ELECTRON IMPACT FRAGMENTATION
OF SILYL-SUBSTITUTED PHENYLDIMETHYLSILANES*

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Electron impact fragmentation of silyl-substituted phenyldimethylsilanes $(CH_3)_2HSiC_6H_4SiX_n$.
$.(CH_3)_{3-n}$ (X = OCH$_3$, Cl, and F; $n = 1-3$) was studied. The fragmentation was found to
depend on substitution of the silyl group; the latter factor affects above all a relative importance
of fragmentations occurring competitively on silicon atoms of the dimethylsilyl group and
substituted silyl group —$SiX_n(CH_3)_{3-n}$. Ionisation energies of substituted phenyldimethyl-
silanes show satisfactory linear dependence on σ constants of silyl groups. However, because
of great experimental errors ionisation energies could not be used to determine σ constants of silyl
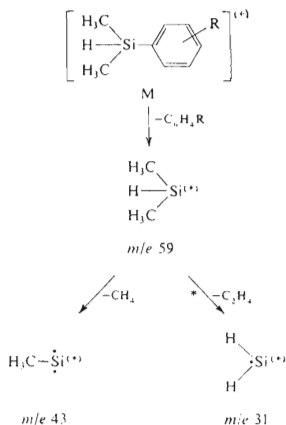groups.

Fragmentation Schemes

With silyl-substituted phenyldimethylsilanes $(CH_3)_2HSiC_6H_4SiX_n(CH_3)_{3-n}$ of
which *m*-substituted derivatives with X = OCH$_3$ ($n = 1-3$) and X = Cl ($n = 1-3$)
and *p*-substituted compounds with X = F ($n = 0,1-3$), X = OCH$_3$ ($n = 1, 2$),
and X = Cl ($n = 1, 3$) were studied, two groups of primary fragmentations are
taking place on electron impact. The first group includes the fragmentations accom-
panied by cleavage of the bonds of the dimethylsilyl group silicon (silicon *I*). These
fragmentations were already described by us[1] for phenyldimethylsilanes bearing
simple substituents. In the case of silyl-substituted compounds there occurs also
the splitting-off of the dimethylsilyl group to give a fragment bearing positive charge,
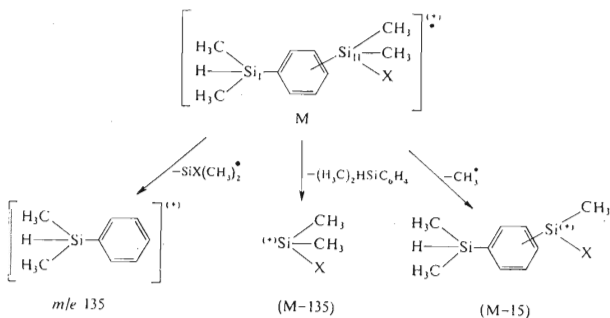which undergoes further fragmentation in two ways (Scheme 1).

The second group involves fragmentations that lead to the cleavage of the bonds
of the silicon of the substituted silyl group (silicon *II*). These fragmentations are for
the silanes $(CH_3)_2HSiC_6H_4SiX(CH_3)_2$ depicted in Scheme 2. The two groups of
fragmentations compete with one another. This is evident from the mass spectrum
of *p*-trimethylsilylphenyldimethylsilane, shown in Fig. 1*a*, which exhibits the peaks

