Barrier Heights and Transition States for the Interconversions of Sila-olefins (Silenes) and Silanediyls. A Theoretical Study

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Ab initio calculations including polarization functions and electron correlation show that sila-olefin–silanediyl interconversions *via* 1,2-hydrogen, 1,2-methyl, and 1,2-silyl shifts proceed only at high temperatures.

In recent years there have been dramatic developments in sila-olefin chemistry.[1] The possible interconversions of sila-olefins and their isomeric silanediyls remain a subject of intensive discussion.[2] Several isomerisations proceeding *via* the 1,2-hydrogen shift have been reported in the last few years.[3—5] However, the calculated barrier heights (*ca.* 40 kcal/mol†)[6,7] and further experimental studies[8—11] have led to the conclusion that unimolecular interconversions *via* the 1,2-hydrogen shift are very unlikely to proceed at room temperature.

In contrast, it has recently been found from both experimental[12] and theoretical[13] studies that the 1,2-silyl shift in silylsilanediyl to disila-olefin conversions proceeds rapidly at room temperature while the 1,2-methyl shift does not readily occur. This finding has prompted us to report *ab initio* calculations of the transition states and barrier heights for the 1,2-silyl and 1,2-methyl group shifts in the interconversion of sila-olefins (**1**) and methylsilanediyls (**2**), equation (1).

$$\underset{(\mathbf{1})}{RHSi{=}CH_2} \rightleftharpoons \underset{(\mathbf{2})}{H\ddot{S}i{-}CH_2R}, \quad R = SiH_3 \text{ or } Me \qquad (1)$$

All calculations were for closed-shell singlets. Geometries were fully optimized at the Hartree–Fock (HF) level with three basis sets (3-21G, 6-31G, and 6-31G*)[14] by using the energy gradient method. The optimized geometries at the HF/6-31G* level are shown in Figures 1 and 2. Electron correlation was incorporated in the HF/6-31G* geometries through second- and third-order Møller–Plesset perturbation (MP2 and MP3) theories,[15] with core-like orbitals held doubly occupied. The results are summarized in Table 1. For comparison, our previous results[7] for R = H are also given in Table 1.

As Table 1 shows, the barriers for the 1,2-methyl and 1,2-hydrogen shifts are too sizeable (40—55 kcal/mol) to be surmounted at room temperature. On the other hand, the barriers for the 1,2-silyl shift are much smaller. At the HF/6-31G level the 1,2-silyl shift barriers are 32.0 [(**1**) → (**2**)] and 39.3 kcal/mol [(**2**) → (**1**)]. Upon addition of polarization functions for Si and C, these barriers decrease to 30.1 and 34.8

† 1 kcal = 4.184 kJ.

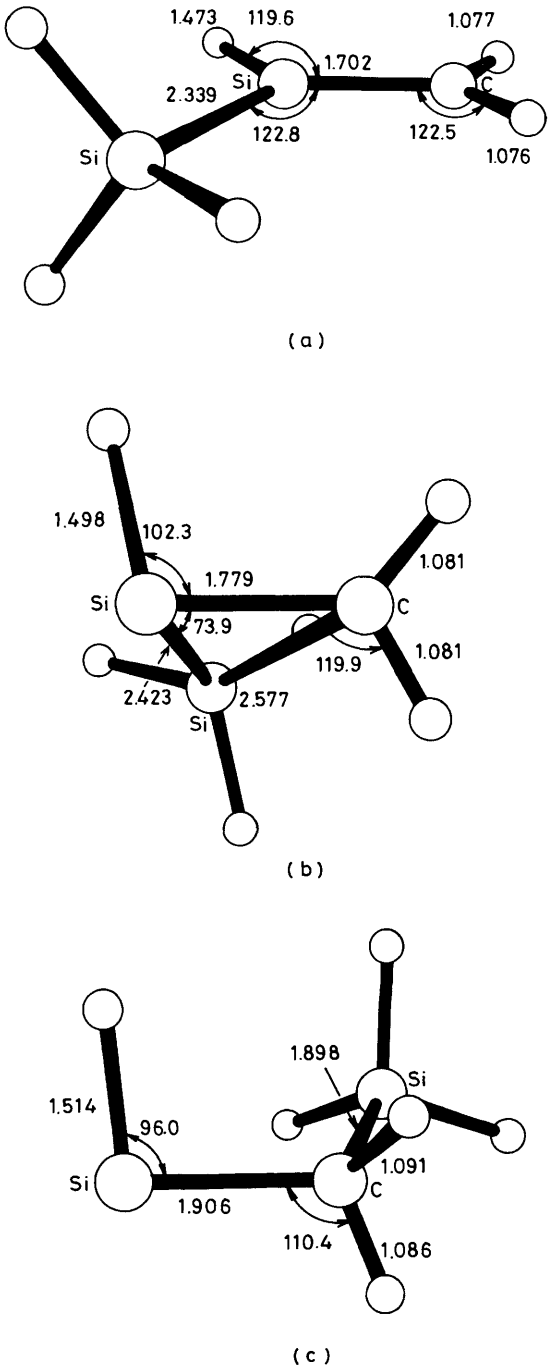

Figure 1. The HF/6-31G* optimized geometries of (a) (SiH_3)-HSi=CH_2, (c) HS̈i–$CH_2(SiH_3)$, and (b) the transition state connecting them in Å and degrees.

