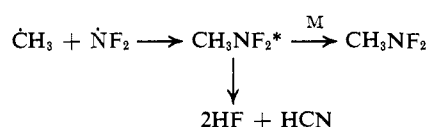


state. The competitive energetics of the two possible reaction routes would then be unimportant, and N-F scission, the reaction with the looser transition state (and thus having the higher preexponential factor in its rate expression), would be dominant.

In the present case, however, the intermediate radical is thermally equilibrated. Moreover, since the rearrangement is 40 to 50 kcal/mol exothermic,¹² whereas the N-F scission is probably close to thermoneutral, the activation energy for b should be considerably lower than that for a. The rates of two reactions are thus competitive, and products from both are observed.

The lower temperature range for decomposition for II corresponds to an E_a for C-N scission of about 45 kcal/mol.⁷ The 10-kcal/mol bond weakening by α -NF₂ substitution is not unexpected; similar findings have been noted for aliphatic nitro compounds.¹³

The minor products, CH₃NF₂ and HCN, can be explained by the sequence⁹



although their formation could also be due to reactions on various surfaces in the system.

Fluorine migration was also observed in a limited study of the low-pressure pyrolysis of CH₃CH₂CH(NF₂)₂ (III) at 650°. Although the major path for de-

(12) This range is based on estimated bond strengths of 106 and 58 kcal/mol for C-F and N-F bonds, respectively; see J. A. Kerr, *Chem. Rev.*, **66**, 465 (1966).

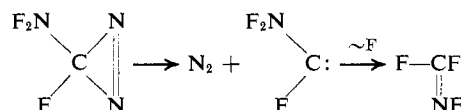
(13) G. M. Nazin, G. B. Manelis, and F. I. Dubovitskii, *Bull. Acad. Sci. USSR, Div. Chem. Sci.*, 374 (1968).

composition of this material was simple dehydrofluorination, significant amounts of HC(NF)F¹⁴ and CH₃-CH₂NF₂ were observed in the product mixture, indicating that such a rearrangement was taking place, the ethyldifluoramine providing good evidence for the presence of ethyl radicals.¹⁵

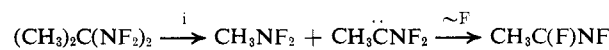
Acknowledgments. The work was supported by the U. S. Office of Naval Research under Contract Nonr 3760(00). The mass spectra were interpreted by Miss Julia Whittick. The authors are grateful for helpful discussions of this work with Drs. D. M. Golden, S. W. Benson, and R. Shaw.

(14) The structure of this material was determined solely from its ¹H nmr spectrum, a double pair of doublets, which suggests *ca.* a 70:30 mixture of the two isomers. The major isomer has a band centered at τ 2.1 with $J_{\text{HNF}} = 33$ cps and $J_{\text{HCF}} = 91$ cps. The band of the minor isomer is centered at τ 3.4 with $J_{\text{HNF}} = 27$ cps and $J_{\text{HCF}} = 84$ cps.

(15) R. Mitsch, E. Newvar, R. Koshar, and D. Dybvig, *J. Heterocycl. Chem.*, **2**, 371 (1965). They observed fluorine migration in an electron deficient species



Thus we might consider for II the generation of a similar species with subsequent rearrangement.



However, at least two facts contraindicate this mode of decomposition. (a) The formation of carbene requires formation of equal amounts of fluorimine and alkyldifluoramine, and at least for II, fluorimine is the major product. (b) We estimate the Arrhenius A factor for a process such as i to be about 10^{10} to 10^{11} sec⁻¹. A lower limit value for the activation energy can be estimated by considering that in i the net process is the breaking of the H₃C-C bond, which requires about 80 kcal/mol. Thus, $k_i \geq 10^{11-80/4.6RT}$ sec⁻¹, a value much too small to account for the observed rate of decomposition of II at 450°.

