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MASS SPECTRA OF 6-AZA AND 11-AZA STEROIDS

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Abstract—A study on the behavior of a considerable number of 6-aza and 11-aza steroids in the mass spectrometer is recorded and discussed. The results illustrate that the hetero atom has a predominant effect in directing the fragmentation of these substances, and interesting differences from the normal steroid fragmentation patterns are therefore observed.

MASS spectrometry has become a particularly effective physical method in the structural elucidation of natural products, and in recent years a tremendous effort has been put forth on investigations with this technique. One of these areas, namely steroids, has received a great deal of attention at Stanford,[1] and more recently, in other laboratories.[2] All of these researches have involved the fragmentation processes in the normal steroid systems and it has been established that the general fragmentation pattern is highly susceptible to the directing influence of substituents. For example, the ethylene ketal and aromatic functions stabilize the positive charge so effectively that they often have the ability to direct the fragmentation in a specific manner.

The marked effect of the nitrogen atom in directing the fragmentation process was well demonstrated from the numerous investigations in the alkaloid field. Also of relevance to this discussion was the examination of the mass spectra of a number of steroidal alkaloids and dimethylamino steroid derivatives in which the nitrogen function is connected in different ways to the steroid skeleton.[1]

The successful syntheses of 6-aza and 11-aza steroids in our laboratory[3-6] has provided us with a rather unique opportunity to investigate the mass spectra of these compounds and thereby evaluate what effect the hetero atom exerts on the fragmentation of the steroid skeleton.

In connection with the mass spectra of 6-aza steroids, a recent publication on 6-aza equilenin and its derivatives has appeared.[7] As may be expected, the fragmentation of these compounds is closely related with the one in the normal equilenin series as already described in detail by Djerassi *et al.*[8] In other words, the presence of a hetero

[1] H. Budzikiewiez, C. Djerassi and D. H. Williams, *Structure Elucidation of Natural Products by Mass Spectrometry* Vol. II. Holden-Day N.Y. (1964).
[2] See for example, N. S. Wulfson, V. I. Zaretskii, V. I. Sadovskaya, S. N. Ananchenko, V. M. Rzheznikov and I. V. Torgov, *Tetrahedron* **22**, 1885 (1966) and Refs cited therein.
[3] J. P. Kutney, R. A. Johnson and I. Vlattas, *Canad. J. Chem.* **41**, 613 (1963).
[4] J. P. Kutney, I. Vlattas and G. V. Rao, *Canad. J. Chem.* **41**, 958 (1963).
[5] J. P. Kutney and I. Vlattas, *Steroids* **4**, 595 (1964).
[6] J. P. Kutney and C. Gletsos, *Steroids* **7**, 67 (1966).
[7] U. K. Pandit, W. N. Speckamp and H. O. Huisman, *Tetrahedron* **21**, 1767 (1965).
[8] C. Djerassi, J. M. Wilson, H. Budzikiewiez and J. W. Chamberlin, *J. Am. Chem. Soc.* **84**, 4549 (1962).

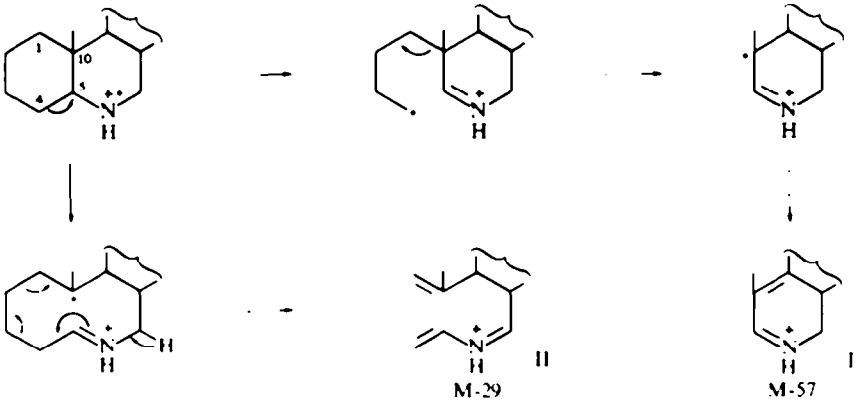
atom in these compounds does not provide a significant difference in the fragmentation pattern, since this atom is part of a stable aromatic system. On the other hand, it is anticipated that if the nitrogen atom is present in a saturated system, the fragmentation pattern may reveal some interesting differences. We wish to report that this latter situation does indeed prevail.

For the sake of clarity, we will discuss the mass spectra of 6- and 11-aza steroids in separate sections. In each instance, plausible mechanisms are presented to illustrate possible fragmentation modes in the molecules. Clearly, alternative mechanisms are often available, but these are not included in order to avoid lengthy discussions.

A. *The mass spectra of 6-aza-5ξ-steroids*

For studies in the 6-aza series, the mass spectra of 6-aza-5ξ-cholestane (**1**) and 17β-hydroxy-6-aza-5ξ-androstane (**2**) were first examined.

The 6-aza cholestane derivative indicates significant peaks at *m/e* 358 (M-15), 344 (M-29), 330 (M-43), 316 (M-57), 302 (M-71), 164 and 124. Similarly, the corresponding fragments in the mass spectrum of the androstane analogue **2** are also present (*m/e* 262, 248, 234, 220, 206, 164 and 124) (Figs 1 and 2). Several of the possible fragmentations of the 6-aza steroid system are indicated below.



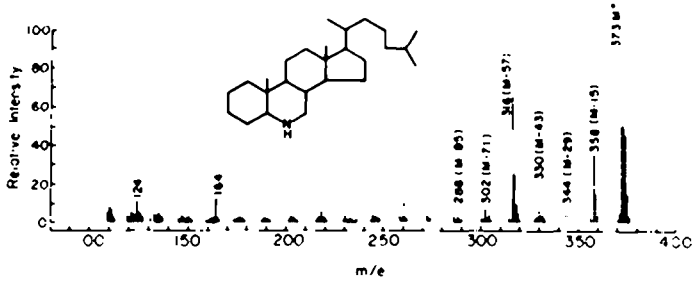


FIG. 1.

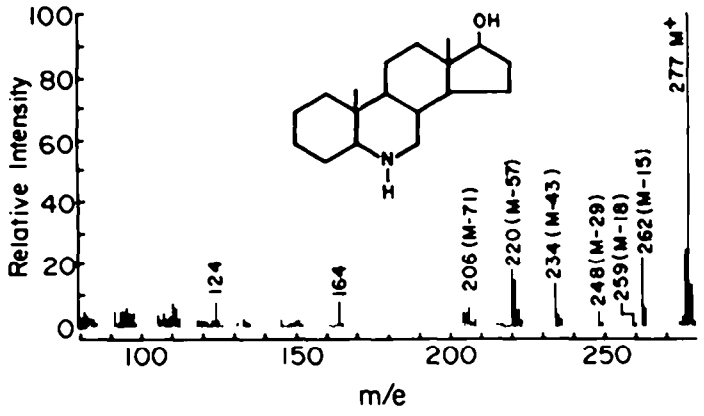
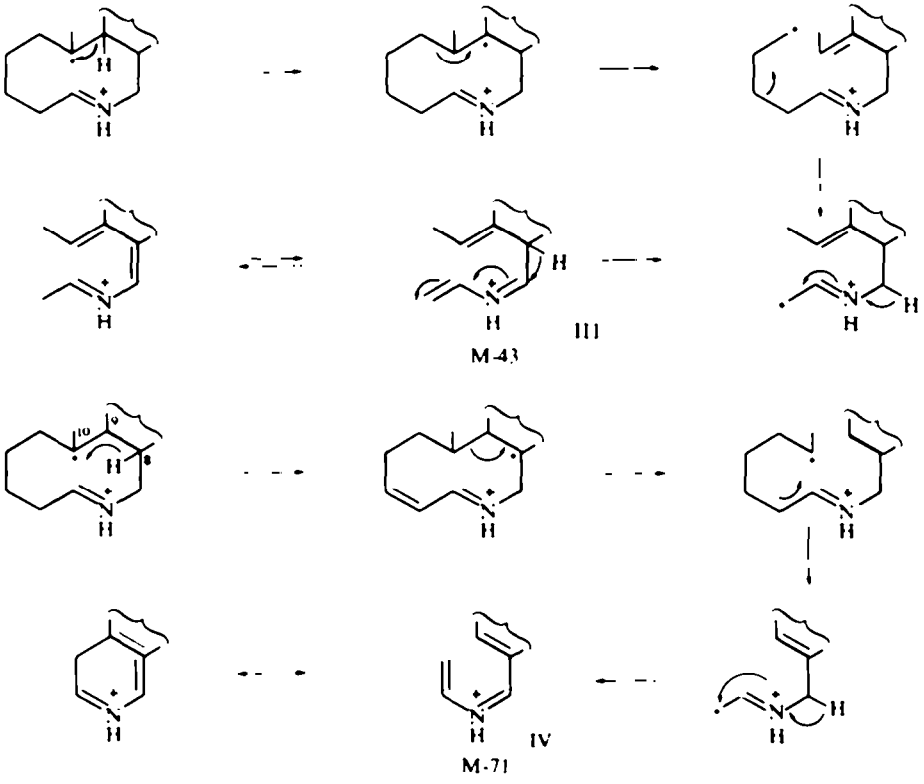


FIG. 2.

