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Photochemical 1,3-Silyl Migration in Allylsilanes Occurring with Inversion of Silyl Configuration[1]

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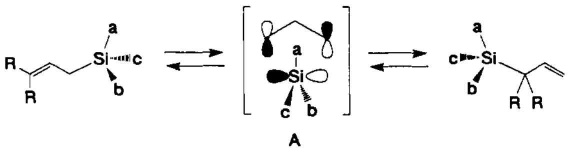
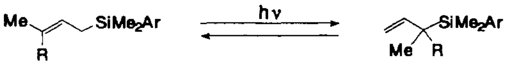
Summary: In apparent disagreement with the prediction by the Woodward–Hoffmann rule, facile intramolecular 1,3-silyl migration of allyl- and propargylsilanes with aromatic substituents at the silicon atom took place reversibly in various solvents under irradiation with 254-nm light, accompanied by the inversion of the silyl configuration.

Sir: Among a large number of facile 1,3-silyl migrations reported, the migration between carbon atoms in an allylsilane system is of particular interest from a mechanistic point of view. Whereas many 1,3-silyl migrations are attributed to intramolecular nucleophilic substitutions proceeding with retention of configuration at silicon,[2] the carbon to carbon migration has been fully characterized as a symmetry-allowed [1,3] sigmatropic rearrangement accompanied by the inversion of configuration at silicon. The transition state has been represented as the structure A in eq 1.[3] The thermal migration requires, however, rather high activation energy of ca. 50 kcal/mol.



(1)

Photochemical 1,3-silyl migration from carbon to carbon[4] and a number of the related migrations[5,6] have been reported but mostly without the stereochemical and mechanistic details. We report herein the first detailed mechanistic study of photochemical 1,3-silyl migration from carbon to carbon in allylsilanes with aromatic substituents at the silicon atom, occurring with inversion of silyl configuration.



(2)

1a, R= Me, Ar= Ph
1b, R= Me, Ar= Naphthyl
1c, R= H, Ar= Ph

2a, R= Me, Ar= Ph
2b, R= Me, Ar= Naphthyl
2c, R= H, Ar= Ph

Typically, irradiation of ca. 0.05 M hexane solution of prenyldimethylphenylsilane (**1a**)[7] with a 125-W low-pressure mercury arc lamp for 1 h gave a mixture of **1a** and the isomer (2-methyl-3-buten-2-yl)dimethylphenylsilane (**2a**)[8] in 29 and 52% yields, respectively, together with 5% of phenyldimethylsilane (**3**).[9] Similar irradiation of **2a** gave **1a** in 32% yield with 59% recovery of **2a**. The results of the photoisomerization are summarized in Table I. In contrast to the reported thermal reaction,[3] the present photomigration occurs reversibly, giving a sterically more crowded allylsilane as the major product at the photostationary state.

Table I. Product Distribution for Photoreactions of Allyldimethylarylsilanes[a]

allylsilane	solvent	products and yields,[b] % 1	2	$ArMe_2SiH$
1a	hexane	29	52	5
1a	benzene	31	54	8
1a	methanol	30	32	4
2a	hexane	32	59	–[c]
1b	hexane	26	57	–[c]
1c	hexane	28	53	2

[a] A ca. 0.05 M solution of an allylsilane was irradiated for 1–2 h in a quartz tube with a 125-W low-pressure Hg arc lamp. [b] Yield determined by GLC. [c] Yield not determined.

A similar but much slower photoisomerization was observed for propargyldimethylphenylsilane: The 1,3-silyl migration across a linear framework gave allenyldimethylphenylsilane in 28% after irradiation for 18 h with the recovery of the propargylsilane (25%). Prenyltrimethylsilane was inert under the similar photochemical conditions.

Intramolecularity of the reaction was confirmed by a crossover experiment. Thus, when a 1:1 mixture of prenylethylmethylphenylsilane (**4**) and **1c** in hexane was photolyzed for 4.7 h, (2-methyl-3-buten-2-yl)ethylmethylphenylsilane (54%) and **2c** (54%) were obtained together with the recovery of **4** (29%) and **1c** (27%). No cross-products were detected in the reaction mixture.