Rearrangements and Unimolecular Decompositions of Benzenoid C₉H₁₁⁺ Ions

Nicola A. Uccella and Dudley H. Williams*


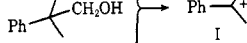
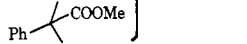
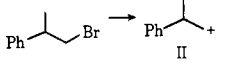
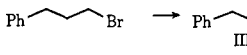
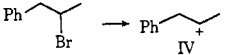
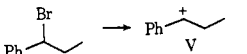

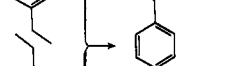
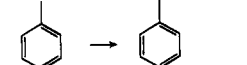
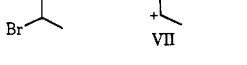


Contribution from the University Chemical Laboratory, Cambridge, United Kingdom. Received May 10, 1972

Abstract: Ions of composition C₉H₁₁⁺ have been generated within a mass spectrometer by electron impact. In terms of the structures of the carbonium ions which are believed to be generated at the threshold, the ions can be subdivided into two groups. Five ions (group 1) are generated as PhC₃H₆⁺ units and in these ions only the six hydrogens of the C₃ side chain become equivalent before unimolecular decomposition *via* loss of C₂H₄, C₃H₄, and C₆H₆. In contrast, CH₄ loss from the C₃ side chains is a specific 1,2 elimination and it is concluded that the reaction occurs in an excited state in which 1,2 shifts are forbidden. Five ions (group 2) are generated as carbonium ions containing di- or trisubstituted benzene rings and side chains of only one or two carbon atoms. These group 2 ions are apparently precluded (by the nature of the initially generated structures) from undergoing any facile unimolecular decompositions, and undergo rearrangements which render all 11 hydrogens in the ion equivalent prior to loss of C₂H₄, C₃H₄, and C₆H₆.

When positive ions decompose in the Nier-Johnson mass spectrometer *via* a metastable transition, they do so after existing for lifetimes of the order of 10 μ sec. Thus, the metastable ion is provided, in a molecular beam following electron impact, with internal energy sufficient for unimolecular decomposition, but

this decomposition does not occur until some 10⁸ vibrations of a given bond have taken place. Metastable transitions therefore normally occur in ions whose internal energies are only slightly (*e.g.*, 0-25 kcal) in excess of the required activation energy. It follows that if a given ion undergoes two or more com-

Table I. Relative Abundances (Per Cent) of Some Metastable Transitions (First Drift Region) from $C_9H_{11}^+$ Ions at 70 eV

Compd no.	$M^+ \rightarrow C_9H_{11}^+$	CH_4	C_2H_4	C_3H_4	C_6H_6
1		0.6	94	3.3	1.7
2		0.8	91	5.5	2.5
3		0.7	93	4.9	1.6
4		0.6	95	2.6	1.7
5		1.2	92	3.9	2.8
6		0.9	95	2.2	1.4
7		1.1	94	2.8	2.1
8		8.4	75	6.6	9.8
9		8.4	73	7.5	12.8
10		10.0	71	5.7	13.3
11		12.7	66	8.8	12.0
12		9.9	69	6.9	13.8
13		17.4	63	8.6	10.5

peting metastable decompositions, the activation energies for the two or more processes must be similar. Further, if two ions of the same elemental composition undergo the same metastable decompositions in the same or similar ratios, this is an excellent criterion that the two ions are decomposing from the *same structure(s)*.¹ This criterion has been used to establish that isomeric $C_2H_5O^+$ ions decompose from two distinct structures,² and that *n*-, *sec*-, *iso*-, and *tert*-butyl bromides provide $C_4H_9^+$ ions which decompose from the same structure(s).³ Evidently, the activation energies required for interconversion of the various

butyl ions are less than that required for unimolecular decomposition. In general, it appears that the presence of the heteroatoms O and N in oxonium and immonium ions increases the barriers for internal rearrangement relative to those for unimolecular decomposition. Thus, isomeric $C_3H_8N^+$ ions can be divided into three distinct classes on the basis of their metastable decompositions.⁴

In the present study, we have replaced the nitrogen atom of $C_3H_8N^+$ by a benzene nucleus to see what kind of a barrier the benzene ring would provide toward interconversion of various $C_9H_{11}^+$ isomers prior to unimolecular decomposition. Thus, at the outset, we were, for example, posing the question as to whether the two carbonium ions shown below would interconvert prior to unimolecular decomposition.

(4) N. A. Uccella, I. Howe, and D. H. Williams, *ibid.*, 1933 (1971).

(1) H. M. Rosenstock, V. H. Dibeler, and F. N. Harlee, *J. Chem. Phys.*, **40**, 591 (1964).

