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The mechanism of methyl loss from ionized methoxypentamethyldisilane: anchimeric assistance versus direct bond cleavage.

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Abstract

Evidence is presented that methyl loss from ionized methoxypentamethyldisilane ($\mathbf{10}^{+\cdot}$) largely involves the methyl ether group and not, as previously suggested, methyl groups attached to the silicon atoms. It is shown that cleavage of the O–C bond is anchimerically assisted by intramolecular migration of the trimethylsilyl group to generate the ion $(CH_3)_2Si^+–O–Si(CH_3)_2$ (**13**). This process involves ca. 66% of molecular ions $\mathbf{10}^{+\cdot}$ dissociating in the ion source (lifetime $< 10^{-6}$ s), and more than 99% of $\mathbf{10}^{+\cdot}$ decomposing as metastable ions (lifetime $\approx 10^{-5}$ s). A minor pathway involves loss of $CH_3^{\cdot}$ from the trimethylsilyl group of $\mathbf{10}^{+\cdot}$, to give a species with a OCH_3 bridged structure **11**. The isomeric ions **11** and **13** do not undergo interconversion at the microsecond time frame.

Introduction

The cleavage of oxygen–carbon bonds according to eq. 1 is extremely disfavoured on energetic grounds and is observed only under exceptional conditions [1–4].

$$[R^1–O–R^2]^{+\cdot}(1) \rightarrow R^1–O^+ + {}^{\cdot}R^2 \qquad (1)$$

As has been demonstrated repeatedly [5–8], however, the process of eq. 1 can be greatly enhanced if R^1 in **1** contains a substituent which has both a high migratory aptitude and a high affinity for oxygen. Extensive studies revealed that in this respect one of the most effective such substituents is a trimethylsilyl group (X = $SiMe_3$), and the overall process is shown in Scheme 1. Noteworthy features of this anchimerically assisted cleavage of the Y–R bond are as follows: (1) If the migrating group X in **2** is not a silyl group but a carbon or germyl substituent, the reaction does not occur. (2) The product ion formed upon loss of R^3 from **2** is

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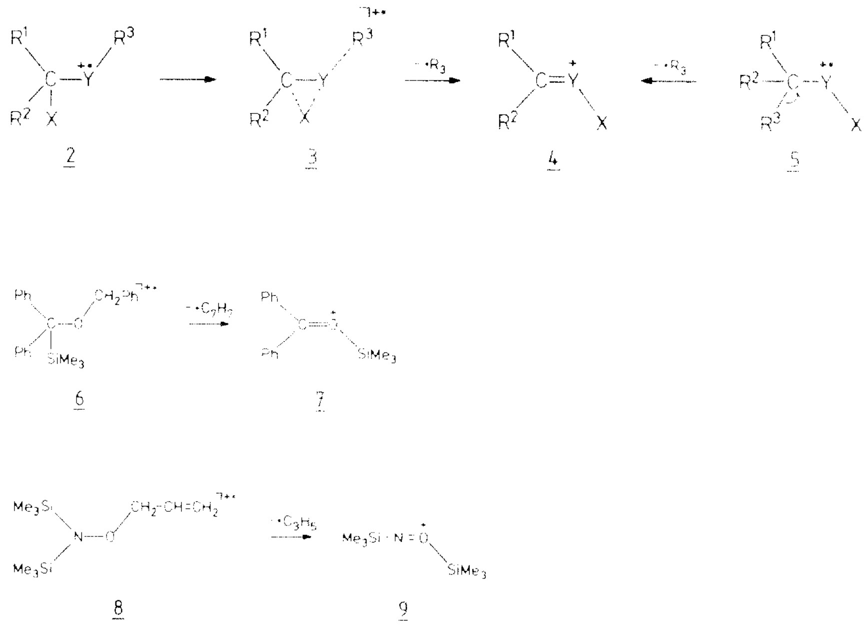
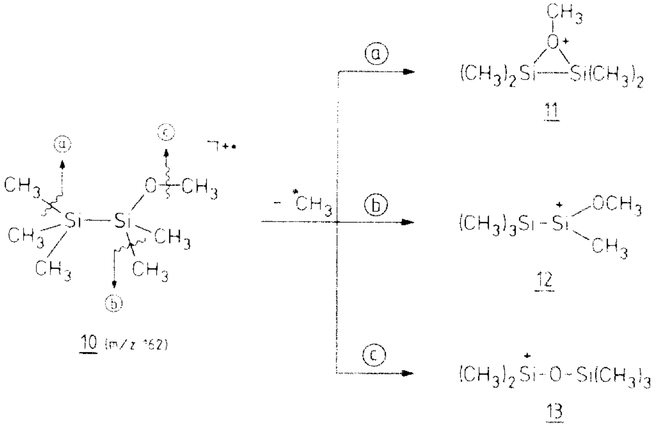


