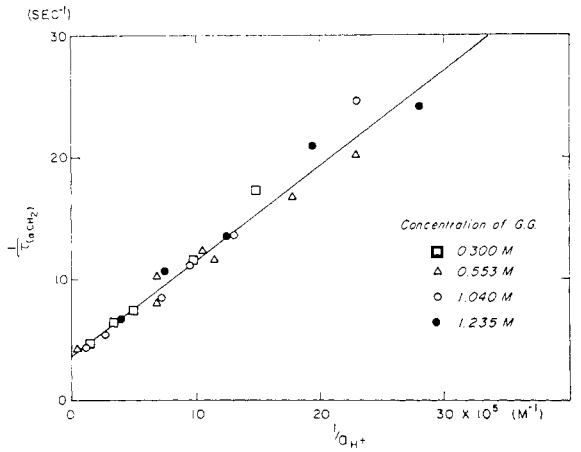

Figure 5. The reciprocal of the mean life time of the peptide hydrogen ($1/\tau$) as measured from the line shape of the α-methylene spectra as a function of $1/a_{H^+}$ (23 ± 1°).

The exchange rate is given by the sum of the exchange reactions

$$\frac{1}{\tau} = k_I[H_2O] + k_{II}[OH^-] = k_I[H_2O] + k_{II}\frac{K_w}{[H^+]}$$

Thus the value of the intercept in Figure 3 equals $k_I[H_2O]$ and the slope $k_{II}K_w$. It was found that $k_I[H_2O] = 3.5$ (sec.$^{-1}$)[16] and $k_{II} = 7.8 \times 10^8$ (M sec.)$^{-1}$.

(16) Another possibility to be considered is the intramolecular reaction

$\langle NH_3^+CH_2CONHCH_2COO^- \rightleftarrows NH_3^+CH_2CO\bar{N}CH_2COOH\rangle$

Since this reaction, as measured by us, must involve a water molecule (see discussion for reaction III for sarcosine in the zwitterion form),[12] we cannot distinguish between the intramolecular reaction and reaction I. The value of the rate constant, k_I, should be looked upon as a sum of the two reactions.

The mechanism and rate of exchange of N-methylacetamide is considered to represent the exchange behavior of short peptides where there are no internal hydrogen bonds. It is natural, therefore, to compare our results to that reported by Berger, Loewenstein, and Meiboom.[10] The rate of exchange reaction of the peptide hydrogen with OH^- ion, k_{II} for GG, is 1.5×10^2 times greater than the corresponding rate constant for N-methylacetamide. This is due probably to the presence of the adjoining positively charged NH_3^+ which will make the peptide hydrogen of GG more positive. A similar behavior of the influence of the NH_3^+ can be drawn when we compare the ionization constant of the carboxylic group of glycine to that of acetic acid.[17] The presence of the positively charged

$$k_{COOH}(\text{glycine})/k_{COOH}(\text{AcOH}) = 2.6 \times 10^2$$

NH_3^+ in glycine causes the proton of the carboxylic group to become more positive and increases the acid dissociation.

The exchange of GG is different, however, from that of N-methylacetamide in one respect. We did not observe any exchange in the acidic range although we went down to pH 0.0. This result is also in contrast to acid-catalyzed exchange reported for glycylglycine.[8]

Acknowledgement. The author wishes to express his gratitude to Dr. E. D. Becker for his valuable discussions and to Mr. R. B. Bradley for maintaining the n.m.r. spectrometer in top condition.

(17) E. J. Cohn and J. T. Edsall, "Proteins, Amino Acids, and Peptides," Reinhold Publishing Corp., New York, N. Y., 1945, p. 77.

Mass Spectrometry in Structural and Stereochemical Problems. LX.[1] The Electron Impact Induced Fragmentation of Steroidal Dimethylamines[2]

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Contribution from the Department of Chemistry, Stanford University, Stanford, California. *Received September 4, 1964*

The mass spectra of a number of dimethylaminoandrostanes and dimethylaminocholestanes have been measured. The most abundant ions in the spectra correspond to immonium species, whose formation is readily understandable, and even predictable, in terms of charge localization on nitrogen in the molecular ion and subsequent fragmentation by rational bond homolyses and hydrogen transfers. Dimethylamino compounds, like ethylene ketals, should be regarded therefore as highly desirable derivatives for mass spectrometric purposes.

Introduction

The ability of a dimethylamino function at C-3 or C-20 in the steroid nucleus to direct electron impact induced fragmentation in such compounds has previously been noted.[3-5] All 3-dimethylamino steroids that have so far been investigated, and which do not

