of the same concentrations in acetic acid were refluxed for 40 hr. In each case, the cooled reaction mixture was diluted with water and extracted with petroleum ether (b.p. 30–60°). The extract was washed with sodium carbonate solution and water and then dried. The crude ester from evaporation of the extract was treated with lithium aluminum hydride in ether and the resulting 2-phenylethanol purified by distillation under reduced pressure.

Examination of the infrared spectra of α- and β-deuterated 2-phenylethanols revealed a number of regions of distinct difference, of which peaks at 9.92 μ (α-deuterated) and 10.5 μ (β-deuterated) appeared most advantageous for analysis (see Fig. 1). The infrared spectra of synthetic mixtures of α- and β-deuterated alcohols in carbon tetrachloride solution were determined and plots relating composition to % transmission at these wave lengths were prepared. Since the standards were not completely deuterated, it was necessary to make some assumption concerning the distribution of deuterium. For simplicity, it was assumed that only undeuterated and dideuterated species were present. This is undoubtedly incorrect, but the error will largely cancel if the actual distribution is similar in the two standards. We also, of course, do not know whether di- or monodeuterated species (or both) contributed to the observed infrared peaks.

Infrared spectra of the alcohols from the solvolyses were determined in carbon tetrachloride solution and their compositions found by reference to the plots of %T *vs.* composition for the synthetic mixtures. The results are recorded in Table III. The difference in results from α- and β-deuterated starting materials provides a check on the error in our original assumption that deuterium distribution is the same in the two standards. The agreement is not excellent, but adequate for our purposes. The sum of percentages of products from the β-deuterated starting material (Ic) is around 106% in both formolysis and acetolysis (Table III), a result also attributable to error in our assumptions about deuterium distribution.

In a control experiment, a 0.3 M solution of 2-phenylethanol-1,1-d_2 in formic acid (about 0.01 M in sodium formate) was heated at 80° for three days. The resulting 2-phenylethyl formate was converted to 2-phenylethanol, which was found by infrared analysis to be identical with the starting material.

Kinetic Methods.—Anhydrous formic acid was obtained from 98–100% formic acid by drying over finely powdered boric oxide.[25] Anhydrous acetic acid was prepared from 99.8% acetic acid by addition of a small excess of acetic anhydride. Sodium acetate and sodium formate were dried thoroughly over phosphorus pentoxide. All materials were Analytical Reagent grade.

The reactions were carried out in a flask fitted with a side arm for withdrawing samples, and a reflux condenser surmounted by a calcium chloride tube. The flask was immersed in a thermostat held at 75.25 ± 0.05°. Formic acid containing 0.107 M sodium formate was brought to thermal equilibrium and a weighed quantity (calculated to give a 0.100 M solution) of the p-toluenesulfonate introduced. Aliquots of 5 ml. were withdrawn periodically, quenched in cold glacial acetic acid, and titrated potentiometrically[25] with 0.05 N perchloric acid in acetic acid.

The acetolyses were carried out by a procedure closely similar to that for the formolyses. Solutions initially 0.030 M in p-toluenesulfonate and 0.032 M in sodium acetate were used. Higher temperatures (93.9°) were necessary to obtain reasonable rates and it was more difficult to maintain constant temperature over a series of runs. Consequently, rates on undeuterated, α- and β-deuterated toluenesulfonates were run simultaneously so that any temperature change would influence equally all three reactions. For this reason, as well as the lower concentrations, precision was somewhat lower than in the formolyses, but still within 2–3%.

Acknowledgments.—We wish to thank Professor A. Streitwieser, Jr., for several interesting discussions and for information in advance of publication. We also thank Professors K. Mislow and V. Prelog for informing us of their results in advance of publication.

[25] S. Winstein and H. Marshall, THIS JOURNAL, **74**, 1120 (1952).

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[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT, BROOKHAVEN NATIONAL LABORATORY]

Electron Impact Dissociation of Camphene-8-C^{13} [1,2]

BY L. FRIEDMAN AND ALFRED P. WOLF

RECEIVED JULY 3, 1957

Specific fragmentation mechanisms for the formation of $C_9H_{13}^+$ and $C_8H_{11}^+$ ions are established from a study of the mass spectrum of camphene-8-C^{13}. A cyclic structure for $C_7H_9^+$, the most abundant ion in the camphene spectrum, is proposed.

The $C_7H_9^+$ ion accounts for approximately 30% of the total ion yield in mass spectra of the terpenes α-pinene, cyclofenchene and tricyclene. It is the most abundant ion produced in spectra of the isomeric exocyclic olefins camphene, β-pinene and α-fenchene, but with these compounds competing processes reduce the $C_7H_9^+$ intensity to roughly 15% of the total ion yield. The monocyclic $C_{10}H_{16}$ isomer dipentene cleaves on electron impact to give $C_5H_8^+$ ions with $C_7H_9^+$ as the second most abundant ion in its mass spectrum. Spectra for these compounds are shown graphically in Figs. 1, 2 and 3.

