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## CHEMISTRY OF ORGANOSILICON COMPOUNDS

### CL \*. PREPARATION AND UV SPECTRA OF NITROPHENYLPOLYSILANES \*\*

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#### Summary

Six *p*- and *m*-nitrophenyl-substituted methylpolysilanes have been prepared by the reaction of nitrobenzyne with monohydromethylpolysilanes. UV spectra of *p*-nitrophenylpolysilanes revealed a strong red shift compared with the parent phenylpolysilanes due to the contribution of intramolecular charge transfer to the nitro group.

#### Introduction

Gilman, Atwell and Schwebke [1], Hague and Prince [2], and Sakurai and Kumada [3] reported independently in 1964 that the silicon–silicon bond has a conjugating property with phenyl and vinyl groups [4]. Thus, phenylpentamethyldisilane revealed an intense absorption at 231 nm ( $43\,300\text{ cm}^{-1}$ ) ( $\epsilon$  10 900); the introduction of a pentamethyldisilanyl group into benzene caused a remarkable red shift in the extent of  $6000\text{ cm}^{-1}$  in the  $^1\text{La}$  band, while the trimethylsilyl group has only a small effect on benzene [5].

Photoelectron spectral [6] and stereoelectronic studies [7] have demonstrated that  $\sigma$ – $\pi$  conjugation between the silicon–silicon bond and the  $\pi$  system is the most important factor in determining the electronic properties of

\* For part CIL see ref. 17.

\*\* In honor of Professor Henry Gilman for his many years of outstanding research and teaching in the field of organometallic chemistry.

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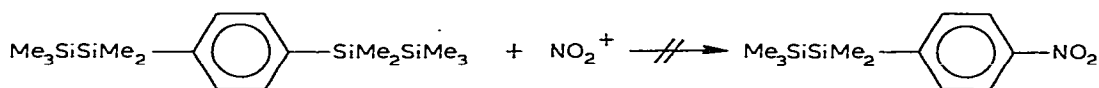
phenyldisilanes. Since polysilyl groups are strongly electron-donating, aryl-polysilanes with an electron-accepting group such as *p*-nitrophenylpolysilanes should exhibit an enhanced red shift in the UV spectra as compared with the parent phenylpolysilanes.

Apart from the interest in the UV spectra, preparation of nitrophenylpolysilane is a challenging problem since the compounds contain both reductive (Si—Si) and oxidative (NO<sub>2</sub>) groups in a molecule. Actually, nitrobenzene can oxidize hexamethyldisilane at an elevated temperature [8].

In this paper, preparation of six novel nitrophenyl-substituted polysilanes and their UV spectra are described.

