Photochemistry of 1-Aryl-4-(pentamethyldisilanyl)buta-1,3-diynes: Photoreaction with Acetone and Dimethyl Fumarate

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Irradiation of 1-aryl-4-(pentamethyldisilanyl)buta-1,3-diynes (**1–3**) with acetone yields site specific and regioselective 1:1 adducts (**4–8**) *via* silacyclopropene intermediates. Photoreaction of 1-aryl-4-(pentamethyldisilanyl)buta-1,3-diynes with dimethyl fumarate gives two-atom insertion products (**9** and **13**) *via* silacyclopropene and/or [2+2] photocycloaddition products (**10–12** and **14**). The silacyclopropene intermediates are formed from singlet excited states in compounds **1** and **2**, but from the triplet excited state in compound **3**.

Since the first report on the silacyclopropene structure by Vol'pin *et al.* in 1962,[1] many attempts have been made to prepare silacyclopropenes. In 1976, Conlin and Gaspar reported that dimethylsilylene generated by thermolysis of 1,2-dimethoxytetramethyldisilane reacts with but-2-yne to give tetramethylsilacyclopropene.[2] Interestingly, photolysis of alkynyl-substituted disilane derivatives affords a convenient route to the silacyclopropenes.[3,4] Most of the silacyclopropenes are extremely unstable toward atmospheric oxygen and moisture and they are trapped by solvents in the photolysis of alkynyl-substituted disilanes in acetone or methanol.[3-5] In this study, we describe the photochemical generation of silacyclopropenes from 1-aryl-4-(pentamethyldisilanyl)buta-1,3-diynes and photoreaction of these silacyclopropenes with acetone and dimethyl fumarate.

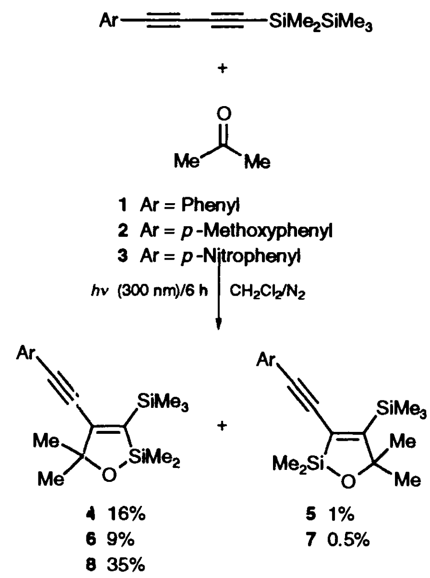
Results and Discussion

Photoreaction of 1-Aryl-4-(pentamethyldisilanyl)buta-1,3-diynes with Acetone.—Irradiation of 1-aryl-4-(pentamethyldisilanyl)buta-1,3-diynes (**1**–**3**) with acetone in deaerated methylene chloride yields site specific and regioselective 1:1 photoadduct(s) (**4**–**8**). Dark-yellow products, probably oligomers and decomposed products, were obtained as byproducts in the reactions.

The UV absorption spectra of photoproducts show less fine structure than that of the parent acetylenes suggesting the loss of the conjugation of diyne unit. The absorption maxima were red-shifted in **4** and **6** compared with parent diynes indicating that the conjugation system is sustained. On the other hand, the absorption maxima of **8** was blue-shifted probably due to the loss of a charge-transfer interaction in the excited state between the nitro and disilanyl group in photoadduct **8**.

The mass spectra of photoadducts show the molecular ion peaks (M^+) indicating that photoadducts are formed by the addition of one acetone molecule to parent diynes. The ^{13}C NMR spectra of photoadducts (**4** and **6**–**8**) show an ethynyl substituted phenyl centre carbon at δ 123.2, 115.2, 116.5 and 129.8, respectively, by the addition rule of ^{13}C chemical shift,[6,7] indicating that the C(3)–C(4) triple bond is the reactive site and the ethynyl aryl moiety remains intact. The ^{13}C NMR spectra also show the characteristic dimethyl substituted sp^3 carbons at δ 87.8, 89.2, 87.8, 89.3 and 87.7, supporting the 1-oxa-2-silacyclopent-3-ene moiety. The location of the trimethylsilyl group on the five-membered ring was confirmed by comparison with the results reported by Shizuka.[5]

Irradiation of 1-aryl-4-(pentamethyldisilanyl)buta-1,3-diynes with acetone in deaerated methylene chloride yields the acetone addition products. These types of photoaddition reactions have been reported to proceed *via* silacyclopropene intermediates formed from the singlet excited states of disilane compounds.[3-5] The silacyclopropene intermediates cannot be isolated in general, because of their high reactivity toward air and moisture except for some cases.



As shown in Fig. 1, the UV absorption spectra of 1-aryl-4-(pentamethyldisilanyl)buta-1,3-diynes change with irradiation time and show an isosbestic point except for compound **1**. For **1**, UV absorption spectra change rather fast upon irradiation and show no isosbestic point. It has been known that (arylethynyl)pentamethyldisilanes give the aryltrimethylsilylacetylene upon irradiation and this acetylene can act as an absorbing species to change the parent UV absorption spectra.[4,8] On the basis of the spectral comparison between the absorption spectra of 1-aryl-4-(trimethylsilyl)buta-1,3-diynes and photolysis products, it is confirmed that 1-aryl-4-(pentamethyldisilanyl)buta-1,3-diynes form an intermediate, probably silacyclopropene, upon irradiation. And these UV absorption spectra are similar to the UV absorption spectra of 1,1-dimethyl-2,3-bis(trimethylsilyl)-1-silacyclopropene,[9] and 1,1-dimesityl-2-phenyl-3-trimethylsilyl-1-silacyclopropene.[10] Furthermore, oxygen does not alter the UV absorption spectra obtained from photolysis of compounds **1** and **2** in aerated solution. Photolysis of compound **3**, on the other hand, is quenched by oxygen showing no change in UV spectra and only the absorption spectrum of starting compound **3** is observed upon irradiation in aerated solution. These results suggest that silacyclopropene intermediates are formed from

