In summary, the results provide theoretical basis for the qualitative experimental observations that an electron-donating nonleaving group, RY, favors expulsion of the more basic phenoxide by depressing the higher barrier, TS2, more than TS1 with a greater extent of bond cleavage, whereas the opposite holds for an electron-withdrawing RY, *i.e.*, favors expulsion of the less basic phenoxide by depressing the lower barrier, TS1, more than TS2 with a greater extent of bond cleavage in TS1 than that in TS2. These trends are also in agreement with the signs of ρ_{XY} (>0) and ρ_{YZ} (<0) established qualitatively based on the experimental results.

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Regioselective Friedel-Crafts Reaction of Allyldichlorosilane with 3,4-Benzo-1,1-dichloro-1-silacyclopentene

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A 86 : 14 isomeric mixture of 3,4-[3'-(dichlorosilyl)isopropyl]benzo-1,1-dichloro-1-silacyclopentene and 3,4-[2'-(dichlorosilyl)isopropyl]benzo-1,1-dichloro-1-silacyclopentene was prepared by the regioselective Friedel-Crafts reaction of allyldichlorosilane with 3,4-benzo-1,1-dichloro-1-silacyclopentene catalyzed by Lewis acid $AlCl_3$. The structure of the products was confirmed by methylation with methylmagnesium bromide and by methoxylation with trimethylorthoformate.

Introduction

There has been considerable interest in the chemistry of 3,4-benzo-1,1-dichloro-1-silacyclopentene (*i.e.*, 2,2-dichloro-2-silaindan) **I** and allyldichlorosilane **II**. The dimethyl derivative of **I**, 3,4-benzo-1,1-dimethyl-1-silacyclopentene undergoes an anionic ring-opening polymerization to give a thermally stable polycarbosilane.[1,2] Allyldichlosilane was also found to undergo Friedel-Crafts reactions with aromatic compounds to produce (2-arylpropyl)chlorosilanes.[3,4] Friedel-Crafts reac-

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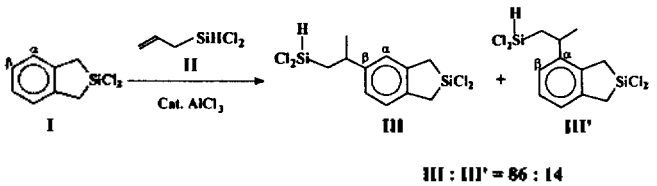


Scheme 1.

tions have been extensively studied for a long time.[5] The recent development of the direct synthesis method for the preparation of allyldichlorosilane[6~8] stimulated an interest in the Friedel-Crafts reactions of allyldichlorosilane with substituted benzenes. 3,4-Benzo-1,1-dichloro-1-silacyclopentene was prepared by a large lab-scale direct synthetic process.[9]

Herein we report the regioselective Friedel-Crafts reaction of allyldichlorosilane with 3,4-benzo-1,1-dichloro-1-silacyclopentene. The structure of the reaction products has been confirmed by chemical reactions of the product 3,4-[3′-(dichlorosilyl)isopropyl]benzo-1,1-dichloro-1-silacyclopentene. Methylation has been achieved by treating with methylmagnesium bromide while methoxylation occurred by reacting with trimethylorthoformate.

Results and Discussion

3,4-Benzo-1,1-dichloro-1-silacyclopentene **I** has the two reactive functional groups: the aromatic benzene ring as well as the chlorine atoms bonded to silacyclopentene ring. Friedel-Crafts reaction of **I** with allyldichlorosilane **II** catalyzed by the Lewis acid of $AlCl_3$ has been carried out to give 3,4-[3′-(dichlorosilyl)isopropyl]benzo-1,1-dichloro-1-silacyclopentene **III** in 55% yield (Scheme 1).

