

Generation and reactivities of ethylmethoxysilylene

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Abstract

Vacuum pyrolysis of 1,2-diethyl-1,1,2,2-tetramethoxydisilane (II) in the presence of 2,3-dimethyl-1,3-butadiene resulted in the formation of 1-ethyl-1-methoxy- (III), 1-ethyl- (IV), and 1-methoxy-3,4-dimethyl-1-silacyclopent-3-ene (V) along with ethyltrimethoxysilane. The observed products might be formed from the addition of ethylmethoxysilylene, ethylsilylene and methoxysilylene into 2,3-dimethyl-1,3-butadiene respectively under thermal conditions. A labelling experiment employing a deuterated precursor of 1,2-diethyl-1,1,2,2-tetramethoxy-*d*₁₂-disilane (II-*d*₁₂) was performed for the purpose of elucidating the conversion of ethylmethoxysilylene into ethylsilylene. Ethylsilylene might be generated from [3 → 2 + 1] cyclo-elimination of an intermediate of 2-ethyloxasilacyclopropane (EtHSi-O-C₁H₂) which can arise from a possible intramolecular silylene insertion into a C–H bond of the methoxy group of ethylmethoxysilylene. The methoxysilylene might be formed from elimination of ethylene of 1-methoxy-1-silacyclopropane (HMeOSi-CH₂-CH₂) derived from intramolecular silylene insertion into a C–H bond of the ethyl group of ethylmethoxysilylene. The temperature dependence of the trapped adduct distribution from the pyrolysis of 1,2-diethyl-1,1,2,2-tetramethoxydisilane was examined.

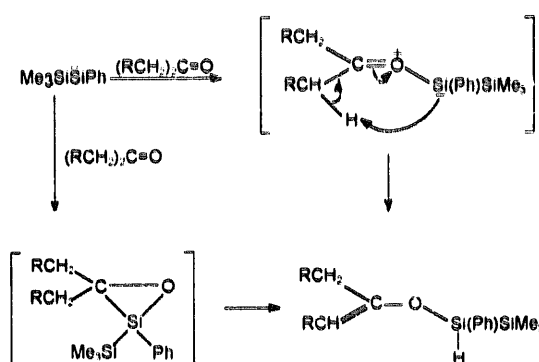
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1. Introduction

It is well known that alkylsilylenes are suggested to insert intramolecularly into the C–H bonds of alkyl groups bigger than CH₃ involving silacyclic intermediates and decompose mainly to alkenes and smaller silylenes [1,2]. It was reported that the reaction pathways involving silacyclopropane type intermediates are much more important than the processes through larger silacyclic intermediates. Seyferth et al. reported evidence for the thermal generation of dimethylsilylene afforded by extrusion of 2,3-dimethyl-2-butene from hexamethylsilirane [3].

Kumada and coworkers reported that photolysis of tris(trimethylsilyl)phenylsilane in the presence of acetone, diethyl ketone and cyclohexanone afforded the corresponding disilanyl enol ethers in moderate yields [4]. The authors suggested a possible mechanism involving initial formation of an ylide, followed by concerted rearrangement to the disilanyl enol ethers. However,

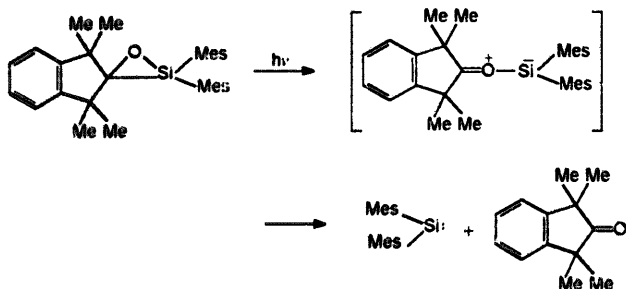
they did not exclude the possibility of initial formation of an oxasilacyclopropane intermediate.



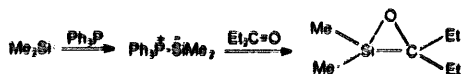
Ando et al. reported that pyrolysis of 1,2-dimethoxy-1,1,2,2-tetramethoxydisilane in the presence of alkyl ketones resulted in the formation of the respective silyl enol ethers and occurred through a mechanism involving initial formation of oxasilacyclopropane intermediate [5,6]. The same authors reported that dimesitylsilenediyl was generated from photolysis and pyrolysis of

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the stable oxasilacyclopropane [7,8] via a $[3 \rightarrow 2 + 1]$ cyclo elimination reaction [7].



The reactions of hexamethylsilacyclopropane with carbonyl compounds in the presence of tertiary phosphines proceeding through an oxasilacyclopropane intermediate were reported by Seyferth and Lim [9].