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of the products of both groups of fragmentations. It cannot be, of course, decided to what extent the $(M - 15)$ ion is formed by abstraction of a methyl radical from silicon I of from silicon II. Secondary and tertiary fragmentations of silyl-substituted phenyldimethylsilanes, which start from dimethylsilyl ion $(m/e\ 59)$ and from sub-
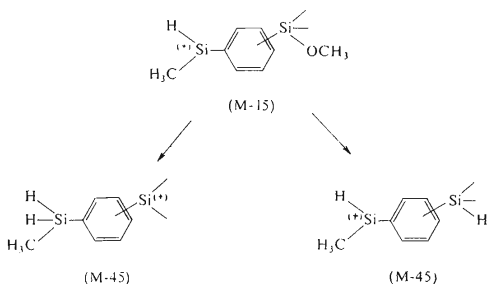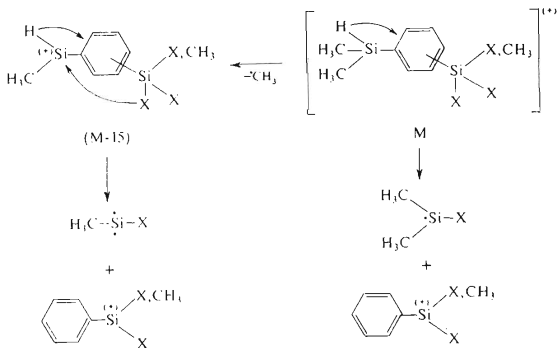
SCHEME 1

SCHEME 2

stituted silyl ions $[SiX_n(CH_3)_{3-n}]^+$, proceed only to a small extent. If, however, the substituent X on silicon *II* is the methoxy group, the $(M - 15)$ ion undergoes further fragmentation to yield formaldehyde, and the mass spectrum shows an intense $(M - 45)$ ion. The spectrum of *m*-dimethoxymethylsilylphenyldimethylsilane, shown in Fig. 1*b*, can be taken as a representative example. In order to explain the formation of this ion, the structure of starting fragmentation ion has to be known. Resulting from the assumptions based on the dependence of fragmentation on substitution[1], in the case of methoxysilyl-substituted phenyldimethylsilanes the methyl radical

SCHEME 3

SCHEME 4

should be cleaved from silicon I. It cannot be decided, however, whether the hydrogen transfer, connected with subsequent abstraction of formaldehyde from the $(M - 15)$ ion, is realised on silicon I or on silicon II. Both possibilities are therefore depicted in Scheme 3.

Apart from fragments arising from simple cleavage of bonds, the mass spectra of the compounds $(CH_3)_2HSiC_6H_4SiX_n(CH_3)_{3-n}$ (where X is halogen and $n = 2$ or 3) show also fragmentation products of the types $(C_6H_5SiX)^+$, $(C_6H_5SiCH_3)^+$, $(C_6H_5SiX_2)^+$, and $(C_6H_5SiXCH_3)^+$. Thus, for example, the spectrum of m-dichloromethylsilylphenyldimethylsilane (Fig. 3b) shows peaks due to $(C_6H_5SiClCH_3)^+$ (m/e 155) and $(C_6H_5SiCH_3)^+$ (m/e 120) ions. These fragments may be formed either from the molecule-ion or from the $(M - 15)$ ions, as shown in Schemes 4 and 5. In such cases it is impossible to ascertain which of the routes is actually followed. Analogous carbon fragments $(C_6H_5CF_2)^+$ and $(C_6H_5CF)^+$ appear in the spectrum of (trifluoromethylphenyl)dimethylsilane[1] as intense peaks at m/e 127 and 108. Although in our previous work[1] these fragments were assumed to arise from the $(M - 15)$ ion, also in this case they may be formed from the molecule-ion.
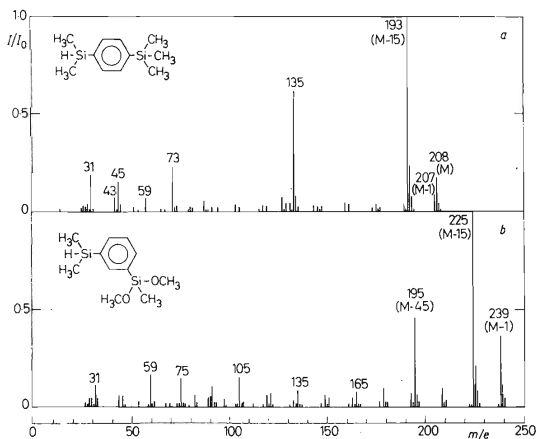

FIG. 1

Mass Spectra of a p-Trimethylsilylphenyldimethylsilane and b m-Dimethoxymethylsilylphenyldimethylsilane

I/I_0 Relative intensity.

