New Aromatic Systems. Part III.* cyclo*Pent*[a]*indene.*

By Wilson Baker and P. G. Jones.

In continuation of experiments designed to synthesise *cyclo*pent[*a*]indene (I) a much improved preparation of the ketone (IV) has been found in the reaction of *cyclo*pent-1-enecarboxyl chloride (II) with benzene in presence of aluminium chloride at the boiling-point. Reduction of (IV) gave the hexahydro*cyclo*pent[*a*]indene (V), but dehydrogenation of this hydrocarbon to *cyclo*pent[*a*]-indene (I) has not been successful. Reaction of the 3-keto-2-phenyl*cyclo*pentane-1-carboxylic acid (X) with phosphoric anhydride proceeded abnormally to give 2-phenyl*cyclo*pent-2-enone (XV) by loss of the elements of formic acid. The action of acetic anhydride in the cold on (X) gave the enol acetate (XI) but, on heating, the reaction proceeded further to give the complex acetoxy-lactone (XIII).

Experiments having as their object the synthesis of the unknown hydrocarbon *cyclo*pent[*a*]indene (I) were described by Baker and Leeds in Part I of this Series (*J.*, 1948, 974). *cyclo*Pent[*a*]indene * is of interest in that it is the simple benzo-derivative of pentalene, the latter being a possible, but as yet unknown, compound of aromatic type consisting of two fused five-membered rings containing, formally, four double bonds (see Part I).

It was shown (*loc. cit.*) that a compound with the desired carbon skeleton, namely 1 : 2 : 3 : 8 : 9 : 10-hexahydro-8-keto*cyclo*pentindene * (IV), could be prepared by condensing benzene with *cyclo*pent-1-enecarboxylic acid and aluminium chloride at the boiling point, isolating the 2-phenyl*cyclo*pentane-1-carboxylic acid, and then cyclising it with a phoshoric anhydride–phosphoric acid mixture to the ketone (IV). This synthesis is, however, not very practicable because the reaction between benzene and *cyclo*pent-1-enecarboxylic acid is complex and gives the desired acid in only about 8% yield; neutral material and much 3-phenyl*cyclo*pentane-1-carboxylic acid are formed owing to migration of the double bond in *cyclo*pent-1-enecarboxylic acid under the influence of the aluminium chloride. Nevertheless this type of reaction appeared to be the most promising for the preparation of the hexahydroketo*cyclo*pent[*a*]indene (IV), and further work was undertaken.

*cyclo*Pent-1-enecarboxyl chloride (II) reacts with benzene at room temperature to give 1-benzoyl*cyclo*pentene (III) by a simple Friedel–Crafts reaction. This ketone is oxidised by potassium permanganate to benzoic acid. The position assigned to the double bond is supported by the bright red colour of the 2 : 4-dinitrophenylhydrazone. The ketone (III) when heated with benzene and aluminium chloride undergoes cycloisomerisation to the desired tricyclic ketone (IV) identical with that previously prepared by Baker and Leeds (*loc. cit.*). In preparing (IV) it is not necessary to isolate the intermediate (III), and it is conveniently made directly from the acid chloride (II) in 58% yield by reaction with benzene and aluminium chloride at the boiling point. Unsuccessful attempts to bring about the addition of benzene to 1-cyano*cyclo*pentene (an intermediate in the preparation of II) in presence of hydrogen chloride

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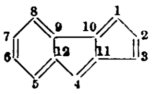
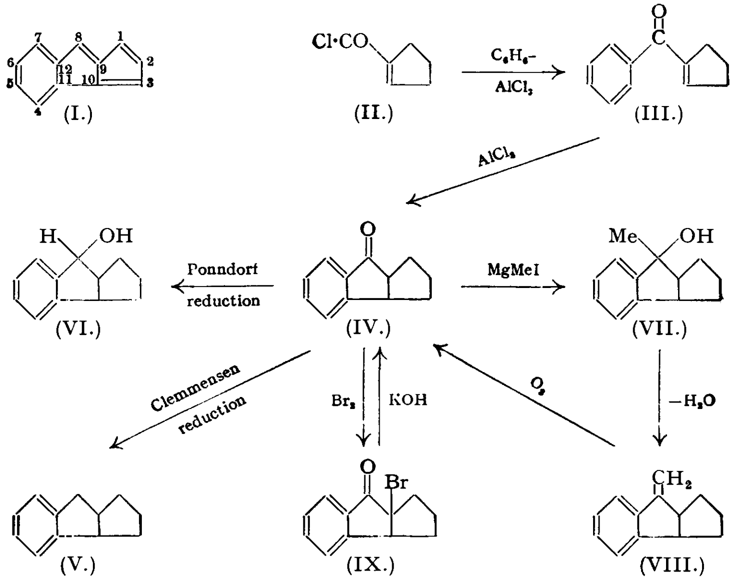
* In *J.*, 1948, 974, this ring-system was numbered  but the Ring Index method (as in I) is now preferred—Editor.

and either aluminium chloride or zinc chloride led to the isolation of 1-chloro-2-cyano*cyclo*pentane and 2-chloro*cyclo*pentan-1-carboxyamide respectively. It is interesting to note that in the preparation of the ketone (IV) by the present method, there is no formation of the isomeric ketone, 1 : 3-*endo*ethylene-4-keto-1 : 2 : 3 : 4-tetrahydronaphthalene, which is produced by reaction of benzene with *cyclo*pent-1-enecarboxylic acid along with much of the intermediate 3-phenyl*cyclo*pentane-1-carboxylic acid (see Part I). It appears that in the acid chloride (II) and in the ketone (III) there is no tendency for the double bond to wander as in *cyclo*pent-1-enecarboxylic acid, and this may be ascribed to the degree of conjugation being greater (owing to increased cationoid character of the carbon atom of the carbonyl group) in the acid chloride (II) and the ketone (III) than in the free carboxylic acid.

