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PENTAMETHYLDISILANYL-SUBSTITUTED PHENOL AND ACETOPHENONE
THE ELECTRONIC EFFECTS OF THE *p*-PENTAMETHYLDISILANYL GROUP

HIDEKI SAKURAI, SEIJI DEGUCHI, MINEO YAMAGATA, SHUN-ICHI MORIMOTO, MITSUO KIRA AND MAKOTO KUMADA
Department of Synthetic Chemistry, Kyoto University, Sakyo-ku, Kyoto (Japan)

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SUMMARY

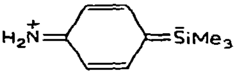
The chemical shifts of the hydroxyl protons of *p*-(trimethylsilyl)- and *p*-(pentamethyldisilanyl)phenol have been measured, and used in the derivation of σ^--constants of +0.06 and +0.02, respectively, for the *p*-Me_3Si and *p*-Me_5Si_2 group. The carbonyl stretching frequencies of *p*-(trimethylsilyl)-, *p*-(pentamethyldisilanyl)-, *p*-(trimethylsiloxy)-, and *p*-(pentamethyldisilanoxy)acetophenone have been determined and used to give σ^+-constants for *p*-Me_3Si, *p*-Me_5Si_2, *p*-Me_3SiO, and *p*-Me_5Si_2O of 0.0, −0.23, −0.60, and −0.60, respectively.

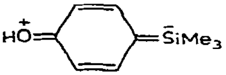
It is concluded that the *p*-Me_5Si_2 group has a larger $+I$ and also a larger $-T$ effect than the *p*-Me_3Si group.

INTRODUCTION

There is much interest in the ultraviolet spectra of polysilanes[1], and these have provided evidence for conjugation between a silicon–silicon bond and an adjacent π-electron system.

There are arguments in favour of $(p \rightarrow d)_\pi$ bonding in the silicon–phenyl bond[2], but it is difficult to provide conclusive evidence for such interactions since silicon exerts an electron-releasing inductive effect ($+I$ effect) that may offset any electron-accepting effect due to $(p \rightarrow d)_\pi$ bonding between the π-electrons of the ring and the d_π-orbitals of silicon ($-T$ effect). For example, Hammett σ-constants for the Me_3Si group are variable depending on varying importance of the $-T$ effect. The positive value of σ_p for the Me_3Si group obtained from acidity constants of anilinium ions or from ionization constants of phenols[2], clearly indicates substantial contributions to the ground state from structures such as

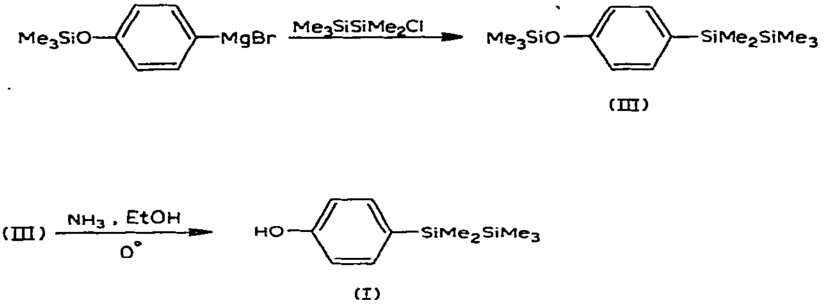




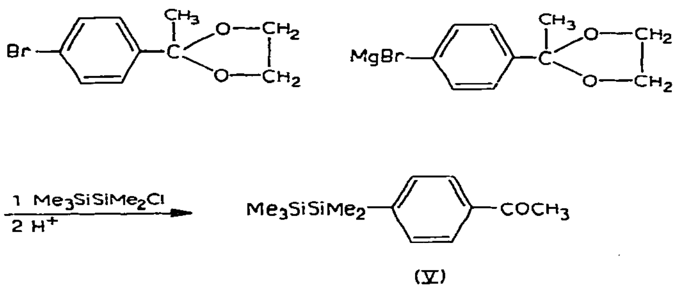
In this paper, the preparation and properties of pentamethyldisilanyl-substituted phenol, acetophenone, and some related compounds are described, and the properties are used in analysing the effects of the silicon–silicon bond on $(p \rightarrow d)_\pi$ ground state interactions.

