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Photo-Induced Electron Transfer Reaction of Polysilanes. Intramolecular Trapping of a Transient Silyl Radical Cation with a Nucleophile[1)]

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The radical cation, produced in photo-induced electron transfer of polysilanyl alkanols, can be trapped efficiently intramolecularly with the hydroxyl group. The silyl radical generated in the process is trapped by the solvent employed. A good Hammett relationship is observed in aryldisilanylalkanols between the relative reactivities of the Si-Si bond and σ^+ constants of the substituent on the aryl group.

Polysilanes undergo photo-induced chlorinative cleavage to give the corresponding chlorosilanes on irradiation in CH_2Cl_2-CCl_4 in the presence of a sensitizer, such as 9,10-dicyanoanthracene (DCA).2) Together with the evidence of diffusion-controlled quenching of DCA fluorescence, the exothermic free energy change on the electron transfer indicated that the Si-Si bond cleavage should proceed via a transient polysilanyl radical cation generated by electron transfer from the polysilane to the singlet excited state of DCA. The radical nature of the intermediate is evidenced by the formation of both chlorosilanes and hexachloroethane in the presence of CCl_4.2) However, trapping of the cationic site of the transient intermediate by a nucleophilic solvent, such as an alcohol is rather difficult under the reaction conditions,3) partly due to the extremely short life time of the radical cation and/or rapid back electron transfer from the DCA radical anion. Therefore, it is desirable to choose an adequate system to prove the cationic nature of the intermediates.

To increase efficiency of the nucleophilic trap, we have designed molecules which contain both nucleophilic and cationic centers in the same molecule, and thus several types of polysilanylalkanols **1** and **2** are prepared from α,ω-chloroalkanols. 3-(Pentamethyldisilanyl)propanol **1** was prepared by the reaction of the Grignard reagent derived from benzyl 3-chloropropyl ether and chloropentamethyldisilane followed by removal of the benzyl group by catalytic hydrogenation (10% Pd).4) 4-Polysilanylbutanols **2** were prepared as shown in Scheme 1. Thus, after protection of the hydroxyl group of 4-chlorobutanol with the (dimethyl)isopropylsilyl group, the silyl ether obtained was converted to the corresponding Grignard reagent which was

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$$\text{HO-(CH}_2)_4\text{-Cl} \xrightarrow{\text{i-PrMe}_2\text{SiCl / Et}_3\text{N}} \text{i-PrMe}_2\text{SiO-(CH}_2)_4\text{-Cl}$$

$$\text{i-PrMe}_2\text{SiO-(CH}_2)_4\text{-Cl} \xrightarrow[\text{2) Cl(SiMe}_2)_2\text{R}]{\text{1) Mg}} \text{i-PrMe}_2\text{SiO-(CH}_2)_4\text{-(SiMe}_2)_2\text{R}$$

$$\xrightarrow[\text{HCl}]{} \underset{\mathbf{2}}{\text{HO-(CH}_2)_4\text{-(SiMe}_2)_2\text{R}}$$