Scheme 1

identical in all respects with a species generated directly from **5**. (3) The leaving radical $\cdot R^3$ may be either a stabilized (benzyl, allyl) or non-stabilized carbon radical (methyl) or are of various other radicals (e.g. silyl functions). (4) The effect of the substituent is the stronger the higher the affinity of Y to the migrating silyl group. Thus, if Y = CH_2, migration of $SiMe_3$ accompanied by cleavage of the Y–R bond does not take place even R^3 corresponds to a stabilized radical. Two typical examples (**6** and **8**) are given in Scheme 1, and it should be mentioned that for metastable ions **6** and **8** the total ion current due to the processes **6** → **7** and **8** → **9** is close to or exceeds 90%.



Scheme 2

As stated in a recent review on the gas-phase chemistry of silicon-containing molecules [9], we believe that the process **2** → **4** is more generally applicable than hitherto acknowledged, and in this paper we present evidence that the previously discussed [10] gas-phase ion chemistry of methoxypentamethyldisilane (**10**) is better described in terms of anchimeric assitance rather than of the mechanisms suggested by Nakadaira et al. [10], who, in the light of the fact that both the 70 eV and low energy mass spectra of **10** exhibit an intense signal at m/z 147 (due to loss of $CH_3^{\cdot}$. from the molecular ion $\mathbf{10}^{+\cdot}$), concluded [10] that the fission of a Si–C bond is a facile reaction generating either **11** or **12** (Scheme 2). The possibility of an anchimerically assisted reaction $\mathbf{10}^{+\cdot} \rightarrow \mathbf{13}$ was not taken into account. We have now shown by a study of the labeled isotopomer **10a** and by using tandem mass spectrometry methodologies [11], that ions $\mathbf{10}^{+\cdot}$ with lifetimes $t < 10^{-6}$ s decompose to **11** and **13** in a roughly 2/3 ratio. With increasing lifetime of $\mathbf{10}^{+\cdot}$ (which corresponds to a decreasing internal energy) the process $\mathbf{10}^{+\cdot} \rightarrow \mathbf{13}$ gains in importance, and for metastable ions $\mathbf{10}^{+\cdot}$ having a lifetime $t \approx 10^{-5}$ s, only cleavage of the O–C bond accompanied by silyl migration is observed.