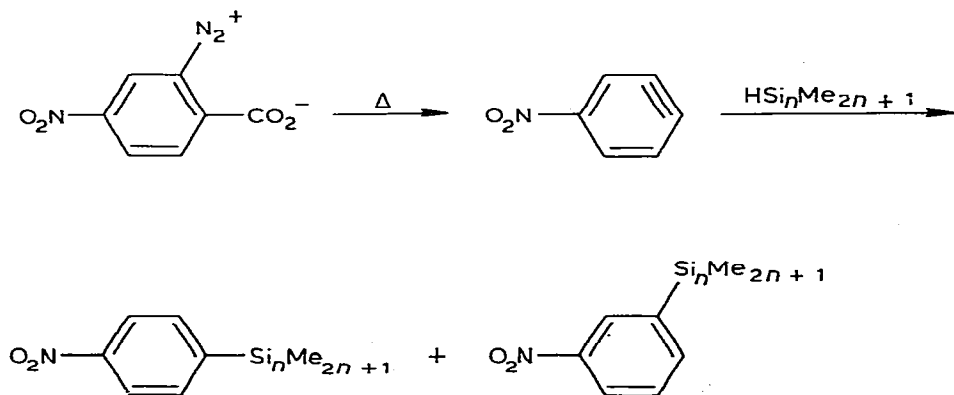
## Results and discussion

The most straightforward method of preparing nitrobenzene derivatives is direct nitration with an appropriate nitration reagent. In fact, phenyltrimethylsilane gave nitrophenyltrimethylsilanes by conventional nitration [9]. We examined nitration of phenylpentamethyldisilane with some nitration reagents, but as expected, only a messy mixture was obtained. Since a route to *p*-nitrophenyltrimethylsilane by nitrodesilylation of *p*-bis(trimethylsilyl)benzene [10] seemed to be applicable to the preparation of *p*-nitrophenylpentamethyldisilane, we examined the following reaction, but it also turned out to be unsuccessful.



Recently, Nagai et al. have demonstrated that Pd(PPh<sub>3</sub>)<sub>4</sub>-catalyzed reactions of hexamethyldisilane with nitrohalobenzenes result in the formation of the corresponding trimethylsilyl-substituted nitrobenzenes [11]. We examined the reaction with octamethyltrisilane and halobenzenes in the hope of introducing a pentamethyldisilyl group into nitrobenzene. However, no trace of the expected products was detected in the reaction mixture. All the silicon—silicon bonds were cleaved with the reagent.

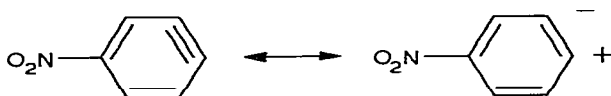
Eventually, the reaction of nitrobenzyne with monohydropolysilanes was found to give the desired products, in spite of low yields.



Nakayama, Yoshida and Simamura have reported that diazonium salts are reduced by triethylsilane or tri-*n*-butylstannane to give the corresponding arenes with elimination of the diazonium group [12]. The reaction of benzenediazonium 2-carboxylate with tri-*n*-butylstannane gave tri-*n*-butylstannyl benzoate quantitatively, while a similar reaction with triethylsilane afforded phenyltriethylsilane in 29% yield together with triethylsilyl benzoate. Apparently, generation of benzyne competes with reduction of the diazonium group in the reaction of benzenediazonium 2-carboxylate with hydrides. It is likely that the more reactive the hydride is, the more reduction product is obtained. In this respect, the use of polysilanyl hydride in the reaction instead of triethylsilane must be disadvantageous, since polysilanyl hydrides are generally more powerful reducing reagent than monosilyl hydrides [13]. Moreover, nitrobenzenediazonium 2-carboxylate generates the benzyne less readily than the unsubstituted one. Therefore, the reaction requires a higher temperature.

The reaction of nitrobenzyne generated in situ from 5-nitrobenzenediazonium 2-carboxylate [14] with polysilicon hydrides is thus not satisfactory, as is reflected in low yields of the products, but in any event, the desired nitrophenylpolysilanes have been prepared by this route.

The reaction of 5-nitrobenzenediazonium 2-carboxylate with pentamethyldisilane afforded *m*- and *p*-nitrophenylpentamethyldisilane in 5.2% yield (*m/p* = 1.6). The fact that the *m*-isomer was obtained preferentially to the *p*-isomer is understandable because of the electronic effect of the nitro group on benzyne. The electrophilicity of the *para* position is enhanced by the electron-withdrawing effect of the nitro group and as a result hydrogen of the hydrosilane tends to add to the *para* position as a hydride.



Generation of nitrobenzyne from 4-nitrobenzenediazonium 2-carboxylate was also examined, but no trace of the desired compound was obtained.

Similar reactions of nitrobenzyne with 1-*H*-heptamethyltrisilane and 2-*H*-heptamethyltrisilane yielded 1-nitrophenylheptamethyltrisilanes (6% yield, *m/p* = 1.4) and 2-nitrophenylheptamethyltrisilanes (4% yield, *m/p* = 1.5), respectively. All the compounds are colorless, but turn to pale yellow on standing in contact with air.

