

## The Structure and Synthesis of Pseudoclovene A

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DEHYDRATION of caryolan-1-ol<sup>1</sup> (I) with phosphorus pentoxide has been reported<sup>2</sup> to yield pseudoclovene (II) and the higher-boiling, rearranged hydrocarbon isoclovene (III). The complete structure of isoclovene was determined by an X-ray crystallographic analysis of the corresponding hydrochloride,<sup>3</sup> but little evidence has been forthcoming in support of the proposed structure (II) for pseudoclovene.

Gas-liquid chromatography of the products from treatment of (I) with P<sub>2</sub>O<sub>5</sub> (or preferably polyphosphoric acid) revealed a complex mixture of, at least, ten hydrocarbons, however the two main components proved to be the most and least volatile, hence careful fractional distillation using a spinning

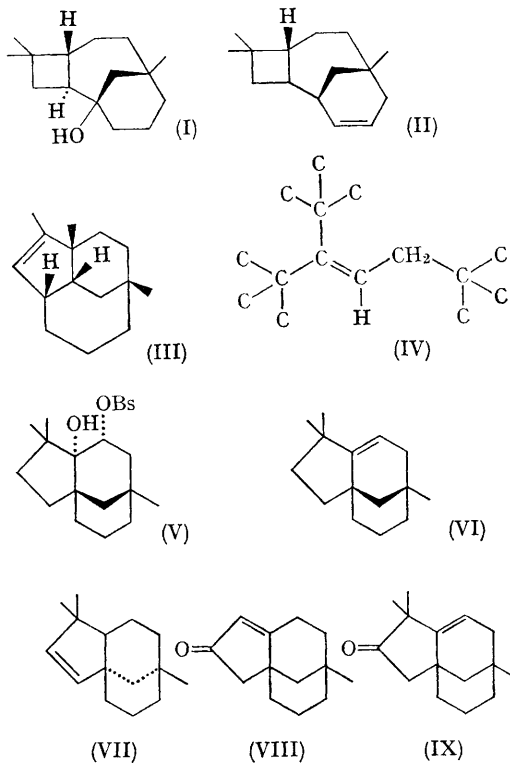
band column served to separate fairly pure (>85%) pseudo- and iso-clovene.

More extensive g.l.c. examination of the lower-boiling pseudoclovene fraction showed it to be a two-component mixture in the ratio of (1:1), which proved separable by silver nitrate-silica gel adsorption column chromatography.† The first component, pseudoclovene-A, was readily eluted with light petroleum, whereas the second hydrocarbon, pseudoclovene B, required the use of 10% ether-light petroleum as eluting solvent.

Pseudoclovene-A, C<sub>15</sub>H<sub>24</sub>-mass spectral parent ion at 204, exhibits maxima at 3030, *ca.* 1670 (very weak) and 820 cm.<sup>-1</sup> in the infrared and shows signals at  $\tau = 4.55$  (1H, triplet,  $J = 4$  c./sec.) and

† 25% AgNO<sub>3</sub> on 140-200 mesh silica gel supplied by Applied Science Laboratories Inc.

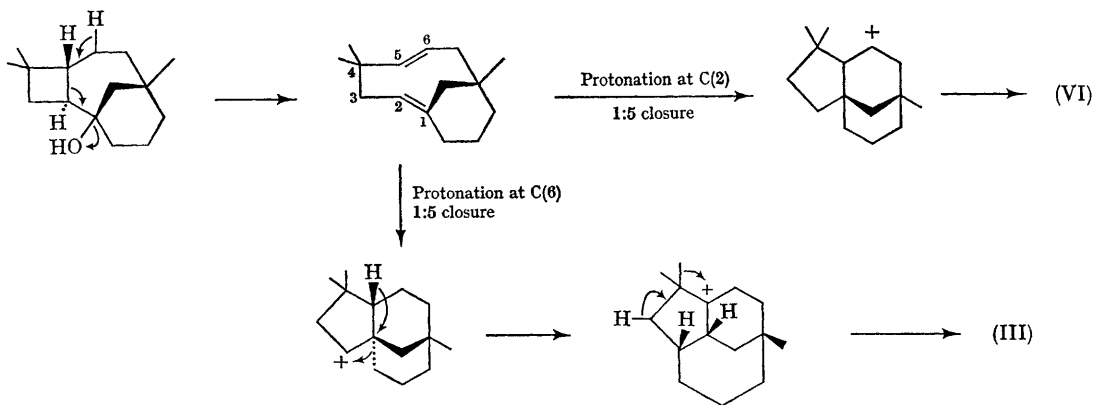
8·15 (2H, doublet,  $J = 4$  c./sec.) with the three expected methyl groups as singlets at  $\tau$  8·94, 9·00, and 9·12. This spectral data is compatible with the partial structure (IV) and hence removes (II) as a structural possibility for pseudoclovene-A. The trisubstituted double-bond in this compound is



