days. The product was washed several times with petroleum ether. It could not be recrystallized because of decomposition in the usual solvents. *Anal.* Calcd. for $C_{12}H_{14}Cl_2NiN_2$: Ni, 18.58; Cl, 22.45. Found: Ni, 18.70; Cl, 24.17.

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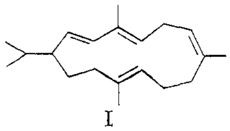
RECEIVED MARCH 21, 1962

CEMBRENE, A 14-MEMBERED RING DITERPENE HYDROCARBON[1]

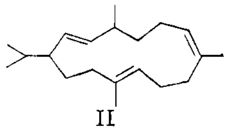
Sir:

Cembrene (I) is a crystalline diterpene hydrocarbon ($C_{20}H_{32}$, mol. wt. 272 (mass spectrum[2]), m.p. 59–60°, $[\alpha]^{23}D$ + 238° (*c* 1.13, chf.)) first isolated by Haagen-Smit, Wang and Mirov,[3] from the oleoresin of *Pinus albicaulis* and subsequently found to occur in exudate of many other pine trees.[4,5] Cembrene,[6] upon catalytic hydrogenation over Pd/C in ethyl acetate, yielded a liquid saturated octahydro derivative ($C_{20}H_{40}$, mol. wt. 280 (mass spectrum[2])), establishing the presence of four double bonds and one ring in the starting material (I). The ultraviolet and infrared spectra of cembrene, $\lambda_{\max}^{\mathrm{EtOH}}$ 245 mμ (ε 17,000), $\nu_{\max}^{\mathrm{CS_2}}$ 1660 (w), 1640 (w), 967 (s), 840 (m), 811 (m) cm.$^{-1}$, indicated the presence of a conjugated diene as well as *trans*-disubstituted and trisubstituted double bonds. From the n.m.r. spectrum[7] (quantitative) of cembrene, it was determined that there was an isopropyl group attached to a saturated carbon (two doublets centered at 9.09 and 9.20 p.p.m., 6 protons), two methyl groups on double bonds (8.47 and 8.38 p.p.m.), and one methyl group on a conjugated diene (8.20 p.p.m.). The presence of five vinyl protons was established by a broad absorption band between 3.80 and 5.30 p.p.m. containing a sharp doublet at 3.80 and 4.07 p.p.m. equal to one proton. The low field position of this doublet characteristic of a proton on a *trans*-disubstituted double bond further indicated that the bond was part of the conjugated diene system.

Reduction of the conjugated diene system of I with lithium in liquid ammonia gave a mixture of dihydrocembrenes,[8] whose ultraviolet spectrum possessed no maximum above 205 mμ, and which consisted of two compounds in the ratio of 85:15 (g.l.c., silicone, 215°). The infrared absorption at 973 cm.$^{-1}$ of the major component (II) indicated the continued presence of the *trans*-disubstituted double bond and the n.m.r. spectrum showed the presence of four vinyl protons.



I

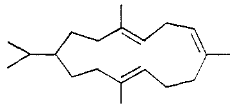


II

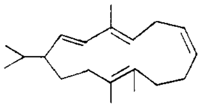
Ozonization of II and treatment with hydrogen peroxide gave 2-isopropyl-5-oxocaproic, 2-methylglutaric, and levulinic acids (isolated as methyl esters by gas-liquid chromatography, silicone, 110°). These three acids account for all twenty carbon atoms of the cembrene molecule. Since all are bifunctional, and since cembrene possesses but one ring, the dihydro derivative and therefore cembrene must contain a fourteen carbon ring. There are eight possible structures for the lithium-liquid ammonia produced dihydrocembrene (II) which could yield these three degradation products.

Ozonization of cembrene and treatment with hydrogen peroxide gave acetic, malonic, 2-isopropyl-5-oxocaproic, and levulinic acids (isolated as methyl esters by gas-liquid chromatography, silicone, 110°). When the ozonide was treated with sodium iodide, then *p*-nitrophenylhydrazine, the *p*-nitrophenylosazone of pyruvaldehyde was isolated. The absence of 2-methylglutaric acid and the appearance of malonic and pyruvic acid moieties permits placement of the olefinic bond which was reduced to form dihydrocembrene II and suggests eight related structures for cembrene.

