[CONTRIBUTION FROM RESEARCH DEPARTMENT, STANDARD OIL COMPANY, (INDIANA)]

Organic Ions in the Gas Phase. I. The Cationated Cyclopropane Ring

BY PAUL N. RYLANDER AND SEYMOUR MEYERSON

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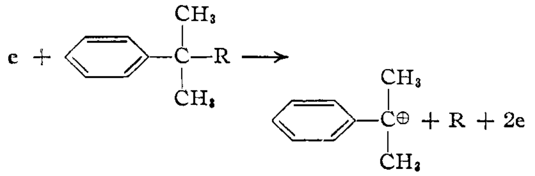
A cyclopropane ring coördinated with a cation is proposed as an ionic intermediate to account for certain rearrangements under electron impact. The cation may be a phenyl group, a methyl group or a proton. Formulation of the propyl ion as a protonated cyclopropane ring resolves many anomalies associated with this ion. The structure is consistent with appearance potential measurements and the spectra of labeled molecules.

Introduction

When polyatomic molecules are subjected to electron bombardment in a mass spectrometer, they react by unimolecular processes to yield a variety of ionized products. Among the products are frequently found ions that cannot be accounted for simply by bond fissions along classical lines.[1] The processes in which they originate must involve intramolecular rearrangements. A shift of hydrogen atoms during dissociation is often adequate to account for such ions. In many cases, however, the experimental data require skeletal rearrangements.

To gain insight into certain observed rearrangements, we synthesized labeled *t*-butylbenzene and 3-ethyl-3-phenylpentane and recorded the mass spectra of these and of the corresponding unlabeled compounds. Study of the spectra has led to the proposal of a cyclic intermediate that can account for many anomalous electron-impact data in the literature.

The Phenylcyclopropane Cation.—Correlation of alkylbenzene structures with mass spectra[2] suggested that 2-methyl-2-phenylalkanes form benzyl ions under electron impact by the path



(1)

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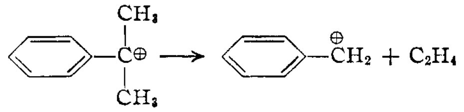


(2)

119 91

The puzzling loss of the elements of ethylene in a single step, as written in reaction 2, is supported by the virtual absence of 8-carbon ions, which would result from the loss of a second methyl carbon in an intermediate step, and by a metastable peak[3] at 69.6, denoting the process

$$(119+) \longrightarrow (91+) + 28$$

in the spectra of *t*-butylbenzene and *t*-pentylbenzene.

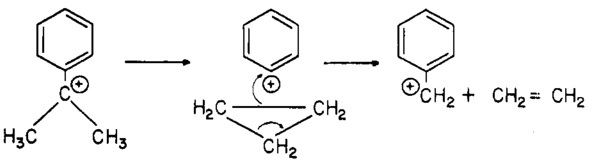
To clarify the mechanism of reaction 2, we synthesized *t*-butylbenzene labeled in the α-position with C^{13} and obtained the mass spectrum, which is shown in Table I with that of unlabeled *t*-butylbenzene. Of the benzyl ions 37.5% contain C^{13} and 62.5% contain no C^{13}. This is, within the limits of the expected isotope effect,[5] a 2-to-1 distribution. The isotopic distribution of benzyl ions is not that to be expected from a shift of the phenyl group or a methyl group followed by cleavage of the β-carbon–carbon bond. In the first case the benzyl ion would be unlabeled, in the second it would be 100% labeled.

TABLE I

PARTIAL SPECTRA OF *t*-BUTYLBENZENE AND *t*-BUTYLBENZENE-α-C^{13}

Mass	Unlabeled	Labeled
135	...	25.2
134	24.5	...
120	...	100.0
119	100.0	1.0
92	...	20.3
91	53.2	33.9

The data imply that the benzyl ion is derived from a phenyldimethylcarbinyl ion that has rearranged so that the three side-chain carbons have become indistinguishable; that is, they have become symmetric with respect to the phenyl group. The simplest formulation of such an ion is a cyclopropane ring with a phenyl ion symmetrically placed above it. Ethylene and benzyl ion can be simply formed by shift of two electron pairs, as



The spectra of other *t*-alkylbenzenes, in which two or all three substituents on the α-carbon are larger than methyl, are consistent with this formulation. Thus, the dissociation of 3-ethyl-3-phenylpentane may be viewed as proceeding through a rearranged

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[1] A. J. Langer, *J. Phys. Colloid Chem.*, **54**, 618 (1950).