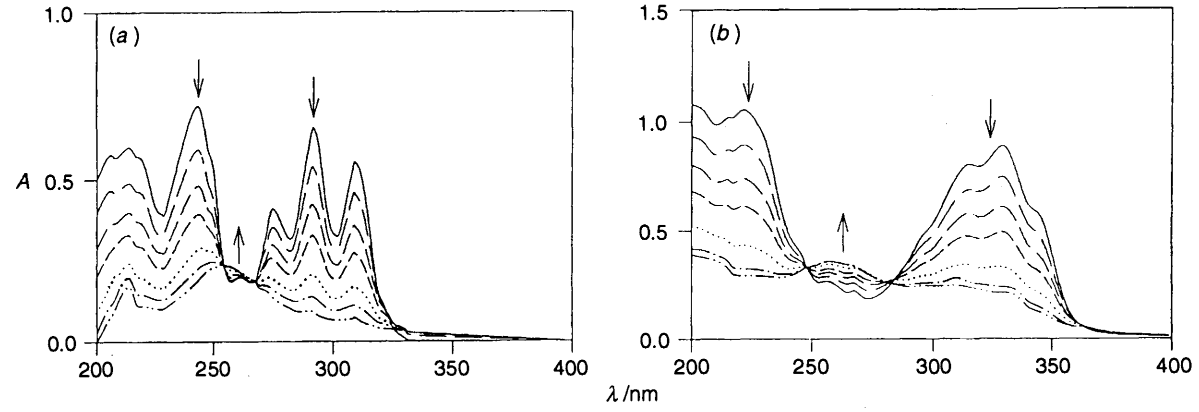


Fig. 1 UV absorption change on irradiation in hexane; (*a*), **2** and (*b*) **3**; at 0, 1, 2, 3, 5, 7 and 8 min

Table 1 Oxygen effects on the photoreaction of 1-aryl-4-(pentamethyldisilanyl)buta-1,3-diynes with acetone

	Φ_{rel}[a]
Reactions	Aerated
1–acetone; **4**	0.13
2–acetone; **6**	0.10
3–acetone; **8**	0.29

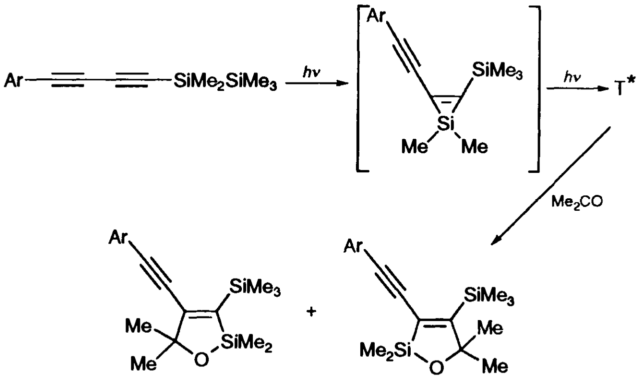
[a] Relative quantum yields with respect to deaerated solutions.

the singlet excited states in compounds **1** and **2**, but from the triplet excited state in compound **3**. This is consistent with the observation that intersystem crossing is highly efficient in nitro aromatics.[11]

After irradiation of 1-aryl-4-(pentamethyldisilanyl)buta-1,3-diynes (4 mmol dm^{-3}) in dry methylene chloride in the absence of acetone for 2 h, the addition of acetone to the reaction mixture in the dark did not give acetone addition products. As (phenylethynyl)pentamethyldisilane,[3–5] no dark reaction occurred for silacyclopropenes with acetone in these cases. The photoreaction of **1** and **2** with methanol proceeds *via* the singlet excited states of **1** and **2**, and the addition of methanol to the intermediate formed proceeds without irradiation.[12] After irradiation of **3** in deaerated and aerated dry methylene chloride in the absence of methanol for 30 min, methanol was added to the reaction mixture to investigate the oxygen effect on the formation of the silacyclopropene.* The addition product was detected by HPLC and this reaction was effectively quenched by oxygen in aerated solution and 9-fluorenone (E_T = 210 kJ mol^{-1}),[13] supporting that the silacyclopropene is formed *via* the triplet excited state of compound **3**.

The oxygen effects on the photoreaction of 1-aryl-4-(pentamethyldisilanyl)buta-1,3-diynes with acetone are summarized in Table 1. The quantum yields of photoadducts decreased to 10–29% in aerated solution indicating that triplet excited states are involved in this photoreaction. For **1** and **2**, the silacyclopropenes are formed from singlet excited states,[12] therefore the photoreaction of silacyclopropenes with acetone proceeds *via* the triplet excited states of silacyclopropenes. With 300 nm irradiation, acetone can absorb the light and the triplet excited state of acetone can be involved. For compound **3**, therefore, the photoreaction and oxygen effect experiments were carried out using a 350 nm lamp as the light source in which **3** absorbs all the light and none is absorbed by acetone. The same results were obtained suggesting that the triplet excited state of acetone is not involved in this reaction.

From these results, we propose a plausible photoreaction mechanism as follows. The formation of acetone addition photoproducts (**4**–**8**) is consistent with the two-atom insertion mechanism suggested in the photoreaction of (phenylethynyl)pentamethyldisilane with acetone.[5] The silacyclopropene intermediates are formed from singlet excited states in **1** and **2**, but from the triplet excited state in **3**. The silacyclopropene intermediates absorb the light and react with acetone in the triplet manifold to give acetone addition photoproducts.



