Journal of Organometallic Chemistry, 271 (1984) 289–297
Elsevier Sequoia S.A., Lausanne – Printed in The Netherlands

1-SILAPHENALENES, POTENTIAL PRECURSORS TO AROMATIC SILYLENIUM IONS AND AROMATIC SILYL ANIONS. SPECTROSCOPIC AND CHEMICAL STUDIES *

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(Received October 4th, 1984)

Summary

Appearance potential measurements on 1,1-dimethyl-1-silaphenalene (**2**, R = X = CH_3) and related molecules show that silaphenalenium ions do not delocalize the positive charge throughout the entire π system like the hydrocarbon phenalene. Evidence for short range delocalization by a vinyl group attached to silicon was found in comparing appearance potentials of the silaphenalenium ion **2a** with acyclic and saturated analogs. Hydride abstraction reactions using hydride derivatives of **2**, **7**, and **8** with Ph_3C^+ $SnCl_5^-$ did not produce detectable silylenium ions. NMR studies of the 1-silaphenalenyl anion (**2c**) and related anions indicate that the anion is not highly delocalized. Ultrasound accelerates the reaction between potassium hydride and several of the silanes.

Introduction

While carbenium ions are ubiquitous throughout organic chemistry, there are only a few cases where experimental evidence supports the existence of silylenium ions in solution [1a,b] even though they are readily observable in the vapor phase by mass spectrometry [2] and ion cyclotron resonance techniques [3]. Our approach to preparing silylenium ions in solution or as a salt has been to try to incorporate Si^+ in an extended π-system. Based on the known chemistry of phenalene (**1**) [4,5] a unique hydrocarbon that generates a cation **1a**, radical **1b** and anion **1c**, each of which is aromatic with a resonance energy of approximately 105 kcal/mol (439 kJ/mol), we felt that 1-silaphenalenes (**2**) were reasonable candidates for producing detectable, or perhaps even isolable, silylenium ions of the type **2a**.

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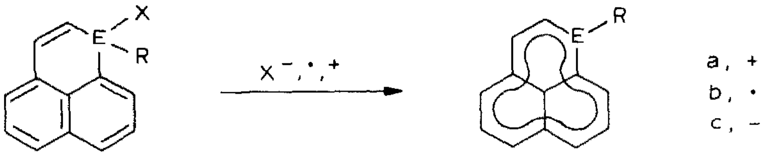
* Dedicated to Prof. M. Kumada

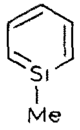
** Taken in part from R. Sooriyakumaran, M.S. Thesis 1982, North Dakota State University, Fargo, ND.



(1: E = C, R = X = H,
2: E = Si, X = H, Cl)

By analogy to **1**, 1-silaphenalenes could also lead to aromatic silyl radical **2b** and aromatic silyl anion **2c**. Although silyl radicals and anions have been known for some time, aromatic silyl radicals and anions are not known [6]. A most attractive feature of **2** is that these are accessible, in theory at least, by simply removing a leaving group of one's choice from silicon. Moreover, derivatives of the 1-silaphenalene system have been prepared and characterized [7].

While isolable silylenium ions have proven to be elusive, species in which silicon participates in a delocalized π-network have been prepared. Barton and coworkers have generated the highly reactive 1-methyl-1-silabenzene (**3**) at high temperatures [8] and more recently, Maier's group trapped silabenzene in an argon matrix at 10 K [9]. The matrix isolated species gave a UV spectrum consistent with a π-perturbed benzene. Ab initio calculations predict silabenzene to have a resonance energy approximately two-thirds that of benzene [10]. Relevant to the above and to our work is a study by Cartledge and Mollere on the potentially aromatic silylenium ion **4** using mass spectrometry [11]. The appearance potential of **4**, a 14 π electron system, was found to be essentially the same as that for the dihydro analogue **5**, demonstrating that the former ion possessed no additional stability attributable to aromaticity.



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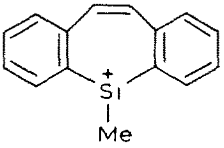

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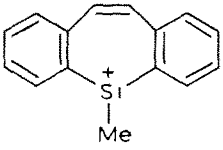

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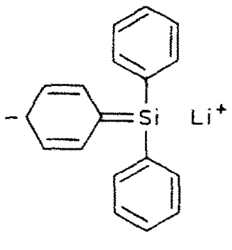
The question of Si–C p_π–p_π delocalization has been studied extensively using phenyl substituted anions in solution [12]. Waack and Doran found that triphenylsilyllithium exhibited a strong absorption maximum at 335 nm (log $\epsilon \approx 4$) and accepted this as evidence for p_π–p_π delocalization in Ph_3SiLi (**6**) [12a].