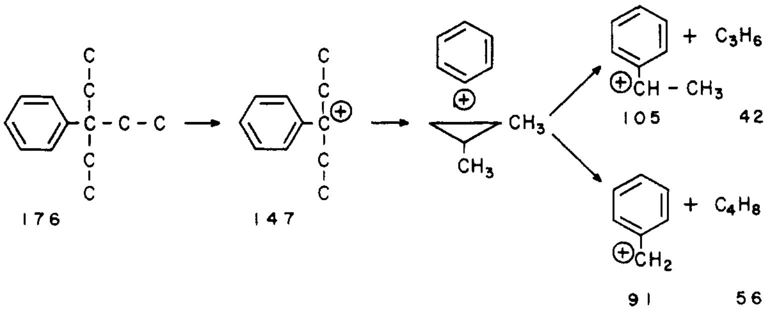
[2] S. Meyerson, *Appl. Spectroscopy*, **9**, 120 (1955).

[3] Metastable peaks are small, diffuse peaks in mass spectra formed by the same processes as ordinary peaks but usually at non-integral masses.[4] They stem from decompositions that occur near the slit between the accelerating region and the analyzer. The apparent mass, m_a, of a metastable peak is equal to m^2_f/m_i, where m_i is the mass of the dissociating ion, and m_f is the mass of the ion produced from the dissociation. Both m_i and m_f are always integers, and the spectrum always shows ordinary peaks at these masses—usually with heights greater than 5% of the largest peak in the spectrum. Consequently, the mass of a metastable peak nearly always determines a unique pair of values for m_i and m_f, and thus defines one step in a decomposition process.

[4] H. M. Rosenstock, A. L. Wahrhaftig and H. Eyring, *J. Chem. Phys.*, **23**, 2200 (1955), and references cited there.

[5] D. P. Stevenson, *Phys. Rev.*, **73**, 537 (1948).

structure consisting of a phenyl ion coördinated with a dimethylcyclopropane ring