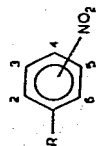
Table 1 lists NMR spectral data of six new nitrophenylpolysilanes. Figures 1 and 2 show UV spectra of *p*- and *m*-nitrophenylpolysilanes, respectively, including nitrobenzene.

As can be seen in Fig. 2, the UV spectra of *m*-nitrophenylpolysilanes are approximately made up by the superposition of the spectrum of nitrobenzene and those of phenylpolysilanes. UV spectral data of phenylpolysilanes are in nm ( $\epsilon$ ): PhSiMe<sub>3</sub> 211.0 (10 000), PhSiMe<sub>2</sub>SiMe<sub>3</sub> 231.0 (10 900), PhSiMe<sub>2</sub>SiMe<sub>2</sub>-SiMe<sub>3</sub> 221.3 (13 000) and 240.0 (15 400), PhSiMe(SiMe<sub>3</sub>)<sub>2</sub> 243.0 (13 000) [3]. However, *p*-nitrophenylpolysilanes exhibit a large bathochromic shift compared with nitrobenzene. In a polar solvent such as ethanol, these absorption maxima shift further to longer wavelength. Table 2 summarizes these data.

Therefore, the intramolecular charge-transfer configuration is important in

(Continued on p. 168)

TABLE 1

NMR SPECTRAL DATA OF NITROPHENYLPOLYSILANES (200 MHz, in acetone- $d_6$ )

R	Chemical shift ( $\delta$ , ppm) and $J$ (Hz)									
	H(2)	H(3)	H(4)	H(5)	H(6)	SIMe	SIMe <sub>2</sub>	SIMe <sub>2</sub> '	SIMe <sub>3</sub>	$J$
Me <sub>3</sub> SISiMe <sub>2</sub> *	7.83	8.24	—	8.24	7.83	—	0.44	—	0.09	<sup>a</sup>
m-	8.33	—	8.24	7.71	7.97	—	0.46	—	0.11	<sup>b</sup>
Me <sub>3</sub> SISiMe <sub>2</sub> SiMe <sub>2</sub> *	7.84	8.27	—	8.27	7.84	—	0.40	0.14	0.06	<sup>c</sup>
m-	8.35	—	8.27	7.74	7.99	—	0.51	0.16	0.07	<sup>d</sup>
(Me <sub>3</sub> Si) <sub>2</sub> SiMe-	7.77	8.23	—	8.23	7.77	0.51	—	—	0.17	<sup>e</sup>
m-	8.30	—	8.22	7.70	7.91	0.53	—	—	0.18	<sup>f</sup>

<sup>a</sup>  $J_{2,3} = 9.0$ , <sup>b</sup>  $J_{2,6} = 1.2$ ,  $J_{2,4} = 2.5$ ,  $J_{4,6} = 8.2$ ,  $J_{4,6} = 1.2$ ,  $J_{5,6} = 7.4$ , <sup>c</sup>  $J_{2,3} = 9.0$ , <sup>d</sup>  $J_{2,6} = 1.2$ ,  $J_{2,4} = 2.5$ ,  $J_{4,5} = 8.1$ ,  $J_{4,6} = 1.2$ ,  $J_{5,6} = 7.3$ , <sup>e</sup>  $J_{2,3} = 9.0$ , <sup>f</sup>  $J_{2,6} = 1.2$ ,  $J_{2,4} = 2.4$ ,  $J_{4,5} = 8.1$ ,  $J_{4,6} = 1.2$ ,  $J_{5,6} = 7.4$ .

