Journal of Organometallic Chemistry, 439 (1992) 107–113
Elsevier Sequoia S.A., Lausanne
JOM 22885

Generation and reactivities of methoxyphenylsilylene

Young-Woo Kwak, Ill-Hyeon Jeong, Jae-You Ko
Department of Chemistry, Kyungpook National University, Taegu, 702-701 (South Korea)

and Bong Hyun Boo
Department of Chemistry, Chungnam National University, Taejon, 305-764 (South Korea)

(Received October 4, 1991)

Abstract

From the vacuum pyrolysis of 1,1-dimethoxy-1-phenyl-2,2,2-trimethyldisilane (I) in the presence of 2,3-dimethyl-1,3-butadiene, two major products, 1-methoxy-1-phenyl-3,4-dimethyl-1-silacyclopent-3-ene (II) and 1-phenyl-3,4-dimethyl-1-silacyclopent-3-ene (III) along with methoxytrimethylsilane have been observed. Methoxyphenylsilylene has been suggested as the primary intermediate that may produce phenylsilylene by the extrusion of formaldehyde from Ph–$\ddot{\mathrm{Si}}$–OMe. These two silylenes may be responsible for the formation of products II and III. It is proposed that the phenylsilylene was generated from the [3 → 2 + 1] cycloelimination of an intermediate of the 2-phenyloxasilacyclopropane ($\mathrm{PhH\underbrace{Si–O–C}H_2}$) which can arise from a possible intramolecular silylene insertion into the C–H bond of the methoxy group in Ph–$\ddot{\mathrm{Si}}$–OMe. A labelling experiment employing a partially deuteriated precursor of 1,1-dimethoxy-d_6-1-phenyl-2,2,2-trimethyldisilane (I-*d*) checked whether or not product III is a secondary product of the [3 → 2 + 1] cycloelimination of the oxasilacyclopropane. As expected, 1-methoxy-d_3-1-phenyl-3,4-dimethyl-1-silacyclopent-3-ene (II-*d*) and 1-deuterio-1-phenyl-3,4-dimethyl-1-silacyclopent-3-ene (III-*d*) are the major products of pyrolysis of the deuteriated precursor (I-*d*) in the presence of the same trapping agent. The intermediacy to phenylsilylene of the oxacyclopropane in the decomposition of alkoxyphenylsilylene is supported by the observation that pyrolysis of 1,1-diethoxy-1-phenyl-2,2,2-trimethyldisilane (IV) in the presence of the same trapping agent produces 1-phenyl-3,4-dimethyl-1-silacyclopentene (III) as the major product along with a trace of 1-ethoxy-1-phenyl-3,4-dimethyl-1-silacyclopent-3-ene (V). A temperature dependence experiment elucidated the energetics of the conversion of Ph–$\ddot{\mathrm{Si}}$–OMe to Ph–$\ddot{\mathrm{Si}}$–H. As the reaction temperature increases, the product ratio (III/II) increases, indicating that dissociation of Ph–$\ddot{\mathrm{Si}}$–OMe into Ph–$\ddot{\mathrm{Si}}$–H and HCHO may be an activated process, which is consistent with the MNDO semiempirical calculation.

Introduction

Alkylsilylenes have been suggested to insert intramolecularly into the C–H bond of alkyl groups larger than CH_3 involving silacyclopropane intermediates [1]. It has

---

Correspondence to: Dr. Y.-W. Kwak.

been reported that the reaction pathways involving the silacyclopropane intermediates are more important than the processes through larger silacyclic intermediates [2]. Ando and Sekiguchi reported clear evidence of the formation of oxasilacyclopropane from the reaction of silylene with ketone in 1977 and also in 1983 that dimesitylsilanediyl was generated from photolysis and pyrolysis of the stable oxasilacyclopropane *via* a [3 → 2 + 1] cycloelimination reaction [3].

