Notes

Mass Spectrometry of 1-Substituted Adamantanes. The Effect of Functional Groups on the Primary Fragmentation Pathways[1]

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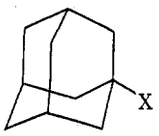
We wish to report on the primary fragmentation pathways of a number of 1-substituted adamantanes, **1** (abbreviated to 1-AdmX), in the light of current interest in mass spectral behavior of adamantanes.[2-8]



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This analysis addresses itself to the origin of the most abundant ions only, Table I, since further fragmentations of these produce similar spectra of lower abundance ions.[9] The fate of the molecular ion of **1** is conveniently classified according to one of the three recognized processes: (a) loss of the substituent, X, as a radical to produce the even-electron ion at *m/e* 135, (b) loss of the neutral molecule, HX, to produce the odd-electron ion at *m/e* 134, and (c) loss of the C_4H_9 hydrocarbon radical to produce an M − 57 ion.

For compounds which produced their most abundant ions by paths a and b, low molecular ion abundance was characteristic, the average from 20 compounds being 10%. For compounds where the base peak arose *via* path c, much higher molecular ion abundance was found, the average from eight compounds being 40%.

Sulfur-Linked Substituents.—Our recent synthetic work on antiradiation drugs[8,10] provided a series of 1-adamantyl sulfides and related compounds[8] [**1**, X = SH,[4] SCH_3, $S(CH_3)_2{}^+I^-$,[11] $S(CH_2)_2NH_2$, $S(CH_2)_5NH_2$, $S(CH_2)_2NHCOC_6H_5$, $S(CH_2)_2NHSO_2C_6H_4CH_3$-*p*, $S(CH_2)_2NHC(=NH)CH_2Cl$, $SCOCH_3$,[11] and $SC(=NH)NH_2$]. Members of this series exhibit a relatively weak molecular ion (2–15% of base peak) which loses the substituent X as a radical to form the stable 1-adamantyl ion, *m/e* 135 (100%).

With the introduction of nitrogen-containing groups into the side chain, other noteworthy ions appear. In the spectrum of **1**, X = $SCH_2CH_2NH_2$, an ion at *m/e* 182 (26%) appears due to the loss of $CH_2{=}NH$ from the parent ion to produce the equivalent to $[1\text{-Adm}SCH_3]^+$. Conversion of the above amine to its benzamide, *p*-toluenesulfonamide, or amidine, represented by 1-Adm$S(CH_2)_2NHY$, produces an ion at *m/e* 194 (18–32%) indicative of the elimination of YNH_2 from the substituent to give $[1\text{-Adm}SCH{=}CH_2]^+$.

For sulfur-linked substituents, bond cleavage of either side of the sulfur atom can also occur, with the charge being retained by the substituent group. For example, in the spectrum of 1-Adm$S(CH_2)_5NH_2$, an abundant fragment at *m/e* 86 (95%) is accounted for by C–S bond cleavage with the loss of 1-adamantyl radical, the charge being retained by the substituent group to produce a $C_5H_{12}N$ ion. An ion also appears in less abundance at *m/e* 118 (18%), representing cleavage of the other C–S bond to produce the $C_5H_{12}NS$ ion. As the complexity of the side chain increases, other processes may lead to the base peak. For example, in 1-Adm$S(CH_2)_5NHCOC_6H_5$, the base peak is *m/e* 105, ($C_6H_5CO^+$) which is not at all unusual, while the *m/e* 135 ion abundance diminished to 5%. However, cleavage of the bridgehead adamantane sulfur bond produces a strong $C_{12}H_{16}NOS$ ion, *m/e* 222 (M − 135, 31%). Among the few ions with 5% abundance or over in this spectrum was one for sulfur side chain cleavage to produce a $C_{12}H_{16}NO$ ion (*m/e* 190, 5%).