RESULTS AND DISCUSSION

The following route was used for the preparation of *p*-(pentamethyldisilanyl)-phenol (I). In solvolysis of the intermediate (III) the procedure used with (trimethylsilyl)phenol (II)[3] had to be modified because ethanolysis in acidic or neutral conditions gave only phenol, because of extensive desilylation. Ethanolysis in the presence of a trace amount of ammonia at 0° was found to be successful. Prolonged heating of (I) also resulted in an extensive rearrangement to phenoxypentamethyldisilane, and flash distillation was indispensable in the purification.



p-(Pentamethyldisilanyl)acetophenone (V) was prepared without difficulty by the procedure used for *p*-(trimethylsilyl)acetophenone (IV)[4].



p-(Trimethylsiloxy)acetophenone (VI) and *p*-(pentamethyldisilanoxy)acetophenone (VII) were prepared by condensation of *p*-hydroxyacetophenone with the corresponding chlorosilanes.

Table 1 lists the hydroxyl chemical shifts of (I) and (II) measured in dimethyl

TABLE 1

THE HYDROXYL PROTON CHEMICAL SHIFTS OF SILYL-SUBSTITUTED PHENOLS

Phenol	δ^a (ppm)	$\Delta\delta$ (ppm)	σ^-
p-$(CH_3)_3SiC_6H_4OH$	9.38	0.08	0.06
p-$(CH_3)_3SiSi(CH_3)_2C_6H_4OH$	9.33	0.03	0.02

[a] The δ values of some other reference phenols were (values in literature are cited in parentheses): phenol, 9.30 (9.22[5], 9.32[6a]); *p*-$MeOC_6H_4OH$, 8.83 (8.83[5], 8.76[6a]); *p*-Cl-*m*-MeC_6H_3OH, 9.49 (9.45[5], 9.50[6a]).

sulfoxide (DMSO) solution. Recent studies of *meta*- and *para*-substituted phenols in DMSO solution have shown a good linear correlation of the hydroxyl chemical shifts with the Hammett σ^--constants[5,6]. Although the chemical shifts were found to vary slightly with temperature the values for some reference compounds agree well with those in literatures. The positions of the hydroxyl chemical shifts of (I) and (II) are definitely at low field relative to those of phenol, though the differences are small. This means that (I) and (II) are more acidic than phenol. The σ^- values were calculated from the equation, $\sigma^- = 0.7\ \Delta\delta$[7], and are listed in the last column of Table 1. The hydroxyl chemical shift of (I) has previously been reported[8], and indicated that (I) was slightly less acidic than phenol. We cannot account for this disagreement, but it is noteworthy that our σ^- value for (I) (+0.06) resembles very closely that calculated from the apparent ionization constants of phenols (+0.07)[9].

TABLE 2

THE CARBONYL STRETCHING FREQUENCIES OF SILYL- AND SILOXY-SUBSTITUTED ACETOPHENONES

Acetophenone	ν(C=O)[a] (cm^{-1})	$\Delta\nu$ (cm^{-1})	σ^+
p-$(CH_3)_3SiC_6H_4COCH_3$	1691.0	0	0
p-$(CH_3)SiSi(CH_3)_2C_6H_4COCH_3$	1688.5	2.5	−0.23
p-$(CH_3)_3SiOC_6H_4COCH_3$	1683.5	7.0	−0.60
p-$(CH_3)_3SiSi(CH_3)_2OC_6H_4COCH_3$	1683.5	7.0	−0.60

[a] The ν(C=O) of some other reference acetophenones were: $C_6H_5COCH_3$, 1691; p-$CH_3C_6H_4COCH_3$, 1688; p-$CH_3OC_6H_4COCH_3$, 1683; p-$NH_2C_6H_4COCH_3$, 1678.

Table 2 lists the carbonyl stretching frequencies of four substituted acetophenones. The C=O stretching frequencies of substituted acetophenones in dilute carbon tetrachloride solution correlated well with Brown–Okamoto's σ^+-constants, according to the equation, $\sigma^+ = 0.0877\ \Delta\nu(C{=}O)$[10]. The frequencies measured in this study are again in good agreement with those of the previous studies, and the equation derived from our values for a limited number of compounds is $\sigma^+ = 0.085\ \Delta\nu(C{=}O)$. The σ^+ values of Me_3Si-, $Me_3SiSiMe_2$-, Me_3SiO-, and $Me_3SiSiMe_2O$-groups calculated from this equation are listed in Table 2.

