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Interaction of trimethylsilyl ions with nitrates of the estrane series in the gas phase

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The interaction of trimethylsilyl ions with nitrates of the estrane series affords the adducts $[M + SiMe_3]^+$, whose fragmentation proceeds through the elimination of the functional groups either along with the trimethylsilyl residue, or in the form of molecules containing no $SiMe_3$.

Key words: mass spectrometry, chemical ionization, trimethylsilyl cation, estrane nitrates.

The interaction of the trimethylsilyl ion with polyfunctional molecules in the gas phase results in the formation of the weakly excited adduct $[M + SiMe_3]^+$, in which the $SiMe_3^+$ group, unlike protons in protonated molecular ions (PMI), is incapable of intramolecular migrating. Therefore, the fragmentation of adducts is determined, to a considerable extent, by the nature of the functional group present in the starting molecule and bound to the trimethylsilyl ion. Note that the decomposition of the $[M + SiMe_3]^+$ ions (IA) usually involves the elimination of the nucleophilic group together with the trimethylsilyl residue.[1—4]

In this work, we studied the interaction of the $SiMe_3$ ion with nitrates of the estrane series[5—8] by mass spectrometry with chemical ionization using $SiMe_4$ as the gas-reactant.

Experimental

Mass spectra were recorded on a Kratos MS-30 mass spectrometer with an energy of ionizing electrons of 200 eV and a temperature of the ion source of 150 °C. The constant pressure of the gas-reactant (0.2 Torr) was maintained by an external pressure gage installed in the feeding system. $SiMe_4$ («Merck») with 99.7% purity was used.

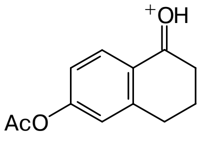
Results and Discussion

The mass spectra of all studied compounds **1—10** (Table 1) contain peaks of the ion-adducts $[M + SiMe_3]^+$ with the intensity varying from 1 to 48%. We failed to find any simple correlation between the stability of the ion-adducts and structure of the studied compounds. The reason probably lies in the occurrence of competing pyrolytic processes because their contribution in each case can barely be determined.

The elimination of trimethylsilyl nitrate to form the $[IA - Me_3SiONO_2]^+$ ions, whose intensity changes from 10 to 100%, is a common feature that characterizes all 10 ions studied (see Table 1). A comparison of the $[IA - Me_2SiONO_2]/IA$ ratios for pairs of stereoisomers (**7—8** and **9—10**) shows that the intensity of the peaks of ions (see Table 1, IV) for the 9-β-hydroxy isomers is more than twofold higher than that of the peaks of the 9-α-isomers. Evidently, the hydroxyl group in the *cis*-position to the nitroxy group favors its elimination.

The spectra of all acetates (compounds **2—8**) exhibit the peak of the $[AcOH + Me_2SiCH_2SiMe_3]^+$ ion (*m/z* 205) formed due to the reaction of the acetoxy groups with the $[Me_2SiCH_2SiMe_3]^+$ ions, which are always present in the plasma of $SiMe_4$,[9—10] followed by the elimination of the remaining part of the molecule in the form of olefin. In the spectra of propionates (compounds **9** and **10**), the peak of a similar ion is observed at *m/z* 219 (see Table 1).

Another way of the formation of an ion with *m/z* 205 (219) available only for nitrates with a substituent at the C(9) position (compounds **3—5**, **7—10**) is related to recharging processes and pyrolytic reactions. In this case, the ion has the bicyclic structure "**A**" similar to that formed by estrane fragmentation under electron impact.[11]



A

The ratio of intensities of peaks of the ion with *m/z* 205 (219) to that of the IA ion differs substantially for the pairs of isomers **4—5**, **7—8**, and **9—10** and is always higher for 9-β-epimers.