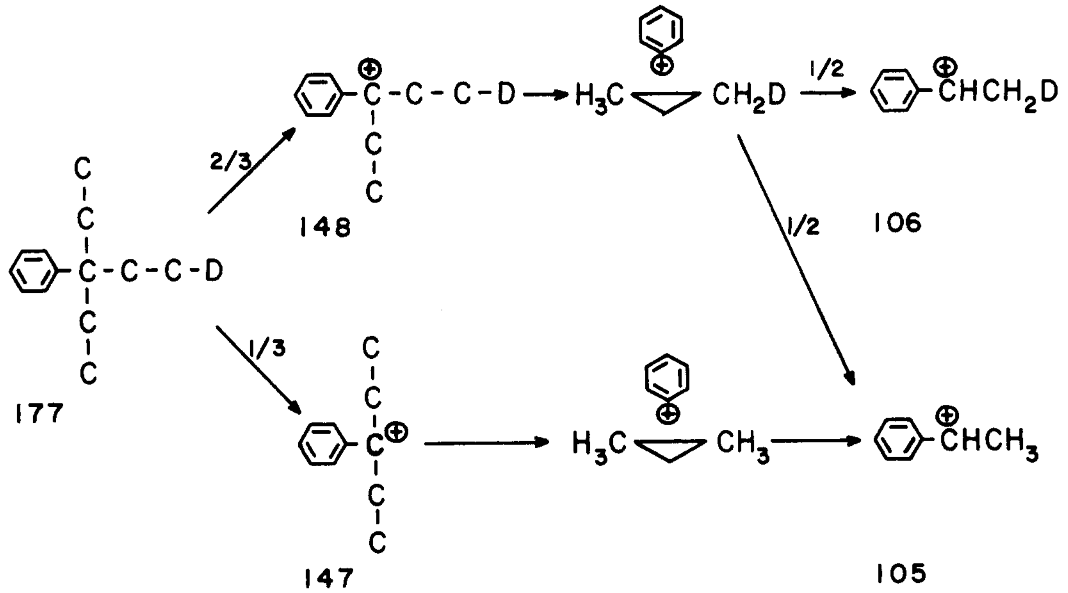


The loss of propylene leads to a phenylethyl ion of mass 105; the loss of butylene to a benzyl ion of mass 91. The derivation of the 105 ion from the 147 ion in a single step is supported by the metastable peak

$$75.0\ (147^+) \longrightarrow (105^+) + 42$$

The relative intensities of the 105 and 91 ions are not in the statistical ratio of 2-to-1, nor should they necessarily be so. The relative amounts of these ions depend upon the activation energies for the two competing reactions in which they are formed.

The spectrum of 1-deutero-3-ethyl-3-phenylpentane gives additional evidence for the postulated rearrangement. This spectrum is compared in Table II with that of the unlabeled compound. Dissociation via a cyclopropane intermediate accounts nicely for the observed distribution of the labeled atoms in the phenylethyl ions



The fractions beside the arrows denote the relative numbers of molecules or ions that react by the indicated paths. The observed distribution of ions agrees well with the distribution predicted from this scheme.

Mass	Obsd., %	Predicted, %
148	64.0	66.7
147	36.0	33.7
106	32.9	33.3
105	67.1	66.7

Benzyl ions from this process should be 100% unlabeled; the 6% labeled benzyl ions at mass 92 result from another process and will be discussed in a future publication.

The Methylcyclopropane Cation.—A cationated cyclopropane ring in which the coördinating group is methyl rather than phenyl can explain the data of Johnson and Langer on labeled neopentanes. They found that neopentane centrally labeled with C^{13} produced, on electron impact, C_4 and C_3 fragments that were 100% labeled, but C_2 fragments that were only 50% labeled.[6] These results readily can be accounted for by rearrangement of the *t*-butyl ion to a methylcyclopropane ion as shown in the next formula chart.

TABLE II

PARTIAL SPECTRA OF 3-ETHYL-3-PHENYLPENTANE AND 3-ETHYL-3-PHENYLPENTANE-1-*d*

Mass	Unlabeled	Labeled
177	...	2.3
176	3.0	..
148	...	19.2
147	29.5	10.8
120	0.5	0.6
119	2.0	0.4
106	...	21.7
105	62.0	44.3
92	...	6.1[a]
91	100.0	93.9[a]

[a] Value of 100.0 assigned to total intensity of $C_7H_7^+$ ions.

Neopentane-1-C^{13} gave C_4 ions that were 75% labeled; C_3, 50%; and C_2, 37%.[7] The same re-

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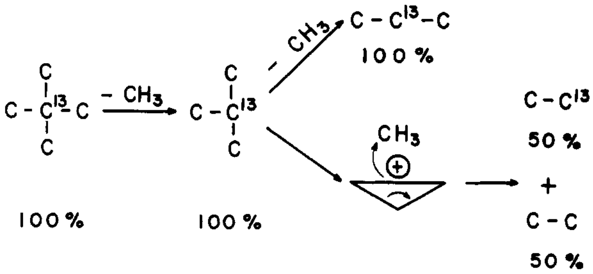
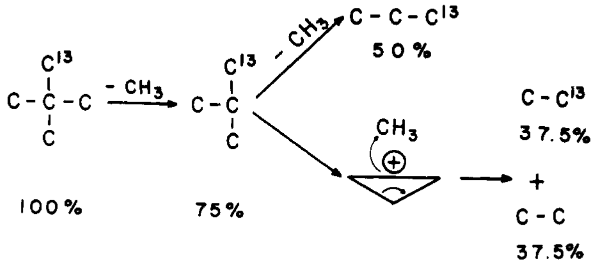
(6) P. Johnson and A. Langer, "Rearrangement Peaks in the Mass Spectra of Centrally C^{13} Labeled Neopentane," presented before ASTM E-14 Committee on Mass Spectrometry, New Orleans, May, 1954.