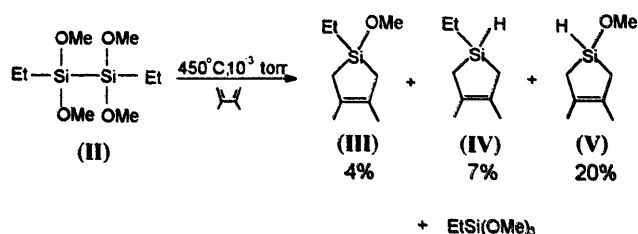


We recently reported that vacuum pyrolysis of 1,1-dimethoxy-1-phenyl-2,2,2-trimethyldisilane in the presence of 2,3-dimethyl-1,3-butadiene was found to proceed through an oxasilacyclopropane intermediate which could arise from a possible intramolecular silylene insertion into a C–H bond of the methoxy group in methoxyphenylsilylene and decompose to phenylsilylene and formaldehyde via a $[3 \rightarrow 2 + 1]$ cyclo elimination [10,11]. After we performed these experiments, the reactions and generation of ethylmethoxysilylene from the vacuum pyrolysis of 1,2-diethyl-1,1,2,2-tetra-methoxydisilane (II) were examined. Here, we wish to report the results of the pyrolyses of alkoxyethylsilylene precursors (alkoxy group; OMe, OMe-*d*₃ and OEt) in the presence of 2,3-dimethyl-1,3-butadiene. We are concerned with a competitive intramolecular silylene insertion into a C–H bond of the methoxy or the ethyl group of ethylmethoxysilylene respectively. In an attempt to elucidate the energetics of the decomposition of ethylmethoxysilylene into ethylsilylene and methoxysilylene, the temperature dependence of the product distribution was examined and AM1 semi-empirical calculations [12] were performed to estimate the energy barriers of the dissociation of ethylmethoxysilylene into ethylsilylene and methoxysilylene respectively.

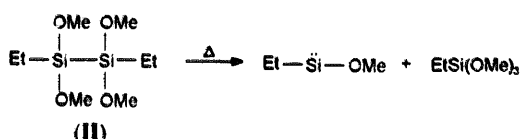
2. Results and discussion

The vacuum pyrolysis of II in the presence of 15-fold excess of 2,3-dimethyl-1,3-butadiene as a good silylene trapping agent at 450 °C affords three major products, 1-ethyl-1-methoxy-3,4-dimethyl-1-silacyclopent-3-ene (III, 4%), 1-ethyl-3,4-dimethyl-1-silacyclopent-3-ene

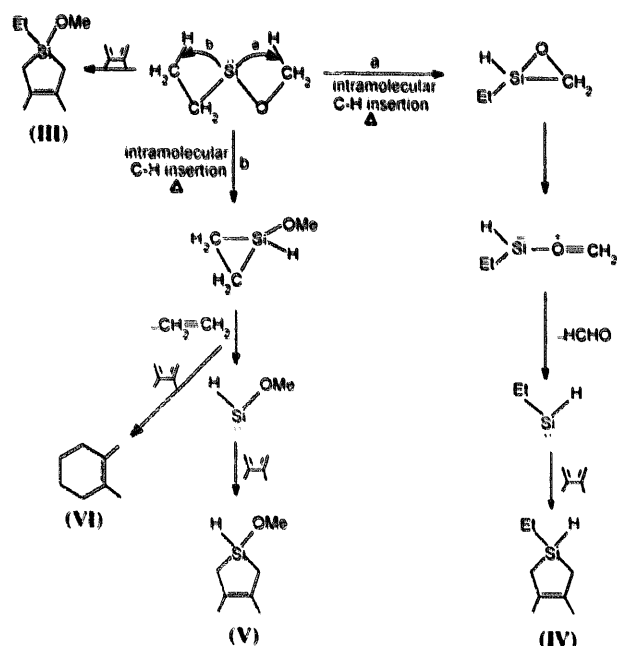
(IV, 7%), and 1-methoxy-3,4-dimethyl-1-silacyclopent-3-ene (V, 20%) along with ethyltrimethoxysilane.



The pyrolysis of the tetramethoxydisilane (II) is initiated by a conventional α -elimination [5,13] of ethyltrimethoxysilane forming ethylmethoxysilylene which is believed to be a primary intermediate.



The formation of IV and V in the trapping reaction suggests that ethylsilylene and methoxysilylene are the secondary intermediates arising from the dissociation of ethylmethoxysilylene. As suggested in Scheme 1, ethylsilylene might be generated from a $[3 \rightarrow 2 + 1]$ cyclo elimination reaction of the 2-ethyloxasilacyclopropane intermediate which can arise from a possible intramolecular silylene insertion into a C–H bond of the methoxy group in ethylmethoxysilylene [5,7,10,11]. The methoxysilylene might be formed from decomposition of a 1-methoxy-1-silacyclopropane intermediate which

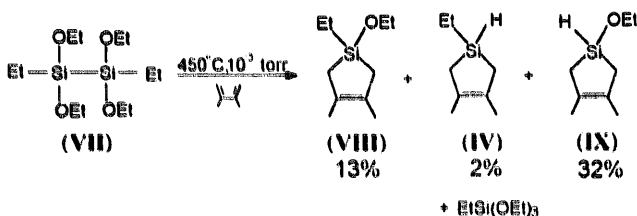


Scheme 1.