The structure of **III** was confirmed by ^1H, ^{13}C NMR spectra, mass spectrum, IR spectrum, and elemental analysis. The IR spectrum of **III** shows that characteristic Si-H stretching frequency which appears at 2200 cm^{-1} but the C=C stretching peak of starting material **II** at 1630 cm^{-1} disappears, which indicates that silyl-isopropylation with keeping the Si-H group has occurred.[10] The electrophilic substitution reaction of **II** to **I** was occurred predominantly at the β position of starting material **I** rather than the α position of **I**. The assignment for the position of Friedel-Crafts alkylation reaction was determined on the basis of fact that the area ratio of α proton to β proton of aromatic ring in ^1H NMR spectrum was changed from 1 : 1 ratio in starting material **I** to approximately 2 : 1 ratio in compound **III**, which indicates that alkylation was favorably occurred at the β position of **I** (*vide infra*) (Figure 1).

The triplet resonance appears at 5.33 ppm for the Si-H (H^a). The multiplet resonances are observed at 1.55-1.61 ppm and 3.07-3.14 ppm for protons H^b and H^c, respectively. The doublet peaks are observed at 1.36 ppm for methyl group (H^d), and 2.57 ppm for two methylene groups (H^e and $H^{e'}$) of cyclopentene ring. The phenylene resonances appear at 7.02-7.05 ppm for H^c (*i.e.*, β proton) and at 7.11-7.20 ppm for H^f and $H^{f'}$ (*i.e.*, α protons). The area ratios between α proton and β proton are approximately 2 : 1 and 2 : 2 for compounds **III** and **I**, respectively, which clearly indicates that alkylation has been occurred at β position. The area ratio of tertiary isopropyl proton (H^c of **III** and H^c of 3,4-[2′-(dichlorosilyl)isopropyl]benzo-1,1-dichloro-1-silacyclopentene **III′**) in the ^1H NMR spectrum shows that a 86 : 14 isomeric mixture of **III** and **III′** has been formed. The ratio of isomers based on the ^1H NMR spectrum was consistent with that of GC peak areas. Molecular ion peak of m/e of 344 was also observed in mass spectrum. In ^{13}C NMR spectrum 6 aromatic resonances appear in the region of 125.37-145.67 ppm, and 5 aliphatic resonances in the region of 24.85-34.60 ppm. Satellite-like peaks in the ^{13}C NMR spectrum of **III** were also observed due to the isomer **III′**. However, it was difficult to separate **III** from **III′** by distillation.

The chlorine atoms bonded to silicon atoms of mixture of **III** and **III′** were easily converted into methyl and

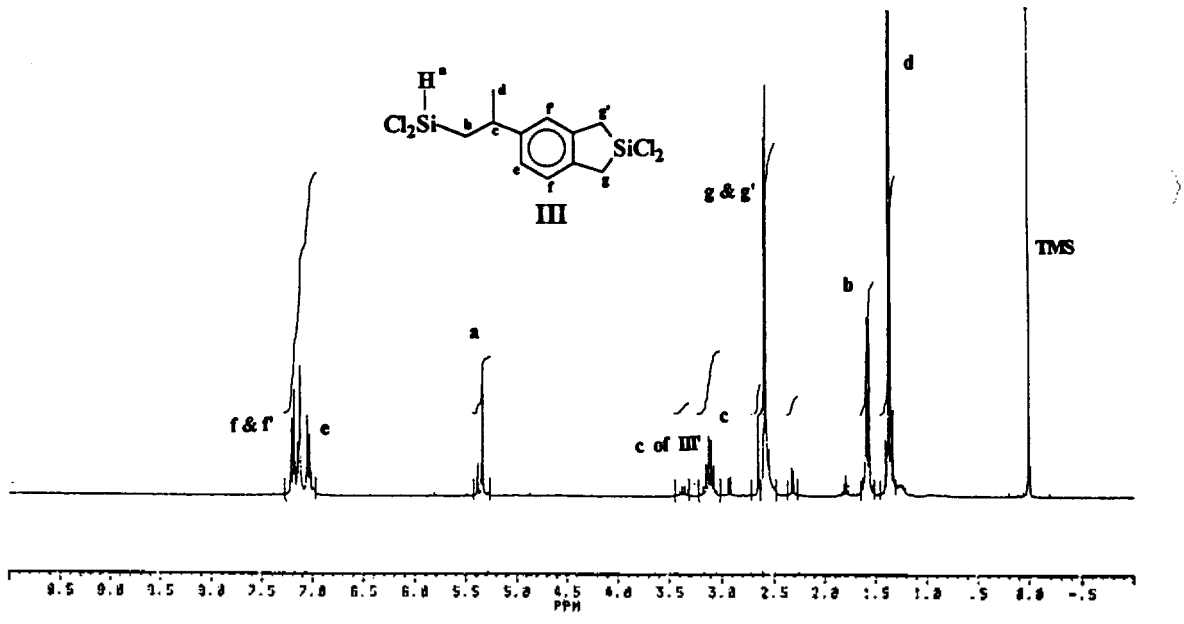
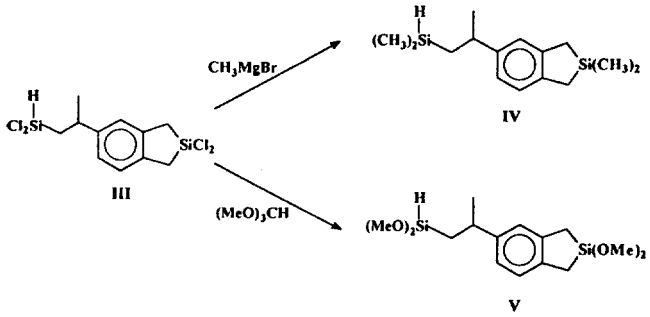


