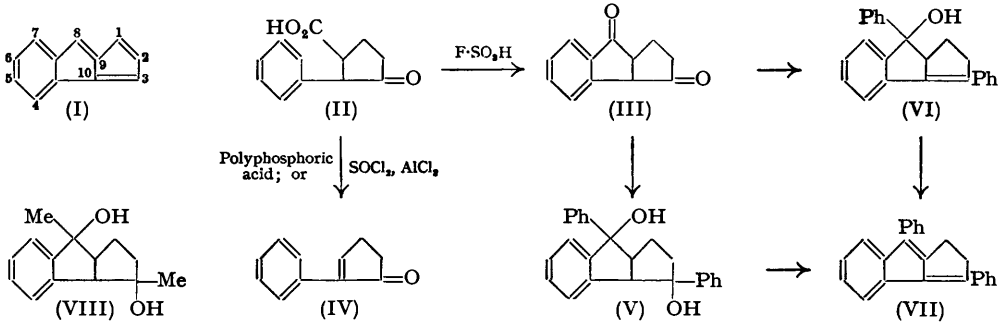
741. *Attempts to Prepare New Aromatic Systems. Part IV.** cyclo*Pent*[a]*indene.*

By Wilson Baker, F. Glockling, and J. F. W. McOmie.

*cyclo*Dehydration of 3-keto-2-phenyl*cyclo*pentane-1-carboxylic acid (II) to 1 : 2 : 3 : 8 : 9 : 10-hexahydro-3 : 8-diketo*cyclo*pent[*a*]indene (III) is readily brought about by fluorosulphonic acid, and this diketone is a promising intermediate for the synthesis of *cyclo*pent[*a*]indene (I). The diketone reacts with phenylmagnesium iodide and with methylmagnesium iodide, giving hexahydro-3 : 8-dihydroxy-3 : 8-diphenyl- and -3 : 8-dimethyl-*cyclo*pent[*a*]indenes (V and VIII); the former is readily dehydrated to the bright orange hydrocarbon, 1 : 2-dihydro-3 : 8-diphenyl*cyclo*pent[a]indene (VII). Catalytic reduction of the diketone has yielded the diol (IX), and the two isomeric hydroxy-ketones (X) and (XI). Nitrosation of the diketone gave 1 : 2 : 3 : 8 : 9 : 10-hexahydro-3 : 8-diketo-2-oximino*cyclo*pent[*a*]indene (XIII), from which the trioximino-compound was obtained by reaction with hydroxylamine.

Preliminary experiments directed towards the synthesis of *cyclo*pent[*a*]indene (I) were described in Parts I (Baker and Leeds, *J.*, 1948, 974) and III (Baker and Jones, *J.*, 1951, 787) of this series. A satisfactory synthesis of a ketone with the required carbon skeleton, namely 1 : 2 : 3 : 8 : 9 : 10-hexahydro-8-keto*cyclo*pent[*a*]indene, was recorded in Part III, and this was reduced to 1 : 2 : 3 : 8 : 9 : 10-hexahydro*cyclo*pent[*a*]indene. Direct dehydrogenation of this hydrocarbon to *cyclo*pent[*a*]indene (I) could not be accomplished in spite of many attempts, showing that either the aromatic ring system of *cyclo*pent[*a*]indene is not formed so readily as those of polycyclic, purely benzenoid compounds, or that if formed it is not stable under the conditions employed. It was, therefore, decided to investigate methods of approach which would involve only mild reactions such as dehydration, exhaustive methylation, or loss of hydrogen halide in the final steps. Preliminary experiments directed towards the same end have also been described by others (Clemo, Groves, Munday, and Swan, *J.*, 1951, 863; Groves and Swan, *J.*, 1951, 867; Dahn, *Helv. Chim. Acta*, 1951, **34**, 1087).



In the following account stereochemical problems are ignored though it is probable that the two five-membered rings are fused in the *cis* position in all the hexahydro*cyclo*pent[*a*]indene derivatives described.

