194. *Indene Series. Part III. The Cyclisation of* 1-*Benzyl*cyclo*pentene and Isomeric Compounds.*

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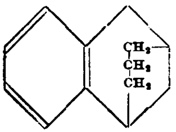
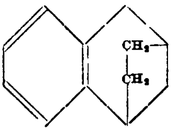
1- and 2-Benzyl*cyclo*pentanol and α-hydroxybenzyl*cyclo*pentane have been dehydrated, and the resulting olefins cyclised, but the only saturated hydrocarbon isolated was 1 : 3-*endo*ethylene-1 : 2 : 3 : 4-tetrahydronaphthalene.

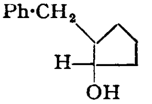
CYCLISATION of the dehydration product of 1-benzyl*cyclo*pentanol was investigated as a possible route to the *cyclo*pent[*a*]indene ring system. Cook and Hewett (*J.*, 1936, 62) have shown the dehydration product of benzyl*cyclo*hexanol to cyclise to give the bridged-ring compound (I), rather than the isomeric fluorene derivative; and our results in the benzyl*cyclo*pentanol series have been analogous—cyclisation occurs to give (II) rather than hexahydro*cyclo*pent[*a*]indene.



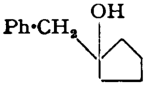
(I.)



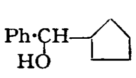
(II.)



(III.)



(IV.)



(V.)

2-Benzyl*cyclo*pentanol (III), prepared by reduction of 2-benzyl- (Baker and Leeds, *J.*, 1948, 974) or 2-benzylidene-*cyclo*pentanone, was dehydrated with phosphoric oxide and the resulting olefin cyclised by aluminium chloride. The saturated hydrocarbon obtained was, however, 1 : 3-*endo*ethylene-1 : 2 : 3 : 4-tetrahydronaphthalene [*tricyclo*(5 : 4 : $1^{3:6}$)dodeca-7 : 9 : 11-triene] (II), as on chromic acid oxidation it yielded 1 : 3-*endo*ethylene-1 : 2 : 3 : 4-tetrahydro-4-ketonaphthalene (Baker and Leeds, *loc. cit.*).

Dehydration of 1-benzyl*cyclo*pentanol (IV) and cyclisation of the product gave mainly the same product (II), although nitration then yielded a dinitro-derivative in about 10% yield, while no nitro-derivatives could be obtained from the saturated hydrocarbons from (III) or (V). The ultra-violet absorption of the olefin from (IV) suggested that about 10% of the olefin mixture had the double bond conjugated with the benzene ring.

α-Hydroxybenzyl*cyclo*pentane (V) has previously been obtained in low yield by Edwards and Reid (*J. Amer. Chem. Soc.*, 1930, **52**, 3325) by interaction of *cyclo*pentylmagnesium bromide and benzaldehyde. We prepared it by the reduction (by potassium ethoxide in ether) of benzoyl*cyclo*pentane, obtained by the condensation of benzene and *cyclo*pentanecarboxyl chloride. The carbinol (V) was dehydrated with phosphoric oxide and the olefin mixture again appeared to have about 10% of the conjugated isomer; (II) was the only product isolated after cyclisation.

Use of anhydrous oxalic acid instead of phosphoric oxide for the dehydrations gave the same results, except that in the case of the olefin from (V) cyclisation followed by oxidation yielded no recognisable product. Here, however, the ultra-violet absorption indicated that nearly all the olefin mixture had the double bond conjugated with the benzene nucleus.

Catalytic dehydrogenation of (II) with palladium at 255° yielded diphenyl.

EXPERIMENTAL.

(All m. p.s are uncorrected.)

2-*Benzyl*cyclo*pentanol.*—2-Benzylidene*cyclo*pentanone was prepared in the analogous way to that described by Vorländer and Kunze (*Ber.*, 1926, **59**, 2081) for 2-benzylidene*cyclo*hexanone. It was hydrogenated quantitatively to 2-benzyl*cyclo*pentanol, b. p. 145—146°/15 mm., in glacial acetic acid with Adams's catalyst at 7 atmospheres and room temperature.

