The Mass Spectra of Small-ring Heterocycles. III. Aroylaziridines

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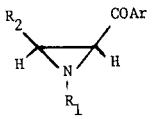
Received January 27, 1972

The mass spectra of *cis-trans* isomeric aroylaziridines are presented. Attempts to extend the method for distinguishing between *cis* and *trans* isomers previously established for aroylazetidines are described and the results rationalized. A simple fission of the 1-alkylnitrogen bond is described and detailed fragmentation mechanisms are presented and discussed.

No reference to the mass spectra of aroylaziridines has appeared in the chemical literature. In conjunction with other studies being carried out in this laboratory (2), and in an attempt to extend the method previously established for distinguishing between *cis* and *trans* isomers in the case of aroylazetidines (3a), the mass spectra of the following aroylaziridines were determined: *trans* 1-cyclohexyl-2-phenyl-3-benzoylaziridine (*t*-I, Fig. 1), *cis*-1-cyclohexyl-2-phenyl-3-benzoylaziridine (*c*-I, Fig. 2), *trans*-1-benzyl-2-phenyl-3-benzoylaziridine (*t*-II, Fig. 11), *cis*-1-benzyl-2-phenyl-3-benzoylaziridine (*c*-II, Fig. 12), *trans*-1-cyclohexyl-2-phenyl-3-*p*-methylbenzoylaziridine (*t*-III, Fig. 13), *cis*-1-cyclohexyl-2-phenyl-3-*p*-methylbenzoylaziridine (*c*-III, Fig. 14), *trans*-1-cyclohexyl-2-methyl-3-*p*-phenylbenzoylaziridine (*t*-IV, Fig. 15), *cis*-1-cyclohexyl-2-methyl-3-*p*-phenylbenzoylaziridine (*c*-IV, Fig. 16), *trans*-1-ethyl-2-phenyl-3-benzoylaziridine (*t*-V, Fig. 17), *cis*-1-ethyl-2-phenyl-3-benzoylaziridine (*c*-V, Fig. 18), *trans*-1-*i*-propyl-2-*p*-biphenyl-3-benzoylaziridine (*t*-VI, Fig. 19), *cis*-1-*i*-propyl-2-*p*-biphenyl-3-benzoylaziridine (*c*-VI, Fig. 20), *trans*-1-ethyl-2-*p*-biphenyl-3-benzoylaziridine (*t*-VII, Fig. 21), *trans*-1-*t*-butyl-2-*p*-biphenyl-3-benzoylaziridine (*t*-VIII, Fig. 22), *trans*-1-methyl-2-*p*-biphenyl-3-benzoylaziridine (*t*-IX, Fig. 23), *cis*-1-*i*-propyl-2-phenyl-3-benzoylaziridine (*c*-X, Fig. 24) and *trans*-1-*t*-butyl-2-phenyl-3-benzoylaziridine (*t*-XI, Fig. 25).

In addition, in order to confirm the proposed overall fragmentation pattern for the aziridines, the mass spectra of the following deuterated aziridines were determined: *trans*-1-cyclohexyl-2-phenyl-3-deuterio-3-benzoylaziridine (*t*-IA, Fig. 3), *cis*-1-cyclohexyl-2-phenyl-3-deuterio-3-benzoylaziridine (*c*-IA, Fig. 4), *trans*-1-cyclohexyl-2-deuterio-2-phenyl-3-benzoylaziridine (*t*-IB, Fig. 5), *cis*-1-phenyl-2-deuterio-2-phenyl-3-benzoylaziridine (*c*-IB, Fig. 6), *trans*-



	R_1	R_2	Ar
Pair I (*t*-I and *c*-I)	C_6H_{11}	C_6H_5	C_6H_5
Pair II (*t*-II and *c*-II)	$CH_2C_6H_5$	C_6H_5	C_6H_5
Pair III (*t*-III and *c*-III)	C_6H_{11}	C_6H_5	*p*-$CH_3C_6H_4$
Pair IV (*t*-IV and *c*-IV)	C_6H_{11}	CH_3	*p*-$C_6H_5C_6H_4$
Pair V (*t*-V and *c*-V)	C_2H_5	C_6H_5	C_6H_5
Pair VI (*t*-VI and *c*-VI)	*i*-C_3H_7	*p*-$C_6H_5C_6H_4$	C_6H_5
t-VII	C_2H_5	*p*-$C_6H_5C_6H_4$	C_6H
t-VIII	*t*-C_4H_9	*p*-$C_6H_5C_6H_4$	C_6H_5
t-IX	CH_3	*p*-$C_6H_5C_6H_4$	C_6H_5
c-X	*i*-C_3H_7	C_6H_5	C_6H_5
t-XI	*t*-C_4H_9	C_6H_5	C_6H_5

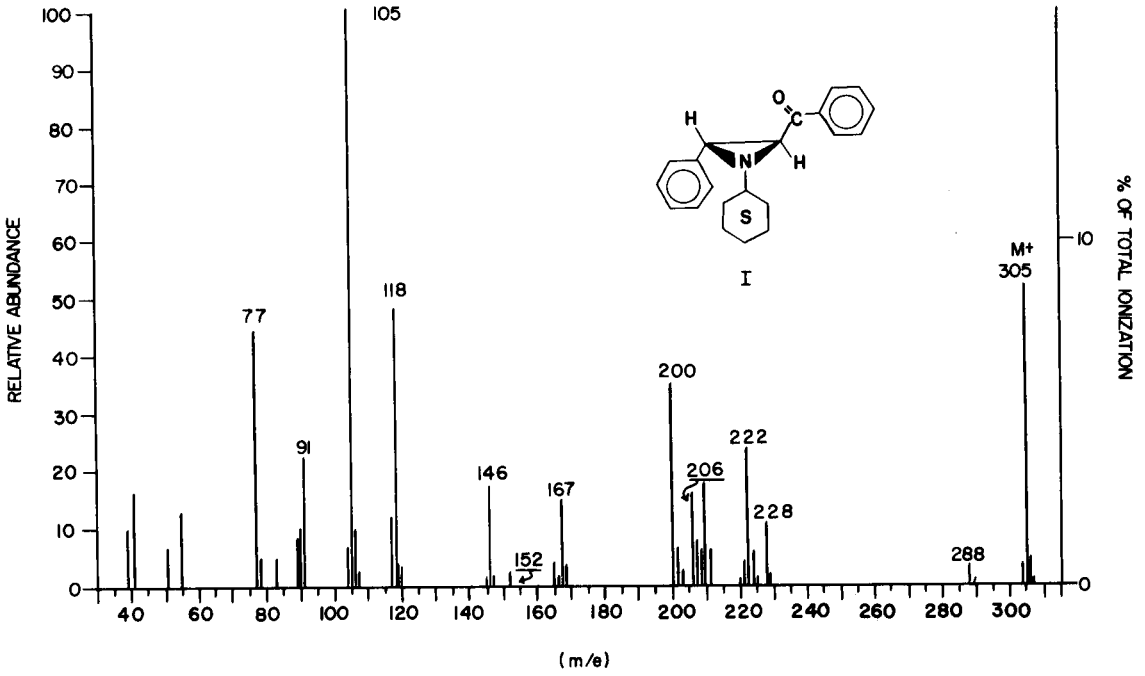


Fig. 1. The mass spectrum of *trans*-1-cyclohexyl-2-phenyl-3-benzoylaziridine (*t*-I).

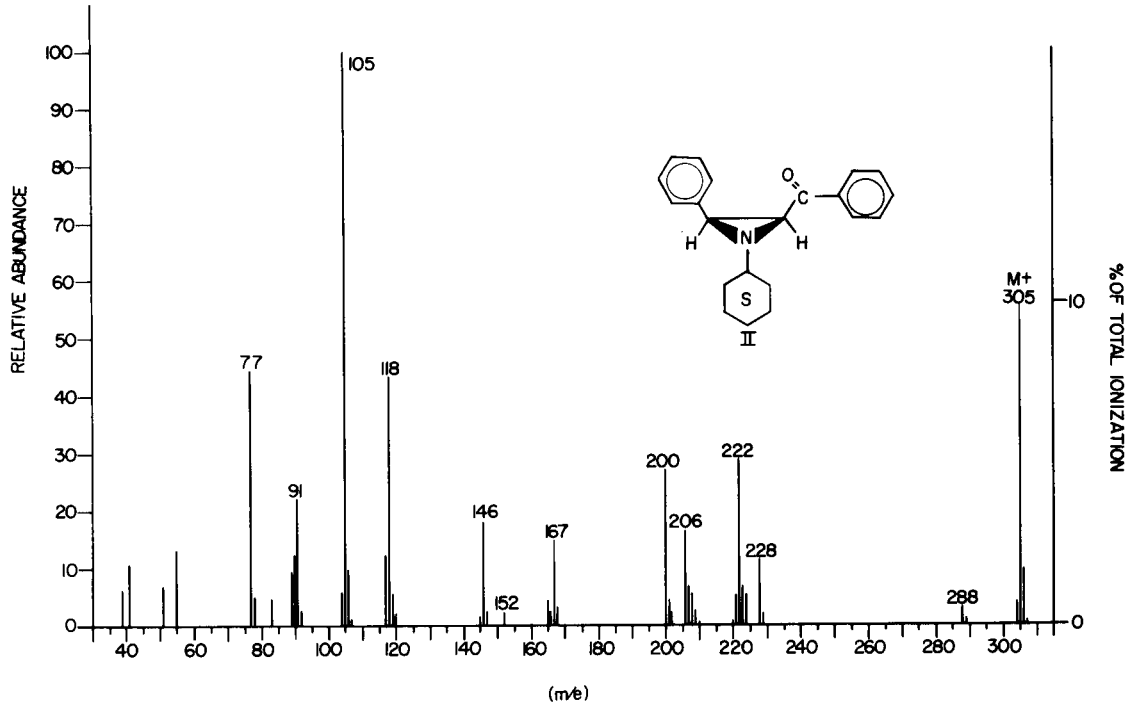


Fig. 2. The mass spectrum of *cis*-1-cyclohexyl-2-phenyl-3-benzoylaziridine (*c*-I).

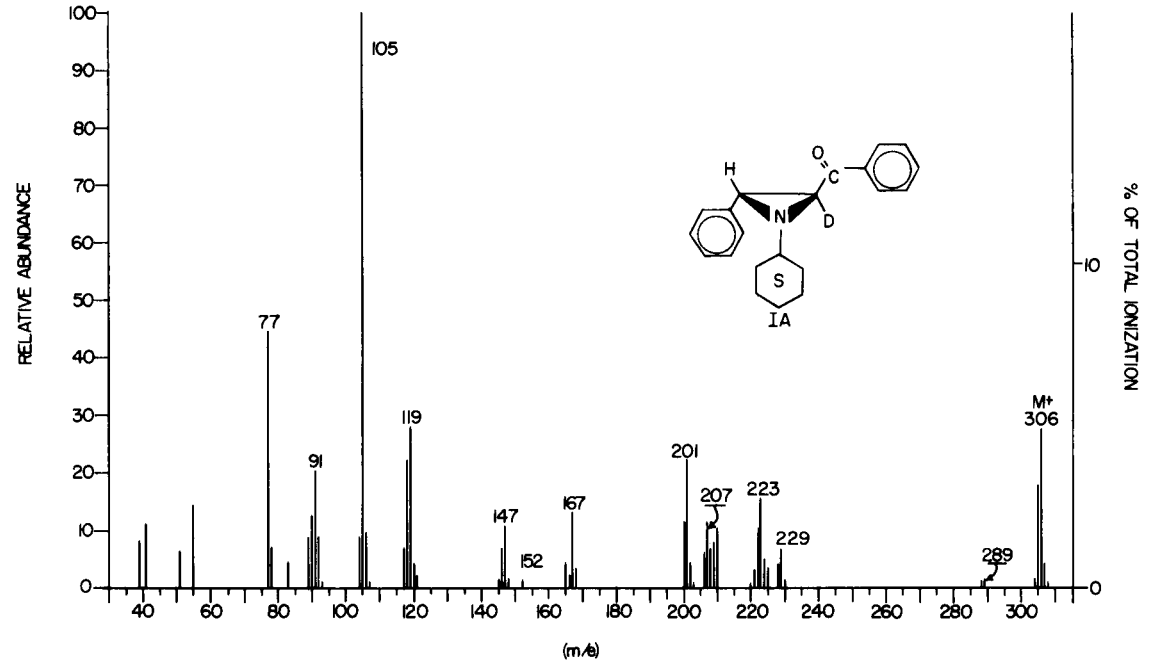


Fig. 3. The mass spectrum of *trans*-1-cyclohexyl-2-phenyl-3-deuterio-3-benzoylaziridine (*t*-IA).

