Simple Cracking and Hydrogen Rearrangement–Cleavage for Oxetanes under Electron Impact. Substituent Effects and Energetics[1]

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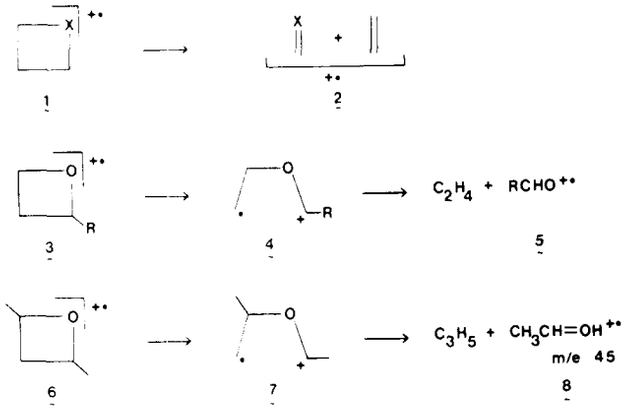
Mass spectral fragmentation of oxetanes substituted with aryl and other groups (**9–16**) gives simple patterns of product ions associated with carbonyl and olefin cycloelimination fragments. For oxetanes substituted with aryl groups in the 2 position, ions resulting from cleavage plus hydrogen rearrangement ($ArRC{=}OH^+$) are also prominent. The direction of two-bond cleavage without rearrangement does not correlate well with electron affinities of fragment ions alone. There is general agreement, however, between regioselectivity and overall stability of ions and neutrals, assessed from heats of formation of product pairs. The regiochemistry of fragmentation for 2-aryloxetanes is also correctly predicted by assessment of the relative stabilities of ring-opened valence isomers of the oxetane molecular ions. The competition between cleavage with and without hydrogen migration for 2-aryloxetanes is dependent on ionizing energy, with the former relatively more important at low voltages. A sizable β-secondary deuterium isotope effect on simple cleavage for **16** is also observed (k_H/k_D = 1.08–1.02, per deuterium, at 10–70 eV). A similarity in regioselectivity for mass spectral and thermal cracking for 2-aryloxetanes is noted.

Mass spectral decomposition of **1**, where X = C, N, O, and C=O, has been the subject of a number of investigations. Results for variously substituted cyclobutanes,[3] azetidines,[4] oxetanes,[5] and cyclobutanones[6] have been reported. For this family of small rings, ring cleavage under electron impact is extremely efficient, presumably due to the release of ring strain (generally >25 kcal/mol) and the stability of molecular products. Molecular ion intensities are low, and large fractions of the total ion current at low ionizing energies can be assigned to cleavage fragments **2**. Where substitution patterns in **1** are



unsymmetrical, cracking is regioselective, providing insight into the effect of substituents on the energetics of bond breaking and charge partitioning. Unlike most mass spectral fragmentations, cycloelimination of **1** may be thermoneutral or even exoergic with relatively large kinetic energy release[4a] as expected for 1,2 eliminations.[7]

A mechanism for mass spectral decomposition of 2-substituted oxetanes (**3** → **5**, R = Me, Et, and Ph) involving initial C–C cleavage to a ring-opened, valence isomeric molecular ion has been proposed,[5b] based on the regioselectivity of fragmentation. The decomposition of other cyclic ethers[8] appears also not controlled by initial C–O cleavage. An isolated case of hydrogen rearrangement for an oxetane (**6** → **8**) has been reported.[5a] This fragmentation which competes with simple cleavage may also involve a ring-opened ion precursor (**7**).

We have extended the survey of oxetane fragmentation in the mass spectrometer, exploring the factors which control the direction of ring cleavage and with pyrolysis chemistry data available for comparison.[9] We note the special importance of hydrogen rearrangement (analogous to **6** → **8**) for aryloxetanes and its requirements of structure for reactivity in competition with simple ring cleavage. The dependence of rearrangement and simple cleavage on ionizing energy and a β-secondary deuterium isotope effect on the direction of cracking are also reported.