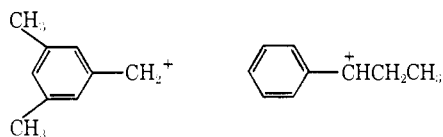
(2) T. W. Shannon and F. W. McLafferty, *J. Amer. Chem. Soc.*, **88**, 5021 (1966).

(3) B. Davis, D. H. Williams, and A. N. H. Yeo, *J. Chem. Soc. B*, 81 (1970).

Table II. Relative Abundances (Per Cent) for Some Metastable Transitions (First Drift Region) for the Decomposition of Some Deuterated Analogs of Ions I-V at 70 eV^a

Compd no.	Precursor	Ion	Neutral particle lost																			
			Methane					Ethylene					Propyne					Benzene				
			d ₀	d ₁	d ₂	d ₃	d ₄	d ₀	d ₁	d ₂	d ₃	d ₄	d ₀	d ₁	d ₂	d ₃	d ₄	d ₀	d ₁	d ₂	d ₃	
14					37		63			11	86	3		28	24	48		58	42			
		Ia								(20)	(60)	(20)		(20)	(60)	(20)		(50)	(50)			
15							100			17	73	10		22	24	54		56	44			
		IIa								(20)	(60)	(20)		(20)	(60)	(20)		(50)	(50)			
16			b	b	b	b	b		9	57	34		13	32	55		58	42				
		IIb							(7)	(53)	(40)		(7)	(53)	(40)		(67)	(33)				
17			c	c	c	c	c		14	55	31		10	37	53		44	56				
		IIIa							(7)	(53)	(40)		(7)	(53)	(40)		(67)	(33)				
18			100					100					100									100
		IIIb																				
19			b	b	b	b	b				64	36		42	58	20	80					
		IVa									(67)	(33)		(67)	(33)	(17)	(83)					
20			100						8	56	36		14	30	56		55	45				
		Va							(7)	(53)	(40)		(7)	(53)	(40)		(67)	(33)				

^a Values in parentheses are those calculated on the basis of H-D randomization in the C₃ side chain, and not involving the aromatic ring; the calculations assume that no isotope effect is operating. ^b See text. ^c Intensities too low to allow reliable measurements.



Results and Discussion

The compounds 1-13 which were used as sources of C₉H₁₁⁺ carbonium ions are given in Table I. Although not essential to our arguments, it is assumed that the carbonium ions I-IX are initially generated without skeletal reorganization at the threshold. This assumption seems reasonable, since in these cases the carbonium ions are formed in reactions of low activation energy (most commonly through loss of a labile bromine atom). In the case of 13 → X, the proposed ring expansion prior to loss of bromine (initially bonded in a less labile *vinyl* position) is in analogy to the behavior of *p*-bromoethylbenzene: when this compound is dideuterated in the benzylic position, there is a deuterium isotope effect discriminating against bromine loss in metastable transitions.⁵ It is of course possible that the ion formed from 11 (and analogous compounds) corresponds to a bridged phenonium ion at the threshold,⁶ and that the primary carbonium ions II and III collapse to other structures with a negligible activation energy, but it is clear that in most cases 1-13 will produce different carbonium ions at the thresh-

(5) I. Howe, N. A. Uccella, and D. H. Williams, submitted for publication in *J. Chem. Soc., Perkin Trans.*

(6) R. H. Shapiro and T. F. Jenkins, *Org. Mass. Spectrom.*, **2**, 771 (1969).

old, and that in some cases the barriers to interconversion of the carbonium ions will be considerable.

Five metastable transitions are found to occur from ions initially generated as the isomeric C₉H₁₁⁺ species listed in Table I; the neutral particles lost in these reactions are H₂, CH₄, C₂H₄, C₃H₄, and C₆H₆. It is not possible to measure accurately the abundance of H₂ loss in the first drift region (using the refocussing technique⁷), and the relative abundance for the other four processes are therefore recorded in Table I. All C₉H₁₁⁺ ions generated from the precursors 1-13 undergo all of these four reactions with ethylene loss always dominant (Table I). However, in those ions in which three contiguous carbon atoms are attached initially to a monosubstituted benzene ring (I-V), ethylene loss accounts for 90-95% of the total metastable ion current from C₉H₁₁⁺, whereas in those ions where the benzene ring is initially di- or trisubstituted (VI-X), the other reactions compete more successfully (ethylene loss 63-75%). The existence of two classes of ions (I-V and VI-X) is confirmed by data for metastable transitions in the second drift region; the losses and relative abundances are C₂H₄ (96 ± 3%) and C₃H₄ (4 ± 2%) for ions I-V, and C₂H₄ (55 ± 3%), H₂ (37 ± 1.5%), CH₄ (3.1 ± 0.5%), C₃H₄ (2.1 ± 0.3%), and C₆H₆ (2.8 ± 0.4%) for ions VI-X.⁸ Thus, only

