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Photochemistry of Conjugated Polyynes: Photochemical Generation of Silacyclopropenes from 1-Aryl-4-(pentamethyldisilanyl)buta-1,3-diyne

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No fluorescence was observed from 1-aryl-4-(pentamethyldisilanyl)buta-1,3-diyne except 1-(1-naphthyl)-4-(pentamethyldisilanyl)buta-1,3-diyne. Irradiation of 1-aryl-4-(pentamethyldisilanyl)buta-1,3-diyne (1) with methanol gives photoaddition products in relatively low yields compared to arylolethynylsilanes which show dual fluorescence. Irradiation of 1 with acetone yields site specific and regioselective 1:1 photoadducts through silacyclopropene intermediates. The triplet excited state of the silacyclopropene reacts with acetone to give addition photoproducts and the triplet energy of the silacyclopropenes lies around 260-286 kJ/mol.

Introduction

The chemical properties of silacyclopropenes have been extensively investigated,¹ since the first report on the silacyclopropene structure by Vol'pin *et al.* in 1962.² Interestingly, photolysis of alkynyl-substituted disilane derivatives affords a convenient route to the silacyclopropenes.³⁻⁵ Ishikawa *et al.* have proposed a mechanism involving a singlet diradical intermediate for the photochemical formation of silacyclopropenes from (phenylethynyl)disilanes.⁵ In general, most of the silacyclopropenes are thermally stable, but they are extremely reactive toward atmospheric oxygen and moisture. These silacyclopropenes formed from the photolysis of alkynyl-substituted disilanes in methanol or acetone react readily with methanol or acetone.³⁻⁵ Silacyclopropenes also react with unsaturated functional groups such as aldehydes, ketones, styrenes, conjugated terminal acetylenes, benzyne, terminal 1,3-dienes, and conjugated imines to give five-membered cyclic organosilicon products in which C=O, C=C, C≡C, or C=N bonds are inserted into the Si-C bond of the silacyclopropene ring.⁶

Although considerable attention has been devoted to investigation of the chemistry of the silacyclopropenes, relatively few results have been reported on the mechanism of the

reaction of silacyclopropenes.^{6,7} We have recently reported the photophysical and photochemical properties of some 1-aryl-4-(pentamethyldisilanyl)buta-1,3-diyne.⁸ In this study, we report the studies on the photochemical generation of the silacyclopropenes from 1-aryl-4-(pentamethyldisilanyl)buta-1,3-diyne in comparison with arylolethynylsilanes.

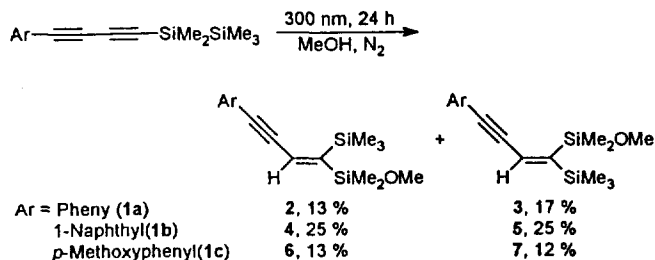
Experimental

Materials. Acetone was dried over K₂CO₃ followed by fractional distillation prior to use. Hexachlorobenzene, fluorene, diphenylacetylene, naphthalene, *p*-terphenyl, and anthracene were purchased from Aldrich and purified by standard methods.⁹

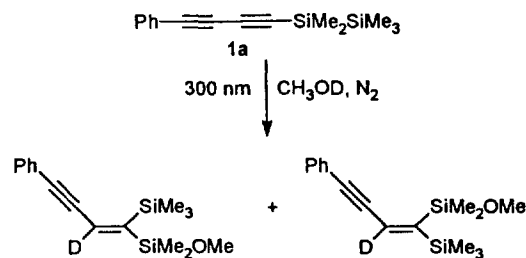
Instruments. High-performance liquid chromatography was performed on a Waters Associates Model 244 liquid chromatograph (Mildford, MA) equipped with a Model 6000A solvent delivery system, Model 440 UV absorbance detector fixed at 254 nm, and Model U6K universal injector.