Results and Discussion

Generation of oxetane molecular ions from **9** to **16** in the mass spectrometer resulted in virtually complete decomposition over a range of ionizing energies (10–70 eV, source temperature 50–70 °C, direct inlet procedure). Product ions which accounted for greater than 90% of the ion current at 10 eV were assigned (1) carbonyl compound and olefin structures expected to result from formal two-bond ring cleavage and (2) protonated carbonyl structures (e.g., $Ph_2C{=}OH^+$ from **11**) resulting from formal rearrangement of hydrogen to oxetane oxygen (with cleavage).[10] Fragmentation patterns, including metastable transitions obtained independently for olefins and carbonyl compounds, accounted for secondary fragmentation of the oxetanes. Metastables were not generally observed for primary oxetane molecular ion decomposition under a limited range of conditions. The exception is the hydrogen rearrangement of **14**, the details for which are shown in Table I along with metastable ion data for the fragmentation of oxetane cleavage products.

The relative abundances of product ions as a function of ionizing energy are shown in Table II. The cleavage modes and resultant ions are identified with reference to the oxetane structures depicted in Table II and the reference formulas **17** and **18**, which illustrate the direction of formal ring cleavage (with [RA, RB] and without [A, B] hydrogen rearrangement) and the residence of charge in product fragments (e.g., B2 for

Table I. Metastable Ions Observed in Oxetane Mass Spectra[a]

Oxetane	Metastable Ion	Transformation	Assignment
9	113.7	118 → 116	$(PhCH{=}CHMe)^{+\cdot} - H_2$
10	113.7	118 → 116	$(PhCH{=}CHMe)^{+\cdot} - H_2$
11	56.7	84 → 69	$(Me_2C{=}CMe_2)^{+\cdot} - Me$
12	56.7	84 → 69	$(Me_2C{=}CMe_2)^{+\cdot} - Me$
	184.0	242 → 211	$(An_2C{=}O)^{+\cdot} - OMe$
13	113.0	117 → 115	$(PhCH{=}CHCH_2)^+ - H_2$
14	121.1	276 → 183	$(M)^{+\cdot} - (Ph_2C{=}OH)^+$
15	82.0	110 → 95	$(MeC{=}CHCH{=}CMe_2)^{+\cdot} - Me$

[a] Also observed in the spectra of the appropriate carbonyl compound or olefin.

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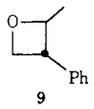
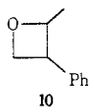
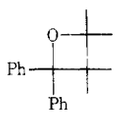
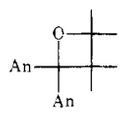
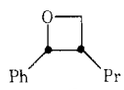
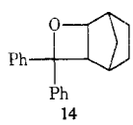
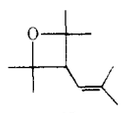
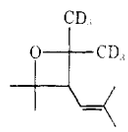
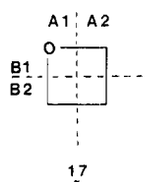
Table II. Mass Spectral Fragmentation of Substituted Oxetanes[a]

Oxetane	Registry no.	Fragmentation	m/e[b]	10 eV	15 eV	20 eV	50 eV	70 eV
 9	53699-68-6	A1	30					
		A2	118 (117)	31	29	22	25	23
		B1	44					
		B2	104	69	71	78	75	77
		RA	31					
		RB	45					
 10	53774-25-7	A1	30					
		A2	118 (117)	19	14	13	17	15
		B1	44					
		B2	104	81	86	84	83	85
		RA	31					
		RB	45					
 11	42245-06-7	A1	84 (69)	45	60	62	67	67
		A2	182 (105)	1	3	6	9	9
		B1	58 (43)	3	3	2	5	6
		B2	208 (193)	8	11	12	6	6
		RA	183	43	23	18	13	12
		RB	59					
 12[e]	56440-24-5	A1	242 (135)	12	22	20	34	33
		A2	84 (69)		2	17	25	24
		B1	58 (43)					
		B2	268 (253)	15	18	12	7	9
		RA	243	73	58	41	25	24
		RB	59					
 13	54541-25-2	A1	106 (105)	17	18	21	23	10
		A2	70	7	5	5	5	5
		B1	30	3	2	3	2	3
		B2	146 (117,115)	23	21	19	24	27
		RA	107	50	54	52	46	46
		RB	31					
 14	42245-07-8	A1	182 (105)	7	10	12	16	17
		A2	94 (79,66)	31	37	41	40	40
		B1	276[c] (248,207,191, 168,167)	29	21	18	18	16
		B2						
		RA	183	33	32	29	26	27
		RB	276[d]					
 15	31058-34-1	A1 = B1	58 (43)	11	13	13	17	14
		A2 = B2	110 (95)	81	77	78	75	81
		RA = RB	59	8	10	9	8	5
 16	65516-98-5	A1	58		9	13	16	18
		A2	116 (101,98)	39	34	29	27	26
		B1	64 (46)		4	6	8	9
		B2	110 (95)	61	48	44	40	39
		RA	59			3	3	2
		RB	64		5	6	6	6