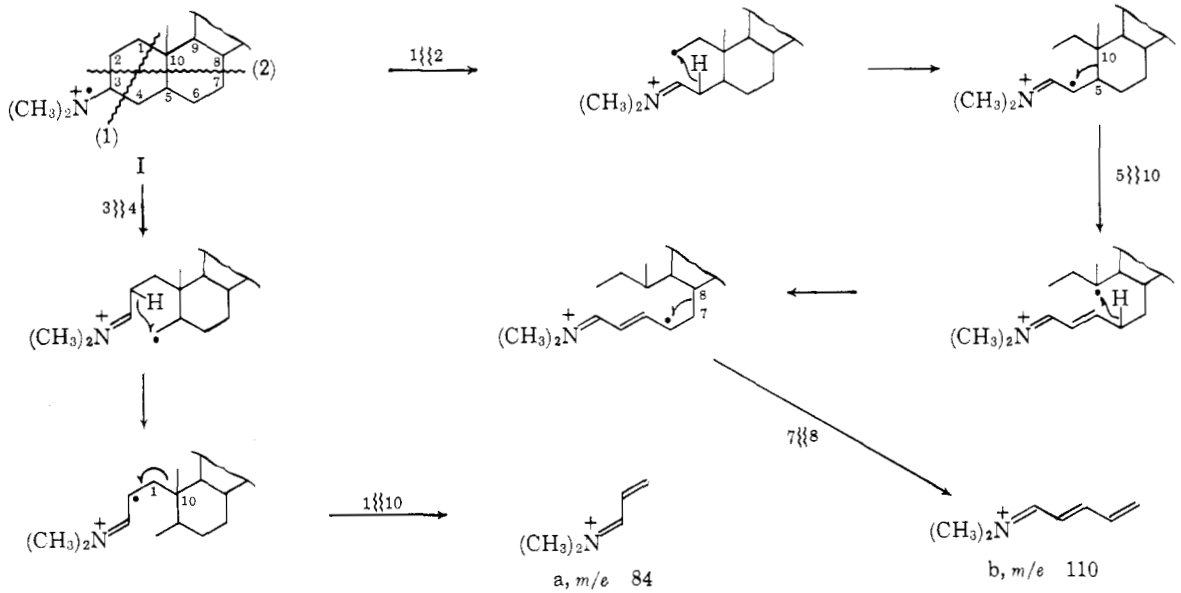
(1) Paper LIX: J. E. Gurst and C. Djerassi, *J. Am. Chem. Soc.*, **86**, 5542 (1964).

(2) We are indebted to the National Institutes of Health of the U. S. Public Health Service for financial support (Grants No. AM 04257 and CA 07195). Thanks are due to Syntex S. A., Mexico City, for supplying certain steroid starting materials.

(3) W. Vetter, P. Longevialle, F. Khuong-Huu-Laine, Q. Khuong-Huu, and R. Goutarel, *Bull. soc. chim. France*, 1324 (1963).

(4) L. Dolejš, V. Hanuš, V. Černý, and F. Šorm, *Collection Czech. Chem. Commun.*, **28**, 1584 (1963).

(5) (a) H. Budzikiewicz, C. Djerassi, and D. H. Williams, "Interpretation of Mass Spectra of Organic Compounds," Holden-Day, Inc., San Francisco, Calif., 1964, pp. 74–80; (b) H. Budzikiewicz, C. Djerassi, and D. H. Williams, "Structure Elucidation of Natural Products by Mass Spectrometry," Vol. II, Holden-Day, Inc., San Francisco, Calif., 1964, pp. 43–49.

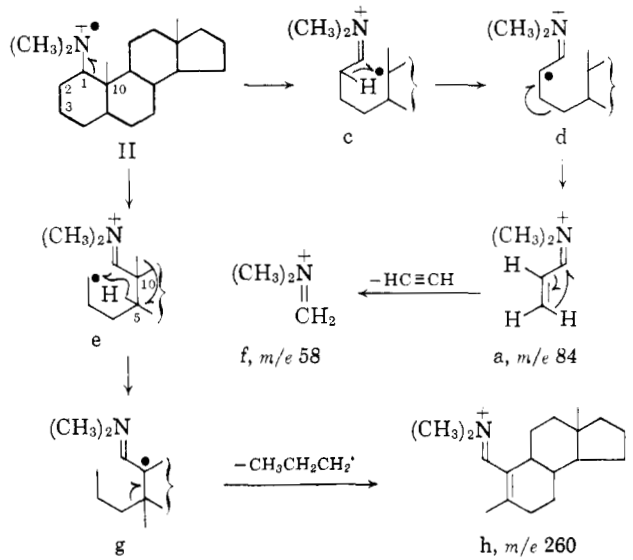


contain other functional groups in rings A and B (see I), show intense peaks in their mass spectra at m/e = 84 (a) and m/e = 110 (b). These ions are formally due to cleavages (1) and (2) (see I) with loss of one and two hydrogens from the nitrogen-containing, charged fragment, respectively.[3-5] The mechanisms which have been proposed[3,5] for the formation of these ions are outlined below since they provide the background for the rationalization of the spectra which will be discussed in this paper. The proposed hydrogen transfers are supported by deuterium-labeling experiments.[6]

As in the case of ethylene ketals,[7] we wished to investigate to what extent analogous modes of breakdown would occur when the dimethylamino function was located at other nuclear sites in the steroid skeleton. The results which were obtained for dimethylamino groups located at C-1, C-2, C-3 (in a 4,4-dimethyl compound), C-6, C-7, C-11, C-16, and C-17 are outlined below. It will be seen that, in those cases where a comparison with the corresponding ethylene ketals[7] can be drawn, the behavior of the two groups is closely analogous. The most important general difference between the spectra of the ethylene ketals and the dimethylamines is that the molecular ions are frequently more abundant in the nitrogen-containing derivatives. In the following discussion all percentages used to express the abundance of an ion are relative to the base peak taken as 100%.

Discussion

1α-Dimethylamino-5α-androstane (II). In the mass spectrum of this compound (II) only one ion (m/e = 58, 53% of the base peak) attains over 10% of the abundance of the m/e = 84 species (a, base peak), which may be formed by the sequence II → c → d → a (m/e = 84). This is not surprising, since the product (e) of the alternative 1–2 cleavage cannot decompose in the conventional manner in the absence of hydrogen attached to C-10. The m/e = 58 ion (f) is frequently important in the spectra of dimethylamino steroids and may be formulated as arising through loss of acetylene from a.



