

ELECTRON IMPACT FRAGMENTATION OF SUBSTITUTED PHENYLDIMETHYLSILANES*

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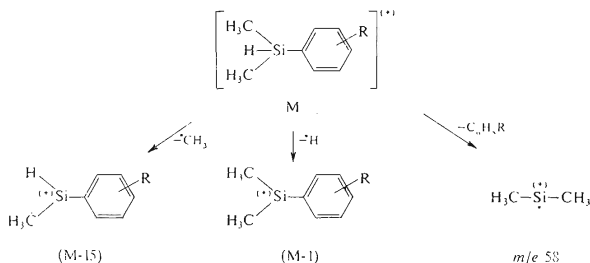
Based on the mass spectra of substituted phenyldimethylsilanes $(\text{CH}_3)_2\text{HSiC}_6\text{H}_4\text{R}$ ($\text{R} = \text{H}$, $p\text{-N}(\text{CH}_3)_2$, $p\text{-OCH}_3$, $p\text{-Cl}$, $m\text{-Cl}$, and $m\text{-CF}_3$), the schemes of their electron impact fragmentation were derived. The fragmentation was found to depend on substituent. Relative abundance of hydrogen and methyl radicals, cleaved from molecule-ions, correlated well with σ constants of the substituents attached to the phenyl group. Substituent effects on fragmentation can, in a first approximation, be explained by the effect of substituents on charge distribution in the molecule-ion, and thus on activation energies of fragmentations. Ionisation energies show satisfactory linear correlation with σ constants of the substituents on the phenyl group of these compounds.

Fragmentation Schemes

Fragmentations of substituted phenyldimethylsilanes on electron impact, proceeding in the first step are depicted in Scheme 1.

In the mass spectra of these compounds, apart from the peak of the molecule-ion, the most intense peaks correspond to the fragments $(M - 1)$ and $(M - 15)$. Only with phenyldimethylsilane and p -methyl-substituted derivative, the abstraction of a neutral species, yielding an ion at m/e 58 (Scheme 1) is more extensive. The very intense peak of this ion is observed in the mass spectra of both compounds. As a representative example, the mass spectrum of p -methylphenyldimethylsilane is shown in Fig. 1a. The above fragmentations are followed by secondary and tertiary fragmentations which are visualized in Scheme 2. If the phenyl group is substituted with polyatomic substituents further fragmentations take place with participation of these substituents. These reactions are for m -methoxyphenyldimethylsilane summarised in Scheme 3. The mass spectrum of p -methoxyphenyldimethylsilane is shown in Fig. 1b. Trifluoromethylphenyldimethylsilane

* Part CXXII in the series Organosilicon Compounds; Part CXXI: This Journal 39, 2616 (1974).



SCHEME 1

differs from the other compounds of the series under study. In its spectrum, shown in Fig. 1c, the peak of the molecule-ion is absent, intense peaks belong, however, to fragments at m/e 127, 108 and 77. Their formation can be depicted, for instance, by Scheme 4.

Dependence of Electron Impact Fragmentation on Substitution

Fragmentation yields depend on substitution of the phenyl group. This dependence is most distinct for both primary fragmentations, leading to the (M - 1) and (M - 15) ions. If a substituent attached to the phenyl group is a good electron donor, fragmentation yields are low. If, on the other hand, the substituent is a poor electron donor, fragmentations proceed with high yields. As a relative measure of the yields of fragmentation routes, the following expressions were used

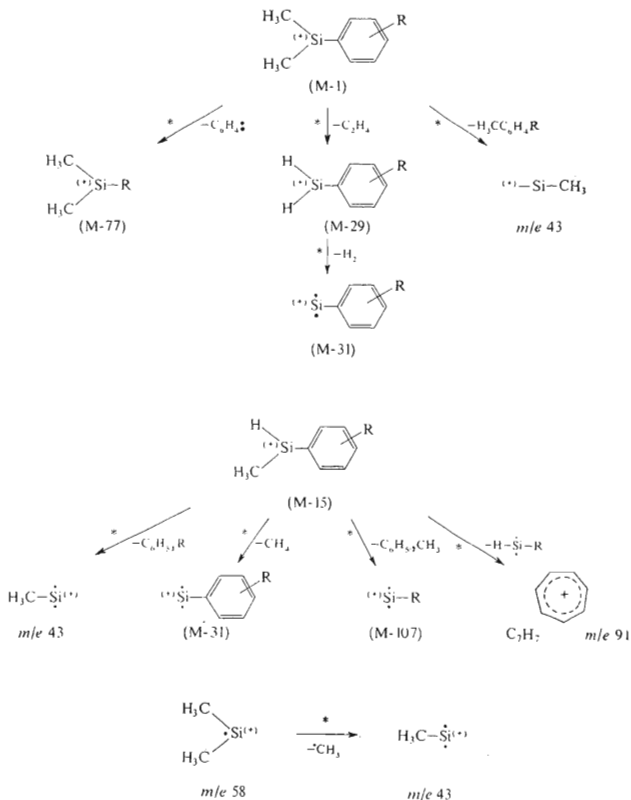
$$\lg \frac{(I_{(M-15)}/I_M)_R}{(I_{(M-15)}/I_M)_H} = \lg (Z/Z_0)_{M-15}$$