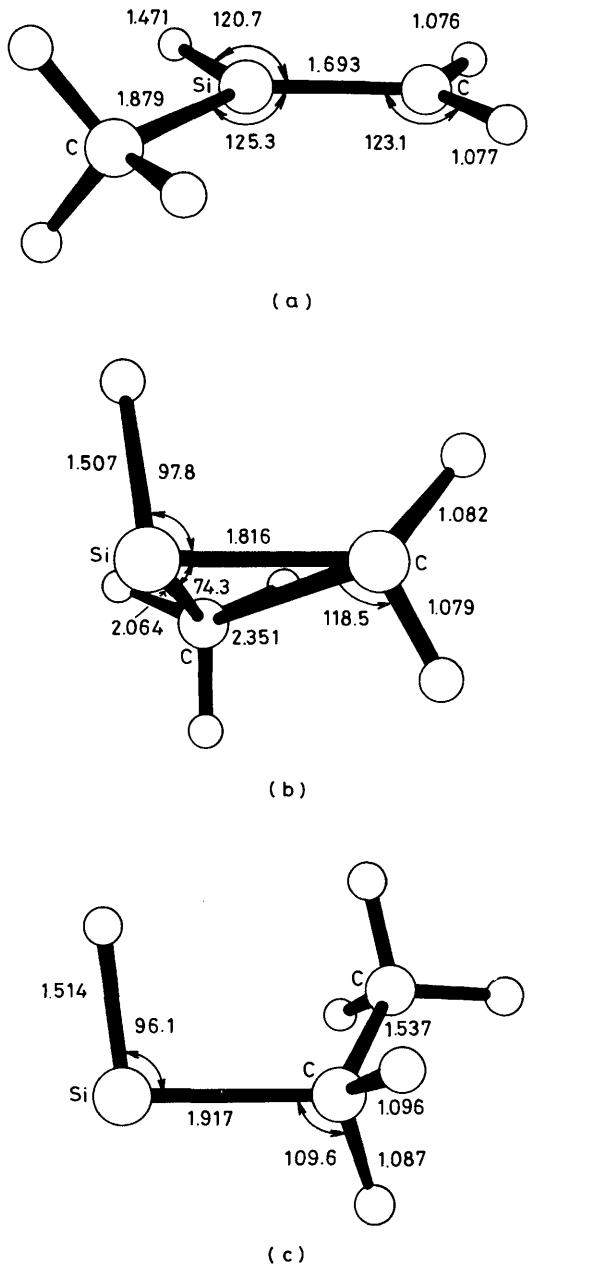

Figure 2. The HF/6-31G* optimized geometries of (a) MeHSi=CH_2, (c) HS̈i-CH_2Me, and (b) the transition state connecting them in Å and degrees.

kcal/mol, respectively. Electron correlation at the MP3/6-31G* level lowers the HF/6-31G* barriers by 3.9 [(**1**) → (**2**)] and 10 kcal/mol [(**2**) → (**1**)]. Here it is instructive to note that the MP3/6-31G* barriers of 26.2 [(**1**) → (**2**)] and 24.8 kcal/mol [(**2**) → (**1**)] are considerably larger than that of 8.5 kcal/mol calculated for the isomerization of $(SiH_3)HSi{=}SiH_2$ to HS̈i–$SiH_2(SiH_3)$.[13] This indicates that silyl groups are much less mobile in sila-olefins and methylsilanediyls than in disila-olefins and silylsilanediyls.

Although calculations at more sophisticated levels of theory may reduce the size of the barriers, the interconversions of sila-olefins and silanediyls are unlikely to proceed rapidly at room temperature. In fact, all the examples observed up to now are restricted to high-temperature experiments: $(Me_3Si)MeSi{=}CH_2$ → MeS̈i–$CH_2(SiMe_3)$ (840 °C)[16,11a] and Me_3Si–S̈i–$CH(SiMe_3)_2$ → $(Me_3Si)_2Si{=}CHSiMe_3$ (450 °C).[17]

The effect of substituents on the ease of the 1,2-shifts has not been discussed. Therefore, we compared the calculated barriers for the 1,2-hydrogen shifts in RHSi=CH_2 → RS̈i–CH_3 for R = H, Me, and SiH_3. At the MP3/6-31G* level the barriers were 42.2 (R = H), 43.5 (R = Me), and 42.8 kcal/mol, (R = SiH_3), there being no significant difference. This suggests that substituents have little effect on the magnitude of the barriers.

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Table 1. Barrier heights for the interconversions of $RHSi{=}CH_2$ (**1**) and $H\ddot{S}i{-}CH_2R$ (**2**) in kcal/mol calculated at several levels of theory.

Level of theory	R = SiH_3		R = Me		R = H[a]	
	(**1**) → (**2**)	(**2**) → (**1**)	(**1**) → (**2**)	(**2**) → (**1**)	(**1**) → (**2**)	(**2**) → (**1**)
HF/3-21G	29.0	43.1	52.4	51.9	42.9	57.8
HF/6-31G	32.0	39.3	53.2	53.7	43.4	57.5
HF/6-31G*	30.1	34.8	55.9	50.5	43.5	49.3
MP2/6-31G*	26.4	23.5	55.5	42.6	44.5	42.4
MP3/6-31G*	26.2	24.8	54.7	44.4	42.2	43.0

[a] Taken from ref. 7.

the Computer Centre of the Institute for Molecular Science using an IMS version of the GAUSSIAN 80 series of programs.[18]

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