Structural Effects in Solvolytic Reactions. 18. The Relative Electron Releasing Properties of Methyl, Phenyl, and Cyclopropyl Groups to the Electron Deficient Center as Indicated by Solvolysis. A Critical Examination of ^{13}C Chemical Shifts as a Basis for Establishing the Electron Densities in Carbonium Ions

Herbert C. Brown* and Edward N. Peters[1,2]

Contribution from the Richard B. Wetherill Laboratory, Purdue University, West Lafayette, Indiana 47907. *Received December 22, 1975*

Abstract: Rate constants (25 °C) for the solvolysis of the *p*-nitrobenzoates, RMe_2COPNB, in 80% aqueous acetone exhibit major increases as the group R is varied from methyl (1.00), isopropyl (2.9), or *tert*-butyl (4.4) to phenyl (969) and to cyclopropyl (503 000). The small difference in the rates for R = methyl, isopropyl, and *tert*-butyl indicates that relief of B strain cannot be a significant factor in the large rate enhancements observed for R = phenyl and cyclopropyl. These large rate enhancements must arise from stabilization of the respective transition states (and the cationic intermediates subsequently produced) by major electron supply from the phenyl and cyclopropyl groups to the electron deficient center. Yet these rates fail to correlate with the ^{13}C chemical shifts for the carbonium carbon of the respective cations (R = methyl, 329.2; R = phenyl, 254.4; R = cyclopropyl, 280.6 ppm), although it has been proposed that such shifts do provide a measure of the electron densities at the carbonium carbon atoms. Consequently, there exists here a major discrepancy between conclusions based on solvolytic data and conclusions based on ^{13}C shifts as to the relative magnitudes of the charge delocalization from the cationic center induced by phenyl and cyclopropyl groups. It is pointed out that rate data for a number of systems are internally consistent in pointing to electron release toward cationic centers from substituents increasing from alkyl to phenyl to cyclopropyl, whereas the data for ^{13}C shifts are not so consistent. The results argue for a reconsideration of the reliability of ^{13}C shifts as a measure of the electron densities in carbonium ions and of the stabilities of these cations, as well as of the application of such shifts as a diagnostic probe for nonclassical structures.

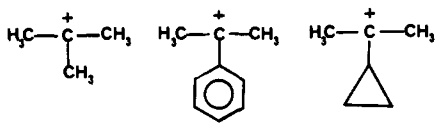
Ever since the pioneering work of Ingold and his co-workers,[3,4] the solvolysis of organic halides and related derivatives has been a major tool for studying the effects of structure on chemical reactivity. In this way, a large body of consistent information has been accumulated on the effects of structure and of substituents on the rates of solvolysis.[4-6] Such studies suffer from the weakness that they give us primarily the difference in energy between the initial and the transition states. However, it is now relatively easy to correct for the energy of the ground state[7] and the Hammond postulate justifies considering the transition state for representative S_N1 solvolyses to be quite close to the actual carbonium ion intermediates.[8]

In recent years, it has become possible to prepare the carbonium ions under stable ion conditions and to observe them spectroscopically.[9] While it is to be hoped that this new tool for the study of carbonium ions will lead us to a better understanding of the relationship between structure and stability,[10] early attempts, based on the idea of a simple relation between ^{13}C chemical shifts and electron density, led to conclusions which run directly counter to positions previously arrived at on the basis of solvolytic data.[11]

For example, Olah and his co-workers examined the *tert*-butyl cation (**1**) and the phenyldimethyl- (**2**) and the cyclopropyldimethylcarbonium (**3**) ions and had reported ^{13}C chemical shifts of 329.2, 254.4, and 280.6 ppm respectively,[11] Chart I. They proposed from these results that the phenyl group must be considerably more electron releasing than a cyclopropyl group,[11] a conclusion which runs counter to that indicated by numerous other results,[12] especially to ^{1}H NMR data for a secondary system.[13]

This paper describes a study of the solvolysis of the three tertiary systems directly related to the three tertiary cations examined in the ^{13}C study of Chart I[2] of which we made a preliminary report in 1973.[2] The study was later extended to include the related tertiary 1-*R*-1-phenyl-1-ethyl series.