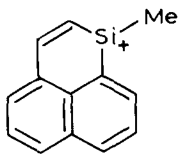
(6)

However, Evans argued that since the λ_{max} decreases markedly from Ph_3CLi to Ph_3SiLi the conjugation between silicon and the phenyl groups is very much less than that between the carbon and phenyl group in Ph_3CLi [12b]. He further concluded that the extent of Si–C conjugation was neglible because replacement of phenyl by methyl had no effect on λ_{max}. In concert with these findings are the recent NMR studies by Olah and Hunadi using ^{13}C and ^{29}Si probes in which a series of phenyl-substituted silyl anions were compared to their carbon analogues and found to have little Si–C p_π–p_π interaction [12c].

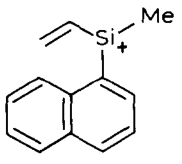
The 1-silaphenalene system presents a unique opportunity to examine p_π–p_π Si–C delocalization in the cationic and anionic states. In this paper we present the results of our mass spectroscopic studies of the silylenium ion **2a** and nuclear magnetic resonance studies of the anion **2c**.

Results and discussion

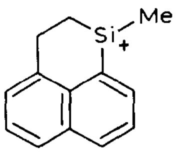
Mass spectral studies. The electron impact data relating to the formation of cations **2a**, **7a**, and **8a** were obtained. Using benzene as the internal standard, the appearance potentials of these ions and the ionization potentials of the parent dimethyl derivatives were determined by the semilog method [13] with an accuracy of 0.05 eV (Table 1).



(2a)



(7a)



(8a)

The difference between the appearance potential (AP) and the ionization potential (IP) can be taken as the activation energy E_a for the relevant fragmentation.

The activation energy E_a can be quantitatively correlated to the delocalization energy of the cation formed [13b,c]. It should be noted that E_a values for the formation of **7a** and **2a** are practically identical while it is significantly higher for **8a**. The higher E_a value for **8a** is consistent with the absence of a double bond adjacent

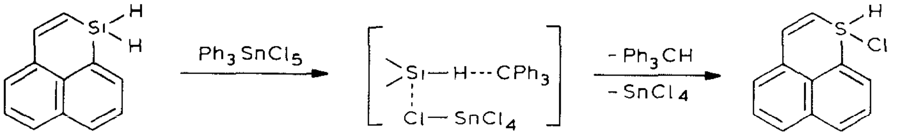
TABLE 1

APPEARANCE POTENTIALS AND IONIZATION POTENTIALS OF **2**, **7** AND **8**

Compound	IP (eV)	AP (M^+ − 15) (eV)	$E_a = AP - IP$ (eV)
2 ($R = X = CH_3$)	7.52	9.72	2.20
7 ($R = X = CH_3$)	7.65	9.80	2.15
8 ($R = X = CH_3$)	7.75	10.28	2.53

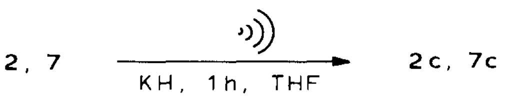
to the silicon. However, **2a** did not show any indication of a delocalized structure similar to that of phenalenium cation **1a**. If **2a** were aromatic the greater delocalization would have resulted in a lower activation energy. That the activation energies for the formation of **7a** and **2a** are the same indicate that the vinyl double bond is the major factor in stabilizing the ions and that there is no significant extended delocalization in **2a**. These results are in agreement with recent ab initio calculations which indicate that vinyl substitution stabilizes the silylenium ion [14].

NMR studies. The NMR spectra of phenalenium ions can be obtained by treating phenalene (**1**) with triphenylcarbenium salts. However, when applied to 1-silaphenalene (**2**) even at $\leqslant -75\,^{\circ}\mathrm{C}$ this approach gave triphenylmethane and 1-chloro-1-silaphenalene as the only products observed in the NMR. No evidence for an independent silylenium ion was found. This result parallels those obtained with other silanes and indicates that a highly associated intermediate like **9**, similar to those postulated for hydride abstractions from simple silanes [15] is responsible for the products observed.