(7) A. Langer and P. Johnson, "Rearrangement Peaks in the Mass Spectrum of Neopentane Terminally Labeled with One C^{13}," presented before the Am. Chem. Soc., Chicago, Sept., 1950



arrangement provides a satisfactory explanation here, too.



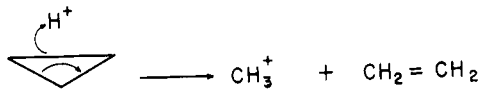
Clearly, it was the butyl ion that rearranged and not the neopentane molecule-ion.

These particular results can be explained equally well by assuming methyl migration in the butyl ion. Even so, the bridged methyl transition state would be but slightly different from the methylcyclopropane cation.

The Protonated Cyclopropane Ring.—The literature abounds with references to anomalous behavior of the propyl ion, which is known to be exceptionally stable.[8] Although the mass spectra of nearly all large aliphatic hydrocarbons show large amounts of $C_3H_7^+$,[9] the structure of this ion is not known with certainty. Those derived from *n*-alkanes should be *n*-propyl if no rearrangement has occurred; those from isoalkanes should be isopropyl. However, the same values are obtained for the ionization potential of C_3H_7 radical when it is calculated from appearance potentials of $C_3H_7^+$ in the spectra of *n*-alkanes and isoalkanes. This observation has led several investigators[8,10,11] to conclude that $C_3H_7^+$ ions from *n*-alkanes and from isoalkanes have the same structure, usually considered to be isopropyl.

Direct measurement of the ionization potential of the isopropyl radical has been reported recently.[12] The value obtained, 7.90 ± 0.05 e.v., is significantly higher than the 7.43 ± 0.1 e.v. derived from the appearance potentials of "i-$C_3H_7^+$" in the mass spectra of isoalkanes and the relevant heats of formation.[13] The discrepancy suggests that $C_3H_7^+$ ions produced by electron impact of hydrocarbon molecules and those produced by ionization of isopropyl radicals do not have the same structure.

A cationated cyclopropane ring in which the cation is a proton can resolve these anomalies and, in addition, the problem of the origin of methyl ions from labeled propanes and butanes. The presence of CH_2D^+ in the spectra[14] of propane-2-*d*, *n*-butane-2-*d* and isobutane-2-*d*, and of $C^{13}H_3^+$ in the spectra[15] of propane-2-C^{13} and isobutane-2-C^{13} can all be accounted for on the assumption that the $C_3H_7^+$ ion is a protonated cyclopropane. The observed fragments are formed by the shift of two electron pairs



A different cyclic structure, in which one hydrogen is shared between the two end carbons, has been proposed[8] to account for certain of the experimental observations.

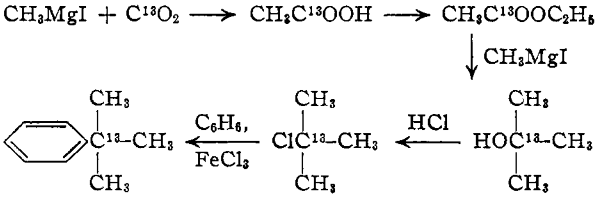
The Cationated Cyclopropane Ring.—Although some other explanation is possible for each case studied, the proposed rearrangement to a cationated cyclopropane ring provides a unified interpretation.

The concept of a cationated cyclopropane ring is new in the interpretation of mass spectra, but similar structures have been proposed[16] to account for certain Wagner–Meerwein rearrangements. A molecular orbital formulation has been made for a substituted protonated cyclopropane, which is viewed as a proton embedded in a molecular orbital containing two electrons and formed by the overlap of three sp^2 orbitals protruding from the three carbons.[16] A cation might be expected to coördinate with cyclopropane because physical and chemical evidence indicates cyclopropane has olefinic character[17] and the coördination of cations with olefins is well established.[18]

