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Journal of Organometallic Chemistry 691 (2006) 541–544

Journal of Organometallic Chemistry

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Kinetic studies on Brook-type isomerization of acylpolysilanes to silenes

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Received 3 March 2005; received in revised form 17 September 2005; accepted 20 September 2005
Available online 2 November 2005

Abstract

First-order rate constants of Brook-type isomerization of acylpolysilanes $(Me_3Si)_3SiCOR$ (R = *iso*-Pr, *tert*-Bu, Ad, 2,6-xylyl, and Mes) leading to silenes $(Me_3Si)_2Si{=}C(OSiMe_3)R$ at various temperatures were determined. Their Eyring plots gave kinetic parameters of $\Delta H^{\ddagger} = 26.6$–$29.4$ kcal mol^{-1} and $\Delta S^{\ddagger} = -11.5$ to -14.6 cal mol^{-1} K^{-1}. The isomerization was accelerated by introducing an electron-donating alkyl substituent on the carbonyl carbon. These results are in accordance with a concerted mechanism involving a four-centered transition state.

Keywords: Kinetic studies; Silene formation; Brook-type isomerization; Acylpolysilane

1. Introduction

Brook-type isomerization of acylpolysilanes is important as a convenient method to generate silenes [1]. The isomerization involves a 1,3-silyl shift from the center silicon atom to the carbonyl oxygen and the formation of a thermally favorable Si–O bond provides a driving force of this isomerization, which would compensate for the formation of thermally unstable Si=C bond. The isomerization can be induced photochemically or thermally. The former produces the rearranged silenes irreversibly [2,3], while the later provides equilibrium between the acylpolysilanes and the respective silenes [2,4].

Although many papers concerning the properties and chemical behaviors of the rearranged silenes have been published to date [2–5], only a little is known for the isomerization mechanism. Recently, it was suggested by theoretical calculations that the isomerization would take place via a concerted way through a four-centered transition state as shown in Scheme 1 [6]. However, no experimental evidences to support this mechanism have been reported so far. In this paper, we report the results of kinetic studies on the isomerization of variously substituted acylpolysilanes, which indicated that the mechanism involving the four-centered transition state is highly probable. Effects of the substituents on the kinetic parameters also are discussed.

2. Experimental

2.1. Preparation of acylpolysilanes

A solution of tris(trimethylsilyl)silyllithium, prepared from tetrakis(trimethylsilyl)silane (2.49 g, 7.78 mmol) and an equimolar amount of methyllithium in 20 mL of THF, was added drop wise to 2,6-dimethylbenzoyl chloride (1.92 g, 11.4 mmol) at −80 °C and the resulting mixture was stirred at room temperature for 3 h. After hydrolysis with water, the solvent was removed and the residue was chromatographed on a silica gel column to give crude solids. Recrystallization of the crude solids twice from hexane gave 0.690 g (23% yield) of **1e** as the pale yellow solids: m.p. 143.5–144.5 °C; MS *m*/*z* 365 ($M^+ - 15$); ^1H NMR ($CDCl_3$) δ 0.17 (s, 27H), 2.17 (s, 6H), 6.93 (d, 2H,

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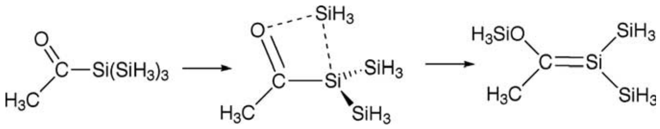
doi:10.1016/j.jorganchem.2005.09.023



Scheme 1.

$J = 7.8$ Hz), 7.08 (t, 1H, $J = 7.8$ Hz); ^{13}C NMR ($CDCl_3$) δ 1.3, 19.6, 128.0, 130.8, 149.5 (q-C), 249.6 (C=O), one aromatic carbon may overlap. Anal. Calc. for $C_{18}H_{36}OSi_4$: C, 56.77; H, 9.53. Found: C, 56.73; H, 9.53%. Acylpolysilanes **1a**–**d** were prepared as reported in the literature [2,3].