Interestingly, the pentamethyldisilanyl group is more electron releasing than the trimethylsilyl group as indicated by the σ^+-constants. Thus, for an electron deficient centre the former group donates electrons more strongly than the latter. Previously we used the free-radical copolymerization of vinylpentamethyldisilane with styrene and acrylonitrile[11] to separate the resonance (*Q*) and polar (*e*) effects in the Price–Alfrey's *Q*–*e* scheme[12], and the more negative *e* value for $Me_3SiSiMe_2$ (−0.6) than for Me_3Si (−0.1) was attributed to a greater electron releasing effect of the former group. The present study confirms this conclusion. Thus, the $+I$ effect of the $Me_3SiSiMe_2$ group is greater than that of Me_3Si. Since the $Me_3SiSiMe_2$ group has practically the same σ^- or σ value* as the Me_3Si group despite the great $+I$ effect suggests that the $Me_3SiSiMe_2$ group exerts a greater $-T$ effect than the Me_3Si group, as would be expected in view of the conjugating effect of the Si–Si bond.

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* Chernyshev *et al.* have reported K_a values of $PhCO_2H$, p-$Me_3SiC_6H_4CO_2H$, and p-$Me_3SiSiMe_2$-$C_6H_4CO_2H$ in 60% EtOH at 25° to be $1.12\cdot10^{-6}$, $1.17\cdot10^{-6}$, and $1.20\cdot10^{-6}$, respectively[13].

Finally it should be noted that Me_3SiO and $Me_3SiSiMe_2O$ groups have the same σ^+-value, which is slightly smaller than that of MeO. The electron-releasing effect of an RO group is a composite of $-I$ effect and $+T$ effect, the latter arising from the electron-pair donation of oxygen to a benzene ring. Since the former effect must be in the order $MeO > Me_3SiO > Me_3SiSiMe_2O$ because the increasing $+I$ effect of R in RO, the observed order for the composite effect may be taken as an evidence for $(n \rightarrow d)_\pi$ interactions in silyl aryl ethers, with such interaction greater for $Me_3SiSiMe_2OAr$ than for Me_3SiOAr. We plan to evaluate this effect more accurately from other results in a forthcoming paper.

EXPERIMENTAL

Spectra

NMR data were obtained with a Jeol model JNM-C-60H spectrometer for DMSO solutions at 23.5°. It was established that the chemical shifts of hydroxyl proton do not depend on concentration, and so 1 mole % solutions were used throughout.

The carbonyl stretching frequencies of ketones were measured as approximately 0.005 *M* solutions in carbon tetrachloride, using a Nippon Bunko model 402G double beam grating spectrophotometer.

Preparation of p-(trimethylsilyl)phenol, (II)

This compound was prepared by Neville's method[3], m.p. 73° (lit. 74°).

Preparation of p-(pentamethyldisilanyl)phenol, (I)

[p-(Trimethylsiloxy)phenyl]pentamethyldisilane, (III). This compound was prepared by the method of Neville[3] with pentamethylchlorodisilane in place of trimethylchlorosilane; b.p. 142°/15 mm, n_D^{20} 1.4983, d_4^{20} 0.9115, MR_D 95.60 (calcd.: 95.46) in 44% yield (Found: Si, 28.50. $C_{14}H_{28}OSi_3$ calcd.: Si, 28.40%.) From the residue, [p-(pentamethyldisilanoxy)phenyl]pentamethyldisilane was obtained in 17% yield, b.p. 118–120°/4 mm, n_D^{20} 1.5020, d_4^{20} 0.8932, MR_D 117.23 (calcd.: 115.81).

p-(Pentamethyldisilanyl)phenol, (I). In repeated attempts, acid hydrolyxis of (III) gave only phenol as a product.