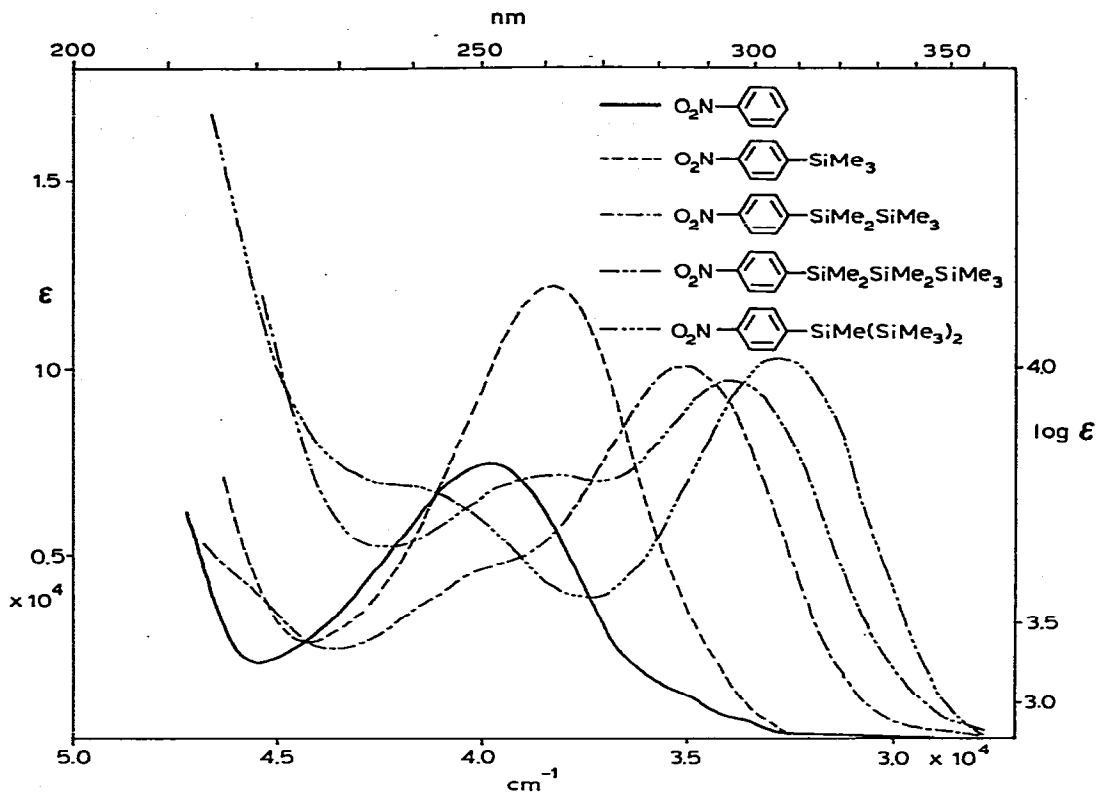


Fig. 1. UV spectra of *p*-nitrophenylpolysilanes in isoctane.