Another fragmentation process which is expected in this system can be initiated by the cleavage of the C_7 C_8 linkage. It is suggested that the fragment at *m/e* 124 may arise in this fashion.

Another common signal at *m/e* 164 in the mass spectra of **1** and **2** is possibly derived by the homolytic cleavage of the C_8 C_{14} and C_{12} C_{13} bonds to generate the fragment VI.

The spectrum of the cholestane analogue also indicates a signal at *m/e* 288 which



can be attributed to the loss of C_6H_{13} from the molecular ion, and we believe that this represents cleavage of the C_{20} C_{22} bond in the side chain.

The N-benzyl-6-aza steroids indicate a very similar fragmentation pattern, but of course, with the additional occurrence of a number of signals due to the presence of the benzyl group. For example, the mass spectra of the N-benzyl-6-aza-5ξ-cholestane (**3**), 17β-hydroxy-N-benzyl-6-aza-5ξandrostane (**4**) and 20β-hydroxy-N-benzyl-6-aza-5ξ-pregnane (**5**) possess a common peak (*m/e* 91) due to the fragment $C_7H_7^+$. Also, the significant M-77 and M-91 fragments which occur at *m/e* 387, 289, 318 and 373, 275, 304 in the three spectra respectively are due to the loss of a phenyl ($C_6H_5\cdot$) or benzyl ($C_6H_5CH_2\cdot$) moiety from the molecular ion. It is to be noted that these peaks are absent in the spectra of the parent 6-aza compound. Again, the most abundant peak (besides the molecular ion peak) in the spectra of these compounds is the one corresponding to the M-57 fragment (Figs 3 and 4).

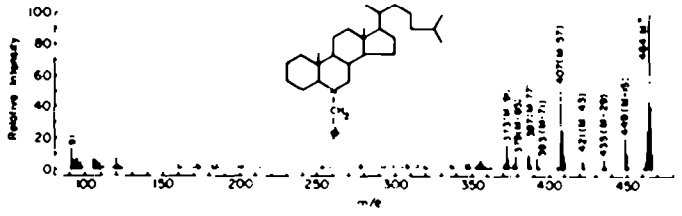


FIG. 3.

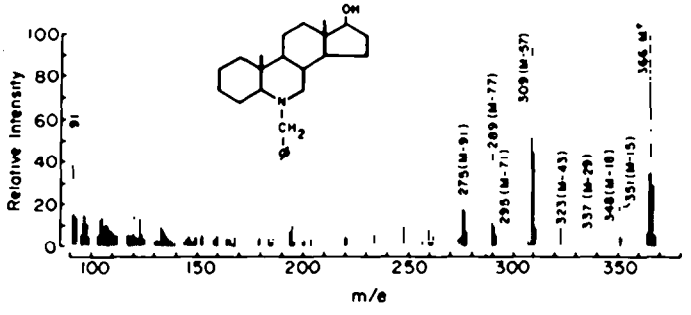
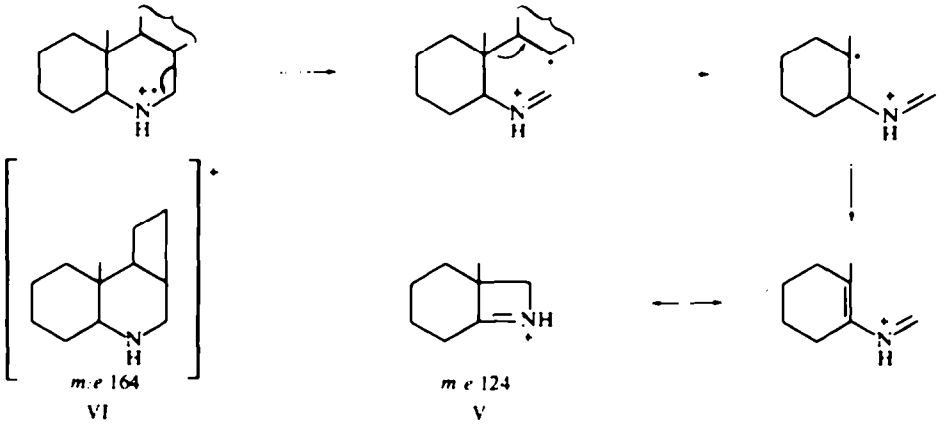


FIG. 4.



The fragments V and VI which would now appear at *m/e* 214 (124 + 90) and 254 (164 + 90) are no longer present in the spectra of these compounds. This is not too surprising when one considers the low abundance of these fragments in the spectra of the parent 6-aza steroids and the competing strong fragmentation which may be expected across the N-benzyl bond in the N-benzyl-6-aza homologues.

B. *The mass spectra of 6-aza-5ξ-7-one steroids*

The presence of a CO group at the C_7 position of the 6-aza steroid skeleton has a dramatic effect on the fragmentation pattern of these compounds. The mass spectra of the compounds which were studied (**6–10**) reveal several significant differences when compared to those discussed in the preceding section. These are: (a) a very strong molecular ion peak, as well as intense M-1 and M-2 peaks; (b) the significant fragments retain the A and B rings of the molecule and arise from cleavage of bonds in rings C and D. The fragmentation of ring A occurs to a minor extent in this series (Figs 5 and 6).

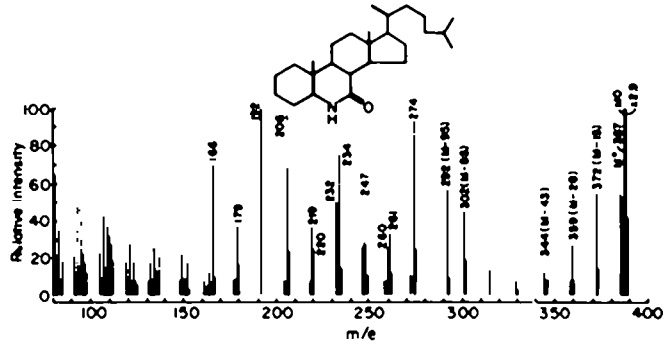


FIG. 5.

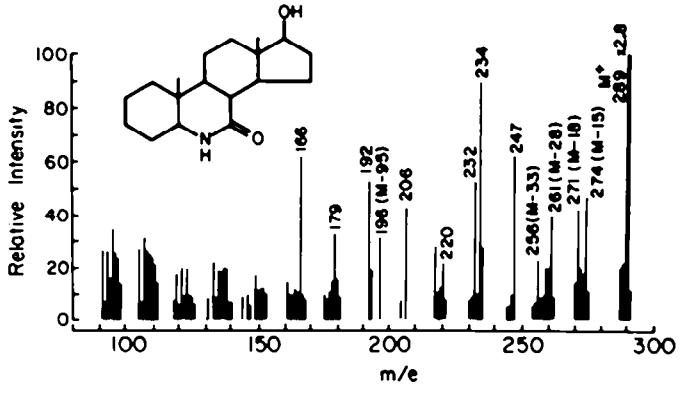
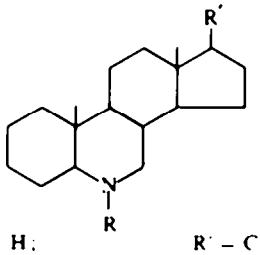


FIG. 6.