[a] Ion intensities from two or more spectra corrected for secondary fragmentation and isotope contribution presented as percent total fragmentation (abundances <5% of base peak not generally included) according to modes indicated by reference structures **17** and **18**. [b] Numbers in parentheses indicate secondary fragment ion for which primary ion abundance was corrected. [c] Charge partitioning for cleavage B cannot be discerned. [d] RB is equivalent to the molecular ion. [e] An = p-$CH_3OC_6H_4$–.

10 = styrene molecular ion; RA for **11** = $Ph_2C{=}OH^+$). The percentages were calculated after correction was made for secondary fragmentation as determined from carbonyl compound and olefin spectra.



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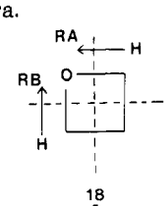

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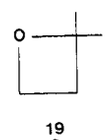
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Relative abundances of product ions were dependent on sample inlet and temperature. For example, introduction of **11** to the ion chamber via the GC inlet virtually eliminated the rearrangement mode RA (*m/e* 183) so that the cracking mode B2 (*m/e* 208) predominated. This change almost certainly results from thermal, surface catalyzed[9b] decomposition of the oxetane in the heated inlet before entering the ion chamber. The preference for fragmentation modes in oxetanes **9–16** at 10 eV, under conditions where the survival of oxetane during the introduction of sample was assured, is presented in simplified fashion in Table III, where values for A, B, and

Table III. Preferred Fragmentation Modes for Oxetanes 9–16 at 10 eV[a]

Oxetane	Fragmentation mode A	B	RA
9	31	69	
10	19	81	
11	46	11	43
12	12	15	73
13	24	26	50
14	38	29	33
15[b]	92		8
16	39	61	

[a] Entries are sums of percentages of principal fragmentations from Table II. [b] Mode A = mode B.

RA represent sums from Table II.

Patterns of structure and reactivity noted for oxetane decomposition especially at, but not confined to, low ionizing energy are as follows. (1) Hydrogen rearrangement is a principal mode of decomposition for oxetanes which are 2-aryl substituted, whereas for 3-phenyl (**9, 10**) and 3-isobutenyl (**15, 16**) substituted oxetanes simple cleavage predominates. (2) Where hydrogen rearrangement occurs readily (**11–14**), the protonated carbonyl fragment (e.g., $Ph_2C{=}OH^+$) is aryl substituted (RA ≫ RB). (3) The pattern of alkyl substitution in **11–14** does not significantly control the competition between hydrogen rearrangement and simple cleavage; the data allow that transfer of hydrogen to oxetane oxygen may occur either from a 2-alkyl or a 3-alkyl or other substituent. Since 2-phenyloxetane does not give protonated benzaldehyde appreciably,[5] transfer of the oxetane ring hydrogen in the formation of protonated carbonyls (for **13** and **14**) appears unfavorable. (4) Since the 2,4-dimethyloxetanes (**6**) but not 2,3,4,-trimethyloxetane undergo hydrogen rearrangement,[5a] a subtle stereoelectronic requirement for hydrogen transfer might have been predicted. This orientation feature for transfer hydrogen may be responsible for the diminution in RA for **14**, but the effect is small. (5) A modest cis–trans effect is observed for **9** and **10**. This influence, in which cis more than trans substituents direct the cleavage which separates them, has been noted for azetidines[4b] and lactams.[6b] (6) For **16**, a β-secondary deuterium isotope effect is observed for simple cleavage (B ≫ A). (7) Cracking of the oxetanes is regioselective, but the preferences for mode A vs. mode B and the distribution of charge within developing fragments do not fit a simple pattern.

