Friedel-Crafts Type Alkylation of 1,2,3,4,5,6,7,8-Octahydroanthracene with Vinylchlorosilanes: Synthesis of Mono, Bis[2-(chlorosilyl)ethyl]-1,2,3,4,5,6,7,8-octahydroanthracenes†

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Friedel-Crafts alkylation reaction of an isomeric mixture of 1,2,3,4,5,6,7,8- (2) and 1,2,3,4,5,6,7,8-octahydrophenanthrene (2') with excess vinylchlorosilanes such as vinyl(methyl)dichlorosilane (1a) and vinyltrichlorosilane (1b) in the presence of aluminum chloride catalyst at 80 °C gives only one dialkylation products, 9,10-bis[2-(chlorosilyl)ethyl]-1,2,3,4,5,6,7,8-octahydroanthrenes [(Cl2XSiCH2CH2)2C14H16: X = Me (4a), Cl (4b)] in good yields, but 9,10-bis[2-(chlorosilyl)ethyl]-1,2,3,4,5,6,7,8-octahydroanthrenes are not obtained. However, monoalkylation of 2 with 1 affords a mixture of both isomeric compounds, 9-[2-(chlorosilyl)ethyl]-1,2,3,4,5,6,7,8-octahydroanthracenes 3 and -phenanthrenes 3'. The yield of product 3' is always higher than that of 3. When a mixture of 3 and 3' is alkylated again with 1, only product 4 without phenanthrene type compounds is obtained, indicating that the isomerizations between 2 and 2', or 3 and 3' occur under the alkylation condition. The alkylation with dimethylvinylchlorosilane or trimethylvinylsilane did not proceed. The structure of 4a is determined by X-ray single crystal diffraction analysis.

Key Words: Friedel-Crafts alkylation, Octahydroanthracene, Organosilicon, Vinylchlorosilanes

Introduction

Polymers with π-electron system such as anthracenes have recently attracted a great deal of interests because of their optical and electric properties due to the delocalization of π-electrons.1-3 Generally, organosilicon compounds containing an anthracene group such as 9,10-bis(trialkylsilyl)anthracene or 9,10-bis(trialkylsilylmethyl)anthracene are prepared by the coupling reaction of chlorosilanes such as chlorotrialkylsilanes or (chloromethyl)trialkylsilanes with an anthracene group such as 9,10-bis(trialkylsilyl)anthracene.4,5 or (chloromethyl)trialkylsilanes6 with an anthracenyl anion generated by the dehalogenation of 9,10-dihaloanthracene with organometallic reagents. However, it is difficult to obtain anthracenylchlorosilanes having reactive chlorine atoms on the silicon by this method because of the strong reactivity of organometallic reagents toward the coupling reaction.7

We have previously reported the Friedel-Crafts alkylations of simple ring compounds such as benzene derivatives,8-11 ferrocene,12 and biphenyl7 with organosilicon compounds such as allylchlorosilanes, vinylchlorosilanes, and (ω-chloroalkyl)chlorosilanes in the presence of Lewis acid catalysts to give (phenylalkyl)chlorosilanes with Si-Cl bonds.13 However, the reaction of poly-annulated anthracene with vinylchlorosilanes in the presence of Lewis acid catalyst was not successful because of the deactivation of catalyst by complexation with anthracene ring.14 Encouraged by the success on the syntheses of these simple benzene derivatives with organochlorosilane, we attempted the Friedel-Crafts alkylation of 1,2,3,4,5,6,7,8-octahydroanthracene (2) as one of simple benzene derivatives with vinylchlorosilanes [CH2 = CHSiCl2X, X = Me (1a), Cl (1b)]. The alkylation products might be aromatized by dehydrogenation15 to give anthracene-substituted chlorosilanes.

The alkylation reaction of 2 with 1 certainly gave 9-alkylated products or 9,10-dialkylated products depending upon the mole ratio of 2 and vinylsilanes 1a, b. Such a process without using expensive organometallic reagents should be attractive to both industry and academia. In this paper, we wish to report the alkylation of 2 with 1a, b to give 1,2,3,4,5,6,7,8-octahydroanthracene-substituted chlorosilanes and also the observations of the isomerizations between 2 and 1,2,3,4,5,6,7,8-octahydrophenanthrene (2'), and between both monoalkylated isomeric products, 9-[2-(chlorosilyl)ethyl]-1,2,3,4,5,6,7,8-octahydroanthracene (3a) and -phenanthrene (3a') etc.

