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A Novel Synthesis of 4B-Element-Containing Styrene Derivatives

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Synopsis. To synthesize 4B-group element-containing styrene monomers, alkylmetalation reactions of 4-methylstyrene (**1**) in the presence of lithium diisopropylamide (**2**) were investigated. Trialkylsilylation of **1** proceeded easily by the reaction with trialkylsilyl chloride in the presence of **2** to form mono- and bis-trialkylsilylated methylstyrene. This synthetic method was expanded to other 4B-element-containing styrenes such as germyl and stannyl compounds.

We have long been studying on syntheses of new functional monomers, oligomers and polymers by using a novel reaction route. In 1986, we found that lithium diisopropylamide (**2**) induced a metalation reaction of 4-methylstyrene derivatives (**1**) to form 4-vinylbenzyllithium derivatives (**3**) without any side reaction such as polymerization or addition reaction at vinyl group of **1**[1] as shown in Eq. 1. The equilibrium constant of the reaction was 0.54 in THF at 20 °C. By using this reaction system, we were able to synthesize a variety of novel monomers and macromonomers.[1—5] For instance, **3a** in the equilibrium system initiates an anionic polymerization of styrene selectively to form polystyrene macromonomers.[1] Mono- and bis-trimethylsilylated methylstyrenes were synthesized in good yield by dropping trimethylsilyl chloride to the equilibrium system.[2]

This paper deals with synthesis of 4B-group element-containing styrene derivatives by the reaction between chlorometal compounds and **3** derived from the reaction between **1** and **2**. Effect of para-substituents in styrene derivatives was also evaluated by ^{1}H NMR.

Experimental

All procedures such as metalation and silylation reactions were carried out under purified nitrogen to eliminate oxygen and moisture.

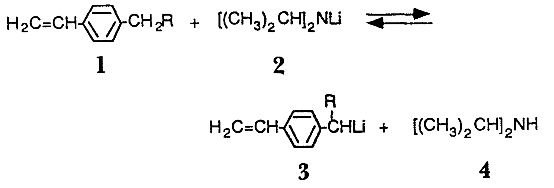
Materials: Commercial tetrahydrofuran (THF), diisopropylamine (DPA), 4-methylstyrene (**1**), *t*-butyl chloride, trimethylsilyl chloride, triethylsilyl chloride, (*t*-butyl)dimethylsilyl chloride, triphenylsilyl chloride, trimethylgermyl chloride, trimethylstannyl chloride, dichlorodimethylsilane, and dimethylsilyl chloride were purified by conventional methods.[7] Methoxydimethylsilyl chloride, *t*-butoxydimethylsilyl chloride and trimethoxysilyl chloride were prepared as reported in previous papers.[8—10] Methods for purification of other materials were described in our previous paper.[2]

Synthesis of 4B-Element-Containing Styrene Monomers: One of the representative procedures for reaction of 4-vinylbenzyllithium and chlorometal compound is described. To a stirred THF solution (15.8 ml) of diisopropylamine (DPA, 2.02 g; 20 mmol), a cyclohexane solution (3.0 ml) of butyllithium (0.65 g; 10 mmol) was added in a 100 ml-round bottomed flask. After stirring for a few minutes to complete the formation of lithium diisopropylamide (**2**), 4-methylstyrene (**1**, 1.18 g; 10 mmol) was added by using a syringe. The color of the mixture was observed to turn yellow immediately. Then, THF solution (11 ml) of triethylsilyl chloride (1.66 g; 11 mmol) was dropped into the mixture for 3 h at 20 °C. After the reaction, low boiling materials were evaporated and the residue was analyzed directly by gas chromatography. The styrene derivatives formed were purified by fractional distillation and analyzed by ^{1}H NMR, UV and GC-mass spectroscopy.