(2 R = X = H) (9) (2 R = H, X = Cl)

Silyl anions. We prepared anions **2c** and **7c** quantitatively from their respective hydrides using potassium hydride in tetrahydrofuran (THF) by irradiating the reaction with ultrasonic waves for 1 h at room temperature [16]. The NMR studies were conducted on samples freshly prepared in the NMR tube. The data are presented in Table 2 along with data on phenalene, **1**, and the phenalene anion, **1c**.



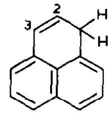
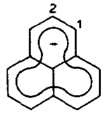
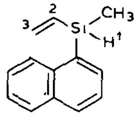
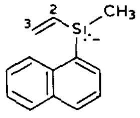
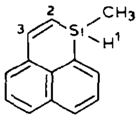
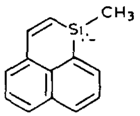
$$2,\ 7 \xrightarrow[\text{KH, 1 h, THF}]{\cdot)))} 2c,\ 7c$$

The NMR spectrum of phenalenyl anion **1c** has only two peaks indicating its delocalized nature [18]. The chemical shifts of the protons attached to carbons 1, 3, 5, 7, 9, and 11 appear as a doublet at 5.17 ppm. Protons attached to 2, 6 and 10 appear as a triplet at 5.91 ppm. The relatively upfield shifts for this aromatic species can be attributed to the presence of negative charge, which opposes the deshielding effect associated with the diamagnetic anistropy of the π-electron systems.

The dramatic change in spectral features observed between **1** and **1c** does not occur between **2** and **2c**. While symmetry considerations eliminate a comparable simplification of spectra the anticipated change in chemical shifts was not realized. For example, the naphthyl protons in **2c** absorb in the same region as those in **2** and the H^3 proton in **2c** is not significantly different in environment from the H^3 proton in **2**. Perhaps more significant is the comparison of the changes in chemical shifts of corresponding protons between the pairs **7** ($R = CH_3$, $X = H$), **7c** and **2** ($R = CH_3$, $X = H$), **2c**. Anion formation leads to an upfield shift of similar magnitudes for the naphthyl, and H^3 protons for the **7** → **7c** and **2** → **2c** transformations. The small

TABLE 2

NMR DATA FOR **1**,**1c**, **7**,**7c** and **2**,**2c**

		Np-H	H^1	H^2	H^3	CH_3	Solvent	
1		6.80-7.45	3.91	5.88	6.49		$CDCl_3$	[18]
1c			5.17	5.91			Et_2O	[18]
7		7.33-7.90 8.15 (*Peri*-H)	5.02	6.46	5.95	0.53	THF-d_8	this work
7c		7.20-7.90 8.60 (*Peri*-H)		6.56	5.70	0.25	THF-d_8	this work
2		7.35-8.00	5.00	6.23	7.60	0.46	THF-d_8	this work
2c		7.16-7.83		6.30	7.36	-0.03	THF-d_8	this work

downfield shifts for the H^2 protons are also of the same magnitude. The change in the chemical shifts of the methyl groups in conversion **7** to **7c** is about half that of the upfield shift for the methyl group in the **2** to **2c** conversion. There is no obvious explanation for this observation but it should be noted that the shifts are small in both methyl groups and directed upfield. The similarity in the spectral features of **7c**, which cannot be aromatic, to those of **2c** leads to the conclusion that there is no significant π-delocalization in the latter.

In conclusion, these studies indicate that the 1-silaphenalenyl system does not delocalize a positive or negative charge throughout the π-network as does the carbon analog. The stabilization of silylenium ion **2a** is due largely to the influence of the vinyl group as shown by comparison of its appearance potential to that of **7a**. The effect of the vinyl group is significant and this data is, to our knowledge, the first to demonstrate this. We are presently investigating vinyl and polyvinyl substituted silylenium ions to determine the limits of this electron stabilization.

Experimental

NMR spectra were taken on a Varian EM390 spectrometer using $CDCl_3$, CCl_4 or THF-d_8 as solvent with tetramethylsilane (TMS), cyclohexane or acetone as internal standard. Chemical shifts are reported in ppm downfield from TMS. Mass spectra were taken on a MAT CH-5DF mass spectrometer at 70 eV. Appearance potentials were measured at the Midwest Center for Mass Spectroscopy at the University of Nebraska at Lincoln. Elemental analyses were done by Galbraith Laboratories, Inc., Knoxville, Tennessee.

