

The Structure of a Hydrocarbon, 2,6,10,10-Tetramethyltricyclo[7,2,0,0^{2,7}]undec-5-ene, Obtained from Caryophyllene Dihydrochloride: X-Ray Analysis of the Dibromo-derivative

By K. GOLLNICK and G. SCHADE

(Max-Planck-Institut für Kohlenforschung, Abteilung Strahlenchemie, 433 Mulheim-Ruhr, Germany)

and A. F. CAMERON, C. HANNAWAY, and J. M. ROBERTSON*

(Department of Chemistry, University of Glasgow, Glasgow, W.2)

Summary The structure of a hydrocarbon, 2,6,10,10-tetramethyltricyclo[7,2,0,0^{2,7}]undec-5-ene (I), obtained by eliminating hydrogen chloride from caryophyllene dihydrochloride, has been determined by the X-ray analysis of its dibromo derivative (II).

DURING early investigations into the chemistry of caryophyllene, several workers used the dihydrochloride (III)† as a suitable crystalline derivative. In an effort to elucidate the structure of caryophyllene and unaware of the com-

plexities inherent in the caryophyllene nucleus, these workers submitted this dihydrochloride to various mild and severe dehydrochlorination conditions.¹ Much confusion then ensued as to the identity of the derived hydrocarbon(s)

because of the limited methods of comparison with other bicyclic and tricyclic hydrocarbons derived from caryophyllene and caryolan-1-ol.

We have now repeated this dehydrochlorination using one of the earliest procedures,^{1(a) viz.}, refluxing in AcOH for 1h, and have found a complex mixture of hydrocarbons from which two main hydrocarbon components could be isolated by fractional distillation and preparative g.l.c. Neither clovene nor the tricyclic hydrocarbon (IV),² each derived from caryophyllene and isocaryophyllene, respectively, were identified as minor components. One of the major hydrocarbons (34%), however, was identified as neoclovene.³

The major hydrocarbon (I) (46%), C₁₅H₂₄, ‡ b.p. 68–69°/3 mm, $d_4^{20} = 0.9111$, $n_D^{20} = 1.4925$, $[\alpha]_D^{24} = -50.0^\circ$ (*c* 2.8, C₆H₆), exhibits maxima at 3040, 1670, and 805 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 9.14, 9.10, and 8.84, a multiplet at 8.24 (CH₃-C=C-H) and an unresolved multiplet at 4.65 (-C=C-H). Catalytic hydrogenation over PtO₂ in acetic acid results in the formation of two saturated hydrocarbons (30:70), thus showing that the parent hydrocarbon is tricyclic. Addition of bromine to an ice-cold solution of the hydrocarbon in CCl₄ yields a crystalline dibromide (II), † m.p. 92–93°, $[\alpha]_D^{20} = +77.2^\circ$ (*c* 0.9, C₆H₆).

This derivative crystallises from benzene to form crystals which are sensitive to light but decompose slowly. The system is orthorhombic, space group $P2_12_12(D_2^3)$ with four molecules of C₁₅H₂₄Br₂ in a unit cell of dimensions $a = 15.47$, $b = 14.02$, $c = 7.01$ Å. The intensities of 1342 reflections were estimated visually from Weissenberg photographs. The structure was solved with some difficulty by the heavy-atom procedure and has been refined, in the latter stages by anisotropic least squares, to $R = 10.6\%$. Calculated bond lengths and angles are as expected and show no anomalies.

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

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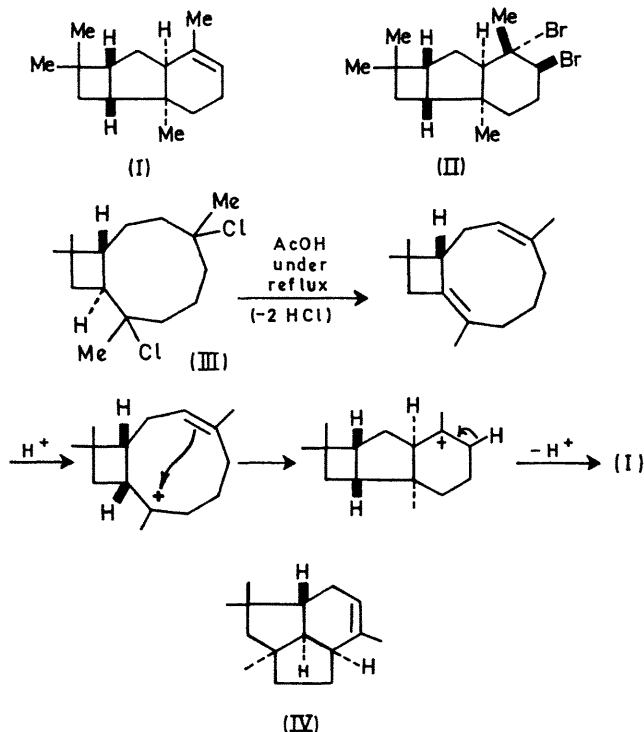
† The structure and stereochemistry of caryophyllene dihydrochloride is at present being confirmed by X-ray analysis.

‡ Satisfactory elemental analyses have been obtained for these compounds.

¹ (a) O. Schreiner and E. Kremers, *Pharm. Arch.*, 1901, **4**, 164; (b) F. W. Semmler and E. W. Mayer, *Ber.*, 1910, **43**, 3451; (c) G. G. Henderson, R. O. O. McCrone, and J. M. Robertson *J. Chem. Soc.* 1929, 1368.

² K. Gollnick, G. Schade, A. F. Cameron, C. Hannaway, J. S. Roberts, and J. M. Robertson, *Chem. Comm.*, 1970, 248.

³ W. Parker, R. A. Raphael, and J. S. Roberts, *J. Chem. Soc. (C)*, 1969, 2634.



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