Oxygen-Linked Substituents.—Unlike the relatively simple 1-adamantanethiol derivatives for which only one of the major modes of molecular ion decomposition is observed, ethers and esters based on 1-adamantanol may follow any of the three pathways mentioned above. However, for a given compound, one mode usually predominates. 1-Adamantanol (**1**, X = OH), on electron bombardment, produces an M − 57 ion as the base peak and indeed with a very minor contribution from the 1-adamantyl ion at *m/e* 135 (5%).[2,4,7] A similar fragmentation is shown by the ethyl ether (**1**, X = OC_2H_5[8]) with the M − 57 ion as the base peak and the *m/e* 135 ion at 19% abundance. Apparently, the amine function in the ether side chain stabilizes the radical produced by substituent cleavage and reverses the above trend. Thus, when X in **1** is $O(CH_2)_2NH_2$,[8] $O(CH_3)_3NH_2$,[12] $OCH(CH_3)CH_2NH_2$,[12] and $O(CH_2)_2NHC(=NH)CH_2Cl$,[8] the base peak was the *m/e* 135

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(9) All ions in the 70-eV mass spectra (5% or over of the base peak) up to *m/e* 28 will appear following these pages in the microfilm edition of this volume of the journal. Single copies may be obtained from the Business Operations Office, Books and Journals Division, American Chemical Society, 1155 Sixteenth St., N.W., Washington, D. C. 20036, by referring to code number JOC-73-1042. Remit check or money order for $3.00 for photocopy or $2.00 for microfiche.

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TABLE I
PRINCIPAL IONS IN FRAGMENTATIONS OF 1-ADMX

X	Mol ion *m/e* (rel int)	*m/e* 135 rel int	*m/e* 134 rel int	[M − 57] ion (rel int)	Registry no.
SH	168 (10)	100		111 (2)	34301-54-7
SCH_3	182 (13)	100			34895-33-5
$S(CH_2)_2NH_2$	211 (6)	100			30771-87-0
$S(CH_2)_2NHCOC_6H_5$	315 (4)	100			30771-90-5
$S(CH_2)_2NHSO_2C_6H_4CH_3$-*p*	365 (2)	100			30771-91-6
$S(CH_2)_2C(=NH)CH_2Cl\cdot HCl$	288 (<1)	100			37817-01-9
	286 (2)				
$S(CH_2)_5NH_2$	253 (4)	100			30771-89-2
$S(CH_2)_5NHCOC_6H_5$	357 (0)	4	5		37817-02-0
$SCOCH_3$	210 (7)	100			37817-03-1
$SC(=NH)NH_2\cdot HBr$	210 (8)	100			30771-94-9
$S(CH_3)_2{}^+I^-$	324 (0)	100			37818-84-1
OH	152 (25)	5		95 (100)	768-95-6
OCH_2CH_3	180 (40)	19		123 (100)	6221-75-6
$O(CH_2)_2NH_2$	195 (13)	100			25225-13-2
$O(CH_2)_3NH_2$	209 (<1)	100		152 (9)	21624-07-7
$OCH(CH_3)CH_2NH_2$	209 (1)	100	3	152 (2)	21623-91-6
$O(CH_2)_2NHC(=NH)CH_2Cl\cdot HCl$	272 (0)	100			30771-83-6
	270 (<1)				
$OCOCH_3$	194 (4)	21	100		22635-62-7
$OCOCH_2CH_3$	208 (5)	57	100		37818-91-0
NH_2	151 (65)			94 (100)	768-94-5
$NHCH_3$	165 (22)			108 (100)	3717-38-2
$N(CH_3)_2$	179 (80)	15		122 (100)	3717-40-6
$NH(CH_2)_2NH_2$	194 (2)	100			37821-93-2
$NH(CH_2)_2OH$	195 (4)	100		138 (26)	3716-66-3
$NH(CH_2)_3OH$	209 (23)	61	9	152 (100)	19984-59-9
$NHCOCH_3$	193 (30)	25	25	136 (100)	880-52-4
$NHCONH_2$	194 (38)	9		137 (84)	13072-69-0
N=C=S	193 (16)	100	2		4411-26-1
CH_2NH_2	165 (29)	100			17768-41-1
$CONH_2$	179 (24)	100			5511-18-2
C≡N	161 (62)	10	100	104 (18)	23074-42-2
C_6H_5	212 (80)	<1		155 (100)	780-68-7

ion and the M − 57 ion is either absent or in low abundance (10%).