Compound **2** substituted with a methoxy group gives the acetone addition photoproduct in lower yield than compound **1**. Further studies on the substituent effects are warranted. However, considering the aromatic stabilization of cyclopropenyl cation, this result may be explained by the stabilization effects of substituents on the silacyclopropene intermediates. The electron-donating methoxy group in **2** probably destabilizes the silacyclopropene. For compound **3**, the high efficiency of intersystem crossing may affect this reaction dominantly.

For **2** and **3**, a stoichiometric amount of acetone cannot trap the triplet excited state of silacyclopropene as effectively as an excess amount. But for **1**, a stoichiometric amount of acetone can trap the triplet excited state of silacyclopropene as effectively as an excess amount (Table 2) indicating that the triplet excited state lifetime of silacyclopropene formed from **1** is long enough to allow it to find a partner in dilute solution but those of silacyclopropenes formed from **2** and **3** are rather short.[14]

Photoreaction of 1-*Aryl*-4-(*pentamethyldisilanyl*)*buta*-1,3-*diynes with Dimethyl Fumarate* (*DMFu*).—Irradiation of 1,4-

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* See ref. 12. Photolysis of **3** in methanol results in the formation of 1-(*p*-nitrophenyl)buta-1,3-diyne through C–Si bond cleavage. But with a stoichiometric amount of methanol, the methanol addition product is obtained as a minor product; δ(CDCl$_3$, 200 MHz) 8.18 (2 H, d), 7.53 (2 H, d), 6.75 (1 H, s), 3.44 (3 H, s), 0.34 (6 H, s) and 0.14 (9 H, s).

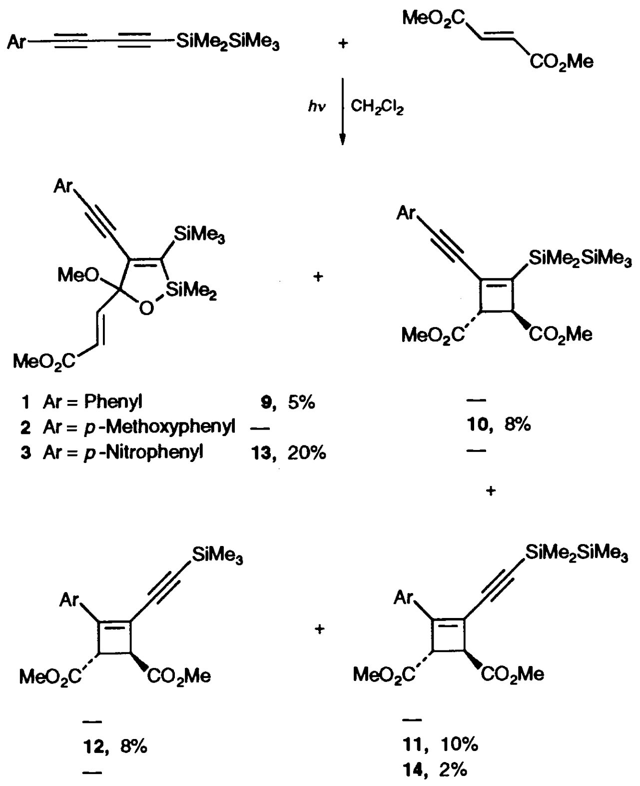
Table 2 Acetone concentration effects on the photoreaction of 1-aryl-4-(pentamethyldisilanyl)buta-1,3-diyne with acetone

Reactions	$\Phi_{1:25}$[a]
1–acetone; **4**	1
2–acetone; **6**	0.17
3–acetone; **8**	0.14

[a] Relative quantum yields with respect to the condition of mole ratio of 1-aryl-4-(pentamethyldisilanyl)buta-1,3-diyne:acetone = 1:2 or 1:25.

diphenylbuta-1,3-diyne with dimethyl fumarate in deaerated tetrahydrofuran (THF) yields a primary 1:1 cyclobutene adduct *via* [2+2] photocycloaddition reaction and further irradiation of the solution results in the formation of novel 1:2 photoadducts as the secondary photoadducts.[15]

Photoreaction of **1** with DMFu in deaerated methylene chloride gives only a two-atom insertion product **9** *via* silacyclopropene. Irradiation of **2** with DMFu gives three [2+2] cycloaddition photoadducts **10–12**. The photolysis of **3** with DMFu in methylene chloride gives two photoproducts, a two-atom insertion product **13** *via* silacyclopropene and a [2+2] photocycloaddition product **14**.



The structures of these photoproducts were determined by various physical methods, including ^{13}C NMR spectroscopy which is vital for the determination of the reaction sites. The UV absorption spectra of photoadducts did not show the typical vibrational fine structure of conjugated diacetylenes. Absorption maxima are red shifted compared with parent 1-aryl-4-(pentamethyldisilanyl)buta-1,3-diynes in photoadducts **11**, **12** and **14**. Mass spectra of all the photoadducts show M^+ peaks, indicating that photoadducts are formed by addition of one DMFu molecule. The ^{13}C NMR spectra show the ethynyl substituted phenyl carbons at δ 122.7 **9**, 115.8 **10** and 129.3 **13**, respectively, indicating that the reactive site is the C(3)–C(4) triple bond.[6,7] On the other hand, cyclobutenyl substituted phenyl carbons appear at δ 125.8 **11**, 125.7 **12** and 138.2 **14**, respectively, by the addition rule of ^{13}C chemical shift.[6] Above all, the appearance of a resonance signal at δ 148–160 (cyclobutene ring sp^2 carbon, deshielded by phenyl ring) is strong evidence of the existence of a phenyl substituted cyclobutene ring.[7] For photoadducts **9** and **13**, there are characteristic methoxy substituted sp^3 carbon peaks at δ 108.1 and 107.9, respectively, suggesting the 1-oxa-2-silacyclopent-3-ene moiety. The ^1H NMR spectra of photoadducts **9** and **13** show olefinic protons of DMFu moiety at δ 6.22 and 7.06, and δ 6.20 and 7.00, respectively, suggesting that the reaction site is not the carbon–carbon double bond, but the carbonyl group of DMFu.

