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SELECTIVE ON-LINE DEUTERATION IN GAS CHROMATOGRAPHY - MASS SPECTROMETRY FOR THE INVESTIGATION OF DISSOCIATIVE IONIZATION OF SILICON-CONTAINING COMPOUNDS

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Summary

A method for specific gas-phase deuteration of unsaturated silicon-containing compounds over pre-heterogenized Wilkinson's catalyst (a solution of $(Ph_3P)_3RhCl$ in Carbowax 20M coated on Chromaton) in the reaction column connected to the mass spectrometer is described. This method was employed to study the dissociative ionization of the corresponding saturated analogues. With the aid of the mass spectra of the dideutero derivatives thus obtained, the main electron-impact-induced reactions of 1,1-dimethyl-1-silacyclopentane, 1,1,2,2-tetramethyl-1,2-disilacyclohexane, 1-methyl-1-ethyl-1-silacyclobutane and ethyl triethoxysilane were elucidated.

Introduction

The value of deuterium-labelling techniques for the investigation of fragmentation mechanisms of organic compounds under mass spectrometric conditions is well known. To obtain labelled derivatives, preparative syntheses involving isolation of the desired products have been used in all known cases. However, the synthesis of deuterium-labelled compounds directly in the inlet system of a mass spectrometer seems to be a rather interesting approach since it permits work at the microgram level and saves time because it eliminates the necessity to isolate the products. Naturally, with this approach only reactions which provide a highly specific incorporation of deuterium can be used. In this context, we have recently reported [1] on the electron-impact reactions of carbonylic compounds, the deuterium-labelled analogues of which were prepared by isotope exchange in the reaction column (KOD and SE-30 on Chromaton) connected directly to the mass spectrometer. In the present paper we describe an efficient method for selective deuteration of unsaturated silicon-containing compounds directly in the inlet system of a gas chromatograph-mass spectrometer. For illustration, the possibilities of the method will be shown by the study of the fragmentation mechanisms of 1,1-dimethyl-1-sila-

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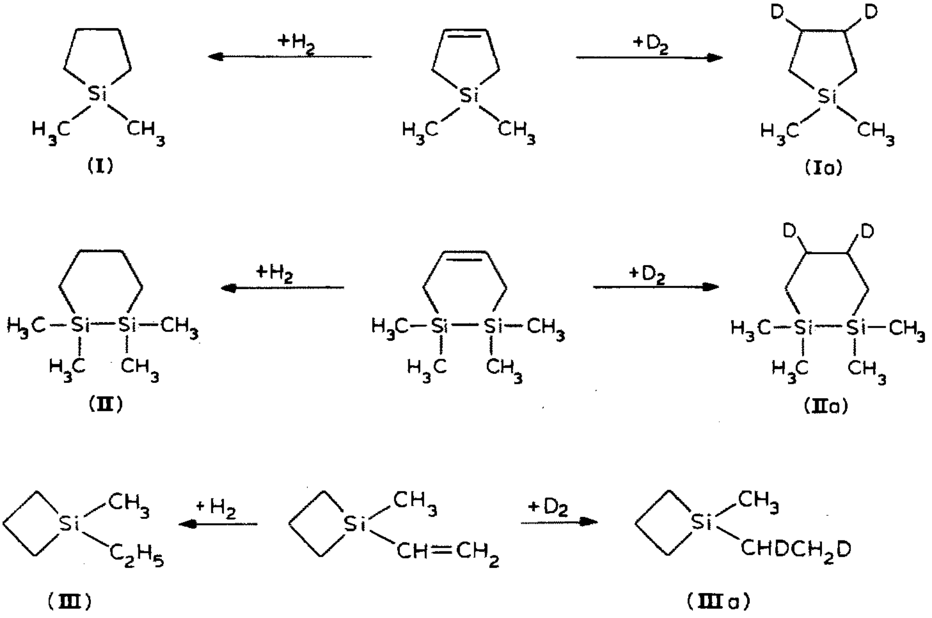
cyclopentane (I), 1,1,2,2-tetramethyl-1,2-disilacyclohexane (II), 1-methyl-1-ethyl-1-silacyclobutane (III) and ethyl triethoxysilane (IV) under electron impact.