Figure 1. ^1H NMR spectrum of mixture of **III** and **III′**.



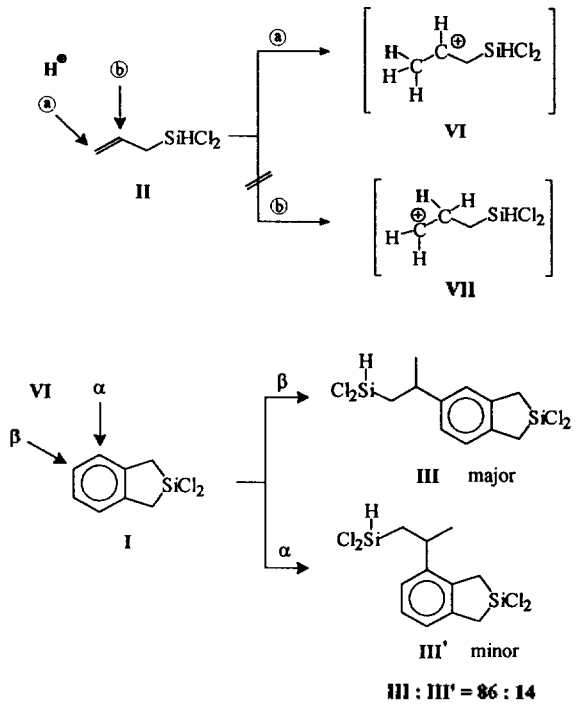
Scheme 2.

methoxy groups. The isomeric ratio of the products **III** and **III'** was confirmed by methylation with methylmagnesium bromide and methoxylation by treatment with trimethylorthoformate (Scheme 2).

Based on the area ratio of ^{1}H NMR spectra, the products **IV** and **V** also contained isomeric 3,4-[2'-(dimethylsilyl)isopropyl]benzo-1,1-dimethyl-1-silacyclopentene **IV'** and 3,4-[2'-(dimethoxysilyl)isopropyl]benzo-1,1-dimethoxy-1-silacyclopentene **V'** in the same ratio of 86 : 14 as **III** and **III'**, respectively (Figure 2).

The possible mechanism for Friedel-Crafts alkylation of **I** by allyldichlorosilane is shown in Scheme 3.

The proton originating from hydrogen chloride due to the reaction of anhydrous aluminum chloride with water inevitably present in the reaction mixture[11] initiates the reaction and results in forming the carbocation intermediate. The pathway (a) through the secondary carbocation intermediate **VI** is more favorable than the pathway (b) *via* the primary carbocation intermediate **VII**. This is attributed to the stability of secondary carbocations[12] as well as the β stabilization effect of intermediate **VI** rather than **VII**.[13,14] The resulting



Scheme 3.

secondary carbocation intermediate **VI** then might attack the β position of **I** much more favorably than the α position due to the steric hindrance.