2.2. Thermal isomerization of acylpolysilanes

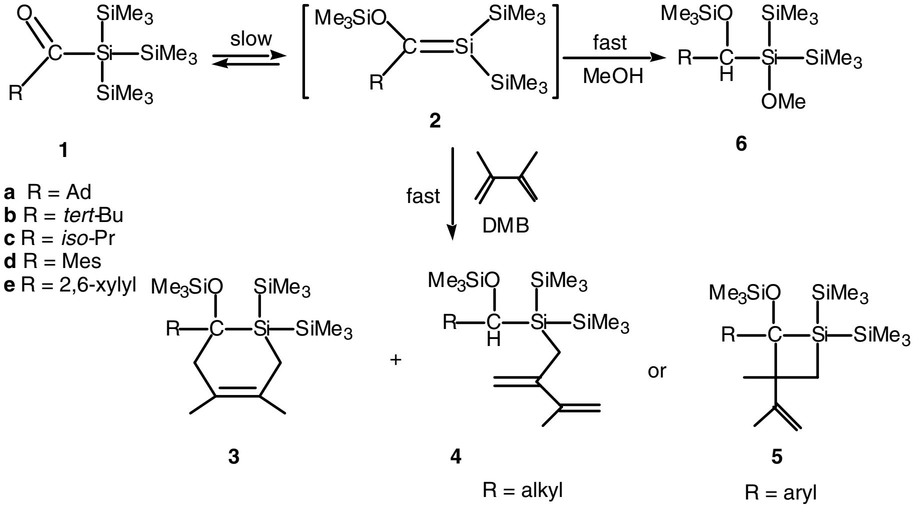
In a 5mϕ NMR tube was placed 50 mg of an acylpolysilane, a 15-fold excess of a trapping agent, and 0.6 mL of a deuterated solvent distilled from sodium–potassium alloy, and the tube was sealed under reduced pressure (ca. 0.1 mmHg). The tube was then heated under fine temperature control and the reaction progress was monitored by the ^{1}H NMR spectra. The NMR data of products **3a**, **4a**, **3b**, **4b** [3c], **3c**, **4c** [4b], **3d** [3c], and **6a** [2] were consistent with those reported previously. Products **5d**, and **3e** and **5e** were separated from the reaction mixtures of **1d** and **1e**, respectively, by silica gel column chromatography. Data for **5d**: GC–MS *m/z* 476 (M^+); ^{1}H NMR (C_6D_6) δ 0.01, 0.16, 0.27 (s, each 9H), 1.06 (3H, s, Me–C(sp^3)), 1.44, 1.73 (d, each 1H, $J = 4.4$ Hz, CH_2Si), 1.75 (s, 3H, Me—C=), 2.09, 2.27, 2.52 (s, each 3H, Mes), 4.96, 4.98 (s, each 1H, olefin CH_2), 6.67, 6.73 (s, each 1H, Mes ring H); ^{13}C NMR (C_6D_6) δ 0.4, 1.2, 2.7, 20.8, 22.7, 23.1, 25.9, 29.6, 33.9, 41.4, 65.6, 114.1 (CH_2=), 129.6, 129.7, 134.4, 136.4, 139.3, 140.0, 148.3 (olefin q-C); Exact MS Calc. for $C_{25}H_{48}OSi_4$: 476.2782. Found: 476.2753. Data for **3e**: GC–MS *m/z* 462 (M^+); ^{1}H NMR (C_6D_6) δ −0.15, 0.019, 0.34 (s, 9H each), 1.34, 1.64 (d, each 1H, $J = 14.9$ Hz, CH_2Si), 1.87, 1.89 (s, each 3H, MeC=), 2.57 (br s, 6H, Me-xylyl), 2.91 (d, 1H, $J = 13.2$ Hz, CH_2C), 3.13 (d, 1H, $J = 13.2$ Hz, CH_2C), 6.81–6.88 (m, 3H, xylyl); ^{13}C NMR (C_6D_6) δ −0.2, 1.8, 3.0, 19.7, 21.4, 21.8, 27.0, 49.2, 84.7, 126.9, 127.4, 131.7 (br), 136.6, 145.4; Exact MS Calc. for $C_{24}H_{46}OSi_4$: 462.2626. Found: 462.2610. Data for **5e**: GC–MS *m/z* 462 (M^+); ^{1}H NMR (C_6D_6) δ −0.01, 0.15, 0.26 (s, each 9H), 1.02 (s, 3H, Me–C(sp^3)), 1.42, 1.71 (d, each 1H, $J = 5.1$ Hz, $SiCH_2$), 1.74, (s, 3H, Me—C=), 2.28, 2.52 (s, each 3H, Me-xylyl), 4.94, 4.95 (br s, each 1H, olefin), 6.82–6.99 (m, 3H, xylyl ring H); ^{13}C NMR (C_6D_6) δ 0.4, 1.2, 2.6, 22.6, 22.8, 23.1, 25.8, 29.7, 114.2, 125.5, 148.1, other signals could not be observed, due to the low intensities and/or overlapping with those of the solvent; Exact MS Calc. for $C_{24}H_{46}OSi_4$: 462.2626. Found: 462.2610.