Results and discussion

For derivatization in the inlet system of a gas chromatograph-mass spectrometer, only gas-phase reactions which proceed over heterogeneous catalysts can be used. The majority of known heterogeneous hydrogenation catalysts are not suitable for the specific saturation of a double bond by deuterium since they lead to extensive isotope scrambling both under gas-phase and liquid-phase conditions, even at room temperature. That is why we studied the homogeneous Wilkinson's catalyst, $(Ph_3P)_3RhCl$, which is widely used for the specific deuteration of various unsaturated compounds in solution chemistry. We decided to employ this catalyst in reaction gas chromatography-mass spectrometry after its pre-heterogenization by coating the solid support (Chromaton W) with a solution of $(Ph_3P)_3RhCl$ in Carbowax 20M. A glass column (1.5 m × 3 mm) was packed with this catalytic system and connected to the mass spectrometer via a molecular separator. Unsaturated silicon-containing compounds were passed through the reaction column in a flow of deuterium gas. It was found that all the unsaturated substrates studied, which were used in amounts of 0.01–0.05 μg, achieved quantitative deuteration to form the dideutero analogues (Ia–IVa) of high isotopic purity (see Figs. 1b–4b) at temperatures of 45–80°C. When hydrogen was used instead of deuterium, the mass spectra of unlabelled saturated compounds (I–IV) were recorded. It should be noted that a recent study on the gas-phase deuteration of alkenes over the same catalytic system showed no migration of the double bond and vicinal dideuteroalkanes contained the label at the site of the original double bond [2]. Therefore the position of the deuterium label in compounds Ia–IVa does not give rise to any doubt.



(I) (Ia)

(II) (IIa)

(III) (IIIa)

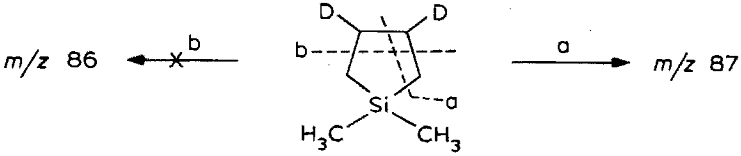
$$(C_2H_5O)_3SiC_2H_5 \xleftarrow{+H_2} (C_2H_5O)_3SiCH{=}CH_2 \xrightarrow{+D_2} (C_2H_5O)_3SiCHDCH_2D$$

(IV) (IVa)

Despite the fact that the electron-impact mass spectrum of 1,1-dimethyl-1-silacyclopentane (I) has been repeatedly discussed [3,4], in neither case were the labelled analogues employed to prove the fragmentation mechanisms. In this connection, the question about the origin of the base ion $[M\text{–}C_2H_4]^{+\cdot}$ which could arise due to the loss of carbon atoms C(2), C(3) and/or C(3), C(4) has not been unambiguously resolved [5,6]. It should be noted that the C_2H_4 molecule lost from the molecular ions of related germacyclopentanes includes C(2) and C(3), as has been proved by the mass spectra of 3,3,4,4-tetradeutero derivatives [7].

The mass spectra of silacyclopentane (I) and its 3,4-dideutero analogue (Ia) recorded after passage of 1,1-dimethyl-1-silacyclopent-3-ene through the reaction column in a flow of hydrogen and deuterium, respectively, are given in Fig. 1. Complete shift of the m/z 86 peak by one mass unit (to m/z 87) on passing from compound I to compound Ia demonstrates that only a C_2H_3D molecule is expelled from the molecular ion of Ia. This gives conclusive evidence that the elimination of the ethylene molecule is a highly regioselective reaction which proceeds exclusively at the expense of carbon atoms C(2) and C(3) (Scheme 1).

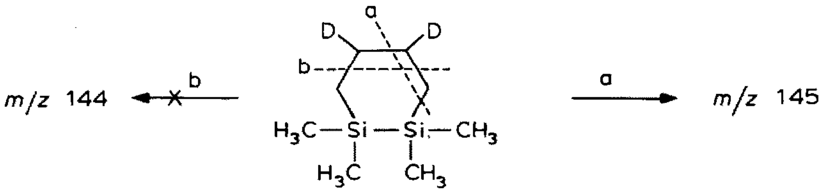
SCHEME 1



(Ia)

A comparative study of the mass spectra of compounds II and IIa (Fig. 2a,b), recorded under the described conditions using 1,1,2,2-tetramethyl-1,2-disilacyclohex-4-ene as the unsaturated substrate, represents the other example of application of the method. As can be seen, the loss of a C_2H_4 molecule from the molecular ion of compound II also appears to be a highly regioselective process taking place at the expense of C(3) and C(4) (Scheme 2). This is corroborated by the complete shift of the m/z 144 peak ($[M - C_2H_4]^{+\cdot}$) to m/z 145 ($[M - C_2H_3D]^{+\cdot}$) on passing from II to IIa (Scheme 2).