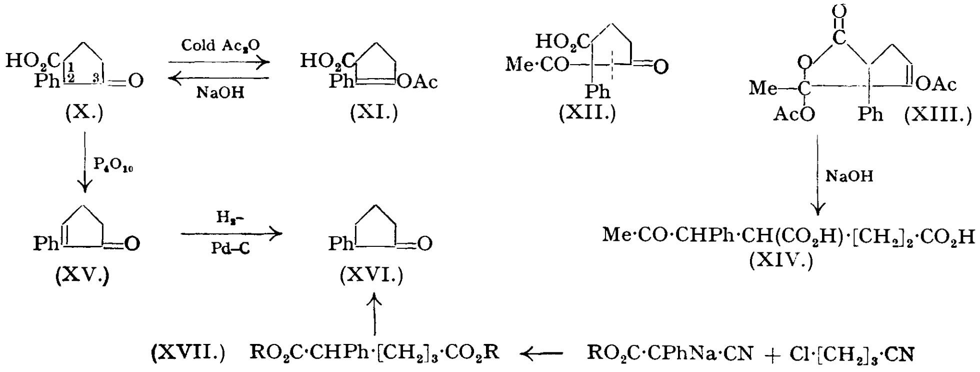
Reduction of (IV) by the Clemmensen method in presence of toluene gave 1 : 2 : 3 : 8 : 9 : 10-hexahydro*cyclo*pent[*a*]indene (V), and this hydrocarbon was characterised as a monosulphonamido-compound, probably the 6-derivative. Many attempts were made to dehydrogenate (V) to *cyclo*pent[*a*]indene (I), but no conclusive evidence was obtained of the production of any less saturated material with aromatic properties. The methods investigated, which are not described in the Experimental section, included boiling with either palladium–charcoal, platinum–charcoal, or selenium, and passage of the vapour over (*a*) palladium–charcoal and asbestos at 330—350° under reduced pressure (see apparatus described by Nunn and Rapson, *J.*, **1949**, 825, 1051) or (*b*) platinum–charcoal at 340° in a stream of nitrogen at atmospheric pressure (see apparatus described by Read and Dewar, *J. Soc. Chem. Ind.*, **1936**, **55**, 347T).



As direct dehydrogenation of (V) had failed, other methods which might lead to *cyclo*pent[*a*]indene were investigated starting from the ketone (IV). Reduction to the secondary alcohol by the Ponndorf method proved difficult and only partial reduction took place giving a mixture of 1 : 2 : 3 : 8 : 9 : 10-hexahydro-8-hydroxy*cyclo*pent[*a*]indene (VI) and much unchanged ketone (IV). The hydroxy-compound was freed from the ketone by several treatments with Girard T reagent, and was finally characterised as the *p*-nitrobenzoyl and the α-naphthylurethane derivatives. Treatment of (IV) with methylmagnesium iodide gave 1 : 2 : 3 : 8 : 9 : 10-hexahydro-8-hydroxy-8-methyl*cyclo*pent[*a*]indene (VII), a solid which underwent dehydration at 120° to the fluid 1 : 2 : 3 : 8 : 9 : 10-hexahydro-8-methylene*cyclo*pent[*a*]indene (VIII). The structure assigned to this product, which may not be homogeneous, is based on the fact that ozonolysis gave the ketone (IV), though in poor yield ; the double bond is unlikely to be between carbon atoms 8 and 9 as this mono-olefin would be considerably strained. Bromination of the ketone (IV) in acetic acid gave 9-bromo-1 : 2 : 3 : 8 : 9 : 10-hexahydro*cyclo*pent[*a*]indene (IX), which was virtually stable towards silver oxide, potassium acetate, pyridine at 120°, or quinoline at 170°. With ethanolic potassium hydroxide the bromine atom was replaced by hydrogen and the ketone (IV) was regenerated. This is clearly a case of " positive " halogen in the α-position to a carbonyl group being replaced by hydrogen; the reaction is much better known in the case of reduction by halogen acids, particularly hydriodic acid, than by alkalis (see Lapworth, *J.*, 1899, **75**, 1134; *Mem. Proc. Manchester Lit. Phil. Soc.*, 1920, **64**, ii, 8; Gilman, "Organic Chemistry," 2nd Edn., 1942, Vol. I, 854).