A mechanism for oxetane decomposition involving direct generation of carbonyl and olefin fragments might include regiochemical control by substituent effects on product ion stability, as illustrated by the preferences of 2-methylcyclobutanone and 3,3-dimethylcyclobutanone for fragmentation to $(methylketene)^{+\cdot}$ and $(isobutylene)^{+\cdot}$, respectively.[6a] This control of regiochemistry and charge development is understood in terms of the relative ionization potentials[11] for ketene (9.6 eV), ethylene (10.5 eV), and isobutylene (9.2 eV) (i.e., a preference for formation of ionic fragment of lowest electron affinity).[6a] This simple analysis is not consistent for the oxetanes. Tetramethylethylene (IP = 8.3 eV) radical ion is an expected and observed major cracking fragment from **11** (A2 cleavage), and cleavage of **12** to ions of dianisyl ketone and 1,1-dianisyl-2-methylpropene (A1 and B2) is favorable, perhaps reflecting the relatively low ionization potentials for the corresponding molecules (IP's for anisole and 4-methoxybenzophenone are 8.2 and 8.8 eV, respectively). However there are anomalies in other cases. The cracking fragments of lowest electron affinity from **9** (**10**) and **13** would be the ions of substituted styrenes (a model olefin is α-methylstyrene, IP = 8.4 eV), yet the ion of styrene (IP = 8.5 eV) is favored for **9** (**10**) (B2 cleavage) and the ions of 1-phenyl-1-pentene and benzaldehyde (IP = 9.5 eV) are formed in about equal amounts from **13** (A1 and B2 cleavage). Additionally, 2,2-dimethyloxetane (**19**) gives primarily the radical ion of acetone[5b] (IP = 9.7 eV) without deference to the ionization potential of isobutylene, and 2-phenyloxetane favors benzaldehyde ion over styrene ion.[5b]

Another quantitative approach to the evaluation of substituent effects involves the assessment of the relative stability of ionic *and* neutral product pairs. Calculations have been carried out for some of the oxetanes shown in Table II, 2,2-dimethyloxetane (**19**), and unsubstituted oxetane (**20**). The data in Table IV include heats of formation which are

Table IV. Heats of Formation (kcal/mol) of Potential Products[a] and Predicted and Observed Modes of Oxetane Decomposition

Registry no.	Oxetane (H_f, M^+)		Fragmentation mode A1	A2	B1	B2	Predicted	Observed[b]
	9 (200)**	C–O	223	−28	196	−40		
		C–C	28*	221**	35	232	B2 > A2	B2 > A2
		Sum	251	193	231	192		
	11 (198)**	C–O	229	13	171	−52		
		C–C	−16	175	44*	229**	B2 > A2	A2 > B2
		Sum	213	188	215	177		
	15 (140)**	C–O	171	−52				
		C–C	−4*	187**	*c*		A2 > A1	A2 > A1
		Sum	167	135				
6245-99-4	**19** (189)**	C–O	233	−28	171	−52		
		C–C	−4	209	12	253	A2 > B1	B1 > A2[d]
		Sum	229	181	183	201		
503-30-0	**20** (208)**	C–O	223	−28	*c*			
		C–C	13	253			A2 > A1	A2 > A1[e]
		Sum	236	225				

[a] Obtained from the sum of heats of formation (25 °C) of carbonyl containing and olefinic ions and neutrals as indicated with reference to general structures **17** and **18** and the orientation of oxetane formulas in Table III and structure **19** (e.g., A1 = vertical cleavage, oxygen containing ion). Calculated heats of formation are starred (* using known group values, or ** using known group equivalents to estimate ΔH_f for neutrals along with ionization potentials: see Supplementary Material). [b] From data at 10 eV, Table II and III, except where noted. [c] Mode A = mode B. [d] Reference 5b. [e] Reference 4c.