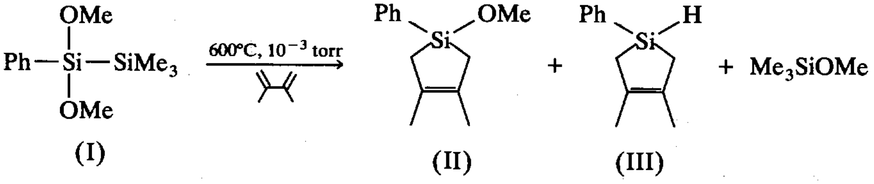
We are concerned with the kind of mechanistics that could be applied to the dissociation of Ph–S̈i–OMe to Ph–S̈i–H and HCHO through the oxasilacyclopropane intermediate containing Si, O and C on the ring. We are also interested in the energetics of the energy barrier to be surmounted in the dissociation of Ph–S̈i–OMe.

We have examined the generation and reactivities of methoxyphenylsilylene formed in the pyrolysis of I in the presence of 2,3-dimethyl-1,3-butadiene. Silylene addition products involving methoxyphenylsilylene and phenylsilylene have been observed. In an attempt to elucidate the reaction mechanism for the generation of phenylsilylene, we performed a labelling experiment employing a deuterium analogue of the precursor (I-*d*). In addition, we have investigated the intramolecular reactivity of ethoxyphenylsilylene relative to that of methoxyphenylsilylene.

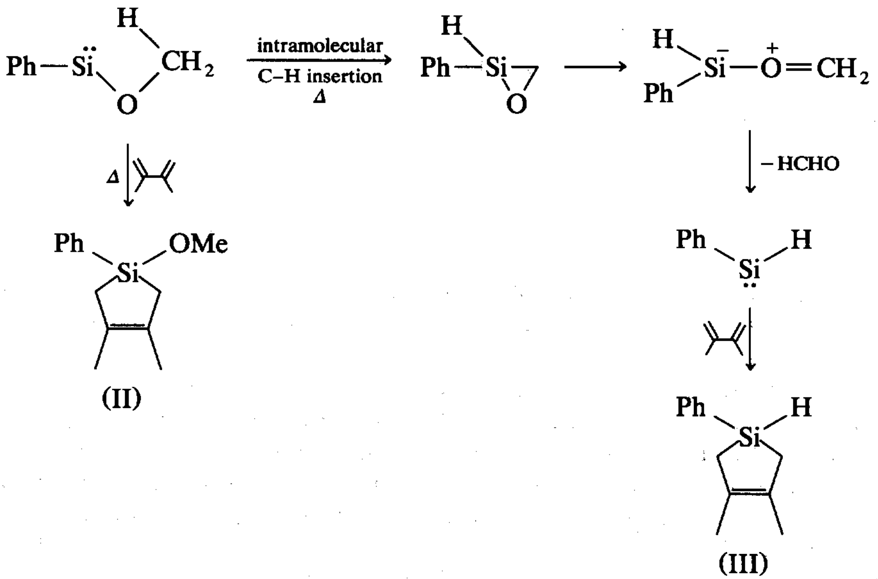
Here, we report and compare the results of the pyrolyses of alkoxyphenylsilylene precursors (alkoxy group = OCH_3, OCD_3 and OCH_2CH_3) in the presence of the trapping agent. Temperature dependence of the product yields could provide mechanistic and energetic information about the decomposition of the silylene. In an attempt to elucidate the energetics of the decomposition of Ph–S̈i–OMe, we also performed an MNDO semiempirical calculation [8] to estimate the energy barrier to the dissociation of Ph–S̈i–OMe into Ph–S̈i–H and HCHO.

Results and discussion

The vacuum pyrolysis of I in the presence of a 15-fold excess of 2,3-dimethyl-1,3-butadiene at 600°C gives two major products, II (68%) and III (23%) along with methoxytrimethylsilane.



Ph–S̈i–OMe is believed to be the primary intermediate in the thermal decomposition of I at 600°C. Formation of III in the trapping reaction indicates that Ph–S̈i–H is the secondary intermediate arising from the dissociation of Ph–S̈i–OMe into Ph–S̈i–H and its counterpart HCHO although the latter has not been detected. There are some reports on the direct generation of the Ph–S̈i–H intermediate from the photodissociation of phenylsilane at 193 nm and from the pyrolysis of 1-phenyl-2,2,2-trimethyldisilane [9]. As suggested below in Scheme 1, this phenylsilylene might be generated from a [3 → 2 + 1] cycloelimination reaction of the 2-phenyloxasilacyclopropane intermediate which can arise from the possible intramolecular silylene insertion into the C–H bond of the methoxy group in



Scheme 1.

