gel, *n*-hexane : ether = 1 : 1) afforded 50 mg (89%) of **14**. ^{1}H-NMR (300 MHz) δ 1.05 (s, 9H, *t*-Bu), 2.58 (dd, 1H, J=14.5 and 16.2 Hz), 2.77 (dd, 1H, J=3.0 and 16.2 Hz), 3.38 (dd, 1H, J=3.0 and 16.2 Hz), 6.18 (d, 1H, J=10.0 Hz), 7.50 (d, 1H, J=10.0 Hz).

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Carbonylation of Bromo(Bromomethyl)Benzenes to Alkyl Carboalkoxyphenylacetates Catalyzed by Cobalt Carbonyl

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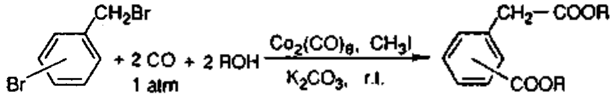
A synthetic method for bis-carbonylation of bromo(bromomethyl)benzenes was described. Alkyl carboalkoxyphenylacetates were easily prepared by the carbonylation of benzylic and arylic bromide moieties in bromo(bromomethyl)benzenes with alcohols in the presence of K_2CO_3, CH_3I, and a catalytic amount of cobalt carbonyl under the atmospheric pressure of carbon monoxide at room temperature in good to excellent yields. The base played a decisive role in the selectivity of product and K_2CO_3 was the best one among bases used.

Introduction

The carbonylation of benzyl- and aryl halides has been systematically developed by the several authors.[1-2] Despite a great amount of the research on the catalytic carbonylation of such organic halides, a little attention has been paid to the catalytic bis-carbonylation of halo(halomethyl)arenes.[3]

Recently, we reported that selective carbonylation of halobenzylhalides gave alkyl (halophenyl)acetates[4] and alkyl (alkoxymethyl)benzoates,[5] respectively depending on reaction conditions used.

We herein wish to report the bis-carbonylation of bromo (bromomethyl)benzenes to give alkyl carboalkoxyphenylacetates catalyzed by cobalt carbonyl.



[1]   [2]

Scheme 1

Results and Discussion

Treatments of bromo(bromomethyl)benzenes with alcohol in the presence of a catalytic amount of $Co_2(CO)_8$, K_2CO_3, and CH_3I as a catalyst promoter under the atmospheric pressure of carbon monoxide at room temperature for 24 h gave the corresponding alkyl carboalkoxyphenylacetates in good

Table 1. Base Effect in bis-Carbonylation of 1-bromo-4-(bromomethyl)Benzene Catalyzed by Cobalt Carbonyl[a]

No.	Base (mmol)	Product	Yield(%)[b]
1	K_2CO_3 (10)	4-$C_2H_5OOCC_6H_4CH_2COOC_2H_5$	98
2	K_2CO_3 (5)	4-$C_2H_5OOCC_6H_4CH_2COOC_2H_5$	73
		4-$BrC_6H_4CH_2COOC_2H_5$	18
3	$KHCO_3$ (10)	4-$C_2H_5OOCC_6H_4CH_2COOC_2H_5$	7
		4-$BrC_6H_4CH_2COOC_2H_5$	68
4	Na_2CO_3 (10)	4-$C_2H_5OOCC_6H_4CH_2COOC_2H_5$	3
		4-$BrC_6H_4CH_2COOC_2H_5$	56
5	$NaHCO_3$ (10)	4-$C_2H_5OOCC_6H_4CH_2COOC_2H_5$	tr
		4-$BrC_6H_4CH_2COOC_2H_5$	12
6	NaOEt (5)	4-$C_2H_5OOCC_6H_4CH_2COOC_2H_5$	5
		4-$BrC_6H_4CH_2OC_2H_5$	38
		4-$C_2H_5OOCC_6H_4CH_2OC_2H_5$	48
		4-$BrC_6H_4CH_2COOC_2H_5$	tr
7	KOH (5)	4-$C_2H_5OOCC_6H_4CH_2COOC_2H_5$	17
		4-$BrC_6H_4CH_2OC_2H_5$	31
		4-$C_2H_5OOCC_6H_4CH_2OC_2H_5$	24
		4-$BrC_6H_4CH_2COOC_2H_5$	24
8	NEt_3 (5)	4-$C_2H_5OOCC_6H_4CH_2COOC_2H_5$	7
		4-$BrC_6H_4CH_2COOC_2H_5$	31

[a] 1-Bromo-4-(bromomethyl)benzene (0.51 g, 2.0 mmol), Base, CH_3I (0.71 g, 5.0 mmol), $Co_2(CO)_8$ (0.034 g, 0.1 mmol), and ethanol (20 m*l*) at room temperature for 24 h. [b] Isolated yield.