(7) K. R. Jennings in "Some Newer Physical Methods in Structural Chemistry," R. Bonnett and J. G. Davis, Ed., United Trade Press, London, 1967, p 105.

(8) The sensitivity for detection of metastable transitions is considerably less in the second drift region than in the first. Thus, the loss of CH₄ and C₆H₆ from ions I-V is not detectable in the second drift region (<1%) but is probably finite.

Table III. Relative Abundances (Per Cent) for Some Metastable Transitions (First Drift Region) for the Decomposition of Some Deuterated Analogs of Ions VI-X at 70 eV^a

Compd no.	Precursor	Ion	Neutral particle lost															
			Methane				Ethylene				Propyne				Benzene			
			d ₀	d ₁	d ₂	d ₃	d ₀	d ₁	d ₂	d ₃	d ₀	d ₁	d ₂	d ₃	d ₀	d ₁	d ₂	d ₃
21			54 (38)	38 (51)	8 (11)		38 (38)	50 (51)	12 (11)		43 (38)	47 (51)	10 (11)		19 (18)	54 (55)	27 (27)	
22			54 (21)	31 (51)	15 (25)	1 (2)	26 (21)	49 (51)	22 (25)	3 (2)	20 (21)	53 (51)	26 (25)	2 (2)	9 (6)	44 (36)	35 (46)	12 (12)
23			56 (38)	36 (51)	8 (11)		41 (38)	48 (51)	11 (11)		39 (38)	50 (51)	11 (11)		21 (18)	51 (55)	28 (27)	
24			63 (38)	25 (51)	12 (11)		33 (38)	46 (51)	21 (11)		35 (38)	50 (51)	15 (11)		21 (18)	53 (55)	26 (27)	
25			61 (38)	31 (51)	5 (11)		40 (38)	48 (51)	12 (11)		44 (38)	45 (51)	11 (11)		12 (18)	52 (55)	36 (27)	

^a Values in parentheses are those calculated on the basis of H-D randomization over the whole ion; the calculations assume that no isotope effect is operating.

ions generated as VI-X undergo the abundant transition for loss of H₂.

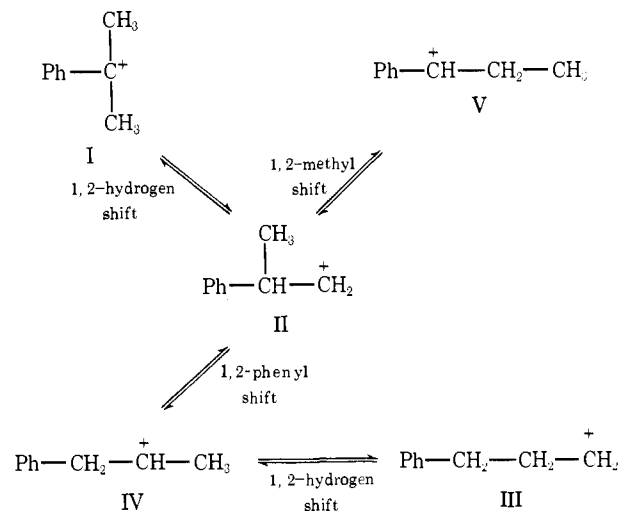
Information as to the extent to which the initially generated structures isomerize prior to metastable decomposition has been sought by specific deuterium labeling in all cases. The data for deuterated analogs of ions I-V are given in Table II and for ions VI-X are given in Table III.