Table V. Isotope Effects on the Direction of Cracking and Development of Charge in Product Ions for Decomposition of 16

Ionizing energy, eV	10	15	20	50	70
$(k_H/k_D)_{tot}$	1.58	1.22	1.22	1.13	1.10
$(k_H/k_D)_{tot}^{1/6}$	1.08	1.03	1.03	1.02	1.02
F_1	1.00	0.79	0.70	0.62	0.59
F_2	1.00	0.92	0.89	0.83	0.82

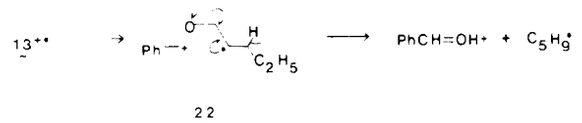
[a] Directions for cleavage and charge location are identified in structure **24.**

known,[11] or which have been calculated by the addition of known thermodynamic groups.[12] Other entries (radical ions) derive from thermodynamic group values for the corresponding molecules along with ionization potential data.[11] Heats of formation of oxetane molecular ions (ring-closed, vide infra), also included in Table IV, derive from group additivity values for oxetane molecules and the ionization potentials of model compounds (see Supplementary Material).

Predicted modes of decomposition are those yielding the product fragments calculated to have the highest stability. Agreement with experiment is good for **15** and **20** (and in general for selecting two favorable paths). The prediction is acceptable for **9** and **19** (considering probable errors in experimentally derived[11,13] and calculated[14] heats of formation) but in error for **11.** Other calculations suggest a driving force for hydrogen rearrangement–cleavage. Thus, the products of RA cleavage for **11** ($Ph_2C{=}OH^+$, ΔH_f = 160; $CH_2CMeC{\cdot}Me_2$, ΔH_f = 11; sum = 171 kcal/mol) are exceptionally stable. On the other hand, where rearrangement–cleavage is not competitive, special stability is not indicated for product pairs; for **9,** CH_2OH^+, ΔH_f = 171[11] and $CH_2CHCH{\cdot}Ph$, ΔH_f = 62 kcal/mol (sum = 233 kcal/mol); for **19,** CH_2OH^+, ΔH_f = 171[11] and $CH_2{=}CMeCH_2{\cdot}$, ΔH_f = 30 kcal/mol (sum = 201 kcal/mol). The stability of aryl-substituted protonated carbonyls ($ArRC{=}OH^+$) which appears to control the preference for and direction of hydrogen transfer would be expected to promote rearrangement for any 2-aryloxetane in which the aryl group is not electron deficient due to further substitution. It is interesting that hydrogen rearrangement with two-bond cleavage is prevalent in aliphatic acyclic ethers[16] and is not general for oxetanes substituted only with alkyl groups,[5] but returns to a competitive position in the 2-aryloxetane series.[17]

The oxetane cycloreversions are not highly endoergic (Table IV) unlike most molecular ion fragmentations (but like most

21



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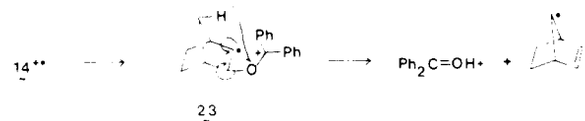