An unusual feature of the high mass range of the spectrum is a peak at m/e = 260 (9%), corresponding to expulsion of 43 mass units from the molecular ion (m/e = 303, 9%). The spectrum of the 2,3-d_2 derivative of 1ξ-dimethylaminocholestane (see II for the numbering of the steroid skeleton) indicates that C-2 and C-3 are expelled in the formation of the M − 43 species and therefore m/e = 260 (M − 43) can reasonably be formulated as arising from the decomposition of e as indicated in the sequence e → g → h (m/e = 260). Hydrogen migration from C-5 to C-2 in a five-membered transition state, with concomitant methyl migration from C-10 to C-5, results in the formation of an allylic ion radical g. This ion radical can then decompose by homolysis of the 4–5 bond to furnish the conjugated immonium ion h (m/e = 260).

2-Dimethylaminocholestane (III).[8] The mass spectrum of this compound is reproduced in Figure 1. As expected, the base peak of the spectrum occurs at m/e = 84, corresponding to cleavage (3) with hydrogen

(6) Z. Pelah, M. A. Kielczewski, J. M. Wilson, M. Ohashi, H. Budzikiewicz, and C. Djerassi, *J. Am. Chem. Soc.*, **85**, 2470 (1963).

(7) Z. Pelah, D. H. Williams, H. Budzikiewicz, and C. Djerassi, *ibid.*, **86**, 3727 (1964); see also G. von Mutzenbacher, Z. Pelah, D. H. Williams, H. Budzikiewicz, and C. Djerassi, *Steroids*, **2**, 475 (1963), and ref. 9 and 10.

(8) This compound was isolated as a mixture of 2α- and 2β-epimers; see C. W. Bird and R. C. Cookson, *J. Chem. Soc.*, 2343 (1960).

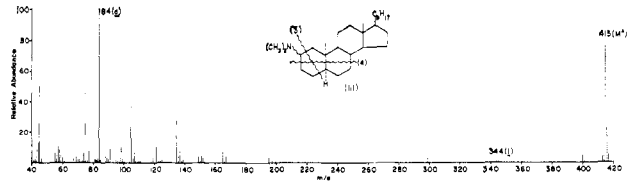


Figure 1. Mass spectrum of 2-dimethylaminocholestane (III).

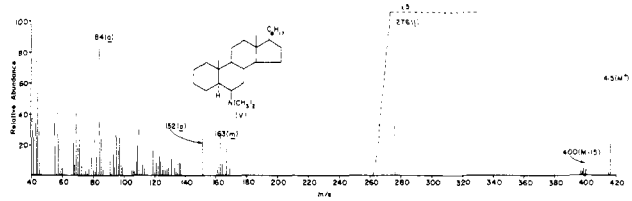
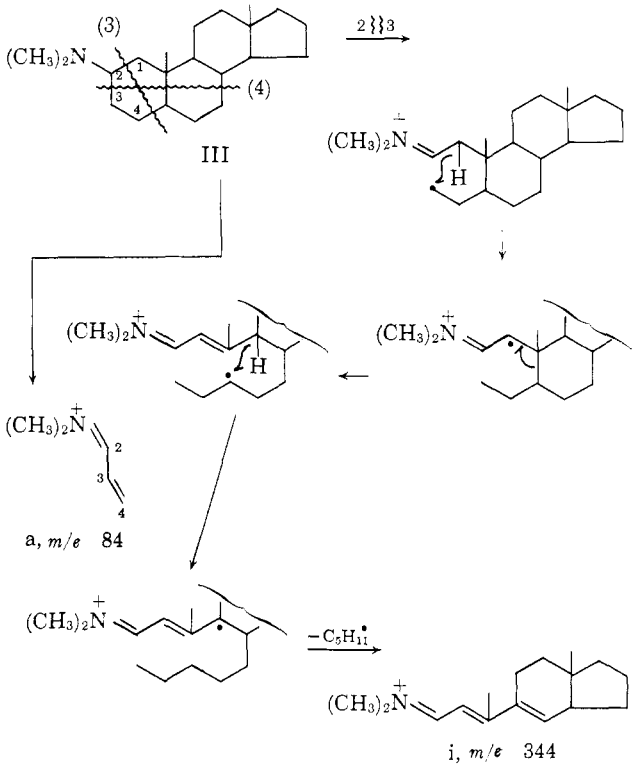
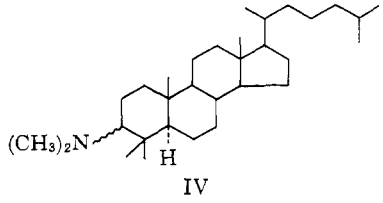


Figure 2. Mass spectrum of 6β-dimethylaminocholestane (V).

transfer from C-3 to the expelled neutral species. A peak is evident at m/e = 344 (i) and corresponds to the ion obtained by cleavage (4) (see III); the intensity of this peak is rather less than might have been anticipated *a priori* and it is interesting to note that a similar state of affairs exists in certain 2-ethylene ketals.[9]

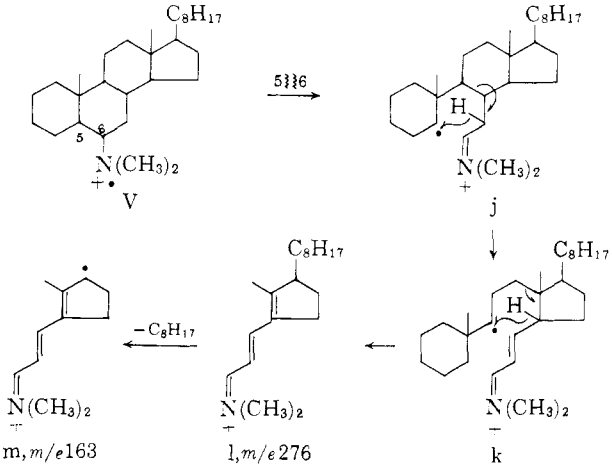


3ξ-Dimethylamino-4,4-dimethylcholestane (*IV*). As with ethylene ketals,[7] disubstitution at C-4 inhibits cleavage across rings A and B (see cleavage (2) in I). Consequently, in the spectrum of IV, the base peak is at m/e = 84 (a) and no other peaks attain even 5% of the abundance of a.