Measurements: ^{1}H NMR spectra were observed on a JEOL GX-270 spectrometer at room temperature, using a 5 mm-glass tube containing a solution of the styrene derivative sample in $CDCl_3$ (0.1 g dm^{-3}). Chloroform and 1,4-dioxane were used as internal references for the measurements. Gas chromatograms were taken with a Hitachi 063 gas chromatograph. For GPC measurements, a Nihon Seimitsu Kagaku NSLC-200 Gel Permeation Chromatograph was used. GC-mass spectra were obtained using a JEOL-DX303.

Results and Discussion

1. Synthesis of 4B-Element-Containing Styrene Monomers. As we reported previously, there are two different anionic species (lithium diisopropylamide, **2**, and 4-vinylbenzyllithium, **3a**) in the equilibrium system between 4-methylstyrene (**1a**) and **2** (Eq. (1)). When trimethylsilyl chloride was dropped to the equilibrium system, mono- and bis-trimethylsilylated **1** were formed in good yield.[2]



(1)

R= -H: **1a, 3a** ; -Si(CH$_3$)$_3$: **1b, 3b**

To synthesize several types of alkylmetal containing **1**, reactions of various types of chlorometal compound in the equilibrium system were carried out, the results of which are listed in Table 1. When trialkyl-substituted silyl chlorides such as triethylsilyl, *t*-butyldimethylsilyl and triphenylsilyl chloride were used as reactant, corresponding coupling compounds with **3a** were formed (Runs 1—7, in Table 1). Yield of the products was strongly dependent on the structure of alkyl substituents adjacent to silicon atom.

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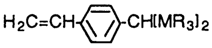
Table 1. Results on Synthesis of 4B-Group Element-Containing Styrene Derivatives[a)]

Run	R_3Cl	[**1a**]$_0$	[**2**]$_0$	[**4**]$_0$	Temp	Yield/%[b)]	
		mol dm^{-3}			°C	Mono[c)]	Bis[d)]
1	$(CH_3)_3SiCl$	0.3	0.3	0.3	20	65.7	15.9
2	$(CH_3)_3SiCl$[e)]	0.5	0.25	0.25	20	82.0	4.7
3	$(CH_3)_3SiCl$[e)]	0.25	0.5	0.5	20	25.5	60.2
4	$(CH_3CH_2)_3SiCl$	0.3	0.3	0.3	20	79.0	5.0
5	$(CH_3CH_2)_3SiCl$	0.15	0.3	0.3	20	57.1	41.2
6	$[(CH_3)_3C](CH_3)_2SiCl$	0.3	0.3	0.3	20	49.1	1.3
7	$(C_6H_5)_3SiCl$[f)]	0.3	0.3	0.3	20	66.8	3.0
8	$H(CH_3)_2SiCl$	0.3	0.3	0.3	20	0	0
9	$CH_3O(CH_3)_2SiCl$	0.3	0.3	0.3	20	0	0
10	$(CH_3O)_3SiCl$	0.3	0.3	0.3	20	0	0
11	$[(CH_3)_3C]O(CH_3)_2SiCl$	0.3	0.3	0.3	20	0	0
12	$(CH_3)_2SiCl_2$	0.3	0.3	0.3	20	0	0
13	$(CH_3O)_3SiCl$	0.3	0.3	0.3	0	2.9	0
14	$(CH_3O)_3SiCl$	0.3	0.3	0.3	−20	4.7	0
15	$(CH_3O)_3SiCl$	0.3	0.3	0.3	−40	7.4	0
16	$(CH_3)_3CCl$	0.3	0.3	0.3	20	0	0
17	$(CH_3)_3GeCl$	0.3	0.3	0.3	20	34.1	1.1
18	$(CH_3)_3SnCl$	0.3	0.3	0.3	20	8.2	1.2
19	$(CH_3)_3SnCl$	0.15	0.3	0.3	20	62.8	32.5

a) Solvent: THF; $[R_3MCl]_0=[\mathbf{2}]_0$; dropping time: 3h. b) Yield to lithium species. c) 4-[Mono(trialkylmetallo)methyl]styrene.  d) 4-[Bis(trialkylmetallo)-methyl]styrene.  e) Ref. 2. f) Small amount of vinyl oligomers was formed (~10%).

