The Structure of Pseudoclovene-B

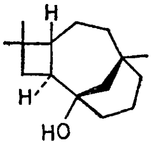
By R. I. Crane (in part), C. Eck, and W. Parker*
(*Department of Chemistry, University of Stirling, Stirling*)

A. B. Penrose
(*School of Physical Sciences, The New University of Ulster, Coleraine, Co. Londonderry, N. Ireland*)

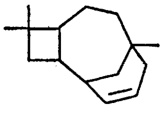
and T. F. W. McKillop, D. M. Hawley, and J. M. Robertson
(*Department of Chemistry, University of Glasgow, Glasgow* W.2)

Summary The structure of pseudoclovene-B, a rearrangement product of caryolan-1-ol, has been determined.

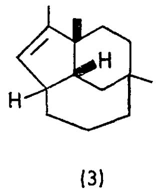
The dehydration of caryolan-1-ol (**1**) with phosphorus pentoxide (or preferably polyphosphoric acid) has been reported[1] to yield pseudoclovene (**2**) and isoclovene (**3**). The complete structure of isoclovene was determined[2] by an *X*-ray crystallographic analysis of the corresponding hydrochloride and subsequent work[3] has shown that pseudoclovene is, in fact, a mixture of two hydrocarbons, pseudoclovene-A and -B, which are separable by silver nitrate–silica gel adsorption chromatography. The structure of pseudoclovene-A (**4**) has since been rigorously established.[3]



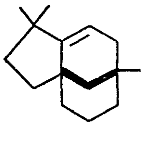
(1)



(2)

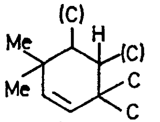


(3)

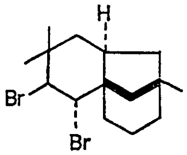


(4)

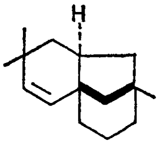
Pseudoclovene-B ($C_{15}H_{24}$, *m/e* parent ion 204), b.p. 111—112° at 10 mmHg, $[\alpha]_D^{20}$ + 33·0° (*c* 1·66 in $CHCl_3$); ν_{max} 3010, *ca.* 1640 vw, 1375, 1360, and 750 cm^{-1}; τ 4·66 (2H, s), 9·03 (6H), and 9·08 (3H). Hydroboration–oxidation[4] of pseudoclovene-B gave a mixture of two ketones separable by chromatography on neutral alumina. The less polar ketone (ν_{max} 1712 cm^{-1}) showed signals at τ 7·59 (1H, d, *J* 11 Hz), 8·07 (1H, d, *J* 11 Hz), 8·95 (3H, s), and 9·00 (6H, s) and the mass spectrum of the corresponding ethylene acetal (parent ion *m/e* 264) had a base peak at *m/e* 179. The more polar ketone (ν_{max} 1700 cm^{-1}) showed τ 7·9 (1H, s), 8·04 (1H, s), 8·95 (3H, s), and 9·00 (6H, s) and the corresponding acetal (parent ion, *m/e* 264) exhibited a base peak at *m/e* 127. These results revealed the presence of a 3,3-dimethylcyclohexene fragment (**5**) in the structure of pseudoclovene-B.



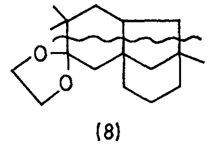
(5)



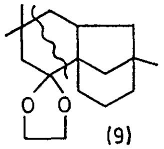
(6)



(7)



(8)



(9)