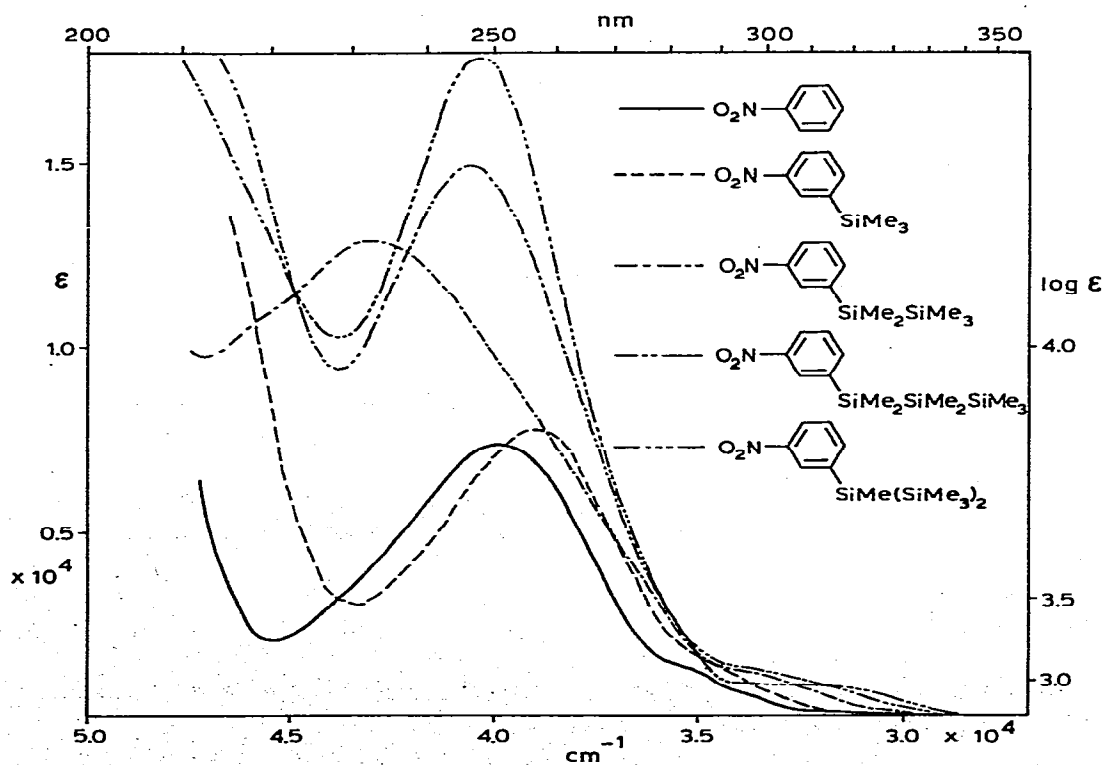
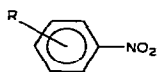


Fig. 2. UV spectra of *m*-nitrophenylpolysilanes in isoctane.

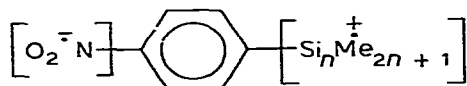
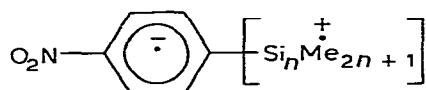
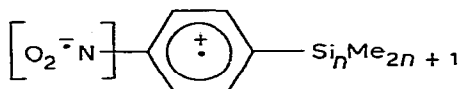
TABLE 2

UV-SPECTRAL DATA OF NITROBENZENE AND NITROPHENYLPOLYSILANES IN ISOCTANE AND ETHANOL ( $\lambda_{\max}$  (nm), log  $\epsilon$ )



R	<i>p</i> -Isomer		<i>m</i> -Isomer	
	<i>i</i> -Octane	EtOH	<i>i</i> -Octane	EtOH
H	251.5 (3.89) 278 (sh) 287 (sh) 298 (sh) 261.5 (4.09)	258.5 (3.91)		
Me <sub>3</sub> Si-		268.0 (4.09) 292 (sh) 302 (sh)	256.5(3.89) 283 (sh) 293 (sh)	262.5 (3.91)
Me <sub>3</sub> SiSiMe <sub>2</sub> -	240 (sh) 250 (sh) 285.5 (4.00)	253 (sh) 291.5 (3.94)	233.0 (4.11) 300 (sh)	232.0 (4.11) 270 (sh)
Me <sub>3</sub> SiSiMe <sub>2</sub> Me <sub>2</sub> -	260.5 (3.95) 295.0 (3.98)	267 (sh) 301.0 (3.90)	246.5 (4.17) 300 (sh)	248.0 (4.15)
(Me <sub>3</sub> Si) <sub>2</sub> SiMe-	240 (sh) 305.5 (4.01)	242 (3.72) 314.5 (3.89)	248.0 (4.25) 308 (3.00)	250.5 (4.24) 320 (sh)

determining the electronic structure of nitrophenylpolysilanes as previously expected. The following charge-transfer structures may be considered.