Photolysis of 1-phenyl-4-(pentamethyldisilanyl)buta-1,3-diyne in CH₃OD. Photolysis was carried out following the reported procedure.^{8(a)} The deuterium incorporation was identified by comparing the ¹H NMR spectra of the photoproducts. The photoadducts formed in CH₃OD did not show the olefinic proton peaks at 6.79 and 6.92 ppm, respec-

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Scheme 1.



Scheme 2.

tively.

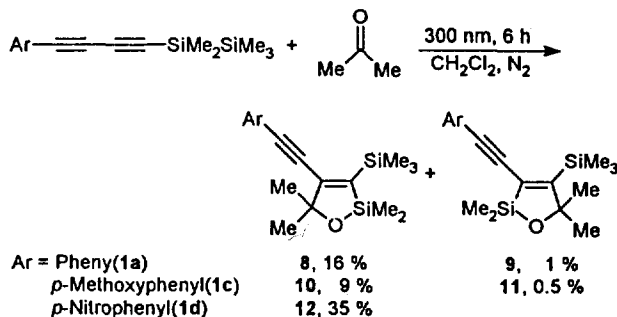
Quenching experiments. Deaerated solutions of 1-phenyl-4-(pentamethyldisilyl)buta-1,3-diyne (4 mM), acetone (10 mM) and quencher (10 mM) in methylene dichloride were irradiated with 300 nm for 3 min. The quantitative analyses were carried out by HPLC under the following conditions: column; Lichrosob Si 60 (12.5×0.4 cm, mean particle size 5 μm), eluent; n-hexane/diethyl ether (40/1, v/v).

Results and Discussion

Photoreaction of 1-aryl-4-(pentamethyldisilyl)buta-1,3-diyne with methanol. Irradiation of 1-aryl-4-(pentamethyldisilyl)buta-1,3-diyne (**1**) in methanol gives the photoaddition products (Scheme 1).^{8(a)}

The silacyclopropene is formed from the singlet excited state of **1**.⁸ We could not isolate the silacyclopropenes because of the high reactivity toward air and moisture. Detection of silacyclopropene intermediates by NMR was attempted but unfortunately the intermediate could not be detected, and the intermediates were detected only by UV spectroscopy.^{8(b)} Irradiation of **1** with methanol gives photoaddition products in relatively low yields compared to arylolethynylsilanes which show dual (local and charge transfer) fluorescence.^{4,5} This low yields can be explained by the low efficiency in the formation of silacyclopropenes, because silacyclopropenes are highly reactive and react exothermally with methanol.⁷

It was reported that photochemical reactions of phenylethynylsilane originate from the singlet excited state, probably ¹CT(charge transfer) state, and the MO calculations supported the ¹CT mechanism for the photochemical formation of silacyclopropenes.^{4,5} No fluorescence was observed from **1** except 1-(1-naphthyl)-4-(pentamethyldisilyl)buta-1,3-diyne (**1b**), neither local nor CT emission, even in rigid organic glasses at 77 K. All the 1-aryl-4-(pentamethyldisilyl)buta-1,3-diyne (**1**) show strong phosphorescence with strong 0-0 bands. The absence of fluorescence and low reaction yields can be explained by the enhanced intersystem crossing. If the intersystem crossing is enhanced, the singlet excited state responsible for the silacyclopropene formation will have a short lifetime to give silacyclopropene and the silacyclopropene formation yields will be low.¹⁰ As a result, in the photolysis of **1** in methanol, photoadducts were obtained in relatively low yields compared to fluorescent arylolethynylsilanes. The compound **1b** which shows fluorescence with a maximum at 353 nm in methanol at 298 K gives methanol addition photoproducts in higher yields. These results support the singlet excited state, probably ¹CT state, mechanism



Scheme 3.

for the photochemical formation of silacyclopropenes from 1-aryl-4-(pentamethyldisilyl)buta-1,3-diyne.