As the foregoing experiments with the ketone (IV) did not appear promising, attention was turned to the possible use of 3-keto-2-phenyl*cyclo*pentane-1-carboxylic acid (X) as an accessible starting point for the synthesis of *cyclo*pent[*a*]indene (I). This acid (X) is an intermediate in one of the syntheses of the ketone (IV) described in Part I, and it was hoped that it might be cyclised to 1 : 2 : 3 : 8 : 9 : 10-hexahydro-3 : 8-diketo*cyclo*pent[*a*]indene which would be a very promising starting point for the preparation of *cyclo*pent[*a*]indene by purely chemical methods rather than by catalytic dehydrogenation at fairly high temperatures. Cyclisation of the acid (X) has not yet been achieved, although a variety of methods has been tried, but the experiments have revealed some rather remarkable properties of this compound.

When treated with acetic anhydride at room temperature in presence of a little sulphuric acid, (X) was converted into its enol acetate, 3-acetoxy-2-phenyl*cyclo*pent-2-ene-1-carboxylic acid (XI), and this substance regenerated the keto-acid (X) on alkaline hydrolysis The position assigned to the double bond in the enol acetate (XI) is the more probable of the two possibilities as it gives the greater degree of conjugation. The action of hot acetic anhydride on the keto-acid (X), $C_{12}H_{12}O_3$, gave a substance which showed neither acidic nor ketonic properties and whose analysis showed it to be a triacetyl derivative of (X), *i.e.*, $C_{18}H_{18}O_6$. Determination of the acetyl groups by alkaline hydrolysis showed that two only were removed as acetic acid and these must be regarded as *O*-acetyl groups, so that the third must be attached to carbon. We regard the compound, $C_{18}H_{18}O_6$, as the acetoxy-lactone (XIII); it probably arises from the enol acetate (XI) as follows. Migration of the acetyl group from oxygen to carbon atom 2 first occurs, to give the diketone (XII); this then forms the enol acetate at the 3-carbonyl group, and, as a γ-keto-acid, gives the lactone (XIII). An analogy for the migration of the acetyl group in (XI) is afforded by the rearrangement of *O*-acetyl- to *C*-acetyl-acetoacetic ester (Claisen and Haase, *Ber.*, 1900, **33**, 3778; Wislicenus and Körber, *Ber.*, 1901, **34**, 218; Bouveault and Borgert, *Bull. Soc. chim.*, 1902, **27**, 1160; Wislicenus, *Ber.*, 1905, **38**, 546; Dieckman and Stein, *Ber.*, 1904, **37**, 3373), and there are many cases, *e.g.*, lævulic acid, of γ-keto-acids which yield acetoxy-lactones when treated with acetic anhydride. Support for the structure (XIII) is afforded by the isolation, after complete hydrolysis by boiling with 10% aqueous sodium hydroxide, of a dicarboxylic acid containing a *C*-acetyl group as proved by a positive iodoform reaction. This dicarboxylic acid has clearly arisen by opening of the *cyclo*pentanone ring in the 1 : 3-diketone (XII) (cf. ring opening of acyl*cyclo*hexanones investigated by Hauser, Swamer, and Ringler, *J. Amer. Chem. Soc.*, 1948, **70**, 4023) which is undoubtedly an intermediate in the alkaline hydrolysis of (XIII). This acid must, therefore, be regarded as 5-keto-4-phenylhexane-1 : 3-dicarboxylic acid (XIV).



Cyclodehydration of the ketonic acid (X) was attempted by heating it with a mixture of phosphoric anhydride and syrupy phosphoric acid, a procedure which has proved very satisfactory for the cyclisation of 2- and 3-phenyl*cyclo*pentane-1-carboxylic acids (Part I). Recent investigation has shown that polyphosphoric acid is probably the active agent in these cases (Snyder and Werber, *J. Amer. Chem. Soc.*, 1950, **72**, 2962, 2965). The reaction yielded a solid, neutral ketone, $C_{11}H_{10}O$, which gave benzoic acid on oxidation with alkaline potassium permanganate and had been derived from the keto-acid (X) merely by the loss of the elements of formic acid. This ketone must be 2-phenyl*cyclo*pent-2-enone (XV); catalytic reduction gave 2-phenyl*cyclo*pentanone (XVI), characterised by a 2 : 4-dinitrophenylhydrazone and an oxime which were identical with those derived from 2-phenyl*cyclo*pentanone synthesised from α-phenyladipic acid (XVII; R = H) by esterification, cyclisation, and final hydrolysis and decarboxylation. The position assigned to the double bond in (XV) is based on the orange-red colour of the derived 2 : 4-dinitrophenylhydrazone and on its almost certain conjugation with both the phenyl and the carbonyl group. α-Phenyladipic acid was previously prepared by Case (*J. Amer. Chem. Soc.*, 1933, **55**, 2929) from the sodio-derivative of ethyl phenylmalonate and γ-iodobutyronitrile; in this work it was prepared from rather more accessible intermediates, namely the sodio-derivative of ethyl α-cyanophenylacetate and γ-chlorobutyronitrile. We find that the preparation of 2-phenyl*cyclo*pentanone from 2-chloro*cyclo*pentanone and phenylmagnesium bromide described by Mitchovitch (*Compt. rend.*, 1935, **200**, 1601) is unsatisfactory, giving a non-homogeneous product in poor yield; the high melting point which he records may be accounted for by the fact that 2-phenyl*cyclo*pentanone is curiously unstable and passes, when kept, into much-higher-melting material (see Experimental).