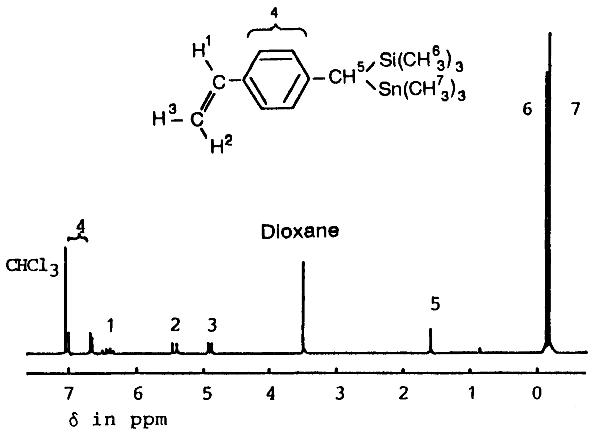


Fig. 1. 270 MHz ^1H NMR spectrum of 4-[(trimethylsilyl)(trimethylstannyl)methyl]styrene formed in the reaction of trimethylstannyl chloride in the equilibrium system containing **1b**, **3b**, and **2**.

When trimethylsilyl chloride was used as a reactant, mono- and bis-trimethylsilylated **1** were formed in good yield under appropriate reaction conditions. With increasing bulkiness of substituent on silyl chloride, the yield of bis-silylated **1** decreased significantly.

Contrary to the reaction of trialkylsilyl chloride in the equilibrium system, silyl chloride having other functional substituents such as an alkoxyl group gave no silylated **1** at 20 °C (Runs 8—12, in Table 1), which suggests that undesired reaction such as coupling reaction of Si-Cl compounds with **2** and/or cleavage reaction of Si-O linkage by a nucleophile might have proceeded preferentially. Actually, with decreasing the reaction temperature, the silylation reaction of **3a** took place (Runs 13—15, in Table 1) though yield of the silylated **1** was still low. The fact suggests that low temperature may prevent the cleavage reaction of Si-O linkage by nucleophiles.

Table 2. Results on Synthesis of Trimethylsilyl and Other 4B-Group Elements-Containing Styrene Derivatives[a)]

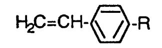
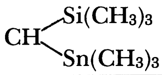
Run	R_3MCl	[**1b**]$_0$	[**2**]$_0$	[**4**]$_0$	Yield[b)]
		mol dm^{-3}			%
1	$(CH_3)_3SiCl$[c)]	0.25	0.25	0.25	65.1
2	$(CH_3CH_2)_3SiCl$	0.3	0.3	0.3	69.2
3	$(CH_3)_3SnCl$	0.3	0.3	0.3	32.5

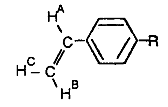
a) Solvent: THF; temp: 20 °C; $[R_3MCl]_0=[\mathbf{2}]_0$; dropping time: 3h. b) Yield to lithium species. c) Ref. 2.

Synthesis of other 4B-group element-containing **1** (C, Ge, and Sn) was also investigated (Runs 16—19, in Table 1). It is seen from the Table that these reactions proceeded smoothly to form several types of 4B-element-containing **1** except for *t*-butyl chloride as a reactant.

As **1b** was also metalated by **2** to form **3b** shown in Eq. 1, 4-methylstyrene derivatives having both trimethylsilyl group and other trialkylmetallo group are easily synthesized. Fig. 1 shows ^1H NMR spectrum of product formed in the reaction of trimethylstannyl chloride with chemical species present in the equilibrium system (see Eq. 1). Assignment of the signals was carried out by using 4-(trimethylsilylmethyl)-styrene,[2)] 4-[bis(trimethylsilyl)methyl]styrene,[2)] and 4-(trimethylstannylmethyl)styrene as reference compounds. As shown in the Fig. 1, methyl protons

