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A Novel Photoinduced Intramolecular Cycloaddition Reaction of 1-(o-Methoxycarbonylmethoxyphenyl)-2-pentamethyldisilanyl Ethyne.

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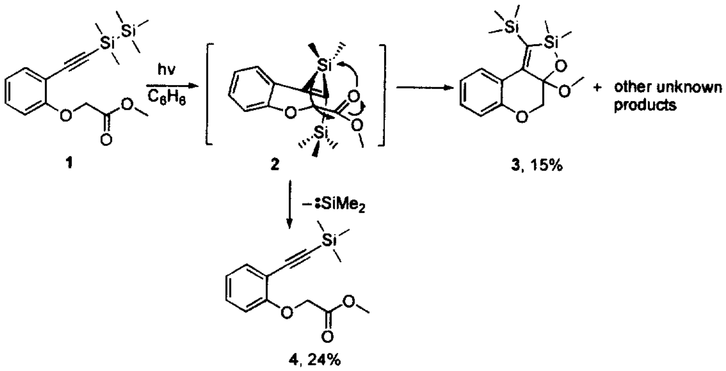
Abstract : Photolysis of 1-(o-methoxycarbonylmethoxyphenyl)-2-pentamethyldisilanyl ethyne **1** in benzene provides a novel intramolecular cycloaddition product **3**.

Silacyclopropene intermediates formed from the photolysis of alkynyl-substituted disilanes in methanol or acetone react readily with hydroxyl or carbonyl group to give the corresponding intermolecular photoaddition products.[1] We have recently reported a photochemical reaction of 1-(o-allyloxyphenyl)-2-pentamethyldisilanyl ethynes[2] affording a novel stereoselective intramolecular cyclization products. Intramolecular cycloaddition of C=O group will provide a novel reaction path and utility for the synthesis of Si containing heterocycles. We ,therefore, synthesized **1** which has a carbonyl group in the ortho position of phenylethynylpentamethyldisilane and now report a novel intramolecular cycloaddition reaction of **1**. Irradiation of **1**[3] ($5x10^{-4}$ mol dm^{-3}) in deaerated benzene with 300nm UV light provided a novel cycloaddition product **3** (15% yield)[4] and 1-(o-methoxycarbonylmethoxyphenyl)-2-trimethylsilyl ethyne **4** (24% yield)[5] along with some decomposition products of unknown structure as shown in Scheme 1. The formation of photoproduct **3** can be rationalized in terms of the initial formation of silacyclopropene intermediate **2** upon irradiation followed by the concerted intramolecular cycloaddition reaction between the carbonyl group in ortho substituent and Si-C bond of silacyclopropene formed. Liberation of dimethylsilylene species from the silacyclopropene intermediate **2** results in the formation of **4**. The structure of the photoproduct **3** was determined by various physical methods including ^{1}H-^{1}H and ^{1}H-^{13}C correlation spectroscopy (COSY), HMBC, nuclear Overhauser and exchange spectroscopy (NOESY).

Scheme 1



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The skeletal structure of **3** was established as shown in Figure 1. Further studies are in progress to elucidate the more detailed mechanism of the reaction.

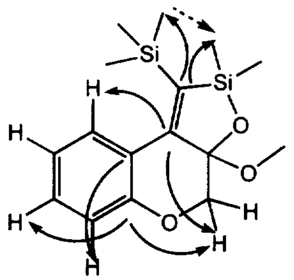

Figure 1. Important correlations observed in HMBC and NOESY spectra of photoproduct **3**.

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3. **1** : Colorless oil ; ^{1}H NMR($CDCl_3$, 300MHz) δ_H 0.14(9H, s), 0.26(6H, s), 3.77(3H, s), 4.69(2H, s), 6.77(1H, dd, J=8.3, 0.9Hz), 6.92(1H, td, J=7.6, 0.9Hz), 7.21(1H, td, J=7.6, 0.9Hz), 7.41 (1H, dd, J=7.6, 1.7Hz) ; ^{13}C NMR($CDCl_3$, 50MHz) δ_C -3.07, -2.60, 52.1, 66.4, 98.2, 102.7, 113.4, 113.9, 121.7, 129.5, 134.1, 158.7, 169.2 ; UV(CH_2Cl_2)λ_{max}303, 294, 261*nm* ; FT-IR (NaCl) 3074.7, 2953.5, 2152.1, 1764.8, 1596.3,1245.9*cm*$^{-1}$; MS (70*eV*) *m/z* 320 (M^+) ; HRMS (M^+) calcd for $C_{16}H_{24}O_3Si_2$ 320.1264, found 320.1333.
   The photolysis of **1** in the presence of nucleophiles such as methanol or acetone will be reported elsewhere.
4. **3** : Colorless oil ; ^{1}H NMR($CDCl_3$, 500MHz) δ_H 0.25(9H, s), 0.30(3H,s), 0.46(3H,s), 3.13(3H, s), 3.92(1H, d, J=11.2Hz), 4.45(1H, d, J=11.2Hz), 6.89(1H, d, J=7.3Hz), 6.90(1H, dd, J=7.3, 8.8Hz), 7.24(1H, ddd, J=8.8, 7.3, 1.5Hz), 7.44(1H, dd, J=7.3, 1.5Hz) ; ^{13}C NMR($CDCl_3$, 125MHz) δ_C 0.62, 0.91, 1.27, 49.56, 72.86, 102.48, 116.82, 119.69, 121.36, 128.49, 130.81, 135.20, 154.77, 157.95; UV(CH_2Cl_2)λ_{max}313, 262, 230*nm* ;FT-IR (NaCl) 2955.1, 1575.9, 1476.9, 1269.6 *cm*$^{-1}$; MS (70*eV*) *m/z* 320 (M^+) ; HRMS (M^+) calcd for $C_{16}H_{24}O_3Si_2$ 320.1264, found 320.1280.
5. **4** : Colorless oil ; ^{1}H NMR($CDCl_3$, 300MHz) δ_H 0.24(9H, s), 3.78(3H, s), 4.69(2H, s), 6.76(1H, dd, J=8.3, 0.9Hz), 6.92(1H, td, J=7.7, 0.8Hz), 7.21(1H, td, J=7.7, 0.8Hz), 7.42(1H, dd, J=7.7, 1.7Hz) ; ^{13}C NMR($CDCl_3$, 50MHz) δ_C -0.05, 52.1, 66.4, 99.2, 100.6, 113.4, 113.5, 121.8, 129.8, 134.2, 158.8, 169.1; UV(CH_2Cl_2) λ_{max} 302, 293, 260, 248*nm*; FT-IR(NaCl) 3073.6, 2957.2, 2158.8, 1764.4, 1596.9, 1250.4*cm*$^{-1}$; MS (70*eV*)*m/z* 262(M^+) ; HRMS (M^+) calcd for $C_{14}H_{18}O_3Si$ 262.1025, found 262.1033.