TABLE I

HYDROCARBON COMPOSITION FROM CAMPHOR *p*-TOLUENESULFONYLHYDRAZONE IRRADIATION

Solvent	Light source	Hydrocarbon, %	Tricyclene,[d] %	Camphene,[d] %
Aqueous 0.1 *N*	Unfiltered	8	18	82
KOH[a]	Filtered	Trace	..	..
Methanolic 0.1	Unfiltered	36	36	64
N KOH[a]	Filtered	44	20	80
Diglyme 0.1 *N*	Unfiltered	93	99	1
NaOMe[b,c]	Filtered	70	87	13

[a] In methanol the other products were methyl ethers and in water the other products were alcohols. In the latter solvent, the main product appeared to be camphene hydrate. [b] In diglyme the *p*-toluenesulfinate anion decomposes photochemically to give toluene and other minor products. These decomposition products were the only species present other than tricyclene and camphene. [c] The sodium salt of the hydrazone is insoluble in diglyme and the irradiations were conducted on the suspended solid. [d] Each entry is an average of two runs which differed by no more than 2%.

fraction obtained by irradiation of I under different conditions and in different solvents is summarized in Table I.

It is to be noted that as the concentration of available protons increases the amount of tricyclene, the product formed by carbenoid decomposition, decreases and the amounts of camphene and alcohols or ethers, the products formed by cationoid decomposition, increase. Such a result is in line with the results obtained by thermal decomposition of the hydrazone.[3,4] Of particular interest is the increase in cationoid decomposition when a Pyrex filter is employed.

Photolysis of I in pure methanol or diglyme (no base added) using a quartz probe proceeded more slowly than the reaction of the salt. The reaction product was contaminated with sulfur-containing materials which must have arisen from the *p*-toluenesulfinic acid generated in the reaction. (No reaction occurred when a Pyrex filter was employed.)

As in the case of the thermal decomposition of the salt of the *p*-toluenesulfonylhydrazone, the room temperature photochemical reaction can be viewed as first forming diazocamphane. The diazocamphane, in turn, either can undergo direct photolysis in the usual fasion to yield a carbene or can react with a proton-donating solvent to yield a diazonium cation which decomposes in the usual fashion. Some evidence for the intermediate formation of the red diazocamphane was found in the irradiations in diglyme with filtered light where a transient red color developed. The utilization of ultraviolet light energy rather than the usual thermal energy for excitation of a bond capable of cleavage again points to the utility of photochemical processes.

In a typical reaction, a solution or suspension of I in an alkaline medium is irradiated until the characteristic maxima of *p*-toluenesulfinate anion at 261 and 268 mμ appear and remain at approximately constant intensity for 15 minutes. For a 2-g. sample, about 20 minutes is required using unfiltered light and 150 minutes using filtered light. The temperature of the solution remains between 25–35°. The reaction mixture is processed as described by Powell and Whiting[3] and the hydrocarbons analyzed by gas-liquid chromatography using a column containing tris-(2-cyanoethoxy)-propane as a stationary phase.

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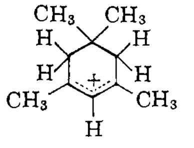
ALIPHATIC ALKENYL (ALLYLIC) CATIONS[1]

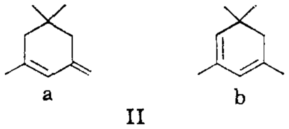
Sir:

Cation I has been prepared and its structure demonstrated with such certainty that its properties should serve as prototypes for those of other aliphatic alkenyl cations.

I is formed by adding to concentrated sulfuric acid the diene mixture (IIa and IIb) obtained from the Grignard addition of methyl iodide to isophorone.[2] I also was formed by shaking a dichloromethane solution of II with moist aluminum chloride.[3] Concentrated (10%) solutions in either medium are stable as evidenced by n.m.r. spectra that are unchanged after one hour.