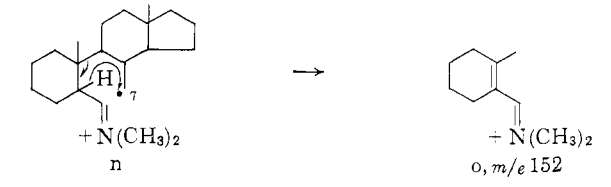


IV

6β-Dimethylaminocholestane (*V*). In the mass spectrum (Figure 2) of V the region above m/e = 265 has been reduced by a factor of five. It can be seen, therefore, that the molecular ion (m/e = 415) and m/e = 276 (l) are by far the most intense peaks in the spectrum. The process by which m/e = 276 is formed follows the usual rational path; in the sequence V → l, outlined below, two steps are occasionally indicated as occurring on one intermediate, in order to condense the representation. Loss of the C-17 side chain from l can occur with the formation of an allylic radical and, indeed, an ion is evident in the spectrum at m/e = 163 (m). A pathway exactly analogous to V → m is followed in the decomposition of cholestan-6-one ethylene ketal upon electron impact.[9,10]



The alternative to the primary homolysis indicated by V → j is homolytic rupture of the 6–7 bond (V → n). Hydrogen transfer from C-5 to satiate the primary radical at C-7 may then occur in n, and associated rupture of the 9–10 bond should then afford o (m/e = 152). This expectation is confirmed by the presence of a medium intensity ion at m/e = 152.



It will be noted that a prominent peak is evident in the spectrum (Figure 2) at m/e = 84 (a), even though the formal structural prerequisite for the formation of this species is a chain of two methylene groups adjacent to the functional group (*e.g.*, as in 1-, 2-, and 3-ketones). As in the case of m/e = 99 ions from ethylene ketals,[7] it seems that the appearance of an m/e = 84 ion several times more intense than any other ion in the spectrum is indicative of such a chain of two methylene groups, but that m/e = 84 ions of somewhat smaller relative abundance (of the same intensity as several other ions in the spectrum—see, for example, Figure 2) may be formed in more compli-

(9) H. Audier, J. Bottin, A. Diara, M. Fétizon, P. Foy, M. Golfier, and W. Vetter, *Bull. soc. chim. France*, 2292 (1964).

(10) H. Audier, A. Diara, M. de J. Durazo, M. Fétizon, P. Foy, and W. Vetter, *ibid.*, 2827 (1963).

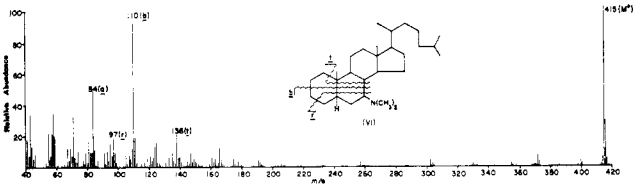
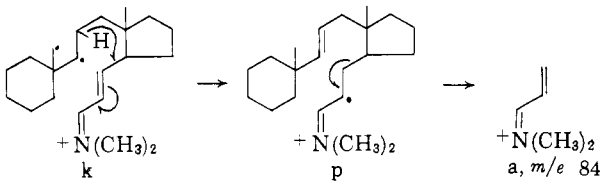
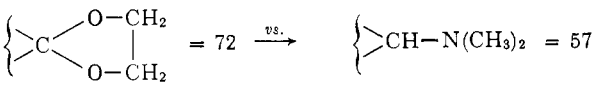


Figure 3. Mass spectrum of 7β-dimethylaminocholestane (VI).

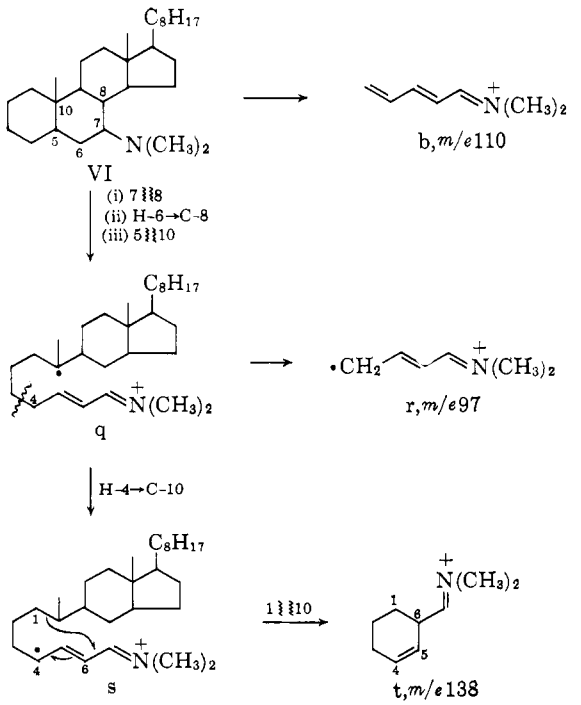
cated rearrangement processes. In analogy to ethylene ketals, in which the phenomenon has been investigated by deuterium labeling,[7] we propose the following sequence for the formation of m/e = 84 in the decomposition of V.