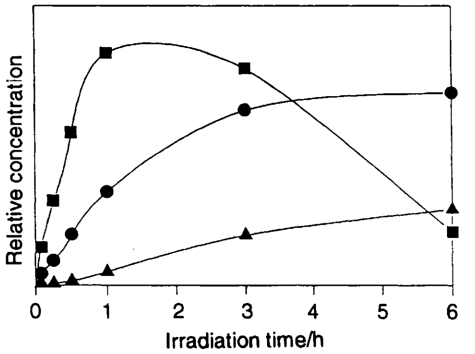
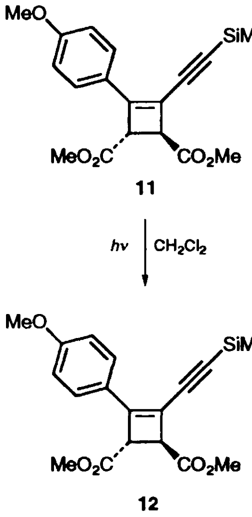


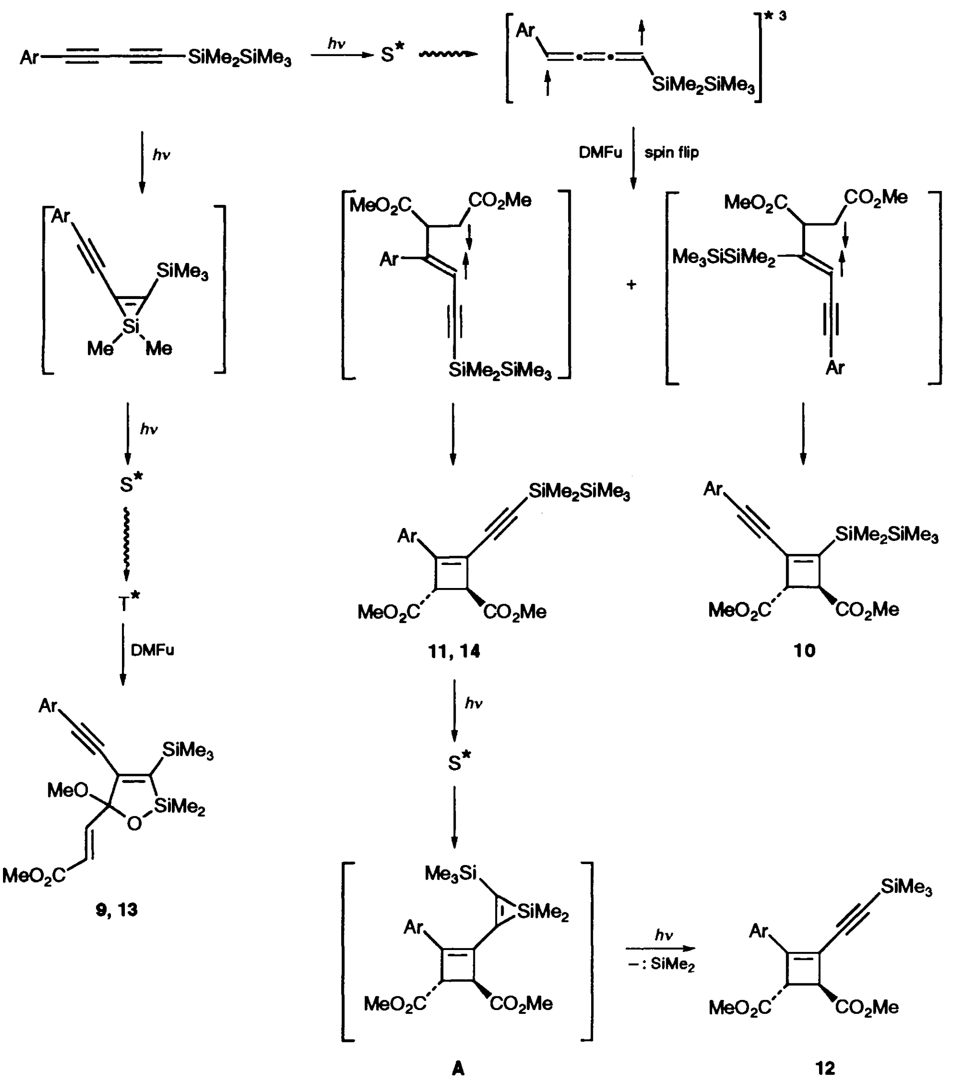
Fig. 2 Kinetics of the photoreaction of **2** with DMFu: ●, **10**; ■, **11**; ▲, **12**

As shown in Fig. 2, the photoadduct **11** is initially formed and prolonged irradiation of the solution results in the formation of the photoadduct **12** indicating that **11** is the primary and **12** is the secondary photoproduct. Photolysis of pure **11** in deaerated methylene chloride results in the formation of **12**, strongly supporting the mechanism.



The oxygen effects on the photoreaction of 1-aryl-4-(pentamethyldisilanyl)buta-1,3-diynes with DMFu are summarized in Table 3. The quantum yields of photoadducts decreased to 25–38% in aerated solution indicating that photoadducts are produced *via* triplet excited states. After irradiation of compound **3** (4 mmol dm^{-3}) in dry methylene chloride in the absence of DMFu for 2 h, the addition of DMFu to the reaction mixture in the dark did not give the DMFu addition product **13**. As for the photoreaction with acetone, no dark reaction occurred for silacyclopropene with DMFu.