A prenylsilane having the 1-pyrenyl group as an aromatic group, prenyldimethyl(1-pyrenyl)silane, was inert, while the facile 1,3-silyl migration of prenyldimethyl(1-naphthyl)silane (**1b**) occurred under the similar photochemical conditions. Comparing the singlet energies among benzene, naphthalene, and pyrene, which values are 110, 92, and 77 kcal/mol, respectively,[10] the result may suggest that the photochemical migration in a prenylarylsilane needs the energy to be more than 80 kcal/mol

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(1) Chemistry of Organosilicon Compounds. 261.

(2) For a review, see: Brook, A. G.; Bassingdale, A. R. *Rearrangements in Ground and Excited States*; de Mayo, P., Ed.; Academic Press: New York, 1980; Vol. 2, Essay 9.

(3) (a) Kwart, H.; Slutsky, J. *J. Am. Chem. Soc.* **1972**, *94*, 2515. (b) Slutsky, J.; Kwart, H. *Ibid.* **1973**, *95*, 8678.

(4) Ishikawa, M.; Nakagawa, K.; Ishiguro, M.; Ohi, F.; Kumada, M. *J. Organomet. Chem.* **1978**, *152*, 155. We have recently reported far less effective 1,3-silyl migration from carbon to carbon in benzyltrimethylsilane: Kira, M.; Yoshida, H.; Sakurai, H. *J. Am. Chem. Soc.* **1985**, *107*, 7767.

(5) Photochemical 1,3-germyl migration in cinnamylgermanes was reported without mechanistic details: Kobayashi, M.; Kobayashi, M. *Chem. Lett.* **1986**, 385. In contrast to our system, the germyl migration should involve direct photoexcitation of the cinnamyl π system.

(6) A number of examples for formal photochemical 1,3-silyl migration have been reported. Si–O: (a) Brook, A. G.; Haris, J. W.; Lennon, J.; Sheikh, M. E. *J. Am. Chem. Soc.* **1979**, *109*, 83. (b) Baines, K. M.; Brook, A. G. *Organometallics* **1987**, *6*, 692. Si–C: (a) Ishikawa, M.; Fuchikami, T.; Sugaya, T.; Kumada, M. *J. Am. Chem. Soc.* **1975**, *97*, 5923. (b) Ishikawa, M.; Fuchigami, T.; Kumada, M. *J. Organomet. Chem.* **1978**, *149*, 37. (c) Sakurai, H.; Kamiyama, Y.; Nakadaira, Y. *J. Am. Chem. Soc.* **1976**, *98*, 7424. C–O: Wright, B. B. *J. Am. Chem. Soc.* **1988**, *110*, 4456.

(7) **1a** was obtained by the in situ Grignard reaction of prenyl chloride, magnesium, and phenyldimethylchlorosilane in ether in 58% yield: ^1H NMR (CCl_4) δ 0.26 (s, 6), 1.47 (s, 3), 1.59 (d, 2, J = 8 Hz), 1.65 (s, 3), 5.09 (t, 1, J = 8 Hz), 7.0–7.5 (m, 5). **1b** and **1c** were prepared by the reaction of prenyldimethylfluorosilane with the corresponding aryllithium. Spectroscopic data will be reported elsewhere.

(8) **2a** was isolated by preparative GLC: ^1H NMR (CCl_4) δ 0.24 (s, 6), 0.97 (s, 6), 4.5–4.9 (m, 2), 5.73 (dd, 1, J = 11, 17 Hz), 7.1–7.5 (m, 5).

(9) The hydrosilane would be formed by simple δ-elimination. Intermediacy of free silyl radicals is incompatible with the results of a crossover experiment. Thus, irradiation of a mixture of $(CH_3)_2C{=}CHCH_2SiMeEtPh$ and $(CD_3)_2C{=}CHCH_2SiMe_2Ph$ in hexane gave only HSiMeEtPh and $DSiMe_2Ph$ as hydrosilanes; neither DSiMeEtPh nor $HSiMe_2Ph$ was detected.