From the data for the deuterated analogs of ions I-V (Table II), a number of conclusions can be drawn. First, all these carbonium ions (with the common feature of a C₃ side chain attached to a monosubstituted benzene ring) undergo, prior to ethylene, propyne,⁹ and benzene loss, randomization of H and D over the side-chain carbons only; no chemical reactions in which hydrogens of the aromatic ring could exchange with those of the side chain occur. Second, it is clear that in the double hydrogen (deuterium) transfer which is necessary prior to propyne loss, there is an isotope effect discriminating against deuterium transfer. Thus, ions which are deuterated to the same extent but initially have different structures (Ia and IIa; IIb, IIIa, and Va) lose only those propynes which are allowed through side-chain H-D rearrangements and lose these in essentially the same ratios. The conclusion that these structures interconvert at rates which are fast prior to their rates of unimolecular decomposition seems inevitable, but the propyne losses deviate from the statistical values inasmuch as the loss of the most highly deuterated propynes is consistently high (Table II), *i.e.*, discrimination against transfer of deuterium from the side chain to the aromatic ring occurs.

(9) The neutral particle C₃H₄ could also correspond to allene; we refer to this reaction as propyne loss of an arbitrary basis.

Taken together, the data in Tables I and II indicate that by some combination of 1,2-hydrogen, -methyl, and -phenyl shifts (*e.g.*, Scheme I), ions I-V interconvert

Scheme I



prior to the unimolecular losses of ethylene, propyne, and benzene.

These conclusions are in accord with previous work. Thus, Ph¹³C⁺(CH₃)₂ loses the ¹³C atom in ethylene expulsion with a frequency that indicates equivalence of the side-chain carbons prior to decomposition even in the source.¹⁰ Also, the C₉H₁₁⁺ ions generated from 3-phenyl-1-bromopropane, 1-phenyl-1-nitropropane, and 1-phenyl-2-nitropropane show equivalence of the side-

(10) R. N. Rylander and S. Meyerson, *J. Amer. Chem. Soc.*, **78**, 5799 (1956).

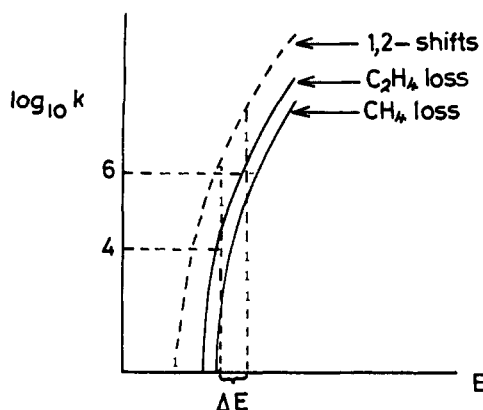
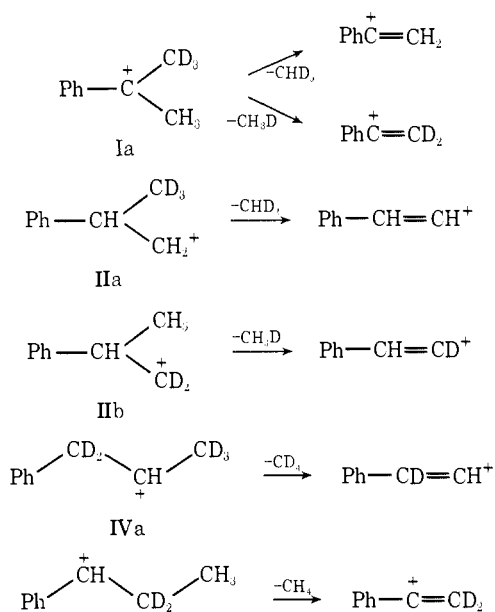


Figure 1. $\log k$ vs. E curve for competing metastable transitions.

chain hydrogens prior to unimolecular decomposition.^{11,12}

The loss of methane and deuterated methanes from ions generated as I-V is in sharp contrast to the other processes. These transitions are in some cases rather weak, and therefore quantitative conclusions are not always possible, but the following conclusions are clear (see also Table II). Ion Ia loses only CH_3D and CHD_3 ; ion IIa loses only CHD_3 ; ion IIb loses CH_3D , does not lose CH_2D_2 , and any loss of CH_4 is zero or small (but cannot be quantitated because of the proximity of this transition to that for loss of CH_3 from an $\text{M}^+ - \text{HBr}$ species); ion IVa gives a weak signal due to loss of CD_4 , and there is no signal for loss of CD_3H above the noise level; ion Va loses only CH_4 . Thus, the data for these ions are in accord with the reactions indicated in Scheme II. In all cases, the data indicate

Scheme II



1,2 elimination of methane without any rearrangement, *i.e.*, from the ion structure which is assumed to be generated at the threshold.

