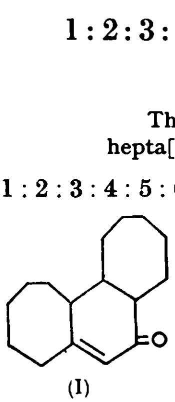
248. *Alicyclic Studies. Part IX.**

1 : 2 : 3 : 4 : 5 : 8 : 9 : 10 : 11 : 12-*Decahydrodi*cyclo*hepta*[a, c]*benzene*.

By Walter J. Rosenfelder and David Ginsburg.

The preparation of 1 : 2 : 3 : 4 : 5 : 8 : 9 : 10 : 11 : 12-decahydrodi*cyclo*hepta[*a*, *c*]benzene is described.



(I)

1 : 2 : 3 : 4 : 5 : 6 : 8 : 9 : 10 : 11 : 12 : 5*a* : 12*a* : 12*b*-Tetradecahydro-6-oxodi*cyclo*hepta[*a*, *c*]-benzene (I) [1] has been reduced with sodium borohydride. Dehydration of the resulting allylic alcohol by several methods yielded a mixture of homoannular diene ($\lambda_{max.}$ 2740 Å) and heteroannular diene ($\lambda_{max.}$ 2450 Å). These maxima are analogous to the absorptions exhibited by cholesta-2 : 4- (2750 Å) and -3 : 5-diene (2340 Å), respectively.[2] Dehydrogenation of the mixture of dienes by bromination with *N*-bromosuccinimide followed by dehydrobromination with lutidine, or by heating with sulphur, yielded 1 : 2 : 3 : 4 : 5 : 8 : 9 : 10 : 11 : 12-decahydrodi*cyclo*hepta[*a*, *c*]benzene.

Experimental

Reduction of 1 : 2 : 3 : 4 : 5 : 6 : 8 : 9 : 10 : 11 : 12 : 5a : 12a : 12b-*Tetradecahydro*-6-*oxodi*cyclo*hepta*[a, c]*benzene*.—To a solution of the ketone (4 g.) in methanol (40 ml.), sodium borohydride (3 g.) was added gradually with shaking. After 1 hr. at room temperature, the solvent was removed at the water-pump. The residue was taken up in ether and washed with dilute hydrochloric acid and with water. After drying (Na_2SO_4) the ether was removed. The main fraction boiled at 160—170°/1·6 mm. The infrared spectrum showed a weak hydroxyl band at 3600 cm.$^{-1}$ but the ultraviolet absorption [$\lambda_{max.}$ 2450 Å (ε 2440 in EtOH)] indicated that considerable dehydration of the allylic alcohol had occurred.

Attempts to isolate the pure allylic alcohol by preparation of an acetate, benzoate, *p*-nitrobenzoate, 3 : 5-dinitrobenzoate, or phenylurethane, failed.

Preparation of Mixture of Dienes.—(*a*) The partially dehydrated allylic alcohol (10 g.) was refluxed in dry benzene (50 ml.) with naphthalene-β-sulphonic acid (0·5 g.), the water being removed in an azeotropic separator. Water removal was complete after 30 min. The solution was then washed with aqueous sodium hydrogen carbonate and with water, dried (Na_2SO_4), and distilled. The main fraction of dienes had b. p. 120—122°/0·5 mm. (Found : C, 88·8; H,

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* Part VIII, preceding paper.

[1] Rosenfelder and Ginsburg, *J.*, 1954, 2955.

[2] Fieser and Fieser, " Natural Products related to Phenanthrene," Reinhold, New York, 1949, 3rd edn., p. 186.

11·3. Calc. for $C_{16}H_{24}$: C, 88·8; H, 11·2%). Ultraviolet absorption : $\lambda_{max.}$ 2450, 2740 Å (ε 5150, 1750 in EtOH). The homoannular diene could not be isolated by means of a maleic anhydride adduct.