Evidence in support of the retention of ring A and B in these fragments is provided from several separate sets of results: (a) the fact that the occurrence of these fragments is independent of the nature of the side chain at C_{17}; (b) the fragmentation of the enol lactams (to be discussed later) which possess an additional double bond at

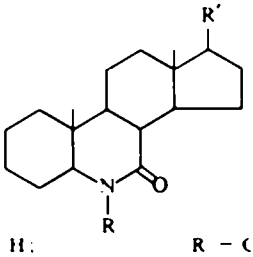
C_4–C_5 indicates, as expected, that these fragments now occur at *m/e* values which are lower by *two* units; and (c) the fragmentation of the N-benzyl-6-aza-7-one derivatives provides fragment ions at *m/e* values which are higher by *ninety* units.



1. R = H; R' = C_8H_{17}-
2. R = H; R' = OH
3. R = CH_2Ph; R' = C_8H_{17}-
4. R = CH_2Ph; R' = OH
5. R = CH_2Ph; R' = CH(OH)Me

We will attempt to provide possible mechanisms for the formation of these fragments which occur at *m/e* 166, 179, 192, 206, 220, etc., in the spectra which were obtained.

The formation of the *m/e* 166 fragment (VII) could be visualized as arising through the homolysis of the C_8 C_{14} and C_9 C_{11} bonds as shown in the following scheme. However, in view of some very recent work,[9] [10] the suggested hydrogen transfer may not occur because of the large interatomic distance between the hydrogen at

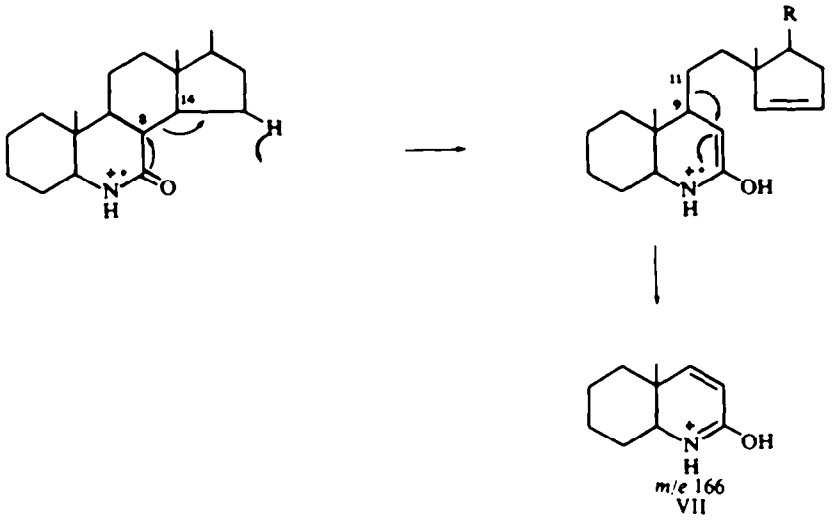


6. R = H; R = C_8H_{17}-
7. R = H; R = OH
8. R = CH_2Ph; R = C_8H_{17}-
9. R = CH_2Ph; R = OH
10. R = CH_2Ph; R = CH(OAc)Me

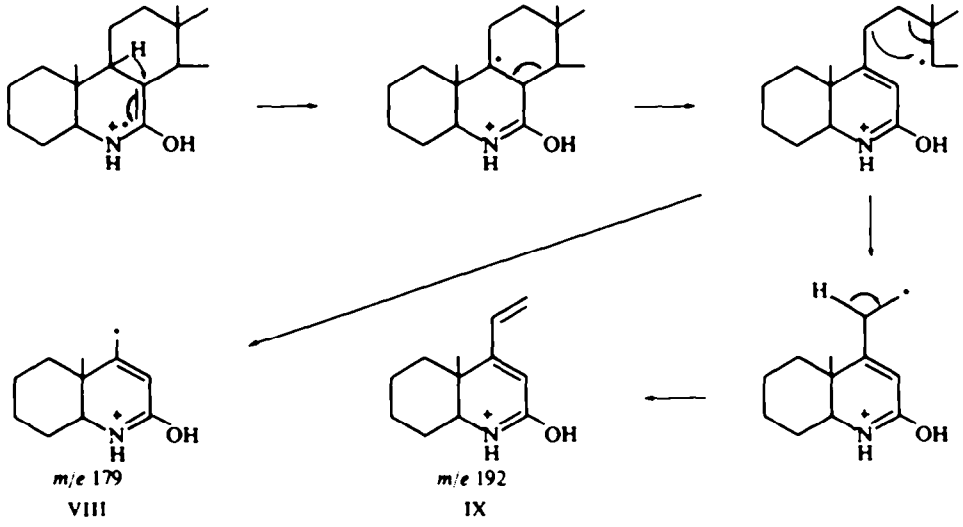
C-15 and the oxygen atom at C-7. Perhaps this fragment arises via homolytic cleavage of the C_8 C_{14} bond.

[9] C. Djerassi and L. Tökes, *J. Am. Chem. Soc.* **88**, 536 (1966).

[10] C. Djerassi, G. Von Mutzenbecher, J. Fajkos, D. H. Williams and H. Budzikiewicz, *J. Am. Chem. Soc.* **87**, 817 (1965).



The fragments VIII (*m/e* 179) and IX (*m/e* 192) may be formed by the appropriate fission of the C_8–C_{14} bond and subsequent loss of ring D as shown below.



A possible rationalization for the formation of some of the other fragments utilizes a cleavage of the C_{13}–C_{14} linkage to generate the species X. The latter may be the intermediate for a number of fragment ions as indicated below. Obviously, other plausible pathways may be postulated for the formation of these fragments, but these invariably must involve the loss of ring D and its side chain. The intermediate X may also serve to provide the fragments at *m/e* 232 and 234.

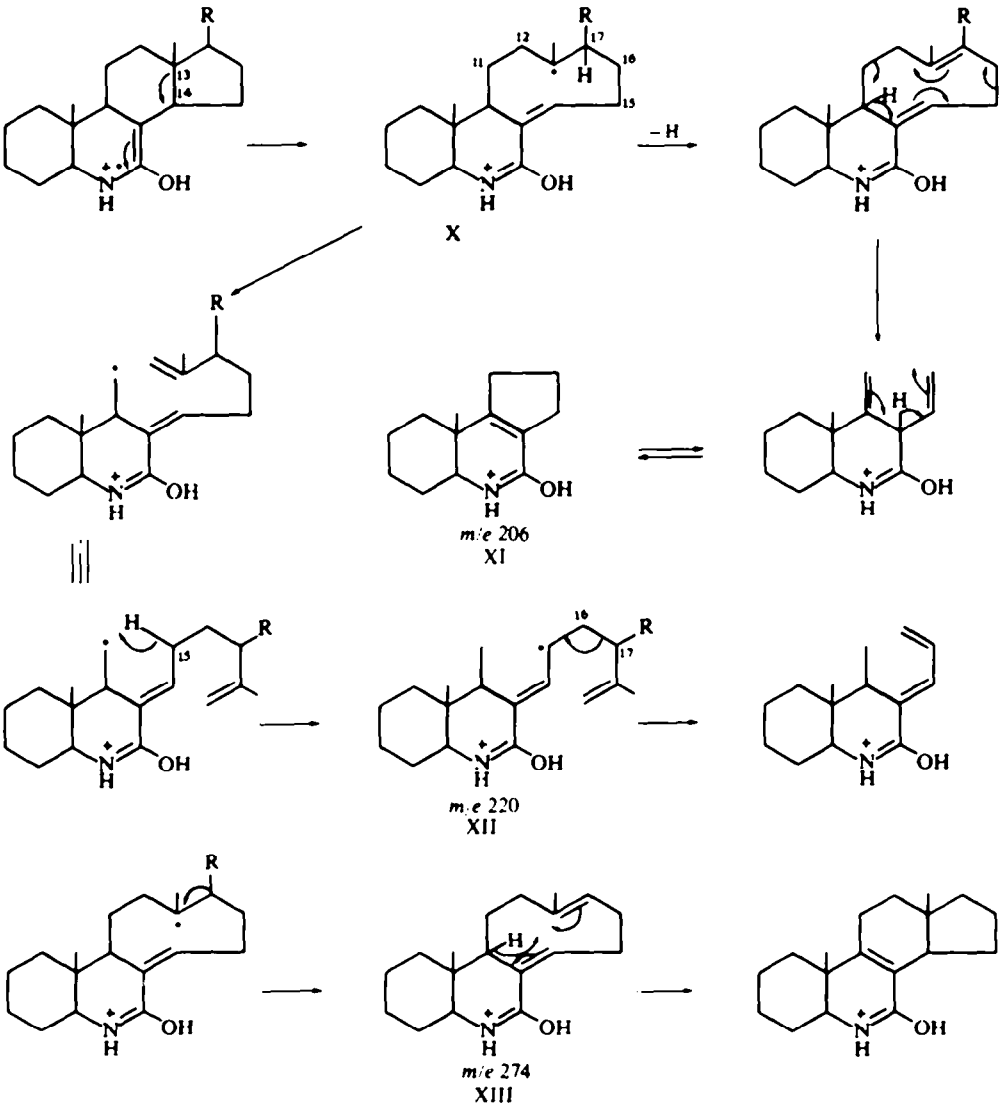
The abundant fragment XIII (*m/e* 274) may arise by homolytic cleavage of the C_{17}–R (R = C_8H_{17} or —OH) bond in the intermediate, as shown.