From these results, we propose a plausible photoreaction mechanism as shown in Scheme 1. The silacyclopropene intermediates formed from the singlet excited state of **1** and from the triplet excited state of **3** absorb the light to give the photoadducts **9** and **13** having the 1-oxo-2-silacyclopent-3-ene



Scheme 1 A plausible mechanism of the photoreaction of 1-aryl-4-(pentamethyldisilanyl)buta-1,3-diynes with DMFu

Table 3 Oxygen effects on the photoreaction of 1-aryl-4-(pentamethyldisilanyl)buta-1,3-diynes with DMFu

Reactions	Φ_{rel}[a] Aerated
1-DMFu; **9**	0.38
2-DMFu; **10**	0.25
11	0.28
12	0.37
3-DMFu; **13**	0.38
14	0.33

[a] Relative quantum yields with respect to deaerated solutions.

moiety, respectively. As for the photoreaction of conjugated polyacetylenes with olefins which we reported previously,[15,16] the [2 + 2] photocycloaddition products are produced *via* the triplet excited states. Interestingly, photoadduct **11** absorbs the light and gives the intermediate **A** having the silacyclopropene moiety. And this intermediate **A** ejects dimethylsilylene to give photoproduct **12**. Probably compound **3** produces the photoadduct of this type, but this adduct is not detected owing to the very low yield.

Compound **2** having the methoxy group produces only [2 + 2] photocycloaddition products, but compound **3** having the nitro group gives a two-atom insertion product in high yield *via* the silacyclopropene intermediate. However, further studies on the substituent effects are necessary. We have reported previously that the triplet excited states of conjugated polyacetylenes have a nucleophilic radical character.[17] These results may be attributed to the substitutent effects on the stability of silacyclopropene intermediates as in the photoreaction with acetone and the nucleophilic character of the 1-aryl-4-(pentamethyldisilanyl)buta-1,3-diyne triplet radical in the [2 + 2] photocycloaddition reaction. The silacyclopropene formed from **2** is rather unstable and the triplet radical has enhanced nucleophilic character due to the electron-donating methoxy group, therefore only [2 + 2] photocycloaddition products are formed. Otherwise, for **3**, owing to the electron-donating nitro group, silacyclopropene is rather stable and the triplet radical has sustained nucleophilic character to give a two-atom insertion product in high yield *via* the silacyclopropene intermediate and the high efficiency of intersystem crossing may play another important role.

Conclusions

Irradiation of 1-aryl-4-(pentamethyldisilanyl)buta-1,3-diynes with acetone yields site specific and regioselective 1 : 1 adducts through two-atom insertion of acetone to silacyclopropene intermediates. Photoreaction of 1-aryl-4-(pentamethyldisilanyl)buta-1,3-diynes with dimethyl fumarate gives two-atom insertion products *via* silacyclopropene and/or [2+2] photocycloaddition products. Compound **2** which has a methoxy group yields only [2+2] photocycloaddition products while **3** which has a nitro group gives both the two-atom insertion product *via* silacyclopropene and the [2+2] photocycloaddition product, the former in higher yield. These results can be attributed to the stabilization of silacyclopropene intermediates by substituents and also to the nucleophilic character of the 1-aryl-4-(pentamethyldisilanyl)buta-1,3-diyne radical in the [2+2] photocycloaddition reaction.

Experimental

Instruments.—^{1}H and ^{13}C NMR spectra were recorded on Bruker AM-300 and Bruker AC-200 spectrometers with chemical shifts being referenced against $SiMe_4$ as an internal standard or the signal of the solvent $CDCl_3$. UV absorption spectra were recorded on a Shimadzu 3100S spectrophotometer. Mass spectra were determined at 70 eV with a Hewlett-Packard 5985A GC–MS by the electron impact (EI) method. FTIR spectra were recorded on a Bomem MB-100 spectrometer in KBr pellets and NaCl cell. High-performance liquid chromatography was performed on a Waters Associates Model 244 liquid chromatography (Mildford, MA) equipped with a Model 6000A solvent delivery system, Model 440 UV absorbance detector fixed at 254 nm, and Model U6K universal injector. Lichrosorb SI-60 column was used for preparative analyses.

Materials.—Dimethyl fumarate was purchased from Aldrich and recrystallized in methanol. Methylene chloride was dried with P_2O_5 and followed by fractional distillation before use. Acetone was dried with K_2CO_3 and followed by fractional distillation before use. Solvents of reagent grade for chromatography were used without further purification. Spectroscopic grade solvents (Tedia) were used for HPLC and UV absorption spectra, respectively. 1-Phenyl-4-(pentamethyldisilanyl)buta-1,3-diyne **1**, 1-(*p*-methoxyphenyl)-4-(pentamethyldisilanyl)-buta-1,3-diyne **2** and 1-(*p*-nitrophenyl)-4-(pentamethyldisilanyl)buta-1,3-diyne **3** were prepared by reported methods.[12]

