Registry No.—Propionic acid, 79-09-4; hydrochloric acid, 7647-01-0.

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The Origin of the $[M - 56]\cdot^+$ Ion in the Mass Spectra of Trimethylsilyl Ethers of Dehydroepiandrosterone and Related Compounds

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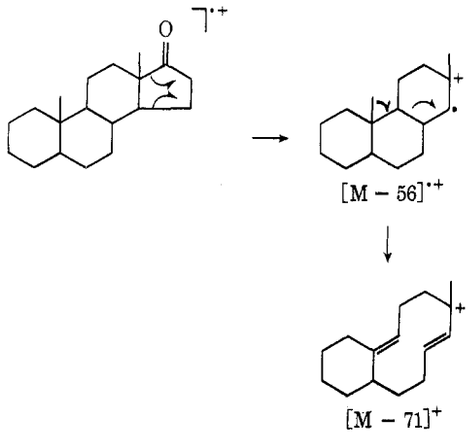
The mass spectra of many 16- and 17-keto steroids contain ions $[M - 56]\cdot^+$, the formation of which has been ascribed to cleavages of the bonds C-13/17 and C-14/15.[1] These ions are often accompanied by ions $[M - 71]^+$ formed by subsequent loss of a methyl radical[2] (Scheme I). During a survey of the mass

SCHEME I

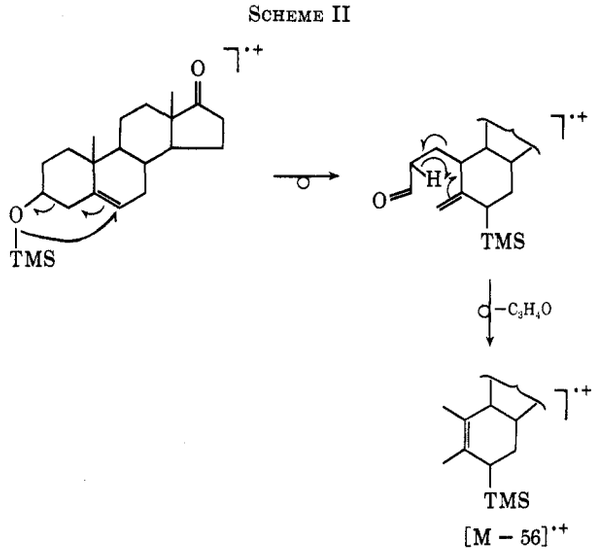


spectra of trimethylsilyl (TMS) ethers of a number of Δ^5-3β-hydroxy steroids it was found that $[M - 56]\cdot^+$ ions, unaccompanied by $[M - 71]^+$ ions, were present in the spectra of 16 and 17 ketones. It has been demonstrated that these $[M - 56]\cdot^+$ ions are formed by electron-impact-induced rearrangement, and not by D-ring cleavage.

The first indication of a duality of mechanisms for the formation of such ions was the presence of $[M - 56]\cdot^+$ ions in the spectra of the TMS ethers of *15,15,17,17-d_4*-3β-hydroxyandrost-5-en-16-one, *16,16-d_2*-3β-hydroxyandrost-5-en-17-one, and *9,12,12,16,16-d_5*-3β-hydroxyandrost-5-ene-11,17-dione.[3] When the 17-oxo group of the TMS ether of 3β-hydroxyandrost-5-en-17-one (dehydroepiandrostereone, DHEA) was selectively replaced[4] by ^{18}O, this atom was found to be retained in the $[M - 56]\cdot^+$ ion. All nine deuterium atoms of the d_9-TMS ether[5] of DHEA were also retained in the $[M - 56]\cdot^+$ ion.

High resolution mass measurement, carried out on the spectrum of the TMS ether of DHEA, showed that the particle eliminated had the composition C_3H_4O (found for ion of nominal *m/e* 304, 304.2198; calcd for $C_{19}H_{32}OSi$, 304.2222). The oxygen atom must, therefore, originate from the 3 position, and it seems likely that the $[M - 56]\cdot^+$ ions of these steroids are formed by a mechanism similar to that proposed for the formation of the $[M - 129]^+$ ion, but with initial transfer of the TMS group. This may proceed *via* a double (silyl and conventional) McLafferty-type rearrangement, as in Scheme II. Because of the relatively large separation

SCHEME II



of C-3 and C-6, the silyl rearrangement is presumed to take place in a stepwise manner.

It should be noted that the TMS ethers of the saturated steroid 3β-hydroxy-5α-androstan-17-one and its 16,16-d_2 analog give rise, respectively, to ions $[M - 56]\cdot^+$ and $[M - 58]\cdot^+$, indicating that such ions are formed by D-ring cleavage as illustrated in Scheme I.[6]

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(2) L. Tökés, R. T. LaLonde, and C. Djerassi, *J. Org. Chem.*, **32**, 1012 (1967).

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(4) A. M. Lawson, F. A. J. M. Leemans, and J. A. McCloskey, *Steroids*, **14**, 603 (1969).

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