There is no evidence to suggest the mechanism of the loss of the elements of formic acid from the ketone (X), which may be either direct, or indirect involving a shift of the double bond of the enol form to the 1 : 2-position followed by an allylic rearrangement and loss of the elements of formic acid from the α-hydroxy-acid so produced.

EXPERIMENTAL.

1-*Benzoyl*cyclo*pentene* (III).—*cyclo*Pent-1-enecarboxylic acid (10·5 g.; Cook and Linstead, *J.*, 1934, 958, and modification given by Baker and Leeds, *loc. cit.*) and thionyl chloride (101 c.c.) were heated on the steam-bath for ¼ hour and distilled, giving *cyclo*pent-1-enecarboxyl chloride (II), b. p. 65—67°/16 mm. (95 g., 78%) (Kenner and Wain, *Ber.*, 1939, **72**, 459, do not record the method of preparation, but give b. p. 179—180°/758 mm.). The chloride (8·1 g., 1 mol.) in dry benzene (100 c.c.) was cooled in ice, and aluminium chloride (25 g., 3 mols.) added during ½ hour. After 20 hours at room temperature, the mixture was poured on ice and concentrated hydrochloric acid (50 c.c.), and the benzene layer separated, washed with dilute aqueous sodium hydroxide, dried ($MgSO_4$), and distilled, giving 1-*benzoyl*cyclo*pentene* (III) as a colourless oil (5·6 g., 52%), b. p. 143°/12 mm., d_{18}^{18} 1·068 (Found : C, 84·1; H, 7·3. $C_{12}H_{12}O$ requires C, 83·7; H, 7·0%). The 2 : 4-*dinitrophenylhydrazone* crystallised from ethanol as red plates, m. p. 162—163° (Found : C, 61·9; H, 4·7; N, 15·9. $C_{18}H_{16}O_4N_4$ requires C, 61·4; H, 4·6; N, 15·9%). Oxidation of this ketone (0·56 g.) by boiling it for 5 hours with alkaline potassium permanganate gave benzoic acid (0·16 g., 40%).

1 : 2 : 3 : 8 : 9 : 10-*Hexahydro*-8-*keto*cyclo*pent*[a]*indene* (IV).—(a) *From* 1-*benzoyl*cyclo*pentene*. The ketone (III) (2·17 g., 1 mol.) in dry benzene (50 c.c.) was treated with aluminium chloride (5·1 g., 3 mols.), the mixture heated on the steam-bath for 1 hour, and the product isolated as in the previous case. 1 : 2 : 3 : 8 : 9 : 10-Hexahydro-8-keto*cyclo*pent[*a*]indene (IV) was obtained as a pale yellow oil (1·34 g., 62%), b. p. 145°/12 mm., n_D^{17} 1·5740 (Found : C, 83·6; H, 7·1. Calc. for $C_{12}H_{12}O$: C, 83·7; H, 7·0%). The 2 : 4-dinitrophenylhydrazone separated from acetic acid as deep red needles, m. p. 214—215° (Found : C, 61·3; H, 4·4; N, 16·1. Calc. for $C_{18}H_{16}O_4N_4$: C, 61·4; H, 4·6; N, 15·9%) unaltered when mixed with the 2 : 4-dinitrophenylhydrazone of the ketone, m. p. 216—217°, prepared as described by Baker and Leeds (*loc. cit.*). The *oxime* of the ketone (IV) separated from dilute ethanol in colourless flakes, m. p. 117—119° (Found : C, 76·6; H, 7·0; N, 7·8. $C_{12}H_{13}ON$ requires C, 77·0; H, 7·0; N, 7·5%).

(b) *From* cyclo*pent*-1-*enecarboxyl chloride and benzene*. The acid chloride (95 g., 1 mol.) in dry benzene (900 c.c.) was cooled in ice, aluminium chloride (292 g., 3 mols.) added with shaking during ½ hour, the mixture heated on the steam-bath for 1 hour, and the ketone isolated next morning. The hexahydroketo*cyclo*pent[*a*]indene (IV), b. p. 145°/12 mm., was isolated as previously described, and obtained in a yield of 58% (73 g.); the 2 : 4-dinitrophenylhydrazone had m. p. and mixed m. p. 214—215°.

1-*Chloro*-2-*cyano*cyclo*pentane and* 2-*Chloro*cyclo*pentanecarboxyamide*.—These compounds were isolated in unsuccessful attempts to effect the addition of benzene to 1-cyano*cyclo*pentene. The cyano-compound (4·7 g.) and aluminium chloride (20 g.) in benzene (20 c.c.) and ether (100 c.c.) was treated with hydrogen chloride at 0°, and after 2 days at room temperature the mixture was heated on the steam-bath for ¼ hour and poured on ice. The benzene layer was washed with dilute aqueous sodium hydroxide, dried ($MgSO_4$), and distilled, yielding 1-cyano*cyclo*pentene, b. p. 60—75°/18 mm. (1·35 g.), and 1-*chloro*-2-*cyano*cyclo*pentane*, b. p. 125—126°/18 mm. (Found : C, 56·0; H, 6·4; N, 10·7. C_6H_8NCl requires C, 55·6; H, 6·2; N, 10·8%). Hydrolysis of the chloro-compound (0·51 g.) with 10% aqueous sodium hydroxide for 4 hours on the steam-bath yielded *cyclo*pent-1-enecarboxylic acid (0·3 g.), m. p. and mixed m. p. 119—120°.