(11) N. M. M. Nibbering and Th. J. de Boer, "Some Newer Physical Methods in Structural Chemistry," R. Bonnett and J. G. Davis, Ed., United Trade Press, London, 1967, p 47.

(12) N. M. M. Nibbering and Th. J. de Boer, *Org. Mass Spectrom.*, **2**, 157 (1969).

We return now to the metastable ion abundance data in Table I and argue from the assumption that the reaction for methane loss is competing with the other reactions and, in particular for the purposes of our argument, with ethylene loss. Now if CH_3 and C_2H_4 losses are indeed competing, then, since the abundance of the metastable peak for ethylene loss is by far the greater (Table I), C_2H_4 loss must be occurring at a faster rate than CH_3 loss in the narrow band of energies ($\sim \Delta E$) which are weighted in metastable transitions, *i.e.*, the assumption of competing reactions demands that C_2H_4 loss is the lower activation energy process (see Figure 1). In addition, it is clear from the deuterium labeling results (Table II) that the rearrangements occurring in the C_3 side chain of ions I-V have lower activation energies than even the most facile unimolecular decomposition of ethylene loss (see Figure 1 for a schematic representation). On the basis of these arguments, it is clear that the loss of methane and deuterated methanes from ions Ia, IIa, IIb, IIIa, IVa, and Va would necessarily occur after H-D randomization. Experimentally, this is not the case (*vide supra*) and therefore we conclude that methane loss is *not* competing with the other three unimolecular decompositions listed in Table I. If the methane loss is not competing with the other decompositions, then it must be occurring from an isolated state, and this state must of necessity be a different electronic state. In summary, we are forced to the conclusions that (i) methane loss occurs from a different electronic state to the other reactions, and that (ii) in this electronic state of the carbonium ions 1,2 eliminations are allowed while 1,2 shifts are forbidden (or, at least, unable to compete). In contrast, the other three unimolecular decompositions probably compete with each other (since all are preceded by H-D side-chain randomization), and in the electronic state from which these decompositions occur, 1,2 shifts are facile. These conclusions are in striking accord with the predictions based on the concept of conservation of orbital symmetry, on the assumption that C_2H_4 , C_3H_4 , and C_6H_6 losses occur from the ground state of $\text{C}_3\text{H}_{11}^+$ carbonium ions, and methane loss occurs from the first excited state of $\text{C}_9\text{H}_{11}^+$ carbonium ions; Woodward and Hoffmann¹³ deduce that in the ground state of a carbonium ion 1,2 shifts are allowed and 1,2 eliminations forbidden, while in the first excited state 1,2 shifts are forbidden and 1,2 eliminations allowed. The present data seem to provide an example which strikingly supports these deductions.

It will be recalled that the carbonium ions VI-X generated from compounds containing di- or trisubstituted aromatic nuclei constitute a second group of ions. This point is confirmed by deuterium labeling experiments (Table III), which establish that in ions VIa-Xa, *all* H and D become equivalent prior to loss of ethylenes, propynes, and benzenes. In general, there is excellent agreement between the losses calculated on a statistical basis (values in parentheses) and the observed results. Apparently, ions generated as VI-X cannot undergo any unimolecular decompositions of relatively low activation energy. Therefore, ions VI-X, generated with sufficient internal energy, largely undergo a relatively high activation energy rearrange-

(13) R. B. Woodward and R. Hoffmann, *Angew. Chem.*, **8**, 781 (1969).

ment process (which results in exchange of side-chain and aromatic hydrogens) in order to gain a configuration which can undergo more facile unimolecular decomposition. All the experimental data can be accommodated by predominant rearrangement of high energy ions, generated as VI-X, to the same decomposing structure as provided from I to V (e.g., Figure 2): H₂ loss, which is unique to the ions VI-X, is interpreted as being competitive with this rearrangement. Figure 2 is a highly simplified and schematic representation of the behavior-determining potential surfaces that one of the ions VI-X might have to surmount before decomposition.