7β-Dimethylaminocholestane (VI). The mass spectrum (Figure 3) of 7β-dimethylaminocholestane (VI) is very similar below m/e = 160 to that of 5α-androstan-7-one ethylene ketal[7,10]; the relative intensities of the prominent ions in these regions of the two spectra are similar, the main difference being a shift of 15 units to lower masses in the amine spectrum, corresponding to the difference between the functional groups, *i.e.*



The most abundant fragment ion (m/e = 110, b) is formed in a manner exactly analogous to that operating in the genesis of its counterpart from 3-dimethylamino steroids (see cleavage (2) in I). Simple homolysis of the 3–4 bond in the decomposition intermediate q yields m/e = 97 (r), whereas s may undergo homolysis of the 1–10 bond with concomitant formation of a six-membered ring to afford t (m/e = 138).



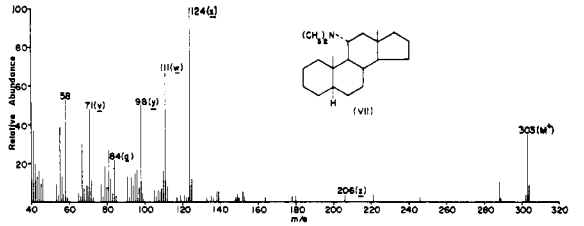


Figure 4. Mass spectrum of 11α-dimethylamino-5α-androstane (VII).

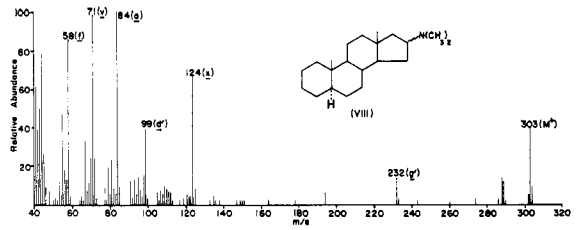
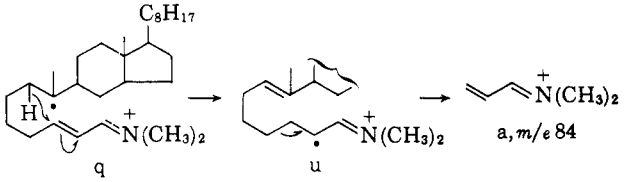


Figure 5. Mass spectrum of 16ξ-dimethylamino-5α-androstane (VIII).

In the absence of two methylene groups adjacent to the functional group, m/e = 84 (a) is less abundant than both the molecular ion (m/e = 415) and m/e = 110; by analogy to ethylene ketals,[7] hydrogen from C-1 may be implicated in its formation (see q → u → a). It is noteworthy that ions formed by reaction paths involving homolysis of the 6–7 bond as the primary process do not appear in the spectrum; the reason for this behavior is not apparent at present.[11]



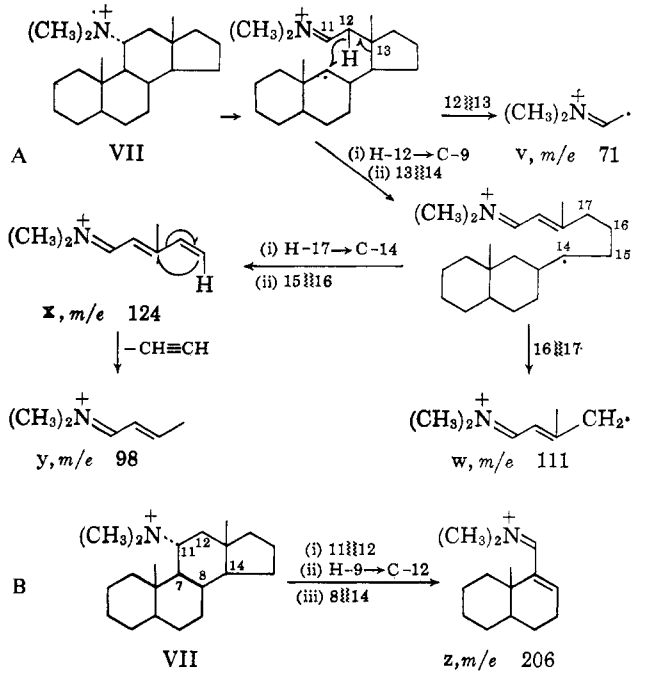
11α-Dimethylamino-5α-androstane (VII). It was of particular interest to examine this compound since the corresponding 11-ethylene ketals have not yet been prepared. A pertinent feature of the mass spectrum (Figure 4) of VII is the very low abundance of the m/e = 84 ion (a). This situation is understandable because a large number of rearrangement processes would be necessary to abstract C-8 and C-9 or C-12 and C-13 from the skeleton with the appropriate number of hydrogen atoms to furnish a. The correspondence between the anticipated and observed peaks n the spectrum is gratifyingly close; the processes involved in the formation of the most abundant ions are indicated in Scheme IA and B, which require little additional comment.

Obviously, there is a great predominance of 9–11 cleavage over the alternative 11–12 fission. These observations seem to indicate that the formation of a secondary radical at C-9 is preferred to the formation of a primary radical at C-12 in the initial α-cleavage processes.