A similar experiment using anhydrous zinc chloride gave, on addition of a little ether to the products of reaction before final distillation, 2-*chloro*cyclo*pentanecarboxyamide* (0·42 g.) as a solid which separated from water in colourless flakes, m. p. 152—153° (Found : C, 49·1; H, 6·8; N, 9·6. $C_6H_{10}ONCl$ requires C, 48·9; H, 6·8; N, 9·5%). Distillation then yielded 1-chloro-2-cyano*cyclo*pentane (1·2 g.). Alkaline hydrolysis of this amide yielded *cyclo*pent-1-enecarboxylic acid.

1 : 2 : 3 : 8 : 9 : 10-*Hexahydro*cyclo*pent*[a]*indene* (V).—A solution of 1 : 2 : 3 : 8 : 9 : 10-hexahydro-8-keto*cyclo*pent[*a*]indene (IV) (10 g.) in toluene (10 c.c.) was added to amalgamated zinc (20 g.), water

(25 c.c.), and concentrated hydrochloric acid (50 c.c.), and the mixture stirred under reflux for 9 hours while heated in an oil-bath at 110—120°. More concentrated hydrochloric acid (5 c.c.) was added every 2 hours. The toluene layer was then shaken with aqueous sodium carbonate, dried ($MgSO_4$), and distilled, giving 1 : 2 : 3 : 8 : 9 : 10-*hexahydro*cyclo*pent*[a]*indene* (V) as a colourless oil (6·95 g., 76%), b. p. 73—75°/1 mm., 107—109°/12 mm., d_{24}^{24} 0·9962; n_D^{17} 1·5511 (Found : C, 91·5; H, 8·8. $C_{12}H_{14}$ requires C, 91·1; H, 8·9%).

This hydrocarbon was characterised as the *monosulphonamido*-derivative, in which substitution has probably occurred in position 6. Chlorosulphonic acid (5 c.c.) was slowly added at 0° with stirring to the hydrocarbon (V) (1·06 g.) in dry chloroform (10 c.c.). After an hour at room temperature the mixture was poured on ice, the chloroform layer was dried, and distilled, and the residual oil heated with powdered ammonium carbonate on the steam-bath for ½ hour. The material, soluble in dilute aqueous sodium hydroxide and precipitated by acid, was crystallised from benzene and then from dilute alcohol, giving minute crystals (0·16 g.), m. p. 130—131° (Found : C, 60·4; H, 6·3; N, 6·2; S, 13·2. $C_{12}H_{15}O_2NS$ requires C, 60·8; H, 6·3; N, 5·9; S, 13·5%).

1 : 2 : 3 : 8 : 9 : 10-*Hexahydro*-8-*hydroxy*cyclo*pent*[a]*indene* (VI).—The ketone (IV) (5 g.), anhydrous *iso*propyl alcohol (50 c.c.), and freshly distilled aluminium *iso*propoxide (5·95 g.) were heated on the steam-bath for 4 hours, whereafter acetone could no longer be detected in the distillate (for apparatus see " Organic Reactions," 1944, **2**, 198). Excess of alcohol was now evaporated off, water (60 c.c.) and concentrated hydrochloric acid (10 c.c.) added with ice-cooling, and the mixture extracted with ether. The extracts yielded a colourless oil (3·3 g.), b. p. 150—160°/18 mm., which contained a considerable amount of unchanged ketone (positive test with 2 : 4-dinitrophenylhydrazine). The crude oil (3·3 g.) in ethanol (25 c.c.) was boiled for 1 hour with glacial acetic acid (6 c.c.) and Girard reagent T (3·3 g.), poured into a solution of sodium carbonate (4·8 g.) in water (100 c.c.) and ice, and extracted with ether. The ether yielded an oil (2·3 g.) which gave a slight precipitate with 2 : 4-dinitrophenylhydrazine, but two further similar treatments with Girard reagent T gave a ketone-free oil (1·5 g.). This 1 : 2 : 3 : 8 : 9 : 10-hexahydro-8-hydroxy*cyclo*pent[*a*]indene (0·49 g.) (VI) gave an *a-naphthylurethane* derivative which separated after the alcohol had been heated with α-naphthyl *iso*cyanate (0·6 c.c.) and light petroleum (15 c.c.; b. p. 80—100°) for 2 hours on the steam-bath; the product (0·53 g.) recrystallised from light petroleum (b. p. 80—100°) or from dilute ethanol in needles, m. p. 152—156° (Found : C, 80·6; H, 6·5; N, 4·7. $C_{23}H_{21}O_2N$ requires C, 80·5; H, 6·1; N, 4·1%). The p-*nitrobenzoyl* derivative formed thin flakes, m. p. 98·5—99·5° (Found : C, 70·4; H, 5·3; N, 5·0. $C_{19}H_{17}O_4N$ requires C, 70·6; H, 5·3; N, 4·3%).