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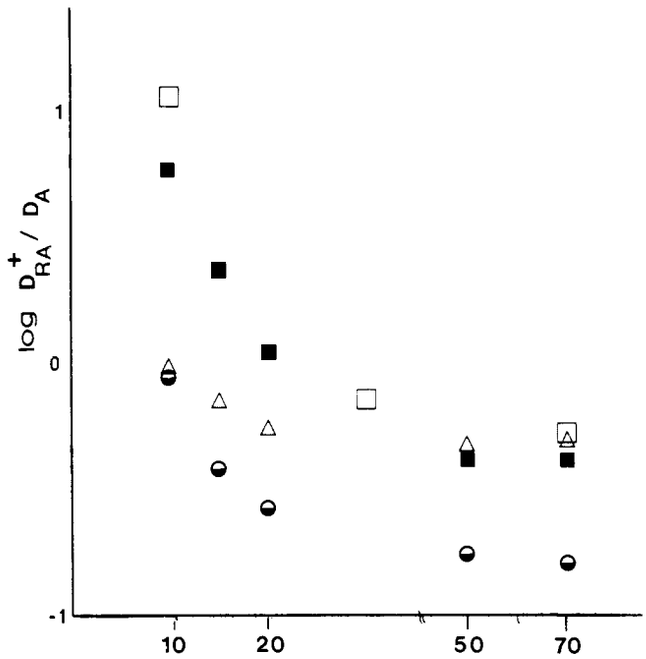


Figure 1. Competing rearrangement and simple cleavage for oxetane molecular ions **6** (□) (data from ref 5a), **11** (◒), **12** (■), and **14** (△) as a function of ionizing energy.

1,2-elimination reactions[7]). The suitability of decomposition paths need not be influenced by the relative energies of product fragments. An attractive alternative to concerted ring fragmentation is stepwise ring opening[5b] controlled by a preference in formation of valence isomeric ions. A very large fraction of the total decomposition of **11–14** (direct cleavage and cleavage–rearrangement) can be accommodated by the two-step mechanism and a preference for breaking the weaker C–C bond. Possible paths for hydrogen transfer in appropriate intermediates are illustrated in **21–23.**[20,21]

An important aspect of the competition of simple ring cleavage and hydrogen rearrangement–cleavage for **11–14** is the dependence on ionizing energy. The rise in daughter ion relative abundance for simple cleavage is shown in Figure 1 for several of the oxetanes. This familiar pattern[22] is anticipated for competing reactions in which theoretical curves depicting the dependence of reaction rate constant on ion internal energy cross. The physical picture in which the most energetic molecular ions preferably undergo simple cleavage, whereas ions of low internal energy favor rearrangement, has been commonly associated with a low activation energy and a low frequency factor for rearrangement and relatively high activation parameters for simple cleavage.[22a] The inference in the present case is that rearrangement proceeds through a tighter activated complex than simple cracking; i.e., that hydrogen transfer is an integral part of the product-determining step which gives $(carbonyl + 1)^+$ ions. Since the dependence of daughter ion ratios on beam energy is found for oxetanes of varying structure, the effect is indeed more likely a potential surface phenomenon than an artifact of internal energy distribution.

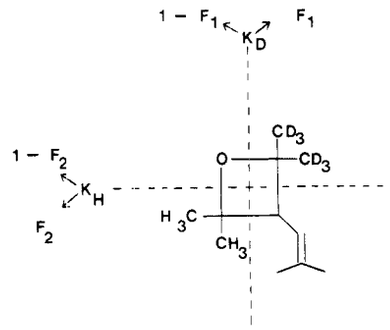
Exploiting the symmetry of **15** and the availability of specifically labeled **16,** we have measured a β-secondary deuterium isotope effect on oxetane cleavage. Data from Table II may be used to calculate a total isotope effect on the direction of cleavage according to eq 1. Scrambling of the deuterium

$$\left(\frac{k_H}{k_D}\right)_{tot} = \frac{(\text{diene-}d_0)^{+\cdot} + (\text{acetone-}d_6)^{+\cdot}}{(\text{diene-}d_6)^{+\cdot} + (\text{acetone-}d_0)^{+\cdot}} = \frac{B1 + B2}{A1 + A2} \quad (1)$$

Table VI. Mass Spectra (20 eV) of Ketones and Olefins Important in the Mass Spectral Fragmentation of Substituted Oxetanes