There are rather intense peaks due to M-28, M-29 and M-43 fragment ions in the spectra of these compounds and these can be attributed to the loss of CO, CHO and CO plus $\cdot CH_3$ from the molecular ion, respectively.

The mass spectra of 6 and 7 possess relatively strong signals at *m/e* 292 and 196, respectively. These signals differ from the corresponding molecular ions by 95 mass units, and therefore, their formation can be considered as being derived by loss of the elements of ring A.

The formation of this M-95 fragment is postulated as arising by cleavage of the C_9–C_{10} bond in the molecular ion XIV and subsequent fission of the C_5–N bond as indicated.

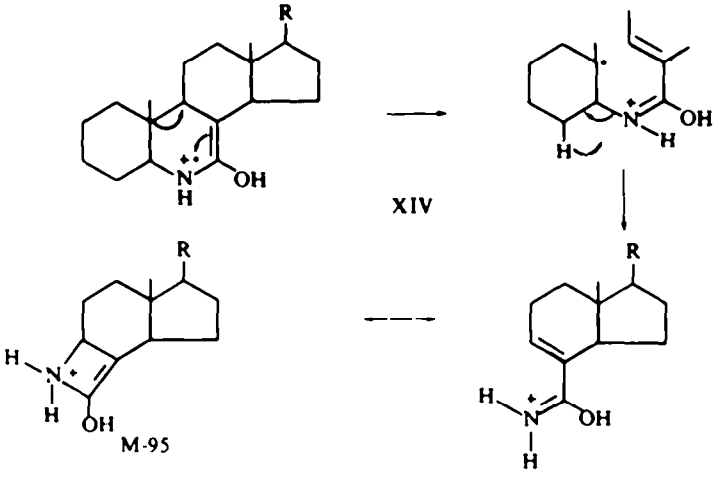
The following mechanistic interpretation for the formation of the M-95 fragment is in good agreement with the main fragmentation of aliphatic amines as described in a recent publication.[11]



[11] C. Djerassi and C. Fenselau, *J. Am. Chem. Soc.* **87**, 5752 (1965).

It is now of considerable interest to compare the mass spectral results obtained in the N-benzyl compounds **8**, **9** and **10** with those discussed above. The abundant fragments which were mentioned above were postulated as resulting from cleavage of the bonds in ring C and D. Such a suggestion would receive support if the significant fragments in the N-benzyl series were now occurring at *m/e* values which were higher by 90 mass units. This situation would of course prevail only if fragmentation in rings C and D occurred prior to any significant loss of the benzyl group. Indeed, inspection of the mass spectra, as for example in the case of **8**, reveals that this is the case—the peaks now occur at *m/e* 256 (166 + 90), 269 (179 + 90), 282 (192 + 90), etc. Although the abundance of these fragments is not very high, it must be recognized that, in general, the intensity of all peaks relative to the molecular ion signal is considerably lower in these spectra than in those of **6** and **7** (Figs 7 and 8).

As in the case of the N-benzyl **3**, **4** and **5**, the mass spectra of the N-benzyl-6-aza-7-one analogues **8**, **9** and **10** indicate the presence of fragments at *m/e* 91, *m/e* 386, 290, 360 (M-91) and *m/e* 400, 304, 374 (M-77), respectively—all due to the presence of the benzyl group.



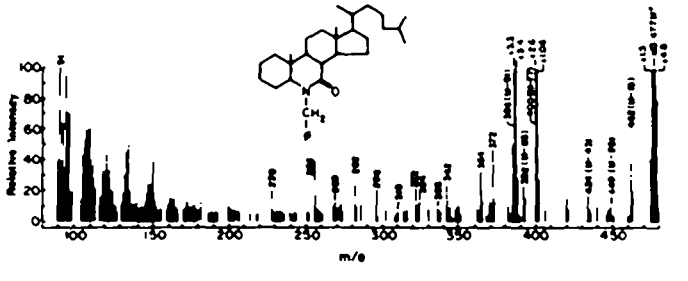


FIG. 7.

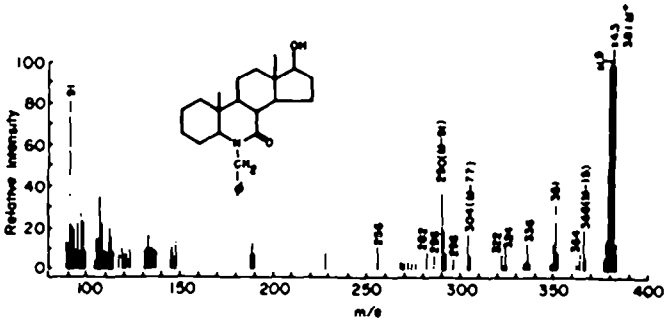


FIG. 8.

C. *The mass spectra of* Δ^4*-6-aza-7-one steroids*

The previous discussion has provided rather lengthy explanations for a variety of fragments in which rings A and B are retained. Consequently, it is immediately obvious that if such species are significant in the fragmentation of the enol lactams, they must occur at *m/e* values which are lower by 2 mass units. Indeed, this situation prevails, since the mass spectra of 6-aza-4-cholestene-7-one (**11**) and 17β-hydroxy-6-aza-4-androstene-7-one (**12**) indicate a number of common signals at *m/e* 164, 177, 190, 204, 218, 230, 232, 244, 245, 246, 258 and 272 due to the Δ^4 analogues of the fragments discussed in the case of the 6-aza-7-one compounds **6** and **7**. The relatively abundant M-28, M-29 and M-43 fragments are again probably due to the loss of CO, CHO and CO plus CH_3, respectively (Figs 9 and 10).

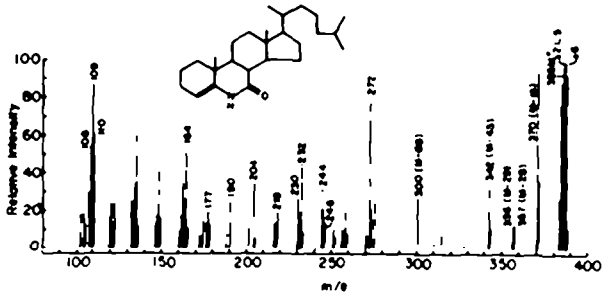


FIG. 9.

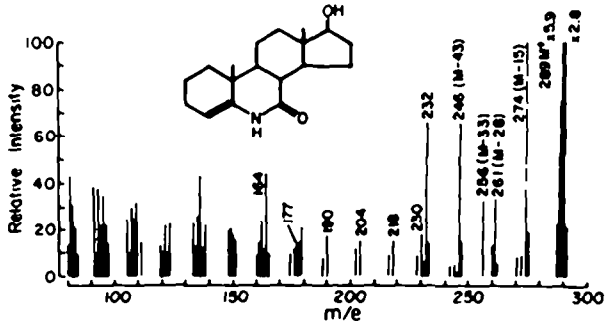
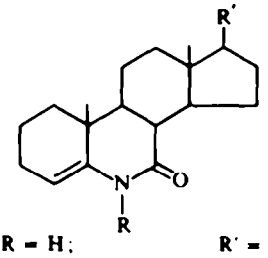


FIG. 10.