Substituent Effects on Electron Impact Fragmentation

Similar to our previous work[1], the yields of electron impact fragmentation of the compounds under study were found to depend on the type of substituents. In the case of silyl-substituted phenyldimethylsilanes, substituents of the silyl group —SiX_n. .$(CH_3)_{3-n}$ affect, of course, also competitive fragmentation reactions occurring both on the silicon of this group (silicon *II*) and on the silicon of the dimethylsilyl group (silicon *I*). This becomes clear from comparison of the spectra of *p*-methoxydimethyl-silylphenyldimethylsilane and *p*-chlorodimethylsilylphenyldimethylsilane (Fig. 2).
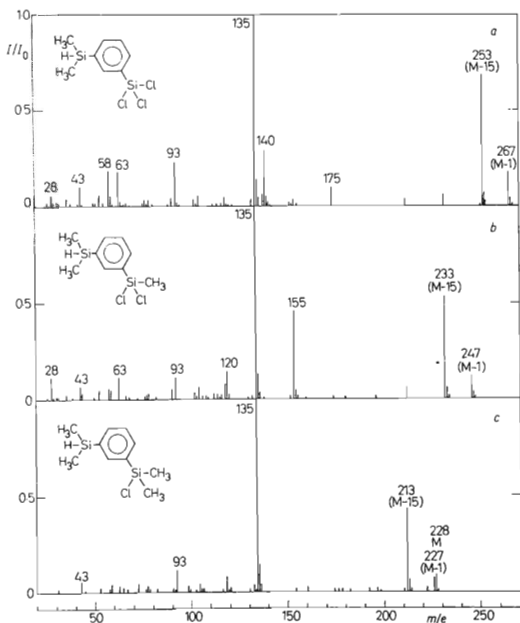

Fig. 2

Mass Spectra of *a p*-Methoxydimethylsilylphenyldimethylsilane, *b p*-Chlorodimethylsilylphenyl-dimethylsilane, and *c p*-Fluorodimethylsilylphenyldimethylsilane

I/I₀ Relative intensity.

Because of the identical mass of fragmentation products formed by cleavage of methyl radicals from both silicon atoms, substituent effects can be discussed only qualitatively. Similar to phenyldimethylsilanes containing simple substituents[1], also here the effect of substituents on other factors determining the intensity of mass spectral peaks had to be neglected. Furthermore, one has to assume that change of substituents affects above all the activation energy of fragmentation. This dependence may also be interpreted in terms of substituent effects on charge distribution in the molecule-ion. Providing that both silicon atoms are identically substituted, then both atoms in the molecule-ion have the same charge. Fragmentations occurring with participation of these reaction centers give then identical fragmentation yields.

SCHEME 5

If silicon *II* is substituted with a group which acts as a stronger electron donor, compared to silicon *I*, the positive charge on this atom decreases. Dissociation energies of the bonds of this silicon atom increase, so that the yields of competitive fragmentations on silicon *I* also increase. If, on the other hand, silicon *II* is substituted with groups which are poorer electron donors than are the groups on silicon *I*, dissociation energies of the bonds of silicon *II* decrease. This would result in a decrease of the yields of competition reactions involving the cleavage of the bonds of silicon *I*. These conditions follow from comparison of Figs 2*a* and 2*b*. While in the mass
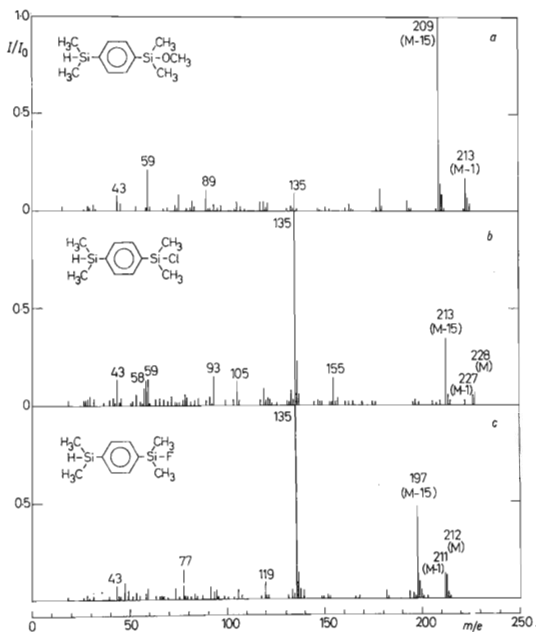