$\mathrm{Ph{-}\ddot{Si}{-}OMe}$ [3a,b]. One possible mechanism for the observed product III is also outlined.

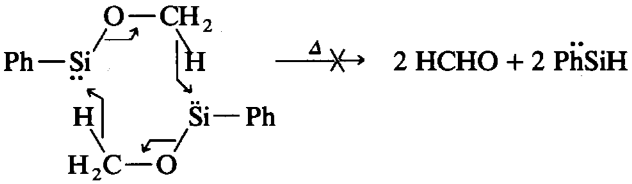
The vacuum pyrolysis of 1,1-dimethoxy-d_6-1-phenyl-2,2,2-trimethyldisilane (I-*d*) in the presence of a 15-fold excess of the same trapping agent at 600°C afforded 1-methoxy-d_3-1-phenyl-3,4-dimethyl-1-silacyclopent-3-ene (II-*d*) and 1-deuterio-1-phenyl-3,4-dimethyl-1-silacyclopent-3-ene (III-*d*). The observed products are also possibly generated by the same mechanism suggested in Scheme 1. From the vacuum pyrolysis of 1,1-diethoxy-1-phenyl-2,2,2-trimethyldisilane (IV) in the presence of the same trapping agent at 600°C we observed 1-phenyl-3,4-dimethyl-1-silacyclopent-3-ene (III) as a major product and a trace amount of 1-ethoxy-1-phenyl-3,4-dimethyl-1-silacyclopent-3-ene (V) along with ethoxytrimethylsilane. The formation of III from the pyrolysis of diethoxydisilane (IV) in the trapping reaction can be explained by the [3 → 2 + 1] cycloelimination reaction of the 2-phenyl-3-methyloxasilacyclopropane intermediate ($\mathrm{PhH\underline{Si{-}O{-}C}HCH_3}$) which can arise from the intramolecular silylene insertion into the methylene C–H bond in the ethoxy group of $\mathrm{Ph{-}\ddot{Si}{-}OCH_2CH_3}$ [11*].

An alternative mechanism for the generation of $\mathrm{Ph{-}\ddot{Si}{-}H}$ involves the 8-membered ring transition state as shown in Scheme 2.

However, this proposed pathway under the gas phase thermal reaction condition seems to be inefficient since the transition state involves the tight 8-membered ring which may give rise to smaller entropy of activation than the direct extrusion of HCHO as shown above in Scheme 1.

---

* Reference number with an asterisk indicates a note in the list of references.



Scheme 2.

The dependence on temperature of the yields of the individual products and of the product ratios from the pyrolysis of the dimethoxydisilane I is summarized in Table 1.

As the reaction temperature increases, the product ratio (III/II) increases. This implies importance of the generation of Ph–S̈i–H from Ph–S̈i–OMe at higher temperature relative to the direct addition of Ph–S̈i–OMe to the trapping agent. Since the addition of silylene to diene trapping agents involves a sufficiently small energy barrier compared with the extrusion of HCHO, the decomposition of Ph–S̈i–OMe into Ph–S̈i–H and HCHO could be an activated process. This suggestion is consistent with our theoretical calculation. Indeed, we performed a MNDO semiempirical calculation to find the thermochemical heats of formation of Ph–S̈i–OMe, PhHSi–O–CH$_2$, and Ph–S̈i–H, as −22.4, −23.8, 73.4 kcal/mol, respectively. Combining ΔH_f° (HCHO) = −26.0 kcal/mol [10] we estimate a value of the energy barrier to the extrusion of HCHO from Ph–S̈i–OMe, E_a = 69.8 kcal/mol. This activation energy is quite high enough to explain the increase of the product ratio (III/II) with the reaction temperature.

Experimental

General procedure

All pyrolyses (injection method) were carried out in a seasoned hot zone consisting of a 10 mm i.d. × 30 cm quartz tube wrapped with nichrome ribbon and covered with asbestos tape. This hot zone was seasoned with hexamethyldisilazane before use. Both residence and pressure were controlled by a 0.8 mm aperture placed at the end of the vertical quartz tube which was attached to a vacuum line [4].