and

$$\lg \frac{(I_{(M-1)}/I_M)_R}{(I_{(M-1)}/I_M)_H} = \lg (Z/Z_0)_{M-1}$$

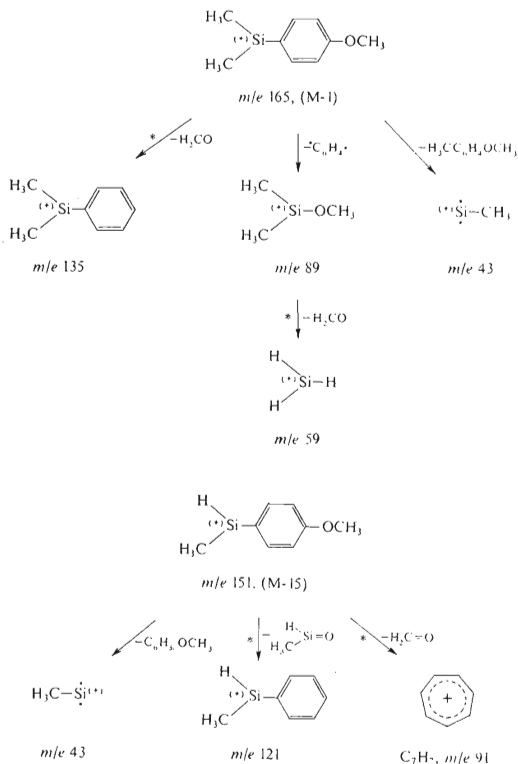
(I peak intensities of the fragment in the mass spectrum; R and H substituted and unsubstituted compound, respectively) and plotted against σ substituent constants¹ (Fig. 2). The yields of both fragmentations strongly depend on the σ values. Correlations of the yields of electron impact fragmentations with σ constants have been known for a long time²⁻⁴. Because of the specificity of fragmentations, these correlations have to be interpreted from different aspects, compared to those used in chemical

reaction kinetics⁵. According to quasi-equilibrium theory of mass spectra^{6,7}, one should consider the effect of substituents on all parameters determining rate constant (activation energy, frequency factor, number of vibration degrees of freedom) and on the energy distribution in molecule-ions. In the system studied the analysis was made for the reaction $M^{\bullet+} \xrightarrow{-CH_3} (M-15)^+$.



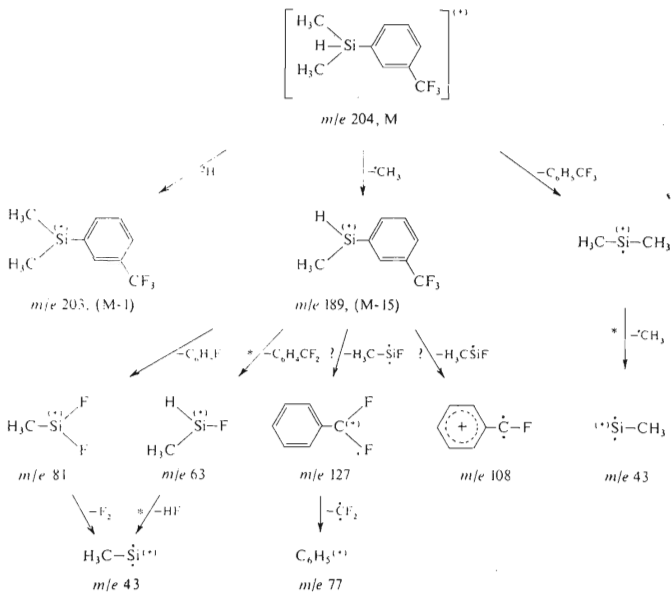
SCHEME 2

The ionisation energies of substituted phenyldimethylsilanes and the appearance energies of $(M - 15)^+$ ions in these compounds were determined by mass spectrometry. The activation energies for the abstraction of a methyl radical, following from the difference between both values, are recorded in Table I. Fig. 3 demonstrates that the yield of the fragmentation considered decreases with increasing activation energy of the reaction. This dependence shows good linearity. It seems therefore justified to explain the correlation shown in Fig. 3, in a first approximation, as solely due



