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Preliminary communication

Substituents effect in the mass spectra of phenylpentamethyldisilanes

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Several attempts[1,2] to generate trivalent silico-cations, "silicenium ions"[2], by means of chemical reactions in solution have failed, though they have been assumed as intermediates in some organosilicon reactions[3]. However, in mass spectra, processes producing silicenium ions are well recognised as favoured paths.

We now describe features of the mass spectra of substituted phenylpentamethyldisilanes, which provide the first examples in which the trimethylsilicenium ion and phenyldimethylsilicenium ions are produced competitively at the same time, and which enable the stabilities of silicenium ions to be compared.

In Table 1, the mass spectral cracking patterns of phenylpentamethyldisilane at 15 eV and 70 eV respectively, are compared. These patterns are quite simple, exhibiting predominantly the parent ion M^+, and the $(M-15)^+$, $(M-73)^+$ and 73^+ ions. The reactions in the ion source must be regarded as comprising the following set of competing consecutive unimolecular reactions, as confirmed by the existence of metastable ions.

Since the value of Z_I/Z_{II}, where $Z_I = [I]/[M^+]$ and $Z_{II} = [II]/[M^+]$, can be taken to correspond to the relative stabilities of the silicenium ions, the stabilization of a silicenium ion by a phenyl group can be regarded as about 10 times as great as that by a methyl

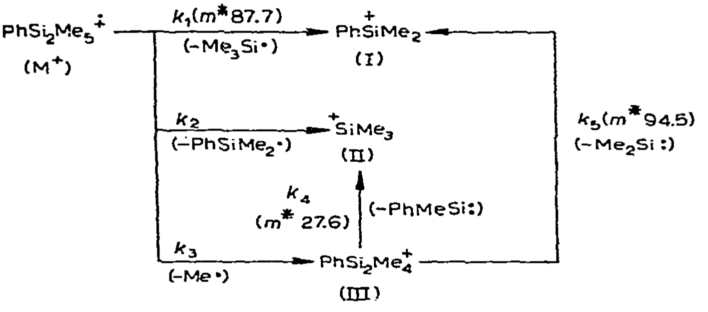

TABLE 1

PREDOMINANT IONS IN THE MASS SPECTRA OF PHENYLPENTAMETHYLDISILANE ($C_6H_5SiMe_2SiMe_3$)

Ion	*Relative intensity*	
	15eV	*70eV*
M (208)	30.0	12.0
M–15	7.1	9.6
M–73	100	100
73	10.3	29.7

group. Assuming that at the lower voltage (15eV) secondary fragmentations such as processes corresponding to k_4 and k_5 are negligible, the term Z_I/Z_{II} can be numerically equated to k_1/k_2 [4]. Since the substituent effect on the rate produced by stabilization of the neutral product is, in general, much less important[5] one can regard the effects of nuclear substituents on Z_I/Z_{II} as a measure of the relative stabilizations of the phenyldimethylsilicenium ions. The values of Z_I/Z_{II} for seven phenylpentamethyldisilanes at 15eV are shown in Table 2. The observed variation of Z_I/Z_{II} ranges over a factor of 26. The relative abundance of the substituted phenyldimethylsilicenium ion increases with the increasing electron-releasing power of the substituent, as would be expected for silicenium ions. Furthermore, there is a good linear relationship between the logarithms of the Z_I/Z_{II} and σ^+ (or σ) constants for the substituents, as shown in Fig. 1. The equations are

$$\log(Z_I/Z_{II}) = -0.67\,\sigma^+ + 1.14 \quad (r = 0.964)$$

and

$$\log(Z_I/Z_{II}) = -1.18\,\sigma + 1.24 \quad (r = 0.953)$$

Significantly, the effects correlate with σ^+ better than with σ, although the difference is not very large. These facts demonstrate that the silicenium ions are stabilized by

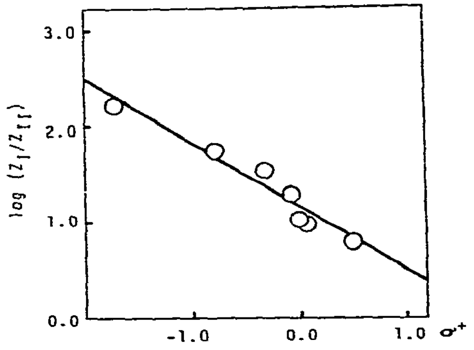

Fig.1. The relationship between $\log(Z_I/Z_{II})$ and σ^+.

TABLE 2

SUBSTITUENT EFFECTS ON Z_I/Z_{II}

Substituent	Z_I/Z_{II}
p-NMe$_2$	157
p-MeO	55.5
p-Me	35.9
m-Me	19.5
H	10.1
m-MeO	9.25
p-Ac	6.02

resonance interaction with the phenyl ring, probably through $2p_\pi$–$3p_\pi$ interaction, although the effects are much smaller than the case of the analogous carbenium ions, $Y{-}C_6H_4CH_2^+$, produced from $Y{-}C_6H_4CH_2CH_2C_6H_5$ compounds by electron impact ($\rho = -3.3$ with σ^+)[6].

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REFERENCES

1 G.A. Olah, Y.K. Mo, *J. Amer. Chem. Soc.*, 93 (1971) 4942.
2 A.G. Brook, K.H. Pannell, *Can. J. Chem.*, 48 (1970) 3679.
3 L.H. Sommer, F.J. Evans, *J. Amer. Chem. Soc.*, 76 (1954) 1186.
4 M.M. Bursey, *Org. Mass Spectrom.*, 1 (1968) 31.
5 F.W. McLafferty, *Chem. Commun.*, (1968) 956.
6 F.W. McLafferty, M.M. Bursey, *J. Amer. Chem. Soc.*, 90 (1968) 5299.