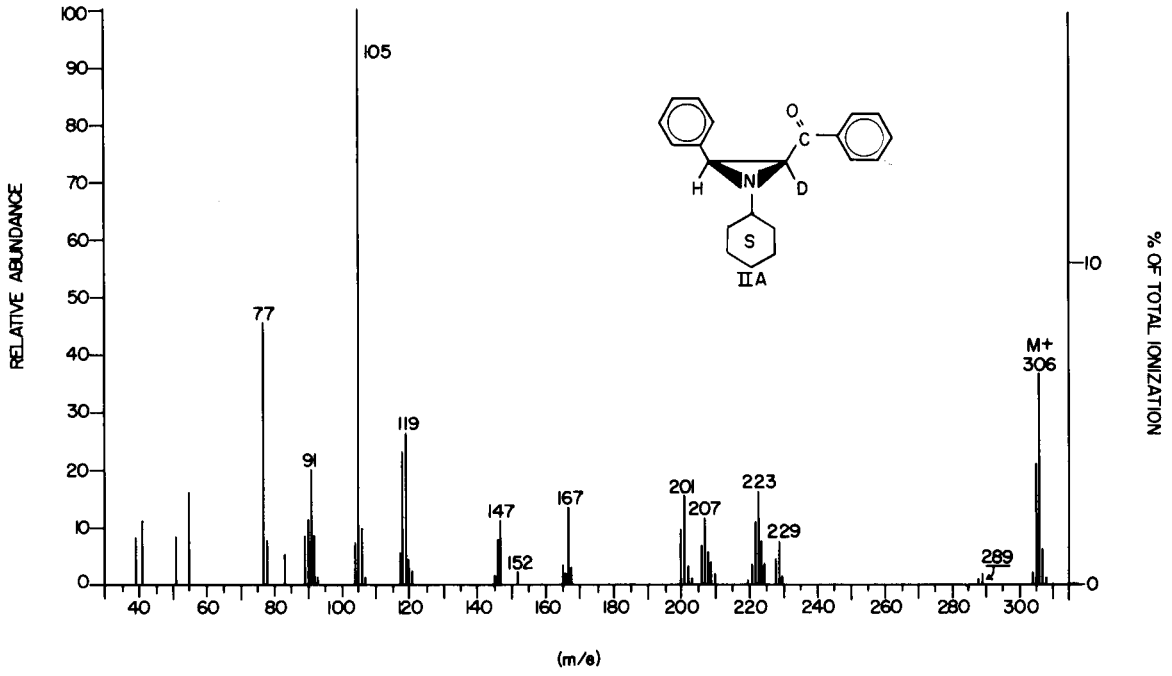


Fig. 4. The mass spectrum of *cis*-1-cyclohexyl-2-phenyl-3-deuterio-3-benzoylaziridine (*c*-IA).

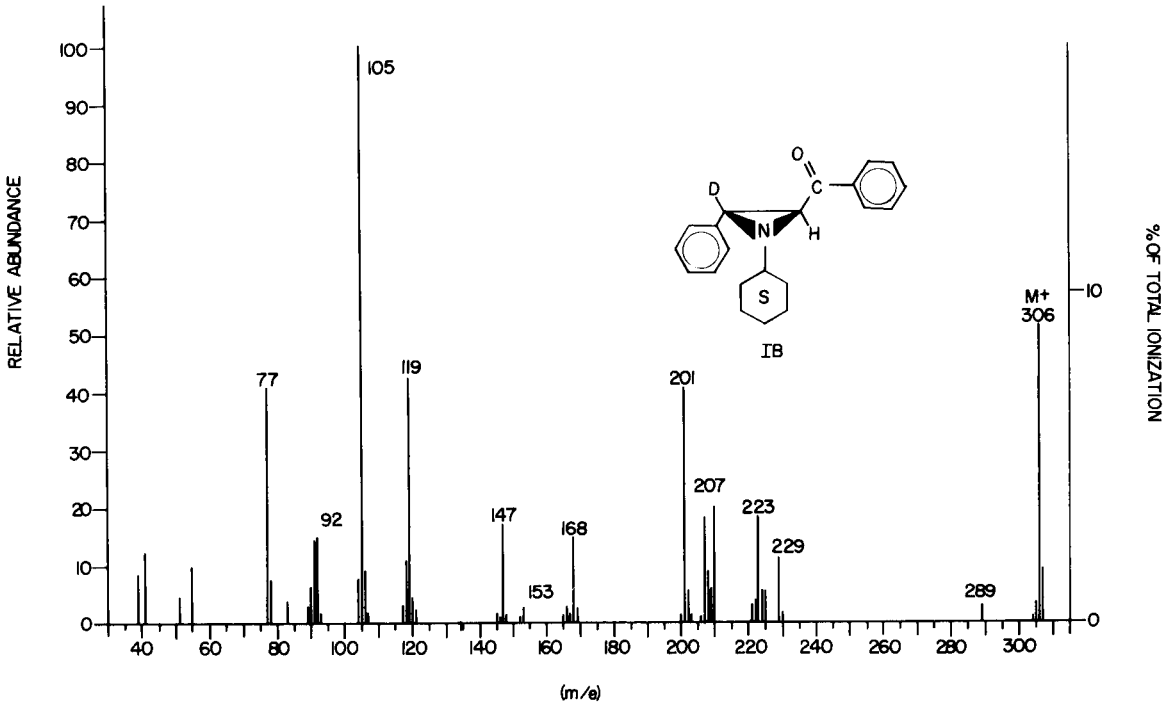


Fig. 5. The mass spectrum of *trans*-1-cyclohexyl-2-deuterio-2-phenyl-3-benzoylaziridine (*t*-IB).

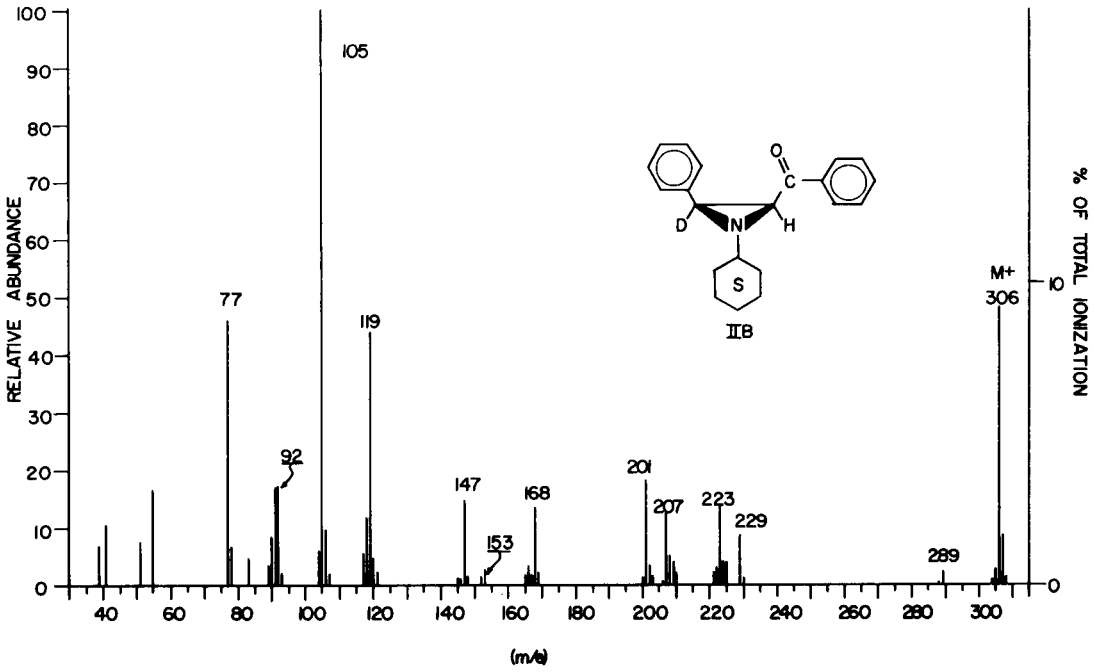


Fig. 6. The mass spectrum of *cis*-1-cyclohexyl-2-deuterio-2-phenyl-3-benzoylaziridine (*c*-IB).

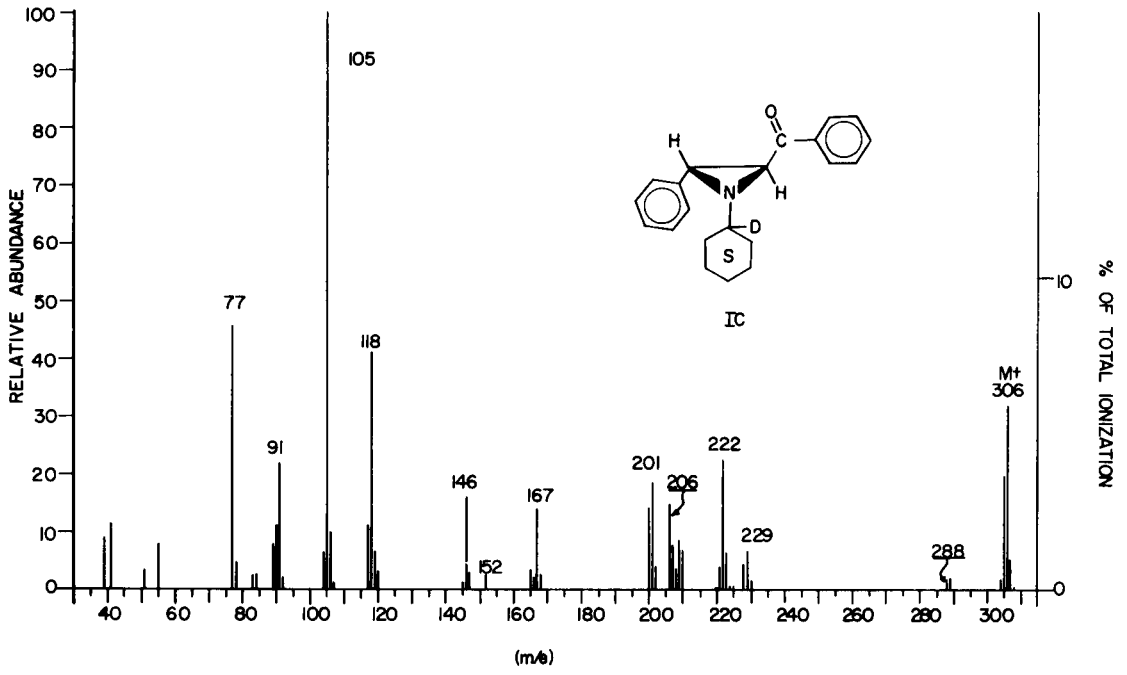


Fig. 7. The mass spectrum of *trans*-1-(1-deuteriocyclohexyl)-2-phenyl-3-benzoylaziridine (*t*-IC).

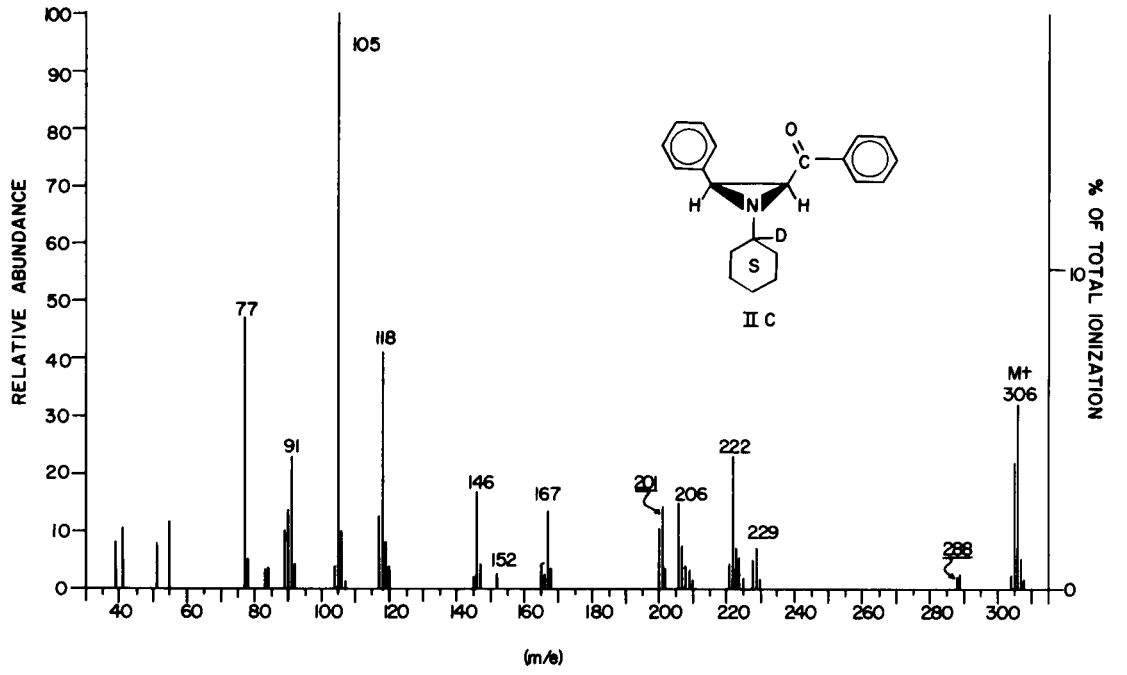


Fig. 8. The mass spectrum of *cis*-1-(1-deuteriocyclohexyl)-2-phenyl-3-benzoylaziridine (*c*-IC).