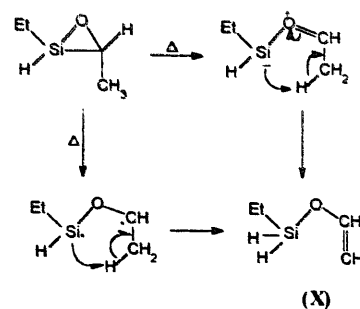
derives from an intramolecular silylene insertion into a C–H bond of the ethyl group in ethylmethoxysilylene [1,2]. Thermally induced extrusion of ethylene from the 1-methoxy-1-silacyclopropane was confirmed from the observation of trapped adduct (VI), 1,2-dimethylcyclohexene, in the reaction mixture.

A labelling experiment employing 1,2-diethyl-1,1,2,2-tetramethoxy- d_{12} -disilane (**II- d_{12}**) may help identification of the reaction pathway for generation of ethylsilylene intermediate. The vacuum pyrolysis of **II- d_{12}** in the presence of an excess of the same trapping agent at 450 °C afforded 1-ethyl-1-methoxy- d_3 -3,4-dimethyl-1-silacyclopent-3-ene (**III- d_3** , 9%), 1-deuterio-1-ethyl-3,4-dimethyl-1-silacyclopent-3-ene (**IV- d** , 3%), and 1-methoxy- d_3 -3,4-dimethyl-1-silacyclopent-3-ene (**V- d_3** , 23%) along with ethyltrimethoxy- d_5 -silane. It seems to us that the observed products are also possibly generated by the same reaction pathway suggested in Scheme 1.

From the vacuum pyrolysis of 1,2-diethyl-1,1,2,2-tetraethoxydisilane (**VII**) in the presence of the same trapping agent at 450 °C, we observed 1-ethoxy-1-ethyl-3,4-dimethyl-1-silacyclopent-3-ene (**VIII**), 1-ethyl-3,4-dimethyl-1-silacyclopent-3-ene (**IV**) and 1-ethoxy-3,4-dimethyl-1-silacyclopent-3-ene (**IX**) as major products along with ethyltriethoxysilane.



Formation of **IV** from the vacuum pyrolysis of tetraethoxydisilane (**VII**) in the trapping reaction can be explained by the [3 → 2 + 1] cyclo elimination reaction [7] of 2-ethyl-3-methoxasilacyclopropane intermediate ($\text{EtHSi}-\text{O}-\text{CHCH}_3$) which can arise from the intramolecular silylene insertion into a methylene C–H bond of the ethoxy group of ethoxyethylsilylene. The product **IX**, 1-ethoxy-3,4-dimethyl-1-silacyclopent-3-ene, was also produced from the trapping reaction of ethoxysilylene intermediate which might be generated from the decomposition of 1-ethoxy-1-silacyclopropane ($\text{HEtOSi}-\text{CH}_2-\text{CH}_2$). From the neat pyrolysis of 1,2-diethyl-1,1,2,2-tetraethoxydisilane (**VII**), we could observe the formation of a trace of silyl enol ether (**X**, $\text{EtH}_2\text{SiOCH}=\text{CH}_2$) which is identified by GC/MS only (Scheme 2). The silyl enol ether (**X**) was not observed in the vacuum pyrolysis of **VII** and the same trapping agent [10]. Formation of **X** can be explained by the reaction pathway involving prior formation of oxasilacyclopropane followed by concerted rearrangement of



Scheme 2.

an ylide or by γ -hydrogen abstraction of a silyl radical through the homolytic cleavage of a silicon–carbon ring bond [4–8].

The temperature dependence of the yields of individual products and of the product ratios from the pyrolyses of the tetramethoxydisilane **II** is summarized in Table 1.

In previous work it was found that the process of direct addition of methoxyphenylsilylene ($\text{Ph}-\text{Si}-\text{OMe}$) to the same diene trapping agent was more favorable than the process of intramolecular C–H insertion of the silylene at 500–700 °C [10], since direct addition of methoxyphenylsilylene to the diene may involve a sufficiently low energy barrier compared with intramolecular insertion into a C–H bond of methoxy group of the silylene. It appears, however, that ethyl substitution at the silicon atom of alkoxydisilanes (alkoxy group; OMe , $\text{OMe-}d_3$ and OEt) leads more predominantly to intramolecular insertion into a C–H bond of the ethyl group of alkoxyethylsilylenes than to direct addition between the silylenes and the trapping agent. This different behavior may be explained in terms of the electronic factor of the ethyl and phenyl group of the silylene intermediates.