FIG. 3

Mass Spectra of *a* m-Trichlorosilylphenyldimethylsilane, *b* m-Dichloromethylsilylphenyldimethylsilane, and *c* m-Chlorodimethylsilylphenyldimethylsilane

I/I_0 Relative intensity.

spectrum of methoxydimethylsilylphenyldimethylsilane most important peaks can be assigned to the $(M - 1)$, $(M - 15)$ and m/e 59 ions that are formed by cleavage of the bonds of silicon I, the spectrum of p-chlorodimethylsilylphenyldimethylsilane show very intense peaks due to $(M - 15)$ ion and to an ion of m/e 135, resulting from the cleavage of the bonds of silicon II. The mass spectrum of p-trimethylsilyl-phenyldimethylsilane, shown in Fig. 1a, lies in this sense in between these cases, since it exhibits the peaks of products of both competitive fragmentations.

Substituents on silicon II do not affect only charge density on this atom, but also electron density on silicon I. As follows from the results of the study of simply substituted phenyldimethylsilanes, the increasing electron donor ability of substituents on silicon II reduces probably also the positive charge on silicon I and decreases thus the yield of fragmentation reactions taking place on this atom. This effect becomes apparent on comparing the mass spectra of p-chlorodimethylsilylphenyl-dimethylsilane (Fig. 2b) and p-fluorodimethylsilylphenyldimethylsilane (Fig. 2c). Due to the stronger electron-accepting ability of the fluorodimethylsilyl group relative to the chlorodimethylsilyl group, the yields of fragmentations involving silicon I are higher for the fluoro derivative than for the chloro derivative. This is why inten-

TABLE I

Ionisation Energies of Silyl-Substituted Phenyldimethylsilanes $(H_3C)_2HSiC_6H_4R$

R	E_I, eV	σ^a (ref.)
m-Si(OCH$_3$)$_3$	9·0	0·09 (10)
m-Si(OCH$_3$)$_2$CH$_3$	8·8	0·03 (10)
m-SiOCH$_3$(CH$_3$)$_2$	8·5	0·04 (10)
m-SiCl$_3$	9·1	0·19 (10)
m-SiCl$_2$CH$_3$	8·6	0·08 (10)
m-SiCl(CH$_3$)$_2$	8·5	0·06 (10)
p-Si(OCH$_3$)$_2$CH$_3$	8·5	0·15 (11)
p-SiOCH$_3$(CH$_3$)$_2$	8·6	0·10 (11)
p-SiCl$_3$	9·3	0·37 (11)
p-SiCl(CH$_3$)$_2$	8·6	0·15 (11)
p-Si(CH$_3$)$_3$	8·4	0·06 (11)
p-SiF$_3$	9·2	0·51 (11)
p-SiF$_2$CH$_3$	8·7	0·28 (11)
p-SiF(CH$_3$)$_2$	8·5	0·15 (11)

^{a} The values, used also in Fig. 4, were determined kinetically[10] or by NMR spectroscopy and by dipole moment measurements[11].