SCHEME 3

to the effect of substituents on the activation energy of the methyl radical abstraction. According to quasi-equilibrium theory of mass spectra, the rate constant of fragmentation decreases with increasing activation energy, which leads to a decrease in fragmentation yield. Furthermore, it also affects the number of molecule-ions with the intrinsic energy high enough for the fragmentation to occur. This effect, too, leads to a decrease of the intensity of fragmentation ions in the mass spectrum. If the change of the activation energy of a fragmentation due to substitution is considered as a decisive factor determining the dependence observed, to substantiate experimental data, the effect of substituent on this quantity has to be explained. The activation energy of electron impact fragmentations depends on distribution of positive charge in the ion which undergoes this reaction. For a given fragmentation the charge density in the bond that is cleaved during the process is a decisive factor. From quantum-chemical calculations of similar systems, *e.g.* substituted phenoxytrimethylsilanes⁸,



SCHEME 4

it can be concluded that also in the molecule-ions formed from substituted phenyldimethylsilanes the positive charge is centered on silicon. The change in substitution on the phenyl group leads to the change of charge distribution in the molecule-ion as a whole and therefore also on silicon atom. The decrease of electron-donating ability of substituents with increasing values of their σ constants results in an increase of positive charge density both on silicon itself and on its bonds, dissociation energies of which hence decrease. This is the reason why activation energies of fragmentations proceeding *via* cleavage of Si—C and Si—H bonds decrease. This is evident for methyl

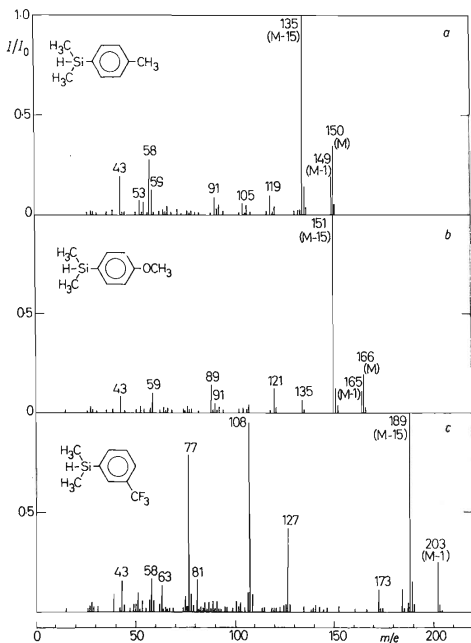


FIG. 1

Mass Spectra of *a* *p*-Methylphenyldimethylsilane, *b* *p*-Methoxyphenyldimethylsilane, and *c* *m*-Trifluoromethylphenyldimethylsilane

I/I_0 Relative intensity.

TABLE I

Ionisation Energy E_I (eV) and Activation Energy (eV) of Cleavage of a Methyl Radical from Substituted Phenyl dimethylsilanes $(\text{CH}_3)_2\text{HSiC}_6\text{H}_4\text{R}$ Induced by Electron Impact

R	E_I	E_A	R	E_I	E_A
<i>p</i> -N(CH ₃) ₂	7.08	2.67	H	8.72	1.34
<i>p</i> -OCH ₃	8.13	1.11	<i>p</i> -Cl	8.84	0.13
<i>p</i> -CH ₃	8.34	1.28	<i>m</i> -Cl	8.90	0.04

radical from Fig. 4, showing a reasonable linear dependence. The figure shows however a limitation of the assumption used. The activation energy of methyl radical abstraction becomes zero when σ substituent constant equals to ca. +0.3. This is why in the mass spectra of substituted phenyl dimethylsilanes the base peak is absent if the σ constant of the substituent is greater than this value. The spectrum of *m*-trifluoromethylphenyl dimethylsilane (Fig. 1c) may serve as an example. This fact can be explained providing that the system of the compounds studied is reduced to biatomic

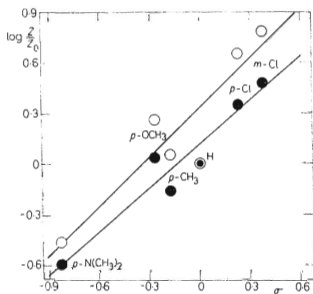


FIG. 2

Dependence of the Yields of Electron Impact Fragmentation of Substituted Phenyl dimethylsilanes on σ Substituent Constants

● Abstraction of hydrogen; $\lg(Z/Z_0) = 0.856\sigma + 0.116$; ○ abstraction of methyl radical; $\lg(Z/Z_0) = 0.974\sigma + 0.327$.