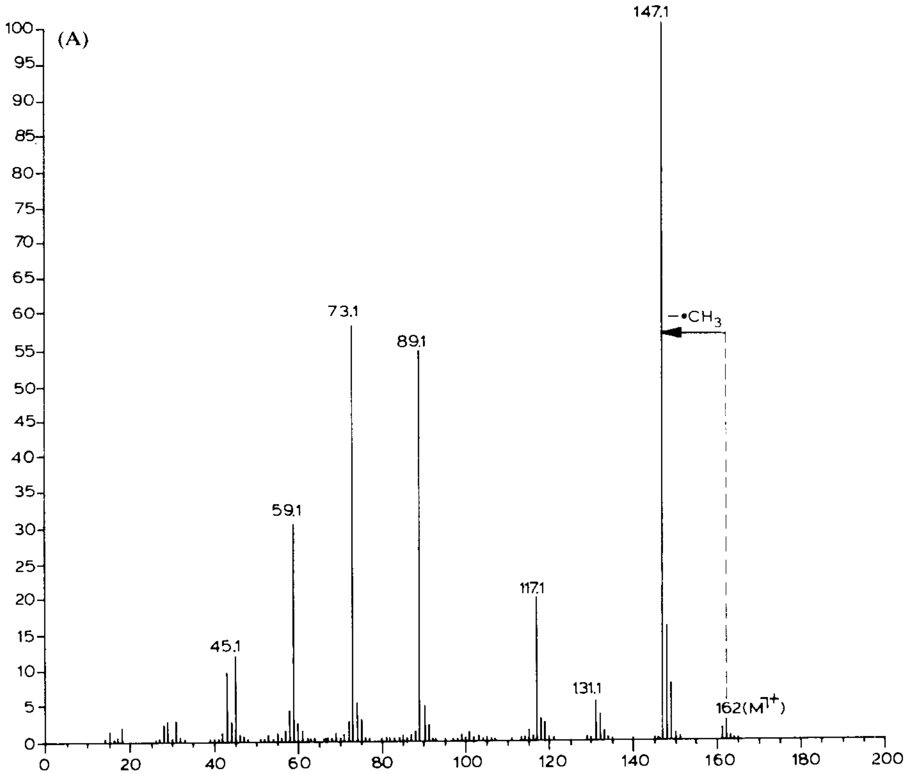
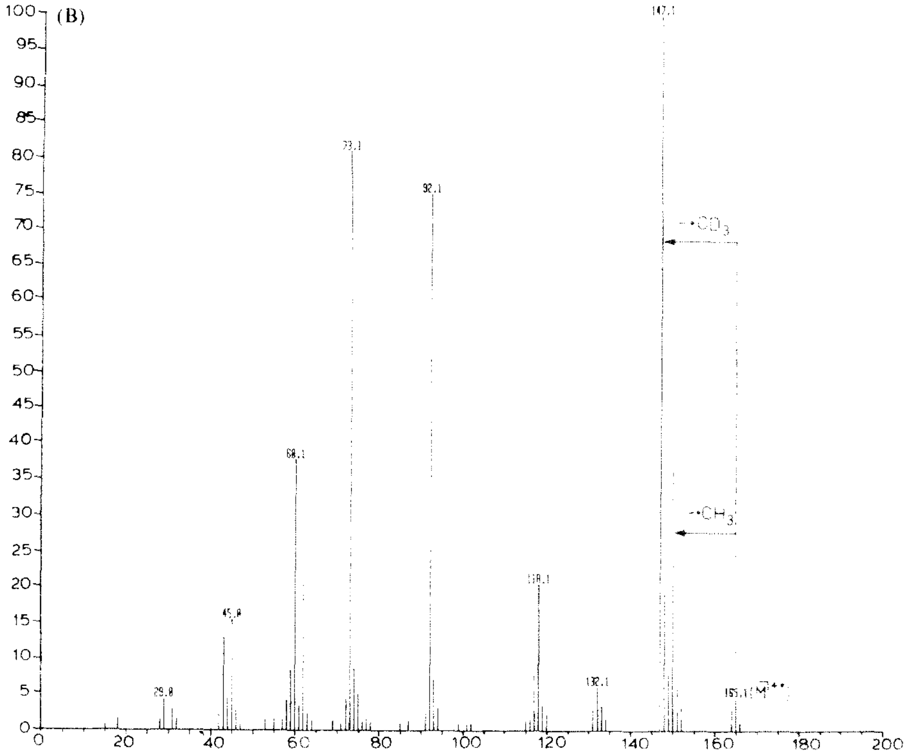


Fig. 1. A: 70 eV mass spectrum of methoxypentamethyldisilane **10**; B: 70 eV mass spectrum of (methoxy-d_3)pentamethyldisilane **10a**; C: metastable ion mass spectrum of **10** (mass selected molecular ions $\mathbf{10a}^{+\cdot}$ which dissociate in the 3rd field free region.