As the reaction temperature increases, the product ratios of **IV** to **III** and **V** to **III** increase. This implies the increasing importance of decomposition of ethylmethoxysilylene into ethylsilylene and methoxysilylene respectively at higher temperatures relative to the direct addition of ethylmethoxysilylene to the trapping agent. Competition experiments indicate the intramolecular C–H insertion product of ethylmethoxysilylene is

Table 1
Temperature dependence of the product ratios from the vacuum pyrolysis of $\text{Et}(\text{MeO})_2\text{SiSi}(\text{OMe})_2\text{Et}$ (**II**) in excess of 2,3-dimethyl-1,3-butadiene

Temperature (°C)	Yield of product (%)			Product ratio			Recovery percentage
	III	IV	V	IV/III	V/III	V/IV	
400	3	2	13	0.7	4.3	6.5	77%
450	4	7	20	1.8	5.0	2.9	64%
500	4	11	28	2.8	7.0	2.5	50%

formed more rapidly from the ethyl group than from the methoxy group. The C–H insertion into the ethyl group of ethylmethoxysilylene may involve a sufficiently small energy barrier compared with the C–H insertion into the methoxy group of the silylene. Increasing reaction temperature favors formation of the 1-ethyl-3,4-dimethyl-1-silacyclopent-3-ene (IV) over 1-methoxy-3,4-dimethyl-1-silacyclopent-3-ene (V). It suggests that the activation barrier for the decomposition of ethylmethoxysilylene intermediate into ethylsilylene is higher than that of ethylmethoxysilylene into methoxysilylene. This suggestion is consistent with our theoretical calculations. An AM1 semi-empirical calculation with the Hyperchem computer program was performed to obtain the heat of formation of Et–Si–OMe, Et–Si–H, H–Si–OMe, EtHSi–O–CH₂, HMeOSi–CH₂–CH₂, HCHO and CH₂=CH₂, as –33.8, 46.1 [2], –10.4, –33.7, –40.6, –26.0 [14] and 12.5 kcal mol^{–1} [2] respectively. Based on their heats of formation [2], we have estimated the crude value of the activation barrier for the decomposition of Et–Si–OMe into Et–Si–H and HCHO (E_a = 53.9 kcal mol^{–1}) and into H–Si–OMe and CH₂=CH₂ (E_a = 35.9 kcal mol^{–1}). The decrease of the product ratio (V/IV) with increasing temperature may be due to the higher activation barrier for the extrusion of Et–Si–H and HCHO from Et–Si–OMe.

3. Experimental

3.1. General

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 connected to a vacuum line [15]. The progress of the pyrolysis was followed by gas chromatography with a flame ionization detector (FID) using a Hewlett-Packard 5890 instrument on a HP-1 capillary column (cross-linked 5% Ph Me silicone, 25 m). Product yields were determined by GC(FID) with cyclohexane as internal standard on the basis of the quantity of 1,2-diethyl-1,1,2,2-tetraalkoxydisilane decomposed. Separation of the products was performed on a Varian Model 920 GC with a thermal conductivity detector (TCD) using 20% OV-17 column (Chromosorb W 80/100, 1/4 in × 13 ft). The ¹H NMR and ¹³C NMR spectra were recorded on a Hitachi R 1200 60 MHz and Bruker AM-300 NMR spectrophotometer in CDCl₃ with tetramethylsilane (TMS) as internal standard. Mass spectra were obtained on a Hewlett-Packard 5890 Series II GC coupled to a 5970 Series mass selective detector. High resolution

mass spectra were obtained by using a Jeol SX-102A double focusing mass spectrometer. Elemental analyses were performed by a Carlo Erba EA-1108.

3.2. Materials

For the synthesis of precursors, aluminum chloride (AlCl₃), dichlorodiphenylsilane, 2,3-dimethyl-1,3-butadiene, ethyl bromide, magnesium and methyl-*d*₃ alcohol-*d* were obtained from Aldrich Chemical Company and used without further purification. All solvents were dried and distilled prior to use. Preparation of the precursors (II, II-*d*₁₂ and VII) has been based on the reaction of 1,2-diethyltetrachlorodisilane (I) with an alcohol [10,16]. However, 1,2-diethyltetrachlorodisilane itself is not readily available. Thus the tetrachlorodisilane (I) was prepared as described previously [10,17,18].

3.3. Preparation of 1,2-diethyl-1,1,2,2-tetrachlorodisilane (I)

For the preparation of chlorodiphenylethylsilane, to a stirred suspension of 3.9 g (0.16 g atm) of Mg turnings in 50 ml of dry ether was slowly added 13.1 g (0.12 mol) of ethyl bromide in 10 ml of dry ether at ice-water temperature. After being stirred for an additional 2 h at room temperature, the liquid was transferred to a dropping funnel by a cannula. The solution was then added dropwise with stirring under nitrogen to 25.2 g (0.1 mol) of dichlorodiphenylsilane in 100 ml of dry ether at room temperature. After addition was complete, the mixture was left overnight followed by filtration of the salts, then fractionally distilled under reduced pressure to afford 16 g (64.8 mmol, 65%, b.p. 128°C/1.5 torr) of chlorodiphenylethylsilane. MS *m/z* (rel. int.): 248 (M⁺ + 2, 28), 246 (M⁺, 12), 219 (37), 217 (100), 199 (12), 181 (11), 165 (1), 163 (2), 141 (4), 139 (2), 121 (3), 105 (3), 91 (4), 77 (4), 65 (4), 63 (8). For the preparation of 1,2-diethyl-1,1,2,2-tetraphenyldisilane, to a suspension of 0.35 g (0.05 g atm) of Li metals and 7.4 g (30 mmol) of the chlorodiphenylethylsilane was slowly added 50 ml of dry THF at ice-water temperature. After being stirred for an additional 4 h at room temperature, the organic layer was transferred through a cannula to the reaction flask. The chlorodiphenylethylsilane (7.4 g, 30 mmol) in 10 ml of dry THF was placed in the dropping funnel, and added to the solution at room temperature. The reaction was exothermic and the mixture was stirred vigorously. After addition was complete, the reaction mixture was stirred overnight at warm temperature followed by filtration of the salts, then the organic layer was treated with water and dried over anhydrous calcium chloride. The volatile solvent was evaporated and the residue was recrystallized with chloroform to afford 8.6 g (20.3 mmol, 68%, m.p. 116–118°C) of 1,2-diethyltetraphenyldisilane. ¹H NMR