Chart I



	1	2	3
^{13}C NMR shifts, ppm from TMS	329.2	254.4	280.6

Results

Synthesis. The tertiary alcohols were prepared by the addition of Grignard reagents to the appropriate ketones. The tertiary alcohols were converted into *p*-nitrobenzoates by treating their lithium salts with *p*-nitrobenzoyl chloride.[14]

Kinetic Studies. The rate constants and thermodynamic parameters of the derivatives selected for solvolysis in 80:20 acetone–water are summarized in Tables I and II.

Discussion

Relative Effectiveness of Phenyl and Cyclopropyl Groups in Facilitating Solvolysis. 1,1-Diphenyl-1-ethyl *p*-nitrobenzoate (**5**) reacts 72 times faster than 2-phenyl-3-methyl-2-butyl *p*-nitrobenzoate (**4**). Thus, both phenyl groups in **5** are helping to stabilize the cation. However, 1-phenyl-1-cyclopropyl-1-ethyl *p*-nitrobenzoate (**6**) reacts over 10^4 times as fast as 2-phenyl-3-methyl-2-butyl *p*-nitrobenzoate (**4**). Clearly, the cyclopropyl group in **6** is stabilizing the adjacent carbonium ion center more than the additional phenyl ring in **5**. In fact, the cyclopropyl ring is 353 times more effective than the additional phenyl in stabilizing the transition state.

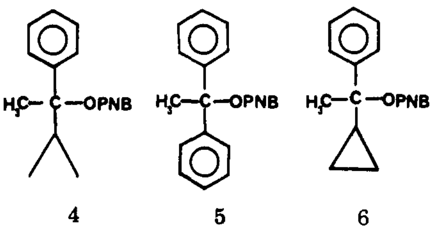
However, it might be argued that these data for the more stabilized phenyl derivatives in Chart II do not provide a fair test of the proposal. Perhaps structures should be examined

Table I. Rate Data for the Solvolysis of the Tertiary 2-Propyl *p*-Nitrobenzoates, $R(CH_3)_2COPNB$, in 80% Acetone

Substituent R	$k_1^{25°} \times 10^6$, s^{-1}	Rel rate, 25 °C	$\Delta H^{\ddagger}$, kcal mol^{-1}	$\Delta S^{\ddagger}$, eu
Methyl[a]	7.45×10^{-5} [b]	1.00	29.2	−7.1
Isopropyl	2.15×10^{-4} [b,c]	2.9	28.5	−7.3
tert-Butyl[d]	3.25×10^{-4} [b]	4.4	29.0	−4.8
Phenyl	7.22×10^{-2} [b,e]	969	24.8	−8.2
Cyclopropyl	37.5[b,f,g]	503 000	20.8	−9.0

[a] H. C. Brown and W. C. Dickason, *J. Am. Chem. Soc.*, **91,** 1226 (1969). [b] Calculated from data at other temperatures. [c] $k_1^{150°} = 419 \times 10^{-6}\ s^{-1}$, $k_1^{125°} = 47.9 \times 10^{-6}\ s^{-1}$. [d] E. N. Peters and H. C. Brown, *J. Am. Chem. Soc.*, **97,** 2892 (1975). [e] $k_1^{75°} = 33.6 \times 10^{-6}\ s^{-1}$, $k_1^{100°} = 391 \times 10^{-6}\ s^{-1}$. [f] $k_1^{50°} = 614 \times 10^{-6}\ s^{-1}$. [g] The product of solvolysis is unrearranged cyclopropyldimethylcarbinol: D. C. Poulter and S. Winstein, *J. Am. Chem. Soc.*, **91,** 3650 (1969).

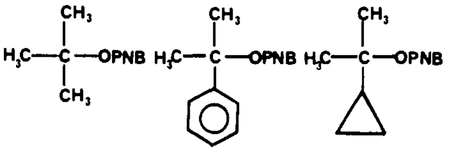
Chart II



	4	5	6
Rel rate	1.00	71.6	25,300

which are directly related to the trimethyl, phenyldimethyl, and cyclopropyldimethylcarbonium ions utilized in the ^{13}C studies of Chart I. Accordingly, we undertook to obtain kinetic data for the solvolysis of the three *p*-nitrobenzoates (Chart III) related to these three cationic intermediates under essentially identical conditions.