The most promising intermediate appeared to be 1 : 2 : 3 : 8 : 9 : 10-hexahydro-3 : 8-diketo*cyclo*pent[*a*]indene (III), which we had previously attempted to make by *cyclo*dehydration of 3-keto-2-phenyl*cyclo*pentane-1-carboxylic acid (II) (Part III, p. 789) by using a mixture of phosphoric anhydride and syrupy phosphoric acid. These reactions led, however, to loss of the elements of formic acid with production of 2-phenyl*cyclo*pent-2-en-one (IV), and the same result has now been obtained by treating the acid (II) with polyphosphoric acid (see Snyder and Werber, *J. Amer. Chem. Soc.*, 1950, **72**, 2962, 2965), and with thionyl chloride followed by aluminium chloride. The final successful production of the diketone (III) from the acid (II) by dehydration with fluorosulphonic acid was briefly reported in a recent note (Baker, Coates, and Glockling, *J.*, 1951, 1376) and, as with other cyclodehydrations with fluorosulphonic acid,

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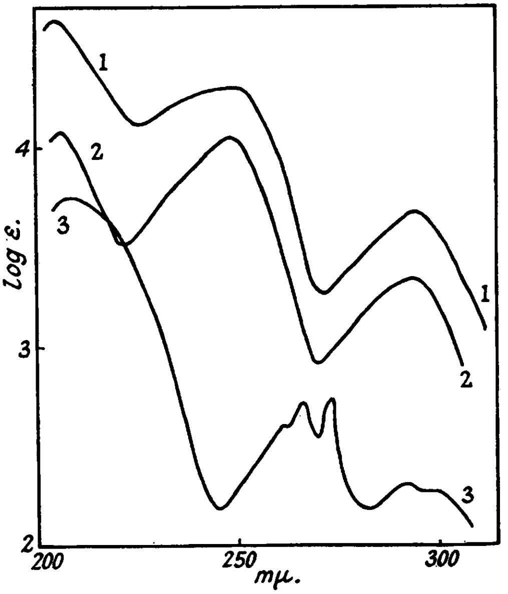
* Part III, *J.*, 1951, 787.

the reaction temperature is critical. Almost complete sulphonation occurs at 100°, and practically no reaction at room temperature; the reaction is best carried out initially at 50—60°, at which temperature little sulphonation occurs and about 50% of the acid is recovered unchanged. The yield of the diketone (III) is 40%, or 82% allowing for the recovered acid.

Reaction of the diketone (III) with two equivalents of phenylmagnesium bromide gave 1 : 2 : 3 : 8 : 9 : 10-hexahydro-3 : 8-dihydroxy-3 : 8-diphenyl*cyclo*pent[*a*]indene (V), though in one experiment which has not so far been repeated a pale yellow, mono-anhydro-derivative of (V) was isolated. The colour of this compound, and the fact that the hydrogen atom in position 10 of the diol (V) is likely to be more reactive than that in position 9 or than the two hydrogen atoms in position 2, makes it likely that this anhydro-derivative is the most fully conjugated possible, namely the stilbene derivative 1 : 2 : 8 : 9-tetrahydro-8-hydroxy-3 : 8-diphenyl*cyclo*pent[*a*]indene (VI). Dehydration of the diol (V) takes place very readily by boiling it in xylene solution with anhydrous copper sulphate, and yields a bright orange hydrocarbon which must be highly conjugated and is regarded as 1 : 2-dihydro-3 : 8-diphenyl*cyclo*pent[*a*]indene (VII). This orange hydrocarbon is also obtained from the unsaturated olefin (VI) by sublimation in a vacuum. The hydrocarbon (VII) is both a 1 : 4-diphenylbutadiene and a stilbene; it is most closely related to 1 : 1 : 4-triphenylbutadiene, $CPh_2{:}CH{\cdot}CH{:}CHPh$ (Staudinger, *Ber.*, 1909, **42**, 4285), the lack of colour of which lends support to the suggestion that the orange-coloured hydrocarbon has the most highly conjugated of the possible structures, namely (VII). The central five-membered ring of (VII) is of fulvene character and would be expected to shift the absorption bands into the visible part of the spectrum. Catalytic hydrogenation of (VII) could not be achieved by using either palladium black or Adams's platinum oxide catalyst at room temperature.