(CDCl₃, 200 MHz): δ 1.09 (t, 6H, SiCH₂CH₃, J = 7.0 Hz), 1.33 (q, 4H, SiCH₂CH₃, J = 7.0 Hz), 7.40 (m, 12H, 4Ph), 7.51 (m, 8H, 4Ph). ¹³C NMR (CDCl₃, 200 MHz): δ 5.87, 8.84, 128.23, 129.33, 136.05, 136.28.

For the preparation of 1,2-diethyl-1,1,2,2-tetrachlorodisilane, 8 g (19 mmol) of the 1,2-diethyltetraphenyldisilane in 50 ml of dry benzene was placed in a three-necked flask fitted with a stirrer, condenser and gas-inlet which was extended into the liquid nearly to the bottom of the flask. To the stirred solution, 0.3 g (2.2 mmol) of sublimed aluminum chloride was added and dry HCl gas was introduced through the gas-inlet tube. The complete consumption of 1,2-diethyl-1,1,2,2-tetraphenyldisilane was confirmed by GC analysis. After reaction was complete, it was mixed well with a small amount of anhydrous acetone in order to deactivate the aluminum chloride remaining in the reaction mixture and then the solvent was evaporated. Bulb-to-bulb distillation of the mixture followed by a preparative GC on an OV-17 column afforded 4 g (15.6 mmol, 82%) of 1,2-diethyl-1,1,2,2-tetrachlorodisilane (I).

Compound I: ¹H NMR (CDCl₃, 200 MHz): δ 0.97 (q, 4H, SiCH₂CH₃, J = 8.0 Hz), 1.37 (t, 6H, SiCH₂CH₃, J = 8.0 Hz). ¹³C NMR (CDCl₃, 200 MHz): δ 1.75, 6.56. MS m/z (rel. int.): 260 (M^+ + 6, 2), 258 (M^+ + 4, 7), 256 (M^+ + 2, 12), 254 (M^+ , 10), 229 (2), 227 (4), 225 (3), 192 (1), 131 (7), 129 (38), 127 (7), 103 (5), 101 (18), 99 (35), 94 (52), 92 (100), 65 (31), 63 (8). HRMS found 253.9063; C₄H₁₀Si₂Cl₄ calc. 253.9077.

3.4. Preparation of 1,2-diethyl-1,1,2,2-tetramethoxydisilane (II)

In a 100 ml three-necked flask equipped with a condenser, funnel, and magnetic stirring bar were placed 3.8 g (0.12 mol) of methanol and 12.1 g (0.12 mol) of triethylamine in 10 ml of benzene at ice-water temperature. The 1,2-diethyl-1,1,2,2-tetrachlorodisilane (5 g, 19.5 mmol) was placed in the dropping funnel and slowly added dropwise to the well stirred solution under nitrogen. After the addition was complete, the reaction mixture was warmed to room temperature and stirred overnight followed by filtration of the salts. Bulb-to-bulb distillation of the mixture followed by preparative GC on a 1/4 in $\times$ 13 ft 20% OV-17 column (detector temp. 200°C, injector temp. 220°C, oven temp. 150°C and flow rate 50 ml min⁻¹) afforded 4 g (16.8 mmol, 86%) of 1,2-diethyl-1,1,2,2-tetramethoxydisilane (II). The spectral properties were as follows: ¹H NMR (CDCl₃, 300 MHz): δ 1.09 (q, 4H, SiCH₂CH₃, J = 8.1 Hz), 1.45 (t, 6H, SiCH₂CH₃, J = 8.1 Hz), 3.99 (s, 12H, SiOCH₃). ¹³C NMR (CDCl₃, 300 MHz): δ 5.58, 7.76, 50.15. MS m/z (rel. int.): 238 (M^+ , 3), 223 (27), 209 (26), 207 (2), 193 (69), 165 (11), 163 (14), 135 (8), 119 (100), 105 (5), 91 (49), 89 (23), 61 (44), 59 (97).

HRMS found 238.1061; C₈H₂₂Si₂O₄ calc. 238.1057. Anal. Found: C, 40.18; H, 9.22. C₈H₂₂Si₂O₄ Calc.: C, 40.30; H, 9.30%.

