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Rearrangement of Silanorbornadienes via Photoinduced Electron-transfer

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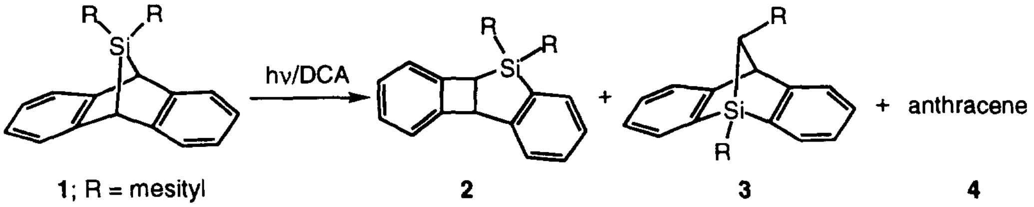
Abstract: Irradiation of silanorbornadienes **1** using 9,10-dicyanoanthracene as a sensitizer afforded two isomers **2** and **3** accompanied with anthracene. In the presence of molecular oxygen, dioxide **5** was obtained as an additional product. These reactions are explained in terms of the initial electron donor-acceptor interaction followed by skeletal rearrangement.

Electron-transfer chemistry of organometallic compounds has attracted considerable attention from the mechanistic and synthetic viewpoints. Numerous studies have revealed that the reactions of group 14 metal radical cations seem to be classified into the following four categories: alcoholysis,1) chlorination,2) oxygenation,3) and addition to electron-deficient π-bonds.4) Recently we indicated that disilabicycloocta-[2.2.2]diene derivatives undergo electron-transfer reaction as electron donors,5) which is consistent with the fact that σ-π conjugation between the benzene π-system and the Si-C σ bond in $(CH_3)_3SiCH_2$-substituted benzenes causes the destabilization and the separation of the degenerated HOMOs of benzene.6) Our continuous interest in the organosilicon radical cations has led us to investigate the electron-donating property of another class of geometrically fixed polycyclic organosilanes, a dibenzosilanorbornadiene (**1**),7) which is also expected to act as a good electron donor due to the σ-π conjugation and its ring strain. We now report photosensitized reaction of **1**, which would provide a new aspect of organosilicon cation radicals.

Irradiation of a solution of **1** (1.5×10^{-2} M) and 9, 10-dicyanoanthracene (DCA, 1.3×10^{-3} M) in 30 ml degassed dry CH_2Cl_2 with two 500 W tungsten-halogen lamps (passing through an aqueous $NaNO_2$ solution filter, cutoff < 400 nm) gave **2**, **3**, and anthracene (**4**) in 31, 36, and 18% yields, respectively.

Scheme 1.



The structures of **2** and **3** were determined on the basis of spectral data and finally established by X-ray crystal analyses.8,9) ORTEP drawings of **2** and **3** are shown in Figure 1. Products **2** and **3** were stable and did not isomerize even on prolonged irradiation. The photoreaction of **1** occurred also in CH_3CN but proceeded slowly in benzene. Previously, we have found that the ultraviolet photolysis of **1** with a medium pressure Hg arc lamp in the presence of silylene trapping reagents gives **2**, **3**, **4**, and the corresponding silylene adducts.7,10) However, no reaction took place when **1** was irradiated with a longer wavelength light than 400 nm in the absence of a sensitizer. Meanwhile, addition of 1,4-diazabicyclo[2.2.2]octane (DABCO), which has a lower oxidation potential than that of **1**,11) suppressed the consumption of **1**. The free energy change (ΔG)12) is -12.9 kcal/mol, and is indicative of exothermic electron-transfer from **1** to the ^{1}DCA*. The fluorescence of DCA was efficiently quenched with **1** ($k_q = 7.9 \times 10^9\ M^{-1}s^{-1}$). On the other hand, neither exciplex emission nor charge-transfer absorption was observed between **1** and DCA. Whereas the results presented above cannot exclude possibilities of initial formation of an exciplex or a charge-transfer complex, it would be reasonable to discuss these reactions as a stepwise process induced by initial electron-transfer from **1** to ^{1}DCA* as outlined in Scheme 2.13)