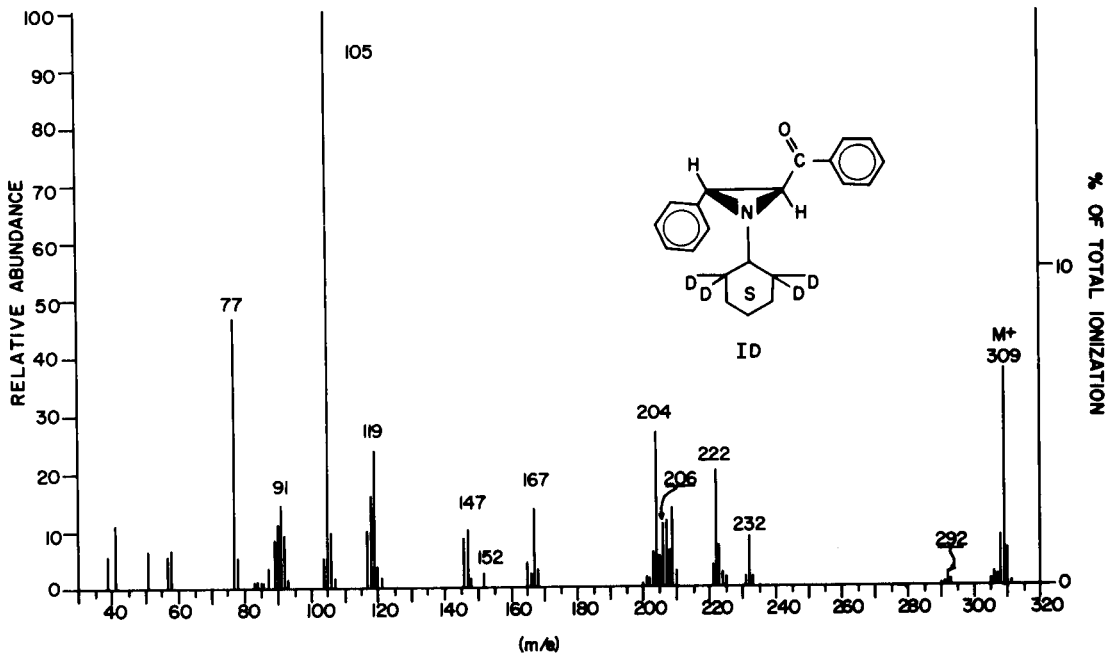


Fig. 9. The mass spectrum of *trans*-1-(2,2,6,6-tetradeuteriocyclohexyl)-2-phenyl-3-benzoylaziridine (*t*-ID).

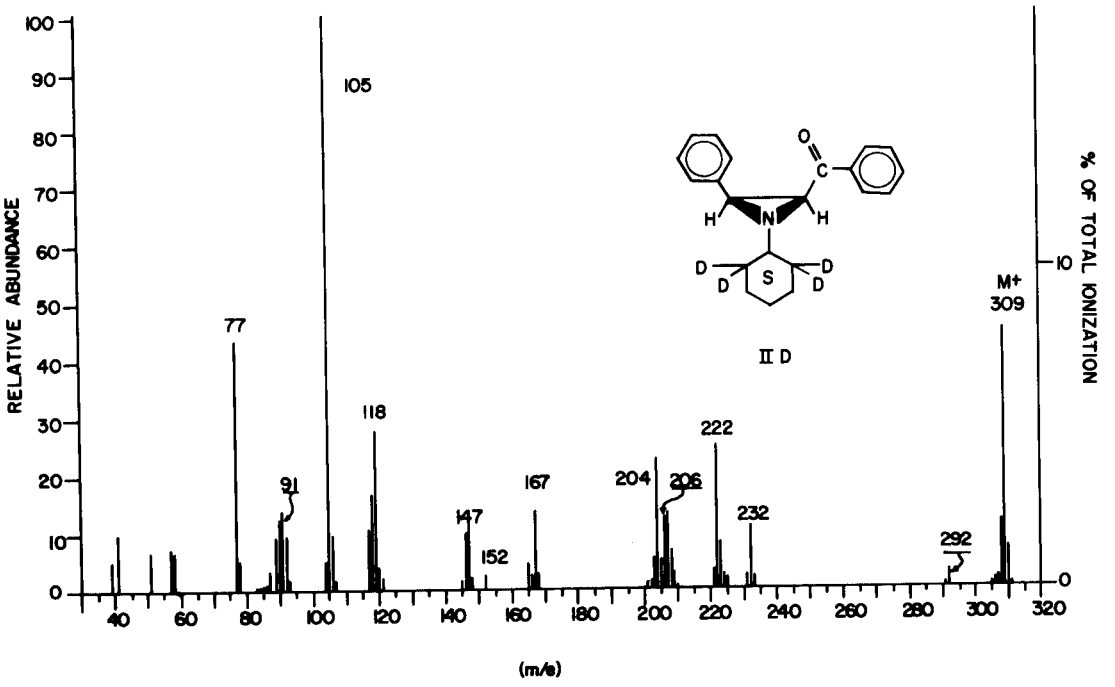


Fig. 10. The mass spectrum of *cis*-1-(2,2,6,6-tetradeuteriocyclohexyl)-2-phenyl-3-benzoylaziridine (*c*-ID).

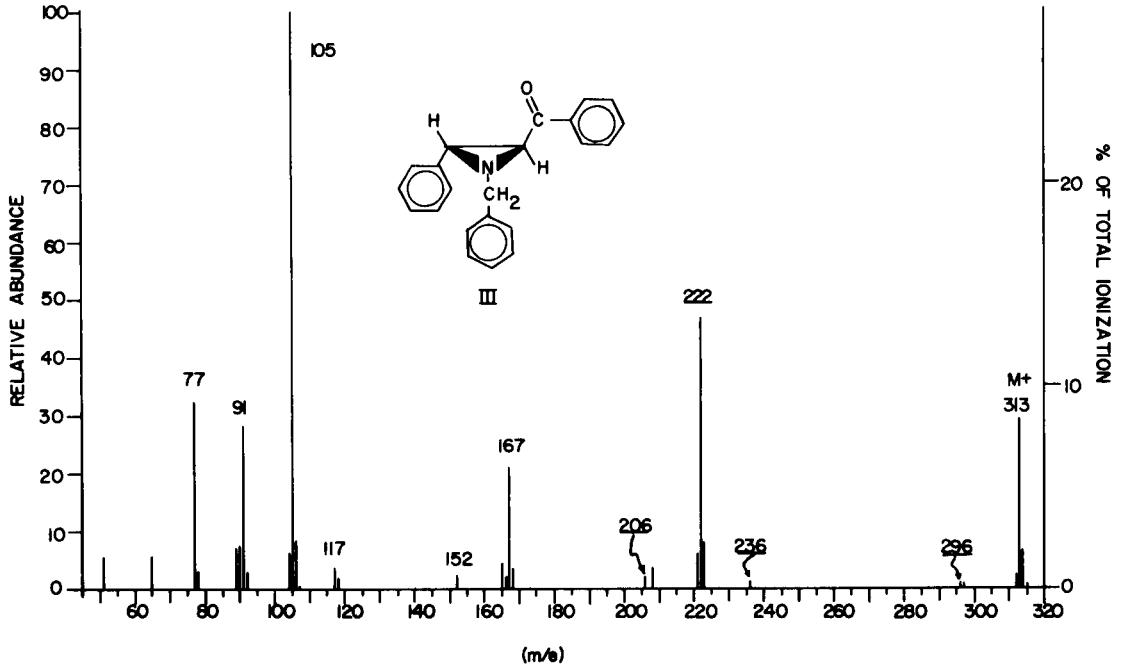


Fig. 11. The mass spectrum of *trans*-1-benzyl-3-phenyl-3-benzoylaziridine (*t*-II).

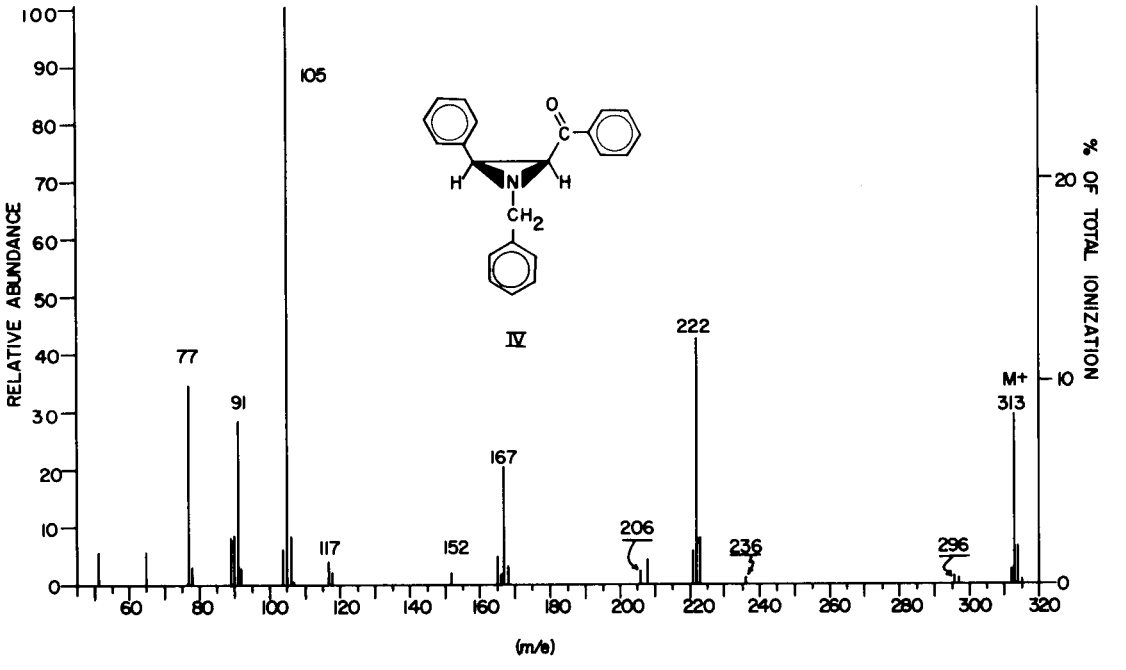


Fig. 12. The mass spectrum of *cis*-1-benzyl-2-phenyl-3-benzoylaziridine (*c*-II).

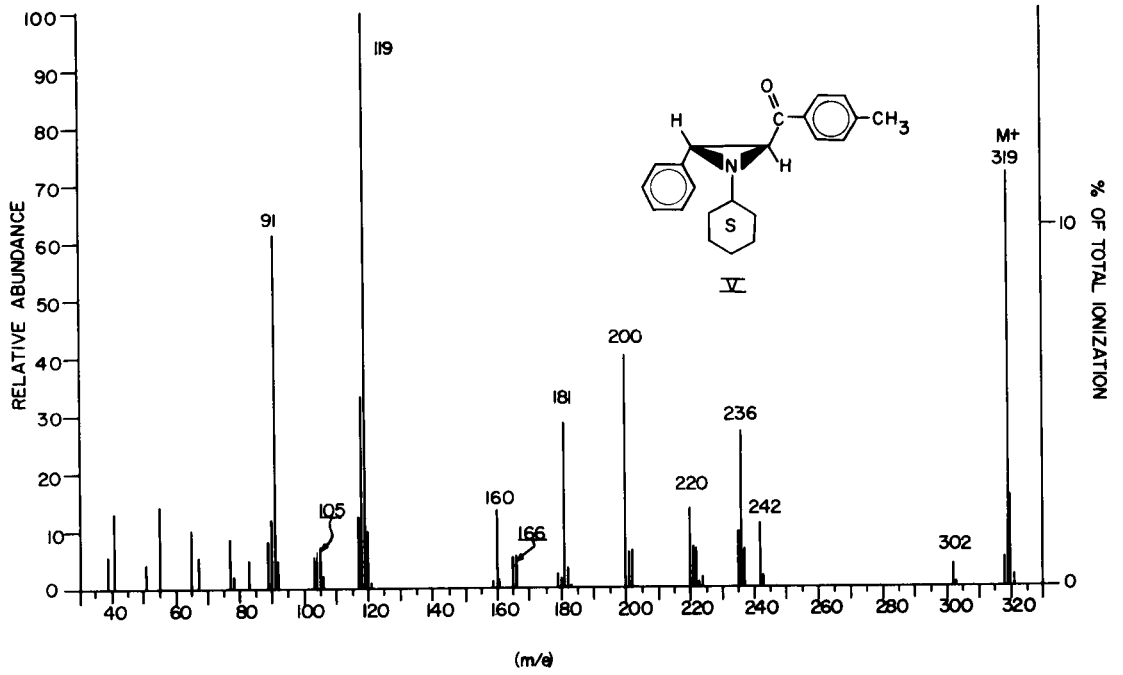


Fig. 13. The mass spectrum of *trans*-1-cyclohexyl-2-phenyl-3-*p*-methylbenzoylaziridine (*t*-III).