Registry no.	Compd	M^+	*m/e* (% base)
100-42-5	$PhCH{=}CH_2$	104	104 (100), 103 (10), 78 (15)
873-66-5	PhCH=CHMe (trans)	118	119 (12), 118 (100), 117 (61)
766-90-5	PhCH=CHMe (cis)	118	119 (10), 118 (100), 117 (75)
563-79-1	$Me_2C{=}CMe_2$	84	84 (100), 69 (66), 56 (7), 55 (7)
781-33-9	$Ph_2C{=}CMe_2$	208	209 (19), 208 (100), 207 (7), 193 (19), 179 (8), 130 (9), 115 (7)
67-64-1	$Me_2C{=}O$	58	58 (33), 43 (100)
119-61-9	$Ph_2C{=}O$	182	183 (24), 182 (100), 105 (67)
666-52-4	$(CD_3)_2C{=}O$	64	64 (45), 46 (100)
498-66-8	Norbornene	94	95 (9), 49 (19), 82 (16), 79 (21), 57 (33), 66 (100)
764-13-6	2,5-Dimethyl-2,4-hexadiene	110	111 (15), 110 (95), 95 (100), 67 (40)
65516-99-6	*cis*-3-(2,2-Diphenylethenyl)cyclopentanecarboxaldehyde	276	277 (14), 276 (47), 258 (12), 248 (30), 207 (100), 191 (40), 180 (92), 168 (90), 167 (81), 166 (20), 165 (63), 152 (23), 129 (28), 128 (58), 115 (43), 91 (81), 85 (41), 83 (55), 81 (19), 77 (27), 59 (38)

label was not apparent, since acetone and diene product ions with intermediate deuteration were not observed. The distribution of label in product ions results from a selection of fragmentation mode and a residence of charge as shown with dissected structure **24**, where k_H and k_D refer to cleavage



24

modes and F_1 and F_2 refer to the fractional distribution of charge for formation of diene-d_6 and diene-d_0, respectively. Using the (B1 + B2)/(A1 + A2) ratios and the individual ion ratios, F_1 and F_2 are calculated using eq 2 and 3. The results

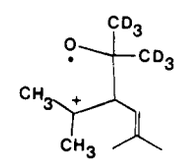
$$\frac{(\text{diene-}d_0)^{+\cdot}}{(\text{diene-}d_6)^{+\cdot}} = \left(\frac{k_H}{k_D}\right)_{tot}\left(\frac{F_2}{F_1}\right) \quad (2)$$

$$\frac{(\text{acetone-}d_0)^{+\cdot}}{(\text{acetone-}d_6)^{+\cdot}} = \left(\frac{k_D}{k_H}\right)_{tot}\left(\frac{1-F_1}{1-F_2}\right) \quad (3)$$

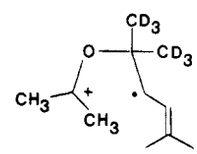
including the values of the isotope effect per deuterium are shown in Table V.

The isotope effect, which represents a ratio of rates for cleavage averaged over the distribution of internal energies of ions undergoing decomposition, is at a maximum at low ionizing energy, paralleling the behavior (temperature dependence) for most isotope effects in molecular thermal chemistry[23] and that of a primary deuterium isotope effect observed for mass spectral decomposition.[24] If ratios of daughter ion abundances at low voltage reflect ratios of rate constants for decomposition of **16**, the isotope effect (1.08 at 10 eV) may be nominally compared with k_H/k_D values (per deuterium) for nucleophilic substitution of labeled secondary and tertiary substrates in solution (limiting solvolyses, k_H/k_D = 1.09–1.10).[25] Another reference point is the negligible β-secondary effect (k_H/k_D = 1.00) observed[26] for a thermal retrograde Diels–Alder reaction in which rate-determining homolytic C–C cleavage is presumably important.

