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MASS SPECTRAL DECOMPOSITION OF ARYLOXETANES.

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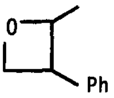
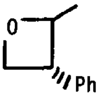
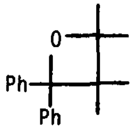
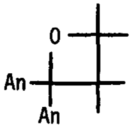
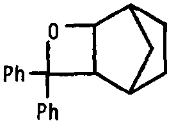
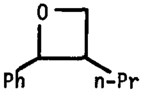
The decomposition of simply substituted oxetanes under electron impact has been reported.[1] Simple ring cleavage into carbonyl and olefin fragments dominates even at high voltage. Hydrogen rearrangement with two-bond cleavage, a common fragmentation for acyclic ethers,[2] has been noted only for 2,4-dimethyloxetane.[1a] We note here the special importance of hydrogen transfer with cleavage for aryloxetanes, the dependence on substituent pattern and energetics for its prominence in competition with simple cracking, and the regioselectivity for simple cracking which disregards product ion stability.

Fragmentation data for oxetanes 1 - 6 are shown in the Table. Cracking and rearrangement ions accounted for >95% of current at 10 eV. Product ions are identified with reference to the orientation of structures in the Table and general structure 7, which indicates direction of cleavage and residence of charge. Spectra of the corresponding carbonyl compounds and olefins were used to identify oxetane secondary fragmentation, for which primary ion abundances were corrected. Rearrangement ions (mode R) were identified as $Ar_2C=OH+$ (for 3 - 5) and PhCH=OH+ (for 6).

Structure-reactivity patterns are as follows: (1) 2-Aryl substitution promotes rearrangement and directs hydrogen transfer to give aryl substituted protonated carbonyl ions. (2) The pattern of alkyl substitution in 3 - 6 does not significantly control the competition between rearrangement and simple cleavage; the source of transfer

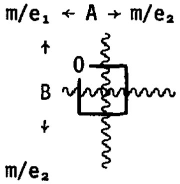
Table. Mass Spectral Data for Aryloxetanes at 10 eV.[a]

Oxetane		Mode	m/e_1	m/e_2	% Rel. Abundance[b]
1		A	-	118 (31)	31
		B	-	104 (69)	69
		R	-	-	-
2		A	-	118 (19)	19
		B	-	104 (81)	81
		R	-	-	-
3		A	182 (1)	84 (45)	46
		B	58 (3)	208 (8)	11
		R	183 (43)	-	43
4[c]		A	242 (12)	-	12
		B	-	268 (15)	15
		R	243 (73)	-	73
5		A	182 (7)	24 (31)	38
		B	276 (29)	-	29
		R	183 (33)	-	33
6		A	106 (17)	70 (7)	24
		B	30 (3)	146 (23)	26
		R	107 (50)	-	50

[a] % rel abundance in parenthesis

[b] Sums of % rel abundance according to mode

[c] An = p-MeOC$_6$H$_4$-



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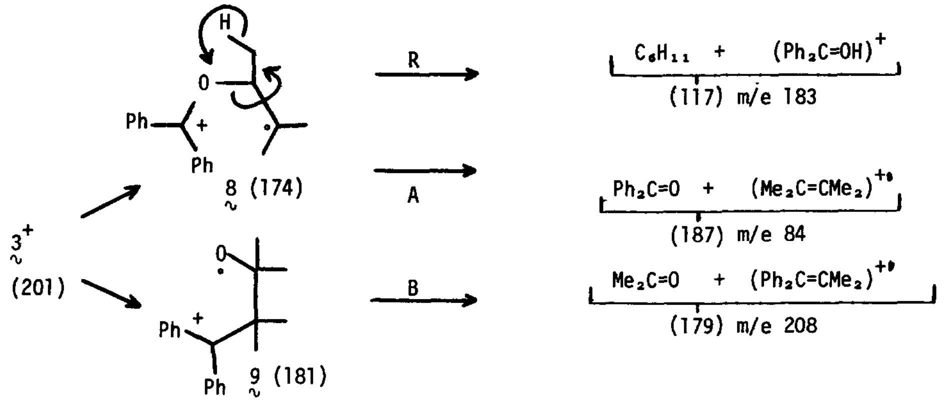
hydrogen may be a substituent at the 2 or 3 ring positions with little if any stereoelectronic requirement. (3) Ring cleavage (A *vs*. B) is regioselective. (4) A modest stereochemical dependence (a cis-trans effect[3]) on cracking is apparent for **1** and **2**.