Irradiation of 1-*Aryl*-4-(*pentamethyldisilanyl*)*buta*-1,3-*diynes with Acetone.*—Deaerated solutions of 1-aryl-4-(pentamethyldisilanyl)buta-1,3-diynes (**1–3**, 4 mmol dm^{-3}) and acetone (100 mmol dm^{-3}) in methylene chloride were irradiated at 300 nm UV light in a Rayonet photochemical reactor, Model RPR-208, equipped with RUL 300 nm lamp. After irradiation for 6 h, the resulting photoreaction mixture was concentrated *in vacuo*. The photoadducts (**4–5**, **6–7** and **8**) of **1**, **2** and **3** were isolated in (16%, 1%), (9%, 0.5%) and 35% yields, respectively, by silica gel column chromatography using the following conditions: eluents; **4–5**: hexane–diethyl ether (20:1, v/v), (**6–7**, **8**): hexane–diethyl ether (10:1, v/v). The products were purified by normal phase HPLC using the following conditions: eluents; (**4–5**): hexane–diethyl ether (25:1, v/v); (**6–7**): hexane–diethyl ether (15:1, v/v); **8**: hexane–diethyl ether–methylene chloride (10:1:1, v/v/v). The photoadducts **4** and **5** could not be resolved and the chemical yields were determined by ^{1}H NMR integration of methyl proton of $-SiMe_3$ and ^{1}H and ^{13}C NMR spectra were obtained as a mixture. The photoproducts **4–7** were obtained as pale-yellow liquids and are unstable in daylight. The photoproduct **8** was an orange solid. Compound **4**: δ_H($CDCl_3$, 300 MHz) 7.40–7.31 (5 H, m), 1.58 (6 H, s) 0.30 (6 H, s) and 0.25 (9 H, s); δ_C($CDCl_3$, 75 MHz) 156.6, 144.9, 131.3, 128.5, 128.3, 123.2, 96.4, 87.8, 87.5, 29.5, 1.7 and −0.5; λ_{max}(MeOH)/nm 302.9, 285.4 and 239.3; ν_{max}(NaCl)/cm^{-1} 2964.9, 1525.4, 1249.3, 994.6, 867.0 and 688.6; *m*/*z* (70 eV) 314 (M^+, 8.0%), 299 (M^+ − Me, 35) and 241 (M^+ − $SiMe_3$, 100) (Calc. for $C_{18}H_{26}OSi_2$, 314.1522. Found, 314.1523). Compound **5**: δ_H($CDCl_3$, 300 MHz) 7.40–7.31 (5 H, m), 1.40 (6 H, s), 0.35 (9 H, s) and 0.32 (6 H, s); δ_C($CDCl_3$, 50 MHz) 177.6, 132.6, 131.0, 128.4, 127.8, 124.3, 100.1, 89.2, 88.0, 30.2, 0.32 and 0.27. Compound **6**: δ_H($CDCl_3$, 300 MHz) 7.38 (2 H, d) 6.86 (2 H, d), 3.60 (3 H, s), 1.47 (6 H, s), 0.27 (6 H, s) and 0.23 (9 H, s); δ_C($CDCl_3$, 75 MHz) 159.9, 156.8, 143.5, 132.8, 115.2, 114.0, 96.6, 87.8, 86.5, 55.2, 29.5, 1.9 and −0.45; λ_{max}(MeOH)/nm 313.7, 298.1 and 200.4; ν_{max}(KBr)/cm^{-1} 2949.9, 1525.5, 1248.9, 994.2, 866.2 and 683.5; *m*/*z* (70 eV) 344 (M^+, 19.7%), 329 (M^+ − Me, 48.9), 271 (M^+ − $SiMe_3$, 100) and 73 ($SiMe_3$, 39.2) (Calc. for $C_{19}H_{28}O_2Si_2$, 344.1629. Found, 314.1609). Compound **7**: δ_H($CDCl_3$, 200 MHz) 7.33 (2 H, d), 6.83 (2 H, d), 3.80 (3 H, s), 1.38 (6 H, s), 0.32 (9 H, s) and 0.29 (6 H, s); δ_C($CDCl_3$, 50 MHz) 176.5, 159.4, 132.9, 132.5, 116.5, 114.0, 100.1, 89.3, 86.7, 55.3, 30.2, 0.4 and 0.3; λ_{max}(hexane)/nm 316.9 and 298.9; ν_{max}(KBr)/cm^{-1} 2964.9, 1519.2, 1249.1, 982.1, 834.8 and 788.4. Compound **8**: δ_H($CDCl_3$, 200 MHz) 8.20 (2 H, d), 7.55 (2 H, d), 1.44 (6 H, s), 0.26 (6 H, s) and 0.22 (9 H, s); δ_C($CDCl_3$, 50 MHz) 155.1, 148.9, 147.1, 132.0, 129.8, 123.0, 129.8, 123.7, 93.9, 92.3, 87.7, 29.5, 1.8 and −0.5; λ_{max}(hexane)/nm 302.7; ν_{max}(KBr)/cm^{-1} 2863.2, 1591.8, 1517.9, 1345.9, 1250.4, 993.7 and 854.0; *m*/*z* (70 eV) 359 (M^+, 4.6%), 344 (M^+ − Me, 69.8), 286 (M^+ − $SiMe_3$, 60.9) and 73 ($SiMe_3$, 100) (Calc. for $C_{18}H_{25}NO_3Si_2$, 359.1373. Found, 359.1353); m.p. 102–103 °C.