The abundant M-95 fragment present in the spectra of the 6-aza-7-one steroids is no longer present in the spectra of the Δ^4-compounds, **11** and **12**. This is to be expected, since the postulated mechanistic interpretation for the formation of this fragment in the case of 6-aza-7-one steroids, cannot be applied in the case of the Δ^4 analogues.



11. R = H;	R' = C_8H_{17}
12. R = H;	R' = OH
13. R = CH_2Ph;	R' = C_8H_{17}
14. R = CH_2Ph;	R' = OH
15. R = CH_2Ph;	R' = CH(OAc)Me

In the case of the N-benzyl-Δ^4-6-aza-7-one steroids (**13**, **14** and **15**), the expected signals at *m/e* 254 (164 + 90), 267 (177 + 90), 280 (190 + 90), etc., due to the fragmentations in ring C and D are very weak. The most intense peak, besides the molecular ion signal, is now due to the M-28 fragment and is probably due to the loss of CO from the molecular ion. Similarly, the M-29 and M-43 fragments are relatively abundant in the spectra of these compounds, and they are again probably due to the loss of CHO and CO plus CH_3, respectively (Figs 11 and 12).

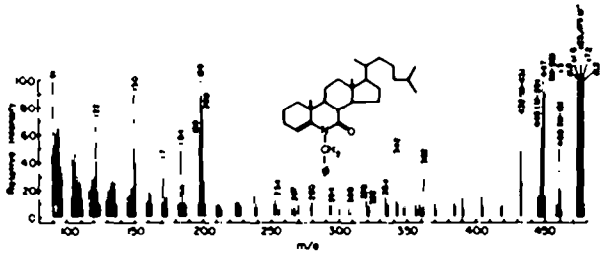


FIG. 11.

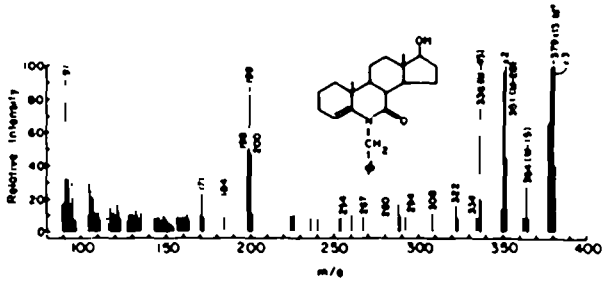
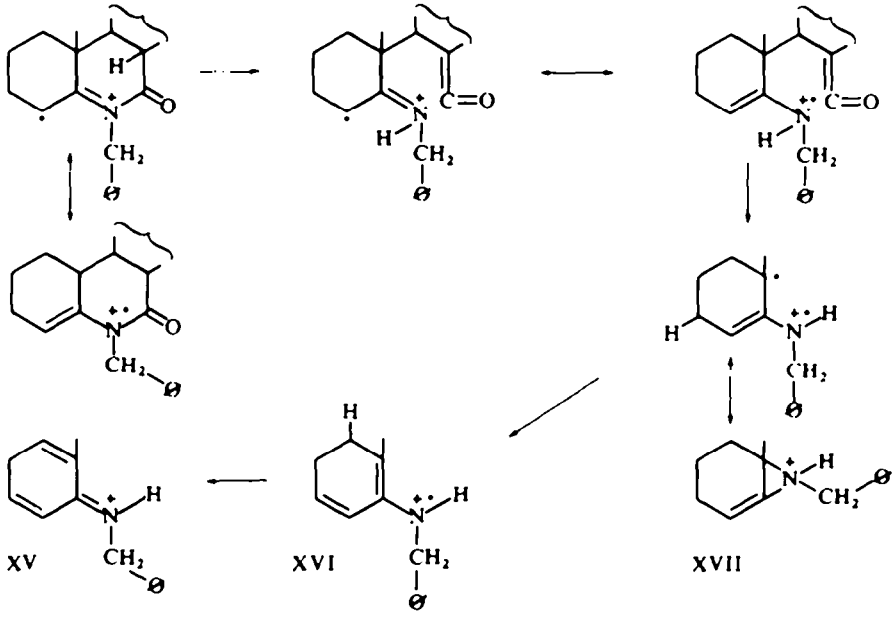


FIG. 12.

On the other hand, these aza steroids indicate three very characteristic signals at *m/e* 198, 199 and 200, with the most intense peak occurring at *m/e* 199. We postulate that the formation of the corresponding fragments XV (*m/e* 198), XVI (*m/e* 199), and XVII (*m/e* 200) may be visualized via the following scheme.



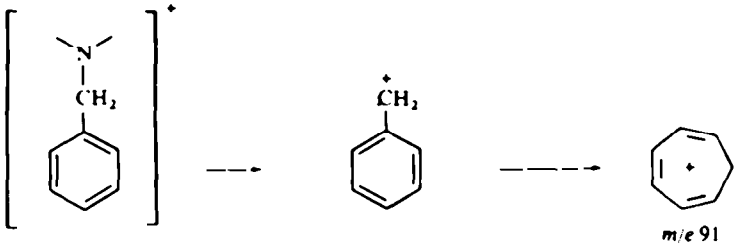
If such a fragmentation was taking place in this series of compounds, one would expect that the spectra of the Δ^4-6-aza steroids which do not contain the benzyl substituent would possess signals at *m/e* 108 (198 − 90), 109 (199 − 90) and 110 (200 − 90). Inspection of this region in the spectrum of 11 reveals clearly that this is actually the case (Fig. 9). The relatively intense signals at *m/e* 171 and 184 are also very characteristic in the spectra of the N-benzyl-Δ^4-6-aza-7-one series.

It has been mentioned in the previous discussion that the presence of the N-benzyl group in the 6-aza and 6-aza-7-one series is associated with the formation of fragments such as $C_7H_7^+$ (*m/e* 91), M-77 and M-91 due to the loss of $C_6H_5\cdot$ and $C_7H_7\cdot$ from the corresponding molecular ions, respectively. Therefore, one would expect the formation of the above fragments in N-benzyl-Δ^4-6-aza-7-one series as well. Although the $C_7H_7^+$ fragment does appear as indicated by a very strong signal at *m/e* 91 in the spectra of the latter series, signals due to fragment ions corresponding to M-77 and M-91 are no longer present in these spectra.

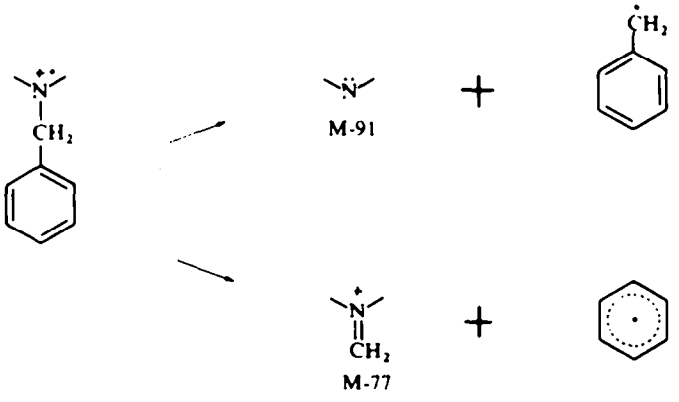
In order to provide an explanation for the absence of the above signals, it is necessary to comment on the fragmentation responsible for the formation of the fragment ions represented by $C_7H_7^+$, M-91 and M-77. It is well known that a benzyl bond is easily cleaved to provide the benzyl ion in which the positive charge is stabilized by resonance. Meyerson[12] has shown that this fragment is present rather as a tropilium ion (*m/e* 91).

[12] S. Meyerson, *Applied Spectroscopy* **9**, 120 (1955).