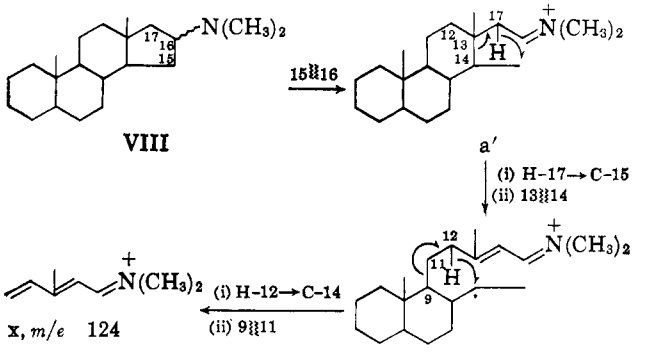
16ξ-Dimethylamino-5α-androstane (VIII). In the spectrum (Figure 5) of VIII, m/e = 84 (a) is of com-

(11) Obviously, 7–8 cleavage will be favored over 6–7 cleavage as the primary process, since secondary and primary radicals, respectively, are generated by these processes. However, one would not anticipate such large differences to be caused by this factor alone.

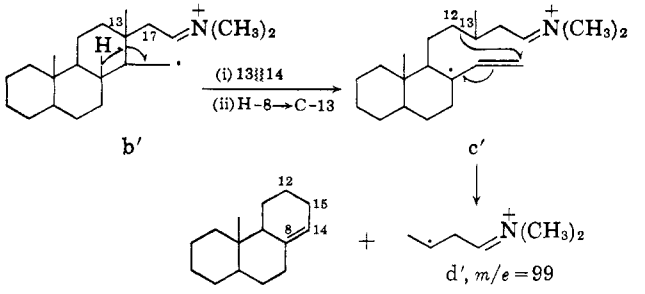
Scheme I. Primary 9–11 Cleavage (A) and 10–11 Cleavage (B)



parable abundance to several other ions, a feature which suggests the presence of a methylene group next to the functionality with a methine group (CH) adjacent to the methylene moiety, as is indeed the case. Cleavage of the 15–16 bond in the molecular ion gives rise to the prominent peak at m/e = 124 (x).

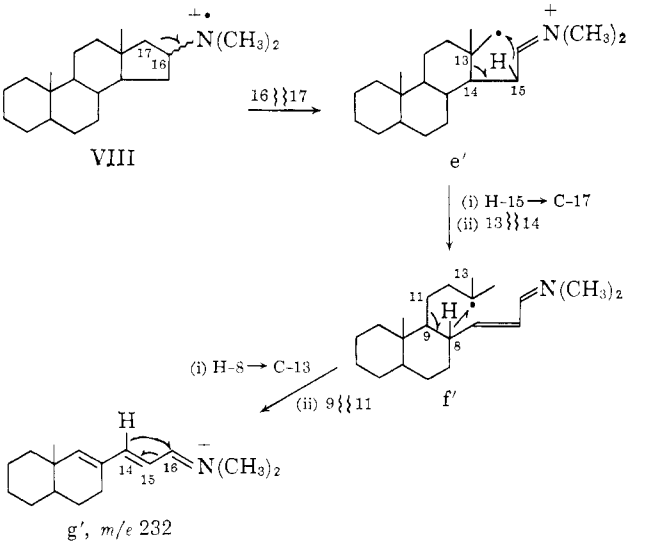


An alternative process for the decomposition of a′ is one in which homolysis of the 13–14 bond occurs (see b′) without associated hydrogen transfer from C-17 to C-15. The species obtained under these circumstances may be converted by hydrogen migration from C-8 to C-13 (see b′) to an allylic radical c′, in which rupture of the 12–13 bond can occur with concomitant formation of a six-membered ring (see c′ → d′). This fragmentation sequence rationalizes the appearance of a prominent peak at m/e = 99 and is identical with that which has been proposed[7] for the formation of an

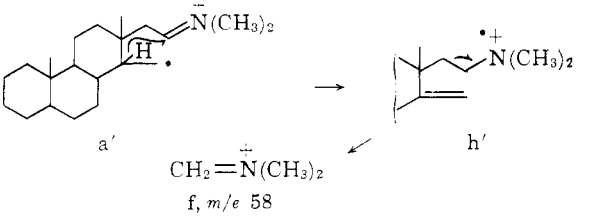


analogous ion at m/e = 114 in the mass spectrum of androstan-16-one ethylene ketal.

If scission of the 16–17 bond occurs in the molecular ion (VIII → e′), the usual series of bond ruptures (e′ → f′ → g′) affords m/e = 232 (g′).