Table 3. Proton Chemical Shifts δ for 4-Substituted Styrenes and Estimated σ-Values for R_3MCH_2 Group[a)]

R in	δ(H_A)	δ(H_B)	δ(H_C)	σ_1	σ_R	σ
		ppm				(=$\sigma_1+\sigma_R$)
H	6.582	5.594	5.093	0	0	0
CH_3[b)]	6.545	5.537	5.028	−0.04	−0.11	−0.15
$CH_2Si(CH_3)_3$[c)]	6.528	5.505	4.987	−0.10	−0.15	−0.25
$CH_2Si(CH_2CH_3)_3$	6.518	5.501	4.981	−0.11	−0.15	−0.26
$CH_2Si(CH_3)_2[C(CH_3)_3]$	6.552	5.503	4.982	−0.12	−0.14	−0.26
$CH_2Sn(CH_3)_3$	6.506	5.478	4.956	−0.12	−0.20	−0.32
$CH[Si(CH_3)_3]_2$[d)]	6.517	5.495	4.972	−0.14	−0.15	−0.29
$CH[Sn(CH_3)_3]_2$	—	5.455	4.927	−0.16	−0.23	−0.39
 $CH\begin{cases}Si(CH_3)_3\\Sn(CH_3)_3\end{cases}$	6.492	5.481	4.953	−0.17	−0.17	−0.34

a)  . b) Ref. 12. c) Ref. 11. d) Ref. 4.

appearing around 0 ppm separated into two signals, indicating the product to have both trimethylsilyl and trimethylstannyl group. Detailed reaction conditions and results are summarized in Table 2.

2. Estimation of Reactivities of Alkylmetal Containing 1 toward Nucleophilic Reagents. We reported[4)] previously that the double bond of 4-(trimethylsilylmethyl)styrene has much lower reactivity toward nucleophilic reagents than styrene itself owing to the electron-releasing effect of para-standing trimethylsilylmethyl group (σ-π hyperconjugation). The effect of 4-bis(trimethylsilyl)methyl group is much higher as compared with 4-trimethylsilylmethyl group, which may be caused by an additional σ-π hyperconjugation between second C-Si bond and the phenyl π-orbital in addition to the σ-π hyperconjugation of the first C-Si bond in vertical position. Substituent effect of several 4B-element-containing **1** was estimated by Hammett's σ-value of para-substituents.

Reynolds, et al. reported that the effect of para-substituents in styrene derivatives can be evaluated from the chemical shifts in their ^1H NMR spectra.[11)] They also reported that the nature of the electron-releasing effect of $-CH_2-MR_3$ in para-substituted styrenes was attributable to the electrically polarized C-M bond.[11)] Hammett's σ-values for para-substituents in styrene derivatives estimated according to Reynolds are listed in Table 3. The electron-releasing effect of the three trialkylsilylmethyl groups is almost invariable regardless of the structure of alkyl group, which is consistent with Reynolds' consideration. The effect of dimetallomethyl substituents was also influenced by the electrically polarized C-M bond as shown in Table 3. Thus, order of the electron-releasing effect of trialkylmetalmethyl substituents are as follows:

$$(R_3Sn)_2CH- > (R_3Sn)(R_3Si)CH- > R_3SnCH_2- \\ > (R_3Si)_2CH- > R_3SiCH_2-$$

We reported previously that trialkylmetal substituted 4-methylstyrenes have higher alternative tendency than that of common styrene derivatives in radical copolymerization with electron-poor vinyl monomers such as methacrylic esters owing to the electron-releasing effect of para substituent of the 4-(trialkylmetalmethyl)styrene.[4)] For example, monomer reactivity ratios (r_1 and r_2) in radical copolymerization of 4-[bis(trimethylsilyl)methyl]styrene (M_1) with methylmethacrylate (M_2) were 0.1 and 0.2, respectively.

4B-Element-containing styrene monomers obtained by the method described here should have similar tendency in radical copolymerization to that of corresponding mono- and bis-trimethylsilylated **1**.

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