On the other hand, the ability of a nitrogen atom to stabilize a positive charge similarly can favour a fragmentation across the $N—CH_2C_6H_5$ or $NCH_2—C_6H_5$ bonds to provide the M-91 and M-77 fragments and the stable radicals $C_6H_5CH_2^{\cdot}$ and $C_6H_5^{\cdot}$, respectively. The fact that these fragments are not present implies that the above mechanism is either not operative to any significant extent in these compounds, or else the species so generated are immediately fragmented further before they can

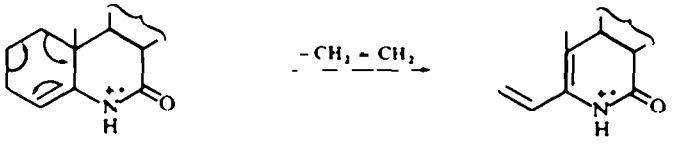


be recorded in the mass spectrometer. We feel that a more preferable explanation lies in an alternate mechanism (already postulated previously for the formation of the fragments XV, XVI and XVII) in which we suggest that a fission of the N—C=O bond occurs in the initial stages.



The pregnane derivatives 10 and 15 indicate three very characteristic signals at *m/e* 149, 270 and 261 (M-90 in 10), 359 (M-90 in 15), which are probably due to the nature of the side chain in these compounds.

The mass spectra of Δ^4-6-aza-7-one steroids, as in the case of the 6-aza-7-one series, can be also compared with the mass spectrum of 2-piperidone. The intensity of the signals corresponding to the M-28 fragment in the mass spectra of these steroids (and particularly in the case of their N-benzyl analogues) is relatively higher than the one observed in the spectra of the 6-aza-7-one series. We feel that the loss



of ethylene via retro-Diels-Alder reaction in the former compounds may contribute significantly to the intensity of these signals.

We also wish to indicate at this point the similarity of the mechanistic interpretation postulated above for the formation of the intense signals at *m/e* 198 (XV), 199 (XVI) and 200 (XVII) in the spectra of the N-benzyl derivatives **13**, **14** and **15** (*m/e* 108, 109 and 110 in the spectrum of **11**) and the one postulated for the formation of the most intense signal at *m/e* 30 in the spectrum of 2-piperidone.[13]

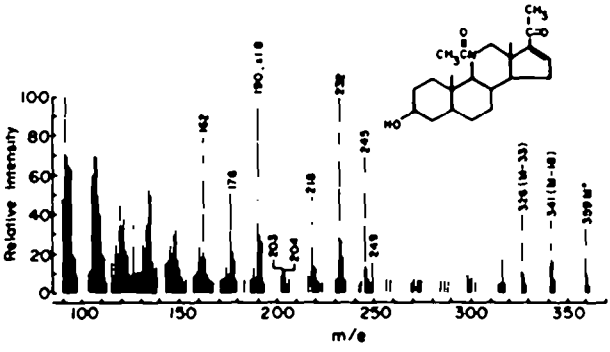


FIG. 13.

m/e 30

D. *The mass spectra of the* 11*-aza steroids*

For the studies of the mass spectra of the 11-aza series, we first examined the spectra of **16** and **17** and **18** (Figs 13–15). Compounds **16** and **17** indicate a series of common significant peaks at *m/e* 176, 190, 202, 203, 204, 206, 216, 218, 230, 232, 245, 249 and 262. On the other hand, **18** indicates an analogous series of signals which differ from those of the previous compounds by only two mass units (*m/e* 178, 192, 204, 205, 206, 208, 218, 220, 232, 234, 247, 251 and 264). Therefore, it becomes obvious from the above comparison that ring A, or part of ring A, is not present in the above

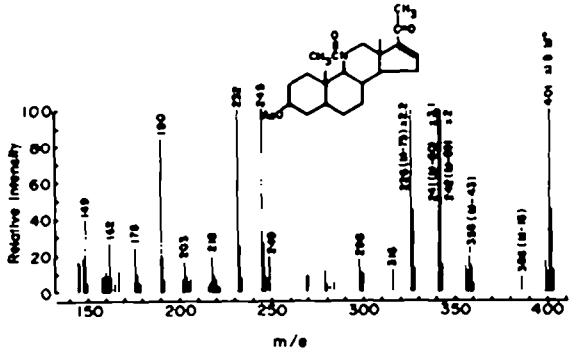


FIG. 14.

[13] A. M. Duffield, H. Budzikiewicz and C. Djerassi, *J. Am. Chem. Soc.* **86**, 5536 (1964).

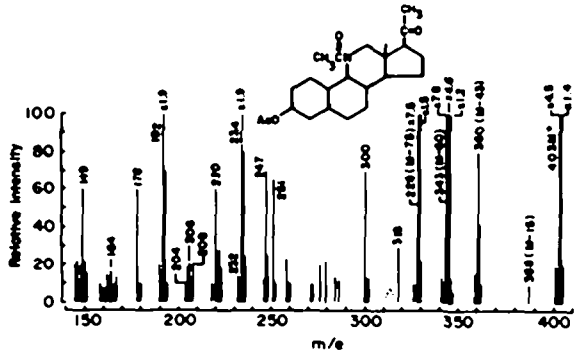


FIG. 15.

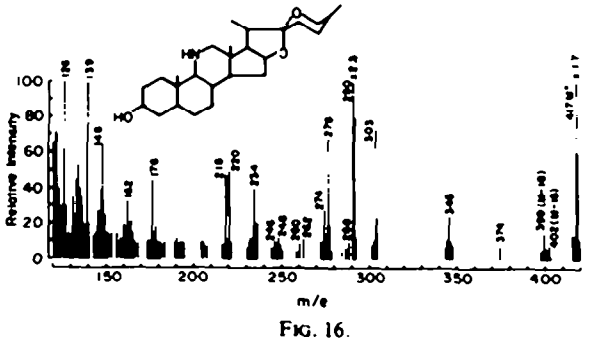


FIG. 16.

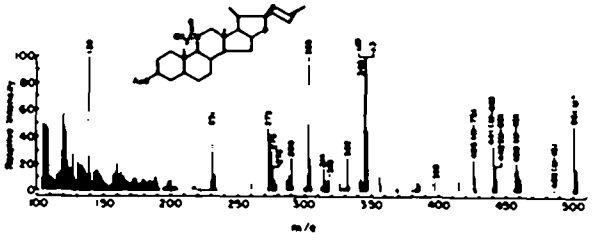
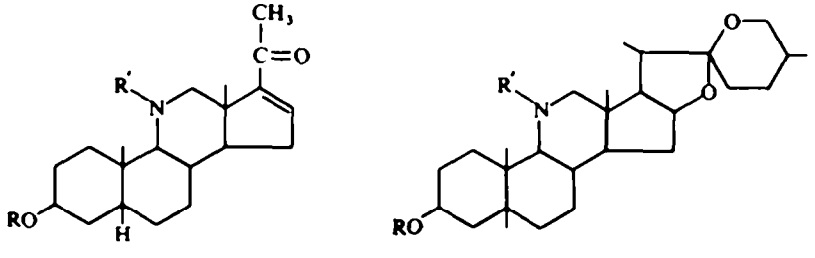


FIG. 17.

fragments, since the substituents at C_3 do not alter the mass of these fragments. On the other hand, these species must retain ring D, since the positions at which they occur are dependent on the functionality in this ring.



16. R = ; R' = Ac
17. R = R' = Ac
18. R = R' = Ac; no double bond at C_{16} C_{17}
19. R = R' = H
20. R = R' = Ac

The mass spectra of **19** and **20** are in further support of this conclusion (Figs 16 and 17). If we accept the above postulate, one would expect to observe that the corresponding fragment ions in the spectra of the latter compounds must shift by the appropriate values. In **20**, the peaks should occur at *m/e* values which are higher by 98 units due to the presence of the sapogenin side chain. Indeed, the spectrum of this compound does possess signals at *m/e* 276, 290, 302 (weak), 303, 304 (weak), 316 (weak), 318 (weak), 330 (weak), 332 and 345. On the other hand, the spectrum of **19**, which bears no N-acetyl function, indicates a series of signals at *m/e* 220, 234, 248, 260, 261 (weak), 262, 264 (weak), 274, 276, 290 and 303. These values differ, as expected, by 56 mass units from those of **18** and by 42 mass units from those of **20**. The latter observation also indicates clearly the presence of the nitrogen function in these fragment ions. It is, therefore, reasonable to conclude that the fragmentation responsible for these signals occurs via homolysis of bonds involving rings B and/or C.