3.5. Preparation of 1,2-diethyl-1,1,2,2-tetramethoxy-d₁₂-disilane (II-d₁₂)

For the synthesis of Et- $\ddot{\text{Si}}$ -OCD₃ precursor (II-d₁₂), 2 g (7.8 mmol) of 1,2-diethyltetrachlorodisilane (I) was added dropwise to the well stirred solution of 1.71 g (47.4 mmol) of methyl-d₃ alcohol-*d* and 4.8 g (47.4 mmol) of triethylamine in 4 ml of dry benzene at ice-water temperature. After the addition was complete, the reaction mixture was warmed to room temperature and stirred overnight, and the mixture was filtered to remove salts. Bulb-to-bulb distillation of the mixture followed by preparative GC on the same OV-17 column afforded 1.5 g (6.0 mmol, 77%) of II-d₁₂. ¹H NMR (CDCl₃, 300 MHz): δ 1.08 (q, 4H, SiCH₂CH₃, J = 8.0 Hz), 1.44 (t, 6H, SiCH₂CH₃, J = 8.0 Hz). ¹³C NMR (CDCl₃, 300 MHz): δ 5.56, 7.76, 49.30. MS m/z (rel. int.): 250 (M^+ , 4), 232 (40), 221 (29), 216 (1), 200 (7), 172 (9), 168 (12), 125 (100), 97 (30), 93 (9), 65 (21), 62 (55). HRMS found 250.1813; C₈H₁₀D₁₂Si₂O₄ calc. 250.1809.

3.6. Preparation of 1,2-diethyl-1,1,2,2-tetraethoxydisilane (VII)

The 1,2-diethyltetrachlorodisilane (2 g, 7.8 mmol) was slowly added dropwise to the well stirred solution of 2.2 g (47.4 mmol) of ethanol and 4.8 g (47.4 mmol) of triethylamine in 4 ml of dry benzene at ice-water temperature under nitrogen gas. After the addition was complete, the mixture was warmed to room temperature and stirred overnight. The mixture was separated by a preparative GC on the same OV-17 column to afford 1.7 g (5.8 mmol, 74%) of VII. ¹H NMR (CDCl₃, 300 MHz): δ 1.05 (q, 4H, SiCH₂CH₃, J = 7.8 Hz), 1.43 (t, 6H, SiCH₂CH₃, J = 7.8 Hz), 1.62 (t, 12H, SiOCH₂CH₃, J = 7.0 Hz), 4.22 (q, 8H, SiOCH₂CH₃, J = 7.0 Hz). ¹³C NMR (CDCl₃, 300 MHz): δ 5.97, 8.38, 18.55, 58.59. MS m/z (rel. int.): 294 (M^+ , 0.4), 265 (31), 249 (5), 237 (8), 221 (100), 193 (42), 191 (36), 181 (25), 177 (40), 165 (36), 163 (20), 153 (8), 149 (11), 147 (36), 137 (11), 135 (20), 123 (9), 121 (5), 119 (16), 117 (19), 107 (12), 105 (8), 103 (27), 91 (21), 89 (7), 75 (15), 73 (16), 63 (36). HRMS found 294.1686; C₁₂H₃₀Si₂O₄ calc. 294.1683. Anal. Found: C, 48.84; H, 10.21. C₁₂H₃₀Si₂O₄ Calc.: C, 48.93; H, 10.27%.

3.7. Pyrolysis of 1,2-diethyl-1,1,2,2-tetramethoxydisilane (II) in the presence of 2,3-dimethyl-1,3-butadiene

The mixture of 0.29 g (1.2 mmol) of II and 1.5 g (18 mmol) of 2,3-dimethyl-1,3-butadiene as a trapping

agent was injected into the rubber septum at the inlet of the vertical quartz tube mentioned above using a gas tight syringe over a period of 4 h. The vacuum pyrolysis of the mixture at 400–500°C and 10^{-3} torr afforded quantitative recovery of the starting material II. The pyrolysate was collected in a trap cooled with a liquid nitrogen and separated by a preparative GC. The observed major products were 1-ethyl-1-methoxy-3,4-dimethyl-1-silacyclopent-3-ene (III), 1-ethyl-3,4-dimethyl-1-silacyclopent-3-ene (IV), and 1-methoxy-3,4-dimethyl-1-silacyclopent-3-ene (V). The spectral properties of these products were as follows.

Compound III: ^1H NMR (CDCl_3 , 300 MHz): δ 0.83 (q, 2H, SiCH_2CH_3 , $J = 8.1$ Hz), 1.09 (t, 3H, SiCH_2CH_3 , $J = 8.1$ Hz), 1.43 (m, 4H, $\text{Si}(\text{CH}_2)_2$), 1.80 (s, 6H, CCH_3), 3.52 (s, 3H, SiOCH_3). ^{13}C NMR (CDCl_3 , 300 MHz): δ 5.69, 6.76, 19.12, 21.42, 50.73, 130.36. MS m/z (rel. int.): 170 (M^+ , 73), 155 (0.2), 141 (89), 138 (45), 127 (2), 119 (6), 113 (16), 111 (11), 109 (16), 105 (7), 99 (5), 95 (5), 75 (6), 67 (7), 61 (9), 59 (100), 55 (5), 53 (5). HRMS found 170.1131; $\text{C}_9\text{H}_{18}\text{SiO}$ calc. 170.1127.