Table 2. Secondary Organic Halide Effect in bis-Carbonylation of 1-bromo-4-(bromomethyl)Benzene Catalyzed by Cobalt Carbonyl[a]

No.	R'X	Product	Yield(%)[b]
2	CH_3I	4-$C_2H_5OOCC_6H_4CH_2COOC_2H_5$	73
		4-$BrC_6H_4CH_2COOC_2H_5$	18
9	$ClCH_2COOC_2H_5$	4-$C_2H_3OOCC_6H_4CH_2COOC_2H_5$	30
		4-$BrC_6H_4CH_2COOC_2H_5$	68
10[c]	$ClCH_2COOC_3H_5$	4-$C_2H_5OOCC_6H_4CH_2COOC_2H_5$	26
		4-$BrC_6H_4CH_2COOC_2H_5$	69
11	$ClCH_2COOH$	4-$C_2H_5OOCC_6H_4CH_2COOC_2H_5$	9
		4-$BrC_6H_4CH_2COOC_2H_5$	54
12	None	4-$C_2H_5OOCC_6H_4CH_2COOC_2H_5$	27
		4-$BrC_6H_4CH_2COC_2H_5$	51

[a] 1-Bromo-4-(bromomethyl)benzene (0.51 g, 2.0 mmol), Base, $K_2CO_3CH_3I$ (0.75 g, 5.0 mmol), R'X (0.75 g, 5.0 mmol) $Co_2(CO)_8$ (0.034 g, 0.1 mmol), and ethanol (20 m*l*) at room temperature for 24 h. [b] Isolated yield. [c] at 60℃.

Table 3. Alcohol Effect in bis-carbonylation of bromo(bromomethyl)Benzenes Catalyzed by Cobalt Carbonyl[a]

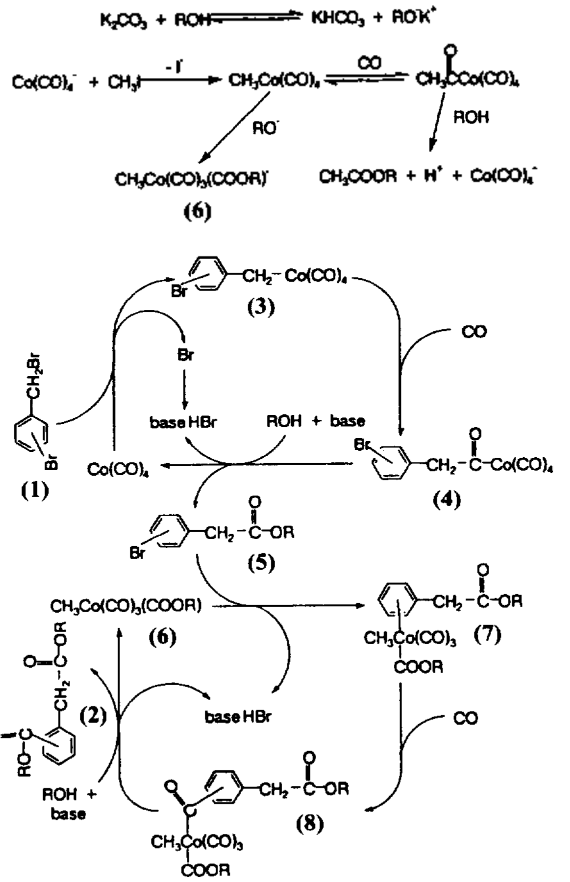
No.	BrPhCH$_2$Br	ROH	Product	Yield (%)[b]
1	4-Br	C_2H_5OH	4-$C_2H_5OOCC_6H_4CH_2COOC_2H_5$	98
			4-$BrC_6H_4CH_2COOC_2H_5$	tr
13	4-Br	CH_3OH	4-$CH_3OOCC_6H_4CH_2COOCH_3$	62
			4-$BrC_6H_4CH_2COOCH_5$	2
			4-$CH_3OOCC_6H_4CH_2OCH_3$	24
			4-$BrC_6H_4CH_2OCH_3$	3
14	4-Br	$^nC_3H_7OH$	4-$^nC_3H_7OOCC_6H_4CH_2COO^nC_3H_7$	91
			4-$BrC_6H_4CH_2COO^nC_3H_7$	tr
15	4-Br	$^nC_4H_9OH$	4-$^nC_4H_9OOCC_6H_4CH_2COO^nC_4H_9$	62
			4-$BrC_6H_4CH_2COO^nC_4H_9$	9
16	2-Br	CH_3OH	2-$CH_3OOCC_6H_4CH_2COOCH_3$	60
			2-$BrC_6H_4CH_2COOCH_3$	tr
			2-$CH_3OOCC_6H_4CH_2OCH_3$	29
17	2-Br	C_2H_5OH	2-$C_2H_5OOCC_6H_4CH_2COOC_2H_5$	76
			2-$BrC_6H_4CH_2COOC_2H_5$	9
			2-$C_2H_5OOCC_6H_4CH_2OC_2H_5$	0
18	2-Br	$^nC_3H_7OH$	2-$^nC_3H_7OOCC_6H_4CH_2COO^nC_3H_7$	32
			2-$BrC_6H_4CH_2COO^nC_3H_7$	40
			2-$^nC_3H_7OOCC_6H_4CH_2O^nC_3H_7$	0
19	2-Br	$^nC_4H_9OH$	2-$^nC_4H_9OOCC_6H_4CH_2C$[illegible]C_4H_9	18
			2-$BrC_6H_4CH_2COO^nC_4H_9$	38
			2-$^nC_4H_9OOCC_6H_4CH_2O^nC_4H_9$	0
20	3-Br	CH_3OH	3-$CH_3OOCC_6H_4CH_2COOCH_3$	61
			3-$BrC_6H_4CH_2COOCH_3$	tr
			3-$CH_3OOCC_6H_4CH_2OCH_3$	36
21	3-Br	C_2H_5OH	3-$C_2H_5OOCC_6H_4CH_2COOC_2H_5$	90
			3-$BrC_6H_4CH_2COOC_2H_5$	tr
			3-$C_2H_5OOCC_6H_4CH_2OC_2H_5$	0