2.3. Theoretical studies

MO calculations were carried out using the Becke3-Lee–Yang–Parr (B3LYP) density functional theory (DFT) at the 6-311G*level within the GAUSSIAN 03 suite of programs (revision B.05; Gaussian, Inc.: Pittsburgh, PA, 2003). For the calculations of transition states (TSs), opt = QST3 and nosymm were employed as the keywords. The initial inputs of the TS geometries were based on that reported for the isomerization of $CH_3COSi(SiH_3)_3$ [6].

3. Results and discussion

Generally, heating acylpolysilanes in hydrocarbons gives rise to equilibrium between the acylsilanes and the corresponding rearranged silenes, the later of which may be trapped by alcohols and unsaturated organic compounds [3]. When acylpolysilane **1a** was heated at 120 °C in the presence of a 15-fold excess of 2,3-dimethyl-1,3-butadiene (DMB) in C_6D_6 and the reaction progress was monitored by ^{1}H NMR spectra, [2 + 4] and ene adducts (**3a** and **4a**) were found to be formed in a ratio of 63:37 (Scheme 2). No other products were detected in the reaction mixture by



Scheme 2.

the NMR spectra throughout the reaction. Pseudo first-order kinetic plots exhibit a linear relationship as shown in Fig. 1(a), giving a rate constant of $k = 2.3 \times 10^{-5}$ s^{-1}. Using a less amount of DMB (8 eq.) little affected the results ($k = 2.3 \times 10^{-5}$ s^{-1}). The apparent reaction rates of the present reactions are much slower than those expected for the addition reactions of the rearranged silenes. Indeed, the second-order rate constants of the ene- and [2 + 4] reactions of 2-methy-2-trimethylsiloxy-1,1-bis(trimethylsilyl)silene (**2**, R = Me), generated by the flash photolysis of acetyltris(trimetnylsilyl)silane (**1**, R = Me) at 299.8 K, with DMB were reported to be 0.04 and 0.19 M^{-1} s^{-1}, respectively [5]. These results clearly indicate that the isomerization from **1a** to **2a** is the rate-determining step of the reactions.

Similar experiments were carried out at different temperatures for acylpolysilanes **1a**–**e** to determine the kinetic parameters by Eyring plots, as illustrated in Fig. 1(b). The reactions of **1a**–**1c** always gave the mixtures of [2 + 4] adducts (**3a**–**c**) and ene adducts (**4a**–**c**), while those of **1d** and **1e** afforded [2 + 2] adducts (**5d** and **5e**) together with [2 + 4] adducts (**3d** and **3e**). Products **5d** and **5e** were obtained as the single isomer, although we could not determine their stereo chemistries. In the reactions of **1d** and **1e**, other unidentified 1:1 adducts of the silenes **2** and DMB were also found to be formed in less than each 2% yield by the NMR analyses. That no ene addition occurred for aryl-substituted acylpolysilanes **1d** and **1e** is not unexpected. In fact, it was reported that heating **1d** with DMB [4b] and treatment of photochemically generated **2d** with DMB at room temperature gave **3d** as the sole isolable product [4b]. In contrast to the present reactions of **1d** and **1e**, however, no formation of **5d** was reported in these previous studies, probably due to its low yield. Fig. 2 represents the temperature dependence of product distribution from the reactions of **1a**–**e** with DMB. Interestingly, the ratio of [2 + 4] addition/ene addition or [2 + 2] addition increased as increasing the temperature, although the origin of this temperature dependence is unclear.

The kinetic parameters obtained by Eyring plots are listed in Table 1. Changing the trapping agent from DMB to methanol did not exert an unambiguous influence, again indicating that the trapping process of silenes **2** does not considerably affect the rate constants (see Scheme 2 and Table 1). We also examined the solvent effects on the reaction rates. However, as shown in Table 2, no evident effects were observed when the solvent was changed form C_6D_6 to less polar C_6H_{12} (Table 2). Ionic process is unlikely to be involved in these reactions.