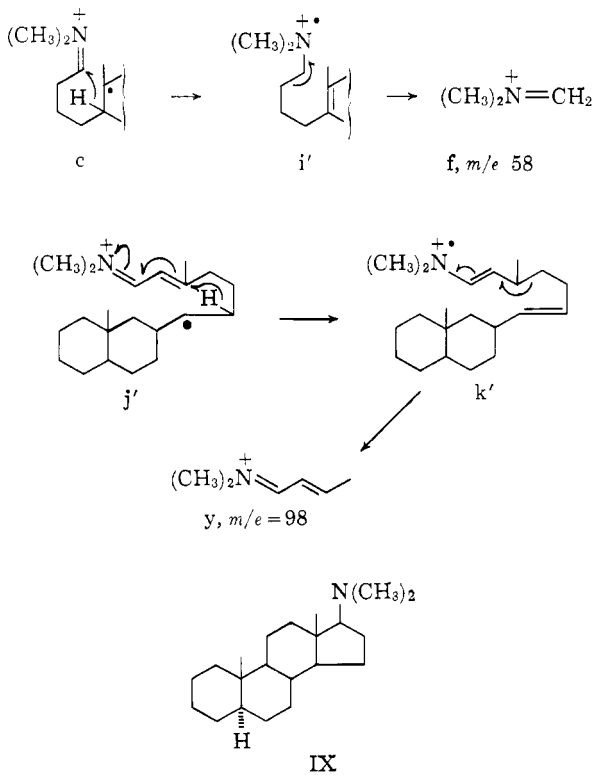


Obviously, homolysis of the 13–17 bond in a′ or of the 14–15 bond in e′ can lead to m/e = 71 (v). In addition, m/e = 58 (see Figure 5), which corresponds to species f, can in principle be formed, for example, in a process in which hydrogen is transformed from C-14 to C-16 with associated rupture of the 15–16 bond (see g′). If this mode of decomposition were to occur in the fragment ion g′, an acetylene would be eliminated as a neutral particle. The formation of such acetylenic neutral particles has been indicated previously in this paper (see a → f and x → y) but, in the absence of metastable ions to confirm such processes, it should be pointed out that the necessary hydrogen rearrangements can equally well (or perhaps even more desirably) be invoked as occurring in some form of the molecular ion. For example, a′ could decompose to f through h′. Deuterium labeling would not, of course, distinguish between these two possibilities since hydrogen is transferred from C-14 in both instances.



However, a′ → f (see 1α-dimethylandrostane (II)) and x → y (see 11α-dimethylaminoandrostane (VII)) can be replaced by c → i′ → f and j′ → k′ → y, respectively, and deuterium labeling would be required to differentiate between these possibilities.

17β-Dimethylamino-5α-androstane (IX). This spectrum requires no discussion other than to note that as expected, m/e = 84 (*a*) is the base peak of the spectrum, being more than 13 times as abundant as any other fragment ion.



Conclusion

This study establishes that dimethylamino derivatives are equally as desirable as ethylene ketal derivatives[7,9,10] for mass spectrometric purposes. The fragmentation patterns of the two classes of compounds run closely parallel. The principles which have been outlined above should prove applicable to any, predominantly saturated, polycyclic molecules and hence will undoubtedly prove valuable in aiding the structure elucidation of natural products. The great advantage of these two types of derivatives is that they control fragmentation even in the presence of other substituents. For instance, the fragmentation of ring D with associated hydrogen rearrangement,[12] so typical of cholestanes, is greatly suppressed (see Figures 1–3) in the presence of the dimethylamino moiety. The highly characteristic ions which are formed in the breakdown processes retain only a portion of the carbon skeleton; therefore, the mass shifts of a given peak caused by other functional groups permit their location or confinement to a certain portion of the molecule.

Most gratifying is the extremely consistent manner in which the basic principles of ground-state organic chemistry permit a facile interpretation of the spectra. The complexities, such as double reciprocal hydrogen transfers[13] and partially random hydrogen migrations,[14] which at times plague the interpretation of the mass spectra of steroidal ketones disappear when charge localization is specific. Under the latter circumstances, bond ruptures proceed in a rational, stepwise manner and structural information may readily be gained.

(12) See C. Djerassi, *Pure Appl. Chem.*, **9**, 159 (2964).
(13) D. H. Williams, J. M. Wilson, H. Budzikiewicz, and C. Djerassi, *J. Am. Chem. Soc.*, **85**, 2091 (1963).
(14) R. H. Shapiro, D. H. Williams, H. Budzikiewicz, and C. Djerassi, *ibid.*, **86**, 2837 (1964).

Experimental[15]

The dimethylamino steroids were prepared by the general procedure of converting the ketone to the oxime and reducing the latter either by catalytic hydrogenation or by lithium aluminum hydride to the amine. Dimethylation of the amine was then effected by formic acid and formaldehyde.[16] Additional details are given below, along with appropriate references for dimethylamino steroids which have previously been described.

General Procedure for the Preparation of Oximes. The ketone and hydroxylamine hydrochloride (2 equiv.) in pyridine solution were heated on a steam bath for approximately 1 hr. Pyridine was then removed by distillation under vacuum and water and ether were added to the residue. Evaporation of the ether phase gave the crude oxime in almost quantitative yield. Purification could be effected by crystallization from methanol–acetone. This procedure proved satisfactory for all cases with the exception of 5α-androstan-11-one oxime; the preparation of this oxime is described below.

1α-Dimethylamino-5α-androstane (II). 1α-Amino-5α-androstane, prepared[17] by lithium aluminum hydride reduction of 5α-androstan-1-one oxime, was dimethylated by means of formic acid and formaldehyde. The product was purified by high-vacuum distillation, and although not crystalline was homogeneous by thin layer chromatography; mol. wt. (mass spectrum), 303; calcd. for $C_{21}H_{37}N$, 303.

2,3-d_2-1ξ-Dimethylaminocholestane. 2,3-d_2-Cholestan-1-one, prepared by catalytic deuteration of Δ^2-cholesten-1-one,[18] was converted into 2,3-d_2-1ξ-aminocholestane by the literature procedure.[19] Dimethylation of this product by means of formic acid and formaldehyde gave 2,3-d_2-1ξ-dimethylaminocholestane which was purified by high-vacuum distillation; mol. wt. (mass spectrum), 417; calcd. for $C_{29}H_{51}D_2N$, 417.

Mixture of 2α- and 2β-Dimethylaminocholestane (III). The crude epimeric mixture was prepared by the method of Bird and Cookson[8] and purified by high-vacuum distillation; mol. wt. (mass spectrum), 415; calcd. for $C_{29}H_{53}N$, 415.

3ξ-Dimethylamino-4,4-dimethylcholestane (IV). 4,4-Dimethylcholestan-3-one oxime was prepared by the general procedure outlined above and had m.p. 205–206°.