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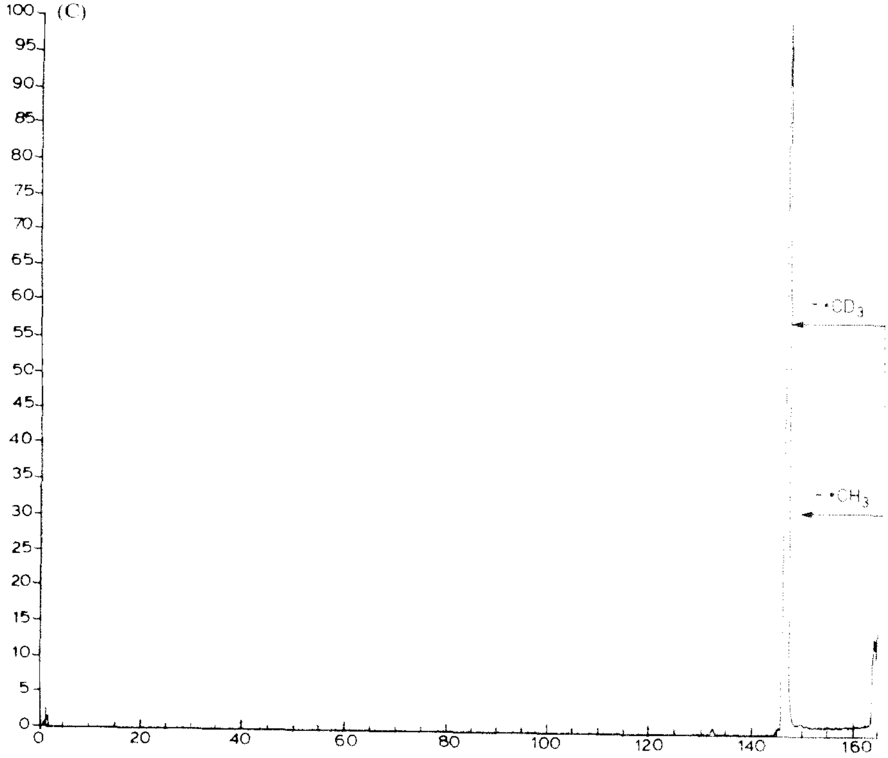

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Experimental

Methoxypentamethyldisilane (**10**), (methoxy-d_3)pentamethylsilane (**10a**) and the bis(trimethylsilyl) ether of 1,4-butanediol were made by standard procedures, purified by preparative gas chromatography, and characterized by H NMR spectroscopy. Electron impact (70 eV) mass spectra were recorded and tandem mass spectrometry experiments carried out with a Vacuum Generator ZAB-HF-3F mass spectrometer. This is a triple sector instrument of B(1)EB(2) configuration (B magnetic and E electric sector), whose characteristics have been described in detail [12,13]. Briefly, ions are generated by 70 eV electron impact ionization (ion trap current 100 μA, accelerating voltage 8 kV). Ions of 8 keV kinetic energy are mass selected using B(1)E at a mass resolution of 2000 for the primary ion beam (10% valley definition), and their unimolecular dissociations recorded by scanning B(2). Collision induced dissociations (CID) [14] were studied by mass selecting the ion of interest (formed either in the ion source or from metastable ions), and subjecting this ion to collisional activation using He as a collision gas (the He gas pressure was adjusted such that the main ion beam intensity was reduced to 80%). 10–20 spectra were accumulated using the Vacuum Generator 11/250 data system.