*Benzoyl*cyclo*pentane.*—*cyclo*Pentanecarboxyl chloride (3·3 g.) (Haworth and Perkin, *J.*, 1894, **65**, 99) in dry benzene (30 ml.) was added to anhydrous aluminium chloride (3·3 g.) in benzene (60 ml.), and the mixture warmed on the water-bath for 1 hour after evolution of hydrogen chloride had ceased. The mixture was then cooled and decomposed with ice and dilute hydrochloric acid. The benzene layer was washed with dilute sodium hydroxide solution, dried (Na_2SO_4), and distilled, giving the *ketone* (3·3 g.) as a colourless oil, b. p. 156—160°/15 mm. (Found : C, 82·6; H, 8·5. $C_{12}H_{14}O$ requires C, 82·75; H, 8·05%). The *semicarbazone* separated from benzene–light petroleum (b. p. 60—80°) as colourless prisms, m. p. 96—97° (Found : C, 67·3; H, 7·35. $C_{13}H_{17}ON_3$ requires C, 67·5; H, 7·35%). The 2 : 4-*dinitrophenylhydrazone* separated from glacial acetic acid as large yellow needles, m. p. 142—143° (Found : C, 61·25; H, 5·2. $C_{18}H_{18}O_4N_4$ requires C, 61·0; H, 5·1%).

*α-Hydroxybenzyl*cyclo*pentane.*—A solution of potassium (4·8 g.) in an excess of absolute ethano was heated on the water-bath under reduced pressure until only a trace of ethanol remained. Benzoyl*cyclo*pentane (6·0 g.) in dry ether (48 ml.) was added, the mixture heated under reflux for 18 hours, cooled, and acidified (dilute hydrochloric acid), and the ethereal layer separated, washed with water, dried (Na_2SO_4), and distilled, giving a colourless alcohol (4·6 g.), b. p. 122°/3 mm. (Found: C, 81·8; H, 9·1. Calc. for $C_{12}H_{16}O$: C, 81·8; H, 9·1%).

Dehydrations with Phosphoric Oxide.—The carbinol (1·0 g.) and phosphoric oxide (2·0 g.) were heated at 120° (oil-bath) for 30 minutes. The temperature of the bath was then raised to 150°, the olefin distilling directly, under reduced pressure, as a colourless mobile oil (0·7 g.), b. p. 109—111°/12 mm. In all cases the product contained no active hydrogen, decolorised bromine in carbon tetrachloride, and absorbed one mol. of hydrogen at room temperature and atmospheric pressure in presence of Adams's catalyst.

The olefin from 1-benzyl*cyclo*pentanol had light absorption in hexane: $\lambda_{\text{max.}}$ 2473 A.; $\log \varepsilon_{\text{max.}} = 3{\cdot}18$; $\lambda_{\text{min.}}$ 2320 A.; $\log \varepsilon_{\text{min.}} = 3{\cdot}05$.

The olefin from α-hydroxybenzyl*cyclo*pentane had light absorption in ethanol: $\lambda_{\text{max.}}$ 2466 A.; $\log \varepsilon_{\text{max.}} = 3{\cdot}26$; $\lambda_{\text{min.}}$ 2297 A.; $\log \varepsilon_{\text{min.}} = 2{\cdot}78$.

Dehydrations with Anhydrous Oxalic Acid.—Equal weights of the carbinol and oxalic acid were heated on the water-bath for 3 hours. Water was then added, the mixture extracted with ether, and the extract washed with sodium carbonate solution, dried (Na_2SO_4), and distilled.

1-Benzyl*cyclo*pentanol (1·25 g.) gave the olefin (0·7 g.), b. p. 115°/14 mm., as a colourless mobile oil.

α-Hydroxybenzyl*cyclo*pentane (3·0 g.) gave a colourless oil (1·0 g.), b. p. 120—125°/15 mm. (the required olefin) (Light absorption in ethanol: $\lambda_{\text{max.}}$ 2485 A.; $\log \varepsilon_{\text{max.}} = 3{\cdot}71$; $\lambda_{\text{min.}}$ 2280 A.; $\log \varepsilon_{\text{min.}} = 3{\cdot}36$), and a pale yellow oil of unknown constitution (0·8 g.), b. p. 220°/15 mm. (Found: C, 85·3; H, 8·8%).