We postulate that any one of what we will call the "group 2 ions" (VI-X) will require a minimum energy E_2 to isomerize to one of the "group 1 ions" (I-V) and that this minimum energy is comparable to that required for H₂ loss (Figure 2). However, it is experimentally established that group 1 ions do not interconvert with group 2 ions (the former group equilibrates H and D *only* in the side chain), and therefore the barrier to decomposition of group 1 ions is less than that to the reverse isomerizations of group 1 to group 2. It follows that the rate-determining step in the decomposition of group 2 ions will be their rearrangement to group 1 ions, and that their subsequent decomposition will be from a more highly energized state, and faster than a normal "metastable decomposition," *i.e.*, the "metastable process" would be rearrangement. If this is the case, then the expectation is that (i) any isotope effects will be smaller in the decomposition of group 2 ions (more internal energy) relative to group 1 ions, and (ii) for competing decompositions, the processes of low abundance for group 1 ions should gain in relative abundance for group 2 ions (higher activation energy processes compete more successfully with lower activation energy processes at higher internal energies). Expectation ii is strikingly confirmed by the data presented in Table I, and expectation i is confirmed by contrasting the considerable isotope effect for propyne loss from group 1 ions (Table II) with the negligible isotope effect for loss of propyne from group 2 ions (Table III). The basis for expectation ii has in fact already been experimentally demonstrated in this paper, in noting the low abundances of transitions for CH₄ ($3.1 \pm 0.5\%$), C₃H₄ ($2.1 \pm 0.3\%$), and C₆H₆ ($2.8 \pm 0.4\%$) losses from group 2 ions in the second drift region relative to the first drift region (12.9 ± 4.9 , 7.2 ± 1.6 , $11.8 \pm 2.0\%$, respectively). In addition, a representative ion of group 1 (ion I) has been made to undergo collision-induced decomposition by collision with helium in the second drift region. In this way, the decomposition of a highly energized group 1 ion can be observed in the form of a metastable spectrum.¹⁴ The relative abundances for C₂H₄, C₃H₄, and C₆H₆ losses were 81.0, 5.7, and 13.3% in this experiment. Methane and hydrogen losses could not be examined due to broadening of the normal peaks associated with ion scattering, but clearly these highly energized decompositions of a group 1 ion closely resemble in their relative abundances those for group 2 ions in the first drift region (Table I), as might be expected on the basis of our proposals.

The occurrence of CH₄ loss from group 2 ions

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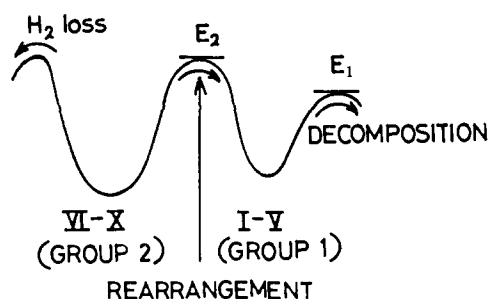
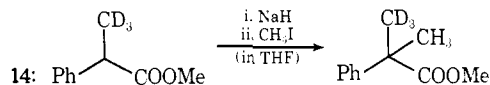
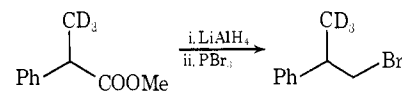
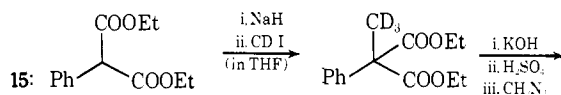
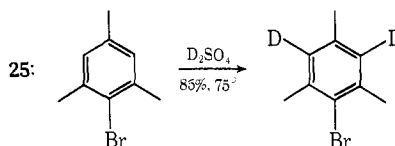
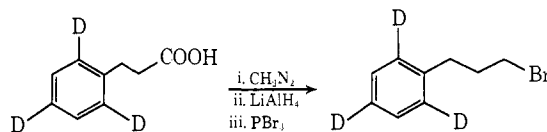
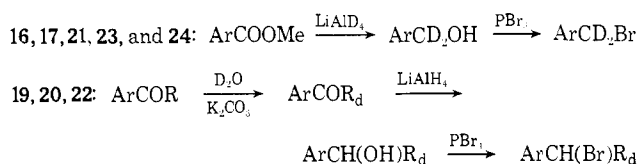


Figure 2. Proposed relative energy requirements for decomposition of ions VI-X.