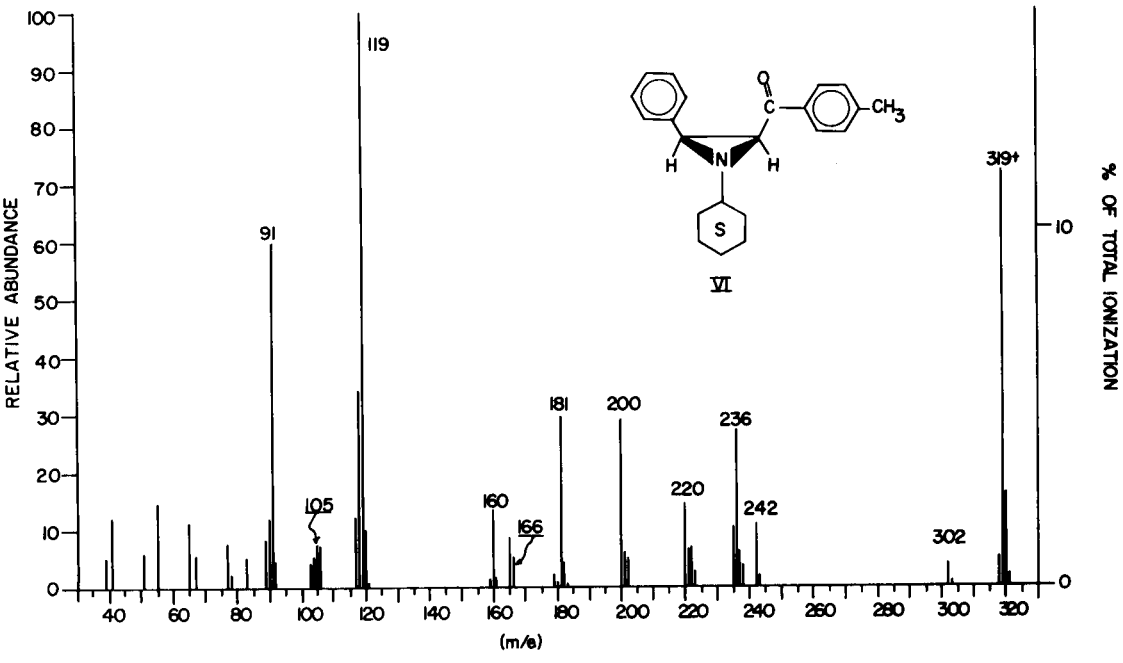


Fig. 14. The mass spectrum of *cis*-1-cyclohexyl-2-phenyl-3-*p*-methylbenzoylaziridine (*c*-III).

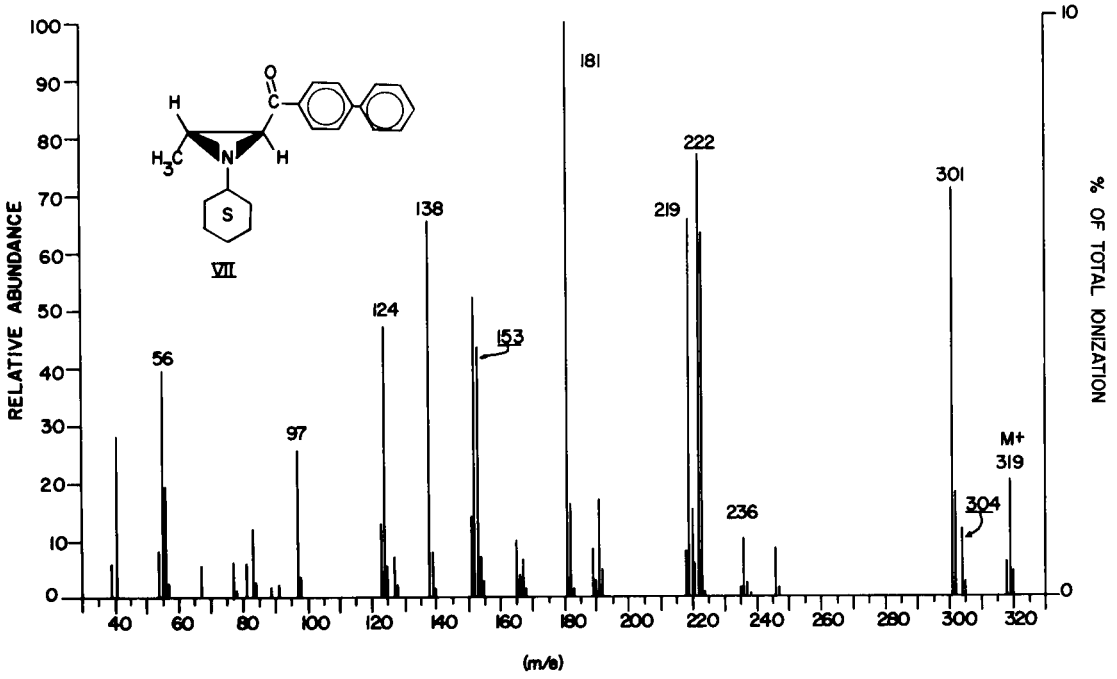


Fig. 15. The mass spectrum of *trans*-1-cyclohexyl-2-methyl-3-*p*-phenylbenzoylaziridine (*t*-IV).

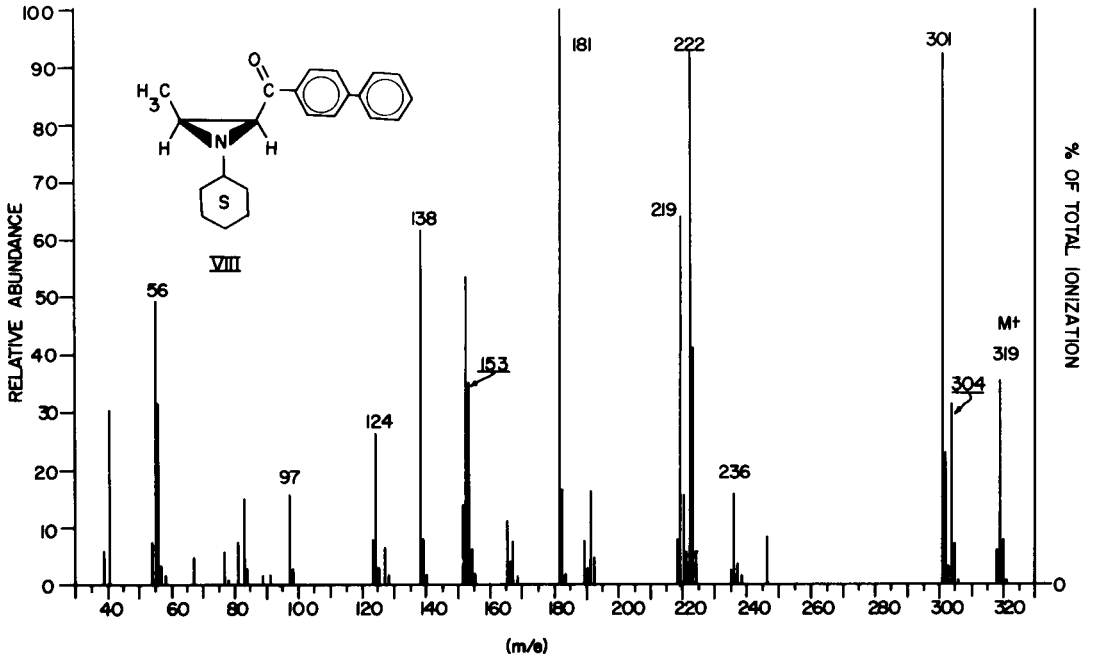


Fig. 16. The mass spectrum of *cis*-1-cyclohexyl-2-methyl-3-*p*-phenylbenzoylaziridine (*c*-IV).

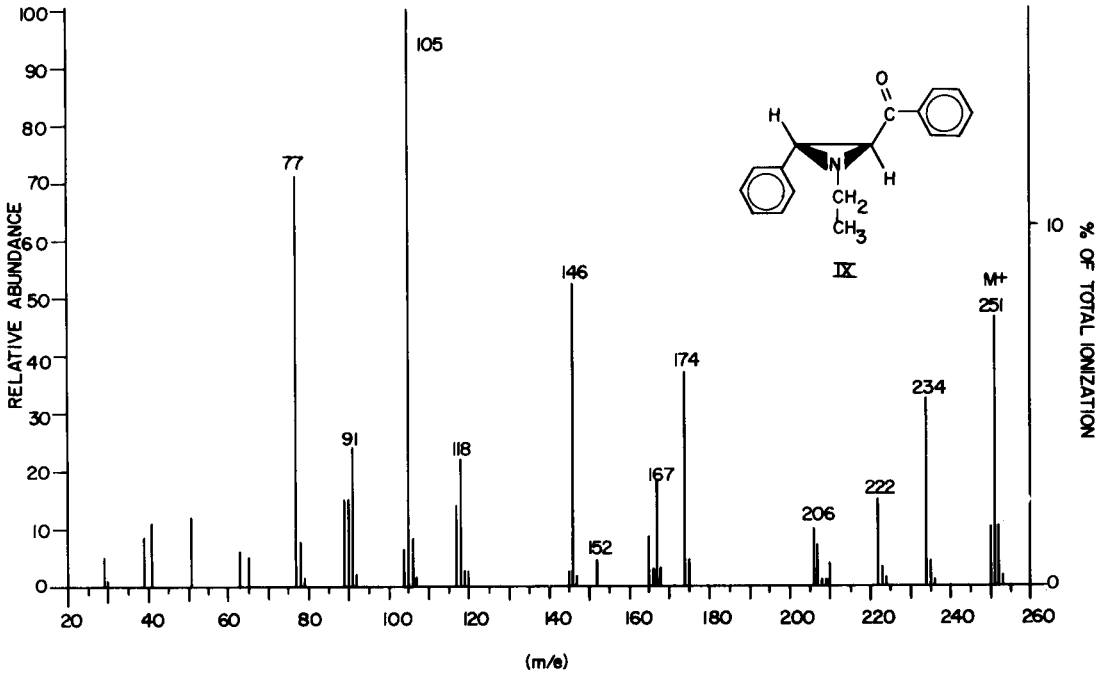


Fig. 17. The mass spectrum of *trans*-1-ethyl-2-phenyl-3-benzoylaziridine (*t*-V).

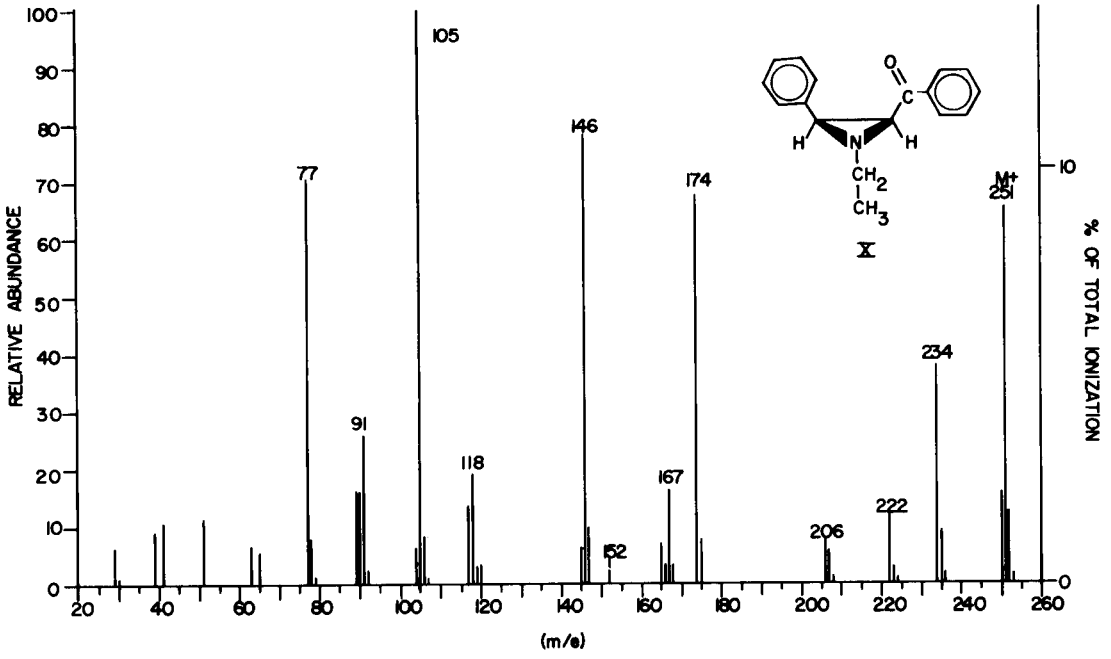


Fig. 18. The mass spectrum of *cis*-1-ethyl-2-phenyl-3-benzoylaziridine (c-V).