(10) Murov, S. L. *Handbook of Photochemistry*; Marcell Dekker: New York, 1973.

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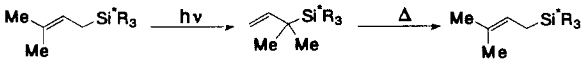
of the exited singlet state, which would be an aromatic π,π^* state. Triplet sensitized excitation of a prenylarylsilane results in no 1,3-silyl migration: **1c** was intact when irradiated in the presence of benzophenone with longer wavelength light than 350 nm. In order to obtain kinetic profile for the photochemical 1,3-silyl migration, we have determined the fluorescence life time (τ_f) and the quantum yield (ϕ_f) for allyldimethylnaphthylsilane (**5**) and propyldimethylnaphthylsilane (**6**): τ_f values were 58.5 and 62.6 ns for **5** and **6**, respectively, and $\phi_f(\mathbf{5})/\phi_f(\mathbf{6})$ was 1.08. The rate and the quantum yield for the 1,3-silyl migration of **5** were thus estimated to be 1.03×10^6 s^{-1} and 0.06, respectively, where the rate constants for fluorescence, intersystem crossing, and the radiationless processes other than 1,3-silyl migration were assumed to be the same between **5** and **6**.

Irradiation of optically active prenylmethyl(1-naphthyl)phenylsilane (**7**, $[\alpha]_D$ −3.6°, *c* 3.6, cyclohexane)[11] in hexane gave (2-methyl-3-buten-2-yl)silane **8**,[13] which showed $[\alpha]_D$ −3.8° (*c* 3.2, cyclohexane) after purified with GPC. Although absolute configuration as well as optical purities of both the starting **7** and produced **8** were not determined, the stereochemical consequence of the photochemical migration was derived from the result of the further thermolysis of the isolated **8** ($[\alpha]_D$ −3.8°) at 590 °C: The thermal isomerization of **8** gave **7** having $[\alpha]_D$ −3.5° (*c* 2.3, cyclohexane) after purification, whose value was essentially the same as that for the starting **7**, being indicative of the overall retention of configuration at silicon during the reaction sequence from **7** to **8** to **7** (eq 3).



(3)

7, $[\alpha]_D$ -3.6 8, $[\alpha]_D$ -3.8 7, $[\alpha]_D$ -3.5

Si*R$_3$ = SiMePhNaph-1

Repeated runs gave similar results. Since the thermal 1,3-silyl migration has been confirmed to occur with complete inversion of configuration at the silicon atom,[3] the photochemical migration must also take place with inversion of configuration!

The results imply that the photochemical 1,3-silyl migration of allylsilanes follows suprafacial [1,3]-shift with inversion at silicon, in apparent disagreement with the prediction by the Woodward–Hoffmann rules:[14] During the migration the allylsilane molecule would jump from the funnel on the singlet excited surface to the ground-state surface at the similar molecular geometry to A in eq 1.

The isomer ratio between **1a** and **2a** at the photostationary state in pentane changed dramatically depending on temperatures. The ratio, **2a**/**1a**, changed from 2.06 to 6.22 between 0 and −90 °C. Excellent linear correlation between ln (**2a**/**1a**) and 1/*T* was observed with the correlation coefficient of 0.999$_6$. Further works should be required to reach the origin of this interesting temperature dependence.

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[11] Optically active **7** was prepared by the reaction of excess prenylmagnesium chloride with optical active chloro(1-naphthyl)phenylmethylsilane ($[\alpha]_D$ −6.2°, cyclohexane; 98% ee)[12] in ether in 47% yield: ^{1}H NMR (CDCl$_3$) δ 0.59 (s, 3), 1.34 (s, 3), 1.54 (s, 3), 2.04 (d, 2, *J* = 8 Hz), 5.10 (t, 1, *J* = 8 Hz), 7.1–7.9 (m, 12).

[12] Sommer, L. H.; Frye, C. L.; Parker, G. A.; Michael, K. W. *J. Am. Chem. Soc.* **1964**, *86*, 3271.