Results and Discussion

Synthesis of 9,10-bis[2-(chlorosilyl)ethyl]-1,2,3,4,5,6,7,8-octahydroanthracenes. 9,10-Bis[2-(chlorosilyl)ethyl]-1,2,3,4,5,6,7,8-octahydroanthrenes [(Cl2XSiCH2CH2)2C14H16: X = Me (4a), Cl (4b)] were synthesized by two step reactions: first, compounds of 2 and 2' were prepared, starting from 1,2,3,4-tetrahydrophenanthrene and 1,4-dichlorobutane, second, the one potted Friedel-Crafts alkylations of 2 or 2' with excess vinylsilanes 1a, b gave the desired dialkylation products 4a and 4b (Scheme 1).

A 2 : 1 mixture of both isomers 2 and 2' was prepared in
43% yield by the Friedel-Crafts alkylation of 1,2,3,4-tetrahydroanaphthalene with 1,4-dichlorobutane in the presence of \( \text{AlCl}_3 \) as a catalyst as described in literature.\(^ {16} \) The compound \( 2 \) was isolated by recrystallization from n-pentane solution of a mixture of \( 2 \) and \( 2' \).

When \( 2 \) was alkylated with \( 1a \) in the presence of \( \text{AlCl}_3 \), monooalkylated compounds of \( 3a \) and \( 3a' \) were obtained along with dialkylated compound \( 4a \). The isomeric compound \( 2' \) was detected during the reaction, indicating the isomerization between \( 2 \) and \( 2' \) under the reaction condition. Thus, the \( 2 : 1 \) isomeric mixture of \( 2 \) and \( 2' \) was used for dialkylation without purification. The reaction conditions for the dialkylation were optimized by varying the mole ratios of \( 1 \) and \( 2 \) and reaction time. The results are summarized in Table 1.

As shown in Table 1, the yield of dialkylation product \( 4 \) increases as the mole ratio of \( 1 \) to \( 2 \) increases from 1 : 1 to 1 : 3, but it did not increase higher than 85% even with the use of \( 2 \) in 4-fold excess. When a 1 : 1 reaction of \( 1 \) and \( 2 \) was carried out, mono-alkylation products of \( 3 \) and \( 3' \) were the major products and \( 3' \) was obtained 4 times more than \( 3 \). These results indicate that phenanthrene type compound \( 2' \) is more favorable than \( 2 \) for the alkylation due to the less steric hindrance in the nucleophilic attack of vinylchlorosilanes to 9-positioned carbon of benzene-ring. In the dialkylation reaction, anthracene type products \( 4a, b \), were only obtained from the alkylation of \( 3 \) or \( 3' \) with vinylchlorosilanes \( 1a, b \), but no phenanthrene type products were observed. The results suggest that \( 3' \) isomerized to \( 3 \), followed by the second alkylation with \( 1 \) to give \( 4 \). The reactivity of \( 1a \) was slightly higher than \( 1b \) in the alkylation. But the alkylation of \( 2 \) with vinyldimethylchlorosilane or vinyltrimethylsilane did not proceed, probably due to the presence of bulkier silyl group.

New compounds \( 3a, 3a', 3b, 3b', 4a, \) and \( 4b \) were characterized by the analysis of NMR spectroscopy. \(^ {13} \)C NMR spectra are helpful for the identification of such alkylation products. Both types of isomeric compounds \( 3a, b \) and \( 3a', b' \) showed 4 peaks and 6 peaks in aromatic region, respectively, due to their symmetries. For the dialkylated products \( 4a \) and \( 4b \), two peaks in the aromatic region appeared due to their higher symmetries, respectively.

The structure of \( 4a \) was determined by X-ray single crystal diffraction. Details of the structure determinations of \( 4a \) are given in Tables 2 and 3. The molecular structures are shown in Figure 1. In Figure 1, \( 4a \) showed a good symmetric structure that two silyl-groups substituted at the C9 and C10 of \( 4a \) are symmetrically located in the opposite side.