The progress of the pyrolysis was followed by GLC analysis with a Hewlett-Packard 5890 instrument on a HP-5 capillary column (cross-linked 5% phenyl-

Table 1

Dependence on temperature of the product yields from the vacuum pyrolysis of $Ph(MeO)_2SiSiMe_3$ (I) in excess of 2,3-dimethyl-1,3-butadiene

Temp. (°C)	Yields of Products [a] (%)		Product Ratio (III/II)	Recovery percent (I) (%)
	II	III		
500	89	0	0	81
600	68	23	0.33	60
700	54	39	0.73	26

[a] Yields are based on the unrecovered starting material.

methylsilicone, 30 m) and a HP-FFAP capillary column (cross-linked polyethylene glycol-TPA phase, 50 m). Product yields were determined by GLC (flame ionization detector) with cyclohexane as an internal standard on the basis of the quantity of 1,1-dialkoxy-1-phenyl-2,2,2-trimethyldisilane decomposed. Preparative gas chromatography was performed on a Varian model 920 GLC (thermal conductivity detector) using an OV-17 (20% on Chromosorb W 80/100, 1/4 in ×13 ft) for separating the reaction mixtures.

Proton NMR spectra were recorded on a Bruker AM-300 spectrometer using methylene chloride as an internal standard and carbon NMR spectra were obtained on the same instrument with $CDCl_3$ as a lock solvent. Mass spectra were obtained on a Shimadzu GCMS-QP 1000A coupled to a Shimadzu GC-9A gas chromatograph.

Materials

1,1,1-Triphenyl-2,2,2-trimethyldisilane and 1,1-dichloro-1-phenyl-2,2,2-trimethyldisilane were prepared as described previously [5,6]. The spectral properties of the two materials were in agreement with literature values. For the preparation of $Ph-\ddot{S}i-OMe$ precursor, I, a solution of 2.5 g (10 mmol) of 1,1-dichloro-1-phenyl-2,2,2-trimethyldisilane and 5.9 g (56 mmol) of trimethylorthoformate was placed in a dry 100 ml flask equipped with a magnetic stirring bar, a reflux condenser, and a $CaCl_2$ drying tube [7]. Preparative GLC on the 13 ft OV-17 (detector temp. 210°C, injector temp. 190°C, oven temp. 180°C and flow rate 46 (ml/min) afforded 1.9 g (79% yield) of (I).

Compound I: ^1H NMR (neat) δ 0.25 (9H, s, $SiMe_3$), 3.65 (6H, s, $Si(OMe)_2$), 7.41–7.68 (5H, m, C_6H_5-); ^{13}C NMR (neat) δ -1.64 (q), 50.72 (q), 127.98 (d), 129.85 (d), 133.92 (d), 135.52 (s); mass spectrum, m/e (relative intensity) 240 (parent, 1), 225 (20), 209 (2), 195 (55), 167 (47), 137 (37), 107 (23), 91 (49), 73 (31), 59 (100).

For the synthesis of $Ph-\ddot{S}i-OCD_3$ precursor, 1,1-dimethoxy-d_6-1-phenyl-2,2,2-trimethyldisilane(I-*d*), 1.3 g (5.2 mmol) of 1,1-dichloro-1-phenyl-2,2,2-trimethyldisilane was added dropwise to a well stirred solution of 0.4 g (11 mmol) of methyl-d_3 alcohol-*d* and 1.1 g (11 mmol) of triethylamine at ice-water temperature. After addition was complete, the reaction mixture was warmed to room temperature and stirred overnight and the mixture was filtered through celite, Bulb-to-bulb distillation of the mixture followed by preparative GLC on the same OV-17 column afforded 0.9 g (70% yield) of the 1,1-dimethoxy-d_6-1-phenyl-2,2,2-trimethyldisilane(I-*d*).

Compound (I-*d*): mass spectrum m/e (relative intensity) 246(parent, 8), 228(100), 196(63), 173(42), 154(2), 135(27), 109(15), 93(60), 73(13), 62(37).

The precursor of ethoxyphenylsilylene, 1,1-diethoxy-1-phenyl-2,2,2-trimethyldisilane(IV), was prepared by the same method as described above (73% yield).