The electron impact dissociation reactions of these compounds present an interesting problem since the processes are essentially those of intramolecular rearrangement and dissociation of excited $C_{10}H_{16}^+$ ions.

The statistical theory of mass spectra[3a,b] gives rate equations for unimolecular ion decomposition reactions which involve energetics of the reaction and frequency factors which are related to steric factors or entropy of activation. Since energetics for dissociation reactions in isomeric systems are expected to be very similar, differences in reaction rates probably arise from differences in the frequency factors. If one assumes that the theory applies, one could assert that the relatively large yield of $C_3H_5^+$, etc., from the exocyclic olefins can be explained by higher excitation of the latter on electron impact. This is a very improbable assumption that would do serious damage to any attempt to apply the statistical theory to systems observable with the mass spectrometer. One is left then with considerations of the effect of structure on mechanisms, and it was for this reason that a C^{13} tracer procedure was investigated.

[1] Research performed under the auspices of the U. S. Atomic Energy Commission.

[2] A part of this material was presented at the Chicago A.C.S. Meeting, September, 1953.

[3] (a) L. Friedman, F. A. Long and M. Wolfsberg, *J. Chem. Phys.*, **27**, 613 (1957); (b) H. Rosenstock, A. Wallenstein, A. Wahrhaftig and H. Eyring, *Proc. Natl. Acad. Sci. U. S.*, **38**, 667 (1952).

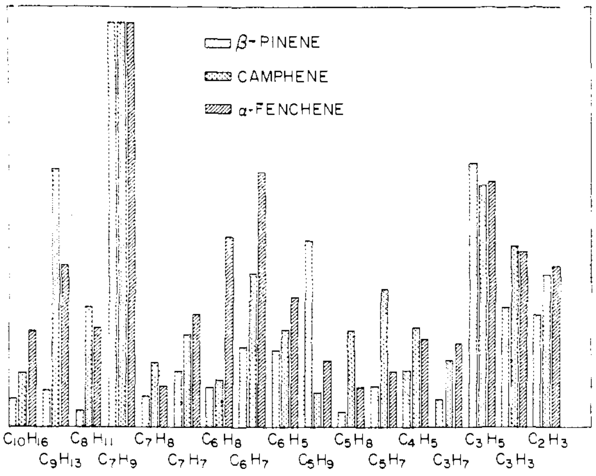
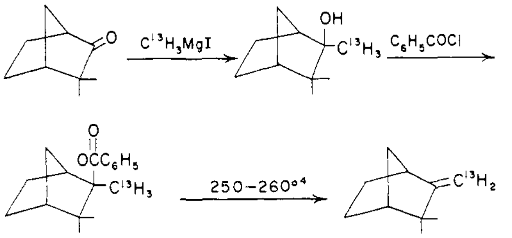


Fig. 1.—Mass spectra of exocyclic olefins.

The following reaction sequence was employed to obtain an excess of 60% C^{13} in the olefin methylene position of camphene.



Camphene-8-C^{13}. Preparative Methods.[5]—The preparation was essentially that described by Roberts and Yancey.[6] Eastman methyl iodide, 68.4 atom % C^{13}, was used. Extra care was taken in purifying the 2-methyl-C^{13}-camphenilyl benzoate by fractionation in a 4-cm. column packed with Podbielniak Heli-Pak no. 3365 model. The material distilled at b.p. 105° (0.2 mm.). The pyrolysis was carried out at a substantially lower temperature (250–260°) than that used by Roberts. Additional purification of the camphene-8-C^{13} produced was necessary in order to remove traces of benzoic acid which complicated the mass spectrum. This was accomplished by multiple fractional sublimation. The samples were sealed in break seals which had been extensively cleaned and finally washed with base. The packaged samples were stored in Dry Ice until ready for use.

Mass spectra of the product were taken with 70 volt ionizing electrons. The samples were sealed directly to a tube going into the ionization chamber and were run from the vapor pressure of camphene at Dry Ice temperature. This method eliminated the need for a heated sample inlet system before the leak which could have induced intramolecular rearrangements in the tagged camphene. The spectra obtained were subdivided into ion groups having the same number of carbon atoms. The natural C^{13} component was removed from each group and a monoisotopic C^{12} camphene spectrum then was used as a basis for computing the relative amounts of C^{12} and C^{13} containing species for the major processes responsible for the production of C_9^+, C_8^+, C_7^+, etc., fragments from camphene. The computation assumed no C^{13} isotope effect on electron impact and was concerned only with the most abundant ion fragments in each carbon group. The results are given in Table I.