I


a

b

II

The n.m.r. spectrum of a dichloromethane solution of I has four bands at 1.98, 6.67, 6.93, and 8.79 τ[4] (bands in nearly the same relative positions are exhibited in the spectrum of a 96% sulfuric acid solution of I) with relative areas of 1:4:6:6. The sharp band corresponding to one hydrogen is at lowest field (1.98 τ) as would be expected for a hydrogen attached to a carbon that is both multiply bonded and part of a positively charged conjugated system. The four methylene hydrogens and six of the twelve methyl hydrogens are alpha to the allylic system and exhibit bands at 6.67 and 6.93 τ (both bands show partially resolved fine structure), the τ-values reflecting the proximity of a positive charge. The six hydrogens (gamma to the allylic system) of the gem-dimethyl grouping gave a sharp band at 8.79 τ, a value only slightly lower than that of hydrogens of methyl groups of saturated hydrocarbons.[5]

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(2) M. S. Kharasch and P. O. Tawney, *J. Am. Chem. Soc.*, **63**, 2308 (1941); J. Schmitt, *Ann.*, **547**, 256 (1941); J. P. Ferrin, T. B. Tom, N. L. Koslin, K. W. Greenlee, J. M. Derfer, and C. E. Boord, *J. Org. Chem.*, **19**, 923 (1954); G. Chiurdoglu and A. Maquestiau, *Bull. soc. chim. Belges*, **63**, 357 (1954); O. H. Wheeler, *J. Org. Chem.*, **20**, 1672 (1955).

(3) This procedure has been used to prepare stable solutions of a number of carbonium ions (Herman G. Richey, Jr., unpublished work).

(4) G. V. D. Tiers, *J. Phys. Chem.*, **62**, 1151 (1958).

(5) L. M. Jackman, "Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry," Pergamon, New York, N. Y., 1959.

The mixture of dienes (II) can be recovered in at least 60% yield by dilution of a sulfuric acid solution of I with water.

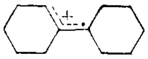
The classic freezing point depression technique[6] gives an *i*-factor of 2.08 ± 0.08 (unchanged after 24 hours) for solutions prepared by adding II to 99% sulfuric acid. This is in accord with the equation for simple protonation

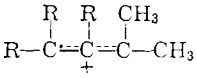
$$C_{10}H_{16} + H_2SO_4 \longrightarrow C_{10}H_{17}^+ + HSO_4^-$$

The most striking feature in infrared spectra of I (in 96% sulfuric acid or dichloromethane solutions) is an intense band at 1533 cm.$^{-1}$, the only band between 2850 and 1450 cm.$^{-1}$. This absorption is intermediate in frequency between ordinary carbon–carbon single bond and double bond stretching absorptions. The extinction of this band is approximately ten times as great as the average extinction of the two carbon–carbon double bond stretching absorptions exhibited in the infrared spectrum of the diene (II).

The ultraviolet spectrum of I (sulfuric acid) has λ_{max} 314 mμ (ϵ 9130). The equilibrium between I and II (determined spectrophotometrically) is 1:1 in 50% sulfuric acid.

The cation III and a series based on IV are half-formed in 50–75% sulfuric acid and have absorption maxima between 310 and 335 mμ. Their chemical stability is less than that of I but sufficient to allow equilibrium studies to be performed.

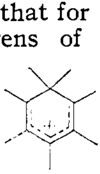

III

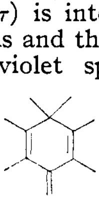


$$\mathrm{R{-}\overset{\displaystyle R}{\overset{|}{C}}{=}\underset{+}{\overset{\displaystyle R}{\overset{|}{C}}}{=}\overset{\displaystyle CH_3}{\overset{|}{C}}{-}CH_3}$$

IV, $R = CH_3$ or H

The properties of I are in excellent agreement with those of the stable cation V prepared by Doering and co-workers.[7] The bands due to α-hydrogens in n.m.r. spectra of both I and V are between 6 and 7 τ (6.15, 6.35, and 6.63 τ for V[8]). The band for the β-hydrogens of V (7.45τ) is intermediate between that for the α-hydrogens and that for the γ-hydrogens of I. The ultraviolet spectra of V[9] (λ_{max} 397 mμ, ϵ 8500, concentrated hydrochloric acid) and I exhibit comparable extinctions and have absorption maxima in agreement with the energy of the long wave length absorption calculated by simplest LCAO MO theory (β for V and $\sqrt{2}\beta$ for I).