In conclusion, 3,4-[3'-(dichlorosilyl)isopropyl]benzo-1,1-dichloro-1-silacyclopentene has been prepared by the regioselective Friedel-Crafts reaction of allyldichlorosilane with 3,4-benzo-1,1-dichloro-1-silacyclopentene in the presence of $AlCl_3$ as a Lewis acid catalyst. The product of regioselective

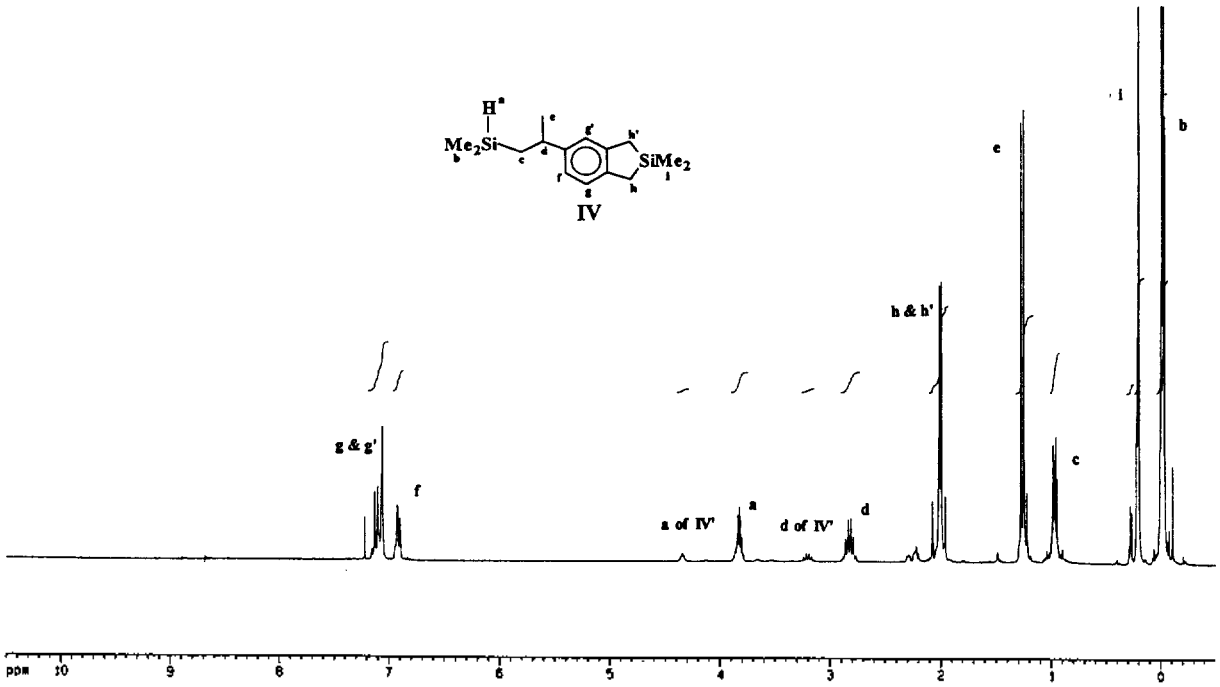


Figure 2. ^{1}H NMR spectrum of mixture of **IV** and **IV'**.

Friedel-Crafts reaction was composed of the isomeric mixture of **III** and **III'** in the manner of 86 : 14 ratio, respectively. The structure of the products was also confirmed by methylation with methylmagnesium bromide and by methoxylation with trimethylorthoformate.

Experimental

All chemicals were purchased from Aldrich Chemicals Inc., U.S.A., or Yakuri Chemical Inc., Japan. Tetrahydrofuran (THF), *n*-hexane, and diethylether were distilled from sodium metal/benzophenone ketyl prior to use. Hexamethylphosphoramide (HMPA) was distilled from calcium hydride and stored over 4 Å molecular sieves. All glassware were dried overnight in an oven at 120 ℃. The apparatus was assembled and was then flamed-dried while being swept with argon.