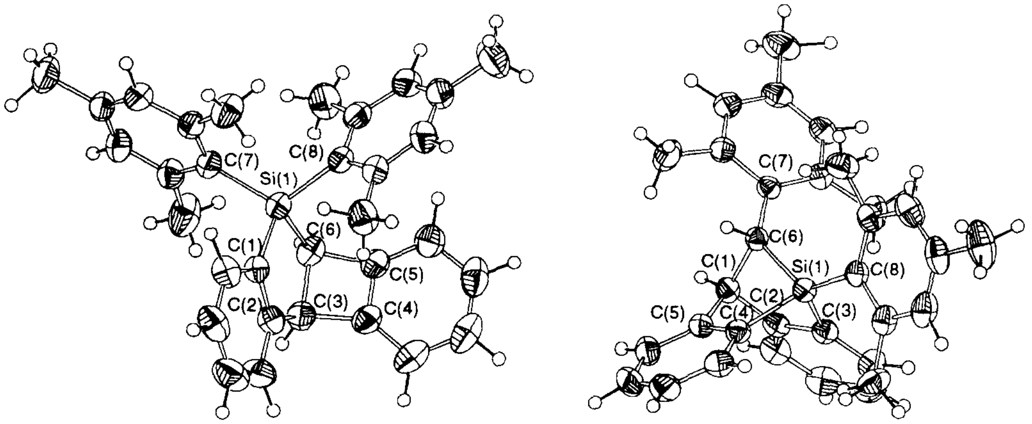
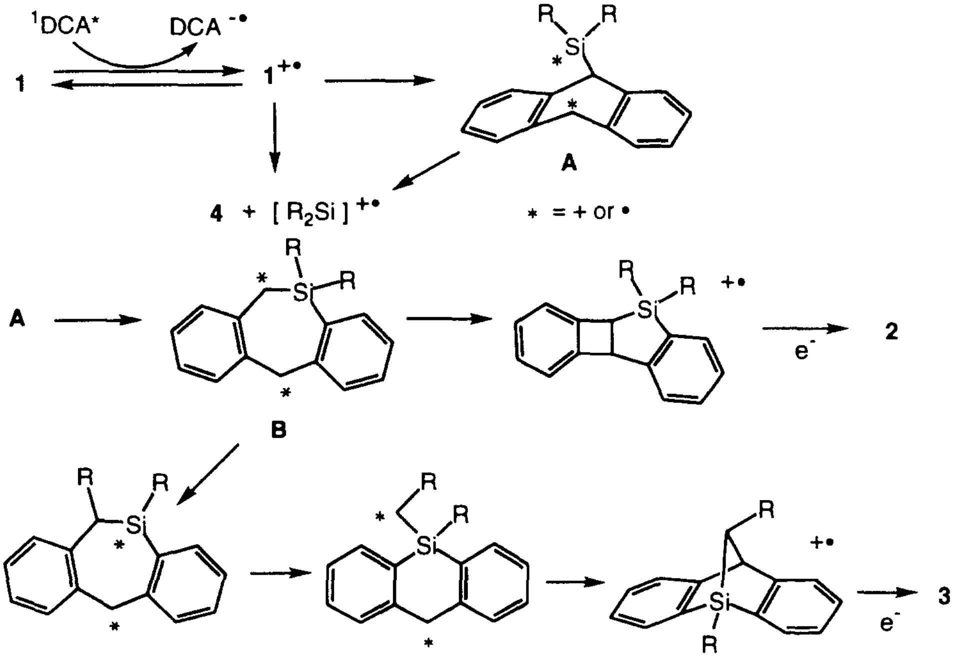


Figure 1. ORTEP drawings of 2 (left) and 3 (light). Selected bond lengths (Å) and angles (°) of **2**: Si(1)-C(6) 1.904(2), Si(1)-C(7) 1.901(2), Si(1)-C(8) 1.896(2), Si(1)-C(1) 1.882(2), C(3)-C(6) 1.597(3), C(3)-C(2) 1.510(3), C(3)-C(4) 1.527(3), C(6)-C(5) 1.531(3), C(1)-C(2), 1.398(3), C(4)-C(5) 1.374(3), C(6)-Si(1)-C(7) 121.5(1), C(6)-Si(1)-C(8) 104.3(1), C(6)-Si(1)-C(1) 93.1(1), C(7)-Si(1)-C(8) 112.1(1), C(7)-Si(1)-C(1) 105.5(1), C(8)-Si(1)-C(1) 119.9(1), C(6)-C(3)-C(2) 111.5(2), C(6)-C(3)-C(4) 86.1(2), C(2)-C(3)-C(4) 114.9(2), Si(1)-C(1)-C(2) 111.5(2), Si(1)-C(6)-C(3) 106.5(1), Si(1)-C(6)-C(5) 115.6(2), C(3)-C(6)-C(5) 85.6(2), C(3)-C(2)-C(1) 117.4(2), C(6)-C(5)-C(4) 94.3(2), C(3)-C(4)-C(5) 94.0(2). Selected bond lengths(Å) and angles(°) of **3**: Si(1)-C(6) 1.915(2), Si(1)-C(8) 1.869(3), Si(1)-C(3) 1.886(3), Si(1)-C(4) 1.884(3), C(1)-C(6) 1.591(4), C(1)-C(2) 1.531(4), C(1)-C(5) 1.528(4), C(6)-C(7) 1.523(3), C(3)-C(2) 1.409(4), C(4)-C(5) 1.408(3), C(6)-Si(1)-C(8) 128.2(1), C(6)-Si(1)-C(3) 92.9(1), C(6)-Si(1)-C(4) 88.9(1), C(8)-Si(1)-C(3) 122.6(1), C(8)-Si(1)-C(4) 117.3(1), C(3)-Si(1)-C(4) 98.8(1), C(6)-C(1)-C(2) 106.7(2), C(6)-C(1)-C(5) 103.6(2), C(2)-C(1)-C(5) 108.4(2), Si(1)-C(6)-C(1) 90.5(2), Si(1)-C(6)-C(7) 134.0(2), C(1)-C(6)-C(7) 113.2(2), Si(1)-C(3)-C(2) 103.2(2), C(1)-C(2)-C(3) 114.0(2), Si(1)-C(4)-C(5) 104.6(2), C(1)-C(5)-C(4) 112.4(2).