[a] 1-Bromo-4-(bromomethyl)benzene (0.51 g, 2.0 mmol), Base, CH_3I (0.71 g, 5.0 mmol), $Co_2(CO)_8$ (0.034 g, 0.1 mmol), and ethanol (20 m*l*) at room temperature for 24 h. [b] Isolated yield. [c] at 60℃.

to excellent yields.

The results of base effect for bis-carbonylation were summarized in Table 1. Of the bases employed in Table 1, potassium carbonate was the most effective one in the formation of ethyl 4-carboethoxyphenylacetate in 98% yield (No. 1). The use of excess K_2CO_3 was indispensable in order to quench HI produced during the reaction. Decreasing the amount of K_2CO_3 reduced the formation of product to lower yield (73%), at the same time, ethyl 4-bromophenylacetate as an intermediate was obtained in 18% yield (No. 2). In cases of other carbonate bases such as $KHCO_3$, $NaHCO_3$, and Na_2CO_3, the yields of product were very lower (trace-7%) along with formation of monoester and unreacted reactant (Nos. 3, 4, and 5). Therefore, these three bases are capable to activate $Co_2(CO)_8$ to $Co(CO)_4^-$ but incapable to activate $Co(CO)_4^-$ with CH_3I to $CH_3Co(CO)_3(COOR)^-$, which might be a true catalyst in the arylic carbonylation. Potassium hydroxide, sodium ethoxide, and triethylamine were not effective due to their inefficiency in connection with product yields (Nos. 6, 7, and 8).

As shown in Table 2, iodomethane as a catalyst promotor showed the highest activity in these reaction (No. 2). Other catalyst promoters were less effective than iodomethane in giving the bis-carbonylated products in 9-30% yields, respectively (Nos. 9, 10, and 11). Chloroacetic acid showed a poor yield because of the consumption of the base by the carboxylic acid group. In the absence of the second organic halide, benzylic halide moiety of bromo(bromomethyl)benzene took partially the role of the second organic halide, thus occurring



Scheme 2

the carbonylation of aryl bromide moiety (No. 12).

Table 3 shows solvent dependence for the yields of bis-carbonylated products. In the case of methanol, Williamson etherification was proceeded in noticeable amounts due to higher nucleophilicity of methanol than that of ethanol (Nos. 13, 16, and 20) and bis-carbonylated products were also given in about 60% yield. The reaction of 1-bromo-4-(bromomethyl) benzene with 1-propanol or 1-bromo-3-(bromomethyl)benzene with ethanol afforded the corresponding ^{n}propyl 4-carbo-^{n}propoxyphenylacetate or ethyl 3-carboethoxyphenylacetate in good to excellent yields, respectively (Nos. 14 and 21). But reactions of ^{n}butanol with 1-bromo-4-(bromomethyl)benzene or sterically hindered 1-bromo-2-(bromomethyl)benzene with ethanol proceeded to give the products in 62% and 76% yields, respectively (Nos. 15 and 17). Finally, 1-bromo-2-(bromomethyl)benzene reacted with ^{n}propanol and ^{n}butanol to give the corresponding bis-carbonylated products in lower yields (32% and 18%) (Nos. 18 and 19). But, in cases of ^{i}propanol and ^{t}butanol, the bis-carbonylation of bromo(bromomethyl)benzene was not successful.