Ultra-violet absorption spectra in ethanolic solution.



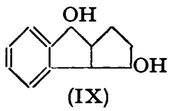
Curve 1. 1 : 2 : 3 : 8 : 9 : 10-*Hexahydro*-3 : 8-*diketo*cyclo*pent*[a]*indene* (III).

Curve 2. 1 : 2 : 3 : 8 : 9 : 10-*Hexahydro*-3-*hydroxy* - 8 - *keto*cyclo*pent*[a]*indene* (X).

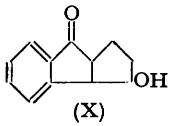
Curve 3. 1 : 2 : 3 : 8 : 9 : 10-*Hexahydro*-8-*hydroxy* - 3 - *keto*cyclo*pent*[a]*indene* (XI).

Methylmagnesium iodide reacted with the diketone (III) to give 1 : 2 : 3 : 8 : 9 : 10-hexahydro-3 : 8-dihydroxy-3 : 8-dimethyl*cyclo*pent[*a*]indene (VIII), and this compound readily yielded a liquid mono-anhydro-derivative which may not be entirely homogeneous; the structure is unknown, as five isomerides can result from simple loss of water. Attempts to obtain a hydrocarbon from (VIII) by complete dehydration led to high molecular weight material.

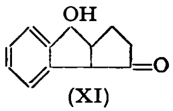
Catalytic reduction of the diketone (III) with two mols. of hydrogen gave the diol, 1 : 2 : 3 : 8 : 9 : 10-hexahydro-3 : 8-dihydroxy*cyclo*pent[*a*]indene (IX), but with one mol. of hydrogen the hydroxy-ketone, 1 : 2 : 3 : 8 : 9 : 10-hexahydro-3-hydroxy-8-keto*cyclo*pent[*a*]indene (X), was isolated. The structure assigned to (X) is based on the similarity of its ultra-violet absorption curve to that of indane-1-one (Ramart Lucas, *Bull. Soc. chim.*, 1935, [5], **2**, 327; Biquard, *ibid.*, 1941, [5], **8**, 55). In one experiment the catalytic reduction of (III) took place slowly and incompletely, and led to the isolation of the isomeric hydroxy-ketone 1 : 2 : 3 : 8 : 9 : 10-hexahydro-8-hydroxy-3-keto*cyclo*pent[*a*]indene (XI), the absorption spectrum of which was quite unlike that of the conjugated ketone (X), and closely resembled that of indane-2-one (Biquard, *loc. cit.*). Ultra-violet absorption curves for the diketone (III) and the hydroxy-ketones (X) and (XI) are shown in the figure. Reduction of the diketone (III) by the Ponndorf method gave a mono-anhydro-derivative of the diol (IX), which is probably 1 : 2 : 8 : 9-tetrahydro-8-hydroxy*cyclo*pent[*a*]indene, but further dehydration led to high molecular weight material.



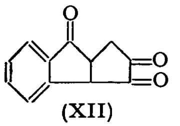
(IX)



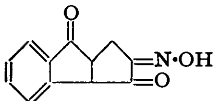
(X)



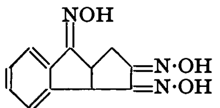
(XI)



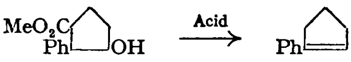
(XII)



(XIII)



(XIV)



(XV) (XVI)

In a direct attempt to introduce a third oxygen atom into the diketone (III) it was oxidised with selenium dioxide but no definite products could be isolated. Nitrosation with amyl nitrite, however, gave 1 : 2 : 3 : 8 : 9 : 10-hexahydro-3 : 8-diketo-2-oximino*cyclo*pent[*a*]indene (XIII), but attempts to hydrolyse this to the triketone (XII) by means of hydrochloric acid in presence of formalin were not successful. With the object of obtaining a derivative of triaminohexahydro*cyclo*pent[*a*]indene which might be converted into *cyclo*pent[*a*]indene by exhaustive methylation, the oximino-compound (XIII) was converted into its dioxime, 1 : 2 : 3 : 8 : 9 : 10-hexahydro-2 : 3 : 8-trioximino*cyclo*pent[*a*]indene (XIV); the subsequent steps have not yet been fully investigated.