We now wish to discuss the spectrum of **18**, since the salient features of the 11-aza series can be well illustrated with this example.

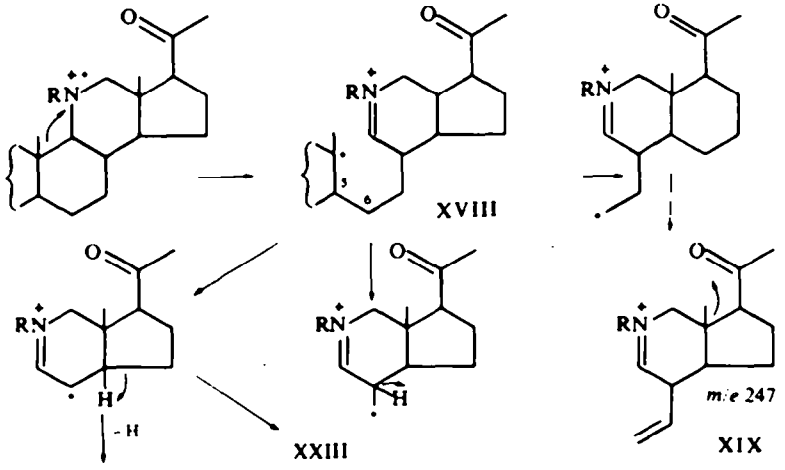
A reasonable postulate for the fragmentation responsible for the generation of the most of the above fragments can be visualized as shown in the scheme below. Homolytic cleavage of the C_9-C_{10} bond in the parent system results in radical XVIII, which in turn may fragment in two different ways. For instance, cleavage of the C_5-C_6 bond in the latter could eventually generate the fragments XIX (*m/e* 247) and XX (*m/e* 232).

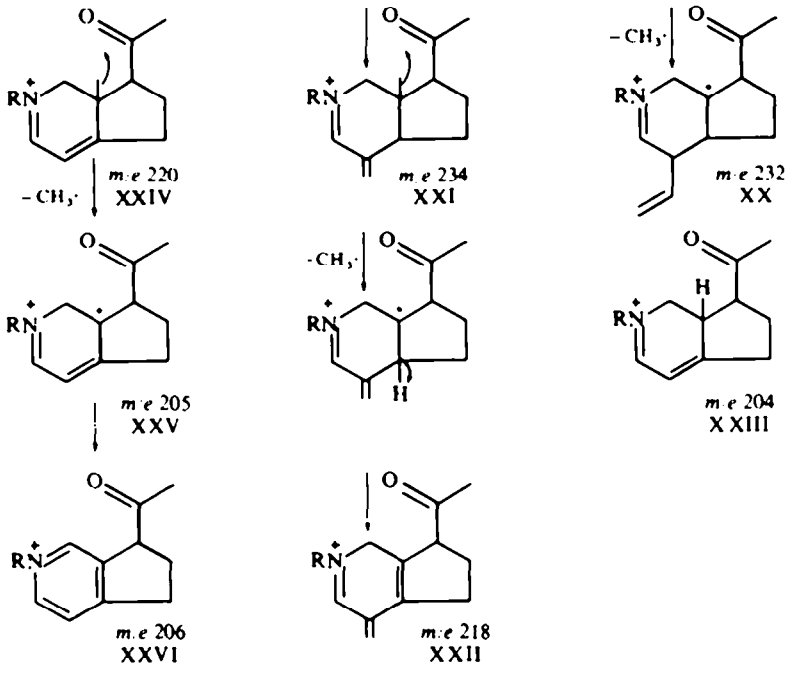
On the other hand, homolysis of the C_6-C_7 bond in XVIII could provide the species XXI (*m/e* 234), and in turn, the fragment XXII (*m/e* 218).

Furthermore, homolysis of the activated C_7-C_8 bond in XVIII would lead to the fragments XXIII (*m/e* 204), XXIV (*m/e* 220), XXV (*m/e* 205), and XXVI (*m/e* 206).

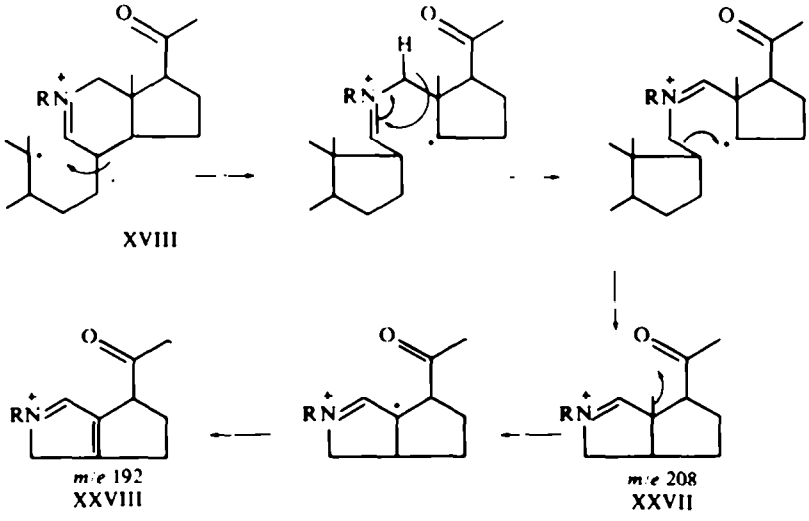
A further series of fragments can be obtained from the intermediate XVIII by further cleavage of the activated C_8-C_{14} and the C_8–C_9 linkages as indicated below for the formation of the fragment XXVII (*m/e* 208). The fragment XXVIII (*m/e* 192) is available from the latter by cleavage of the C_{13}–C_{18} bond and subsequent loss of the C_{14} hydrogen atom.

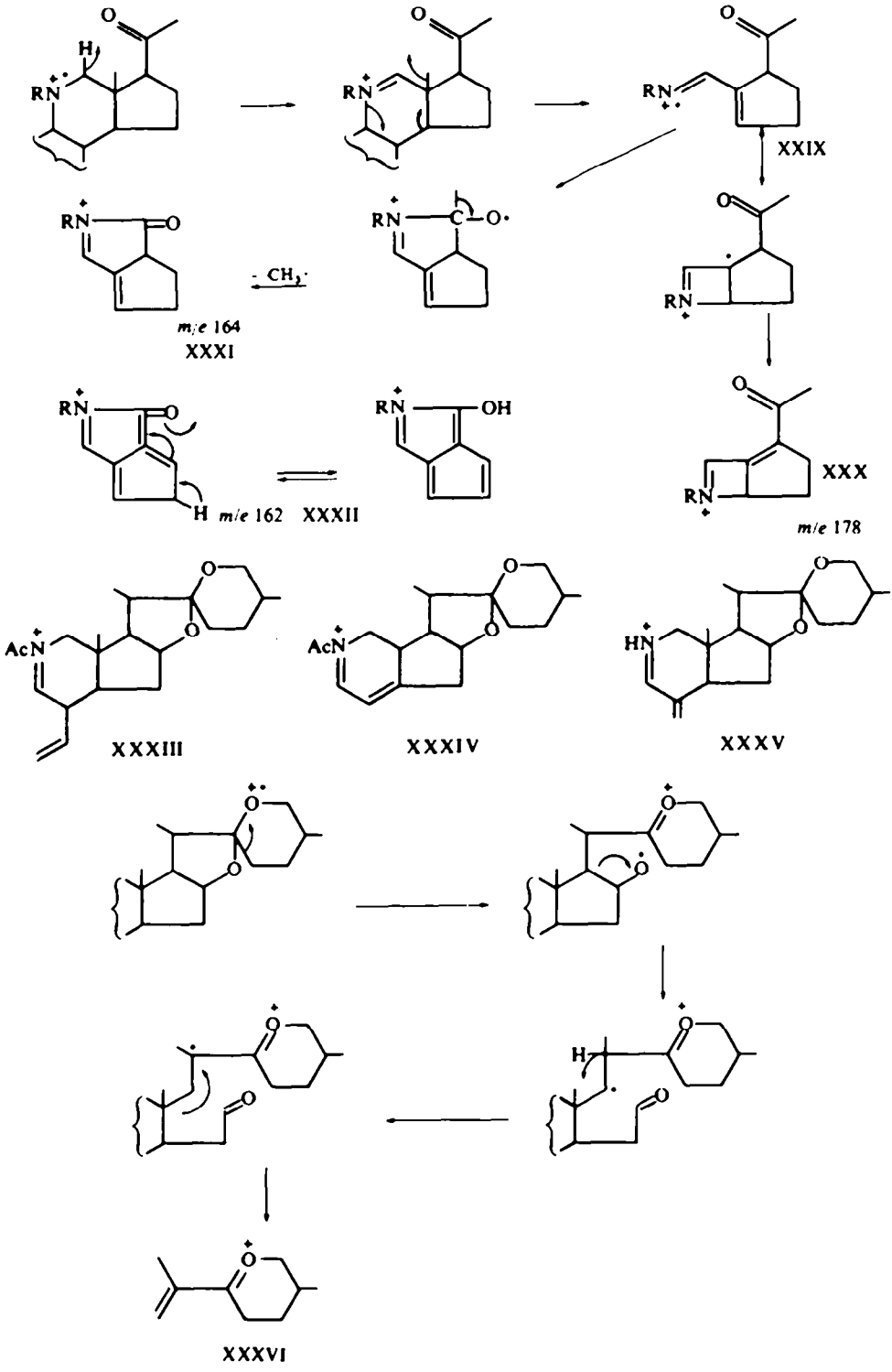
Another series of fragments—XXX (*m/e* 178), XXXI (*m/e* 164) and XXXII (*m/e*