Table 1. Friedel-Crafts Alkylation of \( 2 \) with vinylchlorosilanes\(^ a \)

<table>
<thead>
<tr>
<th>vinylsilane (1)</th>
<th>mole ratio (1/2(^ 2 ))</th>
<th>reaction time (h)</th>
<th>products (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>( a )</td>
<td>1.0</td>
<td>2</td>
<td>8</td>
</tr>
<tr>
<td>( a )</td>
<td>2.0</td>
<td>3</td>
<td>2</td>
</tr>
<tr>
<td>( a )</td>
<td>3.0</td>
<td>4</td>
<td>0</td>
</tr>
<tr>
<td>( a )</td>
<td>4.0</td>
<td>4</td>
<td>0</td>
</tr>
<tr>
<td>( b )</td>
<td>1.0</td>
<td>3</td>
<td>7</td>
</tr>
<tr>
<td>( b )</td>
<td>2.0</td>
<td>4</td>
<td>2</td>
</tr>
<tr>
<td>( b )</td>
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<td>0</td>
</tr>
<tr>
<td>( b )</td>
<td>4.0</td>
<td>5</td>
<td>0</td>
</tr>
</tbody>
</table>

\(^{a}\) The reaction was carried out at 80 °C and using 20 mol % of \( \text{AlCl}_3 \) based on \( 2 \) used. \(^{b}\) The 2 : 1 mixture of \( 2 \) and \( 2' \) was used. \(^{c}\) GLC yields based on \( 2 \) used. \(^{d}\) Isolation yields.
Mechanism. On the basis of our results, a plausible mechanism for the alkylation of 2 with vinylsilane 1a is outlined in Scheme 2. In the Friedel-Crafts alkylation of arenes with aluminum chloride as a catalyst, a small amount of hydrogen chloride resulting from the reaction of anhydrous aluminum chloride with moisture inevitably present in the reactants would initiate the reaction. The proton from the α-bond of the aromatic ring generates a cation on the aromatic ring, which is followed by deprotonation to give silylalkylated aromatic compounds 3a along with the regeneration of a proton. This proton initiates the catalytic cycle of the Friedel-Crafts alkylation with 1a. Finally the intermediate 1 attacks 3a to give dialkylated product 4a.

In conclusion, Friedel-Crafts alkylation reaction of 2 with vinylchlorosilanes at 80 °C in the presence of AlCl3 gave dialkylated products 4 in good yields. In these reactions, the reactivity of 1a is higher that that of 1b. However, no alkylation of 2 was observed in the case of vinylchlorosilanes having two or more methyl groups on the silicon atom. In monoalkylation reactions, the formation of phenanthrene type compounds 3a is more favorable than anthracene type compounds 3. In the dialkylation reaction, 9,10-dialkylated anthracene type compounds 4a were only produced, indicating the rearrangement of monoalkylated phenanthrene type product 3 to anthracene type product 3 under the alkylation condition and followed by the second alkylation because of the less steric hindrance of 3. The structure of 4a was determined by X-ray single crystal diffraction.

Experimental Section

General Comments. All reaction and manipulations were carried out under purified dinitrogen atmosphere using Schlenk techniques. Glasswares were flame-dried before use. Dried solvents were employed in all the reactions. Aluminum chloride (99%) and 1,2,3,4-tetrahydronaphthalene were purchased from Aldrich Chemical Co. Vinylchlorosilanes 1a, 2b were purchased from Gelest, Inc. and used without purification. The reaction products were analyzed by GLC using a packed column (10% SE-30 or SE-54 on 80-100 mesh chromosorb W/AW, 1/8 in. × 1.5 m) or a capillary column (SE-30, 30 m) with a Varian 3300 gas chromatograph, thermal conductivity detector, and dectrom 99 program connected to a computer. The progress of the reaction was monitored by GLC, NMR spectra were recorded on a Bruker Avance 300 (300 MHz, 1H; 75 MHz, 13C) spectrometer in CDCl3 or benzene-d6 solvent. Mass spectra were obtained using a Hewlett Packard 6890GC/5973MSD. High-resolution mass spectra (EI) were obtained at the Korea Basic Science Institute, Seoul, Korea on a JEOI JMS-J070 mass spectrometer at an ionizing voltage of 70 eV. Elemental analyses of new compounds were performed at the chemical analysis laboratory of Korea Institute of Science and Technology.