Catalytic hydrogenation of cembrene over 5% Pd/C in ethyl acetate gave a mixture of three dihydrocembrenes (gas-liquid chromatography, silicone, 200°). The major component III (no maximum in the ultraviolet; n.m.r., 3 vinyl protons; no 970 cm.$^{-1}$ band) was different from dihydrocembrene II and was formed by the hydrogenation of the *trans*-disubstituted double bond of the conjugated diene.



III



IV

Ozonization of III and treatment with hydrogen peroxide gave rise to approximately equal amounts of neutral and acidic materials. The major components of the latter were levulinic and malonic acids.

The eight possible structures of cembrene may be reduced to four by elimination of all structures not containing a *trans*-disubstituted double bond as part of the conjugated system. Two of the remaining four structures also may be eliminated, since the product from their dihydrogenation would not yield levulinic and malonic acids upon ozonization. The two remaining structures are isoprenoid I and the non-isoprenoid IV.

Hydroboration of III, then oxidation, gave a triol mixture V, whose n.m.r. spectrum showed a broad peak at 6.28 p.p.m. corresponding to three protons attached to carbon atoms bearing hydroxyl groups. Acetylation of V with acetic anhydride and sodium acetate at 145° gave the triacetate VI whose n.m.r. spectrum showed a broad band at 5.20 p.p.m. corresponding to three protons at-

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[1] This work was supported in part by Grant No. 14526, National Science Foundation.

[2] We are indebted to Dr. D. P. Stevenson of Shell Development Company for all the mass spectral data quoted in this work.

[3] A. J. Haagen-Smit, T. H. Wang, and N. T. Mirov, *J. Am. Pharm. Assn., Sci. Ed.*, **40**, 557 (1951).

[4] N. T. Mirov, "Composition of Gum Turpentines of Pines," Technical Bulletin No. 1239, U. S. Department of Agriculture, June, 1961.

[5] W. G. Dauben and C. Ashcraft, unpublished observations.

[6] We are indebted to Dr. N. T. Mirov for the supply of oleoresin.

[7] All chemical shifts are quoted in reference to the τ scale.

[8] Satisfactory analyses were obtained for all new compounds.

tached to carbons bearing acetoxyl groups. The downfield shift of 1.08 p.p.m. is characteristic of an acetate of a secondary alcohol.[9] These data agree with structure VI, a structure derived from dihydrocembrene II and cembrene I and would not agree with a similar group of structures derived from IV.

Thus, I represents the structure of cembrene. Although no information is available with regard to the stereochemistry of the trisubstituted double bonds, from a study of models the structure written containing one *cis* bond appears to be more favored than an all *trans* structure. This diterpene hydrocarbon, the first naturally-occurring fourteen carbon ring compound, is specially significant from the biogenetic standpoint, since it is the monocyclic diterpene derived from geranylgeraniol in a manner analogous to the formation of the sesquiterpene humulene from farnesol.[10,11]

(9) L. M. Jackman, "Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry," Pergamon Press, London, 1959, p. 55.

(10) J. B. Hendrickson, *Tetrahedron*, **9**, 82 (1959).

(11) M. D. Sutherland and O. J. Waters, *Aust. J. Chem.*, **14**, 596 (1961).

(12) National Science Foundation Predoctoral Fellow, 1957–1959.

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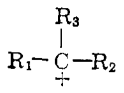
PHYSICAL PROPERTIES OF THE TRICYCLOPROPYLMETHYL CATION[1]

Sir:

Recently the physical properties of a simple aliphatic alkenyl cation were reported.[2] We now report the physical properties of the tricyclopropylmethyl cation, an aliphatic carbonium ion containing no formal double bonds.

Hart and Sandri[3] showed from solvolysis studies that cyclopropyl groups stabilize carbonium ions. The *p*-nitrobenzoates of IIb, IIc, and IId solvolyzed with relative rates of 23,500:246:1, indicating that the effect of cyclopropyl groups was nearly additive.[3]



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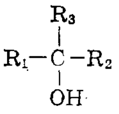
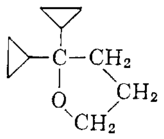


II



III

a, $R_1 = R_2 = R_3 =$ cyclopropyl
b, $R_1 = R_2 =$ cyclopropyl
$R_3 =$ isopropyl
c, $R_1 =$ cyclopropyl
$R_2 = R_3 =$ isopropyl
d, $R_1 = R_2 = R_3 =$ isopropyl
e, $R_1 = R_2 =$ cyclopropyl
$R_3 = -CH_2CH_2CH_2OH_2^+$