1 : 2 : 3 : 8 : 9 : 10-*Hexahydro*-8-*hydroxy*-8-*methyl*cyclo*pent*[a]*indene* (VII).—1 : 2 : 3 : 8 : 9 : 10-Hexahydro-8-keto*cyclo*pentindene (IV) (20 g.) in ether (20 c.c.) was added at 0° to a solution of the Grignard reagent prepared from magnesium (5·64 g.), methyl iodide (38 g.), and ether (100 c.c.). After being kept overnight the mixture was poured into dilute hydrochloric acid and ice, and the ethereal layer yielded a solid (19·1 g., 87%) which separated from light petroleum (b. p. 60—80°) in thick, hexagonal plates, m. p. 67—69° (Found : C, 82·9; H, 8·6. $C_{13}H_{16}O$ requires C, 83·0; H, 8·5%). This 1 : 2 : 3 : 8 : 9 : 10-*hexahydro*-8-*hydroxy*-8-*methyl*cyclo*pent*[a]*indene* (VII) appears to be dimorphic; when kept the crystals became opaque and then melted at 72—74°, but recrystallisation gave again the clear plates, m. p. 67—69°. The m. p. range of this apparently pure compound is doubtless connected with its dimorphism.

Dehydration of 1 : 2 : 3 : 8 : 9 : 10-*Hexahydro*-8-*hydroxy*-8-*methyl*cyclo*pent*[a]*indene* (VII). *Formation of* 1 : 2 : 3 : 8 : 9 : 10-*hexahydro*-8-*methylene*cyclo*pent*[a]*indene* (VIII).—The hydroxy-derivative (VII) (19·1 g.) was kept at 120° for 1 hour, then dissolved in ether, dried ($MgSO_4$), and distilled, finally over sodium, giving a colourless oil (10·9 g.), b. p. 90—92°/4 mm., n_D^{17} 1·5770 (Found : C, 91·6; H, 8·4. $C_{13}H_{14}$ requires C, 91·8; H, 8·2%). This hydrocarbon may not be homogeneous, but it is with little doubt essentially 1 : 2 : 3 : 8 : 9 : 10-*hexahydro*-8-*methylene*cyclo*pentindene* (VIII); it decolourises solutions of bromide in carbon tetrachloride and of potassium permanganate in water. Ozonolysis (of 0·39 g.) yielded a ketonic material giving a red 2 : 4-dinitrophenylhydrazone from ethanolic sulphuric acid solution (yield : 0·105 g., 13%), which after crystallisation from acetic acid formed dark red needles, m. p. 214—215°, undepressed when mixed with a specimen of the 2 : 4-dinitrophenylhydrazone of 1 : 2 : 3 : 8 : 9 : 10-hexahydro-8-keto*cyclo*pent[*a*]indene (IV).

9-*Bromo*-1 : 2 : 3 : 8 : 9 : 10-*hexahydro*-8-*keto*cyclo*pent*[a]*indene* (IX).—1 : 2 : 3 : 8 : 9 : 10-Hexahydro-8-keto*cyclo*pent[*a*]indene (IV) (18·3 g.) in acetic acid (50 c.c.) was gently heated on the steam-bath with bromine (18·7 g.) for ½ hour, then poured into water, and shaken with ether. The ethereal extract was washed with excess of aqueous sodium hydrogen carbonate, dried, and distilled, giving 9-*bromo*-1 : 2 : 3 : 8 : 9 : 10-*hexahydro*-8-*keto*cyclo*pent*[a]*indene* (IX) as a yellow oil (22·7 g., 85%), b. p. 125—127°/1 mm., n_D^{11} 1·6080 (Found : C, 57·6; H, 4·4. $C_{12}H_{11}OBr$ requires C, 57·4; H, 4·4%). The 2 : 4-*dinitrophenylhydrazone* separated from acetic acid in orange flakes, m. p. 197° (Found : C, 50·0; H, 3·6; N, 13·0. $C_{18}H_{15}O_4N_4Br$ requires C, 50·1; H, 3·5; N, 13·0%).

Reaction of 3-*Keto*-2-*phenyl*cyclo*pentane*-1-*carboxylic Acid* (X) *with Acetic Anhydride*.—(a) *Formation of* 3-*acetoxy*-2-*phenyl*cyclo*pent*-2-*ene*-1-*carboxylic acid* (XI). The keto-acid (X) (2 g.) in acetic anhydride (20 c.c.) was treated with a few drops of concentrated sulphuric acid, and after 22 hours at room temperature, the mixture was evaporated at 40° under diminished pressure, and the residue shaken with water and ether. The ethereal layer was dried ($MgSO_4$) and yielded an oil which was obtained crystalline from benzene–light petroleum (b. p. 60—80°). 3-*Acetoxy*-2-*phenyl*cyclo*pent*-2-*ene*-1-*carboxylic acid* (XI) separated as colourless needles (0·75 g.), m. p. 145° (Found : C, 68·3; H, 5·6. $C_{14}H_{14}O_4$ requires C, 68·3; H, 5·7%). This acid is precipitated unchanged after dissolving in dilute aqueous sodium hydrogen carbonate at 0°, but, when a solution in cold 5% aqueous sodium carbonate was acidified after being kept overnight, it regenerated 3-keto-2-phenyl*cyclo*pentane-1-carboxylic acid (X), m. p. and mixed m. p. 114—115°.