Before the cyclisation of the acid (II) to the diketone (III) had been achieved by means of fluorosulphonic acid, it was hoped to prevent the loss of the elements of formic acid during attempted cyclodehydration by first reducing the carbonyl group in (II) to a secondary alcohol. Catalytic reduction of the methyl ester of (II) gave methyl 3-hydroxy-2-phenyl*cyclo*pentane-1-carboxylate (XV), but this substance showed marked instability towards acids, being converted even on boiling with dilute hydrochloric acid into 1-phenyl*cyclo*pent-1-ene (XVI) with loss of carbon dioxide and water. The same product was also obtained when the acid (II) was submitted to the normal Ponndorf conditions of reduction and isolation of the product.

EXPERIMENTAL.

M.p.s are uncorrected. Analyses are by Drs. Weiler and Strauss, Oxford, and Mr. W. M. Eno, Bristol.

1 : 2 : 3 : 8 : 9 : 10-*Hexahydro*-3 : 8-*diketo*cyclo*pent*[a]*indene* (III).—3-Keto-2-phenyl*cyclo*pentane-1-carboxylic acid (II) (11·8 g.) was treated with fluorosulphonic acid (35 c.c.) in two portions so that the temperature rose spontaneously to 50—60°. The homogeneous mixture was left at room temperature for 1¾ hours with occasional shaking, poured into water (500 c.c.), and after 1 hour extracted thoroughly with ether. The extract was shaken with excess of aqueous sodium hydrogen carbonate, dried ($MgSO_4$), and distilled, leaving 1 : 2 : 3 : 8 : 9 : 10-*hexahydro*-3 : 8-*diketo*cyclo*pent*[a]*indene* (III) (4·33 g.), m. p. 86—88°. For analysis a portion was distilled at 1 mm. pressure (bath-temp. 160°) and then crystallised from light petroleum (b. p. 80—100°), giving long needles, m. p. 91° (Found : C, 77·5; H, 5·3. $C_{12}H_{10}O_2$ requires C, 77·4; H, 5·4%). The aqueous alkaline solution yielded unchanged keto-acid (II) (6·03 g.), m. p. and mixed m. p. 115—116°.

The *dioxime* of the diketone (III) was twice crystallised from light petroleum (b. p. 60—80°) containing a little ethanol, and formed needles, m. p. 167° (Found, in material dried at 78° *in vacuo* : C, 66·7; H, 5·8; N, 13·0. $C_{12}H_{12}O_2N_2$ requires C, 66·7; H, 5·6; N, 13·0%).

1 : 2 : 3 : 8 : 9 : 10-*Hexahydro*-3 : 8-*dihydroxy*-3 : 8-*diphenyl*cyclo*pent*[a]*indene* (V).—The diketone (III) (4·0 g.) in dry benzene (50 c.c.) was added slowly to a solution of phenylmagnesium bromide prepared from bromobenzene (8·1 g.) and magnesium (1·25 g.) in dry ether (25 c.c.), the mixture boiled for 10 minutes, left overnight, and, after the addition of aqueous ammonium chloride, extracted several times with ether. The extracts yielded a yellow oil (7·1 g.), which when dissolved in ethanol yielded colourless needles (4·3 g.), m. p. 169—170°, of 1 : 2 : 3 : 8 : 9 : 10-*hexahydro*-3 : 8-*dihydroxy*-3 : 8-*diphenyl*cyclo*pent*[a]*indene* (V) (Found, in material crystallised three times from ethanol: C, 83·9; H, 6·4. $C_{24}H_{22}O_2$ requires C, 84·2; H, 6·4%).

