

Novel Photocycloaddition of Aromatic Ketones to Cyclic Oligosilanes

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Photolysis of aromatic ketones (2,2,2-trifluoroacetophenone, acetophenone, and benzophenone) in the presence of cyclic oligosilanes afforded two types of cycloadducts depending on the nature of the ketone employed. The quenching of the excited triplet state of benzophenone by oligosilanes was investigated by laser flash photolysis.

Since oligosilanes are known to act as good electron-donors due to the σ -conjugation along Si–Si chains, the chemistry of electron-transfer reactions of oligosilanes has been studied extensively.¹ Recently, we reported that phenanthraquinone triplet reacts with oligosilanes to yield silylene transfer products via S_H2 type radical displacement at silicon atoms.² Meanwhile, Alberti and co-workers investigated the photoreaction of ketones with $Me_3SiSiMe_3$ and $(Me_3Si)_4Si$ by EPR spectroscopic method and indicated the intermediacy of silylated ketyl and semiquinone radicals.³ Steinmetz et al. explored the quenching of the excited state of ketones by oligosilanes $Me_3Si(Me_2Si)_nSiMe_3$ ($n = 0, 2$), which afforded silylated pinacol products.⁴ These results naturally prompted us to investigate the reactivity of cyclic oligosilanes with photo-excited carbonyl compounds. We now report the photo-induced cycloaddition of ketones to oligosilanes, which provides a novel example of insertion reaction of Si–Si σ bonds.

A benzene solution of dodecamethylcyclohexasilane **1** (1.1×10^{-2} M) and 2,2,2-trifluoroacetophenone (TFA, 2.2×10^{-2} M) was irradiated with a 500-W medium pressure mercury lamp through a Pyrex filter for 2 h. Preparative HPLC separation of the reaction mixture afforded a TFA insertion product **4** as

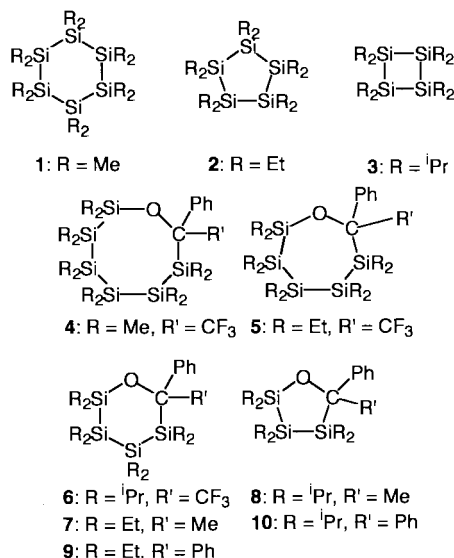


Table 1. Photochemical addition of ketones to oligosilanes

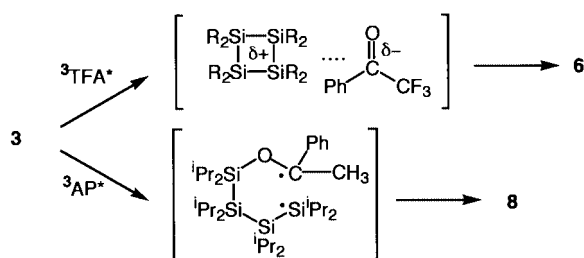
| Entry | Silane | Ketone | Time/h | Product (Yield/%) ^a |
|-------|----------|--------|--------|--------------------------------|
| 1 | 1 | TFA | 2.0 | 4 (85) |
| 2 | 2 | TFA | 2.0 | 5 (20) |
| 3 | 3 | TFA | 2.0 | 6 (29) |
| 4 | 2 | AP | 2.0 | 7 (57) |
| 5 | 3 | AP | 1.0 | 8 (28) |
| 6 | 2 | BP | 1.5 | 9 (12) |
| 7 | 3 | BP | 3.0 | 10 (7) |

^aYields were determined based on the amounts of consumed silanes.

shown in Table 1.⁵ Under similar reaction conditions five- and four-membered cyclic oligosilanes, **2** and **3** gave the corresponding adducts **5** and **6**, respectively, but in rather lower yields.