According to these results, a possible reaction mechanism for the bis-carbonylation reaction is outlined in Scheme 2. Two types of catalysts participate in this reaction. First, Co$_2$(CO)$_8$ undergoes disproportionation in alcohol, giving Co(CO)$_4^-$.[6] Attack of Co(CO)$_4^-$ to benzyl bromide moiety generate **3**, which equilibrates with **4** absorbing a CO. Cleavage of **4** by alcohol gives **5**, H$^+$, and Co(CO)$_4^-$. Second, a part of Co(CO)$_4^-$ reacts with CH$_3$I to afford CH$_3$Co(CO)$_4$, which is converted into **6** as the true catalyst to activate arylic bromide moiety by alkoxide.[3,7] During the formation of **6**, CH$_3$Co(CO)$_4$ equilibrates with CH$_3$COCo(CO)$_4$ absorbing a CO. CH$_3$COCo(CO)$_4$ affords alkyl acetate and Co(CO)$_4^-$ by alcohol. Single electron transfer (SET)[8] from **6** to **5** would generate cobalt complex (**7**) losing bromide anion, which on carbonylation to **8** and subsequent reaction with alcohol gives diester (**2**).

Experimental

^{1}H-NMR spectra were obtained at 60 MHz on a Varian EM 360 or at 300 MHz on a Bruker AM 300 spectrometer. All chemical shifts were measured relative to TMS (δ 0.00). ^{13}C-NMR spectra were obtained at 75.5 MHz on a Bruker AM 300 spectrometer. Chemical shifts were measured relative to solvent ^{13}C resonance (δ CDCl$_3$ 77.0). Mass spectra (MS) were obtained on a Shimadzu-QP1000 spectrometer at 70 eV. FT-IR spectra were recorded on Matton Instrunents 6030 using a thin film of the sample sandwiched between NaCl plates. Gas-liquid chromatography (GLC) was performed on a Shimadzu GC-3BT gas chromatograph using 15% Silicone GE SE 52 on 60-80 mesh Smimalite W.

General reaction procedure is as follows: A mixture of 1-bromo-4-(bromomethyl)benzene (0.51 g, 2.0 mmol), K$_2$CO$_3$ (1.4 g, 10 mmol), ethanol (20 m*l*), CH$_3$I (0.71 g, 5.0 mmol), and Co$_2$(CO)$_8$ (0.034 g, 0.1 mmol) was stirred under CO (1 atm) at room temperature for 24 hours. During this time, ca. 210 m*l* of CO was absorbed for the carbonylation. The mixture was concentrated, filtered by the short column chromatography (silica gel, 3 cm, ether), concentrated, and separated by the preparative thin layer chromatography (silica gel, ethyl acetate : ^{n}hexane = 3 : 10) to give ethyl 4-carboethoxyphenylacetate (R_f = 0.58, 0.370 g, 98%). Ortho and meta-bromobenzyl bromides were also reacted on the similar condition described above.

Analytical data of alkyl (carboalkoxyphenyl)acetates as follows;

Methyl 4-carbomethoxyphenylacetate. colorless oil; ^{1}H-NMR (CCl$_4$) δ 3.49 (s, 2H, CH$_2$), 3.61 (s, 3H, CH$_3$), 3.83 (s, 3H, CH$_3$), 7.28 (d, 2H, J=8 Hz, aromatic H-3, 5), 7.90 (d, 2H, J=8 Hz, aromatic H-2, 6); Mass (m/e) 209 (5), 208 (M$^+$, 42), 177 (74), 149 (100), 118 (13), 105 (15), 90 (32), 89 (32), 60 (40), 59 (40); IR (ν_{CO}) 1720 and 1740 cm^{-1}.