Compound IV: ^1H NMR (CDCl_3 , 300 MHz): δ 0.70 (dq, 2H, SiCH_2CH_3 , $J = 7.2$ Hz, $J = 3.0$ Hz), 1.01 (t, 3H, SiCH_2CH_3 , $J = 7.2$ Hz), 1.53 (m, 4H, $\text{Si}(\text{CH}_2)_2$), 1.73 (s, 6H, CCH_3), 4.07 (septet, 1H, SiH, $J = 3.0$ Hz). ^{13}C NMR (CDCl_3 , 300 MHz): δ 4.11, 7.93, 19.14, 20.98, 130.80. MS m/z (rel. int.): 140 (M^+ , 51), 139 (5), 125 (5), 111 (100), 110 (7), 109 (27), 105 (0.4), 97 (15), 95 (12), 85 (9), 83 (23), 69 (14), 67 (9), 55 (11), 53 (8). HRMS found 140.1022; $\text{C}_8\text{H}_{16}\text{Si}$ calc. 140.1022.

Compound V: ^1H NMR (CDCl_3 , 300 MHz): δ 1.53 (m, 4H, $\text{Si}(\text{CH}_2)_2$), 1.80 (s, 6H, CCH_3), 3.55 (s, 3H, SiOCH_3), 4.97 (quintet, 1H, SiH, $J = 1.5$ Hz). ^{13}C NMR (CDCl_3 , 300 MHz): δ 19.07, 22.69, 51.83, 130.08. MS m/z (rel. int.): 142 (M^+ , 32), 141 (15), 127 (17), 112 (6), 110 (26), 108 (6), 105 (9), 100 (6), 95 (9), 67 (9), 61 (9), 59 (100), 55 (4), 53 (5). HRMS found 142.0815; $\text{C}_7\text{H}_{14}\text{SiO}$ calc. 142.0814. The fourth product, ethyltrimethoxysilane, from the copyrolysis was formed and identified with GC/MS only. MS m/z (rel. int.): 150 (M^+ , 0.4), 121 (100), 91 (60), 77 (3), 61 (15), 59 (18). A trace of 1,2-dimethylcyclohexene (VI) in the reaction mixture was observed and compared with the MS of an authentic sample. Compound (1,2-dimethylcyclohexene): MS m/z (rel. int.): 110 (M^+ , 31), 95 (55), 93 (26), 91 (22), 82 (35), 81 (26), 79 (20), 77 (22), 68 (33), 67 (100), 65 (13), 55 (27), 53 (27), 51 (11).

3.8. Pyrolysis of 1,2-diethyl-1,1,2,2-tetramethoxy- d_{12} -disilane (II- d_{12}) in the presence of 2,3-dimethyl-1,3-butadiene

The vacuum copyrolysis of 0.30 g (1.2 mmol) of II- d_{12} and 1.5 g (18 mmol) of the trapping agent at 450°C was conducted in the same procedure as de-

scribed above. The pyrolysate was separated by a preparative GC to afford unreacted reactant II- d_{12} (62%), 1-ethyl-1-methoxy- d_3 -3,4-dimethyl-1-silacyclopent-3-ene (III- d_3 , 9%), 1-deuterio-1-ethyl-3,4-dimethyl-1-silacyclopent-3-ene (IV- d , 3%), and 1-methoxy- d_3 -3,4-dimethyl-1-silacyclopent-3-ene (V- d_3 , 23%).

Compound III- d_3 : ^1H NMR (CDCl_3 , 300 MHz): δ 0.84 (q, 2H, SiCH_2CH_3 , $J = 8.2$ Hz), 1.10 (t, 3H, SiCH_2CH_3 , $J = 8.2$ Hz), 1.44 (m, 4H, $\text{Si}(\text{CH}_2)_2$), 1.82 (s, 6H, CCH_3). ^{13}C NMR (CDCl_3 , 300 MHz): δ 6.08, 7.19, 19.56, 21.82, 51.13, 130.79. MS m/z (rel. int.): 173 (M^+ , 27), 158 (0.4), 144 (42), 138 (23), 119 (2), 112 (6), 109 (8), 91 (3), 78 (4), 67 (4), 64 (9), 62 (100). HRMS found 173.1310; $\text{C}_9\text{H}_{15}\text{D}_3\text{SiO}$ calc. 173.1316.