Experimental

The spectra of *t*-butylbenzene and 3-ethyl-3-phenylpentane, labeled and unlabeled, were obtained on a Consolidated model 21-102 mass spectrometer. The *t*-butylbenzene was an API standard sample; the other three were synthesized.

t-Butylbenzene-α-C^{13}.—t-Butylbenzene-α-C^{13} was prepared from $BaC^{13}O_3$ of 64.5% isotopic purity by the sequence



$$CH_3MgI + C^{13}O_2 \longrightarrow CH_3C^{13}OOH \longrightarrow CH_3C^{13}OOC_2H_5 \xrightarrow{CH_3MgI} HOC^{13}(CH_3)_2\text{-}CH_3 \xrightarrow{HCl} ClC^{13}(CH_3)_2\text{-}CH_3 \xrightarrow[FeCl_3]{C_6H_6,} C_6H_5C^{13}(CH_3)_2\text{-}CH_3$$

Benzene present as a contaminant did not interfere with interpretation of the mass spectrum. The mass-134 peak was attributed to unlabeled *t*-butylbenzene, and the contributions of this compound were removed from the spectrum. The product was found to be 63.9% labeled. Relative intensities at masses 135 and 120 in the spectrum

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(8) M. B. Wallenstein, A. L. Wahrhaftig and H. Eyring, "The Mass Spectra of Large Molecules. I. Saturated Hydrocarbons," Inst. for the Study of Rate Processes, University of Utah, Salt Lake City, 1951.

(9) American Petroleum Inst., Research Project 44, "Catalog of Mass Spectral Data," Carnegie Institute of Technology, Pittsburgh, Pa., 1947-56.

(10) D. P. Stevenson, *Trans. Faraday Soc.*, **49**, 867 (1953).

(11) F. H. Field and J. L. Franklin, *J. Chem. Phys.*, **22**, 1895 (1954).

(12) J. B. Farmer and F. P. Lossing, *Can. J. Chem.*, **33**, 861 (1955).

(13) D. P. Stevenson, *Disc. Faraday Soc.*, **10**, 35 (1951).

(14) D. P. Stevenson and C. D. Wagner, *J. Chem. Phys.*, **19**, 11 (1951).

(15) D. P. Stevenson, *ibid.*, **19**, 17 (1951).

(16) J. D. Roberts, C. C. Lee and W. H. Saunders, THIS JOURNAL, **76**, 4501 (1954).

(17) A. D. Walsh, *Trans. Faraday Soc.*, **45**, 179 (1949).

(18) M. J. S. Dewar, "The Electronic Theory of Organic Chemistry," Oxford Univ. Press, London, 1949, pp. 141-144.

of the labeled compound are indistinguishable from those at 134 and 119 for the unlabeled compounds; thus no rearrangement occurred during the synthesis and the C^{13} is in the α-position exclusively.

3-Ethyl-3-phenylpentane and 3-Ethyl-3-phenylpentane-1-*d*.—3-Ethyl-3-phenylpentane and 3-ethyl-3-phenylpentane-1-*d* were prepared from phenylpropane and 3-phenylpropane-1-*d* by sodium-catalyzed ethylation.[19] The unlabeled product boiled at 132° (50 mm.), $n^{20}D$ 1.5015; the labeled at 130° (50 mm.), $n^{20}D$ 1.5015. The mass-176 peak in the spectrum of the labeled product was attributed to the unlabeled compound, and the spectrum was corrected accordingly. The 3-phenylpropane-1-*d* was 96 ± 1% labeled; the 3-ethyl-3-phenylpentane-1-*d* was 91 ± 1% labeled. 3-Phenylpentane-1-*d* isolated from the synthesis was 92 ± 1% labeled.

Acknowledgment.—The authors thank D. L. Esmay, Peter Fotis and C. J. Norton for help in the syntheses.