Chart III



	7	8	9
Log k_1, s^{-1}	−10.13	−7.14	−4.43
^{13}C NMR shifts, ppm from TMS	329.2	254.4	280.6

It was observed that the replacement of a methyl group in the *tert*-butyl system (**7**) by a phenyl group (**8**) increases the rate at 25 °C by a factor of 10^3. Replacement of the phenyl group by a cyclopropyl group (**9**) increases the rate at 25 °C by another comparable factor of $10^{2.7}$.

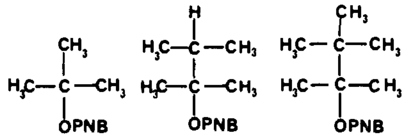
Before we can proceed to interpret these results, it is necessary to establish that differences in B strain[7] are not a significant factor in the observed rates. An isopropyl group has steric requirements similar to those of a phenyl or a cyclopropyl group,[15] and a *tert*-butyl group must have considerably larger steric requirements than a methyl, phenyl, or cyclopropyl group[16] (Chart IV). Solvolysis of isopropyldimethylcarbinyl (**10**) and *tert*-butyldimethylcarbinyl *p*-nitrobenzoate (**11**) yields rates of 2.9 and 4.4[17] larger than that of **7**. Clearly, relief of B strain cannot represent a major contribution in the factors of 969 and 503 000 observed for the respective effects of a phenyl and cyclopropyl group in the corresponding derivatives.

Table II. Rate Data for the Solvolysis of the Tertiary 1-Phenyl-1-ethyl *p*-Nitrobenzoates, $R(Ph)CH_3COPNB$, in 80% Acetone

Substituent R	$k_1^{25°} \times 10^6$, s^{-1}	Rel rate, 25 °C	$\Delta H^{\ddagger}$, kcal mol	$\Delta S^{\ddagger}$, eu
Isopropyl[a]	9.51×10^{-3} [a,b]	1.00	26.7	−5.7
Phenyl	0.681[b,c]	71.6	26.0	−0.3
Cyclopropyl[a]	241	25 300	20.8	−5.5

[a] E. N. Peters and H. C. Brown, *J. Am. Chem. Soc.*, **95,** 2397 (1973). [b] Calculated from data at other temperatures. [c] $k_1^{75°} = 424 \times 10^{-6}\ s^{-1}$, $k_1^{50°} = 21.8 \times 10^{-6}\ s^{-1}$.

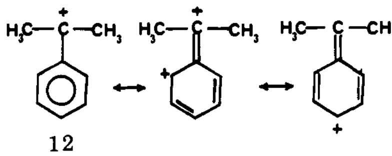
Chart IV



	7	10	11
Rel rate	1.00	2.9	4.36

Since differences in the ground state energies are not significant in the *tert*-butyl and *tert*-cumyl derivatives, the factor of 10^3 in rates indicates that the transition state of the *tert*-cumyl derivative is stabilized by approximately 4 kcal/mol. The stabilization of the free ion is presumed to be modestly larger.[8] This stabilization is attributed to charge delocalization in the carbonium ion (**12**) from the cationic carbon into the aromatic ring (Chart V). Indeed, the large rate enhancement effects of methyl[18a] (× 26) and methoxy[18b] (× 3360) substituents in the para position of *tert*-cumyl derivatives support this interpretation.

Chart V



12

Similarly, the large rate enhancing effect of the cyclopropyl group in **9** ($10^{5.7}$) indicates that the transition state is stabilized by approximately 7.5 kcal/mol. This stabilization must also be the result of major charge delocalization from the carbonium center into the cyclopropane ring. Indeed, here also large rate enhancing effects, following σ^+, have been observed for methyl (× 11) and ethoxy (× 940) substituents in the cyclopropyl ring in the solvolysis of cyclopropylcarbinyl esters.[19]

The major increase in rate observed for the cyclopropyl derivative **9**, as compared to the phenyl derivative **8**, indicates that more charge must be delocalized from the developing cation center in the transition state for **9** than is the case for **8**. The same should be true for the fully developed cations.

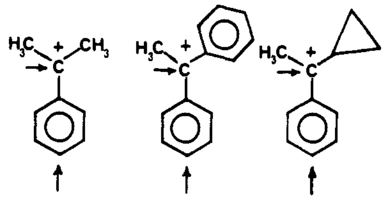
Consequently, all of the solvolytic data are internally consistent in revealing that electron supply to an electron deficient center increases from alkyl (methyl or isopropyl) to phenyl and increases further to cyclopropyl.