Compound (IV): ^1H NMR(neat) 0.18 (9H, s, $SiMe_3$), 1.23 (6H, t, CH_3-C), 3.81 (4H, q, $O-CH_2-C$), 7.33–7.69 (5H, m, C_6H_5-); mass spectrum m/e (relative intensity) 268 (parent, 0), 253 (4), 239 (50), 211 (14), 195 (100), 179 (19), 151 (25), 139 (30), 135 (27), 133 (49), 105 (27), 91 (12), 73 (31), 45 (61).

Pyrolysis of I in the presence of 2,3-dimethyl-1,3-butadiene. The mixture of 0.3 g (1.2 mmol) of I and 1.5 g (18 mmol) of the trapping agent 2,3-dimethyl-1,3-butadiene was injected into the rubber septum at the inlet of the quartz tube mentioned above using a gas tight syringe over a period of 2 h. Pyrolysis of the mixture (500–700°C) afforded quantitative recovery of the starting material I. Bulb-to-bulb distillation of the pyrolysate followed by preparative GLC on an OV-17 column afforded the two products, II and III. The spectral properties of these two products are given below.

Compound II: ^1H NMR (neat) δ 1.55 (4H, broad s, CH_2–Si), 1.73 (6H, broad s, CH_3–C), 3.45 (3H, s, CH_3O–Si), 7.28–7.59 (5H, m, C_6H_5–); ^{13}C NMR (neat) δ 19.16, 22.59, 47.74, 127.81, 129.59, 130.09, 133.42, 134.92; mass spectrum m/e (relative intensity) 218 (parent, 28), 203 (4), 187 (4), 186 (21), 141 (49), 140 (28), 105 (17), 59 (100), 53 (11)

Compound III: ^1H NMR (neat) δ 1.58–1.65 (4H, m, CH_2–Si), 1.76 (6H, broad s, CH_3–C), 4.61–4.69 (1H, m, H–Si), 7.35–7.57 (5H, m, C_6H_5–); ^{13}C NMR (neat) δ 19.13, 22.61, 127.93, 129.49, 130.77, 134.43, 135.84; mass spectrum m/e (relative intensity) 188 (parent, 64), 173 (19), 145 (24), 131 (14), 121 (11), 110 (100), 105 (81), 95 (47), 53 (51).

Pyrolysis of I-d in the presence of 2,3-dimethyl-1,3-butadiene. The mixture of 0.3 g (1.2 mmol) of I-*d* and 1.5 g (18 mmol) of the trapping agent was copyrolyzed at 600°C. Bulb-to-bulb distillation of the reaction mixture followed by preparative GLC on the same column as mentioned above yielded unreacted I-*d* (62%), 1-methoxy-d_3-1-phenyl-3,4-dimethyl-1-silacyclopent-3-ene (II-*d*, 61%) and 1-deuterio-1-phenyl-3,4-dimethyl-1-silacyclopent-3-ene (III-*d*, 21%).

Compound II-*d*: mass spectrum m/e (relative intensity) 221 (parent, 66), 186 (98), 171 (14), 143 (24), 139 (13), 108 (15), 105 (10), 78 (4), 62 (100).

Compound III-*d*: mass spectrum m/e (relative intensity) 189 (parent, 75), 174 (20), 145 (24), 131 (13), 111 (100), 105 (67), 95 (34), 79 (22), 67 (21), 53 (26).

Pyrolysis of IV in the presence of 2,3-dimethyl-1,3-butadiene. The mixture of 0.4 g (1.5 mmol) of 1,1-diethoxy-1-phenyl-2,2,2-trimethyldisilane (IV) and 1.9 g (23 mmol) of trapping agent was copyrolyzed at 600°C. Bulb to bulb distillation of the pyrolysate followed by preparative GLC on the same column yielded unreacted IV (56%), 1-phenyl-3,4-dimethyl-1-silacyclopent-3-ene(III, 80%) and a trace amount of 1-ethoxy-1-phenyl-3,4-dimethyl-1-silacyclopent-3-ene (V) [12*] along with ethoxytrimethylsilane.

Compound V: mass spectrum m/e (relative intensity) 232 (parent, 66), 186 (100), 171 (10), 154 (12), 123 (10), 110 (19), 105 (25), 78 (14), 73 (15), 45 (43).