2a : R = Me 43%

2b : R = Me_3Si 46%

2c : R = C_6H_4-X, X = H, 64%

2d : R = C_6H_4-X, X = p-Me, 58%

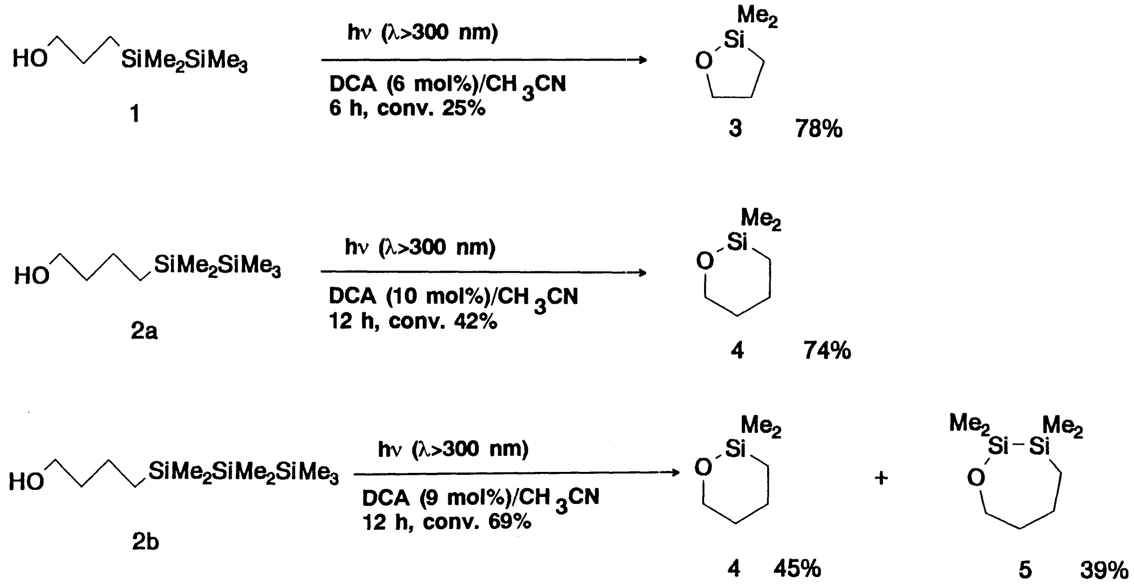
2e : R = C_6H_4-X, X = p-MeO, 50%

2f : R = C_6H_4-X, X = p-CF_3, 64%

Scheme 1.

allowed to react with chloropolysilanes. The coupling products yield polysilanylbutanols **2** on acid hydrolysisunder usual conditions.[5] Yields were 36 – 64% based on the silyl ether.

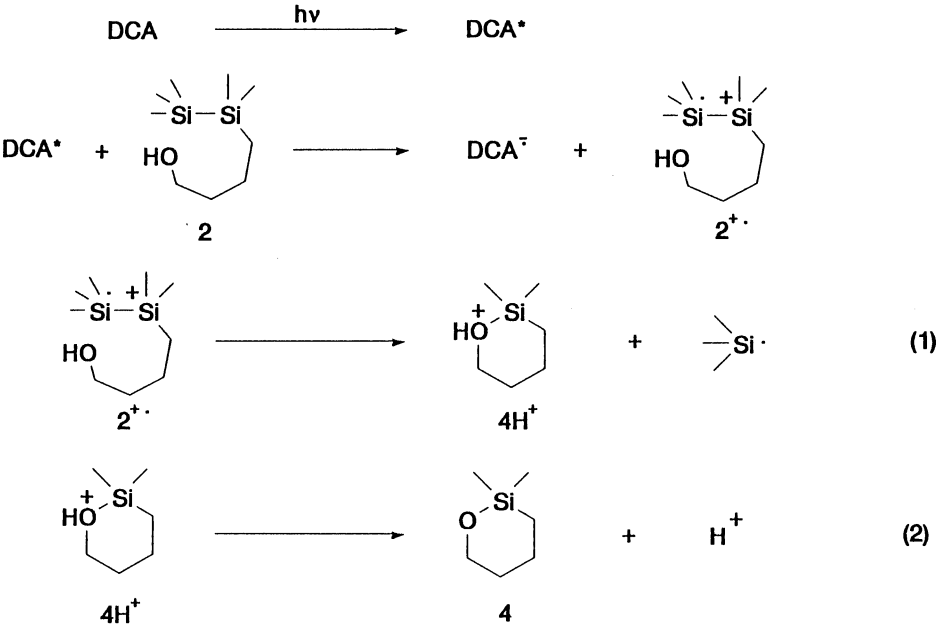
Photolysis of **1** in CH_3CN containing a small amount of DCA (0.1 mol/l) with a high pressure Hg arc lamp through a Pyrex filter caused cleavage of the Si–Si bond by intramolecular participation of the hydroxyl group to give a cyclic silyl ether **3**[6] in 78% yield. Similar photolysis of the disilanylbutanol **2a** gave a six-membered cyclic silyl ether **4**[7] but the trisilanylbutanol **2b** afforded **4** and **5** in 45 and 39% yield, respectively, as shown in Scheme 2.[8]



Scheme 2.

Similarly, the DCA sensitized photoreaction of phenylpentamethyldisilanylbutanol **2c** gave **4** in high yield. Interestingly, the fate of the phenyldimethylsilyl moiety was quite dependent on the reaction media. Thus, in CH_2Cl_2–CCl_4, chlorodimethylphenylsilane (91% with **4**, 96%), in benzene, dimethyldiphenylsil–

ane (22% with **4**, 53%), and in EtOH–CH_3CN (1:3), ethoxydimethylphenylsilane (100% with **4**, 100%) were obtained, respectively. These results can be accounted for by Scheme 3. Electron transfer from **2** to the singlet excited state of DCA (DCA*) generates the geminate radical ions composed of the DCA radical anion and the polysilanyl radical cation $\mathbf{2}^{+\bullet}$, in which the hydroxyl group attacks cationic site intramolecularly to give the protonated cyclic silyl ether $\mathbf{4}H^+$ and the corresponding silyl radical (Eq. 1). Deprotonation of $\mathbf{4}H^+$ yields **4** (Eq. 2). It is noteworthy that the intramolecular nucleophilic trapping prevails over the intermolecular. Chemical evidence for the intervention of the silyl radical is provided by photolysis of **2c** in the presence of DCA mentioned above; namely, the formation of the dimethyldiphenylsilane in benzene is readily rationalized by the reaction of the dimethylphenylsilyl radical with the solvent benzene.[9)] This is further substantiated by the formation of chlorodimethylphenylsilane on the photolysis in CH_2Cl_2–CCl_4. Chlorodimethylphenylsilane should arise from the dimethylphenylsilyl radical by abstraction of a chlorine from CCl_4. On the other hand, the formation of ethoxydimethylphenylsilane is not straightforward. A possibility is that the silyl radical is transformed to the silyl cation by means of electron transfer to the ground state of DCA followed by trapping with ethanol to give ethoxydimethylphenylsilane.[3,10)] Addition of the radical to CH_3CN followed by ethanolysis is another possibility, though.



