Photochemically Induced [2 + 2] Cycloaddition of a Silacyclopentadiene with Carbon Disulfide

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abstract: A silacyclopentadiene (silole) undergoes photo-induced [2+2] cycloaddition with CS₂ to afford the corresponding β -dithiolactones. The electron transfer from singlet excited state of the silole to CS₂ is shown to play an important role in the cycloaddition reaction.

Although Diels-Alder reactions of a silacyclopentadiene (silole) with various kinds of 2π components, such as acetylenes, singlet oxygen, and cyclopropene, have been known, la only a few examples of photochemical cycloadditions of a silole have been reported, namely [2 + 2] dimerization of 1,1-dimethyl-2,5-diphenylsilole (1)^{1b,1c} and [2 + 2] cycloadditions with 1,1-dimethoxyethylene^{1b} and with benzophenone.^{1d} On the other hand, there are a few examples of thermally induced cycloaddition involving carbon disulfide,² however no photochemical cycloaddition of CS₂ acting as a 2π component has been reported as far as we are aware of. We now report that on irradiation some siloles undergo photochemical [2 + 2] cycloaddition with CS₂ to give the corresponding β -dithiolactones.

Irradiation of a CS₂ solution (0.1 M) of 1 in an NMR tube with a medium pressure Hg lamp through a Pyrex filter for 2 hr was found to give two kinds of [2 + 2] photoadducts in 1:1 ratio almost quantitatively.³ Thus, on irradiation the reaction mixture shows at first, a pair of two Si-Me signals (δ 0.04 and 0.65 for 2a, and δ -0.11 and 0.60 for 2b) and doublets (δ 4.99 for 2a and δ 5.27 for 2b) on the ¹HNMR spectrum together with those of the starting material 1, and these signals increase their intensities with consumption of 1. These spectroscopic features indicate these photo-products should be a pair of [2 + 2] adducts between 1 and CS₂. However, only one of these two adducts could be isolated by TLC on silica gel as yellow crystals, mp 108 - 109 °C (33% yield).⁴ The other product was decomposed quite readily on silica gel and could not be isolated successfully from large reddish polymeric materials produced from the photo-decomposition of CS₂.⁵

Presence of a thiocarbonyl group in 2a is supported by a strong IR absorption at 1151 cm⁻¹ together with a quite low field resonance at 238.6 ppm in ¹³CNMR spectrum.^{7,8} The β -dithiolactone structure of 2a is also suggested from the remarkable similarity of chemical reactivities to those of the [2 + 2] photodimer of 1,^{1c} thus, irradiation of the THF solution of 2a in a quartz tube with a low



pressure Hg arc lamp for 67 hr gave 1 in a 40% isolated yield and thermolysis of 2a in vacuo at 180 $^{\circ}$ C for 1.5 hr gave 1 in a 40% yield. The structure of 2a was confirmed finally by its conversion to silole 4 as shown in Scheme. At first, thiolactone 2a was reduced with LiAlH4⁹ followed by desulfurization with Raney Ni to give a silacyclopentane 3 as a stereoisomeric mixture in a 57% yield.¹⁰ Then, bromination of 3 with NBS followed by dehydrobromination with potassium acetate¹² afforded unsymmetrically substituted silole 4 as an yellow oil in a 41% yield.¹³ Consequently, together with the characteristic NMR spectral pattern described above, this leads to the conclusion that the other photoproduct should be the positional isomer 2b.

The fluorescence of 1 in CH₃CN is quenched by CS₂ with nearly diffusion controlled quenching rate constant kg, 1.0 x 10¹⁰ M⁻¹·s⁻¹ determined from a Stern-Volmer plot, where the life time of the lowest singlet excited state (S_1) of 1 was measured to be 1.1 ns. Reduction potential of CS₂ is -1.53 V in CH3CN.¹⁵ Since 1 has been shown to be an efficient electron donor,^{1d} CS₂ is expected to act as an efficient electron acceptor. This is further supported by the Rehm-Weller equation, namely it shows that the single electron transfer (SET) from S_1 of 1 to CS₂ should be highly exothermic and the free energy change of the process is estimated to be -5.6 kcal·mol^{-1,16} These show that the SET participation should play an important role in the photo-induced [2+2] cycloaddition of 1 with CS2 in CH3CN, and the [2+2] cycloaddition of this kind in non-polar solvent such as CS2 proceeds possibly through the exciplex with high degree of charge transfer character. In connection with a Woodward-Hoffman rule,¹⁷ it is interesting that 1 undergoes [2+2] instead of [4+2] cycloaddition reaction with a good electron acceptor N-chlorosulfonyl isocyanate at 0 °C without light, 1a, 18 From comparisons of the reduction potential,19 carbon dioxide, oxygen analog of CS2, is not conceivable to be an efficient electron acceptor as CS₂. In fact, the fluorescence of 1 is not quenched with carbon dioxide. In conformity with this view, carbon dioxide does not undergo photo-induced [2+2] cycloaddition with 1 and this gives only [2+2] dimers of 1.1b, 1c

Although the reduction potential of 5 is quite similar to that of $1,^{20}$ C-tetraphenylated silole 5 did not afford any cycloadduct corresponding to 2 under similar irradiation conditions. The life time of fluorescence of 5 is found to be quite short and the order of pico second. Together with steric crowding imposed by the four phenyl groups, this would be partly due to the life time of 5_1 of 5being too short to undergo electron transfer.

