

THE MASS SPECTRA OF SOME HEXAALKYL DISILOXANES

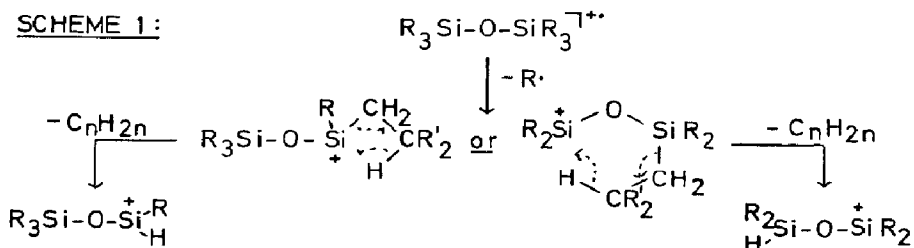
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ABSTRACT

The electron impact induced fragmentations of some hexaalkyl disiloxanes have been studied with respect to the effect of the size and the positions of different alkyl substituents at the Si-atoms. Positional isomers of hexaalkyl disiloxanes differing by the distribution of alkyl groups over both Si-atoms can be easily distinguished by large intensity differences of fragment ions in the 70eV EI-mass spectra. D-labelling studies and MIKE-spectra of relevant ions show that this effect is due to an unusual preference for the loss of a small alkyl group flanked by two larger ones at the same Si-atom from molecular ions. The results also indicate that after the initial loss of an alkyl radical the structural identity of the fragment ions is lost probably by migrations of alkyl groups.

INTRODUCTION

Hexaalkyl disiloxanes are simple members of the large family of organo siloxanes. To establish the analytical application of mass spectrometry for these technical important compounds the mass spectra of some hexaalkyl disiloxanes and related compounds have been investigated before (ref. 1-5). The most important fragmentation route corresponds to loss of an alkyl radical followed by consecutive eliminations of C_nH_{2n} in analogy to the mass spectra of aliphatic ethers (ref. 6). However, elimination of C_nH_{2n} in pentaalkyl disiloxane ions may occur either by a four membered transition state as proposed for triethyl silyl



ethers of alkanols (ref. 2) or by a six membered one as proposed for triethyl silyl derivatives of alkanediols (ref. 7; scheme 1). To get some further insight into the fragmentation mechanisms the following hexaalkyl disiloxanes including positional isomers have been studied

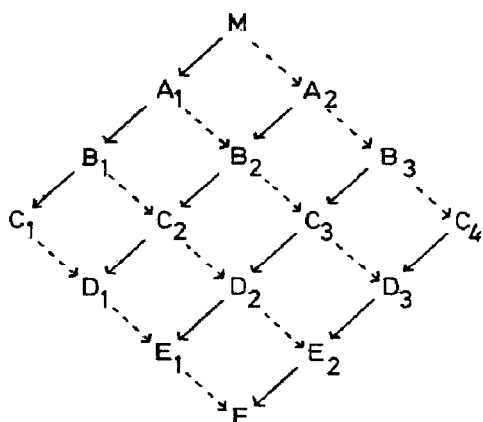
'(anti-)symmetrical'			'unsymmetrical'		
$R_3^1Si-O-SiR_3^2$			$R_2^1R^2Si-O-SiR^1R_2^2$		
	R ¹	R ²		R ¹	R ²
1	C ₂ H ₅	CH ₃	6	C ₂ H ₅	n-C ₃ H ₇
2	C ₂ H ₅	C ₂ H ₅	7	C ₂ H ₅	i-C ₄ H ₉
3	C ₂ H ₅	C ₂ D ₅	(C ₂ H ₅) ₂ iC ₄ H ₉ Si-O-SiC ₂ D ₅ (iC ₄ H ₉) ₂		
4	C ₂ H ₅	n-C ₃ H ₇	8		
5	C ₂ H ₅	i-C ₄ H ₉			

METHODS

The disiloxanes 1 - 8 were synthesized either by coupling of the appropriate trialkylchloro silane with sodium trialkyl silanolate (ref. 8) or by a catalytic dehydrocondensation of trialkyl silanes with trialkyl silanols in the presence of Ni (ref. 9). The disiloxanes were purified by preparative gas chromatography. The mass spectra were obtained by a MAT 311A mass spectrometer (electron energy 70eV, acceleration voltage 3 kV, temp. of ion source and inlet system 150°C) coupled to a SS 200 data system. The MIKE-spectra were measured on a VG ZAB 2F mass spectrometer (electron energy 70 eV, accelerating voltage 6 kV, temp. of ion source and septum inlet system 180-200°C). All signals observed in the MIKE-spectra were narrow Gaussian shaped peaks.

RESULTS AND DISCUSSION

The intensities of the molecular ions in the 70 eV mass spectra are small (as expected) and can be hardly detected in the spectra of 4 - 8. The spectra of 4 and 6 are shown in fig. 1 and the intensities of relevant ions in the spectra of 1 - 7 are given in table 1. It is seen clearly that the genesis of all prominent fragment ions in these spectra can be explained by scheme 2. However, the peaks of the ions B₃, C₃, C₄, D₂, D₃ and E₂ around the left corner of scheme 2 are small or absent in the spectra of 4 - 7 which contain larger alkyl substituents besides C₂H₅ groups.