162) -are plausibly derived from a common ion radical XXIX which may be formed as shown. It is interesting to indicate here that, in the case of the C_{16}–C_{17} dehydro analogues **16** and **17**, the fragment XXXII (*m/e* 162) arising via the above postulated fragmentation is much more abundant than the fragment XXXI (*m/e* 164) in the dihydro series. This situation is possibly due to the fact that the C_{16}–C_{17} double bond in the former compounds is able to provide an aromatic bicyclic system.

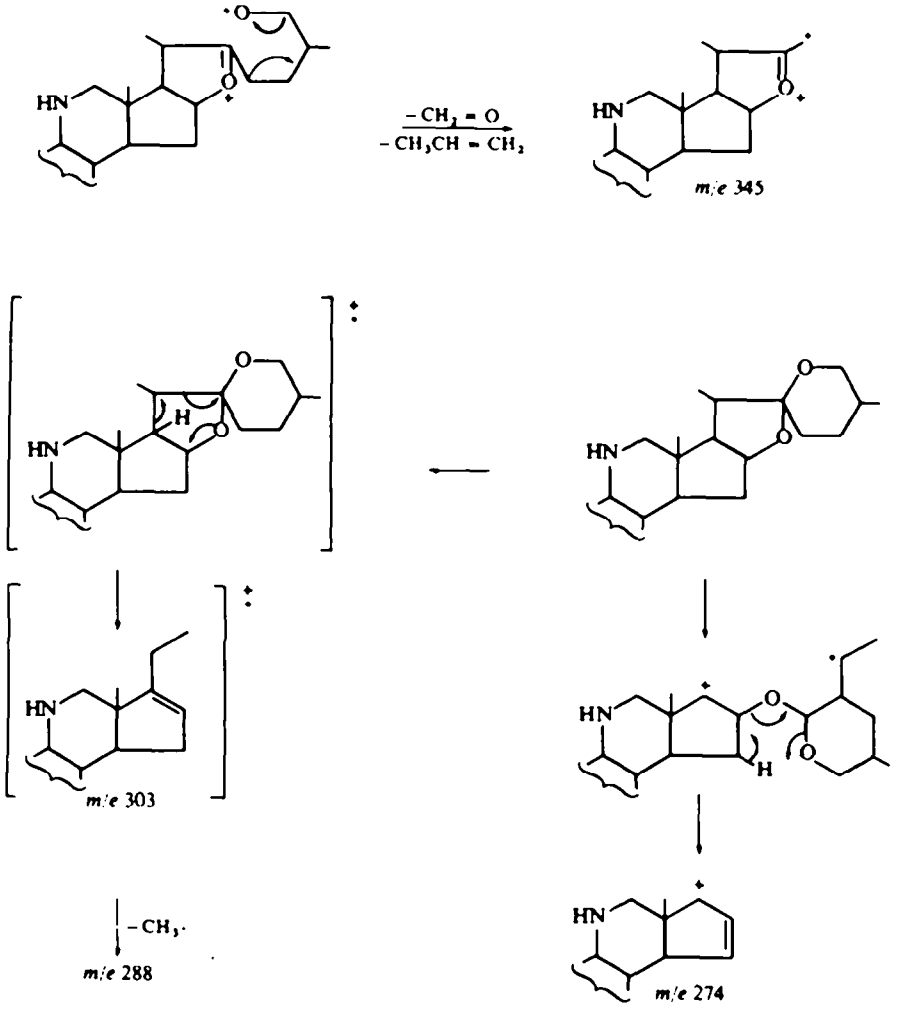



XXIX
- CH2·
m/e 164
XXXI
m/e 162
XXXII
XXX
m/e 178
XXXIII
XXXIV
XXXV
XXXVI

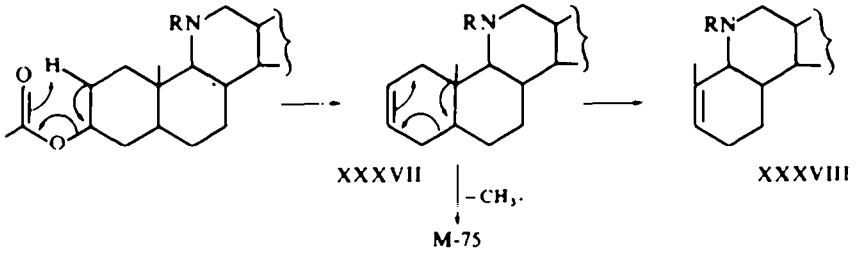
It is of further interest to emphasize at this point that the intensity of the signals due to the fragment ions discussed above, with the exception of those at *m/e* 345 and 303, is considerably lower in the spectrum of **20**. Similarly, an analogous difference in the intensity of signals (with the exception of the one at *m/e* 290) is observed in the mass spectrum of **19** and those of **16**, **17** and **18**. It is not possible at this time to provide any conclusive explanation for the high intensity of the signals at *m/e* 345, 303 in the spectrum of **20** and at *m/e* 290 in the one of **19**, but it is suggested they are perhaps due to the fragments XXXIII (as XIX in **18**), XXXIV (as XXV in **18**) and XXXV (as XXI in **18**), respectively.

The important signal at *m/e* 139 (XXXVI), common in **19** and **20**, is due to the fragmentation of the spiroketal side chain and is a characteristic feature in the mass spectra of sapogenins.[1]

The signals at *m/e* 274, 288, 303 and 345 in the spectrum of **19** can be derived via a fragmentation process of the spiroketal side chain as shown below.[1]



The abundant fragment M-60 (XXXVII) and M-75 (XXXVII-CH_3) in the spectra of **17**, **18** and **20** are very reminiscent of the spectrum of cholestan-3β-ol acetate,[1] and are due to the loss of AcOH and AcOH plus a Me group from the molecular ion. In the case of **18**, the corresponding signals occur at *m/e* 341 and 326, respectively. The metastable peak at *m/e* 313 (which is also present in the spectrum of **17** at *m/e* 312) strongly supports the relationship between those two fragments. The subsequent retro-Diels-Alder reaction which would normally provide the fragment XXXVIII is apparently not occurring in our system, since there is no signal corresponding to this fragment in **17**, **18** and **20**. On the other hand, **16**, **17** and **18** and **20** indicate signals at *m/e* 316, 360, 358 and 458 (M-43), respectively, which are due to the loss of the acetyl group from the N-acetyl functions.



In conclusion, we hope that these results have demonstrated that the presence of nitrogen as a hetero atom in the steroid system can have a profound effect on the fragmentation pattern of these molecules. Indeed, the application of this physical tool to problems in this series will undoubtedly provide valuable structural information. We will present results in this direction in future publications.

EXPERIMENTAL

The mass spectra were obtained with an Atlas CH4 mass spectrometer, using the direct insertion technique. The ionizing energy was maintained at 70 ev.