Scheme 3.

Next, the substituent effect on the disilanyl part of the alkanol **2** was examined. The relative reaction rates among **2c** – **2f** have been obtained by the competitive photolysis in CH_3CN–MeOH containing a small amount of DCA. The values are $k_{2c} : k_{2d} : k_{2e} : k_{2f} = 1.0 : 1.2 : 1.9 : 0.68$. The logarithm of these relative rates against substituent constant σ^+ affords a good linear relationship where reaction constant ρ is -0.32 ($r = 0.996$). The small but negative ρ value is consistent with the view that the Si–Si bond acts as an electron donor. Quenching rate constants of DCA fluorescence with **2c** – **2f** also depend on the substituent on the phenyl group as shown in Table 1. Thus, the quenching rate increases with increasing electron donating nature of substituents and *vice versa*. Similar trends are observed in the oxidation peak potentials and the calculated free energy change on the electron transfer as shown in Table 1. These results accord with the reaction sequence shown in Scheme 3.

Table 1. DCA Fluorescence Quenching with Aryldisilanylbutanols **2**

Compound	$k_q/10^{10}mol^{-1}s^{-1}$ a)	E_{ox} b)	ΔG/kcal mol^{-1} c)
2e (X = p–OMe)	1.36	1.26	-21.4
2d (X = p–Me)	0.97	1.68	-11.7
2c (X = H)	0.70	1.76	- 9.9
2f (X = p–CF_3)	0.60	1.82	- 8.5

a) Rate constants for fluorescence quenching of DCA in CH_3CN obtained by Horiba NAES–1000 time–resolved fluorimeter.

b) Oxidation peak potentials obtained by cyclic voltammetry: Pt electrode, tetrabutylammonium perchlorate in CH_3CN vs. SCE.

c) Calculated free energy change on the electron transfer in CH_3CN.[11)]

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4) **1**: ^{1}HNMR ($CDCl_3$) δ 0.15 (s, 6H), 0.18 (s, 9H), 0.58–0.82 (m, 2H), 1.42–1.78 (m, 2H), 2.05 (s, 1H), 3.62 (t, 2H).
5) **2a**: ^{1}HNMR($CDCl_3$) δ 0.12 (s, 6H), 0.18 (s, 9H), 0.55–0.82 (m, 2H), 1.28–1.83 (m, 4H), 2.12 (s, 1H), 3.72 (t, 2H). **2b**: ^{1}HNMR ($CDCl_3$) δ 0.12–0.17 (br. s, 21H), 0.58–0.85 (m, 2H), 1.25–1.78 (m, 5H), 3.72 (t, 2H). **2c**: ^{1}HNMR ($CDCl_3$) δ 0.15 (s, 6H), 0.45 (s, 6H), 0.58–0.85 (m, 2H), 1.22–1.82 (m, 5H), 3.68 (t, 2H), 7.52–7.58 (m, 5H). **2d**: ^{1}HNMR ($CDCl_3$) δ 0.20 (s, 6H), 0.30 (s, 6H), 0.56–0.78 (m, 2H), 1.09 (s, 1H), 1.23–1.41 (m, 2H), 1.46–1.56 (m, 2H), 2.32 (s, 3H), 3.57 (t, 2H), 7.14 (d, 2H), 7.32 (d, 2H). **2e**: ^{1}HNMR ($CDCl_3$) δ 0.15 (s, 6H), 0.45 (s, 6H), 0.55–0.88 (m, 2H), 1.22–1.85 (m, 5H), 3.65 (t, 2H),3.88 (s, 3H), 6.95 (d, 2H), 7.42 (d, 2H). **2f**: ^{1}HNMR ($CDCl_3$) δ 0.02 (s, 6H), 0.35 (s, 6H), 0.51 - 0.62 (m, 2H), 1.24–1.36 (m, 2H), 1.47–1.58 (m, 3H), 3.58 (t, 2H), 7.54 (s, 4H).
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