(b) 2 : 3′-*Diacetoxy*-2 : 3 : 4 : 5-*tetrahydro*-5-*keto*-2-*methyl*-3-*phenyl*cyclo*pent*-3-*eno*(2′ : 1′-3 : 4)*furan* (XIII). The keto-acid (X) (1 g.) and acetic anhydride (10 c.c.) were boiled for 12 hours, then evaporated under diminished pressure, and the residue crystallised from ethanol. The *acetoxy-lactone* (XIII) separated as thin plates (0·35 g.), m. p. 137—178° [Found : C, 65·7; H, 5·6; Ac, 24·9. $C_{14}H_{12}O_2(OAc)_2$ requires C, 65·5; H, 5·5; Ac, 26·1%].

5-*Keto*-4-*phenylhexane*-1 : 3-*dicarboxylic Acid*.—The preceding acetoxy-lactone (XIII) (0·2 g.) was boiled with 10% aqueous sodium hydroxide (4 c.c.) for ½ hour, the solution cooled and acidified, giving 5-*keto*-4-*phenylhexane*-1 : 3-*dicarboxylic acid* (XIV) as fine crystals, m. p. 154—155° [Found : C, 63·5; H, 6·5%; equiv., 126. $C_{12}H_{14}O(CO_2H)_2$ requires C, 63·6; H, 6·1%; equiv., 132]. When warmed with 10% aqueous sodium hydroxide, sodium hypochlorite, and potassium iodide, it readily gave a precipitate of iodoform, m. p. and mixed m. p. 119—120°.

2-*Phenyl*cyclo*pent*-2-*enone* (XV).—3-Keto-2-phenyl*cyclo*pentanecarboxylic acid (9 g.) was added with stirring to a previously prepared and cooled mixture of syrupy phosphoric acid (45 c.c.; *d* 1·75) and phosphoric anhydride (45 g.), and after 3 hours' heating on the steam-bath the product was cooled, poured on ice, and extracted with ether. The ethereal solution was washed with dilute aqueous sodium hydroxide, dried, and distilled, giving 2-*phenyl*cyclo*pent*-2-*enone* (XV) (3·1 g.) as an oil, b. p. 110—113°/2 mm., which solidified on cooling. It crystallised from light petroleum (b. p. 60—80°) as colourless plates, m. p. 72° (Found : C, 83·7; H, 6·3. $C_{11}H_{10}O$ requires C, 83·5; H, 6·3%). The 2 : 4-*dinitrophenylhydrazone* separated from dioxan in thick, orange-red needles, m. p. 209—210° (Found : C, 60·4; H, 4·2; N, 16·5. $C_{17}H_{14}O_4N_4$ requires C, 60·4; H, 4·1; N, 16·6%). The *semicarbazone* formed nacreous flakes from ethanol, m. p. 235—237° (decomp.) (Found : C, 66·6; H, 6·0; N, 19·4. $C_{12}H_{13}ON_3$ requires C, 67·0; H, 6·0; N, 19·5%). Oxidation of this ketone with alkaline potassium permanganate solution at the b. p. for ½ hour gave benzoic acid (49%), m. p. and mixed m. p. 122°.

2-*Phenyl*cyclo*pentanone* (XVI).—(a) *By reduction of* 2-*phenyl*cyclo*pent*-2-*enone* (XV). The ketone (XV) in methanol was shaken in hydrogen for 3 hours at one atm. pressure in presence of a small quantity of 30% palladium–charcoal, and the solution filtered and evaporated, leaving an oil which solidified at 0° but melted at room temperature. It yielded a 2 : 4-dinitrophenylhydrazone, m. p. 142—144° after crystallisation from ethanol; on admixture with the 2 : 4-dinitrophenylhydrazone prepared by method (b) the m. p. was 142—145°. The oxime formed colourless needles (from light petroleum), m. p. and mixed m. p. with the oxime prepared by method (b), 141—142°.