Reactions were monitored by analytical GLC of Hewlett Packard 5890 II equipped with HP-1 capillary column (0.53 mm×30 m) coated with cross-linked methyl siloxane gum and with FID detector. The column was deactivated immediately before use by the injection of 50 μL of hexamethyldisilazane.

^{1}H and ^{13}C nuclear magnetic resonance (NMR) spectra were recorded on a Bruker ARX 300 spectrometer. Chemical shifts were measured using tetramethylsilane as an internal standard or the solvents as standard. IR spectra were recorded by a Shimadzu IR 430 or Bruker IFS-48 FTIR spectrometers. Low resolution mass spectra were measured on Mass Hewlett Packard 5971A instrument by EI ionization at 70 eV.

Elemental analyses were performed by the Advanced Analysis Center of the Korea Institute of Science and Technology, Seoul, Korea.

3,4-Benzo-1,1-dichloro-1-silacyclopentene (I) and **allyldichlorosilane (II)** were generously provided by Dr. Il Nam Jung, Korea Institute of Science and Technology. Compound **I** had the following spectral properties. ^{1}H NMR ($CDCl_3$) δ: 2.63 (s, 4H), 7.17-7.22 (m, 2H), 7.25-7.29 (m, 2H). ^{13}C NMR ($CDCl_3$) δ: 25.25, 126.99, 129.08, 137.16. IR (KBr) ν: 3065, 3010, 2950, 2880, 1595, 1570, 1490, 1475, 1460, 1450, 1390, 1380, 1280, 1210, 1160, 1130, 1090, 1070, 1030, 940, 840, 810-740, 600, 560-500 cm^{-1}. MS m/e (relative intensity): 202 [M^+, 83], 166 [$(M\text{-}HCl)^+$, 97], 104 [$(M\text{-}SiCl_2)^+$, 100], 98 [$SiCl_2^+$, 28], 78 [$C_6H_6^+$, 70]. Compound **II** had the following spectral properties. ^{1}H NMR ($CDCl_3$) δ: 2.18 (d, 2H, J=7 Hz), 5.12-5.18 (m, 2H), 5.47 (t, 1H, J=2 Hz), 5.71-5.85 (m, 1H). ^{13}C NMR ($CDCl_3$) δ: 27.00, 118.68, 128.12. IR (KBr) ν: 3095, 3020, 2990, 2950, 2900, 2210 (Si-H), 1640, 1630 (C=C), 1420, 1415, 1400, 1390, 1385, 1300, 1170, 1120-1030, 990, 910, 825, 810, 760, 720, 610, 560 cm^{-1}. MS m/e (relative intensity): 148 [M^+, 68], 127 [28], 125 [$(M\text{-}CH_3)^+$, 43], 112 [$(M\text{-}CH_2CH_2)^+$, 30], 107 [64], 105 [$(M\text{-}Cl)^+$, 100], 101 [51], 99 [$SiHCl_2^+$, 71], 65 [61].