THF and ether were distilled as needed from benzophenone-sodium ketyl under nitrogen. Chlorosilanes were from the Dow Corning Co. or Petrarch System, Inc. and were used as obtained. Before use, all glassware was oven dried, assembled hot, and cooled under a stream of dry nitrogen. All reactions were run under a nitrogen atmosphere. Stirring of solutions was done with a magnetic stirrer and all reactions were continuously stirred unless otherwise specified. All additions were dropwise from a pressure-equalizing addition funnel unless stated otherwise.

The statement "worked-up in the usual manner" refers to removal of solvent by rotoevaporator under aspirator vacuum followed by dissolving the residue in ether. The ether was washed with saturated sodium chloride solution. All Grignard reactions were first washed with saturated ammonium chloride solution, then dried with Na_2SO_4 or $MgSO_4$, filtered by gravity, and the ether removed under aspirator vacuum using a rotoevaporator. Analytical samples were obtained by preparative gas chromatography. 1-Naphthylvinyldichlorosilane (**7**,: R = X = Cl), 1,1-dichloro-1-silaphenalene (**2**: R = X = Cl), 1-silaphenalene (**2**: R = X = H), 1-methyl-1-silaphenalene (**2**: R = Me, X = H), 1,1-dimethyl-1-silaphenalene (**2**: R = X = Me) and 1,1-dimethyl-1-silaphenalane (**8**: R = X = CH_3) were prepared using literature procedures [7a–c].

Preparation of (1-naphthyl)vinylmethylchlorosilane (7: R = CH_3, X = Cl)

Magnesium turnings (18 g, 0.75 mol) were suspended in THF (300 ml) in a three liter three-necked flask equipped with mechanical stirrer, addition funnel and nitrogen inlet. 3 ml of 1,2-dibromomethane was added and stirred for 15 min to activate the magnesium. To this mixture vinylmethyldichlorosilane (130 ml, 1.00 mol) was added at once. The flask was cooled in ice and 1-bromonaphthalene (70 ml, 0.50 mol) in THF (150 ml) was added dropwise over a period of 2 h. The mixture was stirred for another 2 h and dioxane (90 ml, > 1 mol) was added. The white precipitate obtained was allowed to settle. The supernatant liquid was collected. More pentane was added to the precipitate, stirred well, allowed to settle and the supernatant liquid was collected again. This was repeated one more time. After removing the solvent from these fractions using a rotoevaporator, the remaining liquid was distilled under reduced pressure. 116.50 g (60%) of (1-naphthyl)vinylmethylchlorosilane was collected at 110–130 °C/0.2 torr. NMR (CCl_4): δ 7.36–8.40 (m, 7H, NpH), 5.93–6.80 (m, 3H, ViH), 0.96 ppm (s, 3H, $SiCH_3$). Anal. Found: C, 67.00; H, 5.65. $C_{13}H_{13}SiCl$ calcd.: C, 67.07; H, 5.63%.

Preparation of 1-methyl-1-silaphenalene (2: R = CH_3, X = H) and 1-methyl-1-silaphenalane (8: R = CH_3, X = H)

Pyrolysis of 7 (R = CH_3, X = Cl) (40 g) at 695 °C was carried out as described for

7 (R = X = Cl) [7]. 8 g (25%) of colorless liquid containing **2** (R = CH_3, X = Cl) and **8** (R = CH_3, X = Cl) in 2/1 ratio (by NMR) was collected at 120–160 °C/0.2 torr.

This mixture (5 g, 21 mmol) in ether (25 ml) was slowly added to a cold suspension of $LiAlH_4$ (0.30 g, 7 mmol) in ether (25 ml). This was refluxed for 1 h and worked up in the usual manner. Distillation gave 3.16 g (70%) of pale yellow liquid at 100–125 °C/0.2 mmHg, containing **2** (R = CH_3, X = H) and **9** (R = CH_3, X = H) in a 2/1 ratio (by NMR). The compounds were separated by preparative gas chromatography. The spectral properties of **8** were identical to those of an authentic sample [7c]. For **2** (R = CH_3, X = H): NMR (THF-d_8): δ 7.35–8.00 (m, 6H, NpH), 7.60 (d, 1H, NpCH), coupled to SiCH_A as shown by spin decoupling experiments, 6.23 (d, 1H, SiCH_4=CH_B), 5.00 (q, 1H, Si–H) 0.46 ppm (d, 3H, $SiCH_3$). Anal. Found: C, 79.35; H, 6.30. $C_{13}H_{12}Si$ calcd.: C, 79.33; H, 6.16%.