SCHEME 2: Genesis of fragment ions

—→ : loss of C_nH_{2n}
 - - - → : loss of C_2H_4

Obviously, elimination of a large alkyl group as C_nH_{2n} is preferred over loss of C_2H_4 . Further, it is seen that the spectra of the positional isomers 4/6 and 5/7 are distinctly different by the intensities of the primary fragment ions of type A and their daughter ions B and C. These differences may arise from the loss of different alkyl groups during the first fragmentation step and/or the subsequent alkene elimination.

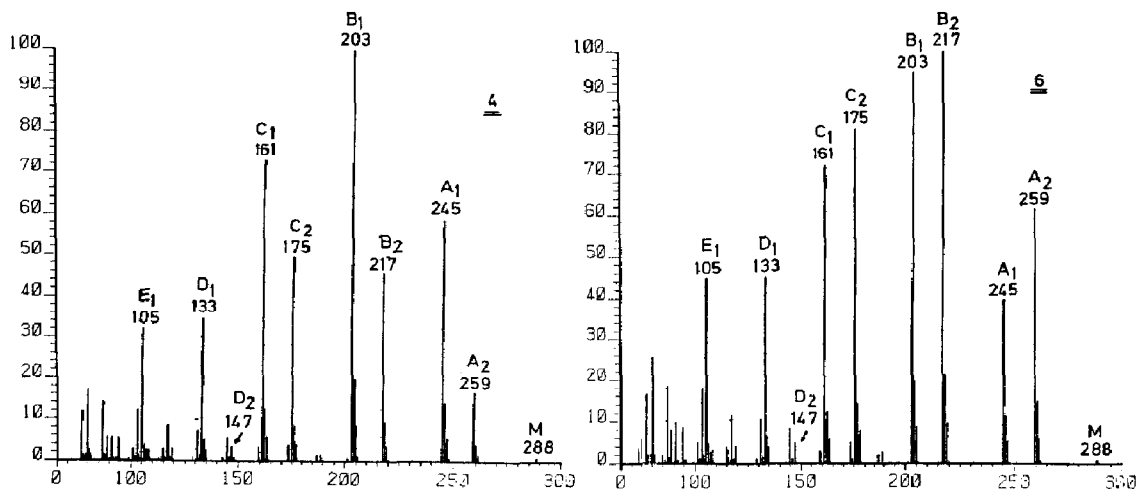


Fig. 1. EI mass spectra (70eV) of 1.1.1-triethyl-3.3.3-tri-n-propyl disiloxane (4) and 1.1.3-triethyl-1.3.3-tri-n-propyl disiloxane (6)

Loss of alkyl radical. The intensity of ion A_1 exceeds that of ion A_2 in the mass spectra of the anti-symmetrically substituted disiloxanes 4 and 5, indicating preferred loss of the larger alkyl group during the first reaction step. Similarly, the daughter ions B_1 and C_1 of A_1 are more abundant than daughter ions B_2 and C_2 of A_2 . Therefore, the intensity ratio A_1/A_2 reflects different rates of formation of these ions. Surprisingly, the intensity ratio A_1/A_2 is reversed in the mass spectra of the unsymmetric isomers 5 and 7, indicating the unusual preference for the loss of a small

TABLE 1

Characteristic Ions in the EI Mass Spectra of 1 - 7

	(Type of ion ^a), rel.int., % B)												
	A ₁	A ₂	B ₁	B ₂	B ₃	C ₁	C ₂	C ₃	D ₁	D ₂	E ₁	E ₂	F
<u>1</u>	84	14	100	13		55	12		12				
<u>2</u>	← 100 →			← 41 →			← 20 →		← 8 →		← 12 →		5
<u>3</u> b)	70	100	9	48	20	1	12	20					
<u>4</u>	59	17	100	46	<1	73	50	2	35	4	31	3	12
<u>5</u>	25	1	83	13	c)	100	29	c)	31	c)	27	c)	8
<u>6</u>	40	62	95	100	<1	72	81	2	45	5	45	4	16
<u>7</u>	33	54	100	97	c)	90	91	c)	37	c)	31	c)	8

a) see scheme 2 b) C_nH_{2n} = C₂D₄ c) overlapping with other ions

alkyl group. The mass spectrum of 8 shows peaks for loss of C₂H₅ (17%), C₂D₅ (35%) and i-C₄H₉ (31%), corresponding to 0.8:3.4:1.0 for the loss of one of these groups from M⁺. Clearly an alkyl group flanked by two large alkyl groups at the same Si-atom is lost with special ease. This steric effect is characteristic for R₃Si-groups in radical cations and leads to different mass spectra for positional isomeric disiloxanes. Note also the unusually large secondary isotope effect k_H/k_D = 1.43 for loss of C₂H₅/C₂D₅ from M⁺ of 3.

Elimination of C_nH_{2n}: Preferred elimination of large alkyl groups (iC₄H₉ > nC₃H₇ > C₂H₅) from disiloxonium ions of Type A, B and C is confirmed by the MIKE spectra of these fragment ions. Furthermore, the MIKE spectra of corresponding ions of isomers 4/6 and 5/7 are identical. Hence different elimination mechanisms have no effect on the reaction of metastable disiloxonium ions of different origin. Competitive loss of C₂H₄ and C₂D₄ is observed in the MIKE spectra of all fragment ions of 3 with the same k_H/k_D of 1.8 ± 0.1, in spite of expected differences in the structure and elimination mechanisms of these ions. A plausible explanation for this result is the loss of structural identity by alkyl group migrations in metastable pentaalkyl disiloxonium ions.

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