The mass spectra of all studied compounds contain peaks of ions corresponding to the elimination of HNO_3 from IA. Usually the functional groups X eliminate in the form of HX from IA of polyfunctional compounds if

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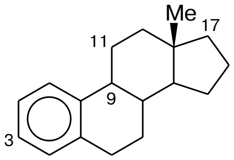
Table 1. Mass spectra of chemical ionization ($SiMe_4$ as the gas-reactant) of nitrates of the estrane series



Compound	Estrane, substituents	m/z (I (%)) I [a]	II [b]	III [c]	IV [d]	V [e]	VI [f]	Other ions, (assignment)
1	3,17β-OH, 11β-ONO_2	406(~2)	—	343(70)	271(25)	—	—	253 (100) (C—H_2O)
2	3-OAc, 17β-ONO_2	432(40)	385(12)	369(6)	297(100)	205(24)	—	—
3	3-OAc, 9α-OH, 11β-ONO_2 (17O)	462(~1)	415(100)	399(50)	327(10)	205(20)	—	—
4	3,9α-OAc, 11β-ONO_2 (17O)	504(20)	—	441(20)	369(20)	205(100)	—	372(21) [IA − $AcOSiMe_3$]
5	3,9β-OAc, 11β-ONO_2 (17O)	504(15)	—	441(3)	369(12)	205(100)	—	372(20) [IA − $AcOSiMe_3$]
6	3-OH, 11α-ONO_2, 17β-OAc, 17α-CH≡CH	472(7)	425(10)	409(10)	337(60)	205(100)	—	340(20) [IA − $AcOSiMe_3$]
7	3,17β-OAc, 9α-OH, 11β-ONO_2, 17α-CH≡CH	530(48)	483(34)	467(100)	395(72)	205(52)	—	
8	3,17β-OAc, 9β-OH, 11β-ONO_2, 17α-CH≡CH	530(7)	—	467(25)	395(33)	205(100)	—	
9	3,17β-EtCOO—, 9α-OH, 11β-ONO_2	534(25)	487(15)	471(65)	399(30)	—	219(100)	—
10	3,17β-EtCOO—, 9β-OH, 11β-ONO_2	534(6)	487(22)	471(15)	399(16)	—	219(100)	—

[a] I — $[M + SiMe_3]^+$ (IA).

[b] II — $[IA - HNO_2]^+$.

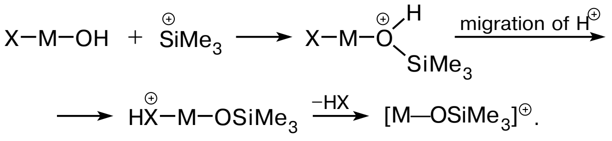
[c] III — $[IA - HNO_3]^+$.

[d] IV — $[IA - Me_3SiONO_2]^+$.

[e] V — $[AcOH + Me_2SiCH_2SiMe_3]^+$.

[f] VI — $[EtCOOH + Me_2SiCH_2SiMe_3]^+$.

the starting substance contains substituents bearing the mobile H atom, for example, OH group. The scheme of this transformation can be presented as follows



$$X{-}M{-}OH + \overset{\oplus}{SiMe_3} \longrightarrow X{-}M{-}\overset{\oplus}{O}{<}^{H}_{SiMe_3} \xrightarrow{\text{migration of } H^{\oplus}}$$
$$\longrightarrow H\overset{\oplus}{X}{-}M{-}OSiMe_3 \xrightarrow{-HX} [M{-}OSiMe_3]^{\oplus}.$$

According to this scheme, when the groups acting as proton donor and acceptor are spatially separated, HX elimination is poorly probable if occurs at all.[12] However, the data in Table 1 contradict this assumption: HNO_3 is eliminated from compounds that either contain no OH group (compound **4**), or contain OH groups spatially separated from the nitroxy groups (**1**, **3**, **6**, **7**, and **9**). Therefore, the $[IA — HNO_3]^+$ ions can partially be formed due to pyrolytic processes.

We also may assume that the $[IA - HNO_2]^+$ ions, whose intensities do not correlate with the structures of the studied compounds, have the pyrolytic origin.

Thus, the fragmentation of estrane nitrates can occur by both the elimination of functional groups together with the $SiMe_3$ group and elimination of the functional groups in the form of molecules containing no $SiMe_3$ group. In the first case, the decomposition of the ion-adduct mainly follows the regularities previously found for simple model compounds. In the second case, the competing parallel pyrolytic reactions violate these regularities.

Recharging processes, which can result in decompositions inherent in electron impact, exert a specific effect on the character of estrane decomposition.

Therefore, a possibility of recharging and thermodestruction processes should be taken into account in an attempt to make conclusions about the structure and stereochemistry of relatively complex and thermally unstable molecules from their mass spectra of chemical ionization using $SiMe_4$ as a gas-reactant.

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