Preparation of (1-naphthyl)vinylmethylsilane (7: R = CH_3, X = H)

(1-Naphthyl)vinylmethylchlorosiliane (**7**: R = CH_3, X = Cl) (3 g, 13 mmol) in ether (15 ml) was slowly added to a cold suspension of $LiAlH_4$ (0.20 g, 5 mmol) in ether (15 ml). This was refluxed for 1 h and worked up in the usual manner to give a yellow liquid. This was chromatographed on neutral alumina using pentane as elutent. After removal of pentane 2 g (80%) of colorless liquid was obtained. NMR (THF-d_8): δ 7.33–8.15 (m, 7H, NpH), 6.46 (m, 1H, SiCH_A=CH_B), 5.95 (m, 2H, $SiCH_A$=CH_B), 5.02 (Octet, 1H, SiH), 0.53 ppm (d, 3H, $SiCH_3$). Anal. Found: C, 78.59; H, 6.68. $C_{13}H_{14}Si$ calcd.: C, 78.76; H, 7.07%.

Preparation of (1-naphthyl)vinyldimethylsilane (7: R = X = CH_3) from 1-naphthylvinyldichlorosilane (7: R = X = Cl)

To a 20 ml ethereal solution of **7** (R = X = Cl) (2.5 g, 10 mmol) was added 12 ml (24 mmol) of a 2 *M* solution of MeMgI in ether (Alfa). This was refluxed for 1 h, cooled to room temperature and worked up in the usual manner. 1.80 of **7** (R = X = CH_3) (85%) was collected on distillation at 105–110 °C/0.2 mmHg. NMR ($CDCl_3$): δ 7.28–8.10 (m, 7H, NpH); 5.56–6.63 (m, 3H, ViH), 0.45 ppm (s, 6H, $SiCH_3$). Anal. Found: C, 79.37; H, 7.55. $C_{14}H_{16}Si$ calcd.: C, 79.19; H, 7.59%.

Low temperature NMR of 1-silaphenalene (R = X = H) with Ph_3C^+ $SnCl_5^-$

1-Silaphenalene (12 mg, 0.05 mmol) in CD_2Cl_2 (0.15 ml) was placed in an NMR tube and the contents were cooled in a mixture of dry ice and ether. To this solution Ph_3C^+ $SnCl_5^-$ (26 mg, 0.05 mmol) in CD_2Cl_2 was added dropwise under N_2 and agitated. NMR of the mixture was taken at −75, −50 °C and ambient temperature. At −75 °C the ^1H NMR spectrum showed the formation of 1-chloro-1-silaphenalene (**2**: R = H, X = Cl) along with triphenylmethane. At −50 °C the intensity of the peaks belonging to 1-chloro-1-silaphenalene decreased and at room temperature only triphenylmethane remained in the solution. Presumably this arises from the well-known Lewis acid catalyzed polymerization of styrenes [17]. A white precipitate was found on the bottom of the NMR tube. This material did not dissolve in excess acetonitrile or dichloromethane but was soluble in ether and THF. NMR spectra of these solutions could not be interpreted. Analysis of this solution for radicals by ESR spectroscopy gave negative results.

Electron impact data

The ionization and appearance potentials were determined by the "semi-log" method [13]. Using this method, a plot was obtained of log (i/i_0) vs. eV where "i" is the intensity of the ion in question at any given ionizing energy and "i_0" is the intensity of the same ion at 40 eV. In each case, benzene, whose ionization potential is known, was run as a benchmark (*IP* benzene 9.2 eV). By reading across the graph in the linear region, one can easily read changes in eV. By referring to the benzene reference, these values of eV were translated into absolute values.

Preparation of the anions ***2c*** *and* ***7c***

An oven dried NMR tube was charged with KH (13 mg, 0.325 mmol) under nitrogen. 1-Methyl-1-silaphenalene (**2**: $R = CH_3$, $X = H$) (30 mg, 0.156 mmol) in THF-d_8 (0.40 ml) with a few drops of cyclohexane was added at once. A syringe needle attached to a rubber septum was used as a nitrogen inlet. The contents were agitated in a common ultrasonic laboratory cleaner (Branson model 220, 55 kH_3, 150 W, 117 V) for approximately 1 h. Afterwards, the NMR tube was centrifuged and the spectrum of the resultant dark violet solution was recorded. A pale yellow solution of **7c** was prepared in the same fashion.

Acknowledgements

Acknowledgement is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society for partial support of this research. Financial support from the National Science Foundation (Grant No. 7911812) and the Air Force Office of Scientific Research (Grant No. AFOSR 84-0008) is also gratefully acknowledged.

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