sity of the peaks due to the $(M - 15)$ ions increases on going from the chloro to the the fluoro derivative. The same effect takes place also in the series $(CH_3)_2HSiC_6H_4 . .SiX_n(CH_3)_{3-n}$ with the same X and varying n. As follows from comparison of the mass spectra shown in Figs $3a-c$, in the series $m-(CH_3)_2HSiC_6H_4SiCl_n(CH_3)_{3-n}$ the substitution of chlorine on silicon II in m-trichlorosilylphenyldimethylsilane for the methyl group affects the decrease of the positive charge on silicon I. This diminishes the yield of the cleavage of a methyl radical from this centre, and in the mass spectra of the compounds of this series the $(M - 15)$ and $(M - 1)$ ions become gradually less abundant on going from m-trichlorosilylphenyldimethylsilane (Fig. $3a$) to m-chlorodimethylsilylphenyldimethylsilane (Fig. $3c$).

Ionisation Energies

Ionisation energies of silyl-substituted phenyldimethylsilanes are recorded in Table I. A detailed interpretation of these values is not possible due to relatively great experimental errors $(\pm 0.2 \text{ eV})$. Nevertheless, it can be stated that all values lie below the value for benzene (9·245 eV). The ionisation energies of trihalogenosilylphenyldimethylsilanes are highest energies so far measured. In the series $(CH_3)_2HSiC_6H_4 . .SiX(CH_3)_{3-n}$, with the same X and varying n, ionisation energies increase with decreasing number of methyl groups.

These effects can be discussed only qualitatively. According to Koopmans theorem[2] the ionisation energy corresponds to the HOMO energy. It can be then assumed that due to the $+I$ effect of substituents on the aromatic ring the HOMO energy increases as a result of inductive perturbation. Increasing electronegativity and number of substituents X on silicon II affect back donation of electrons in the bond of phenyl group with silicon, this leading to strengthening of the bond. This is accompanied by a decrease of the HOMO energy and by an increase of the ionisation energy. This effect becomes weaker again if back donation takes place on the
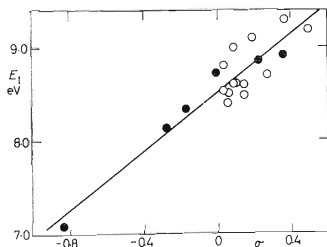

Fig. 4

Relationship Between Ionisation Energies and σ Constants of Substituted Phenyldimethylsilanes

● Simply substituted phenyldimethylsilanes, ○ silyl-substituted phenyldimethylsilanes, $E_I = 0.157\sigma + 8.51$.

silicon of the Si—X bond[3],[4]. The same situation arises with methoxysilyl-substituted compounds, whose ionisation energies are in general lower than the energies of analogous chlorine- and fluorine-containing compounds. As correlations of ionisation energies with σ substituent constants are already known[5−7], we attempted to find a similar relationship also for the silyl substituents studied. Fig. 4 shows the relationship between ionisation energies of simply substituted phenyldimethylsilanes[1] and reported[8] values of σ constants. The dependence is satisfactorily linear, having $\varrho = +0.157$. Due to relatively great error of ionisation energy measurements, σ constants of the silyl substituents could have been determined with the accuracy of ± 1.3 units, *i.e.* with quite insufficient accuracy. As σ constants of the silyl groups $SiX_n(CH_3)_{9-n}$ were determined by different methods with other model compounds[9−11], the values used in Fig. 1 and Table I were taken from the above literature. As follows from Fig. 4, the deviations found for this series of compounds are greater than the error of the measurements. The fact that even in the series with relatively limited changes of substituents there are deviations from the relationship between ionisation energies and σ constants was observed, however, also with compounds of other types, *e.g.* with halogenobenzenes.

EXPERIMENTAL

The compounds studied were prepared and characterised in a previous work[10]. Their mass spectra were recorded with a spectrometer equipped with simple focusation, using conditions reported earlier[1]. The mass spectra were not corrected. Ionisation and appearance potentials were determined from the ionisation yields measured at a constant number of mass units in dependence on the energy of impact electrons. The accuracy of measurements was ± 0.2 eV.

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