severely sterically hindered as indicated by its chromatographic behaviour on silver nitrate-silica gel and by its complete inertness to attempted catalytic hydrogenation under a wide variety of conditions. Treatment of pseudoclovene-A with  $\text{OsO}_4$ -pyridine in ether even for periods up to *one week* led only to partial transformation into a single crystalline secondary-tertiary diol which was readily converted into the corresponding mono-*p*-bromobenzenesulphonate ester.

This derivative when crystallised from ether-light petroleum was monoclinic, space group  $P2_1$ , with four molecules per unit cell of dimensions  $a = 9.97$ ,  $b = 21.41$ ,  $c = 9.97$  Å and  $\beta = 90^\circ$ . Some 3000 visually estimated intensity data were obtained from a small crystal rotating about the  $a$ -axis and the arrangement of the molecules in the unit cell, closely approximating to a tetragonal system, was put to full use in solving the structure. The positions of the heavy atoms were determined from a 3D Patterson distribution and the remaining atoms were found by the heavy-atom method.<sup>4</sup> The absolute configuration was determined from a consideration of the intensity differences of 26 Bijvoet pairs<sup>5</sup> of reflections using  $\text{Cu-K}\alpha$  radiation. The agreement index,  $R$ , now stands at 17.9% and refinement by Fourier and least squares methods is progressing.<sup>†</sup> Formula (V) illustrates the full stereochemical result of this X-ray analysis hence pseudoclovene-A must have structure (VI).

The similarity of (VI) and clovene (VII) suggested a simple synthesis of (VI) in its racemic form. The enone (VIII), a precursor in the total synthesis of clovene,<sup>6</sup> was treated with  $\text{KO}^t\text{Bu}/\text{Bu}^t\text{OH}$  and methyl iodide<sup>7</sup> to give (IX), which on Wolff-Kishner reduction gave an olefin identical in high



<sup>†</sup> Using programmes devised by the Glasgow Group: Fourier programme—Dr. J. G. Sime; least-squares programme—Professor D. W. J. Cruickshank and J. G. F. Smith.

resolution infrared,  $^1\text{H}$  n.m.r., and gas-chromatography mass spectra with pseudoclovene-A.

Several formal mechanisms can be devised to rationalise the formation of pseudoclovene-A, but those which involve an initial Wagner-Meerwein rearrangement of one of the cyclobutyl bonds to the bridgehead cation<sup>3</sup> can be excluded as such a step

would lead to prohibitively strained intermediates. An alternative proposal (Figure) overcomes this difficulty and has the added advantage of encompassing with the correct stereochemistry the co-formation of isoclovene. The structural elucidation of pseudoclovene-B is in hand.

(Received, September 13th, 1967; Com. 981.)

<sup>1</sup> A mixture of caryolan-1-ol, clovene, and neoclovene is produced by treatment of caryophyllene with sulphuric acid. See W. Parker, R. A. Raphael, and J. S. Roberts, *Tetrahedron Letters*, 1965, 2313; and references cited therein.

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<sup>3</sup> J. S. Clunie and J. M. Robertson, *Proc. Chem. Soc.*, 1960, 82; *J. Chem. Soc.*, 1961, 4382.

<sup>4</sup> J. M. Robertson and I. Woodward, *J. Chem. Soc.*, 1937, 219; 1940, 36; G. A. Sim in "Computing Methods and the Phase Problem in X-ray Crystal Analysis", ed. R. Pepinsky, J. M. Robertson and J. C. Speakman, Pergamon Press, Oxford, 1961.

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<sup>7</sup> S. K. Malhotra and H. J. Ringold, *J. Amer. Chem. Soc.*, 84, 3402.