Polar solvents can stabilize the charge-transfer structures and cause a red shift in the absorption maxima. Virtually no solvent effect was observed for the *m*-isomers.

A theoretical treatment of the UV spectra of substituted phenylpolysilanes, including nitrophenylpolysilanes, based on the configuration interaction method [15] will be published elsewhere.

## Experimental

NMR and UV spectra were taken with a Varian HA-200 spectrometer and a Hitachi EPS-3 spectrophotometer, respectively.

Commercial nitrobenzene was purified with a preparative GLC. Samples of *p*- and *m*-nitrophenyltrimethylsilane were prepared according to the literature [11].

#### *Preparation of p- and m-nitrophenylpentamethyldisilanes*

In a 50 ml two-necked flask, fitted with a reflux condenser were placed 0.619 g (3.84 mmol) of 5-nitrobenzenediazonium 2-carboxylate [14] 0.610 g (4.61 mmol) of pentamethyldisilane, and 15 ml of toluene. The suspension was heated at 90–95°C for 3 h with stirring by a magnet bar under nitrogen. The reaction mixture was passed through a silica gel column and then an isomeric mixture of *p*- and *m*-nitrophenylpentamethyldisilane was separated from impurities with a silica gel TLC. The yield was 50.1 mg (0.198 mmol, 5.2%). The ratio of the *m*-isomer to the *p*-isomer was determined by GLC to be 1.6. Each isomer was separated by GLC.

*p*-Nitrophenylpentamethyldisilane: m.p. 48–49°C; MS, calcd. for C<sub>11</sub>H<sub>19</sub>NO<sub>2</sub>Si<sub>2</sub> 253.0953, found 253.0958.

*m*-Nitrophenylpentamethyldisilane: an oil; MS, found 253.0952.

#### *Preparation of 1-(p- and m-nitrophenyl)heptamethyltrisilanes*

These compounds were prepared by the same procedure. The yield of the isomeric mixture was 6% (*m/p* = 1.4).

1-(*p*-Nitrophenyl)heptamethyltrisilane: m.p. 40–41°C; MS, calcd. for C<sub>13</sub>H<sub>25</sub>NO<sub>2</sub>Si<sub>3</sub> 311.1193, found 311.1208.

1-(*m*-Nitrophenyl)heptamethyltrisilane: an oil; MS found 311.1210.

#### *Preparation of 2-(p- and m-nitrophenyl)heptamethyltrisilanes*

Similarly, 2-(*p*-nitrophenyl)heptamethyltrisilane: an oil, MS, found 311.1222, and 2-(*m*-nitrophenyl)heptamethyltrisilane: an oil, MS found 311.1209 were prepared in 4% yield (*m/p* = 1.5).

#### *Results of some unsuccessful attempts*

Nitration of phenylpentamethyldisilane with 90% fuming nitric acid in acetic anhydride at 0°C as well as with a 1.3/1.0 mixture (v/v) of conc. H<sub>2</sub>SO<sub>4</sub> and conc. HNO<sub>3</sub> (*d* = 1.4) gave complex mixtures in which only nitrobenzene was detected by GLC.

Nitrodepentamethyldisilanylation of *p*-bis(pentamethyldisilanyl)benzene [16] with fuming nitric acid in acetic anhydride by the same procedure of Deans and Eaborn [10] as well as with nitronium tetrafluoroborate in acetonitrile afforded mixtures of unidentified materials.

The reaction of *p*-bromonitrobenzene with octamethyltrisilane (1 : 2 to 1 : 8 molar ratio) catalyzed by tetrakis(triphenylphosphine)palladium in an aromatic solvent (benzene, toluene or xylene) at 85 ~ 150°C (6 experiments) resulted in the formation of mixtures from which *p*-nitrophenyltrimethylsilane and *p*-nitrophenylpentamethyldisiloxane (GC-MS) were identified. The reaction of *p*-nitrochlorobenzene gave similar results.

## Acknowledgements

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