295. *Alicyclic Studies. Part XVII.* Preparation and Reactions of Bicyclodec-1-enyl.*

By Jacob Strumza and David Ginsburg.

Bicyclodec-1-enyl has been prepared by dehydration of bicyclodecyl-1,1′-diol. Diels–Alder reactions of this new diene with a number of dienophiles are described.

CYCLODECANONE was reduced to the pinacol, bicyclodecyl-1,1′-diol with aluminium amalgam in dry benzene. A very small amount of self-condensation of cyclodecanone occurs during the reduction, leading to the formation of 2-cyclodecylidenecyclodecanone. The latter through 1,4-reduction with lithium aluminium hydride gave 2-cyclodecylcyclodecanol.

The pinacol was dehydrated by our improved procedure with phosphorus oxychloride in pyridine.[1] We had hoped that we might isolate several geometrical isomers of the diene but the steric course of the elimination appears to be unique as the resulting bicyclodec-1-enyl was easily obtained crystalline. Unfortunately, however, its infrared spectrum does not show clear bands for either *cis*- or *trans*-double bonds.

The diene gave adducts in high yields with maleic anhydride, *p*-benzoquinone, and 1,4-naphthaquinone (see Experimental section). Conditions could not be discovered to

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* Part XVI, Strumza and Ginsburg, preceding paper.

[1] Greidinger and Ginsburg, *J. Org. Chem.*, 1957, **22**, 1406.

shift the equilibrium with dimethyl acetylenedicarboxylate in the direction of the adduct. Further transformations of the maleic anhydride adduct will be reported in the following paper in connexion with analogous adducts of bicyclohex-1-enyl and bicyclo-oct-1-enyl.[2]

EXPERIMENTAL

Bicyclodecyl-1,1'-*diol*.—A mixture of coarse aluminium powder (14·4 g.) and mercuric chloride (10·8 g.) was added to a stirred solution of cyclodecanone [3] (40 g.) in dry benzene (80 ml.). The resulting exothermic reaction caused the solvent to reflux gently. The mixture was heated under reflux with stirring overnight. Wet benzene (60 ml.) was added, followed by water (60 ml.) with stirring. After 30 minutes' heating the solid was removed and was extracted twice with boiling benzene. The benzene from the combined extracts was removed at the water-pump. Distillation gave unchanged ketone, b. p. 126—128°/26 mm. (5·7 g.). A pentane solution of the residual oil afforded after 12 hr. at 5° colourless prisms (15·8 g., 55%) of the *pinacol*, m. p. 106° (from 2,2,4-trimethylpentane), $\nu_{\max.}$ (in $CHCl_3$) 3550 cm.$^{-1}$ (OH) (Found: C, 77·25; H, 12·4; O, 10·5. $C_{20}H_{38}O_2$ requires C, 77·4; H, 12·3; O, 10·3%).

Distillation afforded more cyclodecanone (5·6 g.). The residual oil was dissolved in ethanol; in 12 hr. at 5° the solution deposited colourless needles (830 mg.) of a dimer assumed to be 2-*cyclodecylidenecyclodecanone*, m. p. 81° (from ethanol), $\nu_{\max.}$ (in $CHCl_3$) 1695 cm.$^{-1}$ (–C=C·C=O), $\lambda_{\max.}$ (in dioxan) 300 mμ (log ε 1·51) (Found: C, 81·9; H, 12·4; O, 5·9. $C_{20}H_{34}O$ requires C, 82·7; H, 11·8; O, 5·5%).

Reduction of this ketone with lithium aluminium hydride in ether gave 2-*cyclodecylcyclodecanol* as colourless prisms, m. p. 81—82° (from ethanol), $\nu_{\max.}$ (in $CHCl_3$) 3630 cm.$^{-1}$ (OH) (Found: C, 81·2; H, 13·3; O, 5·6. $C_{20}H_{38}O$ requires C, 81·6; H, 13·0; O, 5·4%).

Bicyclodec-1-*enyl*.—A solution of the pinacol (20 g.) in dry pyridine (400 ml.) was heated under reflux with phosphorus oxychloride (20 ml.) for 2 hr. Most of the pyridine was removed at the water-pump and water (10 ml.) was shaken with the ice-cold residue for 30 min. Extraction with pentane (3 × 300 ml.), washing with dilute hydrochloric acid and with water, drying ($MgSO_4$), and removal of the pentane, gave the oily *diene* (12·5 g., 71%) that crystallised as rhombs, m. p. 64—65°, from propan-2-ol. It had $\lambda_{\max.}$ (in methylcyclohexane) 235 mμ (log ε 4·06) but in $CHCl_3$ did not show infrared bands of either a *cis*- or a *trans*-double bond (Found: C, 87·45; H, 12·4. $C_{20}H_{34}$ requires C, 87·5; H, 12·5%).