V


VI

The properties reported[10] recently for a species thought to be one of the isomeric cyclohexenyl cations VIIa or VIIb are not in agreement with those of I. There was no band comparable to the intense absorption of I at 1533 cm.$^{-1}$; a weak band at 1692 cm.$^{-1}$ was the only band reported between 2850 and 1450 cm.$^{-1}$ in infrared spectra (Nujol–Fluorolube mixed mulls) of VII. The n.m.r. spectrum of VII (a sharp band at −0.09τ and a broad band at 9.13τ with areas in the ratio of 1:2.06)[11] does not contain the expected complex absorption at about 2τ for the allylic hydrogens nor the absorption expected for α-hydrogens at 6–7τ. The extinction of 234 for the maximum at 307 mμ (dioxane) is but a shadow of the extinctions found for I and V.


VIIa


VIIb

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[6] L. P. Hammett and A. J. Deyrup, *J. Am. Chem. Soc.*, **55**, 1900 (1933).

[7] W. von E. Doering, M. Saunders, H. G. Boynton, H. W. Earhart, E. F. Wadley, W. R. Edwards, and G. Laber, *Tetrahedron*, **4**, 178 (1958).

[8] The spectrum[7] was of a hydrochloric acid solution standardized against a benzene capillary. The reported values have been converted to parts per million from benzene and 2.73 added to correct to a tetramethylsilane standard. For n.m.r. spectra of similar ions see C. MacLean, J. H. van der Waals, and E. L. Mackor, *Mol. Phys.*, **1**, 247 (1958).

[9] Ultraviolet spectra of similar compounds have been reported: C. Reid, *J. Am. Chem. Soc.*, **76**, 3264 (1954); G. Dallinga, E. L. Mackor, and A. A. Verrijn Stuart, *Mol. Phys.*, **1**, 123 (1958).

[10] G. A. Olah and W. S. Tolgyesi, *J. Am. Chem. Soc.*, **83**, 5031 (1961).

[11] The spectrum[10] was of a nitromethane solution standardized against water as an external reference.

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MASS SPECTROMETRY IN STRUCTURAL AND STEREOCHEMICAL PROBLEMS. V.[1] REFRACTINE AND ASPIDOFRACTINE

Sir:

Recently structural formulas have been assigned to several complicated alkaloids[1,2,3] without resorting to any classical chemical degradations, based largely on interpretations of mass spectral fragmentation patterns, and coupled in several instances[1,3] with n.m.r. measurements. We wish now to report the application of this new approach to the structure elucidation of the hexacyclic alkaloids refractine[4] and aspidofractine isolated from the Brazilian tree *Aspidosperma refractum* Mart. Refractine[4] (polymorphic forms m.p. 157.5–159° and 191–192°, $[\alpha]_D$ −23° (all rotations in chloroform)) is a N-acetyl-7-methoxydihydroindole (with an additional carbomethoxy function) with analyses compatible with $C_{22}H_{26}N_2O_4$ or $C_{23}H_{28}N_2O_4$ (396), the latter being correct as shown by mass spectrometric molecular weight determination (found, 396). We are now proposing the hexacyclic structure IA for refractine on the basis of the following evidence.

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[1] Paper IV, C. Djerassi, S. E. Flores, H. Budzikiewicz, J. M. Wilson, L. J. Durham, J. Le Men, M.-M. Janot, M. Plat, M. Gorman and N. Neuss, *Proc. Natl. Acad. Sci. U. S.*, **48**, 113 (1962).

[2] K. Biemann, M. Friedmann-Spiteller and G. Spiteller, *Tetrahedron Letters*, 485 (1961).

[3] (a) C. Djerassi, H. W. Brewer, H. Budzikiewicz, O. O. Orazi and R. A. Corral, *Experientia*, **18**, March (1962); (b) B. Gilbert, J. M. Ferreira, R. J. Owellen, C. E. Swanholm, H. Budzikiewicz, L. J. Durham and C. Djerassi, *Tetrahedron Letters*, No. 2, 59 (1962); (c) C. Djerassi, H. Budzikiewicz, J. M. Wilson, J. Gosset, J. Le Men and M.-M. Janot, *Tetrahedron Letters*, 235 (1962).

[4] B. Gilbert, L. D. Antonaccio, A. A. P. G. Archer and C. Djerassi *Experientia*, **16**, 61 (1960).