SCHEME 2



(IIa)

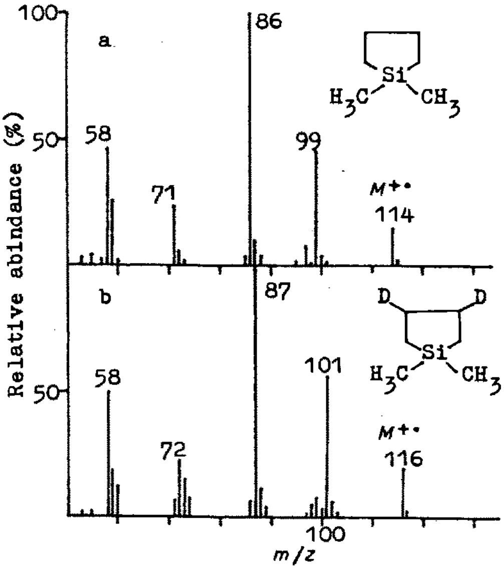


Fig. 1. Mass spectra of: (a) 1,1-dimethyl-1-silacyclopentane; (b) 1,1-dimethyl-3,4-dideutero-1-silacyclopentane.

In a similar manner, a C_2H_4 molecule may also be eliminated from the $[M-CH_3]^+$ ion (m/z 157) formed due to the loss of a methyl radical from the silicon atom. In fact, the appearance of the m/z 130 ion in the spectrum of IIa is due to the loss of a C_2H_3D species from $[M-CH_3]^+$ (m/z 159). The presence of the m/z 131 ion in the latter case is most likely associated with the elimination of C_2H_4 after skeletal rearrangement of $[M-CH_3]^+$.

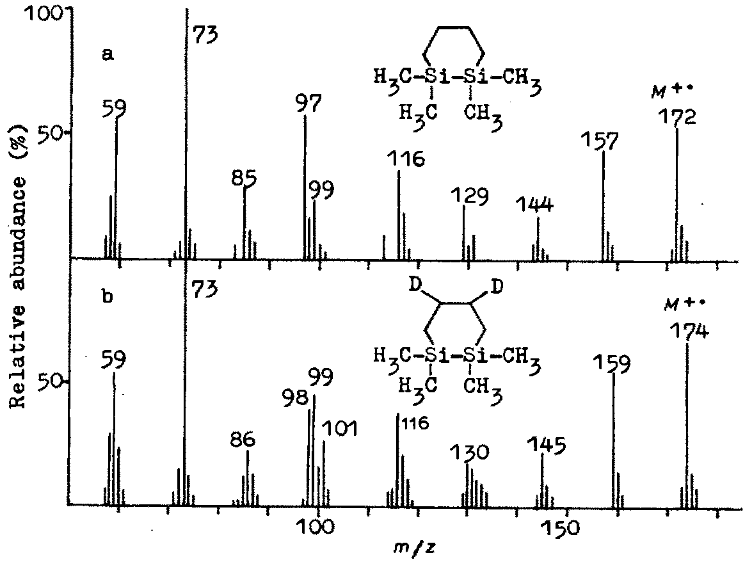


Fig. 2. Mass spectra of: (a) 1,1,2,2-tetramethyl-1,2-disilacyclohexane; (b) 1,1,2,2-tetramethyl-4,5-dideutero-1,2-disilacyclohexane.

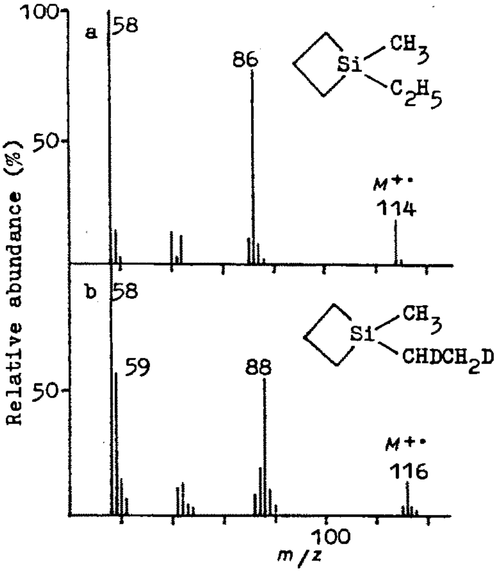
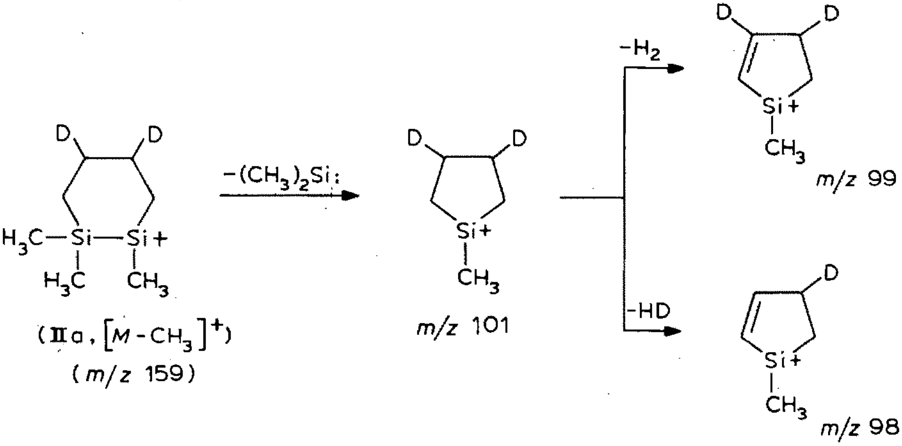