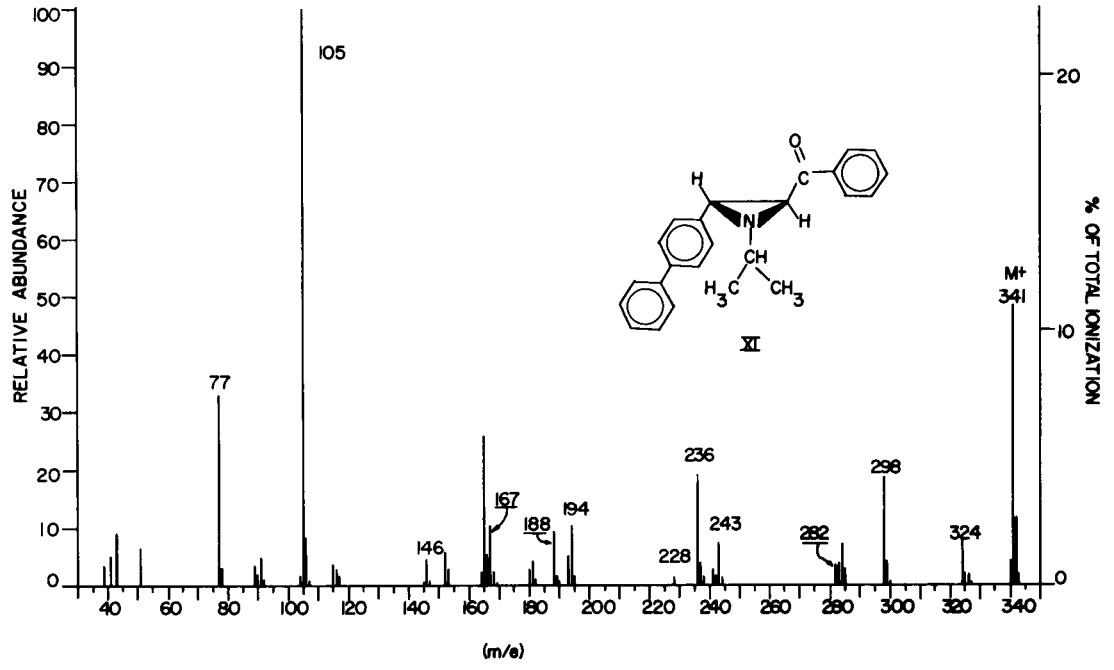


Fig. 19. The mass spectrum of *trans*-1-*i*-propyl-2-*p*-biphenyl-3-benzoylaziridine (*t*-VI).

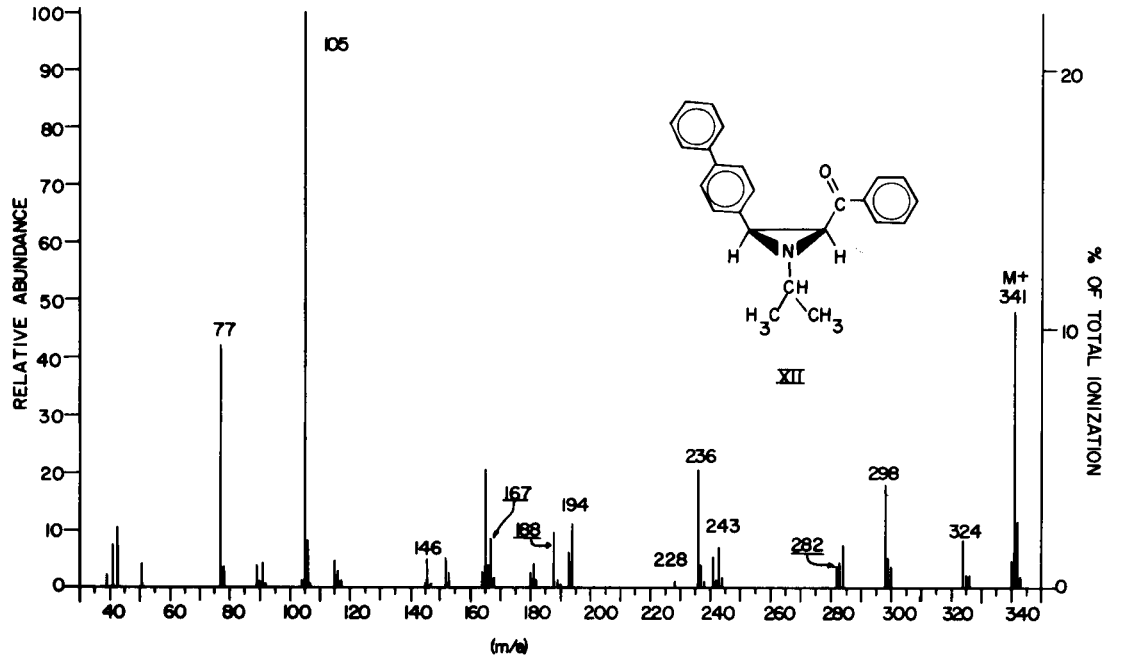


Fig. 20. The mass spectrum of *cis*-1-*i*-propyl-2-*p*-biphenyl-3-benzoylaziridine (*c*-VI).

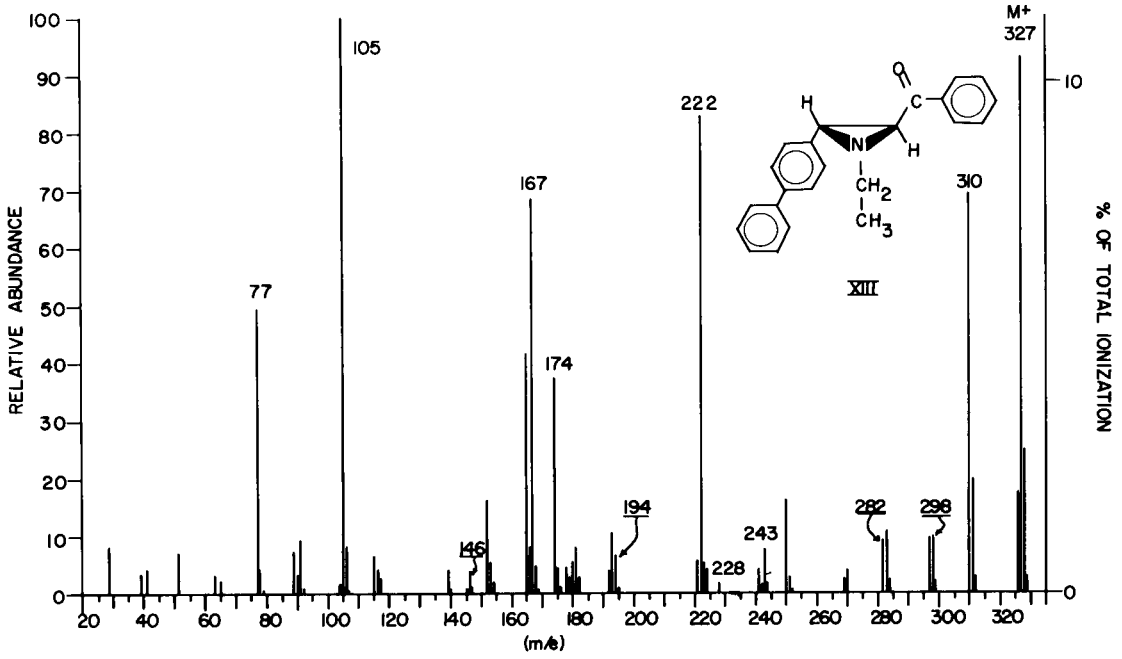


Fig. 21. The mass spectrum of *trans*-1-ethyl-2-*p*-biphenyl-3-benzoylaziridine (*t*-VII).

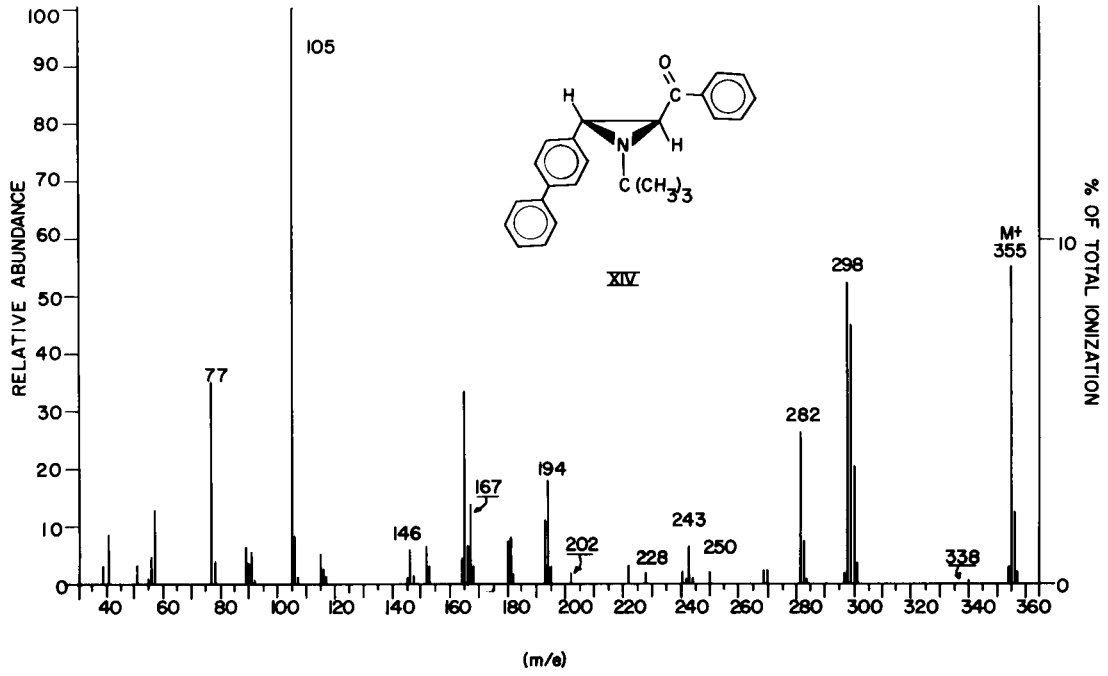


Fig. 22. The mass spectrum of *trans*-1-*t*-butyl-2-*p*-biphenyl-3-benzoylaziridine (*t*-VIII).

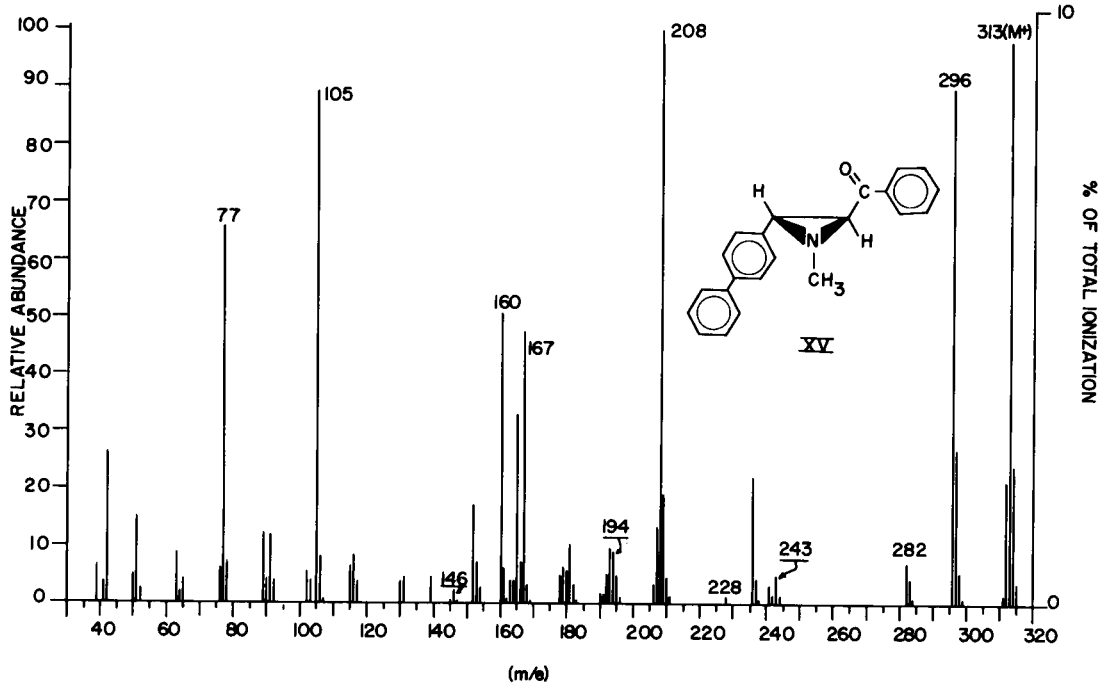


Fig. 23. The mass spectrum of *trans*-1-methyl-2-*p*-biphenyl-3-benzoylaziridine (*t*-IX).