1 : 2 : 8 : 9-*Tetrahydro*-8-*hydroxy*-3 : 8-*diphenyl*cyclo*pent*[a]*indene* (VI).—The diketone (III) (1·0 g.) in benzene (15 c.c.) was added to a solution of phenylmagnesium bromide, prepared from bromobenzene

(1·7 g.) and magnesium (0·26 g.) in ether (30 c.c.), the mixture boiled for 5 minutes, and the product isolated as in the previous case. The yellow solid (1·2 g.), after several crystallisations first from aqueous ethanol (charcoal) and then from ethanol, formed pale yellow needles, m. p. 161—162°, of 1 : 2 : 8 : 9-*tetrahydro*-8-*hydroxy*-3 : 8-*diphenyl*cyclo*pent*[a]*indene* (VI) (Found : C, 88·3; H, 6·2. $C_{24}H_{20}O$ requires C, 88·9; H, 6·2%).

1 : 2-*Dihydro*-3 : 8-*diphenyl*cyclo*pent*[a]*indene* (VII).—(*a*) The dihydroxy-compound (V) (0·27 g.) was boiled for 4 hours in dry xylene (15 c.c.) in the presence of anhydrous copper sulphate (1·0 g.) and then filtered, and the residue washed with ether. Evaporation of the solvents and crystallisation of the residue from ethanol gave 1 : 2-*dihydro*-3 : 8-*diphenyl*cyclo*pent*[a]*indene* (VII) as bright orange needles (0·21 g.), m. p. 168—174°. Further purification first by sublimation *in vacuo* and then by two crystallisations from ethanol gave the pure compound, m. p. 180° (Found : C, 94·1; H, 5·8. $C_{24}H_{18}$ requires C, 94·1; H, 5·9%).

(*b*) The monohydroxy-compound (VI) (0·1 g.) was heated in a sublimation apparatus (160—180°/0·1 mm.), and the orange-red, glassy sublimate which collected on the cold finger was crystallised from ethanol, giving the hydrocarbon (VII) (0·04 g.), m. p. and mixed m. p. 180°.

1 : 2 : 3 : 8 : 9 : 10-*Hexahydro*-3 : 8-*dihydroxy*-3 : 8-*dimethyl*cyclo*pent*[a]*indene* (VIII).—The diketone (III) (2·0 g.) in dry benzene (15 c.c.) was added to methylmagnesium iodide prepared from methyl iodide (3·7 g.) and magnesium (0·62 g.) in ether (10 c.c.). After the mixture had been left overnight, aqueous ammonium chloride was added, the oil extracted with ether, and after the removal of the solvent, the residue was dissolved in aqueous methanol. 1 : 2 : 3 : 8 : 9 : 10-*Hexahydro*-3 : 8-*dihydroxy*-3 : 8-*dimethyl*cyclo*pent*[a]*indene* (VIII) separated as needles, which after recrystallisation had m. p. 110—111° (yield 1·4 g.) (Found, in material dried at room temperature *in vacuo* : C, 77·3; H, 7·9. $C_{14}H_{18}O_2$ requires C, 77·0; H, 8·3%).

Anhydro-derivative of 1 : 2 : 3 : 8 : 9 : 10-*Hexahydro*-3 : 8-*dihydroxy*-3 : 8-*dimethyl*cyclo*pent*[a]*indene*.—(*a*) The dihydroxy-compound (VIII) (0·34 g.) was heated at 120° in a cold-finger sublimation apparatus at 1 mm. pressure. Rapid evolution of steam occurred, and the residue then distilled (bath temp. 140—160°) as a thick, pale yellow oil (0·22 g.). This *anhydro*-derivative was similarly redistilled with partial conversion into a residual orange glass (Found, in distillate : C, 84·0; H, 8·5. $C_{14}H_{16}O$ requires C, 84·0; H, 8·0%).

(*b*) The dihydroxy-compound (VIII) (1·6 g.) was boiled in toluene (20 c.c.) with anhydrous copper sulphate (3 g.) for 8 hours. The toluene solution yielded what is probably the same anhydro-derivative as a yellow oil (0·2 g.), b. p. 110°/1 mm. (Found : C, 84·8; H, 8·4%).