Relative Effectiveness of Phenyl and Cyclopropyl Groups in Facilitating ^{13}C Shifts. Since our study was completed, many data have accumulated which indicate the difficulty in relating ^{13}C shifts to electron density in phenyl and cyclopropyl systems. In fact, Olah has recently reported further studies of the trend of charge distribution and the relative delocalization afforded by methyl, phenyl, and cyclopropyl groups and has modified his original position, concluding that the relative order of charge delocalization in substituted secondary allylic carbonium ions is cyclopropyl $\gtrsim$ phenyl $\gg$ methyl,[20] quite different from that arrived at in the earlier studies.[21,22] Olah now suggests that this modified order is the result of significant neighboring-group deshielding of the carbonium ion center by the cyclopropyl substituent.

Some of Olah's own data illustrate the same difficulties. For example, cyclopropylcarbonium ions, $Cp_xMe_{3-x}C^+$ ($x = 0$ to 3), exhibit much smaller changes in the ^{13}C shift as compared to the corresponding phenyl series, $Ph_xMe_{3-x}C^+$ ($x =$ 0 to 3). The data would appear to be in better agreement with a swamping effect resulting from larger electron supply from the cyclopropyl substituents than from the phenyl groups.

Furthermore, if the ^{13}C shift is simply related to charge delocalization,[23] the observed ^{13}C shifts would be expected to vary in the same order methyl, cyclopropyl, and phenyl, according to Olah's own proposed interpretation, irrespective of whether the comparison is based on the $^+$C or p-C values (Chart VI). However, this is not observed in the dimethylphenyl- (13), diphenylmethyl- (14), and the cyclopropylmethylphenylcarbonium ions (15). Indeed, the trend of the ^{13}C shifts observed for the para carbons parallels that for the solvolysis of the corresponding p-nitrobenzoates, as reported here (i.e., **8**, **5**, and **6**, respectively), whereas the trend of the values for the $^+$C shifts is different.

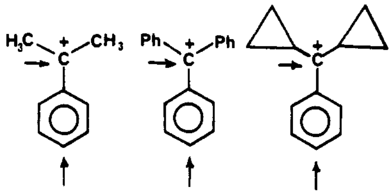
Chart VI



	13	14	15
^{13}C NMR shifts ($^+$C)	254.4	229.3	246.3
^{13}C NMR shifts (p-C), ppm from TMS	156.0	148.2	145.6
Log k (ROPNB)	−7.14	−6.17	−4.62

Similarly, the same trend of the ^{13}C shift of the para carbon atoms is observed in the series in Chart VII of *tert*-cumyl- (**13**), triphenylmethyl- (**16**), and dicyclopropylphenylcarbonium ions (**17**), whereas the trend for the carbonium carbons differs. The results can be rationalized in terms of Olah's latest proposal of a deshielding of the carbonium carbon by neighboring cyclopropyl.[20]

Chart VII

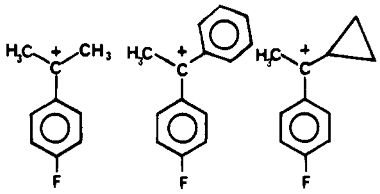


	13	16	17
^{13}C NMR shifts ($^+$C)	254.4	211.9	261.1
^{13}C NMR shifts (p-C), ppm from TMS	156.0	144.1	136.6

Further support is provided by a recent study of Volz and his co-workers of the ^{19}F chemical shifts of cations **18**, **19**, and **20**[24] (Chart VIII). These authors concluded that their results are in agreement with solvolytic, equilibrium, and polarographic studies with the cyclopropyl group stabilizing the carbonium ion better than the phenyl group.

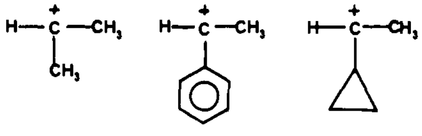
It is of interest that Olah's own earlier ^{1}H NMR results led him to a conclusion opposite to that he reached on the basis of his ^{13}C results, namely, that the cyclopropyl group stabilizes the carbonium ion better than the phenyl group in a related series of secondary ions (**21–23**)[13] (Chart IX).