WHITING, INDIANA

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[19] H. Pines, J. A. Vesely and V. N. Ipatieff, THIS JOURNAL, **77**, 554 (1955).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, NORTHWESTERN UNIVERSITY]

The Nature of Hydrogen Bonded Ion-Pairs: The Reaction of Pyridine and Carboxylic Acids in Chloroform

BY GORDON M. BARROW

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The determination of relative base strengths from the equilibrium constants from the reaction of acids and bases in a non-dissociating solvent is shown to require a detailed understanding of the nature of the reaction product. A series of carboxylic acids are studied for which the weakest and strongest acids form, respectively, a simple hydrogen bonded complex and an ion-pair salt with the base pyridine. The infrared spectra of the 1:1 reaction products of acids of intermediate strength with pyridine show these products to consist of a simple hydrogen bonded complex in tautomeric equilibrium with an ion-pair species rather than a single resonating species. For the acids studied a 2:1 reaction product is shown to exist only for an ion-pair species. The equilibrium constants for the reaction of pyridine and acetic acid in CCl_4 and $CHCl_3$ are reported and are compared with the results for other bases.

The reaction of protonic acids with bases in non-dissociating solvents leads, for acids and bases of sufficient strength, to the formation of an ion-pair salt associated through a hydrogen bond.[1-3] For such systems the acidic proton is said to be transferred and the hydrogen bonding back to the anion is considered to be essentially electrostatic. For weaker acids and bases[4,5] in similar solvents the reaction product consists of a simple hydrogen bonded complex. In these cases the proton is considered to remain covalently bonded to the acid and the base is associated to the acidic hydrogen through an electrostatic attraction. It is of interest to consider here the distinction between these two extreme situations and to inquire into the nature of the reaction in non-dissociating solvents between protonic acids and bases of intermediate strength.

This intermediate case can be considered as a structural problem involving the equilibrium position, or positions, of the proton through which the acidic and basic groups are associated. For a proton equally attracted to the parent acid and to the base the potential energy can be represented either by a curve with a single minimum between the two groups or by a curve with two minima, each minimum approximately a covalent bond length from each of the two groups. Neither possibility can be immediately ruled out. It now appears that for a number of hydrogen bonds in crystalline materials the single minimum is more probable.[6] The only suitable comparison, where the groups are not held in a crystal lattice, would appear to be in the system of a hydronium ion associated to a water molecule.[7] Although the many complexities of this system allow only a remote comparison, it is of interest to note the probable existence of a double minimum with the proton attached to one or the other of the adjacent water molecules.

This question of the nature of the acid–base reaction product bears on the study of acid and base strengths in non-dissociating solvents. Equilibrium constant studies, to determine relative base strengths have been made by Bell and Bayles[1] in which the reaction results in a proton transfer. It is customary, also, to make use of shifts in the acidic OH frequency to estimate base strengths where the proton is not transferred.[4] Two potential difficulties are introduced by these approaches.

It is, firstly, necessary to know if equilibrium constants obtained at the two extremes are to be taken as limiting examples of the same type of reaction or whether they represent results for two essentially different reactions. The first would apply if, for increasing acidity and basicity, the potential minimum for the proton shifted continuously from a position near the acid to one near the base *i.e.*, if the single minimum potential was appropriate. If, on the other hand, a double minimum applies, the proton transfer and simple hydrogen bonding reactions are different reactions and no straightforward comparison of the results of the two reactions with each other, or with the base strength, can be expected. It follows, therefore, that comparison of acids or bases with a wide range of strengths in non-dissociating solvents by means of equilibrium constants requires a detailed understanding of the reaction product.

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(1) R. P. Bell and J. W. Bayles, *J. Chem. Soc.*, 1518 (1952).

(2) M. M. Davis and H. B. Hetzer, *Bur. Standards J. Research*, **48**, 381 (1952).

(3) G. M. Barrow and E. A. Yerger, THIS JOURNAL, **76**, 5211 (1954); **77**, 4474 (1955); **77**, 6206 (1955).

(4) W. Gordy, *J. Chem. Phys.*, **9**, 215 (1941).

(5) M. Tamres, S. Searles, E. M. Leighly and D. W. Mohrman, THIS JOURNAL, **76**, 3983 (1954).

(6) R. E. Rundle and M. Parasol, *J. Chem. Phys.*, **20**, 1487 (1952).

(7) B. E. Conway, J. O'M. Bockris and H. Linton, *ibid.*, **24**, 834 (1956).