(*b*) The partially dehydrated alcohol (5 g.) and aluminium oxide (10 g.; 100-mesh, activated at 150° for 3 hr. and allowed to cool in a desiccator immediately before use) were heated at 170—180°/2 mm. for 1 hr. in a Claisen flask. The temperature was then raised to 200° and the product was distilled. The wet distillate was taken up in ether, and the ether layer separated, dried, and distilled. The main fraction of dienes distilled at 127—128°/1 mm. but the ultraviolet absorption spectrum indicated that some rearrangement to the heteroannular diene had taken place. Ultraviolet absorption : $\lambda_{max.}$ 2450, 2740 Å (ε 5100, 1750 in EtOH).

(*c*) Treatment of the partially dehydrated allylic alcohol (7 g.) in pyridine (30 ml.) with phosphorus oxychloride (7 g.) at 0°, followed by storage overnight at room temperature and working up in the usual way, gave a product which was still highly coloured after two high-vacuum distillations. Ultraviolet absorption : $\lambda_{max.}$ 2460 Å (ε 7100), indicating a high content of the heteroannular diene.

Reactions of the Mixture of Dienes.—(a) *With one mol. of* N-*bromosuccinimide*. To the diene mixture (12 g.) in dry carbon tetrachloride (100 ml.), *N*-bromosuccinimide (11·9 g., 1·1 mol.) was added with swirling and cooling during 10 min. An immediate vigorous reaction set in with some evolution of hydrogen bromide. To complete the bromination, the solution was heated under reflux for 10 min. After the usual working up, the residue was heated under reflux with lutidine (50 ml.) for 90 min. The solution was concentrated in a vacuum to 10 ml. and the lutidine hydrobromide was removed by filtration. This salt was washed with ether and the filtrate and washings were combined. The residual lutidine was removed by shaking five times with dilute hydrochloric acid and after three washings with water the ethereal layer was dried and distilled. After a small forerun, b. p. 138—143°/2·3 mm., the main fraction, b. p. 144—147°/2·3 mm. (6 g.), was obtained. Recrystallisation from ether–methanol gave large plates of 1 : 2 : 3 : 4 : 5 : 8 : 9 : 10 : 11 : 12-*decahydrodi*cyclo*hepta*[a, c]*benzene*, m. p. 56—57°. The analytical sample, m. p. 57—57·5°, was obtained by three recrystallisations from ether–methanol (Found : C, 89·7; H, 10·3. $C_{16}H_{22}$ requires C, 89·7; H, 10·3%). Ultraviolet absorption : $\lambda_{max.}$ 2600, 2690 Å (ε 321, 345 in heptane).

(b) *With sulphur*. A mixture of the dienes (6 g.) and sulphur (6 g.) was heated at 180°/25 mm. for 1 hr. The temperature of the metal-bath was then raised to 220°, material distilling at 184—186°/25 mm. The distillate was taken up in light petroleum (30 ml.), filtered from a little sulphur, and chromatographed on alumina (100 g.). On elution with light petroleum the first 100 ml. afforded merely traces, whereas the next 100 ml. gave 1 : 2 : 3 : 4 : 5 : 8 : 9 : 10 : 11 : 12-decahydrodi*cyclo*hepta[*a*, *c*]benzene (2·3 g.), plates, m. p. and mixed m. p. 56—57° (from ether–methanol). Further elution with light petroleum gave only traces of material.

(c) *With selenium*. A mixture of the dienes (10 g.) and selenium (15 g.) was heated for 2 hr. at 200°, and the temperature was then raised during 1 hr. to 345°. This temperature (±5°) was maintained for 24 hr., the product was cooled, and the solid mass was repeatedly extracted by heating under reflux with benzene. The benzene extract was concentrated in a vacuum and filtered through a column of alumina (200 g.) to remove most of the selenium. Upon distillation, the product (8·4 g.) had b. p. 146—150°/3 mm. Redistillation from sodium gave the analytical sample, b. p. 146—148°/4 mm., n_D^{25} 1·5255 (Found : C, 88·0; H, 11·5%). The analytical figures indicate that disproportionation may take place and the oil isolated is a more reduced product. A more dehydrogenated product was not isolated. Kuhn–Roth determination showed no rearrangement to a product containing *C*-methyl groups had occurred and no absorption at 1375 cm.$^{-1}$ was found in the infrared spectrum of the product.

DANIEL SIEFF RESEARCH INSTITUTE, REHOVOT.
ISRAEL INSTITUTE OF TECHNOLOGY, HAIFA, ISRAEL.

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