Chart VIII



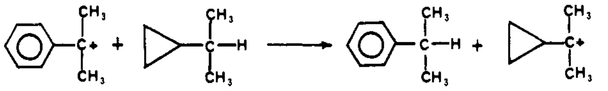
	18	19	20
^{19}F shift, ppm from CCl_3F	−59.7	−78.7	−81.99

Chart IX



	21	22	23
^{1}H NMR shifts, ppm from TMS	13.5	9.8	8.14

Finally, in a study of the relative stabilizing effects of phenyl and cyclopropyl substituents, Taft, Hehre, and co-workers have noted that NMR chemical shift-energy correlations are not general.[25] Using pulsed ion cyclotron resonance spectroscopy and ab initio molecular orbital theory to provide information on the ionic species in the gas phase (eq 1), they concluded that neither the calculated π charge densities nor the ^{13}C shifts properly reflect the relative stabilizing effects of the phenyl and cyclopropyl group on the tertiary ions in the gas phase. They concluded that the phenyl group is superior to cyclopropyl in stabilizing a secondary carbonium center, but that the reverse is true for tertiary carbonium centers. However, these calculations are for the gas phase and their applicability to solution phenomena is uncertain.



(1)

A Critical Examination of ^{13}C Shifts as a Basis for Establishing Electron Densities in Carbocations. The question we now face is whether the phenyl-cyclopropyl question we have explored in the present study represents an exception, so that we can rely on such interpretation of ^{13}C shifts in other systems, or are there reasons to exercise caution in utilizing such interpretations of ^{13}C shifts in other systems.

Examination of the ^{13}C chemical shifts of *tert*-cumyl cations does reveal the existence of a linear relationship with σ^+ constants.[26] However, many reactions involving changes in substituents in the meta and para positions of the aromatic ring are correlated by the Hammett relationship, but the same kind of quantitative treatment cannot be carried over to other systems where structural variations are made at or near the reaction center.

Certain data already available suggest the hazards involved in applying this procedure to cations involving such structural modifications at the cationic center. The isopropyl cation is far less stable than the *tert*-butyl cation and must possess a much higher concentration of charge at the cationic carbon,[27] but their ^{13}C shifts are 318.8 and 329.2 ppm, respectively.[11]

This apparent anomaly might be a consequence of the tendency for such highly active secondary species to exist as tight ion pairs. If so, the anomaly might vanish with more stable cationic species. Both thermodynamic and kinetic data reveal the triphenylmethyl cation to be more stable than the di-

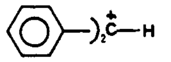
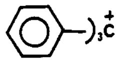
Table III. Preparation of Tertiary Alcohols

Compd	Bp or mp, °C	$n^{20}{}_D$	Lit. bp or mp, °C	Lit. $n^{20}{}_D$
2,3-Dimethyl-2-butanol	120–121	1.4158	117–118 (740 mm)[a]	1.415 1[b]
2-Phenyl-2-propanol	90 (10 mm)		93–94 (13 mm)[c]	
2-Cyclopropyl-2-propanol	123	1.4331	123.4–123.6 (752 mm)[d]	1.432 57[d]
1,1-Diphenyl-1-ethanol	80.5–81.2		81[e]	

[a] J. Lindner, *Monatsh. Chem.*, **32,** 419 (1911). [b] V. J. Shiner, *J. Am. Chem. Soc.*, **76,** 1603 (1954). [c] A. Kloges, *Ber.*, **35,** 2633 (1902). [d] P. Bruylants, *Bull. Soc. Chim. Belg.*, **36,** 153 (1927). [e] A. Jung and F. Jung, *Bull. Soc. Chim. Fr.*, 269 (1966).

phenylmethyl cation.[28] However, the observed chemical shifts are 211.9 and 199.4 ppm, respectively.[21] Thus, even these relatively stable cations do not obey the proposed relationship (Chart X).

Chart X

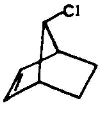
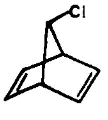
		
pK_{R^+}[28a]	−13.3	−6.63
Log k_1 (RCl in EtOH)[28b]	−4.27	−1.90
^{13}C NMR shifts, ppm from TMS	199.4	211.9

It might be argued that a structural change from a secondary to a tertiary carbonium ion is so large that the ^{13}C shifts should not be expected to obey the proposed relationship. Perhaps the relationship should be applied only to a closely related family of secondary or of tertiary cations.