1,2,3,4,5,6,7,8,8a,9,10,10a,11,12,13,14,15,16,17,18-*Eicosahydrodicyclodeca*[a,c]*benzene*-9,10-*dicarboxylic Anhydride*.—A solution of bicyclodec-1-enyl (5 g.) and maleic anhydride (2·7 g.) in xylene (15 ml.) was heated under reflux for 3 hr. The cooled mixture solidified and gave white needles of the *anhydride* (5·45 g., 80%), m. p. 184° (from methylcyclohexane), $\nu_{\max.}$ (in $CHCl_3$) 1845, 1775 cm.$^{-1}$ (C=O of anhydride) (Found: C, 77·3; H, 9·8; O, 12·9. $C_{24}H_{36}O_3$ requires C, 77·4; H, 9·7; O, 12·9%).

Aromatisation of the six-membered ring was effected by refluxing the adduct (0·74 g., 0·002 mole) in chloroform (50 ml.) with bromine (0·32 g., 0·004 mole) for 5 hr. After washing of the solution with 5% sodium hydrogen carbonate solution and with water, the chloroform was removed. Trituration of the residue with methanol gave colourless needles of the aromatic *anhydride* (80 mg., 11%), m. p. 191° (from acetic acid), $\nu_{\max.}$ (in $CHCl_3$) 1835, 1765 cm.$^{-1}$ (C=O of anhydride) (Found: C, 78·0; H, 8·8; O, 13·1. $C_{24}H_{32}O_3$ requires C, 78·2; H, 8·75; O, 13·0%).

1,2,3,4,5,6,7,8,8a,8b,9,10,11,12,13,14,14a,14b,15,16,17,18,19,20,21,22-*Hexacosahydrodicyclodeca*[a,c]*anthracene*-9,14-*dione*.—A nitrobenzene (20 ml.) solution of bicyclodec-1-enyl (2·19 g., 0·008 mole) and 1,4-naphthaquinone (1·26 g., 0·008 mole) was heated at 150° for 3 hr. Steam-distillation to remove nitrobenzene was followed by extraction of the dark residue with chloroform. Removal of the chloroform and extraction with hexane, removal of the solid by filtration and of the hexane from the mother-liquor gave an oil which upon trituration with propan-2-ol gave slender yellow needles (1·24 g., 36%) of the *diketone*, m. p. 141° (from propan-2-ol), $\nu_{\max.}$ (in $CHCl_3$) 1660 cm.$^{-1}$ (C=O conjugated to aromatic nucleus), $\lambda_{\max.}$ (in dioxan) 247, 277, 337 mμ (log ε 4·24, 4·10, 3·47) (Found: C, 83·6; H, 9·1; O, 6·8. $C_{30}H_{40}O_2$ requires C, 83·3; H, 9·3; O, 7·4%).

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[2] Strumza and Ginsburg, following paper.

[3] Cope, *Org. Synth.*, 1956, **36**, 79.

Dehydrogenation of this diketone (0·5 g.) was effected in acetic acid (20 ml.) with *p*-benzoquinone (2 g.) at 100° for 4 hr. *p*-Benzoquinone (2 g.) was again added and heating prolonged for another 4 hr. The black precipitate was removed from the ice-cold mixture and washed with cold methanol. The *docosahydro-diketone* (350 mg., 59%) was obtained as yellow needles, m. p. 218° (from dioxan), $\nu_{max.}$ (in $CHCl_3$) 1655 cm.$^{-1}$ (quinonoid C=O), $\lambda_{max.}$ (in dioxan)[4] 241, 269, 361 mμ (log ε 4·54, 4·60, 3·65) (Found: C, 84·2; H, 8·4; O, 7·6. $C_{30}H_{36}O_2$ requires C, 84·1; H, 8·5; O, 7·5%).

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[4] Cf. Friedel and Orchin, " Ultraviolet Spectra of Aromatic Compounds," John Wiley and Sons, Inc., New York, 1951, No. 395.