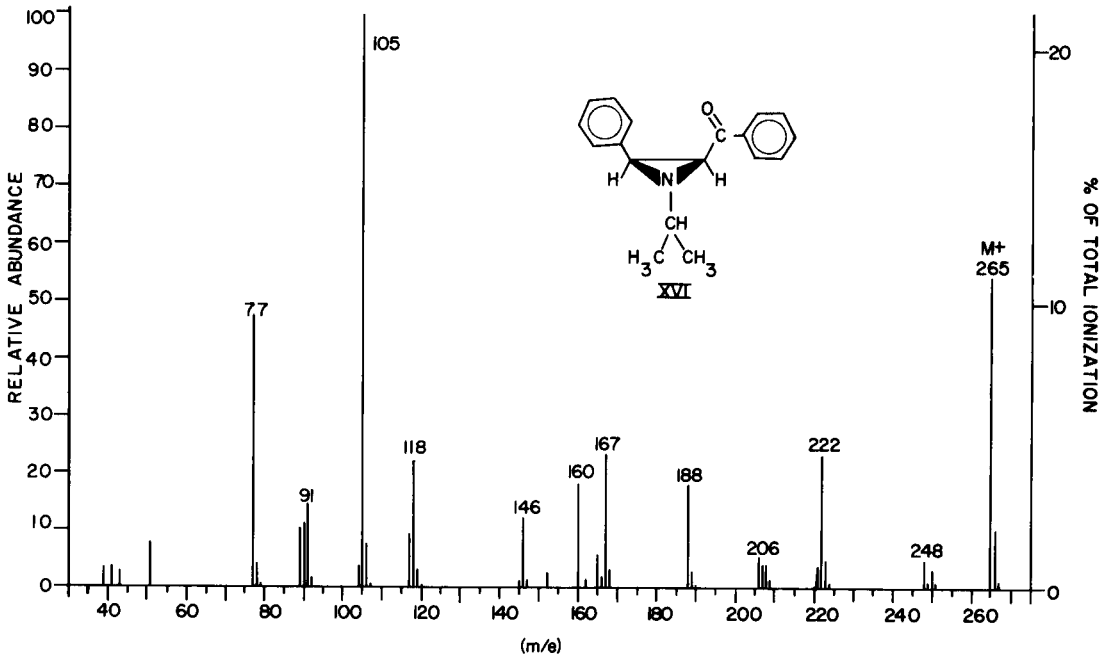


Fig. 24. The mass spectrum of *cis*-1-*i*-propyl-2-phenyl-3-benzoylaziridine (*c*-X).

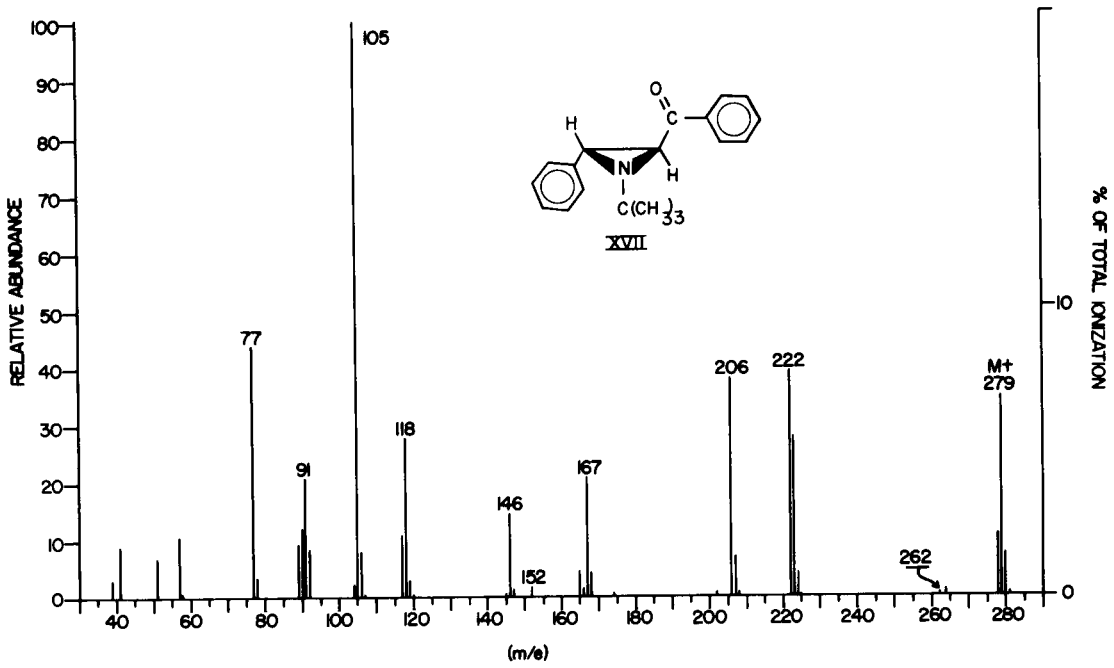


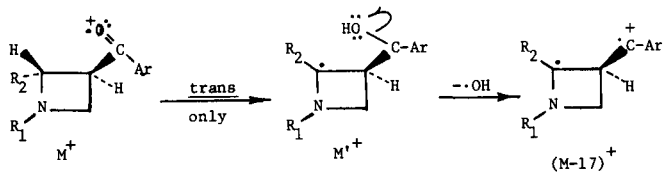
Fig. 25. The mass spectrum of *trans*-1-*t*-butyl-2-phenyl-3-benzoylaziridine (*t*-XI).

1-(1-deuteriocyclohexyl)-2-phenyl-3-benzoylaziridine (*t*-IC, Fig. 7), *cis*-1-(1-deuteriocyclohexyl)-2-phenyl-3-benzoylaziridine (*c*-IC, Fig. 8), *trans*-1-(2,2,6,6-tetradeuteriocyclohexyl)-2-phenyl-3-benzoylaziridine (*t*-ID, Fig. 9), and *cis*-1-(2,2,6,6-tetradeuteriocyclohexyl)-2-phenyl-3-benzoylaziridine (*c*-ID, Fig. 10). Pair IA was shown to be 64.6% deuterated, Pair IB was in excess of 93% deuterated, Pair IC was 61.4% deuterated, while Pair ID was 82.3% tetradeuterated, 16.0% trideuterated, 1.4% dideuterated, 0.2% monodeuterated, and 0.1% non-deuterated.

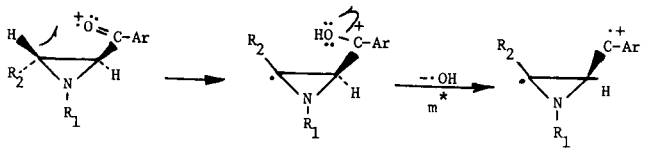
It appears reasonable that the predominant initial process occurring when an aroylaziridine is subjected to electron impact is removal of one of the non-bonding electrons from one of the heteroatoms. It is generally accepted that nitrogen is more capable of stabilizing a positive charge than oxygen because of the lower electronegativity (4), of nitrogen, and, in analogous cases where both nitrogen and carbonyl functions are present (5), the entire fragmentation pattern may be rationalized on the basis of the initial removal of an electron from nitrogen. However, in the present case, the carbonyl function is adjacent to an aromatic system, and a positive charge on oxygen may be stabilized by resonance interactions with the aromatic ring. Therefore, although electron-shift mechanisms can be drawn to account for the origin of all major fragments by removal of an electron from nitrogen, the removal of a nonbonding electron from oxygen is considered to be an equally, if not more, important process for these aziridines.

Previous studies of *cis* and *trans* isomers of various types have generally been more or less successful in establishing distinct fragmentation patterns for each isomer (3), usually being based on relative differences in intensities of certain key fragments. This technique requires that the spectra of both *cis* and *trans* isomers be available for comparison.

The mass spectra of the *cis*- and *trans*-arylaroylazetidines studied in this laboratory were unusual in that they showed a marked and explainable difference between the isomers (3). The mass spectrum of each *trans*-azetidine studied showed a peak at $[M\text{-}17]^+$ and an easily observable metastable peak corresponding to the transition $[M]^+ \rightarrow [M\text{-}17]^+$. Both of these peaks were absent in the mass spectra of the *cis*-azetidines. This obvious difference in the spectra was rationalized on the basis of a rearrangement of the C-2 hydrogen to the carbonyl group in the *trans*-isomers, followed by loss of a hydroxyl radical. This rearrangement is not geometrically possible in the *cis*-azetidines.



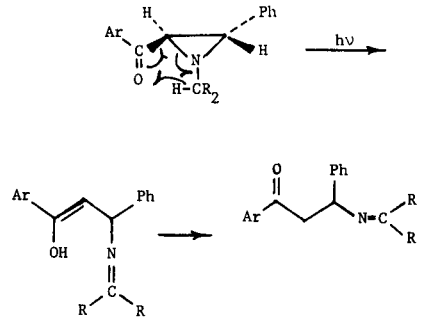
In the aroylaziridines, both *cis*- and *trans*-isomers show an $[M-17]^+$ peak of low to high abundance and a metastable peak corresponding to an $[M]^+$ to $[M-17]^+$ transition (except for pair IV, which showed an $[M-18]^+$ peak). The appearance of the $[M-17]^+$ peak in both isomers of the aziridines can be rationalized by either of the following fragmentations. In the *trans*-isomers, either the C-2 hydrogen is being transferred to the carbonyl function ($a_O \rightarrow aa$), followed by the loss of a hydroxyl radical to yield ion *b*, a process similar to that shown above for *trans*-azetidines. Alternatively, ion a_O is undergoing a McLafferty-type rearrangement of the hydrogen attached to the carbon at the 1-position to the carbonyl function



Ia$_o$	(305)	VIa$_o$	(341)	aa	Ib	(288)	VIb (324)
IIa$_o$	(313)	VIIa$_o$	(327)		IIb	(296)	VIIb (310)
IIIa$_o$	(319)	VIIIa$_o$	(355)		IIIb	(302)	VIIIb (338)
IVa$_o$	(319)	IXa$_o$	(313)		IVb	(---)	IXb (296)
Va$_o$	(251)	Xa$_o$	(279)		Vb	(234)	Xb (262)
		XIa$_o$	(279)				XIb (262)

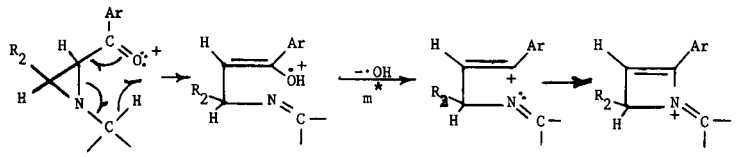
($a_O \rightarrow ab$), followed by the loss of the hydroxyl radical to yield ion *ba* or *bb*. Since the McLafferty-type rearrangement is not geometrically forbidden in either isomer (rapid inversion of the ring nitrogen removes any geometrical restrictions on the stereochemistry at C-3), such a process would also lead to an $[M-17]^+$ ion in the *cis*-isomers. This process, of course, is forbidden for the *N*-*t*-butylaroylaziridines VIII and XI.

The McLafferty-type process seems to be supported by recent articles by Padwa in which the following mechanism for the photochemical reaction of aziridines was proposed (6).



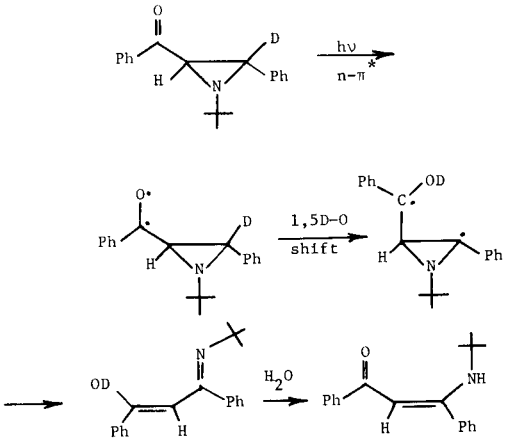
This hydrogen transfer is analogous to a Norrish type II cleavage observed in the irradiation of aliphatic ketones containing γ hydrogens (7).

The process involving the hydrogen at C-2 seems to be inoperative in aroylaziridines, since labelling with deuterium at the C-2 position of aziridine *I* (pair *IB*) does not give a $[M-18]^+$ peak corresponding to a loss of OD radical from the molecular ion. Labelling of the cyclohexyl ring at the carbon on the 1-position of aziridine *I* (pair *IC*) did not conclusively establish process $a \rightarrow ab \rightarrow bb$ because the labelling was just in excess of 50%. It is also possible that isotope discrimination was occurring with this isomer pair (8). Labelling at the C-3 position and at the 2′ and 6′ of the cyclohexyl ring of aziridine *I* (pairs *IA* and *ID*, respectively) eliminated these positions as sites for hydrogen transfer. However, the spectra of aziridines substituted with methyl, ethyl, isopropyl, and *t*-butyl groups at the 1-position appear to establish the process ($a_O \rightarrow ab \rightarrow bb$) as the one responsible for the loss of ·OH from the molecular ions, since the $[M-17]^+$ peak



Ia$_o$	(305)	VIa$_o$	(341)	ab	Iba	(288)	VIba (324) bb
IIa$_o$	(313)	VIIa$_o$	(329)		IIba	(296)	VIIba (312)
IIIa$_o$	(319)	VIIIa$_o$	(355)		IIIba	(302)	VIIIba (338)
IVa$_o$	(319)	IXa$_o$	(313)		IVba	(---)	IXba (296)
Va$_o$	(251)	Xa$_o$	(265)		Vba	(234)	Xba (248)
		XIa$_o$	(279)				XIba (262)

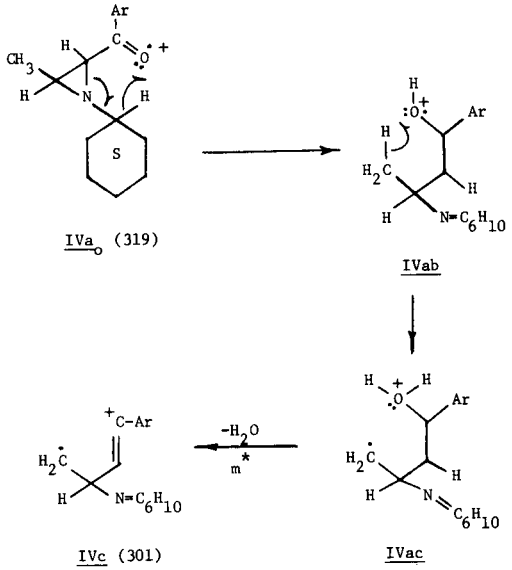
in the *N*-*t*-butyl aziridines (VIII and XI) is less than 0.1% of the base peak Σ_{29}, 0.02%), about 8% (Σ_{29}, 1.9%) for aziridine pair VI, about 5% (Σ_{29}, 1.1%) for aziridine X, nearly 40% (Σ_{29}, 5.6%) for aziridine pair V, 69% (Σ_{29}, 8.2%) for aziridine VII, and 90% (Σ_{29}, 8.9%) for aziridine IX. Thus, as the carbon atom attached to the 1-position become more substituted, the peak at $[M-17]^+$ decreases in relative intensity and in percent of the total ionization, indicating the degree of steric hindrance caused by additional methyl groups. The relatively small $[M-17]^+$ peak in aziridines VIII and XI could be attributed to a seven-center rearrangement (9), or perhaps to a small amount of hydride transfer from the C-2 position, as observed by Padwa in his photochemical study of *trans*-1-*t*-butyl-2-deuterio-2-phenyl-3-benzoylaziridine (6c).