As shown in Table 1, the $\Delta S^{\ddagger}$ values are negatively large, agreeing with the mechanism including a four-centered transition state predicted by the previous theoretical studies (Scheme 1) [6]. The $\Delta H^{\ddagger}$ values for acylpolysilanes

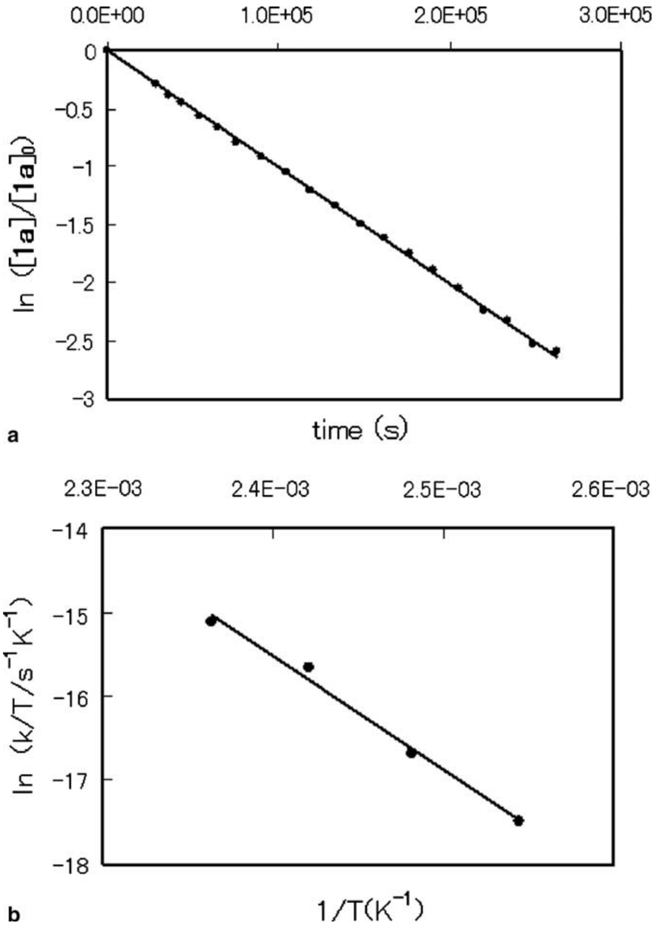


Fig. 1. (a) First-order kinetic plots for the reaction of **1a** in the presence of DMB at 120 °C; (b) Eyring plots of the reactions of the reaction of **1a** in the presence of DMB.

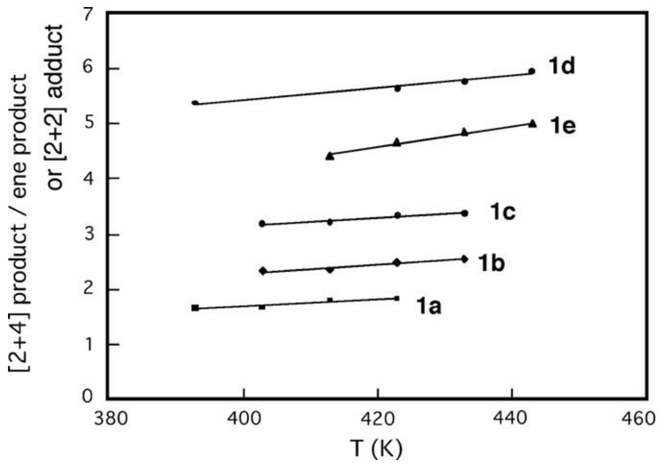


Fig. 2. Temperature dependent product distribution of the reactions of acylpolysilanes **1a**–**e** with DMB.

Table 1
Kinetic parameters of Brook-type isomerization of acylpolysilanes in C_6D_6, based on Eyring plots

Reactant	Trapping agent	$\Delta H^{\ddagger}$ (kcal mol^{-1})	$\Delta S^{\ddagger}$ (cal mol^{-1} K^{-1})
1a	DMB	26.6	−14.2
1a	MeOH	26.8	−13.7
1b	DMB	27.2	−13.9
1c	DMB	27.4	−14.6
1d	DMB	29.4	−11.8
1e	DMB	29.3	−11.5

Table 2
Solvent dependence of the rate constants of the reactions of **1** in the presence of DMB (15 eq.)