Fig. 3. Mass spectra of: (a) 1-methyl-1-ethyl-1-silacyclobutane; (b) 1-methyl-1-(1,2-dideuteroethyl)-1-silacyclobutane.

SCHEME 3



The origin of abundant ions at *m/z* 99 and 97 in the case of II can also be established from the labelling results. They show that the *m/z* 99 ion contains carbon atoms C(4) and C(5) and probably arises due to the loss of $(CH_3)_2Si$: from the $[M–CH_3]^+$ ion. Further dehydrogenation of the *m/z* 99 ion then leads to the ion at *m/z* 97, the peak of which is converted into the doublet at *m/z* 98 and 99 in the spectrum of IIa (Scheme 3).

The appearance of the *m/z* 85 ion in the spectrum of II may be attributed to "in half" cleavage of the molecular ion which is accompanied by hydrogen migration to the leaving species. The shift of the corresponding peak to *m/z* 86 after deuteration gives evidence that this ion includes the C(3) and C(4) atoms. The possible structure $(CH_3)_2\overset{+}{Si}CH{=}CH_2$ may be ascribed to the ion.

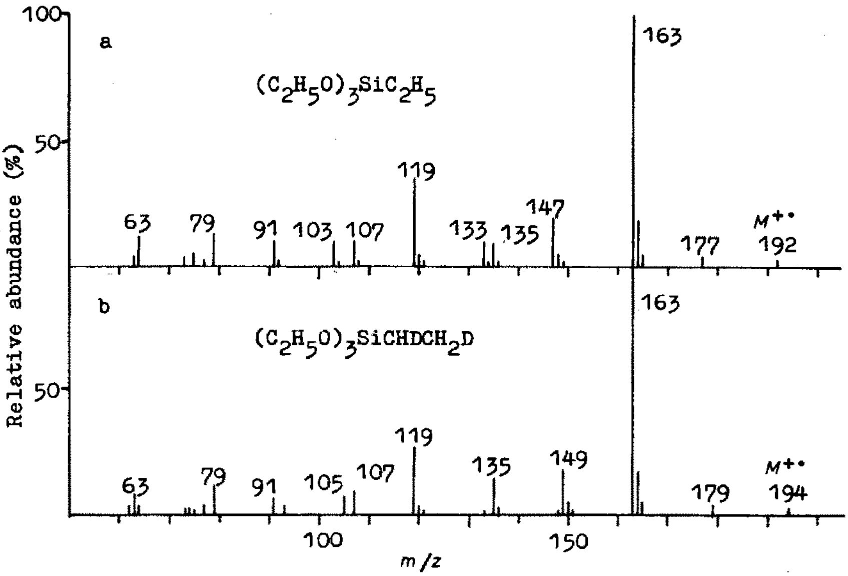
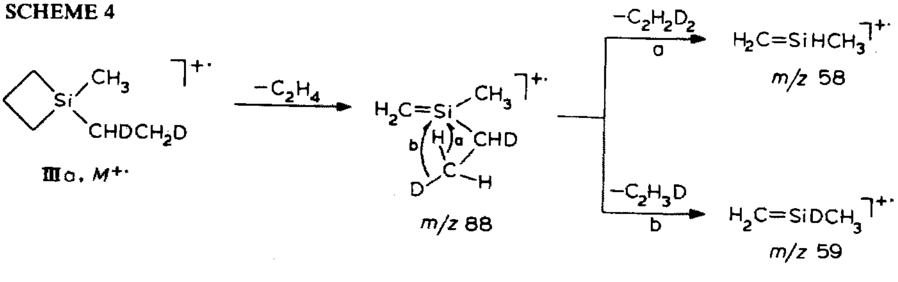


Fig. 4. Mass spectra of: (a) ethyl triethoxysilane; (b) 1,2-dideuteroethyltriethoxysilane.