Irradiation of 1-*Aryl*-4-(*pentamethyldisilanyl*)*buta*-1,3-*diynes with DMFu.*—Deaerated solutions of 1-aryl-4-(pentamethyldisilanyl)buta-1,3-diynes (**1** and **2**, 4 mmol dm^{-3}) and DMFu (100 mmol dm^{-3}) in methylene chloride were irradiated at 300 nm UV light in a Rayonet photochemical reactor, Model RPR-208, equipped with RUL 300 nm lamps. After irradiation of **1** for 24 h and **2** for 12 h, the resulting photoreaction mixture was concentrated *in vacuo*. The photoadducts **9** from compound **1** and **10–12** from **2** were isolated in 5, 8, 10 and 8% yields, respectively, by silica gel column chromatography: eluents; **9**: *n*-hexane–diethyl ether (4:1, v/v), **10–12**: *n*-hexane–diethyl ether (3:1, v/v). This was followed by normal phase HPLC with the following conditions: eluents; **9**: *n*-hexane–ethyl acetate–methylene chloride (14:1:2, v/v/v), **10–12**: *n*-hexane–diethyl ether–methylene chloride (9:1:2, v/v/v). All photoproducts, except photoproduct **12**, were obtained as a pale-yellow liquid and were unstable in daylight. Compound **9**: δ_H($CDCl_3$, 300 MHz) 7.43–7.31 (5 H, m), 7.06 (1 H, d, *J* 15 Hz), 6.22 (1 H, d, *J* 15 Hz), 3.73 (3 H, s), 3.23 (3 H, s), 0.38 (3 H, s), 0.32 (3 H, s) and 0.24 (9 H, s); δ_C($CDCl_3$, 75 MHz) 166.8, 152.1, 147.7, 146.7, 131.7, 128.9, 128.4, 122.7, 121.9, 108.1, 97.2, 86.3, 51.7, 49.9, 0.4 and −0.7; λ_{max}(hexane)/nm 308.4 and 290.7; ν_{max}(KBr)/cm^{-1} 2954.9, 2193.4, 1726.1, 1531.6, 1259.8, 1038.4, 842.1 and 688.9; *m*/*z* (70 eV) 400 (M^+, 3.4%), 341 (M^+ − CO_2Me, 3.1), 241 (M^+ − Me − DMFu, 100) and 73 ($SiMe_3$, 46.4) (Calc. for $C_{21}H_{28}O_4Si_2$, 400.1526. Found, 400.1512). Compound **10**: δ_H($CDCl_3$, 300 MHz) 7.31 (2 H, d), 6.82 (2 H, d), 3.79 (3 H, s), 3.70 (3 H, s), 3.69 (3 H, s), 3.00 (1 H, d, *J* 3.47 Hz), 2.93 (1 H, d, *J* 3.47 Hz), 0.28 (3 H, s), 0.25 (3 H, s) and 0.10 (9 H, s); δ_C($CDCl_3$, 75 MHz) 169.8, 169.3, 159.5, 137.2, 132.9, 117.8, 115.8, 113.9, 96.3, 87.0, 55.3, 52.3, 27.6, 25.5, −2.2 and −4.7; λ_{max}(hexane)/nm 314.5 and 296.7; ν_{max}(NaCl)/cm^{-1} 2950.8, 1734.6, 1509.2, 1249.3, 1165.6 and 832.9; *m*/*z* (70 eV) 430 (M^+, 0.3%), 357 (M^+ − $SiMe_3$, 22.5%) and 73 ($SiMe_3$, 100%) (Calc. for $C_{22}H_{30}O_5Si_2$, 430.1632. Found, 430.1578). Compound **11**: δ_H($CDCl_3$, 300 MHz) 7.63 (2 H, d), 6.83 (2 H, d), 4.04 (1 H, d, *J* 2.2 Hz), 3.90 (1 H, d, *J* 2.2 Hz), 3.80 (3 H, s), 3.73 (3 H, s), 3.70 (3 H, s), 0.25 (6 H, s) and 0.14 (9 H, s); δ_C($CDCl_3$, 75 MHz) 171.4, 170.9, 160.4, 148.1, 127.7, 125.7, 116.3, 113.2, 102.9, 100.7, 55.3, 52.3, 52.2, 47.9, 45.7, −2.6 and −3.2; λ_{max}(hexane)/nm 316.5; ν_{max}(NaCl)/cm^{-1} 2938.7, 1729.7, 1508.4, 1250.7, 1171.6 and 835.9; *m*/*z* (70 eV) 430 (M^+, 0.2), 371 (M^+ − CO_2Me, 1.2), 357 (M^+ − $SiMe_3$, 0.9), 73 ($SiMe_3$, 69.9) and 59 (CO_2Me, 27.7)

(Calc. for $C_{22}H_{30}O_5Si_2$, 430.1632. Found 430.1605). Compound **12**: δ_H($CDCl_3$, 300 MHz) 7.62 (2 H, d), 6.85 (2 H, d), 4.03 (1 H, d, *J* 2.2 Hz), 3.89 (1 H, d, *J* 2.2 Hz), 3.79 (3 H, s), 3.74 (3 H, s), 3.70 (3 H, s) and 0.23 (9 H, s); δ_C($CDCl_3$, 50 MHz) 171.3, 170.9, 163.3, 148.7, 128.0, 125.7, 115.9, 113.8, 103.5, 98.7, 55.3, 52.3, 52.2, 46.1, 45.0 and −0.2; λ_{max}(hexane)/nm 313.4 and 227.2; ν_{max}(KBr)/cm^{-1} 2960.3, 2136.9, 1730.6, 1541.5, 1254.2, 1171.2 and 851.4; *m/z* (70 eV) 372 (M^+, 3.2%), 313 ($M^+ - CO_2Me$, 100), 59 (CO_2Me, 48.8) (Calc. for $C_{20}H_{24}O_5Si_1$, 372.1393. Found, 372.1403); m.p. 97–98 °C.