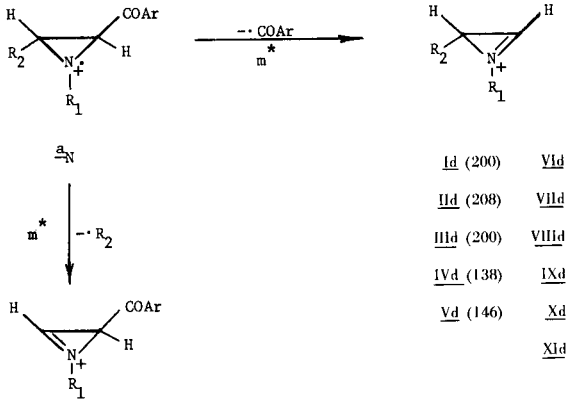
It is probable that the smaller bond angle of the aziridines relative to that of the azetidines is a prime reason that process $a_O \rightarrow aa \rightarrow b$ does not occur, since the smaller bond angle places the hydrogen at the 2-position farther from the carbonyl group than is the case with the *trans*-azetidines. Also, from models, it is apparent that a hydrogen on the carbon attached to the 1-position of the aziridine ring can align itself with the carbonyl function in the arrangement required for the McLafferty-type rearrangement more readily than can the hydrogen attached to the 2-position.

The presence of an $[M-18]^+$ peak rather than an $[M-17]^+$ peak in the spectra of Pair IV can be rationalized on the basis of a double McLafferty-type rearrangement (10), followed by the loss of a molecule of water ($IVa_O \rightarrow$ IVc). It should be noted that the $[M-17]^+$ peak in Pair IV, as confirmed by calculation (11), is due to the isotopic "plus-one" ion of the $[M-18]^+$ fragment.

The overall fragmentation pattern for the aziridines was established by varying the substituents at the three positions of the aziridine ring, labelling of the aziridine Pair *I*, and use of the metastable ions (12), which were confirmed by the electrostatic sector scan defocused metastable technique developed by Major (12).

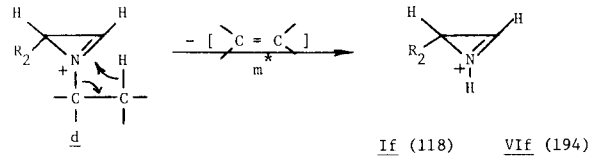


The main fragmentation process for each series proceeds *via* homolytic or heterolytic cleavage of the bonds β to the nitrogen. All pairs, except Pair *II*, show fragments of large relative abundance resulting from the α-cleavage of the aroyl group ($a_N \rightarrow d$) and the 2-substituent ($a_N \rightarrow e$). In Pair *II*, the corresponding ions are present in small abundance (less than 5% of the base peak).



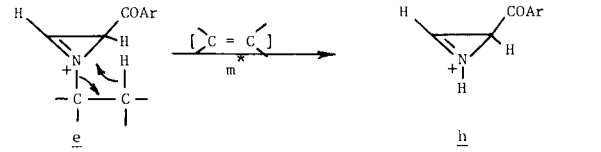
Id (200)	VId (236)	Ie (228)	VIe (188)
IId (208)	VIId (222)	IIe (236)	VIIe (174)
IIId (200)	VIIId (250)	IIIe (242)	VIIIe (202)
IVd (138)	IXd (208)	IVe (304)	IXe (160)
Vd (146)	Xd (160)	Ve (174)	Xe (188)
	XId (174)		XIe (202)

An interesting 1,3 C-to-N hydrogen shift occurs in ions *d* and *e* to give ions *f* and *g*, respectively.



d

If	(118)	VIf	(194)
IIf	(---)	VIIf	(194)
IIIf	(118)	VIIIf	(194)
IVf	(56)	IXf	(194)
Vf	(118)	Xf	(118)
		XIf	(118)

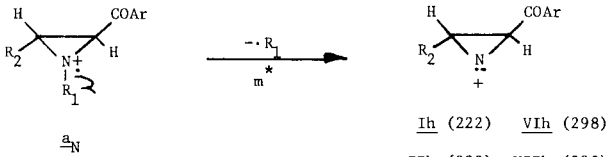


e h

Ig	(146)	VIg	(146)
IIg	(---)	VIIg	(146)
IIIg	(160)	VIIIg	(146)
IVg	(222)	IXg	(146)
Vg	(146)	Xg	(146)
		XIg	(146)

This 1,3 C-to-N hydrogen rearrangement is supported by the mass spectra of Pairs *IC* and *ID* (Figs. 7 and 8 and Figs. 9 and 10, respectively), in which the peaks for ion *f* and *g* are not shifted for Pair *IC* while those for *ID* are shifted one mass unit higher. The driving force for these two rearrangements appears to be the loss of a neutral molecule (an alkene). With aziridines *IX* and *II*, these fragmentation processes are unfavorable since the portion lost from ion *d* and *e* would be $:CH_2$ and $:CHC_6H_5$ (from *IX* and *II*, respectively).

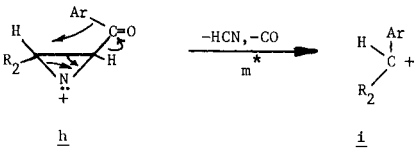
Simple scission of the 1-alkyl-nitrogen bond ($a_N \rightarrow h$) is generally considered to be an unusual process in the spectra of amines (13); however, it is one of the major fragmentations in the spectra of α-lactams (1). This process also appears to be a favored one in the aziridines, where relief of steric strain may be part of the driving force. Another factor in the formation of *h* is the stability of the radical formed in this fragmentation. For example, loss of $\cdot CH_3$ from *IX* results in ion *IXh* which accounts for less than 1% of the total ionization; loss of ·Et from *VII* gives *VIIh* which accounts for ~1% of the total ionization; while loss of $\cdot C(CH_3)_3$ from *VIII* and loss of $\cdot CH_2Ph$ from *II* yields ions *VIIIh* and *IIh* which accounts for 9% and 13% of the total ionization, respectively.



a_N

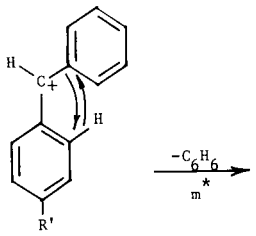
Ih	(222)	VIh	(298)
IIh	(222)	VIIh	(298)
IIIh	(236)	VIIIh	(298)
IVh	(236)	IXh	(298)
Vh	(222)	Xh	(222)
		XIh	(222)

The formation of fragment *h* leads to the subsequent formation, as indicated by the presence of the appropriate metastable ions, of the arylmethyl cation *i* (which then further fragments to ions *j* and *k*).



h i

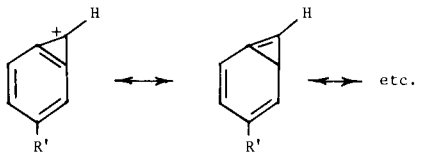
Ii	(167)	VIi	(243)
IIi	(167)	VIIi	(243)
IIIi	(181)	VIIIi	(243)
IVi	(181)	IXi	(243)
Vi	(167)	Xi	(167)
		XIi	(167)



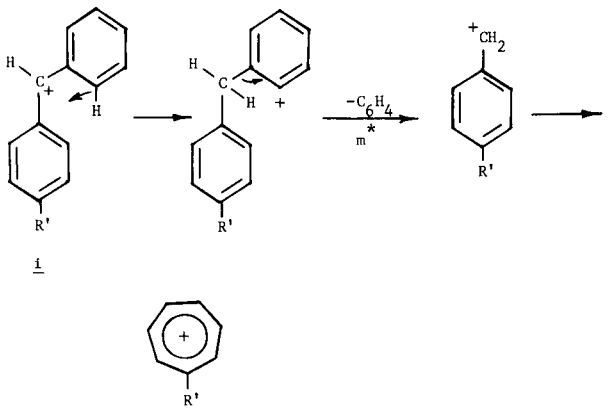
R' = H for pairs, I, II, V, and IX

R' = C_6H_5 for pairs VI, VII, VIII, and X

R' = CH_3 for Pair III



Ij	(89)	VIj	(165)
IIj	(89)	VIIj	(165)
IIIj	(103)	VIIIj	(165)
Vj	(89)	IXj	(165)
		Xj	(89)
		XIj	(89)

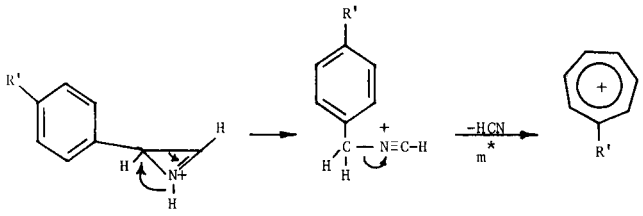


i

Ik (91) VIk (167)
IIk (91) VIIk (167)
IIIk (105) VIIIk (167)
Vk (91) IXk (167)
Xk (91)
XIk (91)

Ions *IVj* m/e 165) and *IVk* (m/e 167) appear to occur *via* the loss of methane and $:CH_2$, respectively, from the arylmethyl cation *i*.

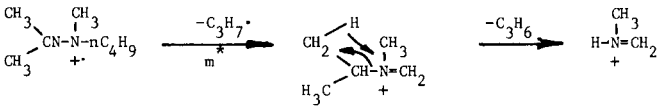
Ion *k* arises from ion *f*, where a hydrogen migration followed by loss of neutral HCN yields the tropylium ion.



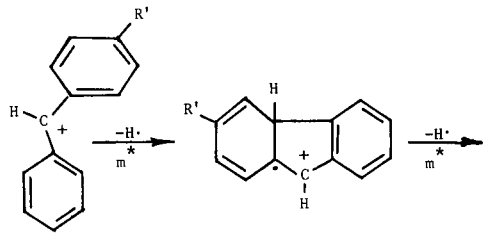
f k

This H-migration seems to be supported by the mass spectra of Pair II), in which the peak at m/e 91 is shifted to m/e 92. Whether the ring system is intact in ion *f* or not is open for debate. If the aroylaziridine is envisioned as undergoing a ring opening of the type ($a_N \rightarrow af \rightarrow ff$), the hydrogen migration from the R′ group followed by the loss of a neutral alkene has an analogy in the mass spectra of *n*-alkyl secondary and *n*-alkyl tertiary amines.

A similar rearrangement is seen in the mass spectrum of *N*-methyl-*N*-isopropyl-*N*-*n*-butylamine (14).

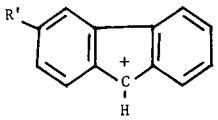


Ion *i* may also undergo further fragmentation to form ions *l*, *m*, and *n*, similar to the fragmentation found in the electron impact spectrum of triphenylmethane (15).



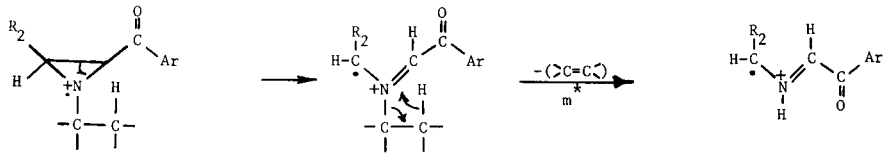
i

I1 (166) VII1 (242)
III (166) VIII1 (242)
IIII (180) IX1 (242)
V1 (166) X1 (166)
VI1 (242) XI1 (166)

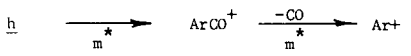


Im (165) VIIm (241)
IIm (165) VIIIm (241)
IIIm (179) IXm (241)
Vm (165) Xm (165)
VIm (241) XIm (165)

Ion *h* further fragments to form ion *o*, which is the base peak in the spectra of most of the aroyl aziridines. Ion *o* then fragments to form aryl cation *p*.