Dry ammonia was bubbled into dry ethanol to make an ethanol solution of ammonia. The solution was diluted to about 0.1 *N* with absolute ethanol. To 50 g of (III) in 300 ml of ethanol added 8 ml of 0.1 *N* ethanol solution of ammonia thus prepared as above with external cooling by ice/salt bath. After stirring for 1 h, the mixture was kept over night in a refrigerator. Ethanol was then removed *in vacuo*, and the residue was distilled quickly through a 13 cm-column packed with a glass helices to give 14 g (41% yield) of pure (homogeneous to GLC) (II), b.p. 124°/13 mm, m.p. 38° (Found: C, 58.84; H, 8.89. $C_{11}H_{20}OSi_2$ calcd.: C, 58.86; H, 8.98%.)

Preparation of p-trimethylsilyl- and p-pentamethyldisilanyl-substituted acetophenone, (IV) and (V)

Compound (IV), b.p. 120–130°/20 mm, n_D^{20} 1.5161, d_4^{20} 0.9688, was prepared by Neville's method[4]. (V) was prepared by a similar method, b.p. 120°/5 mm, n_D^{20} 1.5283, d_4^{20} 0.9442, MR_D 81.72 (calcd.: 80.46) (Found: C, 62.11; H, 8.69. $C_{13}H_{22}OSi_2$

calcd.: C, 62.34; H, 8.85%.)

Preparation of p-(trimethylsiloxy)acetophenone, (VI)

A benzene solution of *p*-hydroxyacetophenone (13.6 g, 0.1 mole) and trimethylchlorosilane (13 g, 0.12 mole) was refluxed for 50 h in the presence of triethylamine (11 g, 0.11 mole). After removal of triethylamine hydrochloride by filtration, 15 g (0.072 mole, 72.1% yield) of *p*-(trimethylsiloxy)acetophenone was distilled from the mixture, b.p. 117–119°/4 mm, n_D^{20} 1.5131, d_4^{20} 1.0100 (Found: C, 63.19; H, 7.65. $C_{11}H_{16}O_2Si$ calcd.: C, 63.42; H, 7.74%.)

Preparation of p-(pentamethyldisilanoxy)acetophenone, (VII)

By essentially the same procedure as above, 11 g (0.081 mole) of *p*-hydroxyacetophenone and 15 g (0.090 mole) of pentamethylchlorodisilane in the presence of 10 g of triethylamine gave 17 g (0.064 mole, 79.0% yield) of *p*-(pentamethyldisilanoxy)acetophenone, b.p. 126–127°/3 mm, n_D^{20} 1.5204, d_4^{20} 0.9749 (Found: C, 58.60; H, 8.39. $C_{13}H_{22}O_2Si_2$ calcd.: C, 58.59; H, 8.32%.)

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REFERENCES

1 H. Sakurai, H. Yamamori and M. Kumada, *Chem. Commun.*, (1968) 198; and references cited therein.
2 C. Eaborn, *Organosilicon Compounds*, Butterworths London, 1960, p. 86–116.
3 R. G. Neville, *J. Org. Chem.*, 25 (1960) 1063.
4 R. G. Neville, *J. Org. Chem.*, 24 (1959) 111.
5 R. J. Ouellette, *Can. J. Chem.*, 43 (1965) 707.
6 (a) J. G. Trayham and G. A. Knesel, *J. Org. Chem.*, 31 (1966) 3350;
(b) M. T. Tribble and J. G. Trayham, *J. Amer. Chem. Soc.*, 91 (1969) 379.
7 Foot note 18 (b) in ref. 6 (b).
8 D. E. Fenton and J. J. Zuckerman, *Inorg. Chem.*, 7 (1968) 1323.
9 R. A. Benkeser and H. R. Krysiak, *J. Amer. Chem. Soc.*, 75 (1953) 2421.
10 T. G. Traylor and J. C. Ware, *J. Amer. Chem. Soc.*, 89 (1967) 2304.
11 H. Sakurai, K. Tominaga and M. Kumada, *Bull. Chem. Soc. Jap.*, 39 (1966) 1279.
12 T. Alfrey and C. C. Price, *J. Polym. Sci.*, 2 (1947) 101.
13 E. A. Chernyshev, N. G. Tolstikova, A. A. Ivashenko, A. A. Zelenetskaya and L. A. Leites, *Izv. Akad. Nauk. SSSR, Otd. Khim. Nauk*, (1963) 660.