Alkylation of 1,2,3,4-tetrahydronaphthalene with 1,4-dichlorobutane. To a mixture of 1,2,3,4-tetrahydronaphthalene (198.3 g, 1.5 mol) and aluminum chloride (6.7 g, 0.05 mol) under nitrogen atmosphere at 0 °C was added 1,4-dichlorobutane (63.5 g, 0.5 mol) for 20 min. After addition, the temperature was raised to room temperature. The reaction mixture was stirred for 1 h at room temperature and then quenched with water. Benzene (400 mL) was added to the reaction mixture. The organic layer was separated and dried over anhydrous magnesium sulfate. The reaction mixture was vacuum-distilled to give the 2:1 mixture (20.0 g) of 2
and 2' in 43% yield (based on 1,4-dichlorobutane used) and dodecahydrotriphenylene (40.1 g). Compound 2 was purified as colorless crystals by the repeated recrystallization of n-pentane solution of a mixture of 2 and 2'. Compound 2 was identified by comparing the spectral data with those of commercial compound from Aldrich Chemical Co.

Data for 2b: 1H NMR (300 MHz, CDCl3) δ 2.01 (s, 8H, ring-CH2), 2.79 (t, J = 6.3 Hz, 8H, benzylidene-CH2), 7.01 (s, 2H, aromatic-H); 13C NMR (75 MHz, CDCl3) δ 23.45 (ring-CH2), 26.38, 30.01 (benzylidene-CH2). 123.74, 135.83, 137.77, 140.17 (aryl-carbons); HRMS (m/z) calcd for C16H21Cl3Si (M+), 346.0478; found, 346.0478. Data for 3a: 1H NMR (300 MHz, CDCl3) δ 0.81 (s, 3H, PhSiH3), 1.40 (t, J = 3 Hz, 4H, SiCH2CH2), 1.79 (s, 8H, PhCH2CH2), 2.54 (s, 8H, benzylidene-CH2), 2.70-2.76 (m, 2H, SiCH2CH2), 6.74 (s, 1H, aryl-H); 13C NMR (75 MHz, CDCl3) δ 55.12 (SiCH2), 22.86 (SiCH2), 29.90 (ring-CH2), 25.92 (SiCH2), 26.83 (benzylidene-CH2), 123.74, 135.83, 137.77, 140.17 (aryl-carbons); HRMS (m/z) calcd for C17H22ClSi (M+), 362.1024; found, 362.0988. Data for 3a': 1H NMR (300 MHz, CDCl3) δ 0.81 (s, 3H, PhSiH3), 1.40 (t, J = 3 Hz, 4H, SiCH2CH2), 1.79 (s, 8H, PhCH2CH2), 2.54 (s, 8H, benzylidene-CH2), 2.70-2.76 (m, 2H, SiCH2CH2), 6.74 (s, 1H, aryl-H); 13C NMR (75 MHz, CDCl3) δ 55.12 (SiCH2), 22.86 (SiCH2), 23.09, 23.56 (PhCH2CH2), 26.19 (SiCH2), 26.42, 29.98 (benzylidene ring-CH2), 126.34, 133.45, 134.34, 135.83, 137.77, 143.60 (aryl-carbons); HRMS (m/z) calcd for C17H22ClSi (M+), 362.1024; found, 362.1004. Data for 4a: mp: decomposed slowly at 230 °C; 1H NMR (300 MHz, benzene-d6) δ 0.43 (s, 6H, SiCH3), 1.04 (t, J = 3 Hz, 4H, SiCH2), 1.66 (s, 8H, ring-CH2), 2.61 (s, 8H, benzylidene-CH2), 2.72 (t, J = 3 Hz, 4H, SiCH2CH2); 13C NMR (75 MHz, benzene-d6) δ 54.95 (SiCH3), 20.87 (SiCH2), 21.00 (ring-CH2), 23.67 (SiCH2CH2), 27.16 (benzylidene ring-CH2), 132.17, 137.21 (aryl-carbons); Anal. Calcd. for C20H16Cl3Si: C, 51.28; H, 6.64. Found: C, 51.40; H, 6.52.