The loss of HX as the chief fragmentation mode is observed in several 1-adamantyl esters. When X = $OCOCH_3$[13] or $OCOCH_2CH_3$[11] in **1**, elimination of the corresponding carboxylic acid molecule produces the parent ion at *m/e* 134, with a smaller loss of the X moiety alone to give the *m/e* 135 ion in 21 and 57% relative abundance, respectively.

Nitrogen-Linked Substituents.—For the nitro[2] and isothiocyanato compounds (**1**, X = NO_2 and N=C=S), *m/e* 135 is the base peak with little contribution from the other pathways (<2%).

Loss of the X substituent as a radical from the parent ion of simple amines [**1**, X = NH_2,[2,7] $NHCH_3$,[10] and $N(CH_3)_2$[2]] is not favored (<15%), and the base peak in each instance arises from the M − 57 ion. In some polyfunctional amines apparent stabilization of the substituent group as a leaving radical again occurred such that for **1**, when X = $NH(CH_2)_2OH$[13] and $NH(CH_2)_2NH_2$,[14] the parent ion was the adamantyl ion, *m/e* 135, and the contribution from the M − 57 ion was reduced to 26 and less than 2%, respectively. However, in the spectrum of an homologous amino alcohol, **1**, X = $NH(CH_2)_3OH$,[15] the M − 57 ion is restored as the base peak, with a *m/e* 135 fragment amounting to 61%.

Decomposition of the molecular ion of 1-acetamidoadamantane[2] (**1**, X = $NHCOCH_3$) involves all three modes of fragmentation, with the M − 57 ion as the base peak. The loss of X and HX also occurs since the *m/e* 134 and 135 ions are present, both in 25% relative abundance. 1-Adamantylurea (**1**, X = $NHCONH_2$) is unique in that neither the M − 57 ion (84%) nor the *m/e* 135 ion (9%) but an ion at *m/e* 94 represents the base peak. The ion can be attributed to the loss of 43 (HNCO) from the M − 57 ion.

Carbon-Linked Substituents.—The fragmentation results in *m/e* 135 ion as the base peak when the substituents, X, in **1** are alkyl,[2] cycloalkyl,[2] CH_2OH,[2] $COCH_3$,[2] $CO_2C_2H_5$,[2] CH_2COCH_3,[6] $(CH_2)_2CO_2H$,[16] and from the present study, CH_2NH_2[17] and $CONH_2$. In a surprising departure from this pattern the molecular ion from 1-adamantanecarbonitrile (**1**, X = CN) eliminates HCN to create *m/e* 134 (100%) and gives rise to a small M − 57 ion (18%), while the *m/e* 135 ion is completely absent.

Not all carbon-linked substituents conform to either of these two patterns, since 1-phenyladamantane[2] (**1**,

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X = C_6H_5) has the M − 57 ion as base peak and the *m/e* 135 and 134 ions are absent. Apparently, different types of carbon-linked substituents control fragmentation of the molecular ions, albeit paths a, b, and c are predominantly involved.

Phosphorus-Linked Substituents.—In a recent report,[18] the mass spectrum of methyl 1-adamantanephosphonate [1, X = $P(O)(OCH_3)_2$] indicates that the 1-adamantyl ion, *m/e* 135, is also the base peak.

Registry No.—1-AdmO$(CH_2)_2NH_2\cdot$HCl, 21623-89-2; 1-AdmNHCH$_3\cdot$HCl, 3717-39-3; 1-AdmNH$(CH_2)_2$-$NH_2\cdot$HCl, 37819-00-4; 1-Adm$CH_2NH_2\cdot$HCl, 1501-98-0.