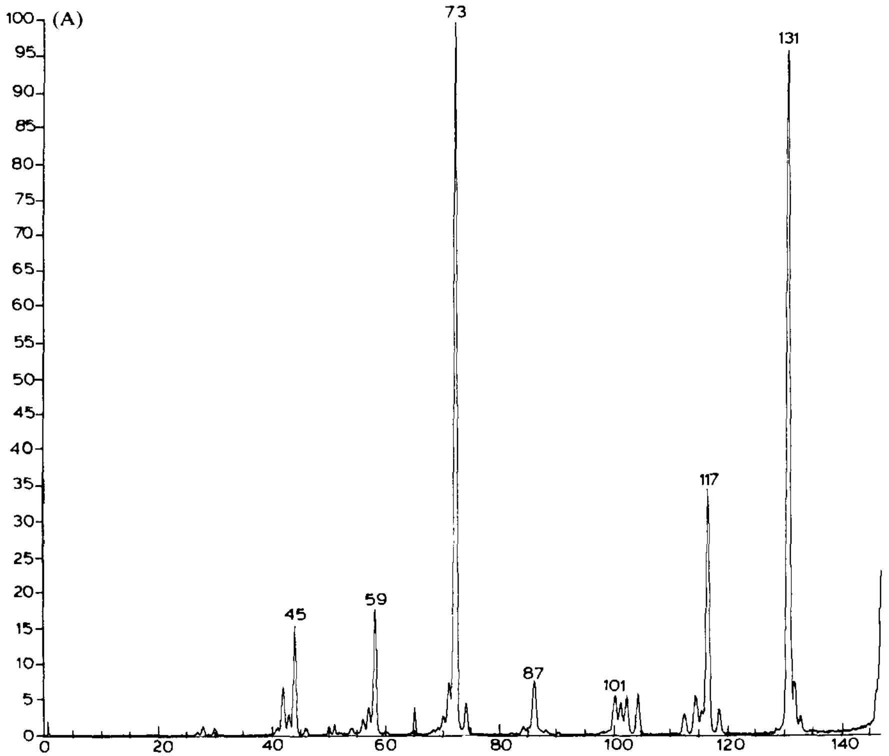
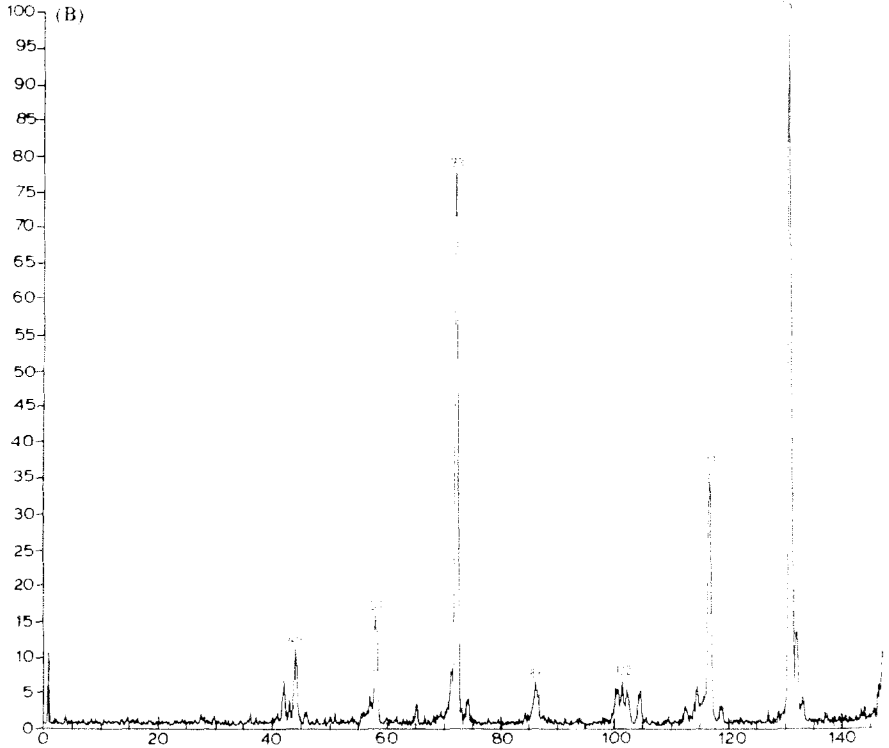


Fig. 2. A: 3rd field-free region (3FFR) collisional activation (CA) mass spectrum of m/z 147 generated from the bis(trimethylsilyl)ether of 1,4-butanediol; B: 3FFR CA mass spectrum of m/z 147 generated via 2nd field-free region loss of $CH_3^{\cdot}$ from $\mathbf{10}^{+\cdot}$; C: 3FFR CA mass spectrum of m/z 147 generated from ion source decomposition of $\mathbf{10}^{+\cdot}$; D: 3FFR CA mass spectrum of m/z 150 generated via loss of CH_3 from $\mathbf{10a}^{+\cdot}$ in the ion source.