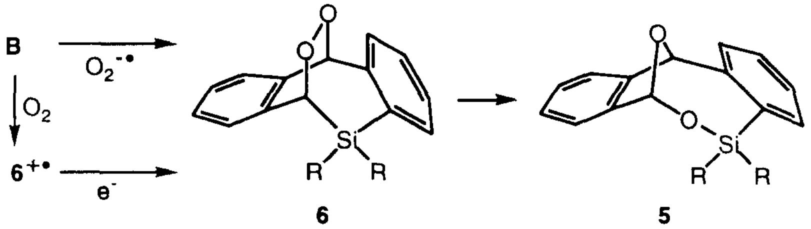
Probably, electron transfer occurs from the bridge C-Si bond of **1** affording a cation radical $1^{+\bullet}$. Then, $1^{+\bullet}$ would collapse to give **A** by the C-Si bond cleavage, and isomerize to an open intermediate **B** by migration of an aromatic group. Ring closure and subsequent back-electron-transfer furnish **2**. Meanwhile, the formation of **3** would be accounted for by the two-fold 1,2-migration of two aromatic groups followed by ring closure and back-electron-transfer. In these reduction steps, $DCA^{-\bullet}$ or neutral **1** probably serves as the electron sources.13-15) Formation of **4** in substantial yields in all the reaction conditions employed suggests that the second C-Si bond cleavage in **A** or spontaneous extrusion of the R_2Si moiety from $\mathbf{1}^{+\bullet}$ would occur. However, no product derived from the eliminated R_2Si moiety was detected even in the presence of 2,3-dimethyl-1,3-butadiene, which is a known trapping reagent for silylenes.16)

To obtain insight into the rearrangement mechanism, we tested the photoreaction of **1** in the presence of molecular oxygen, which has been reported to trap various cation radicals efficiently.3,13-15) When DCA-sensitized photolysis of **1** was carried out under bubbling oxygen, an oxygen-adduct (23%) was obtained while the yields of **2** and **3** were decreased (16 and 19%, respectively). With careful analysis of spectral data, we assigned **5**8) instead of endoperoxide **6** to the oxygen-adduct since it was thermally stable and could not be reduced by Ph_3P. It was confirmed that **2** and **3** were inert under the oxygenation condition. Therefore, it is suggested likely that the intermediate **B** is trapped by $O_2^{-\bullet}$ giving **6**, which would be unstable and undergo isomerization *via* the O-O bond cleavage. It should be noted that, as another route, **6** could be formed by O_2 addition to **B** followed by reduction (Scheme 3).15) To our knowledge, the isomerization described here represents the first example of photosensitized skeletal rearrangement of organosilicon compounds. Further studies are underway to explore the mechanistic details of this reaction.

Scheme 2.



Scheme 3.



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8. All new compounds gave consistent spectroscopic and analytical data.
9. Crystal data for **2**: $C_{32}H_{32}Si$ (fw 444.69), triclinic $P\bar{1}$; a=12.824(2)Å; b =10.133(2)Å; c=10.223(2)Å; α=99.98(1)°; β=100.88(1)°; γ=96.27(2)°; V=1270.9(4) Å^3; Z=2. Data were collected with Mo Kα radiation (graphite monochrometer λ=0.71073Å) on a Rigaku AFC-4 diffractometer. A total of 6548 reflections within 2θ =55° by the 2θ - ω scan method with a scan rate of 4°/min. The final R factor was 0.052 (Rw=0.069) for 4515 reflections with $|Fo| > 3\sigma$ (Fo). Crystal data for **3**: $C_{32}H_{32}Si$ (fw 444.69), monoclinic C2/c; a=35.739(5) Å; b =8.289(2) Å; c=17.156(3) Å; β=93.64(2)°; V=5072(2) Å^3; Z=8. Data were collected with Mo Kα radiation (graphite monochrometer λ=0.71073Å) on a Rigaku AFC-5R diffractometer. A total of 6426 reflections within 2θ = 55° by the ω scan method with a scan rate of 4°/min. The final R factor was 0.059 (Rw=0.074) for 4094 reflections with $|Fo| > 3\sigma$ (Fo). A reflection (-202) was omitted from the least-squares refinements.
10. Although the formation of **3** was not reported in the previous paper, 7) reexamination of the photolysis of **1** revealed the formation of **3**; irradiation of **1** in benzene with a medium pressure Hg arc lamp gave **2**, **3**, and **4** in 14, 32, and 4% yields, respectively.
11. Oxidation potentials (E_{OX}) of **1** and DABCO are + 1.40 and + 0.70 V vs SCE, respectively.
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