For example, is it safe to conclude that the 2-methylnorbornyl cation is 50% nonclassical,[29] in spite of the mass of chemical evidence favoring the classical structure,[7] merely because the 2-methylnorbornyl cation exhibits a ^{13}C chemical shift of 269.9, as compared to 329.2 for *tert*-butyl? Is it safe to conclude that the 2-bicyclo[2.1.1]hexyl and 2-methylbicyclo[2.1.1]hexyl cations are classical, merely on the basis of ^{13}C shifts,[30] in spite of the arguments that this system is a far better candidate for σ bridging than the related 2-norbornyl derivatives?[31,32]

Difficulties are evident even when we restrict ourselves to very closely related secondary or tertiary derivatives. For example, the ^{13}C chemical shifts of the 7-norbornenyl and 7-norbornadienyl cations and the logarithms of their rates of solvolysis for the corresponding chlorides do not follow the proposed relationship[29,33] (Chart XI). Finally, it is quite clear that the relationship is not operative, even for the closely related group of three tertiary derivatives that was the main objective of this study (Charts I and III).

Chart XI

		
Log k_1	−6.09	−3.22
^{13}C NMR shifts (C7) for cation, ppm from TMS	31.6	41.1

It is to be hoped that further work will place on a quantitative basis the factors influencing the ^{13}C shift in carbocations. With a sound theoretical foundation, it should be possible to utilize such shifts to determine the charge densities in such ions. This is not possible now.[10] An empirical approach to utilizing ^{13}C shifts for estimating charge densities is of value only so long as major exceptions are not encountered. Several such exceptions have been pointed out here.[10,34]

Table IV. Preparation of *p*-Nitrobenzoates

p-Nitrobenzoate	Mp, °C	Lit. mp, °C	Anal.
5	135 dec		C, H, N
8	133–134	136–137[a]	
9	86.5–87.5	89–90[b]	
10	78.8–79.5	82[c]	

[a] L. F. King, *J. Am. Chem. Soc.*, **61,** 2383 (1939). [b] M. Hanack and K. Goerler, *Ber.*, **96,** 2121 (1963). [c] M. D. Cameron et al., *J. Org. Chem.*, **19,** 1215 (1954).

Conclusion

In view of these developments, it is highly questionable if ^{13}C shifts can be used in their present state of understanding[10] to prove unequivocally the structure of the 2-norbornyl cation,[29b] the 2-bicyclo[2.1.1]hexyl cation,[30] or of other proposed classical and nonclassical ions.[35,36]

Experimental Section

Preparation of Tertiary Alcohols and *p*-Nitrobenzoates. 2-Isopropyl-, 2-phenyl-, and 2-cyclopropyl-2-propanols and 1,1-diphenyl-1-ethanol were prepared by the addition of methylmagnesium chloride to commercially available 3-methyl-2-butanone, acetophenone, cyclopropyl methyl ketone, and benzophenone, respectively. The physical data are listed in Table III. The *p*-nitrobenzoates were prepared by treating the lithium salt of the alcohols with *p*-nitrobenzoyl chloride.[14] The physical and analytical data are listed in Table IV.

Kinetic Procedure. The procedure employed in determining the rate constants of *p*-nitrobenzoates followed that described earlier.[14]

References and Notes

(1) Postdoctoral research associate on a grant (GP 31385) provided by the National Science Foundation.
(2) For a preliminary report, see H. C. Brown and E. N. Peters, *J. Am. Chem. Soc.*, **95,** 2400 (1973).
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(17) E. N. Peters and H. C. Brown, *J. Am. Chem. Soc.*, **96,** 263 (1974).
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(20) G. A. Olah and R. J. Spear, *J. Am. Chem. Soc.*, **97,** 1539 (1975).
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Ring Opening Reactions in Cycloalkane Molecular Ions. A Collisional Activation and Field Ionization Kinetic Study[1]

Friedrich Borchers,[2a] Karsten Levsen,*[2a] Helmut Schwarz,[2b] Chrysostomos Wesdemiotis,[2b] and Roland Wolfschütz[2b]

Contribution from the Department of Physical Chemistry, University of Bonn, D 5300 Bonn, and the Department of Organic Chemistry, Technical University, D 1000 Berlin, Germany. *Received August 3, 1976*

Abstract: Collisional activation and field ionization kinetic measurements demonstrate that alkyl substituted cycloalkane molecular ions with three-, four-, and five-membered rings (*n*-pentylcyclopropane, *n*-butylcyclobutane, 1,2-diethylcyclobutane, and *n*-propylcyclopentane) undergo ring opening within ca. 10^{-9} s to form initially the 1-alkene molecular ions which isomerize to some extent to double bond isomers. However, six-, seven-, and eight-membered rings (ethylcyclohexane, 1,2-dimethylcyclohexane, 1,3-dimethylcyclohexane, methylcycloheptane, and cyclooctane) remain intact *prior* to decomposition.

