The Structure of an Isocaryophyllene Rearrangement Product, 1,5,9,9-Tetramethyltricyclo[6,2,1,$0^{4,11}$]undec-5-ene: *X*-Ray Analysis of the Dibromo-derivative

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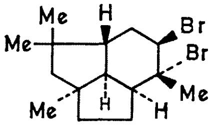
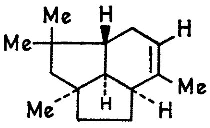
Summary The structure of an isocaryophyllene rearrangement product, 1,5,9,9-tetramethyltricyclo[6,2,1,$0^{4,11}$]-undec-5-ene, has been determined by the *X*-ray analysis of its dibromo-derivative.

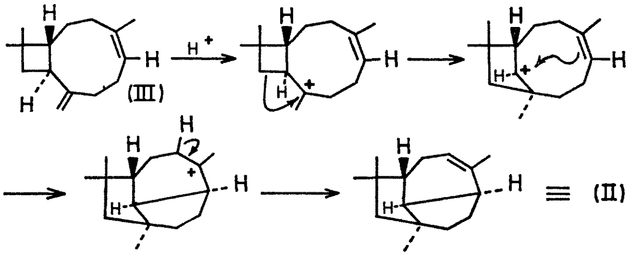
THE acid-catalysed rearrangement of caryophyllene has been shown[1] to produce three major products, caryolan-1-ol, clovene, and neoclovene.[2] We have now studied the rearrangement of isocaryophyllene (III) under similar conditions. We find that pure (—)-isocaryophyllene, on treatment with sulphuric acid in ether, yields a complex mixture of hydrocarbons from which two main components (each 35%) can be isolated in a pure state by fractional distillation and preparative g.l.c. In agreement with the findings of Nickon *et al.*,[1c] neither caryolan-1-ol nor clovene are detected in the crude reaction mixture.



(I)



(II)



The first major hydrocarbon, $C_{15}H_{24}$,† n_D^{20} 1·5094, $[\alpha]_D^{25}$ $-87{\cdot}69°$ (c 3·1, $CHCl_3$) has been shown to be identical to neoclovene by comparison of i.r. and n.m.r. spectra and R_T values on various g.l.c. columns.

The second major hydrocarbon, $C_{15}H_{24}$,† n_D^{20} 1·4922, $[\alpha]_D^{25}$ $-72{\cdot}3°$ (c 2·0, C_6H_6), exhibits maxima at 3020, 1645 (very weak), 808, and 794 cm^{-1} in the i.r. which are compatible with a trisubstituted double bond. The n.m.r. spectrum shows three methyl singlets at τ 9·17, 9·02, and 8·93, a slightly broadened singlet at τ 8·46 (CH_3–C=C–H), and an unresolved multiplet at τ 4·72 (CH_3–C=C–H). Two saturated hydrocarbons (30 : 70) are obtained by catalytic hydrogenation over PtO_2 in acetic acid, thus demonstrating that the parent hydrocarbon is tricyclic. Addition of bromine to an ice-cold solution of the hydrocarbon in CCl_4 yields a crystalline dibromide,† m.p. 95—97°, $[\alpha]_D^{29}$ $-121{\cdot}5°$ (c 0·94, C_6H_6).

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† Satisfactory elemental analyses have been obtained for these compounds.

This derivative crystallises from ethyl acetate as long needles which are sensitive to light, but rapid decomposition can be prevented by coating with varnish. The system is orthorhombic, space group $P2_12_12_1$ (D_2^4) with four molecules of $C_{15}H_{24}Br_2$ in a unit cell of dimension s$a = 6{\cdot}63$, $b = 9{\cdot}00$, $c = 26{\cdot}44$ Å. From Weissenberg photographs 865 structure amplitudes were evaluated by visual estimation. The co-ordinates of the bromine atoms were obtained from an analysis of the Patterson function. Structure factors were calculated from these positions ($R = 31\%$) and the three-dimensional electron density distribution calculated on this basis gave the positions of seven carbon atoms in addition to bromine atoms. Four further cycles of structure factor calculation and Fourier syntheses revealed all the atomic positions and reduced R to 19·1%. Three cycles of isotropic least-squares refinement reduced R to 14·9% and refinement is continuing. Bond lengths and angles appear to be reasonable at the present stage.

Our results define the structure of the dibromide as (I) and consequently the structure and stereochemistry of the parent hydrocarbon as (II). It is probable that the formation of this new hydrocarbon from isocaryophyllene (III) proceeds by the mechanism shown.

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[1] For leading references, see (a) A. Nickon, *Perfumery Essent. Oil Record,* 1954, **45**, 149; (b) D. H. R. Barton and P. de Mayo, *Quart. Rev.*, 1957, **11**, 189; (c) A. Nickon, F. Y. Edamura, T. Iwadare, K. Matsuo, F. J. McGuire, and J. S. Roberts, *J. Amer. Chem. Soc.*, 1968, **90**, 4196.

[2] W. Parker, R. A. Raphael, and J. S. Roberts, *Tetrahedron Letters*, 1965, 2313; T. F. W. McKillop, J. Martin, W. Parker, and J. S. Roberts, *Chem. Comm.*, 1967, 162.