On the other hand, when acetophenone (AP) was used in place of TFA, **2** and **3** were converted to **7** and **8**, respectively, in which one of the silylene unit of the cyclic organosilyl chain is eliminated during the photolysis (Table 1, entries 4 and 5). Irradiation of benzophenone (BP) in benzene containing **2** and **3** afforded similarly **9** and **10**, respectively, but in only poor yields (Table 1, entries 6 and 7). Under the above irradiation conditions, the ketones should be excited selectively. Furthermore, at this stage, the generation of free dialkylsilylene (R_2Si): during the photolyses has not been substantiated by the trapping experiment using hydrosilanes and 1,3-butadienes since these conventional trapping reagents quenched the triplet ketones efficiently to suppress the reaction with oligosilanes.

Since the present photoreactions did not proceed in the presence of naphthalene, the photocycloaddition is indicated to be induced by the triplet states of ketones as suggested by the comparison of the singlet and the triplet energies of AP ($E_S =$ ca. 79, $E_T =$ ca. 74 kcal/mol) and BP ($E_S =$ ca. 76, $E_T =$ ca. 69 kcal/mol) with those of naphthalene ($E_S =$ ca. 92, $E_T =$ ca. 61 kcal/mol).⁶ Electron-transfer processes between **1–3** and the triplet states of TFA, AP and BP are calculated to be endothermic in benzene based on the Rehm–Weller equation,⁷ and hence the formation of radical ion pairs may be improbable. Previously, the formation of benzyl radicals by hydrogen abstraction of *p*-cymene by the triplet states of various ketones was reported.⁸ Wagner and co-workers indicated that the ketones with π , π^* lowest triplet (such as TFA), and those with n , π^* lowest triplet (such as AP and BP) afforded primary, and tertiary benzyl radicals, respectively, as main products. This chemoselectivity was suggested to be ascribed to the differences in the orientation and the degree of charge transfer of the exciplexes formed from those ketones with *p*-cymene. In this regard, following explanation is possible as exemplified by the case of **3** as shown in Scheme 1. Thus, the electron withdrawing group of TFA may be responsible to form a polar and tight exciplex (or transition state) to give **6**, whereas the electron



Scheme 1.

donating group of AP may contribute to form a more loose complex (or transition state) collapsing to the extended diradical, in which one silylene unit is allowed to be expelled by S_H2 displacement on the silicon atom next to the silyl radical for some steric demands to afford **8**. The bulkiness of substituents Et and i Pr may be responsible for the ring size of the products **7** and **8**, respectively.

In order to clarify the initial interaction of the substrates, we carried out quenching experiment of BP triplet ($^3BP^*$) by means of laser flash photolysis.⁹ The third harmonic pulse of Nd: YAG laser (355 nm) was used as an exciting light source. Triplet-triplet (T-T) absorption of $^3BP^*$ was detected around 530 nm¹⁰ after laser excitation of BP in a mixed solvent ($CH_3CN/CH_2Cl_2 = 4:1$). In the presence of **1** and **3**, T-T absorption of $^3BP^*$ decayed faster due to quenching by **1** and **3**, as observed for **3** in Figure 1. From the dependence of lifetime of $^3BP^*$ upon the concentration of **1** and **3**, the quenching rate constants (k_q) were calculated to be 1.46×10^7 ($M^{-1} s^{-1}$) for **1**, 1.50×10^8 ($M^{-1} s^{-1}$) for **3**, respectively. Furthermore, electron-transfer between BP and oligosilanes seems not to operate since the absorption due to BP radical anion was not detected at all in the region from 600 up to 700 nm.¹⁰ Therefore, we concluded that quenching of $^3BP^*$ should proceed via an exciplex or a diradical intermediate as mentioned above. Coupled with our previous observation that phenanthraquinone triplet and **3** did not afford radical ions in non-polar media,² it is probable that weaker oxidizing species $^3TFA^*$ and $^3AP^*$ would react with oligosilanes without electron-transfer at least in benzene.

