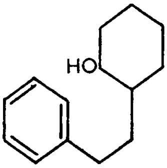
271. *Synthesis of Polycyclic Compounds. Part III.* The Formation of* as-*Octahydrophenanthrene from the Isomeric 2-Phenethyl*cyclo*hexanols.*

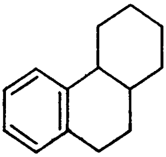
By (Mrs.) Manjuli Ray, J. C. Bardhan, and K. C. Bhattacharyya.

A synthesis of 3-phenethyl*cyclo*hexanol is described. This on cyclodehydration, like other isomeric alcohols examined in this connection, affords *as*-octahydrophenanthrene.

It was shown by Bardhan and Sengupta[1] that 2-phenethyl*cyclo*hexanol (I) on treatment with phosphoric anhydride at 140° passed smoothly into *as*-octahydrophenanthrene (II), which could be readily dehydrogenated to phenanthrene. The same octahydrophenanthrene (II) was obtained later by others[2] by the action of sulphuric acid or phosphoric acid on the tertiary alcohol (III). It is now generally recognised, however, that in all such cases the cyclisation proceeds through the olefin (IV), and the resultant product invariably contains also the spiran[3] (V).



(I)



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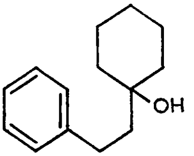

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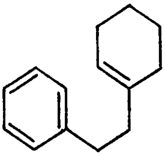

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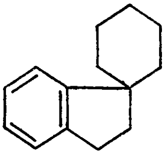

(V)

It has been shown[4] that 7-benzyl*iso*menthol[5] undergoes phenanthrene ring closure in the presence of phosphoric anhydride, and the product on dehydrogenation furnishes 3-*iso*propylphenanthrene. As the reaction is somewhat unusual, it seemed of interest to examine the behaviour of 3-phenethyl*cyclo*hexanol (VI) under analogous conditions.

5-Styryl*cyclo*hexane-1 : 3-dione[6] (VII) was allowed to react with phosphoryl chloride,[7] giving 3-chloro-5-styryl*cyclo*hex-2-enone (VIII), which on hydrogenation over colloidal

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* Part II, *J.*, 1956, 355.

[1] Bardhan and Sengupta, *J.*, 1932, 2520, 2798.

[2] Bogert, *Science*, 1933, **77**, 289; Perlman, Davidson, and Bogert, *J. Org. Chem.*, 1936, **1**, 288; Cook, *Chem. and Ind.*, 1933, 451; Cook and Hewett, *J.*, 1933, 1098.

[3] Cook, Hewett, and Lawrence, *J.*, 1936, **71**; Cook, Hewett, and Robinson, *J.*, 1939, 168; Levitz, Pulman, and Bogert, *J. Org. Chem.*, 1941, **6**, 105.

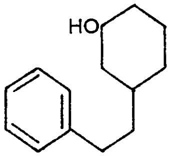
[4] Bardhan and Adhya, *J.*, 1956, 260.

[5] Read, Smith, and Hughesdon, *J.*, 1924, **125**, 135; Read and Smith, *J.*, 1923, **123**, 2270.

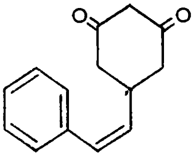
[6] Vorlander, *Annalen*, 1897, **294**, 132.

[7] Crossley and Pratt, *J.*, 1915, **107**, 173.

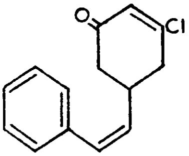
palladium [8] furnished 3-phenethyl*cyclo*hexanone (IX). This on further reduction with sodium and moist ether afforded the corresponding alcohol (VI) which, when heated in a vacuum with phosphoric anhydride, gave *as*-octahydrophenanthrene in a good yield, and this on dehydrogenation with selenium at 300—320° was converted almost quantitatively into phenanthrene.



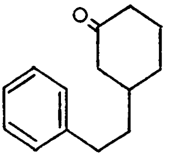
(VI)



(VII)



(VIII)



(IX)

The formation of *as*-octahydrophenanthrene (II) from 3-phenethyl*cyclo*hexanol (VI), which is without precedent, however, presents some interesting analogies with the cyclodehydration [9] of the three isomeric alcohols (X), (XI), and (XII), all of which give 1-methyltetralin in the presence of sulphuric acid or phosphoric acid.

$C_6H_5{\cdot}[CH_2]_2{\cdot}CH(OH){\cdot}CH_2{\cdot}CH_3$ (X) $C_6H_5{\cdot}[CH_2]_3{\cdot}CH(OH){\cdot}CH_3$ (XI) $C_6H_5{\cdot}[CH_2]_4{\cdot}CH_2{\cdot}OH$ (XII)

The physical properties of the *as*-octahydrophenanthrene described above are in good agreement with those previously recorded [3] for this hydrocarbon. From its method of formation it seems highly probable that it is free from contamination with the isomeric spiran (V), although this has not been rigidly established.