Addition of IIa to 96% H_2SO_4 produces the tricyclopropylmethyl cation (Ia). This ion has a most remarkable n.m.r. spectrum consisting of a single sharp band (width at half-height about 3.5 cycles) at 6.85 τ (60 mc., benzene capillary reference, 2.73 used to relate benzene to tetramethylsilane). This is in striking contrast to the n.m.r. spectrum of IIa (CCl_4 solution), which consists of a complex multiplet from 8.9–9.4 τ and a complex multiplet from 9.5–9.8 τ with areas in the approximate ratio of 1:3. This reduction of the complex cyclopropyl n.m.r. pattern to a single band is also found in protonated dicyclopropyl ketone, which exhibits a band (with poorly resolved fine structure) at 7.05 τ in 96% H_2SO_4. These observations both support the identification of Ia and show the close relation between carbonium ions and protonated ketones.

IIa was recovered in 63% yield from solutions of Ia in 96% H_2SO_4. The b.p. and both n.m.r. and infrared spectra are identical with those of the original IIa used to form Ia. Addition of a solution of Ia in 96% D_2SO_4 to ice–10% NaOH yielded a CCl_4 extract. The n.m.r. spectrum of this extract was virtually identical with that of the original IIa demonstrating that no rapid H–D exchange had occurred and that IIa was the only water insoluble product derived from drowning Ia. Even slow H–D exchanges are absent because the n.m.r. spectrum of Ia in 96% D_2SO_4 was essentially unchanged after one hour. This eliminates an olefin as a component of the equilibrium and reflects the high energy of cyclopropylidene derivatives.

The initial *i*-factor of IIa in H_2SO_4 was 4.1 in accord with the equation $ROH + 2H_2SO_4 = R^+ + H_3O^+ + 2HSO_4^-$. The infrared spectrum of Ia exhibits bands at 837, 1279, and 1445 (cm.$^{-1}$).[4] In the ultraviolet, λ_{max} for Ia (270 mμ, ϵ 22,000)[5] bears a relation to alkenyl cations (310–335 mμ) that is comparable to the relation between protonated cyclopropyl ketones (dicyclopropyl ketone·H^+ 235 mμ, tricyclanone·H^+ 250 mμ)[6] and protonated unsaturated ketones (4-methyl-3-penten-2-one·H^+ 284 mμ).[7]

Solutions of Ia in 96% H_2SO_4 show little change in n.m.r. or ultraviolet spectra after one hour although decomposition is progressing. The ion becomes increasingly unstable (chemically) as the % H_2SO_4 is reduced from 85 to 52%. At 25°, the half-life is 700 seconds in 71% acid and 30 seconds in 52% acid. Extrapolations of the first order rate plots suggest that IIa is completely converted to Ia even in 52% acid. The mode of decomposition appears to be nucleophilic attack on the $-CH_2-$

(1) Grateful acknowledgment is made of partial support of this Research by grants from the Petroleum Research Fund of the American Chemical Society, and the National Science Foundation.

(2) N. C. Deno, H. G. Richey, Jr., J. D. Hodge, and M. J. Wisotsky, *J. Am. Chem. Soc.*, **84**, 1498 (1962).

(3) H. Hart and J. M. Sandri, *ibid.*, **81**, 320 (1959).

(4) The H_2SO_4 solution was held in plastic films between NaCl prisms. By taking two spectra, one with high clarity polyethylene and one with high clarity FEP fluorocarbon polymer (kindly supplied by the du Pont Company), the complete 2–15 μ region can be measured. The H_2SO_4 has a strong background absorption throughout this region, but the intense bands pierce through this background.

(5) IIa Solvolyzes at a moderate rate in acetic acid (and probably also methanol and ethanol) so that it was necessary to introduce IIa directly into 96% H_2SO_4 and dilute the resulting solutions.

(6) Simple protonated ketones do not absorb above 220 mμ (H. J. Campbell and J. T. Edward, *Can. J. Chem.*, **38**, 2109 (1960)).

(7) 4-Methyl-3-penten-2-one·H^+ has a strong absorption band at 1540 cm.$^{-1}$ in close agreement with the value 1533 cm.$^{-1}$ found in an alkenyl cation (ref. 2). This is ascribed to a stretching mode of the $C\cdots C\cdots C$ system and suggests that the hydroxyalkyl cation form makes the dominant contribution to the structure of this protonated ketone. A second intense band at 1595 cm.$^{-1}$ may be the second stretching band of the allylic system though a band at 1590-1610 has been found in several simple protonated ketones including acetone·H^+.