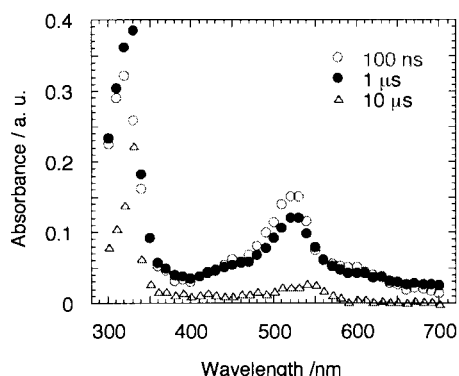


Figure 1. Transient absorption spectra obtained by laser excitation of BP in the presence of **3** in CH_3CN/CH_2Cl_2 .

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con reagents.

Dedicated to Prof. Hideki Sakurai on the occasion of his 70th birthday.

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- Selected spectral data: **4**: MS m/z 522(M^+); 1H NMR ($CDCl_3$) δ 7.24–7.16(m, 5H), 0.19(s, 6H), 0.18(s, 6H), 0.15(s, 6H), 0.12(s, 3H), 0.10(s, 6H), 0.05(s, 3H), –0.12(s, 3H), –0.15(s, 3H); ^{13}C NMR ($CDCl_3$) δ 138.09, 127.77, 127.64, 126.73, 125.37, 79.10, 2.41, 1.99, –3.89, –4.49, –4.94, –5.21, –5.31, –5.39, –5.43, –5.54, –5.80. **5**: MS m/z 604(M^+); 1H NMR ($CDCl_3$) δ 7.40–7.26(m, 5H), 127.44, 126.74, 125.44, 90.76, 11.03, 10.98, 10.88, 10.71, 10.61, 10.20, 10.13, 9.36, 8.80, 8.74, 8.33, 8.27, 7.94, 7.39, 7.04, 5.80, 5.66, 5.34, 4.75, 3.85. **6**: MS m/z 587($M^+ - 43$); 1H NMR ($CDCl_3$) δ 7.72–7.26(m, 5H), 1.74–1.17(m, 50H), 0.88(d, 4H), 0.55(d, 3H); ^{13}C NMR ($CDCl_3$) δ 139.80, 127.50, 126.96, 126.85, 126.56, 79.67, 23.70, 23.69, 23.63, 23.58, 23.26, 23.19, 22.49, 21.60, 21.20, 20.52, 20.44, 19.63, 19.47, 19.32, 19.25, 18.80, 18.73, 15.67, 15.51, 15.40, 15.33, 15.06, 14.72. **7**: MS m/z 464(M^+); 1H NMR ($CDCl_3$) δ 7.30–7.06(m, 5H), 1.70(s, 3H), 1.24–0.50(m, 40H); ^{13}C NMR ($CDCl_3$) δ 149.25, 127.40, 124.68, 124.59, 73.77, 28.52, 11.48, 10.54, 10.45, 10.41, 10.24, 8.75, 8.33, 7.93, 7.31, 6.79, 4.57, 3.79, 3.48, 2.53, 2.38, 2.08. **8**: MS m/z 462(M^+), 1H NMR ($CDCl_3$) δ 7.43–7.10(m, 5H), 1.65(s, 3H), 1.55–0.45 (m, 42H); ^{13}C NMR ($CDCl_3$) δ 150.31, 127.63, 124.76, 124.68, 76.54, 31.59, 23.39, 23.31, 23.24, 23.20, 20.64, 19.85, 19.61, 18.87, 18.61, 17.69, 16.52, 14.56, 14.01, 13.92, 13.70, 13.31, 12.40, 12.15.
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