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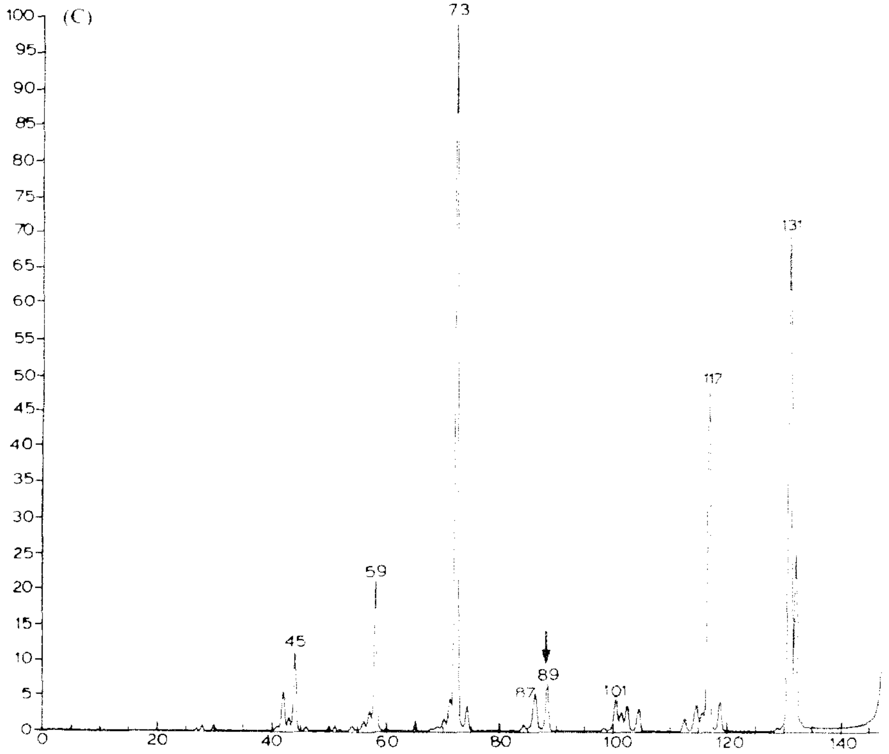

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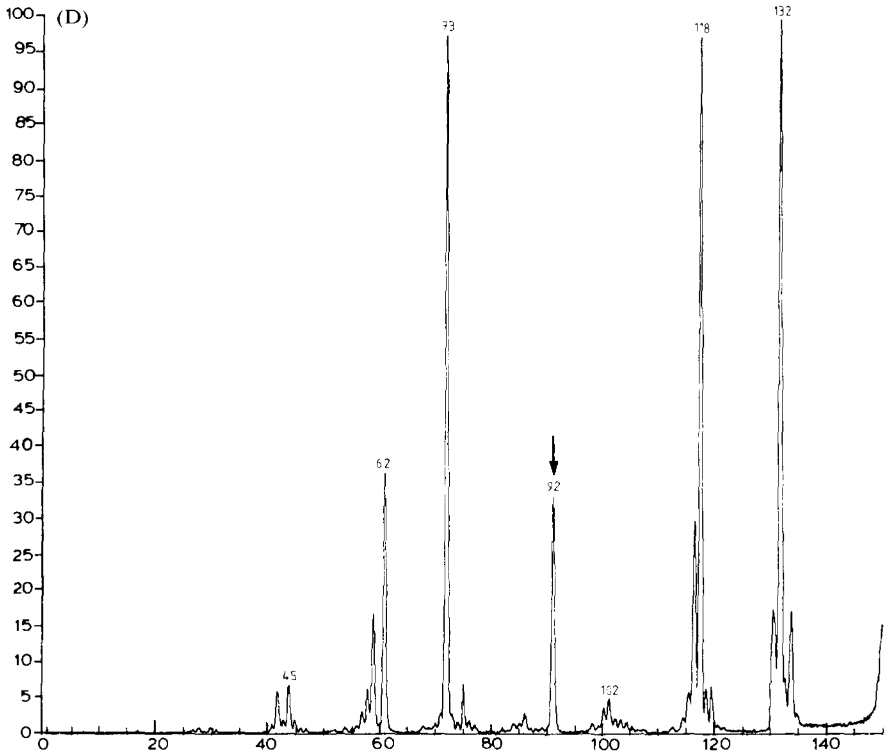

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Results and discussion

A comparison of the mass spectra of **10a** shown in Fig. 1B, C clearly reveals that most of the methyl radicals eliminated from ionized methoxypentamethyldisilane originate from the methoxy group. For reactions occurring in the ion source we observe a ratio of ca. 3/2 for losses of CD_3 versus CH_3 (Fig. 1B); this ratio increases to $> 99/1$ for ions with low internal energy (3rd field-free region unimolecular dissociations, Fig. 1C).