The occurrence of ring-opening reactions in alkylcycloalkane molecular ions prior to fragmentation has been postulated repeatedly. Thus, Stevenson[3] demonstrated that if methylcyclopentane-α-^{13}C undergoes loss of a methyl radical about 50% of the label is retained in the remaining $[C_5H_9]^+$ ion suggesting an isomerization to a linear ion prior to decomposition. More detailed studies by Meyerson et al.[4,5] using compounds labeled with ^2H and ^{13}C in the α position showed that the label retention in the $[C_5H_9]^+$ ion is nearer to 40% and depends on the ionizing voltage; with increasing electron energy the loss of the original side chain becomes more pronounced. From these results the authors concluded that at least two competing mechanisms are operating, i.e., loss of the original side chain from the intact ring and methyl loss after ring opening to a linear intermediate. Similar results were obtained for ethylcyclopentane,[4] although a shift toward simple cleavage has been postulated with increasing length of the side chain. In contrast to these alkylcyclopentane ions the methyl radical lost from methylcyclohexane includes only the original side chain.[4]

An extensive and elegant field ionization kinetic study by Falick and Burlingame[6] fully supported the earlier conclusions and shed further light on the details of these processes. The lifetime measurements of methylcyclopentane-α-^{13}C revealed that at times $<10^{-9}$ s exclusively the side chain is eliminated while the methyl radical loss at longer times included also ring C atoms approaching total randomization at the longest observed times suggesting that the ring is essentially intact at times $<10^{-9}$ s prior to decomposition, but opens up at longer times.

A completely different approach was used by Pottie et al.[7] to obtain information on the structure of cycloalkane ions. From heats of formation data obtained from appearance potential measurements the authors concluded that there is a "strong possibility" that the $[C_nH_{2n-1}]^+$ ions formed from cyclopropane, cyclobutane, and methylcyclopentane have an olefinic rather than a cyclic structure, while the $[C_6H_{11}]^+$ ion from cyclohexane actually may be a cyclohexyl ion.

In this context also a study of the isomerization of $[C_6H_{12}]^{+\cdot}$ ions by Smith and Williams is of interest.[8] Using competing metastable transitions the authors concluded that the decompositions of a large variety of $[C_6H_{12}]^{+\cdot}$ ions proceed via common intermediates. Although in view of the presented data this conclusion is not fully convincing,[9] rather similar metastable abundance ratios were observed for *n*-propylcyclopropane, ethylcyclobutane, and methylcyclopentane.

Finally, in a collisional activation (CA) study[10] of a large number of C_8H_{16} isomers (including some cycloalkanes) identical CA spectra were observed for the molecular ions of 1-octene and *n*-propylcyclopentane which again strongly suggests ring opening of the latter prior to decomposition.

Stimulated by this observation we decided to study a whole series of isomeric cycloalkanes of the elemental composition C_8H_{16} with three-, four-, five-, six-, seven-, and eight-membered rings and varying side chain using both the collisional activation[11] and field ionization kinetic[12] technique to obtain additional information on the following questions: (a) the dependence of the stability of the cycloalkane molecular ion on the ring size, (b) the influence of the length of the side chain on the isomerization behavior, (c) the structure of the molecular ion after ring opening, and (d) the time scale for the isomerization process.

Experimental Section

Materials. Methylcycloheptane. Reaction of cycloheptanone with CH_3MgBr gave 1-methylcycloheptanol, which was thermally dehydrated to 1-methylcycloheptene under addition of I_2.[13] Catalytic hydrogenation ($H_2/PtO_2/AcOH$) led to methylcycloheptane.

***n*-Butylcyclobutane.** Cyclobutanone was transformed into the corresponding alcohol with *n*-C_4H_9Li which was dehydrated (I_2 ad-