Compound IV- d : ^1H NMR (CDCl_3 , 300 MHz): δ 0.72 (q, 2H, SiCH_2CH_3 , $J = 7.7$ Hz), 1.04 (t, 3H, SiCH_2CH_3 , $J = 7.7$ Hz), 1.55 (m, 4H, $\text{Si}(\text{CH}_2)_2$), 1.75 (s, 6H, CCH_3). ^{13}C NMR (CDCl_3 , 300 MHz): δ 4.15, 8.04, 19.25, 21.02, 130.62. MS m/z (rel. int.): 141 (M^+ , 51), 126 (5), 112 (100). HRMS found 141.1085; $\text{C}_8\text{H}_{15}\text{DSi}$ calc. 141.1085.

Compound V- d_3 : ^1H NMR (CDCl_3 , 300 MHz): δ 1.55 (m, 4H, $\text{Si}(\text{CH}_2)_2$), 1.81 (s, 6H, CCH_3), 4.95 (quintet, 1H, SiH, $J = 1.5$ Hz). ^{13}C NMR (CDCl_3 , 300 MHz): δ 19.51, 23.09, 52.23, 130.51. MS m/z (rel. int.): 145 (M^+ , 38), 130 (16), 110 (29), 103 (7), 95 (7), 67 (5), 64 (8), 62 (100), 55 (2), 53 (3). HRMS found 145.0996; $\text{C}_7\text{H}_{11}\text{D}_3\text{SiO}$ calc. 145.1002. The fourth product, ethyltrimethoxy- d_9 -silane, was produced and identified with GC/MS only. MS m/z (rel. int.): 159 (M^+ , 0.3), 130 (100), 98 (47), 81 (3), 66 (10), 62 (15). A trace of VI in the reaction mixture was also observed.

3.9. Pyrolysis of 1,2-diethyl-1,1,2,2-tetraethoxydisilane (VII) in the presence of 2,3-dimethyl-1,3-butadiene

The mixture of 0.3 g (1.0 mmol) of 1,2-diethyl-1,1,2,2-tetraethoxydisilane (VII) and 1.23 g (15 mmol) of the trapping agent was copyrolyzed at 450°C. The pyrolysate followed by preparative GC on the same column afforded unreacted VII (49%), 1-ethoxy-1-ethyl-3,4-dimethyl-1-silacyclopent-3-ene (VIII, 13%), 1-ethyl-3,4-dimethyl-1-silacyclopent-3-ene (IV, 2%), and 1-ethoxy-3,4-dimethyl-1-silacyclopent-3-ene (IX, 32%) as major products along with ethyltriethoxysilane.

Compound VIII: ^1H NMR (CDCl_3 , 300 MHz): δ 0.79 (q, 2H, SiCH_2CH_3 , $J = 8.1$ Hz), 1.05 (t, 3H, SiCH_2CH_3 , $J = 8.1$ Hz), 1.25 (t, 3H, $\text{SiOCH}_2\text{CH}_3$, $J = 6.9$ Hz), 1.39 (m, 4H, $\text{Si}(\text{CH}_2)_2$), 1.77 (s, 6H, CCH_3), 3.73 (q, 2H, $\text{SiOCH}_2\text{CH}_3$, $J = 6.9$ Hz). ^{13}C NMR (CDCl_3 , 300 MHz): δ 6.03, 6.85, 18.43, 19.19, 22.01, 58.95, 130.35. MS m/z (rel. int.): 184 (M^+ , 68), 169 (0.4), 155 (100), 138 (18), 127 (5), 119 (7), 113 (12), 111 (59), 73 (90), 71 (6), 69 (5), 67 (9), 61 (7), 55

(5), 53 (2). HRMS found 184.1290; $C_{10}H_{20}SiO$ calc. 184.1284.

Compound IX: 1H NMR ($CDCl_3$, 300 MHz): δ 1.26 (t, 3H, $SiOCH_2CH_3$, $J = 6.9$ Hz), 1.55 (m, 4H, $Si(CH_2)_2$), 1.78 (s, 6H, CCl_3), 3.73 (q, 2H, $SiOCH_2CH_3$, $J = 6.9$ Hz), 4.76 (m, 1H, SiH). MS m/z (rel. int.): 156 (M^+ , 88), 141 (29), 127 (57), 114 (15), 113 (13), 111 (33), 110 (35), 99 (16), 95 (17), 83 (26), 73 (100), 71 (10), 69 (11), 67 (15), 61 (12), 55 (12), 53 (9). HRMS found 156.0968; $C_8H_{16}SiO$ calc. 156.0971. The ethyltriethoxysilane was identified with GC/MS only. MS m/z (rel. int.): 192 (M^+ , 0.5), 177 (3), 163 (100), 147 (20), 137 (10), 133 (11), 119 (43), 107 (14), 103 (14), 91 (17), 89 (6), 79 (34), 73 (57), 75 (69), 63 (38). A trace of VI in the reaction mixture was also observed. From the neat pyrolysis of VII, the formation of a trace of silyl enol ether ($EtH_2Si-O-CH=CH_2$, X) was observed and identified by GC/MS only. MS m/z (rel. int.): 102 (M^+ , 55), 101 (55), 87 (11), 75 (16), 74 (9), 73 (100), 61 (6), 59 (11), 57 (17), 55 (6).

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