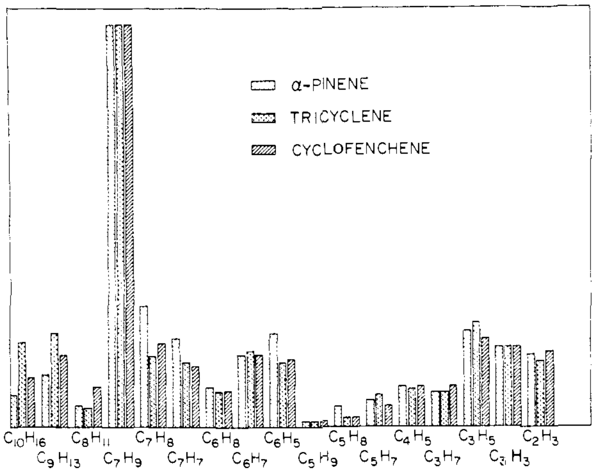


Fig. 2.—Mass spectra of cycloölefins and tricyclics.

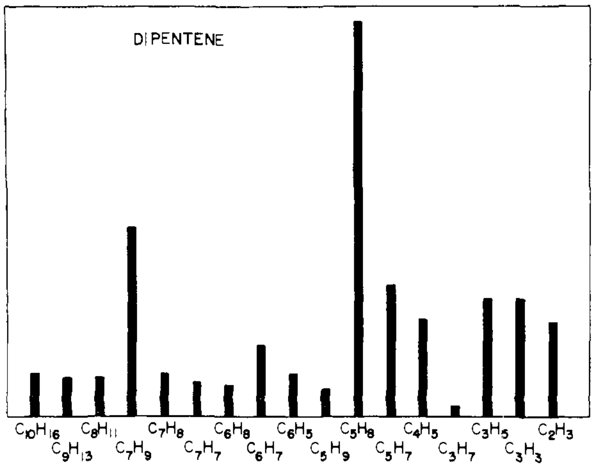


Fig. 3.—Mass spectrum of dipentene.

TABLE I

Process $C_{10}H_{16}^+ \rightarrow$	% C^{13} in ion Fragment	Of 100% C^{13}
$C_9H_{13}^+ + CH_3$	67	97.1
$C_8H_{11}^+ + C_2H_5$	65	96
$C_7H_9^+ + C_3H_7$	55	82.1
$C_6H_7^+ + C_4H_9$	43.3	65.6
$C_5H_7^+ + C_5H_9$	39	60.2
$C_4H_5^+ + C_6H_{11}$	36.7	57.3
$C_3H_5^+ + C_7H_{11}$	15.5	24.6

Processes involving loss of CH_3 and C_2H_5 show practically no loss of C^{13} indicating very little rearrangement in the syntheses or prior to and in the electron impact process. Roughly 20% of the available excess C^{13} is lost in the formation of $C_7H_9^+$. This could be due in part to a prior rearrangement associated with this decomposition process or a multiplicity of mechanisms.

The C^{13} data are insufficient to provide a unique mechanism for dissociation reactions of camphene on electron impact. They do establish specific fragmentation mechanisms not involving C^{13} in the loss of CH_3 and C_2H_5 from the $C_{10}H_{16}^+$ ion fragment. The C^{13} content of C_7^+ and C_3^+ ion frag

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[4] Little or no rearrangement occurs in this step as shown by Roberts (ref. 6). The xanthate ester method (W. R. Vaughan and R. Perry, Jr., THIS JOURNAL, 75, 3168 (1953)) proved unsatisfactory. The mass spectrum of camphene-8-C^{13} prepared in this way was difficult to analyze because of traces of sulfur-containing impurities which could not be removed.

[5] We wish to thank Dr. R. F. Schultz of the Hercules Powder Corp. for supplying a sample of camphene.

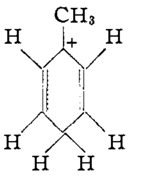
[6] J. D. Roberts and J. A. Yancey, THIS JOURNAL, 75, 3165 (1953).

ments suggests a charge competition reaction in their formation. This could not be the simple reaction of the type

$$\begin{aligned} AB &\longrightarrow A^+ + B \\ &\longrightarrow B^+ + A \end{aligned}$$

because of the hydrogen content of the major C_7^+ and C_3^+ ions. There could be a more complex charge competition process which involved hydrogen loss as a secondary process. The C^{13} content of C_6^+, C_5^+ and C_4^+ ions show a remarkable similarity with relatively small tendency toward loss of C^{13} in processes responsible for the formation of these fragments. The statistical theory predicts rather specific dissociation mechanisms following paths of minimum energy and entropy and the production of stable products that resist subsequent decomposition reactions.