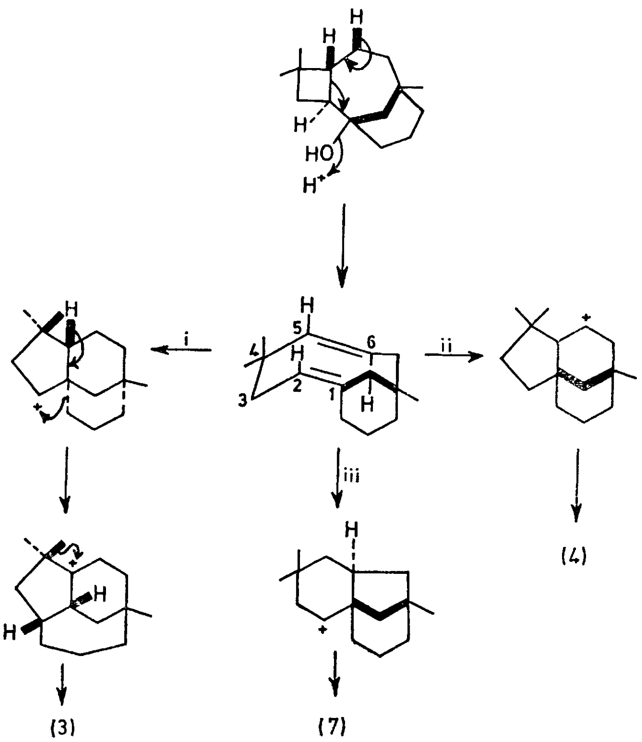
The corresponding dibromide, m.p. 122—123°, $[\alpha]^{21}_{D}$ $+103°$ (c 1·45 in CCl_4) was prepared from the olefin by treatment with pyridinium hydrobromide perbromide[5] in acetic acid and on treatment with zinc–ethanol was converted into a single olefin identical in all respects with pseudoclovene-B.

Crystals of the dibromide are monoclinic, space group $P2_1$; $Z = 2$; $a = 9{\cdot}56$, $b = 7{\cdot}95$, $c = 10{\cdot}95$ Å, $\beta = 115{\cdot}1°$. Three crystals were used in the data collection owing to their decomposition on prolonged exposure to the X-ray beam. Approximately 1300 intensities were estimated visually from equi-inclination Weissenberg photographs taken with Cu-K_α radiation. The Patterson distribution was solved for the bromine positions and the remaining non-hydrogen atoms were located from the ensuing electron-density distributions. The structure was refined by full-matrix least-squares (R 0·125) taking into account the anisotropic vibrational parameters of the bromine atoms. The absolute stereochemistry depicted in (**6**) and thence of pseudoclovene-B was determined (**7**) from a consideration of the intensity differences of several Bijvoet pairs of reflections.[6]

These results allowed a structural assignment to be made to the ethylene acetals (**8**) and (**9**) of the corresponding less and more polar ketones described above, with their associated mass spectral fragmentation[7] behaviour as indicated.

It is notable that the mechanistic Scheme proposed previously[3] to account for the formation from caryolan-1-ol of isoclovene (**3**) and pseudoclovene-A (**4**) can also account for the structure of pseudoclovene-B (**7**).

(*Received*, 19*th January* 1971; *Com.* 083.)



Scheme. i, *Protonation at* C(6), 1:5 *closure;* ii, *Protonation at* C(2), 1:5 *closure;* iii, *Protonation at* C(5), 1:6 *closure.*

[1] A. W. Lutz and E. B. Reid, *J. Chem. Soc.*, 1954, 2265; G. G. Henderson and R. O. O. McCone, *ibid.*, 1929, 1368.

[2] J. S. Clunie and J. M. Robertson, *Proc. Chem. Soc.*, 1960, 82; *J. Chem. Soc.*, 1961, 4382.

[3] P. Doyle, G. Ferguson, D. M. Hawley, T. F. W. McKillop, J. Martin, and W. Parker, *Chem. Comm.*, 1967, 1123.

[4] G. Zweifel and H. C. Brown, *Org. Reactions*, 1963, **13**, 1 (see also H. C. Brown, "Hydroboration", Benjamin, New York, 1962).

[5] L. F. Fieser and M. Fieser, "Reagents for Organic Synthesis", Wiley, New York, 1967, p. 967.

[6] J. M. Bijvoet, *Prok. K. ned. Akad. Wetenschap*, 1949, **52**, 313. See also S. Ramaseshan in "Advanced Methods of Crystallography," Academic Press, London, 1964, pp. 67–95.

[7] See Interpretation of Mass Spectra of Organic Compounds,' by H. Budzikiewicz, C. Djerassi and D. H. Williams, Holden–Day, San Francisco, 1964, and references cited therein.