Irradiation of 1-(p-*Nitrophenyl*)-4-(*pentamethyldisilanyl*)-*buta*-1,3-*diyne* **3** *with DMFu*.—A deaerated solution of **3** (4 mmol dm^{-3}) and DMFu (100 mmol dm^{-3}) in methylene chloride was irradiated at 350 nm UV light in a Rayonet photochemical reactor, Model RPR-208, equipped with RUL 350 nm lamps. After irradiation for 12 h, the resulting photoreaction mixture was concentrated *in vacuo*. The photoadducts **13–14** were isolated in 20 and 2% yields, respectively, by silica gel column chromatography with hexane–diethyl ether (5:1, v/v) as an eluent followed by normal phase HPLC using hexane–ethyl acetate–methylene chloride (7:1:2, v/v/v) as an eluent. The photoproducts **13–14** were obtained as orange solids and product **14** was very unstable. Compound **13**: δ_H($CDCl_3$, 300 MHz) 8.18 (2 H, d), 7.57 (2 H, d), 6.99 (1 H, d, *J* 15.6 Hz), 6.20 (d, *J* 15.6 Hz), 3.72 (3 H, s), 3.21 (3 H, s), 0.38 (3 H, s), 0.32 (3 H, s) and 0.24 (9 H, s); δ_C($CDCl_3$, 50 MHz) 166.6, 155.6, 147.3, 146.5, 146.1, 132.3, 129.3, 123.6, 122.2, 107.9, 94.4, 90.8, 51.7, 49.9, 0.3 and −0.7; λ_{max}(hexane)/nm 317.8; ν_{max}(NaCl)/cm^{-1} 2954.2, 1727.3, 1521.6, 1344.2 and 852.7; *m/z* (70 eV) 445 (M^+, 1.4%), 286 ($M^+ - Me - DMFu$, 47.6), 228 ($M^+ - SiMe_3 - DMFu$, 32.8) and 73 ($SiMe_3$, 82.6) (Calc. for $C_{21}H_{27}NO_6Si_2$, 445.1377. Found, 445.1406); m.p. 90–91 °C. Compound **14**: δ_H($CDCl_3$, 300 MHz) 8.19 (2 H, d), 7.82 (2 H, d), 4.14 (1 H, d, *J* 2.15 Hz), 3.98 (1 H, d, *J* 2.15 Hz), 3.76 (3 H, s), 3.73 (3 H, s), 0.28 (6 H, s) and 0.16 (9 H, s); δ_C($CDCl_3$, 50 MHz) 171.7, 170.6, 160.2, 146.1, 138.2, 126.7, 124.3, 123.9, 108.6, 107.5, 52.6, 52.5, 48.8, 45.9, −2.6 and 3.4; λ_{max}(hexane)/nm 341.7 and 258.6; ν_{max}(NaCl)/cm^{-1} 2963.6, 1738.0, 1520.5, 1342.7 and 854.3; *m/z* (70 eV) 445 (M^+, 0.9%), 386 ($M^+ - CO_2Me$, 3.8) and 73 ($SiMe_3$, 48.7) (Calc. for $C_{21}H_{27}NO_6Si_2$, 445.1377. Found 445.1406).

UV Absorption Change of 1-*Aryl*-4-(*pentamethyldisilanyl*)-*buta*-1,3-*diynes on Irradiation*.—Solutions of 1-aryl-4-(pentamethyldisilanyl)buta-1,3-diynes (2×10^{-5} mol dm^{-3}) in dry *n*-hexane were prepared in quartz cuvettes (1.00 cm). After the solutions were purged with dry nitrogen, the UV absorption spectra were measured on the Shimadzu 3100S spectrophotometer. After irradiation at 300 nm UV light in a Rayonet photochemical reactor, Model RPR-208, equipped with RUL 300 nm lamps, the UV absorption spectra were measured. To investigate the oxygen effect, the UV absorption spectra of the aerated solution were recorded under the same conditions and compared with the results of the deaerated solution.

Acetone Concentration Effects on the Photoreaction of 1-*Aryl*-4-(*pentamethyldisilanyl*)*buta*-1,3-*diynes with Acetone*.—The relative quantum yields of the photoreactions of 1-aryl-4-(pentamethyldisilanyl)buta-1,3-diynes (4 mmol dm^{-3}) with acetone (8 mmol dm^{-3} and 100 mmol dm^{-3}) to give photoadducts **4–8** were measured. The 300 nm UV light in a Rayonet photochemical reactor, Model RPR-208, equipped with RUL 300 nm lamps was shone for 5 min. The quantitative analysis was carried out by HPLC using the following conditions: column, Lichrosorb Si 60 (25 × 1.0 cm, mean particle size 7 μm, E. Merck); eluents, **1**, hexane–diethyl ether (40:1, v/v), **2**, hexane–diethyl ether (25:1, v/v), **3**, hexane–diethyl ether (20:1, v/v).

Oxygen Effects on the Photoreaction of 1-*Aryl*-4-(*pentamethyldisilanyl*)*buta*-1,3-*diynes with Acetone and DMFu*.—The relative quantum yields of the photoreactions of 1-aryl-4-(pentamethyldisilanyl)buta-1,3-diynes (0.8 mmol dm^{-3}) with acetone (20 mmol dm^{-3}) to give photoadducts **4–8** were measured in the presence of oxygen (bubbled with dry oxygen) and compared with those obtained in the deaerated condition (degassed by N_2 bubbling). The 300 nm UV light in a Rayonet photochemical reactor, Model RPR-208, equipped with RUL 300 nm lamps was shone for 5 min. The quantitative analysis were carried out by HPLC using the following conditions: column Lichrosorb Si 60 (25 × 1.0 cm, mean particle size 7 μm, E. Merck); eluents, **1**, hexane–diethyl ether (40:1, v/v); **2**, hexane–diethyl ether (25:1, v/v); **3**, hexane–diethyl ether (20:1, v/v).

The same procedure was used for the photoreaction with DMFu except for 350 nm UV light for **3**. The quantitative analysis was carried out by HPLC using the following conditions: column, Lichrosorb Si 60 (25 × 1.0 cm, mean particle size 7 μm, E. Merck); eluents, **1**: hexane–ethyl acetate–methylene chloride (25:1:1, v/v/v); **2**, hexane–diethyl ether–methylene chloride (9:1:2, v/v/v); **3**, hexane–ethyl acetate–methylene chloride (7:1:2, v/v/v).

Acknowledgements

This investigation was supported by the OCRC-KOSEF and the Korea Advanced Institute of Science and Technology.

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Paper 4/02020K
Received 5th *April* 1994
Accepted 12th *May* 1994