Cyclisation of the Olefins.—The procedure followed was the same in all cases. The olefin (1·0 g.), in dry carbon disulphide (5 ml.), was added during several hours to anhydrous aluminium chloride (1·7 g.) in carbon disulphide (35 ml.) at 0°. The mixture was kept at 0° for 48 hours, and the clear liquid was decanted and decomposed with ice and dilute hydrochloric acid. The organic layer was separated, dried ($CaCl_2$), and fractionated, affording 1 : 3-*endo*ethylene-1 : 2 : 3 : 4-tetrahydronaphthalene (II) (0·4 g.), b. p. 115°/15 mm., as a colourless oil from all the olefins except that obtained by oxalic acid dehydration of α-hydroxybenzyl*cyclo*pentane. In this case, the olefin (1·5 g.) yielded on cyclisation a saturated, unidentified colourless oil (0·3 g.), b. p. 120—125°/15 mm.

*Nitration of the Product obtained by Cyclisation of the Olefin formed on Phosphoric Oxide Dehydration of 1-Benzyl*cyclo*pentanol.*—The saturated hydrocarbon, which consisted mainly of (II), was nitrated in the cold for 2 hours with concentrated sulphuric acid–concentrated nitric acid (3 : 2 by vol.). The *dinitro*-compound precipitated by water solidified on trituration with light petroleum and gave colourless needles, m. p. 154°, from methanol (Found: C, 57·75; H, 4·5. $C_{12}H_{12}O_4N_2$ requires C, 58·05; H, 4·8%). The yields varied from 10 to 20%. The light-petroleum mother-liquors contained the main product of the reaction, a brown oil having a pronounced ketonic odour.

Chromic Acid Oxidation of the Products from the Cyclisations.—The hydrocarbon (0·5 g.), sodium dichromate (1·0 g.), and acetic acid (5·5 ml.) were heated under reflux for 2½ hours. *iso*Propyl alcohol was added to remove the excess of chromic acid, the solvents were removed at 50° (reduced pressure), the residue was extracted with ether, and the extracts were washed with sodium carbonate solution, dried (Na_2SO_4), and distilled. 1 : 3-*endo*Ethylene-1 : 2 : 3 : 4-tetrahydro-4-ketonaphthalene (0·3 g.), b. p. 165°/20 mm., was obtained from the hydrocarbons formed in phosphoric oxide experiments, and in lower yield (0·08 g.) from the hydrocarbon formed by cyclisation of the olefin from oxalic acid dehydration of 1-benzyl*cyclo*pentanol (in this case, 0·2 g. of original material was recovered).

The semicarbazone of the ketone separated as colourless needles (from dilute methanol), m. p. 190—191° (after liquefaction and resolidification at 170—171° owing to loss of methanol of crystallisation), not depressed on admixture with an authentic specimen. The 2 : 4-dinitrophenylhydrazone formed dark red needles (from glacial acetic acid), m. p. 245—246° (decomp.), not depressed on admixture with an authentic specimen.

On oxidation of the cyclised product from the olefin formed by oxalic acid dehydration of α-hvdroxybenzyl*cyclo*pentane, the original material was recovered apparently unchanged, as no 2 : 4-dinitrophenylhydrazone could be isolated from the product.

Catalytic Dehydrogenation of 1 : 3-endo*Ethylene*-1 : 2 : 3 : 4-*tetrahydronaphthalene.*—The hydrocarbon (0·5 g.) was heated under reflux (bath-temp. 255°) for 3 hours with palladium black (0·15 g.). Approx. 1 mol. of hydrogen was liberated. The mixture solidified to a colourless mass of crystals, m. p. 35—37°, which appeared to contain diphenyl. This was confirmed by preparation of the 4 : 4′-dinitro-derivative, colourless needles (from methanol), m. p. 236°, not depressed on admixture with an authentic specimen (Found: C, 58·4; H, 3·45. Calc. for $C_{12}H_8O_4N_2$: C, 58·3; H, 3·3%).

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