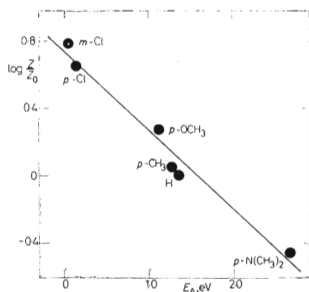


FIG. 3

Relationship between the Yield of the Cleavage of a Methyl Radical from the Molecule-Ion of Substituted Phenyl dimethylsilanes and the Activation Energy of Reaction

$$\lg(Z/Z_0) = -0.468E_A + 0.731.$$

system and changes in the potentials of the neutral molecule $A-B$ and of the molecule-ion $(A-B)^+$ are a function of distance between nuclei (Fig. 5). Franck-Condon transitions from the vibrational ground state of the potential curve of the neutral molecule $A-B$ to the potential curve of the molecule-ion $(A-B)^+$ are represented in Fig. 5 by perpendicular lines and correspond to the ionisation energy E_I and to the appearance energy of fragmentation ion B^+ , denoted as E_{AP} . At a certain form of the potential curve of the molecule-ion $(A-B)^+$ (solid line), the activation energy E_A of the cleavage of a bond appears, which can be determined as a difference between experimental values of E_{AP} and E_I . If the potential curve of the molecule-ion $(A-B)^+$ shifts due to lengthening of equilibrium distance $A-B$ to greater values (broken line), Franck-Condon transitions are possible only in the regions on the curve which lie above dissociation limit. On ionisation there proceeds a spontaneous decomposition of the molecule-ion which does not require any activation energy, and no molecule-ions are present in the mass spectrum. It is obvious that in the system considered the increase of $Si-CH_3$ bond length in the molecule-ion on increasing value of σ constant, and hence decreasing electron-donating ability of a substituent, leads to the experimental results described above.

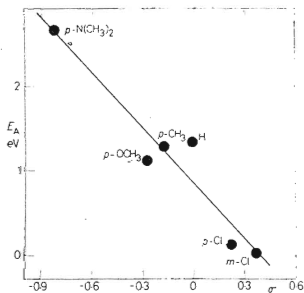


FIG. 4

Relationship between the Activation Energy of the Cleavage of a Methyl Radical from the Molecule-Ion of Substituted Phenyl-dimethylsilanes and σ Substituent Constants

$$E_A = -2.158\sigma + 0.855.$$

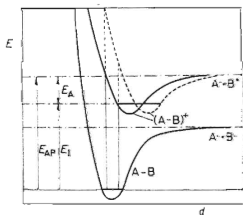


FIG. 5

Potential Energy of Molecules $A-B$ and of the Molecule-Ion $(A-B)^+$ as a Function of Distance between Atomic Nuclei

E_A Activation energy of the cleavage of bonds in $(A-B)^+$, E_I ionisation energy, and E_{AP} appearance energy of B^+ ion.

EXPERIMENTAL

Substituted phenyldimethylsilanes were prepared and described in previous works⁹⁻¹¹. Mass spectra were recorded with a mass spectrometer equipped with simple focussation. An indirect insertion temperature was 150°C, an ion source temperature was 250°C and an electron acceleration voltage was 70 V. The mass spectra shown in Fig. 1 were not corrected. They show for each ion the natural abundance of isotopes of the elements present in the compound studied, with the exception of chlorine for which the data correspond to monoisotopic ³⁵Cl.

On evaluating the mass spectra of substituted phenyldimethylsilanes, the intensities $I_{(M-1)}$ and $I_{(M-15)}$, measured for determination of $\lg(Z/Z_0)$, were corrected with respect to the yields of subsequent fragmentations, by adding the intensities of secondary and tertiary fragmentation products to these values. In the case where a reaction product was formed by several routes, it was assumed that all paths considered yield the product in the same amount. The values for phenyldimethylsilane and its *p*-substituted derivative were further corrected. Because of the high abundance of the product at m/e 58, formed by concurrent reaction, the intensity of the peak due to this ion was in both cases added in the ratio of uncorrected intensities $I_{(M-1)}$ and $I_{(M-15)}$ to the latter values. For determination of the ionisation and appearance energies, the yields of ionisation were measured at a constant mass number in dependence on the energy of impact electrons. The curves so obtained were treated semi-logarithmically¹². The accuracy of measurements was ± 0.2 eV.

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