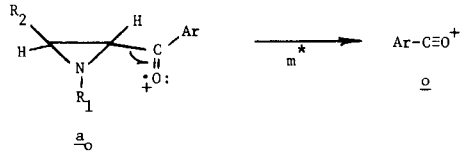


a_N af ff

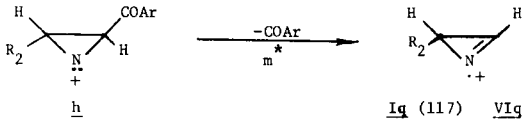


Io (105)	VIo (105)	Ip (77)	VIp (77)
IIo (105)	VIIo (105)	IIp (77)	VIIp (77)
IIIo (119)	VIIIo (105)	IIIp (91)	VIIIp (77)
IVo (181)	IXo (105)	IVp (153)	IXp (77)
Vo (105)	Xo (105)	Vp (77)	Xp (77)
	XIo (105)		XIp (77)

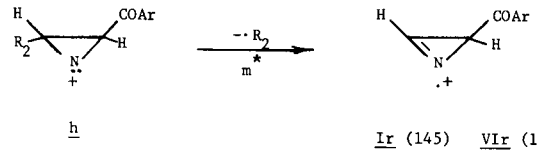
Ion *o* also arises from the molecular ion a_O.



Ion *h* appears to undergo an α-cleavage reaction, with elimination of the aroyl radical, to yield ion *q*. Cleavage of R_2 from *h* to yield ion *r* occurs only to a small extent.

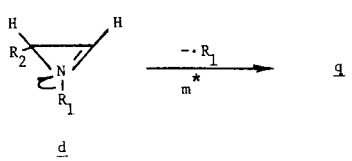


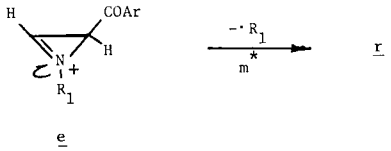
Iq (117)	VIq (193)		
IIq (117)	VIIq (193)		
IIIq (117)	VIIIq (193)		
IVq (55)	IXq (193)		
Vq (117)	Xq (117)		
	XIq (117)		



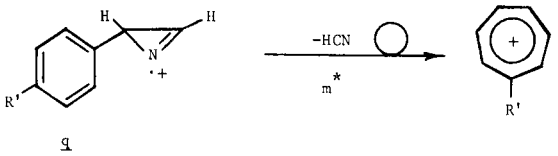
Ir (145)	VIr (145)		
IIr (145)	VIIr (145)		
IIIr (159)	VIIIr (145)		
IVr (221)	IXr (145)		
Vr (145)	Xr (145)		
	XIr (145)		

Ions *d* and *e* give rise to ions *q* and *r*, respectively, through loss of the alkyl function attached to the nitrogen.





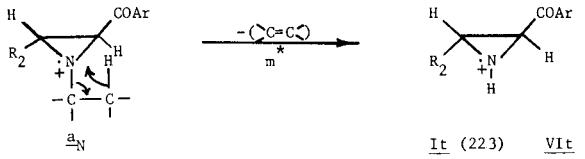
Ion *q* undergoes a loss of HCN as ion *f* to give ion *s*, which can be formulated as a tropylium ion-radical.



R' = H for I, II, V, and XI
R' = C_6H_5 for VI, VII, and X
R' = CH_3 for III

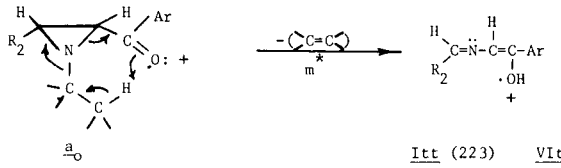
Is (90)	VIIs (166)		
IIs (90)	VIIIs (166)		
IIIs (104)	IXs (166)		
Vs (90)	Xs (90)		
VIs (166)	XIs (90)		

The 1,3- C-to-N hydrogen shift observed in ions *d* and *e* also appears to occur with ion a_N.



It (223)	VIt (299)		
IIt (223)	VIIt (299)		
IIIt (237)	VIIIt (299)		
IVt (237)	IXt (223)		
Vt (223)	Xt (223)		
	XIt (223)		

Alternatively, ion *t* may also arise *via* a hydrogen migration to the carbonyl oxygen.

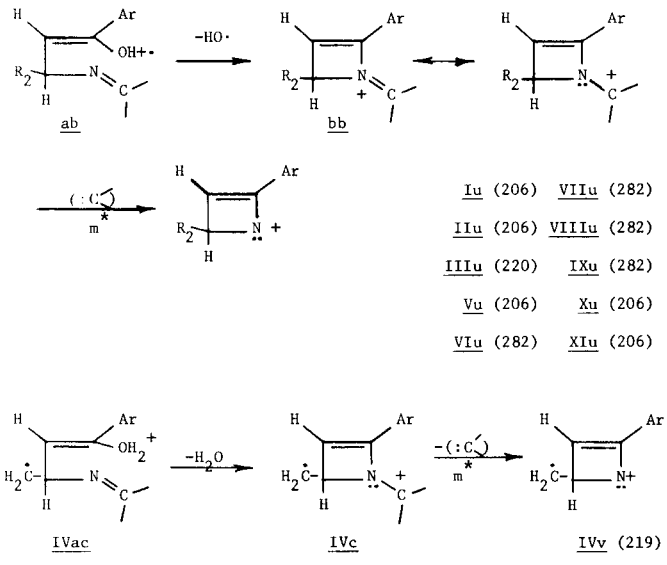


Itt (223)	VItt (299)		
IItt (223)	VIItt (299)		
IIItt (237)	VIIItt (299)		
IVtt (237)	IXtt (223)		
Vtt (223)	Xtt (223)		
	XItt (223)		

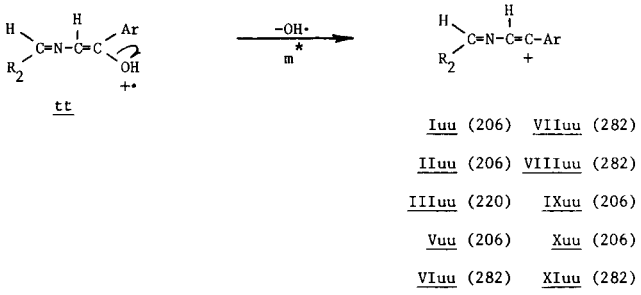
For aziridines *II* and *IX*, the formation of ion *t* (or *tt*) occurs *via* a hydride shift from the benzyl and methyl groups, respectively, to the nitrogen radical. For the *N*-*t*-butyl aziridines (VIII and XI), the ratio of ions *h* to *s* is 1.37 and 1.85 (16), respectively, while the same ratio for the *N*-isopropyl aziridines *VI* and *X* is approximately 24.2 and 28.8 (16), respectively. This indicates that loss of the neutral alkene ($a_N \rightarrow t$) is a much more important process for the *N*-*t*-butyl aziridines.

Although aziridines I, III, IV, V, VI, VII, VIII, IX, X and XI all contain alkyl groups at the 1-position, the alkyl groups do not participate in the fragmentation process to any great extent, and thus, ions attributable to the alkyl functions are in small abundance. Cleavage of the benzyl group from the 1-position in Pair II gives rise to m/e 91 and its daughters.

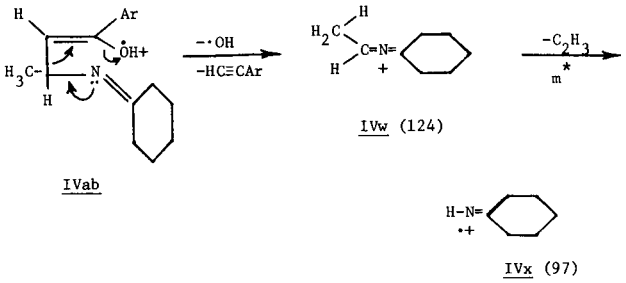
In each pair of aziridines an ion is present whose m/e is given by the formula $[M\text{-}16\text{-}R_1]^+$, except for Pair IV, where the m/e of the ion is given by $[M\text{-}17\text{-}R_1]^+$. This difference in the general formula seems to indicate that the ions in which there is an alkyl function in the 1-position have their origin in the fragment *ab*, through loss of the oxygen, one hydrogen from R_1, and the residual portion of R_1. In Pair IV, the residual portion of R_1 is lost along with a water molecule from *IVac* giving rise to the formula $[M\text{-}17\text{-}R_1]^+$. A possible mechanism for this type of transformation is given below.



Ion *u* also appears to arise from the *tt* or *t* species since appropriate metastable peaks are found for this transition.



The appearance of m/e 124 in the spectra of Pair IV may be attributed to the formation of ion *w*, possibly from a precursor such as *IVab*. The corresponding ion does not appear in the spectra of the other aziridines.



Ion *IVw* also appears to undergo loss of C_2H_3 to form an ion at m/e 97, as indicated by the corresponding metastable ion.

EXPERIMENTAL

Mass Spectra.

The low resolution mass spectra were determined with a Perkin-Elmer Hitachi RMU-6D mass spectrometer operating at 70 eV. The samples were introduced directly into the ion source (17), with the sample heater being maintained at 60-80° and the ion source at 110-130°. The temperature was adjusted in each case to obtain the most useful spectrum. In no case was the temperature of the sample heater greater than the melting point of the sample. (See (12).

The methods of Cromwell (18) and Southwick (19) were successfully applied in the synthesis of the aziridine ketones employed in this study. Those compounds which have not been previously described in the literature gave satisfactory microanalyses and a more detailed description of the synthetic method and the spectral data will appear in a later report. Stereochemical assignment of the *cis*- and *trans*-isomers was made on the basis of nmr, ir and uv spectroscopy (2a,20). A brief description of the synthetic routes to the deuterium-labelled aziridines follows.

Deuterium Labelled 1-Alkyl-2-phenyl-3-benzoylaziridines, *cis* and *trans*. 1-Cyclohexyl-2-d_1-2-phenyl-3-benzoylaziridine.

Base catalyzed condensation of benzaldehyde-d_1 (21) with acetophenone afforded 1,3-diphenyl-3-d_1-2-propen-1-one which

was subsequently brominated and then dehydrohalogenated with *N*-methylpiperidine to give 1,3-diphenyl-2-bromo-3-d_1-2-propen-1-one (α-bromo-β-d_1-chalcone), m.p. 29-31°. Reaction of the labelled α-bromochalcone with cyclohexylamine in benzene according to a known procedure (18) produced *cis*-1-cyclohexyl-2-d_1-2-phenyl-2-benzoylaziridine, m.p. 105-107°, and the corresponding *trans*-isomer, m.p. 99-101°. Mixed melting-point experiments of the respective *cis*- and *trans*-forms of the aziridine with authentic samples (2a) showed no depression. The ring proton nmr spectrum (deuteriochloroform) of the labelled aziridines consisted of slightly broadened singlets located at δ 3.15 and 3.43 for the *cis*- and *trans*-forms, respectively.

1-Ethyl-3-d_1-2-phenyl-3-benzoylaziridine, *cis*- and *trans*.

Treatment of the deuterium labelled α-bromochalcone with two equivalents of ethylamine in benzene afforded 1-ethyl-2-d_1-2-phenyl-3-benzoylaziridine as a mixture of the *cis*- and *trans*-forms. Column chromatography (silica gel) of the crude material gave the *trans*-aziridine as a pale yellow oil. The corresponding *cis*-isomer was obtained as a crystalline material, m.p., 65-66°. Proton magnetic spectroscopy confirmed the introduction of deuterium at C_2 in the aziridines.

1-Cyclohexyl-2-phenyl-3-d_1-3-benzoylaziridine, *cis*- and *trans*.

These compounds were obtained upon reaction of α-bromochalcone (22) with cyclohexylamine-*N*-d_2 (23) in benzene. The pmr spectra (deuteriochloroform) of the *cis*- and *trans*- forms showed singlets at δ 3.28 and 3.50, respectively, for the aziridine ring proton.

1-(1-d_1-Cyclohexyl)-2-phenyl-3-benzoylaziridines, *cis* and *trans*.

Synthesis of 1-d_1-cyclohexylamine was achieved by catalytic hydrogenation of 1-d_1-nitrocyclohexane (24) in d_1-acetic acid with Raney nickel as catalyst. Subsequent reaction with α-bromochalcone produced the labelled *cis*- and *trans*-aziridines.

1-(2,2,6,6-d_4-Cyclohexylamine)-2-phenyl-3-benzoylaziridines, *cis*- and *trans*.

These compounds were prepared by reaction of 2,2,6,6-d_4-cyclohexylamine (25) with α-bromochalcone.

Acknowledgements.

This work was supported in part by grants from the National Institute of General Medicine (grant GM-13122 to H.E.B.) and the Nation Cancer Institute (grant CA-02931 to N.H.C.) as well as fellowships from the Petroleum Research Fund (to P.B.W.), Texaco, Inc. (R.G.P.), and Minnesota Mining and Manufacturing Co. (R.G.P.).

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