A mechanistic problem remains in that the isotope effect in **16** is more consistent with a two-step path involving initial C–O cleavage than one in which preliminary C–C cleavage is important (as proposed above for aryl-substituted systems). If ring opening of the molecular ion is akin to heterolysis in solvolysis chemistry and $k_H/k_D > 1.0$,[25] ions **25** and **26** would



25



26

be favored for C–O and C–C cleavages, respectively. Only **25** leads to the preferred distribution of product ions so that either an "inverse" isotope effect on C–C cleavage is important, C–O cleavage leads the decomposition of **16** (**15**), or another mechanism such as concerted (two-bond) fragmentation prevails. In the transition state for concerted cracking, charge would be partially developed in one or the other of the nascent fragments. The preference for charge residence (F_1 and F_2 values) and the effects of ionizing energy and isotopic substitution thereon are not surprising (ionization potentials for acetone and 2,5-dimethyl-2,4-hexadiene are 9.7 and 7.9[27] eV, respectively). A direct cleavage mechanism with a normal isotope effect influencing the stability of developing charge would rationalize the data.[28]

Although a unified mechanism for oxetane cleavages does not emerge from our study in combination with earlier work,[5] it remains the case that for oxetanes substituted with aryl groups a mechanism involving cleavage of the "weaker" C–C bond followed by the partitioning of tautomeric molecular ions to cleavage products with and without hydrogen rearrangement is consistent with the observed directional selectivity and thermochemistry. A comparison with pyrolysis data is instructive. The effects of substituents on regio- and stereochemistry and on rates of cracking **9**–**11**[9b] are consistent with the intervention of diradicals which result from selective C–C cleavage (analogues of **21** and **22**). Whether these species are bona fide intermediates or descriptions of transitions states is unclear, but the evidence clearly supports a discontinuity between bond breaking and bond making for the reaction profile. The correspondence in the direction of cleavage for pyrolytic and mass spectral decompositions may be fortuitous or may depend on prevailing forces of orbital topology and

symmetry. There have been recent references to orbital symmetry imposed barriers to "four-electron" fragmentation[29] and rearrangement[30] under electron impact. The issue, as applied to oxetane cleavage, involves the potential electronic destabilization predicted for a geometrically favorable (roughly C_{2v}) transition state for concerted decomposition. Molecules could avoid barriers imposed by such unfavorable electronics through discontinuous or stepwise cracking (thermal or under electron impact). Similar mass spectral and thermal regiochemistries then result from a coincidence of substituent influences on the stability of diradicals and tautomeric radical ions.[31]

Experimental Section

Synthesis of the oxetanes,[33] *cis*- and *trans*-2-methyl-3-phenyloxetane (**9** and **10**),[34] 2,2-diphenyl-3,3,4,4-tetramethyloxetane (**11**),[35] 2,2-bis(*p*-methoxyphenyl)-3,3,4,4-tetramethyloxetane (**12**),[35] 2-phenyl-3-propyloxetane (**13**),[36] 4,4-diphenyl-3-oxatricyclo[4.2.1.0^{2,5}]-nonane (**14**),[37] and 2,2,4,4-tetramethyl-3-(2,2-dimethylethenyl)oxetane (**15**),[38] followed literature procedures. 2,2-Bis(trideuteriomethyl)-3-(2,2-dimethylethenyl)-4,4-dimethyloxetane (**16**)[39] was prepared using acetone-d_6 (99.5%, Stohler Isotope Chemicals) following the procedure for **15**. NMR analysis indicated that deuterium label was not scrambled during the photochemical cycloaddition procedure; i.e., **16** was >97% 2,2-dimethyl-d_6. Most of the reference carbonyl compounds and olefins were commercially available. The 1,1-diaryl-2-methylpropenes[40] and *cis*-3-(2,2-diphenylethenyl)cyclopentanecarboxaldehyde[37] were prepared following literature procedures.

Mass Spectra. Spectra were recorded on a Hitachi Perkin-Elmer RMU-6L instrument (chamber temperature 50–70 °C) using a direct sample insertion procedure and base-washed sample holders. Product ions were identified with reference to the spectra of proposed ketone and olefin cracking fragments obtained independently (Table VI) or assigned on the basis of literature data.[41]

Ion intensities were averaged from duplicate runs (average deviation generally 1.0%), primary ion abundances were corrected for secondary fragmentation (along with isotope corrections where necessary), and relative final intensities computed as percent abundance to produce the data in Table II.

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Supplementary Material Available: relative abundances of ions in oxetane mass spectra (Table VII) and details of calculations of heats of formation for radical ions (19 pages). Ordering information is given on any current masthead page.

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