3,4-[3'-(Dichlorosilyl)isopropyl]benzo-1,1-dichloro-1-silacyclopentene (III). In a 250 mL 3-neck round bottom flask equipped with reflux condenser, pressure equalizing dropping funnel, and magnetic stirring bar was placed **I** (10.8 g, 0.05 mol) and $AlCl_3$ (0.67 g, 5.0 mmol) under argon atmosphere. The flask and its contents were immersed in an ice-water bath. **II** (6.20 g, 0.04 mol) was placed in the dropping funnel, and added dropwise to the well stirred mixture over 1 h. The reaction was exothermic and the mixture was stirred for 1 h after cooling. The reaction mixture was stirred vigorously with heating at 50 ℃ for 1 h and treated with NaCl (1.0 g). *n*-Hexane (20 mL) was added, filtered and the volatile solvent removed by evaporation under reduced pressure. The residue was fractionally distilled. A fraction with bp 105-106 ℃/5 mmHg in 7.5 g, 55% yield, was obtained. ^{1}H NMR ($CDCl_3$) δ: 1.36 (d, 3H, J=7 Hz), 1.55-1.61 (m, 2H), 2.57 (d, 4H, J=5 Hz), 3.07-3.14 (m, 1H), 5.33 (t, 1H, J=2 Hz), 7.02-7.05 (m, 1H), 7.11-7.20 (m, 2H). ^{13}C NMR ($CDCl_3$) δ : 24.85, 24.89, 25.37, 30.34, 34.60, 125.37, 127.08, 129.32, 135.39, 137.51, 145.67. IR (KBr) ν: 3070, 3020, 2960, 2930, 2870, 2200 (Si-H), 1600, 1565, 1500, 1490, 1480, 1450, 1440, 1420, 1380, 1330, 1265, 1235, 1210, 1190, 1130, 1100-1000, 900-750, 600-500 cm^{-1}. MS m/e (relative intensity): 344 [M^+, 63], 329 [$(M\text{-}CH_3)^+$, 40], 301 [41], 265 [29], 229 [$(M\text{-}SiHCl_2CH_2)^+$, 71], 193 [23], 129 [29], 115 [22], 83 [100]. Elemental Anal. Cacld. for $C_{11}H_{14}Cl_4Si_2$: C, 38.37; H, 4.10. Found: C, 37.80; H, 4.22. Compound **III** was containing 3,4-[2'-(dichlorosilyl)isopropyl]benzo-1,1-dichloro-1-silacyclopentene **III'** in 14% based on the ^{1}H NMR spectrum.

3,4-[3'-(Dimethylsilyl)isopropyl]benzo-1,1-dimethyl-1-silacyclopentene (IV). In a 100 mL 3-neck round bottom flask equipped with reflux condenser, pressure equalizing dropping funnel, and magnetic stirring bar were placed 3.0 M methylmagnesium bromide (14.5 mL, 0.043 mol) and diethylether (40 mL) under argon atmosphere. **III** (3.00 g, 8.0 mmol) and diethylether (40 mL) was placed in the dropping funnel, and added dropwise to the well stirred solution over 1 h. The reaction mixture was stirred for another 6 h. *n*-Hexane (100 mL) was poured. The organic layer was separated, washed with water (3×100 mL) and with saturated NaCl solution, dried over anhydrous magnesium sulfate, and filtered. The volatile solvent was then removed by evaporation under reduced pressure. The residue was fractionally distilled. A fraction with bp 93-95 ℃/5 mmHg in 1.7 g, 75% yield, was obtained. ^{1}H NMR ($CDCl_3$) δ: 0.08 (d, 6H, J=4 Hz), 0.26 (s, 6H), 1.08 (t, 2H, J=4 Hz), 1.33 (d, 3H, J=7 Hz), 2.05 (d, 4H, J=5 Hz), 2.84-2.91 (m, 1H), 3.86-3.90 (m, 1H), 6.94-6.97 (m, 1H), 7.10-7.17 (m, 2H). ^{13}C NMR ($CDCl_3$) δ: −4.17, −3.67, −2.29, 20.72, 21.30, 24.78, 25.48, 36.23, 123.96, 127.29, 129.00, 139.48, 142.10, 146.94. IR (neat) ν: 3090, 3060, 3000, 2950, 2900, 2860, 2100 (Si-H), 1600, 1560, 1480, 1460, 1450, 1410, 1400, 1390, 1370, 1325, 1250, 1210, 1190, 1125, 1100, 1045, 1010, 1000, 900, 880, 830, 760, 740, 710, 680 cm^{-1}. MS m/e (relative intensity): 262 [M^+, 55), 247 [$(M\text{-}CH_3)^+$, 51], 231 [$(M\text{-}2(CH_3)\text{-}H)^+$, 25], 219 (84), 205 (72), 189 [$(M\text{-}(CH_3)_2SiHCH_2)^+$, 89], 173 (61), 159 (36), 145 (51), 131 (28), 115 (27), 100 (26), 73 [$(CH_3)_2SiHCH_2)^+$, 100]. Elemental Anal. Cacld. for $C_{15}H_{26}Si_2$: C, 68.70; H, 9.92. Found: C, 68.30; H, 9.23. Compound **IV** was containing 3,4-[2'-(dimethylsilyl)isopropyl]benzo-1,1-dimethyl-1-silacyclopentene **IV'** in 14% on the base of ^{1}H NMR spectrum.