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Kinetics of the Peracid Oxidation of Acetylenes. Electrophilic Attack on Phenylacetylenes[1]

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The peracid oxidation of phenyl- and diphenylacetylenes suggests the rate-determining primary formation of oxirenes.[2]

An oxirene intermediate was verified in the peracid oxidation of cyclodecyne,[3] the Wolff rearrangement,[4] and the reaction of methylene with carbon monoxide.[5] Earlier reports[6-8] postulated an electrophilic attack of peracid on a triple bond, but the higher reactivity of triple-bond carbon toward nucleophiles[9] might enable a nucleophilic attack of peroxide ion to occur. Contrary to the anticipation, our kinetic data on the perbenzoic acid (PBA) oxidation of phenylacetylenes showed an electrophilic attack alone as shown below and added an example of electrophilic addition to triple bond similar to the acid-catalyzed hydration.[10]

Results and Discussion

The rate of the reaction of phenylacetylene with perbenzoic acid (PBA) was measured in benzene at 25.0°. The rate was expressed as eq 1.

$$v = k[\text{PhC}{\equiv}\text{CH}][\text{PBA}] \quad (1)$$

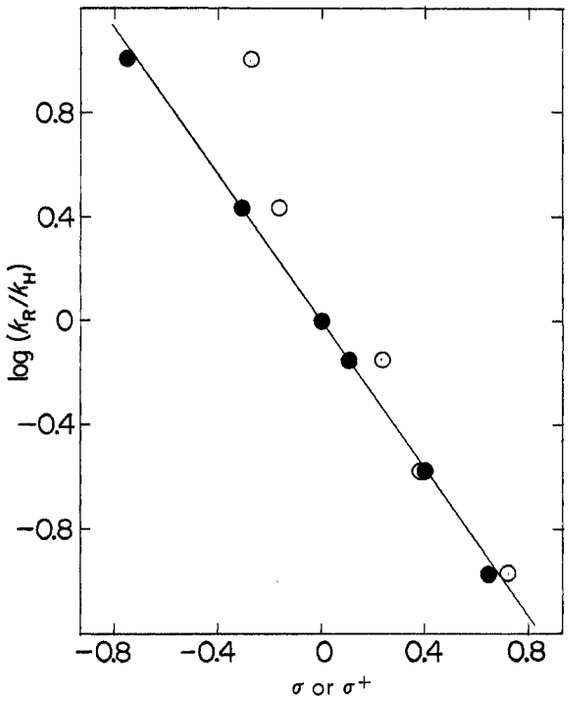

Figure 1.—Hammett plot for the reaction of substituted phenyl acetylenes with perbenzoic acid at 25.0°: open circle, σ; closed circle, σ^+.

TABLE I
RELATIVE RATE CONSTANTS (k_R/k_H) FOR THE REACTION OF SUBSTITUTED PHENYLACETYLENES WITH PERBENZOIC ACID IN BENZENE AT 25.0° ± 0.1°[a]

Registry no.	R in $RC_6H_4C{\equiv}CH$	Relative second-order rate constant (k_R/k_H)
768-60-5	*p*-MeO	10.2[c]
766-97-2	*p*-Me	2.67[b]
536-74-3	H	1.00
873-73-4	*p*-Cl	0.680[b]
766-81-4	*m*-Br	0.263[c]
3034-94-4	*m*-NO_2	0.108[c]

[a] Initial concentrations: [$PhCO_3H$], 0.2–0.4 *M*; [$RC_6H_4C{\equiv}$CH], 0.06–0.25 *M*. [b] Probable error: ±1%. [c] Probable error: ±2%.

The second-order rate constant *k* (1.65×10^{-5} M^{-1} sec^{-1}) with excess phenylacetylene calculated from the pseudo-first-order rate constant agreed with that with excess PBA (1.44×10^{-5} M^{-1} sec^{-1}). This fact shows that phenylacetylene reacts with PBA in a molar ratio of *ca.* 1:1 under these conditions.[11]

Relative rates for substituted phenylacetylenes were determined by the competitive reaction as shown in Table I. The Hammett plot (Figure 1) gives a satisfactory straight line with σ^+ value[12] to give a ρ value of −1.40 with a correlation coefficient *r* of 0.999. The negative ρ value suggests an electrophilic attack of

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