Reaction of the mixture of 2 and 2' with 1b. Using the same procedure as above, the reaction of a 2:1 mixture of 2 and 2' (2.80 g, 15.0 mmol), and 1b (2.42 g, 15.0 mmol) in the presence of AlCl3 (0.2 g, 1.5 mmol) gave a 1:5.6 mixture (2.4 g) of 3b and 3b', and 4b (1.45 g). Compound 4b was purified by the recrystallization of toluene solution. The results obtained from the other reactions using various mole ratio of 1b and 2 were summarized in Table 1, in details.

Data for 3b: 1H NMR (300 MHz, benzene-d6) δ 1.33 (t, J = 3.9 Hz, 2H, SiCH3), 2.37 (s, 8H, ring-CH2), 2.62 (s, 8H, benzylidene-CH2), 2.64-2.67 (m, 2H, SiCH2CH2), 6.58 (s, 1H, aryl-H); 13C NMR (75 MHz, benzene-d6) δ 23.38, 23.69 (ring-CH2), 24.02 (SiCH2CH2), 25.25, 30.39 (benzylidene-CH2), 29.40 (SiCH2), 126.76, 133.47, 134.15, 135.55 (aryl-carbons); HRMS (m/z) calcd for C20H18Cl2Si (M+), 346.0478; found, 346.0475. Data for 3b': 1H NMR (300 MHz, benzene-d6) δ 1.63 (t, J = 4.9 Hz, 2H, SiCH2), 2.37 (s, 8H, ring-CH2), 2.62 (s, 8H, benzylidene-CH2), 2.64-2.67 (m, 2H, SiCH2CH2), 6.87 (s, 1H, aryl-H); 13C NMR (75 MHz, benzene-d6) δ 23.38, 23.44, 23.69, 25.12 (ring-CH2), 25.25, 26.58, 30.39 (benzylidene-CH2), 26.46 (SiCH2CH2), 27.19 (SiCH2), 126.80, 131.65, 132.04, 133.47, 134.16, 136.35 (aryl-carbons); HRMS (m/z) calcd for C14H18Cl2Si (M+), 326.0988; found, 326.0984. Data for 4b: mp: decomposed slowly at 260 °C; 1H NMR (300 MHz, benzene-d6) δ 1.19 (t, J = 4.5 Hz, 4H, SiCH2), 1.59 (s, 8H, ring-CH2), 2.46 (s, 8H, benzylidene-CH2), 2.68 (t, J = 3.9 Hz, 4H, SiH2CH2); 13C NMR (75 MHz) δ 20.65 (ring-CH2), 23.33 (SiCH2CH2), 23.49 (benzylidene ring-CH2), 27.01 (SiCH2), 132.30, 136.31 (aryl-carbons); Anal. Calcd. for C16H22Cl2Si2: C, 42.45; H, 4.75. Found: C, 42.80; H, 4.82.

X-ray Structure Determination. All the X-ray data were collected on an Enraf-Nonius CAD4 automated diffractometer equipped with a Mo X-ray tube and a graphite crystal monochromator. The orientation matrix and unit cell dimensions were determined from 25 machine-centered reflections in the 2θ range of from 15° to 25°. The variations of intensities were monitored by a repeated check of intensities of three reflections every 1 h during the data collection period. A direct method successfully located all the non-hydrogen atoms (SHELXLS-97). The program, SHELXL-97, was used to refine the structure. Hydrogen atoms were included in the structure factor calculation using a riding model. Crystallographic data for the structure reported here have been deposited with the Cambridge Crystallographic Data Center (Deposition No. CCDC-188534). The data can be obtained free of charge via http://www.ccdc.cam.ac.uk/structures/cctng菲 (or from the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033; e-mail: deposit@ ccdc.cam.ac.uk).

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