It is important to understand whether oxetane fragmentation is controlled by product fragment stability or by a tendency to initially break the weakest bond. Considering simple cracking alone, the stability of product ions might have been a controlling feature as in other four-membered ring decompositions.[4] The fragments of lowest electron affinity are the substituted styrenes[5] for **1**,**2** (m/e 118), and **6** (m/e 146) and the diaryl olefins for **3** (m/e 208), **4** (m/e 268), and **5** (m/e 276). In fact, cleavage to these products is barely competitive. Additionally, 2,2-dimethyloxetane gives primarily the radical ion of acetone[1b] (IP = 9.7 eV) without deference to the low ionization potential of isobutylene (9.2 eV), and 2-phenyloxetane favors benzaldehyde ion over styrene ion.[1b]

Thermodynamic control may also be assessed with reference to heats of formation of ionic *and neutral* fragments. Values for the molecular ion, possible ring opened intermediate ions, and possible fragmentation products have been estimated for **1** - **4** using the group additivity method.[6] The results for **3** are representative and illustrated in part below. The calculated heats of formation (kcal/mol) indicate an *exothermicity* for fragmentation (consistent with negligible molecular ion intensity) and a special driving force for rearrangement, the stability of $Ph_2C{=}OH^+$. Overall product stability does not control, however, the regioselectivity of cracking (A vs. B). A preference for intermediate **8** over **9** does rationalize the data and provides a convenient route for rearrangement.[7] Regioselectivity is then viewed as a competition of ring opening modes[1] with subsequent importance of product stability in a second step.

Our results highlight special features of small ring decomposition under electron impact: (1) the small number of competing fragmentations; (2) large substituent influences which provide structure-reactivity relationships for fundamental cleavage processes; and (3) the potential exothermicity of decomposition (unlike most mass spectral fragmentations) which results in the intervention of mechanistic factors other than product development control.



ACKNOWLEDGEMENT

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REFERENCES AND NOTES

(1) (a) K. Pihlaja, K. Polviander, R. Keskinen, and J. Jalonen, Acta Chem. Scand., 25, 765 (1971); (b) P.O.I. Virtanen, A. Karjalainen, and H. Ruotsalainen, Suomen Kemistilehti B, 43, 219 (1970).

(2) F.W. McLafferty, Anal. Chem., 29, 1782 (1957).

(3) M.B. Jackson, T.M. Spotswood, and J.H. Bowie, Org. Mass. Spectrometry, 1, 857 (1968).

(4) H. Audier, J.M. Conia, M. Fetizon, and J. Gore, Bull. Soc. Chim. France, 787 (1967).

(5) The alkyl styrenes should have IP's similar to α-methylstyrene (8.4 eV) while those of the diaryl olefins should be much lower. Other IP reference points (in eV) are tetramethylethylene (8.3), styrene (8.5), benzaldehyde (9.5) and benzophenone (9.4).

(6) S.W. Benson, "Thermochemical Kinetics," John Wiley and Sons, Inc., N.Y., 1968; (b) J.L. Franklin, J. Chem. Phys., 21, 2029 (1953); (c) New thermodynamic groups generated for these estimates will be reported in the full paper.

(7) The ratio R/A as a function of ionizing energy is consistent with the competition of reactions with tight and loose transition states; see G. Jones, II and L.P. McDonnell, Org. Mass. Spectrometry, 10, 1 (1975).