3,4-[3'-(Dimethoxysilyl)isopropyl]benzo-1,1-dimethoxy-1-silacyclopentene (V). In a 100 mL 3-neck round bottom flask equipped with reflux condenser, $CaCl_2$ drying tube, and magnetic stirring bar were placed **III** (3.44 g, 10.0 mmol) and trimethylorthoformate (10.94 g, 100 mmol). The reaction mixture was stirred at 60 ℃ for 3 h. After reaction was completed, the volatile solvent was removed

by evaporation under reduced pressure. The residue was fractionally distilled. Compound V in 1.86 g, 57% yield, was obtained. ^{1}H NMR ($CDCl_3$) δ: 1.04 (m, 2H), 1.29 (d, 3H, J=7 Hz), 2.02 (d, 4H, J=6.9 Hz), 2.95 (m, 1H), 3.48 (s, 3H), 3.51 (s, 3H), 3.56 (s, 6H), 4.42 (t, 1H, J=1.3 Hz), 6.94-6.97 (m, 1H), 7.08-7.15(m, 2H). ^{13}C NMR ($CDCl_3$) δ: 15.01, 15.59, 22.78, 24.99, 34.09, 50.76, 50.98, 51.04, 124.19, 127.24, 129.15, 136.68, 139.17, 146.68. IR (neat) ν: 3030, 2950, 2800, 2170 (vs, Si-H), 1605, 1560, 1480, 1450, 1190, 1100(br), 955, 835(br), 795, 660 cm^{-1}. MS m/e (relative intensity): 326 (M^+, 69), 309 (34), 294[$(M-CH_3OH)^+$, 48], 283 (35), 276 (52), 262(37), 247 (34), 221(M^+-SiH$(OMe)_2CH_2$, 71), 204 (40), 189 (79), 162 (37), 129 (29), 121 (92), 91 [$(SiH(OMe)_2)^+$, 85], 83 (100), 79 (29). Elemental Anal. Cacld. for $C_{15}H_{26}Si_2O_4$: C, 55.19; H, 8.03. Found: C, 55.40; H, 8.11. Compound V was containing 3,4-[2'-(dimethoxysilyl)isopropyl]benzo-1,1-dimethoxy-1-silacyclopentene V' in 14% on the base of ^{1}H NMR spectrum.

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Synthesis of Pyrazinopsoralen: A Pyrazine Ring Fused Monofunctional Psoralen Derivative

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An efficient synthesis of 6,8-dioxa-1,4-diazacyclopenta[b]phenanthren-5-one (Pyrazinopsoralen) (**4**) has been carried out by the Suzuki coupling reaction as a key step starting from 5-bromo-6-methoxybenzofuran (**6**) and methyl 2-iodo-3-pyrazinecarboxylate (**8**).

Introduction

Psoralens have a wide range of photobiological properties. They have shown photosensitizing effects in animals and humans and have been used in PUVA (psoralen + UVA: 320-400 nm) photochemotherapy[1~4] for the treatment of psoriasis, vitiligo, mycosis fungoides, and chronic leukemia. They are known to be phototoxic to insects, fungi, viruses, and bacteria.[5~8] Psoralens are also used as powerful tools in nucleic acid research consequences of defined lesions in DNA.[9,10]

Psoralen (Ps, **1**) is the parent structure of a relatively large number of furocoumarins in which the rings are linearly fused (Figure 1). Their biological properties have been attributed to their ability to photoreact with nucleic acids, especially DNA.[11] It appears that the genotoxic effects, as well as the therapeutically important antiproliferative effects, are due mainly to their capacity to induce photoconjugation to DNA. The modification of DNA by psoralens is a two-step process:[12,13] (a) formation of a molecular complex in the ground state; (b) photoconjugation of the complexed psoralen to pyrimidine bases of DNA, particularly thymine.[11] However, undesirable effects involving the photomutagenecity and photocarcino-