1 : 2 : 3 : 8 : 9 : 10-*Hexahydro*-3 : 8-*dihydroxy*cyclo*pent*[a]*indene* (IX).—The diketone (III) (0·5 g.) in ethanol (50 c.c.) was shaken at atmospheric pressure with hydrogen in the presence of Raney nickel (1 g.) for 4 hours, when 2 mols. of hydrogen had been absorbed. The filtered solution yielded an oil which was distilled at 0·5 mm. pressure (bath temp. 200°). The colourless distillate solidified, and was crystallised from benzene–light petroleum (b. p. 60—80°), giving 1 : 2 : 3 : 8 : 9 : 10-*hexahydro*-3 : 8-*dihydroxy*cyclo*pent*[a]*indene* (IX) as needles, m. p. 75° (Found : C, 75·8; H, 7·4. $C_{12}H_{14}O_2$ requires C, 75·8; H, 7·4%).

1 : 2 : 3 : 8 : 9 : 10-*Hexahydro*-3-*hydroxy*-8-*keto*cyclo*pent*[a]*indene* (X).—The diketone (III) (1·05 g.) in ethanol (20 c.c.) was hydrogenated as in the previous experiment, but the reaction was stopped after the uptake of 1 mol. of hydrogen. The resulting 1 : 2 : 3 : 8 : 9 : 10-*hexahydro*-3-*hydroxy*-8-*keto*cyclo*pent*[a]*indene* (X) (0·6 g.) separated from benzene–light petroleum (b. p. 60—80°) in rectangular prisms, m. p. 115—116° (Found : C, 76·3; H, 6·5. $C_{12}H_{12}O_2$ requires C, 76·6; H, 6·4%). It may be sublimed unchanged under diminished pressure. The 2 : 4-*dinitrophenylhydrazone*, prepared by Brady's method, separated from benzene as red needles, m. p. 208—209° (Found, in twice crystallised material : C, 59·2; H, 4·5; N, 15·4. $C_{18}H_{16}O_5N_4$ requires C, 58·8; H, 4·4; N, 15·2%).

1 : 2 : 3 : 8 : 9 : 10-*Hexahydro*-8-*hydroxy*-3-*keto*cyclo*pent*[a]*indene* (XI).—A somewhat crude specimen of the diketone (III) (5·0 g.) in ethanol (100 c.c.) was hydrogenated at atmospheric pressure in presence of Raney nickel (0·5 g.). After 15 hours, absorption of only 2/3 mol. of hydrogen had taken place, and concentration of the solution (to 25 c.c.) and further slow evaporation at room temperature led to the separation of crystalline material (0·75 g.). After being twice crystallised from benzene–light petroleum (b. p. 60—80°) the 1 : 2 : 3 : 8 : 9 : 10-*hexahydro*-8-*hydroxy*-3-*keto*cyclo*pent*[a]*indene* (XI) separated as needles, m. p. 135° (Found : C, 76·5; H, 6·4. $C_{12}H_{12}O_2$ requires C, 76·6; H, 6·4%). The 2 : 4-*dinitrophenylhydrazone* was twice crystallised from ethanol giving yellow needles, m. p. 208° (Found : C, 59·4; H, 4·1; N, 15·4. $C_{18}H_{16}O_5N_4$ requires C, 58·8; H, 4·4; N, 15·2%).

1 : 2 : 8 : 9-*Tetrahydro*-8-*hydroxy*cyclo*pent*[a]*indene* (?).—The diketone (III) (6·1 g.), freshly distilled aluminium *iso*propoxide (13·5 g.), and dry *iso*propyl alcohol (100 c.c.) were boiled for 6½ hours, while 70 c.c. of distillate were collected. The residue was poured on ice and dilute hydrochloric acid and extracted with ether, and the extracts yielded a product which distilled as a viscous yellow oil (2·84 g.), b. p. 148—151°/1 mm. Redistillation resulted in the formation of much high molecular weight material (Found, in distillate : C, 83·6; H, 7·6. $C_{12}H_{12}O$ requires C, 83·7; H, 7·0%).