Photolysis of 1-phenyl-4-(pentamethyldisilyl)buta-1,3-diyne (**1a**) in CH₃OD was carried out to give insight into the reaction mechanism of the silacyclopropene with methanol. Irradiation of **1a** in CH₃OD gives only deuterium incorporated photoadducts in the olefinic hydrogen, indicating the ionic mechanism for the reaction of the silacyclopropene with methanol (Scheme 2). The deuterium incorporation was identified by comparing the ¹H NMR spectra of the photoproducts. The photoadducts formed in CH₃OD did not show the olefinic proton peaks at 6.79 and 6.92 ppm,^{8(a)} respectively.

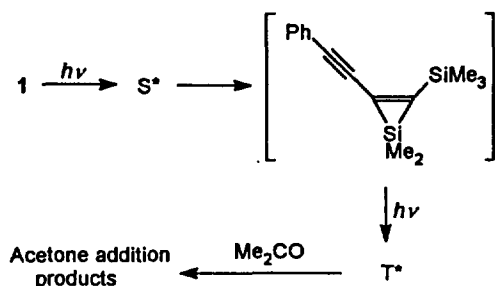
Photoreaction of 1-aryl-4-(pentamethyldisilyl)buta-1,3-diyne with acetone. Irradiation of **1** with acetone in deaerated methylene chloride yields site specific and regioselective 1:1 photoadducts (Scheme 3).^{8(b)}

Seyferth *et al.* had proposed a mechanism involving (*n*, π*)³ of C=O bond which is similar to the photoinduced cycloaddition of carbonyl compounds to simple alkenes, *i.e.* Paterno-Büchi reaction.⁵ But they did not show any direct evidence for the mechanism. Previously, we have proposed a reaction mechanism involving a triplet excited state of silacyclopropenes instead of (*n*, π*)³ of acetone in the photoreaction of **1** with acetone.⁸ To support this mechanism, experiments with various quenchers were carried out to quench the triplet excited state of acetone selectively and results are summarized in Table 1. With hexachlorobenzene which has the triplet energy just below that of acetone, the quantum yield of photoadduct is not decreased indicating that the triplet excited state of acetone is not involved in this reaction, while the quantum yield decreased to 71-78% with fluorene and diphenylacetylene and 22-28% with *p*-terphenyl and anthracene indicating that the silacyclopropene formed from the photolysis of 1-phenyl-4-(pentamethyldisilyl)buta-1,3-diyne

Table 1. Quenching of photoreaction of **1a** with acetone

Quencher	E_T (kJ/mol) ^a	Φ_{rel} ^b
Hexachlorobenzene	307.9	1.10
Fluorene	285.6	0.71
Diphenylacetylene	262.5	0.78
Naphthalene	255.8	0.34
<i>p</i> -Terphenyl	244.9	0.28
Anthracene	176.4	0.22
No quencher		1.00

^aacetone ($E_T=331.8-344.4$ kJ/mol), for E_T see ref. [11]. ^brelative quantum yields with respect to the photoreaction without quencher.

**Scheme 4.**

(**1a**) reacts with acetone *via* the triplet excited state of the silacyclopropene (Scheme 4) and the triplet energy of the silacyclopropene lies around 62-68 kcal/mol. The increased reaction quantum yield with hexachlorobenzene can be explained by the sensitized reaction in which the triplet energy is transferred from the triplet excited state of hexachlorobenzene to the ground state of silacyclopropene.

In conclusion, silacyclopropene intermediates are formed *via* singlet excited state in the photolysis of 1-aryl-4-(penta-methylsilyl)buta-1,3-diyne (**1**). The reaction of the silacyclopropene with methanol gives the photoadducts through an ionic reaction path. From the selective quenching studies, it is confirmed that the triplet excited states of silacyclopropenes react with acetone to give site specific and regioselective 1:1 photoadducts and the triplet energy of the silacy-

clopropenes lies around 260-286 kJ/mol.

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