A structural assignment of the resulting $(M\text{–methyl})^+$ ions is provided by analysis of the collisional activation (CA) mass spectra (Fig. 2). A comparison of the CA mass spectra shown in Fig. 2A, B leaves no doubt that both ions are identical in structure. As the *m/z* 147 ion generated from the bis(trimethylsilyl) ether of 1,4-butanediol is assigned structure **13** [9], we conclude that loss of $CD_3^{\bullet}$ from $\mathbf{10a}^{+\bullet}$ also generates the same species, i.e. process $\mathbf{10}^{+\bullet} \rightarrow \mathbf{13}$ (Scheme 2) occurs exclusively in the case of low-energy ions $\mathbf{10}^{+\bullet}$. If the *m/z* 147 ion is generated from $\mathbf{10}^{+\bullet}$ in the ion source, i.e. from species having higher internal energy, the resulting CA mass spectrum (Fig. 2C) contains all signals present in the spectra of Fig. 2A, B, thus indicating that in the ion source species **13** is also formed. Interestingly, however, there is, in addition, a weak, but structure-diagnostic signal at *m/z* 89, which is due to loss of Me_2Si. In line with the data shown in Fig. 1A, we interpret this signal as an indication that ions $\mathbf{10}^{+\bullet}$ in the ion source co-generate **11** and **13**. The former, upon collisional activation decomposes to, inter alia, Me_2Si and Me_2SiOMe^+ (*m/z* 89). This pathway is not open to the isomer **13**. Further support for this interpretation is provided by the CA mass spectrum of *m/z* 150, generated via loss of $CH_3^{\bullet}$ from $\mathbf{10a}^{+\bullet}$ (Fig. 2D). The signal at *m/z* 92 (mass shifted from *m/z* 89 due to the presence of the CD_3 group) is greatly enhanced in intensity.

That the isomers **12** and **13** do not undergo interconversion is clearly evidenced by a comparison of their unimolecular dissociation products. As shown in Fig. 3, the spectra are so distinct that isomerization in the time available in our experiments (ca. 10^{-5} s) is highly unlikely.

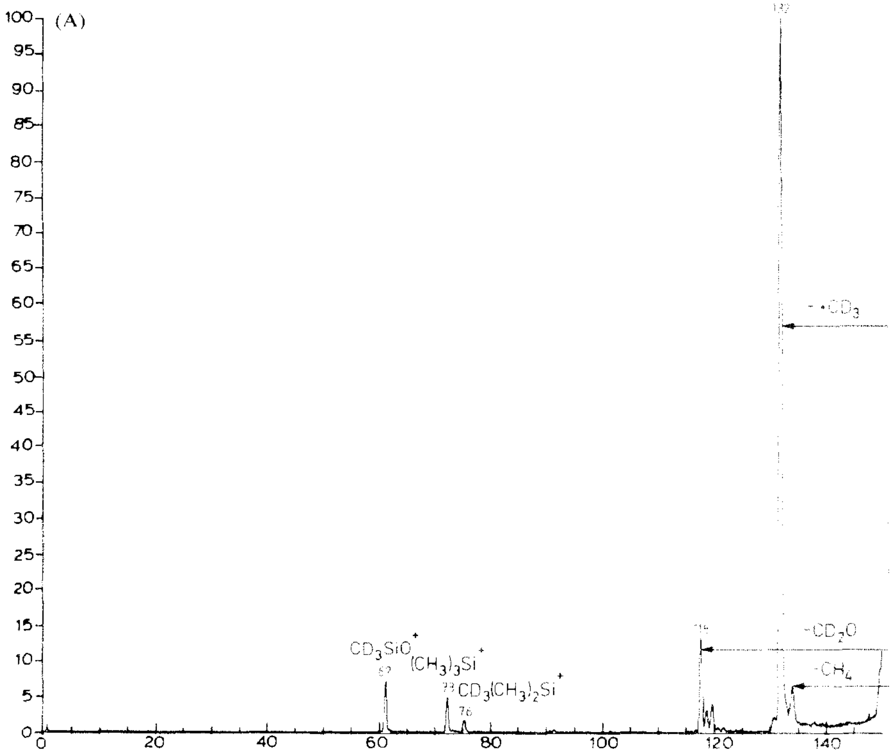

Fig. 3. A: 3FFR metastable ion (MI) mass spectrum of *m/z* 150 generated via loss of $CH_3^{\bullet}$ from $\mathbf{10a}^{+\bullet}$ in the ion source; B: 3FFR MI mass spectrum of *m/z* 147 generated via loss of $CD_3^{\bullet}$ from $\mathbf{10a}^{+\bullet}$ in the ion source.