The cyclic $C_7H_9^+$ ion is expected to have more stability than a simple open chain which would undergo decomposition much more easily than a ring system. Furthermore since it is observed in high abundance, it is expected that it would be formed more readily from the parent species than lower molecular weight fragments and that it would then play the role of precursor of some of the lower molecular weight ion fragments. If one assumes that these ions are products of decomposition of a $C_7H_9^+$ intermediate in a set of consecutive decomposition reactions taking place subsequent to electron impact, then structures for $C_7H_9^+$ must be compatible with the C^{13} data. A C_7 ion with C^{13} randomly distributed in equivalent positions and equal probability of bond rupture for the formation of C_4, C_5 and C_6 ions by bond rupture processes would produce a C_4^+ ion containing 47% C^{13}, C_5^+ containing 60% and C_6^+ containing 70%. The qualitative agreement between % of total C^{13} observed and calculated on the basis of random rearrangement and fragmentation suggests that while specific processes are responsible for C_9^+ and C_8^+, extensive rearrangements must take place in the formation of lower molecular weight species. If the assumption that $C_7H_9^+$ is the parent species of the lower molecular weight, C_6, C_5 and C_4 ions, then structures of the type a are disfavored for C_7H_9, since both equal probability of bond rupture in the formation of C_6 for example is improbable and the mechanism for random distribution of C^{13} among various positions is not obvious from this structure. Structures of type b and c are possible and have the advantage that they represent highly stabilized forms of $C_7H_9^+$, a condition required from consideration of the statistical theory of mass spectra for relatively abundant ions.



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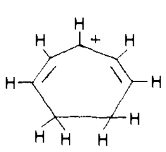

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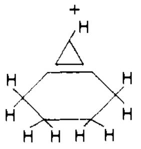

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[CONTRIBUTION FROM CHEMICAL DEPARTMENT, NAGOYA UNIVERSITY]

The Dipole Moments and the Conformations of Matridine and Related Compounds

BY BUNZO EDA, KYOSUKE TSUDA[1] AND MASAJI KUBO

RECEIVED NOVEMBER 8, 1957

The dipole moments of matridine, allomatridine, sparteine, α-isosparteine and related compounds were measured in benzene solutions. The dipole moment data indicate that in the allomatridine molecule, all the neighboring rings are *trans*-fused and that matridine has *cis*-fused rings. The moment of 2-methylperhydropyrido[3,4,5-i,j]quinolizine is close to that of allomatridine, indicating that the molecule of the former compound, like that of the latter, assumes a stable extended structure. The moment of α-isosparteine is in agreement with that calculated for the molecular structure determined by X-ray crystal analysis.

Introduction

When matrine and allomatrine are subjected to reduction with lithium aluminum hydride, they give matridine and allomatridine, respectively.[2] One of the present authors[3] has already succeeded in the total synthesis of allometridine, a stereoisomer of matridine. The conformational analysis of this isomeric pair of compounds has given a clue to the elucidation of the molecular structure of matrine,[4] an alkaloid first isolated from the root nodules of certain leguminous plants found in Japan. The present investigation was undertaken in order to determine the conformations of these compounds from the measurements of dipole moments of matridine and related compounds.

Materials

Matridine (I) and allomatridine (II) were prepared by the method described in a previous paper.[2] The melting points were 56–57° and 76–78°, respectively. 2-Methylperhydropyrido[3,4,5-i,j]quinolizine (or 9-methyl-9-azahexahydrojulolidine) (III) and quinolizidine (or norlupinane) (IV) were synthesized according to the procedure already reported.[5] The former crystallized with one molecule of water and showed a melting point of 74–75°. On drying over phosphorus pentoxide, the crystals turned into an oily anhydrous compound, which was used for dipole moment measurements. The compound IV was purified by recrystallization of its hydrobromide. The free base was an oil boiling at 184°. Hexahydrojulolidine (V) was prepared by

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[1] Institute of Applied Microbiology, University of Tokyo.

[2] E. Ochiai, S. Okuda and H. Minato, *J. Pharm. Soc. Japan*, **72**, 781 (1952).

[3] K. Tsuda and H. Mishima, *Pharm. Bull.*, **5**, 285 (1957).

[4] R. H. F. Manske and H. L. Holmes, "The Alkaloids," Vol. III, Academic Press, Inc., New York, N. Y., 1953, p. 178.

[5] K. Tsuda, S. Saeki, S. Imura, S. Okuda, Y. Sato and H. Mishima, *J. Org. Chem.*, **21**, 1481 (1956).