(Tables I and III) suggests that the proposed excited state accessible *via* ionization and fragmentation of 1-7 is also accessible *via* ionization and fragmentation of 8-13, but that the configurations required for methane loss (e.g., Scheme II) are only available after extensive rearrangement of the group 2 ions (Table III). Thus, the group 2 ions VIa, VIIIa, IXa, and Xa lose CH₄, CH₃D, and CH₂D₂ in very similar ratios, but if these processes follow after all H and D atoms have passed through equivalent positions (as seems likely), then an isotope effect discriminating against D loss is operating. The operation of a relatively large isotope effect in methane loss but *not* in the other processes (Table III) is further evidence to support the contention that methane loss is occurring from a different electronic state.

Scheme III



Experimental Section

All mass spectra were determined on an AEI MS9 double focusing mass spectrometer with an electron beam energy of 70 eV and a

source temperature below 100°. Samples were introduced *via* the heated inlet system at a temperature below 80°. Unimolecular metastable transitions in the second drift region were observed at a nominal 8 kV. Collision-induced metastable transitions were observed using helium at a pressure of 7×10^{-6} τ . The first drift region transitions were obtained using the metastable refocusing technique.⁷

Unlabeled compounds were either available commercially or synthesized by unexceptional methods.

Isotopically labeled compounds were prepared as outlined in Scheme III.

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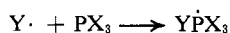
Kinetic Applications of Electron Paramagnetic Resonance Spectroscopy. VIII. Tetraalkoxyphosphoranyl Radicals¹

G. B. Watts,² D. Griller, and K. U. Ingold*

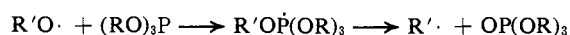
Contribution from the Division of Chemistry, National Research Council of Canada, and the Christopher Ingold Laboratories, University College London, London, England. Received April 28, 1972

Abstract: The reactions of the phosphoranyl radicals formed by the addition of *tert*-butoxy radicals to trimethyl, triethyl, triisopropyl, and tri-*tert*-butyl phosphite have been examined by epr spectroscopy. At temperatures below *ca.* -115° the *t*-BuOP(OMe)₃ and *t*-BuOP(OEt)₃ decay with second-order kinetics. At higher temperatures all four radicals decay with first-order kinetics to yield phosphate and a *tert*-butyl radical. The rates of this β -scission reaction increase by about an order of magnitude at -60° along the series from *t*-BuOP(OMe)₃ to to (*t*-BuO)₄P. Arrhenius parameters for β -scission have been determined by kinetic epr spectroscopy and by a competitive procedure. The latter method has shown that *tert*-butyl radicals react with phosphoranyl radicals with rate constants that are approximately the geometric mean of the rate constants for the bimolecular self-reactions of the *tert*-butyl and phosphoranyl radicals. The mechanism of β -scission is discussed.

The growing importance of free radical reactions in organophosphorus chemistry is well documented.³ The presence of unoccupied low energy d orbitals makes valence shell expansion of trivalent phosphorus compounds possible. Such compounds can therefore react with free radicals to increase their coordination number to four and yield a *phosphoranyl radical*⁴⁻⁶ with nine valence electrons.



Tetraalkoxyphosphoranyl radicals have been proposed as intermediates in the oxidation of trialkyl phosphites by *tert*-alkoxy radicals.^{4,6}



Initial attempts to observe such phosphoranyl radicals directly by the photolysis of di-*tert*-butyl peroxide in the presence of trialkyl phosphites in the cavity of an electron paramagnetic resonance (epr) spectrometer were

unsuccessful, only the spectrum of the *tert*-butyl radical being observed.⁷⁻⁹ However, more recent work has shown that this failure was due to an insufficient sweep of the magnetic field in these experiments.¹¹⁻¹⁴ Trialkoxy(*tert*-butoxy)phosphoranyl radicals and trialkoxy(ethoxy)phosphoranyl radicals¹⁵ have now been detected from a wide variety of trialkyl phosphites. The epr spectra of these radicals show a large doublet splitting from phosphorus (~900 G) with no further fine structure.¹¹⁻¹⁵ Phosphoranyl radicals are believed to have a slightly distorted trigonal-bipyramidal structure, with the orbital of the unpaired electron occupying a position in the equatorial plane.^{12,13,16}

Bentrude and coworkers¹⁷⁻¹⁹ have studied the stereochemistry of the overall oxidation of trialkyl phosphites

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