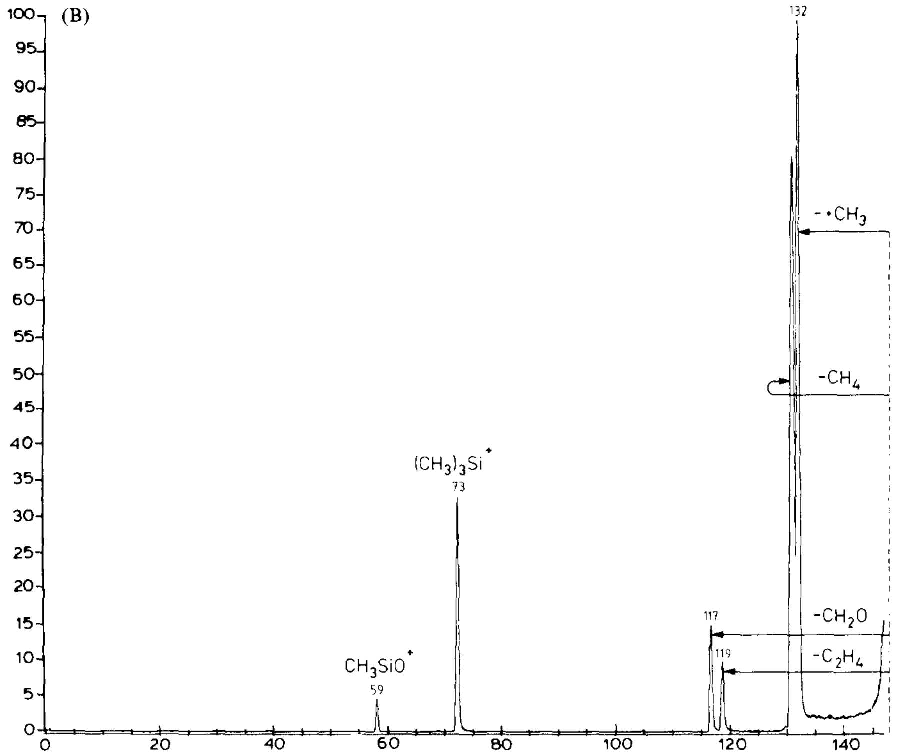

Fig. 3. continued.

Acknowledgements

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References

1 H. Schwarz, Org. Mass Spectrom., 15 (1980) 491.
2 H. Schwarz, Nachr. Chem. Techn. Lab., 28 (1980) 158.
3 H. Schwarz, Top. Curr. Chem., 97 (1981) 1.
4 H. Schwarz, Ann. Chim. (Rome), (1981) 29.
5 H. Schwarz, M. Kliment, M.T. Reetz and G. Holzmann, Org. Mass Spectrom., 11 (1976) 989.
6 H. Schwarz and M.T. Reetz, Angew. Chem., 88 (1976) 726.
7 H. Schwarz, C. Wesdemiotis and M.T. Reetz, J. Organomet. Chem., 161 (1978) 153.
8 B. Ciommer, H., Schwarz, A. Maaroufi, M.T. Reetz and K. Levsen, Z. Naturforsch. B, 36 (1981) 771.
9 H. Schwarz, in S. Patai and Z. Rappoport (Eds.), The Chemistry of Organosilicon Compounds, Wiley, Chichester, in press.
10 Y. Nakadaira, T. Kobayashi, M. Kira, H. Sakurai, Y. Yamada and Y. Shida, J. Organomet. Chem., 113 (1976) 249.
11 F.W. McLafferty (Ed.), Tandem Mass Spectrometry, Wiley Interscience, New York, 1983.
12 T. Weiske, PhD Thesis, TU Berlin D83, 1985.
13 J.K. Terlouw, T. Weiske, H. Schwarz and J.L. Holmes, Org. Mass Spectrom., 21 (1986) 665.
14 K. Levsen and H. Schwarz, Mass Spectrom. Rev., 3 (1983) 77.