Anal. Calcd. for $C_{29}H_{51}NO$: N, 3.26. Found: N, 3.23.

The oxime was reduced by lithium aluminum hydride in ether and converted by the standard methylation procedure[16] directly to IV; m.p. 125.5–127.5°; $[\alpha]_D$ +23° (*c* 1.0, $CHCl_3$); mol. wt. (mass spectrum), 443.

6β-Dimethylaminocholestane (V). This compound was prepared as described by Gent and McKenna[20] and

(15) Melting points are uncorrected. Microanalyses were carried out by Messrs. E. Meier and J. Consul. Mass spectra were measured with a CEC 21-103C mass spectrometer equipped with an all glass heated inlet system (200°). The ionizing energy was maintained at 70 e.v. and the ionizing current at 50 μa.
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purified by high-vacuum distillation; mol. wt. (mass spectrum), 415; calcd. for $C_{29}H_{53}N$, 415.

7β-Dimethylaminocholestane (VI). The hydrochloride salt of VI was prepared as described by Bird and Cookson.[8] Regeneration of the free base and crystallization of this material from methanol–ether gave VI, m.p. 85–86°; mol. wt. (mass spectrum), 415; calcd. for $C_{29}H_{53}N$, 415.

5α-Androstan-11-one Oxime. 5α-Androstan-11-one[12] (0.20 g.) and hydroxylamine hydrochloride (0.20 g.) were dissolved in 80% aqueous pyridine (20 ml.) and the mixture was heated under reflux for 20 hr.[21] Pyridine was then removed under vacuum and water and ether were added to the residue. The ether phase was washed with water, dried, and evaporated giving an oil (0.20 g.) which crystallized on standing. Recrystallization of this material from acetone gave the crude oxime, m.p. 55–57°, which was reduced without further purification.

11β-Amino-5α-androstane. The oxime (0.15 g.) from above and platinum oxide (50 mg.) in acetic acid (12 ml.) were stirred under 1 atm. of hydrogen at 60° for 3 hr. The product, isolated in the usual manner, was crystallized from acetone at −30° giving 11β-amino-5α-androstane (0.13 g.), m.p. 103–104°. Attempts to dimethylate this amine by means of formaldehyde and formic acid were unsuccessful, which is consistent with the β-orientation of the amino group.

Anal. Calcd. for $C_{19}H_{33}N$: C, 82.84; H, 12.08. Found: C, 82.50; H, 12.01.

11α-Dimethylamino-5α-androstane (VII). 5α-Androstan-11-one oxime (0.10 g.) was dissolved in *n*-propyl alcohol (25 ml.) and small pieces of sodium were added to the solution until it became saturated with sodium propoxide. The crude amine was isolated in the conventional manner and then taken up in dry ether. Dry hydrogen chloride was bubbled through the ether solution for a few minutes and the solution was then evaporated to dryness. Hexane was added to the residue and the insoluble salt was isolated by filtration. The salt was shaken with 10% potassium hydroxide and ether. The ether phase was washed with water, dried, and evaporated, and the residue (80 mg.) was chromatographed on alumina (10 g., activity 1). Elution with ether gave traces of 11β-amino-5α-androstane, m.p. 102–103°, undepressed on admixture with the amine obtained by catalytic reduction of the 11-oxime as described above. Further elution with chloroform and then methanol gave 11α-amino-5α-androstane (72 mg.) as an oil. Dimethylation of this material furnished 11α-dimethylamino-5α-androstane (VII, 65 mg.), m.p. 66–68° (from acetone); mol. wt. (mass spectrum), 303; calcd. for $C_{21}H_{37}N$, 303. The α-configuration follows from the known[8] stereochemical course of the sodium–alcohol reduction of steroid oximes and the ease of dimethylation as compared with that of the above-described 11β-amine.

5α-Androstan-16-one Oxime. 5α-Androstan-16-one was converted to the oxime by the standard procedure previously outlined. The oxime had m.p. 198.5–199.5°.

Anal. Calcd. for $C_{19}H_{31}NO$: N, 4.84. Found: N, 4.89.

16ξ-Dimethylamino-5α-androstane (VIII). The above oxime was reduced with lithium aluminum hydride in ether and dimethylated with formic acid and formaldehyde giving, after crystallization of the product from acetone, crystals of VIII, m.p. 77–82°; mol. wt. (mass spectrum). 303; calcd. for $C_{21}H_{37}N$, 303.

17β-Dimethylamino-5α-androstane (IX). 17β-Amino-5α-androstane[22] was dimethylated by the formic acid–formaldehyde procedure furnishing IX, m.p. 101.5–103° (after crystallization from acetone, lit.[23] m.p. 97–98.5°); mol. wt. (mass spectrum), 303, $[\alpha]_D$ 0° (*c* 1.0, $CHCl_3$).

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Mass Spectrometry in Structural and Stereochemical Problems. LXII. Fragmentation and Hydrogen Transfer Reactions of β-Hydrindanones. Synthesis of Deuterated β-Hydrindanones

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The mass spectra of trans-8-methylhydrindan-2-one and analogs deuterated in every ring position have been determined. With the aid of high-resolution measurements, it has been possible to determine the major fragmentation modes and to gain insight into the mechanisms by which these processes occur. The mechanisms leading to the formation of fragment ions as well as the syntheses of deuterated derivatives are discussed.

The mass spectrometric fragmentation patterns of α- and β-decalones have been reported in earlier papers,[2a,b] with the intention of correlating their breakdown processes with those found in polycyclic ketones such as steroids.[3] The decalone system is structurally related to the A–B rings of steroids and, in the same manner, β-hydrindanones may be considered

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