Reactant	Temperature (°C)	Rate constant (s^{-1}) (solvent)
1a	150	1.1×10^{-4} (C_6D_6) 1.2×10^{-4} (C_6D_{12})
1b	140	3.3×10^{-5} (C_6D_6) 3.7×10^{-5} (C_6D_{12})
1c	150	3.2×10^{-5} (C_6D_6) 3.2×10^{-5} (C_6D_{12})
1d	150	1.5×10^{-5} (C_6D_6) 1.7×10^{-5} (C_6D_{12})
1e	160	4.1×10^{-5} (C_6D_6) 4.2×10^{-5} (C_6D_{12})

1a–**c** with an alkyl substituent are smaller than those of **1d**, **e** with an aryl substituent, probably due to the electron-donating properties of alkyl substituents, which enhance the nucleophilicity of the carbonyl oxygen. However, this is in contrast to that substitution of the silene carbon by an electron-donating group would lead to an enhancement of the polarization of $Si(\delta+) = C(\delta-)$ destabilizing the double bond thermally. To know more about the substitution effects, we performed theoretical calculations on model reactions of formyldisilane (**1f**) and acetyldisilane (**1g**) at the level of B3LYP/6-311G* and the results are shown in Fig. 3. The transition states of these reactions were obtained with imaginary frequencies of 397.0*i* and 340.0*i* cm^{-1} for **1f** and **1g**, respectively. Both the optimized geometries of the transition states from **1f** and **1g** are similar to each other and to that previously reported for the isomerization of $CH_3COSi(SiH_3)_3$ (see Scheme 1) [6]. However, the H_3Si–O distance for R = Me in the transition state is a little shorter (1.90 Å) than that for R = H (1.92 Å), indicating that the methyl substitution leads to stronger coordination of carbonyl oxygen to the migrating SiH_3 group in the transition state. In addition, as shown in Fig. 3, the activation energy for the isomerization of **1f** is larger than that for **1g** by 2.2 kcal mol^{-1}, although the reaction heat for the isomerization of **1f** is smaller than that of **1g**. These are in good agreement with the present experimental observations described above.

The $\Delta H^{\ddagger}$ values of acylpolysilanes with an alkyl substituent increase as increasing the size of the alkyl groups in the order of **1a** < **1b** < **1c**. This seems to be ascribed to the enhanced electron-donating properties of the alkyl groups in the order of *iso*-Pr < *tert*-Bu < Ad. An alternative explanation is that steric repulsion between the alkyl and the polysilyl groups brings the carbonyl oxygen close to the polysilanyl unit to facilitate the Me_3Si–O interaction. However, the shortest Me_3Si–O distances in **1a** and **1b**, estimated by MO calculations at the RHF/6-31G* level are almost the same (3.25 Å for **1a** and 3.28 Å for **1b**). This alternative, therefore, seems to be less likely.

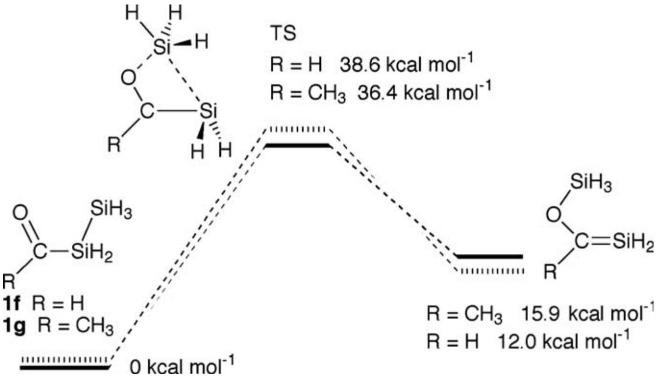


Fig. 3. Energy diagram for the isomerization of **1f** and **1g**, derived from MO calculations at the B3LYP/6-311G* level.

In conclusion, we determined kinetic parameters of Brook-type isomerization of acylpolysilanes, which indicate that the four-centered transition state is important in accordance with the theoretical prediction, reported previously [6]. The isomerization is accelerated by introduction of electron-donating alkyl substituent on the carbonyl carbon, probably due to increased nucleophilicity of the carbonyl oxygen, while the silenes would be destabilized by the same substitution.

Acknowledgments

This work was supported by a Grant-in-Aid for Scientific Research (Nos. 14750687 and 15550038) from the Ministry of Education, Science, Sports, and Culture of Japan, to which our thanks are due. We thank Sankyo Kasei Co., Ltd. and Tokuyama Co., Ltd. for financial support.

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