[13] **8**: ^{1}H NMR (CDCl$_3$) δ 0.70 (s, 3), 1.22 (s, 3), 1.23 (s, 3), 4.94 (d, 1, *J* = 17 Hz), 4.99 (d, 1, *J* = 11 Hz), 6.10 (dd, 1, *J* = 11, 17 Hz), 7.1–8.0 (m, 12). Isolation was achieved by a recycle GPC (Japan Analytical Industry Co., Ltd., an LC-08 Model with JAIGEL-1H and 2H column 20 mm φ × 600 mm).

[14] Woodward, R. B.; Hoffmann, R. *Angew. Chem., Int. Ed. Engl.* **1969**, *8*, 781.

Reversal of the Nature of Substituent Effect by Changing the Number of the α-Substituent. Relative Ease of Formation of the Three α-Fluoromethyl Radicals

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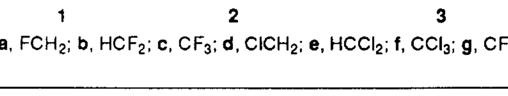
Summary: The nature of α-F substituent effect on the methyl radical was found for the first time to change with the number of C–F bonds, i.e., it changes from the stabilizing effect in mono- and difluoromethyl radicals to the destabilizing effect in trifluoromethyl radical.

Sir: It is usually taken for granted that although the effect of successive substitution by a particular substituent Y on the same carbon atom is not necessarily additive, the nature of Y, e.g., whether electron-attracting or -donating, does not change in the YCH$_2$, HCY$_2$, CY$_3$ series.[1] Apparently, it has never been experimentally demonstrated that the nature of the substituent effect can be reversed in the aforesaid series. Some time ago, however, on the basis of the speculation that there could be two opposing aspects of the substituent effect of α-fluorine on the methyl radical, we proposed the following stability order, i.e., FCH$_2^\bullet$ and HCF$_2^\bullet$ > CH$_3^\bullet$ > CF$_3^\bullet$, in which the nature of the α-F was inverted from spin-stabilizing to spin-destabilizing.[2] This paper presents conclusive epxerimental evidence that the nature of α-F substituent effect on the methyl radical indeed changes with the number of C–F bonds.

In a previous paper we have reported the relative rate of formation of CF$_3^\bullet$ and CH$_3^\bullet$ from the β-scission of a common precursor, the trifluoro *tert*-butoxy radical.[3] By using the same methodology, the relative rates of formation of FCH$_2^\bullet$, HCF$_2^\bullet$, and CF$_3$CH$_2^\bullet$ radicals, as well as ClCH$_2^\bullet$ and HCCl$_2^\bullet$, from the β-scission of alkoxy radicals **3**, have now been measured.


$$\mathrm{R{-}C(CH_3)_2{-}OCl} \text{ or } \mathrm{(R{-}C(CH_3)_2{-}OCO_2)_2} \xrightarrow{\Delta} \mathrm{R{-}C(CH_3)_2{-}O^\bullet} \qquad (1)$$

1 **2** **3**

R = **a**, FCH$_2$; **b**, HCF$_2$; **c**, CF$_3$; **d**, ClCH$_2$; **e**, HCCl$_2$; **f**, CCl$_3$; **g**, CF$_3$CH$_2$

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[1] (a) Merenyi, R.; Janousek, Z.; Viehe, H. G. In *Substituent Effects in Free Radical Chemistry*; Viehe, H. G., et al., Eds.; Reidel Publishing Co.: Dordrecht, The Netherlands, 1986; p 301. (b) Susmann, R. *Ibid.* p 143. (c) Birkhofer, H.; Beckhaus, H. D.; Ruechardt, C. *Ibid.* p 199.

[2] Fluorocarbon Group of SIOC, *Sci. Sin.* (*Engl. Ed.*) **1977**, *20*, 353.

[3] Jiang, X. K.; Li, X. Y.; Wang, K. Y. *J. Chem. Soc., Chem. Commun.* **1986**, 745.

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