Acknowledgments

We are grateful to the Korea Science and Engineering Foundation for financial support (89-0303-04) of this work. We also thank Professor M. Ishikawa of Hiroshima University for useful private communication on the synthesis of 1,1-dichloro-1-phenyl-2,2,2-trimethyldisilane and Professor R.T. Conlin and P.R. Jones of the University of North Texas for advice on the construction of the pyrolysis apparatus and helpful discussion. One of the authors (BHB) is grateful to the Ministry of Education, Korea, for partial financial support from the Basic Science Research Institute Program (1990).

References and notes

1 M.A. Ring, H.E. O'Neal, S.F. Rickborn and B.A. Sawrey, Organometallics, 2 (1983) 1891.

2 M.A. Ring and H.E. O'Neal; cited in J.Y. Corey, E.R. Corey and P.P. Gaspar (Eds.), Silicon Chemistry, Ellis Horwood Ltd, 1988, pp. 427–438.

3 (a) W. Ando, Y. Hamada and A. Sekiguchi, J. Chem. Soc., Chem. Commun. (1983) 952; (b) W. Ando, M. Ikeno and A. Sekiguchi, J. Am. Chem. Soc., 99 (1977) 6447; (c) W. Ando, Y. Hamada and A. Sekiguchi, Tetrahedron Lett. 23 (1982) 5323.

4 (a) R.T. Conlin, Y.-W. Kwak and H.B. Huffaker, Organometallics, 2 (1983) 343; (b) R.T. Conlin and Y.-W. Kwak, *ibid.*, 3 (1984) 918.

5 (a) M.V. George, D.J. Peterson and H. Gilman, J. Am. Chem. Soc., 82 (1960) 403; (b) H. Gilman and T.C. Wu, *ibid.*, 73 (1951) 4031; (c) A.G. Brook and H. Gilman, *ibid.*, 76 (1954) 278; (d) H. Gilman, W.J. Trepka and D. Wittenberg, *ibid.*, 84 (1962) 383.

6 (a) K. Nate, M. Ishikawa, N. Iwamura and Y. Murakami, J. Polym. Sci., Part A, Polym. Chem., 24 (1986) 1551; (b) Ishikawa, private communication.

7 (a) L.M. Shorr, J. Am. Chem. Soc., 76 (1954) 1390; (b) T.J. Barton and D.S. Banasiak, J. Organomet. Chem., 157 (1978) 255; (c) M.E. Childs and W.P. Weber, *ibid.*, 86 (1975) 169.

8 (a) M.J.S. Dewar and W. Thiel, J. Am. Chem. Soc. 99 (1977) 4899; (b) M.J.S. Dewar, J. Friedheim, G. Grady, E.F. Healy and J.J.P. Stewart, Organometallics, 5 (1986) 375.

9 (a) J.E. Baggot, H.M. Frey, P.D. Lightfoot and R. Walsh, Chem. Phys. Lett. 125 (1986) 22; (b) M.E. Lee, D.N. Lee and C.H. Kim, The Third Korea-Japan Joint Symposium on Organometallic and Coordination Chemistry, pp. 11–15, Oct. 19–20, 1990, Choonchon, Korea.

10 J.D. Cox and G. Pilcher, Thermochemistry of Organic and Organometallic Compounds, Academic Press, New York, 1970.

11 From the neat pyrolysis of 1,1-diethoxy-1-phenyl-2,2,2-trimethyldisilane (IV) which is suggested by a referee, we would not observe the formation of phenylvinyloxysilane ($\mathrm{PhH_2SiOCH{=}CH_2}$) from the isomerization of 2-phenyl-3-methyloxasilacyclopropane intermediate ($\mathrm{PhH}\underbrace{\mathrm{Si{-}O{-}C}}\mathrm{HCH_3}$). It seems to us that the decomposition of the oxasilacyclopropane to the phenylsilylene is faster than the isomerization of the oxasilacyclopane into the phenylvinyloxysilane.

12 We could not get a good ^{1}H-NMR spectrum of compound V which was obtained in a trace amount. Thus the compound V was identified from a GC/Mass spectrum only.