Comparison of the mass spectra of compounds II and IIa shows that the formation of the $(CH_3)_3Si^+$ (*m/z* 73) and $[(CH_3)_2SiSi(CH_3)_2]^{+\cdot}$ (*m/z* 116) ions is associated with complete loss of label. This is quite explainable for the latter ion, which may be produced through a simple fission of the Si–C(3) and Si–C(6) bonds. At the same time, migration of a hydrogen atom from C(3) (or C(6)) or of a CH_3 group from the silicon atom should be supposed in order to explain the loss of the deuterium label during the formation of the ion at *m/z* 73.

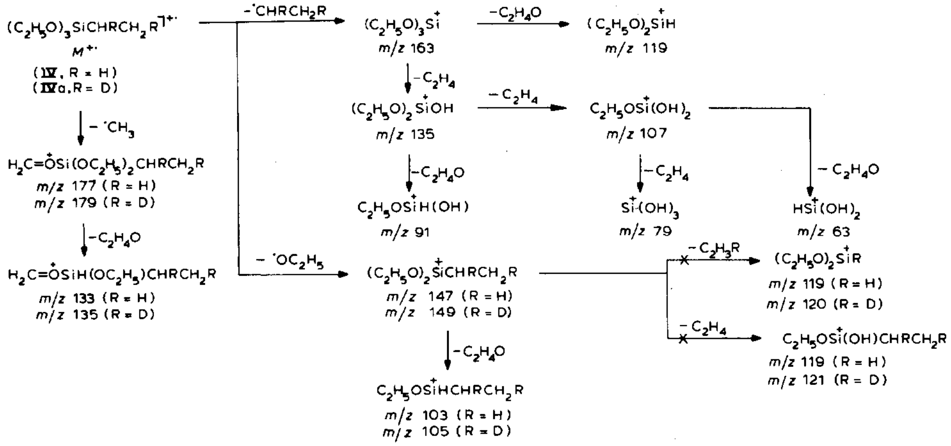
When 1-methyl-1-vinyl-1-silacyclobutane was used as the unsaturated substrate, 1-methyl-1-ethyl-1-silacyclobutane (III) and its labelled analogue IIIa were obtained and their mass spectra were recorded. As has been shown earlier [8], the most abundant ions in the mass spectrum of III (Fig. 3a) are due to step-wise elimination of two C_2H_4 molecules from the molecular ion. It was proposed that "in half" cleavage of the cyclobutane ring was responsible for the loss of the first C_2H_4 molecule. The labelling experiments (Fig. 3b) prove this suggestion and shed light on the mechanism of the elimination of the second C_2H_4. As the intensity ratio of the peaks at *m/z* 58 to *m/z* 59 (nearly 2/1) in the spectrum of IIIa is in good agreement with the probability of migration of H/D atoms (also 2/1), this allows the suggestion that a four-membered transition state is realized (Scheme 4).

SCHEME 4



The electron-impact-induced fragmentation of ethyl triethoxysilane (IV), obtained by the hydrogenation of vinyl triethoxysilane under the described conditions, can proceed at the expense of both O–C_2H_5 and Si–C_2H_5 groups (Fig. 4a). To help resolve this ambiguity, the mass spectrum of the dideutero analogue IVa (Fig. 4b) is rather informative. In Scheme 5, the main fragmentation pathways of compound IV are presented alongside those of compound IVa.

SCHEME 5



Experimental

The syntheses of 1,1-dimethyl-1-silacyclopent-3-ene and 1,1,2,2-tetramethyl-1,2-disilacyclohex-4-ene have been reported previously [9,10]. 1-Methyl-1-vinyl-1-silacyclobutane was synthesized according to the method reported in ref. 11. Vinyl triethoxysilane was a commercial analytical-reagent grade material.

The supported Wilkinson's catalyst (a solution of 5% $(Ph_3P)_3RhCl$ in 15% Carbowax 20M coated on Chromaton W) was prepared according to the method reported earlier [2]. A glass column (1.5 m × 3 mm) was packed with this catalyst system and connected to the mass spectrometer. Unsaturated substrates (0.05–0.1 μl) were passed through the column, which was preheated up to 45–80°C, in a flow of hydrogen or deuterium at a rate of 20 ml/min and the mass spectra of the corresponding saturated compounds or their dideutero analogues were recorded.

The investigation was performed on an LKB-2091 gas chromatograph/mass spectrometer. The mass spectra were obtained at an ionizing energy of 70 eV and an emission current of 50 μA; the temperature of the ionization chamber and molecular separator was 200°C.

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