(b) *From α-phenyladipic acid* (XVII; R = H). α-Phenyladipic acid was prepared from the sodio-derivative of ethyl α-cyano-α-phenylacetate (Wallingford, Jones, and Homeyer, *J. Amer. Chem. Soc.*, 1942, **64**, 576; Horning and Finelli, *ibid.*, 1949, **71**, 3204) by reaction with 3-chloropropyl cyanide (*Org. Synth.*, 1944, Coll. Vol. I, p. 156). The sodio-derivative, prepared from sodium ethoxide (15·4 g.), phenylacetonitrile (26·2 g.), and ethyl carbonate (120 c.c.), was treated without isolation with 3-chloropropyl cyanide (23·2 g.), and the mixture heated in an oil-bath at 120° for 3 hours. The cooled, acidified product was extracted with ether, and the extracts were dried and distilled, giving a fraction (22·5 g.), b. p. 159—165°/1 mm., which was boiled with concentrated hydrochloric acid (150 c.c.) for 12 hours, then cooled, and the α-phenyladipic acid collected (19·5 g., 39%). It separated from water in colourless needles, m. p. 137—138° (Found : C, 65·2; H, 6·6. Calc. for $C_{12}H_{14}O_4$: C, 64·9; H, 6·3%) (Case, *J. Amer. Chem. Soc.*, 1933, **55**, 2929, records m. p. 131—133°, and Kuhn and Michel, *Ber.*, 1938, **71**, 1125, m. p. 135·5°). This acid (19·5 g.) was converted into the ethyl ester (XVII; R = Et), a very pale green oil (19·4 g.), b. p. 135—137°/0·5 mm., n_D^{15} 1·4932, by boiling it with ethanol (50 c.c.) and concentrated sulphuric acid (5 c.c.) for 6 hours, and working up the product in the usual way. Cyclisation of this ester (4·9 g.) was effected by boiling it for 6·5 hours with a solution of sodium (0·41 g.) in dry ethanol (12 c.c.), removing the ethanol by distillation, and hydrolysing and decarboxylating the product by boiling the residue with water (5 c.c.) and concentrated hydrochloric acid (15 c.c.) for 12 hours. The diluted mixture was then extracted with ether, and the extracts were washed with aqueous sodium carbonate, dried, and distilled, giving crude 2-phenyl*cyclo*pentanone (XVI) (1·35 g., 48%), collected at 114—124°/2 mm., which solidified on cooling. It separated from light petroleum (b. p. 60—80°) in colourless, thick plates, m. p. 38° (Found : C, 82·4; H, 7·5. Calc. for $C_{11}H_{12}O$: C, 82·5; H, 7·5%). The 2 : 4-*dinitrophenylhydrazone* formed orange needles, m. p. 146°, from ethanol (Found : C, 60·4; H, 4·8; N, 16·4. $C_{17}H_{16}O_4N_4$ requires C, 60·0; H, 4·7; N, 16·5%). The oxime separated from light petroleum (b. p. 60—80°) in silky needles, m. p. 141—142° (Found : C, 75·2; H, 7·2; N, 7·8. Calc. for $C_{11}H_{13}ON$: C, 75·4; H, 7·4; N, 8·0%). This ketone undergoes change on being kept; after 9 months a specimen had become sticky, and when washed with light petroleum left an insoluble residue, m. p. 110—114°. This observation may account for the erroneous m. p. of 126—127° recorded for this ketone by Mitchovitch (*Compt. rend.*, 1935, **200**, 1601); he gave m. p. 146° (decomp.) for the oxime, and m. p. 228° (decomp.) for the semicarbazone.

(c) *From* 2-*chloro*cyclo*pentanone and phenylmagnesium bromide.* Repetition of this method of preparation described by Mitchovitch (*loc. cit.*) gave the ketone as an oil, b. p. 100—108°/2 mm., which partly solidified at 0°, but melted at room temperature; a crystalline oxime could not be obtained. The derived 2 : 4-dinitrophenylhydrazone had m. p. 144—145°, and the semicarbazone had m. p. 227—228°.

5-*Methyl*-2-*phenyl*cyclo*pentanone*.—Ethyl α-phenyladipate (8·9 g.; above) and a solution of sodium (0·74 g.) in anhydrous ethanol (20 c.c.) were boiled for 5·5 hours, to form the sodio-derivative of ethyl 2-keto-3-phenyl*cyclo*pentanonecarboxylate. Methyl iodide (6·8 g.) was then added and boiling continued for 2 hours, after which the mixture was evaporated and the residue boiled for 14 hours with water (35 c.c.) and concentrated hydrochloric acid (50 c.c.). The diluted solution was then extracted with ether, and the extracts were washed with aqueous sodium carbonate, dried and distilled, giving 5-*methyl*-2-*phenyl*cyclo*pentanone* as a colourless oil (2·1 g.), b. p. 91—93°/0·5 mm., n_D^{13} 1·5361 (Found : C, 82·5; H, 8·2. $C_{12}H_{14}O$ requires C, 82·8; H, 8·1%). The 2 : 4-*dinitrophenylhydrazone* separated from ethyl acetate as yellow plates, m. p. 208° (Found : C, 60·9; H, 4·8; N, 5·6. $C_{18}H_{18}O_4N_4$ requires C, 61·0; H, 5·1; N, 15·8%).

*Methyl 3-Keto-2-phenyl*cyclo*pentanecarboxylate.*—3-Keto-2-phenyl*cyclo*pentanecarboxylic acid (X) (21·8 g.) was boiled for 4 hours with anhydrous methanol (100 c.c.) and concentrated sulphuric acid (6 c.c.), water added, and the solid *ester* collected and dried (20 g.). It separated from aqueous methanol in needles, m. p. 80° (Found : C, 72·0; H, 6·7. $C_{13}H_{14}O_3$ requires C, 71·6; H, 6·4%).

The authors thank the Department of Scientific and Industrial Research for a Maintenance Allowance (to P. G. J.), Mr. D. M. G. Lloyd, St. Andrews, for the ozonolysis of compound (VIII), and Dr. J. F. W. McOmie for help with the experiments on the acid (X).

THE UNIVERSITY, BRISTOL. [*Received, November* 18*th*, 1950.]