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References and Notes

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- 3. The photo-cycloaddition proceeds smoothly with the light (436 nm) through the appropriate filter, where only 1 absorbs most of the light.
- 4. 2a: MS m/z (rel. intensity), M⁺ 338 (1), 262 (100); UV (n-hexane) λ_{max} 255 nm (ε 16500), 296.5 (9700), 314.5 (11800); IR 1250, 1228 cm⁻¹ (SiMe), 1141 (C=S); ¹HNMR (CDCl₃) δ 0.04, 0.65 (3H, s, SiMe), 4.99 (1H, d, J = 4.0 Hz, C₅-H), 7.08 (1H, d, J = 3.7 Hz, C₄H=C), 7.14-7.45 (10H, m, Ar'H); ¹³CNMR (CDCl₃) δ -2.2 (SiMe), -1.9 (SiMe), 46.3 (C₁), 84.7 (C₅), 125.5, 125.7, 126.7, 127.8, 128.6, 128.8, 138.1, 140.0 (C₄), 142.6, 146.0 (C₃ and Ar'C), 238.6 (C₆).
- 5. On irradiation of 1 in CH₃CN containing CS₂, together with the signals due to 1 and some decomposed products, the NMR resonances of 2a emerged but none of signal due to 2b was observed. Under these irradiation conditions, the yield of 2a was estimated to be 39% from the NMR spectrum of the photolysate. In accord with these results, on addition of CH₃CN to the CS₂ solution containing both 2a and 2b, 2a remains unchanged but 2b is found to decompose quite readily. Thus, 2b is highly sensitive to a nucleophilic attack. This may be attributable to the silyl group being located at β -position to the sulfur in 2b.⁶
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- 10. 3: bp 140 ° C /0.5 mmHg; MS m/z (rel. intensity) M⁺ 280 (80), 117 (100); ¹HNMR (CCl4) cis-3: δ -0.42, 0.43 (3H, s, SiMe), 1.24 (3H, d, J = 6.0 Hz, CMe), trans-3: δ 0.01, 0.07 (3H, s, SiMe), 1.25 (3H, d, J =

5.5 Hz, CMe). These NMR spectral data show that 3 is a mixture of cis and trans isomers regarding the phenyl groups. The stereochemical assignment is made on the basis of comparison of these NMR data with those of 1,1-dimethyl-2,5-diphenyl-1-silacyclopentane.¹¹

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- 13. 4: MS m/z (rel. intensity), M⁺ 276 (100); λ_{max} (n-hexane) 231 (17600), 346 (18700); ¹HNMR (CDCl₃) δ 0.47 (6H, s, SiMe), 2.12 (3H, s, CMe), 7.1-7.6 (11H, m, HC= and Ar'H). By monitoring the photoreaction using NMR spectroscopy, irradiation of 4 in CS₂ was found to give [2 + 2] photoadducts also as a mixture of 6, 7, and 8 in ca. 4 : 2 : 1 ratio. Together with their chemical behavior on silica gel, structures of these adducts are elucidated from their NMR spectral features as below. Along with the two Si-Me signals, both 6 and 7 show two types of signals, one due to the Me group on a sp² carbon atom and the other due to the methine proton on an sp³ carbon atom. Compound 6 is purified by means of silica gel TLC,¹⁴ but 7 is found to be decomposed by the treatment with silica gel. On the other hand, 8 is stable on silica gel and shows the C-Me signal to higher field and the methine proton signal at olefinic region.



- 14. 6: mp 106-107.5 °C; MS m/z (rel. intensity) M⁺ 352 (9), 276 (100); UV (n-hexane) 234 nm (sh. 19600), 251 (sh. 13900), 277 (sh. 6700), 319 (12000); ¹HNMR (CS₂) δ 0.03, 0.58 (3H, s, SiMe), 2.20 (3H, s, C₄Me), 4.89 (1H, s, C₅H); 7: ¹HNMR (CS₂) δ -0.15, 0.53 (3H, s, SiMe), 2.11 (3H, s, C₄Me), 5.14 (1H, s, C₅H); 8: ¹HNMR (CS₂) δ 0.33, 0.64 (3H, s, SiMe), 1.49 (3H, s, C₄Me), 6.91 (1H, s, C₅H). These δ values are calculated in reference to the internal p-dioxane signal (δ: 3.70).
- 15. Half-wave reduction potential of CS₂ obtained by polarography: Pt electrode, tetraethylammonium perchlorate (0.1 M) in CH₃CN vs. SCE.
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