EXPERIMENTAL

5-*Styryl*cyclo*hexane*-1 : 3-*dione* [6] (VII).—This substance has been prepared before, but the following procedure is much more expeditious. A solution of sodium (23 g.) in absolute ethanol (375 ml.) was heated with ethyl malonate (160 g.) and cinnamylideneacetone (b. p. 155—156°/4 mm.) (172 g.) on the water-bath for 6 hr. It was treated with water (400 ml.), and ethanol was removed on the water-bath. Aqueous potassium hydroxide (100 g. in 100 ml.) was then added, and the liquid made up to 1250 ml. by water and boiled in an open flask for 25 min. It was filtered, acidified, and boiled as before until no more carbon dioxide was evolved. On cooling, the crystalline product (206 g.) was collected, washed with water, and purified from ethanol (charcoal). It had m. p. 183—184° (lit.,[6] 186°).

3-*Chloro*-5-*styryl*cyclo*hex*-2-*enone* (VIII).—The diketone (VII) (32·1 g.), suspended in dry chloroform (75 ml.), was refluxed with phosphorus trichloride (6·5 ml.) on the water-bath for 3 hr. The chloroform was distilled off, the residue decomposed with ice-water, and the resulting emulsion extracted with ether. The ethereal solution was washed with 4% aqueous sodium hydroxide, then with water, dried, and distilled. The *chloro-ketone* (VIII) (15 g.) distilled almost constantly (b. p. 180—182°/4 mm.) (Found : Cl, 15·7. $C_{14}H_{13}OCl$ requires Cl, 15·3%).

3-*Phenethyl*cyclo*hexanone* (IX).—A solution of the chloro-ketone (VIII) (13 g.) in ethanol (50 ml.) was hydrogenated at 30° in the presence of gum arabic (0·1 g.), dissolved in water (5 ml.), and palladium chloride (0·1 g.) until hydrogen (4216 ml. Calc. : 4156 ml.) was absorbed (3 hr.). After filtration, the solution was evaporated to half its bulk, diluted with water, and extracted with ether. The ethereal solution was washed, dried, and distilled. The *ketone* (10·3 g.), having a faint but characteristic smell, had b. p. 152—153°/6 mm. (Found : C, 83·1; H, 8·8. $C_{14}H_{18}O$ requires C, 83·2; H, 8·9%). The *semicarbazone* crystallised from aqueous ethanol as plates, m. p. 181—182° (Found : C, 69·6; H, 8·3. $C_{15}H_{21}ON_3$ requires C, 69·5; H, 8·2%).

3-*Phenethyl*cyclo*hexanol* (VI).—A mixture of the above ketone (12 g.), ether (60 ml.), and water (50 ml.) was stirred mechanically, and sodium (12 g.) was introduced gradually with occasional cooling in ice-water. When all the sodium had dissolved (4 hr.), the ethereal layer was separated, the alkaline solution was extracted with ether, and the combined ethereal solutions were washed with water, dried (K_2CO_3), and evaporated. 3-*Phenethyl*cyclo*hexanol* (10 g.) had b. p. 152°/4 mm. (Found : C, 82·5; H, 9·9. $C_{14}H_{20}O$ requires C, 82·4; H, 9·8%).

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[8] Skita and Franck, *Ber.*, 1911, **44**, 2862.

[9] Bogert *et al.*, *J. Amer. Chem. Soc.*, 1934, **56**, 185, 959; 1935, **57**, 151.

The 3 : 5-*dinitrobenzoate*, prepared in pyridine, crystallised from ethanol in needles, m. p. 121—122° (Found: C, 63·5; H, 5·7. $C_{21}H_{22}O_6N_2$ requires C, 63·3; H, 5·5%).

1 : 2 : 3 : 4 : 9 : 10 : 11 : 12-*Octahydrophenanthrene* (II).—The foregoing alcohol (3 g.) was heated with phosphoric anhydride (7 g.) for 0·5 hr. at 135—140°/4 mm. The temperature was then allowed to rise slowly and between 160° and 170° a colourless oil (2 g.) distilled. This was dried, and distilled over sodium, giving pure *as*-octahydrophenanthrene, b. p. 128°/6 mm., d_4^{30} 0·99736, n_D^{30} 1·54859, $[R_L]_D$ 59·28 (Found: C, 90·4; H, 9·8. Calc. for $C_{14}H_{18}$: C, 90·3; H, 9·7%), fully saturated towards potassium permanganate and bromine.

The octahydrophenanthrene (2 g.) and selenium (4 g.) were heated at 300—320° for 20 hr., giving an almost theoretical yield of phenanthrene, m. p. and mixed m. p. 100° (Found: C, 94·2; H, 5·5. Calc. for $C_{14}H_{10}$: C, 94·4; H, 5·6%). The picrate had m. p. and mixed m. p. 145°.

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