1 : 2 : 3 : 8 : 9 : 10-*Hexahydro*-3 : 8-*diketo*-2-*oximino*cyclo*pent*[a]*indene* (XIII).—The diketone (III) (10·5 g.), freshly distilled amyl nitrite (9·0 g.), and ethanol (100 c.c.) were treated dropwise at −10° with concentrated hydrochloric acid (2·4 c.c.). The mixture was allowed to reach room temperature, warmed to 50° for 10 minutes, and poured into water (250 c.c.)–ether (100 c.c.). The pink solid which collected at the interface of the two liquids was collected (3·02 g.) and crystallised first from benzene containing a little ethanol and then from benzene, giving 1 : 2 : 3 : 8 : 9 : 10-*hexahydro*-3 : 8-*diketo*-2-*oximino*cyclo*pent*[a]*indene* (XIII) as pale yellow needles, m. p. 202—204° (decomp.) (Found : C, 67·2; H, 4·5; N, 6·6. $C_{12}H_9O_3N$ requires C, 67·0; H, 4·2; N, 6·5%). A further quantity (1·26 g.) of (XIII) was obtained by keeping the aqueous-ethereal mixture at 0° for 48 hours.

1 : 2 : 3 : 8 : 9 : 10-*Hexahydro*-2 : 3 : 8-*trioximino*cyclo*pent*[a]*indene* (XIV).—The crude mono-oximino-compound (XIII) (0·9 g.), hydroxylamine hydrochloride (1·5 g.), sodium acetate (1·5 g.), water (25 c.c.), and ethanol (25 c.c.) were boiled for 4 hours. After cooling and dilution with water the 1 : 2 : 3 : 8 : 9 : 10-*hexahydro*-2 : 3 : 8-*trioximino*cyclo*pent*[a]*indene* (XIV) (1·0 g.) was collected and crystallised three times from aqueous ethanol, being obtained as needles, m. p. 265° (decomp.) (Found : C, 59·1; H, 4·9; N, 17·4. $C_{12}H_{11}O_3N_3$ requires C, 58·8; H, 4·5; N, 17·2%).

Methyl 3-*Hydroxy*-2-*phenyl*cyclo*pentane*-1-*carboxylate* (XV).—Methyl 3-keto-2-phenyl*cyclo*pentane-1-carboxylate (Baker and Jones, *J.*, 1951, 792) (5·0 g.) in methanol (150 c.c.) was shaken with hydrogen at 6 atmospheres' pressure in the presence of Raney nickel (1 g.) for 7 hours. The *methyl* 3-*hydroxy*-2-*phenyl*cyclo*pentane*-1-*carboxylate* was isolated as a colourless, viscous oil, b. p. 136°/1 mm. (4·8 g.) (Found : C, 71·2; H, 7·2. $C_{13}H_{16}O_3$ requires C, 70·9; H, 7·3%).

1-*Phenyl*cyclo*pent*-1-*ene* (XVI).—The preceding ester (XV) (4·6 g.), concentrated hydrochloric acid (100 c.c.), and water (100 c.c.) were boiled for 7 hours, and then steam-distilled. The steam-distillate was extracted with ether, and the extracts washed with aqueous sodium hydrogen carbonate, dried, and distilled, yielding 1-phenyl*cyclo*pent-1-ene as a colourless oil (1·35 g.), b. p. 78—80°/2 mm., which soon solidified and then had m. p. 25° (von Braun, *Ber.*, 1927, **60**, 2555, records m. p. 23°). The sodium hydrogen carbonate extract gave only a trace of acidic material. The 1-phenyl*cyclo*pent-1-ene was characterised by catalytic reduction whereupon 1 mol. of hydrogen was taken up, giving phenyl*cyclo*pentane, b. p. 215—216°/760 mm. (lit. b. p. 213—215°/760 mm.), and by oxidation with alkaline potassium permanganate to γ-benzoylbutyric acid, m. p. 127—128° (Wislicenus and Kuhn, *Annalen*, 1898, **302**, 218, record m. p. 127·5°).

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