Ethyl 4-carboethoxyphenylacetate. colorless oil; ^{1}H-NMR (CCl$_4$) δ 1.21 (t, 3H, J=7 Hz, CH$_2$), 1.35 (t, 3H, J=7 Hz, CH$_3$), 3.56 (s, 2H, CH$_3$), 3.86 (q, 2H, J=7 Hz, CH$_2$), 4.10 (q, 2H, J=7 Hz, CH$_2$), 7.07 (d, 2H, J=8 Hz, aromatic H-3, 5), 7.73 (d, 2H, J=8 Hz, aromatic H-2, 6); Mass (m/e) 236 (M$^+$, 14), 218 (14), 191 (44), 163 (100), 136 (30), 135 (45), 32 (66); IR (ν_{CO}) 1717 and 1738 cm^{-1}.

^{n}Propyl 4-carbo-^{n}propoxyphenylacetate. colorless oil; ^{1}H-NMR (CCl$_4$) δ 0.90 (t, 3H, J=7 Hz, CH$_3$), 1.01 (t, 3H, J=7 Hz, CH$_3$) 1.60 (m, 4H, (CH$_2$)$_2$), 3.57 (s, 2H, CH$_2$), 3.99 (t, 2H, J=6 Hz, CH$_2$), 4.20 (t, 2H,J=6 Hz, CH$_2$), 7.30 (d, 2H, J=8 Hz, aromatic H-3, 5), 7.96 (d, 2H, J=8 Hz, aromatic H-2, 6); Mass (m/e) 223 (7), 222 (7), 206 (4), 205 (25), 181 (7), 180 (10), 178 (5), 177 (26), 137 (4), 136 (40), 135 (17), 118 (9), 107 (9), 92 (4), 91 (9), 90 (17), 89 (12), 43 (100); IR (ν_{CO}) 1720 and 1738 cm^{-1}.

^{n}Butyl 4-carbo-^{n}butoxyphenylacetate. colorless oil; ^{1}H-NMR (CCl$_4$) δ 0.90 (t, 3H, J=7 Hz, CH$_3$), 0.97 (t, 3H, J=7 Hz, CH$_3$), 1.33 (m, 2H, CH$_2$), 1.46 (m, 2H, CH$_2$), 1.59

(m, 2H, CH_2), 1.74 (m, 2H, CH_2), 3.56 (s, 2H, CH_2), 3.97 (t, 2H, J=5 Hz, CH_2), 4.26 (t, 2H, J=6 Hz, CH_2), 7.35 (d, 2H, J=8 Hz, aromatic H-3, 5), 8.01 (d, 2H, J=8 Hz, aromatic H-2, 6); ^{13}C-NMR ($CDCl_3$) δ 13.4 (CH_3), 13.6 (CH_3), 18.9 (CH_2), 19.1 (CH_2), 30.4 (CH_2), 30.6 (CH_2), 40.5 (CH_2), 41.2 (CH_2), 64.6 (CH_2) 64.7 (CH_2), 129.1 (aromatic C-3, 5), 129.2 (aromatic C-1), 129.6 (aromatic C-2, 6), 139.1 (aromatic C-4, 166.2 (COO), 170.7 (COO); Mass (m/e) 292 (M^+, 9), 237 (19), 219 (29), 191 (21), 181 (36), 180 (19), 163 (7), 136 (61), 58 (100), 43 (70), 32 (70); IR (ν_{CO}) 1721 and 1738 cm^{-1}.

Methyl 2-carbomethoxyphenylacetate. colorless oil; ^{1}H-NMR (CCl_4) δ 3.60 (s, 3H, CH_3), 3.80 (s, 3H, CH_3), 3.90 (s, 2H, CH_2), 7.50 (m, 4H, aromatic H); Mass (m/e) 177 (28), 176 (85), 175 (14), 149 (81), 148 (100), 133 (94), 119 (36), 105 (15), 91 (82), 90 (34), 89 (30); IR (ν_{CO}) 1740 cm^{-1}.

Ethyl 2-carboethoxyphenylacetate. colorless oil; ^{1}H-NMR (CCl_4) δ 1.27 (t, 3H, J=7 Hz, CH_3), 1.39 (t, 3H, J=7 Hz, CH_3), 3.98 (s, 2H, CH_2), 4.16 (q, 2H, J=7 Hz, CH_2), 4.35 (q, 2H, J=7 Hz, CH_2), 7.23-8.20 (m, 4H, aromatic H); Mass (m/e) 191 (31), 190 (51), 163 (16), 162 (40), 135 (100), 134 (60), 118 (20), 90 (2), 89 (2); IR (ν_{CO}) 1717 and 1738 cm^{-1}.

^{n}Propyl 2-carbo-^{n}propoxyphenylacetate. colorless oil; ^{1}H-NMR (CCl_4) δ 0.90 (t, 3H, J=7 Hz, CH_3), 1.20 (t, 3H, J=7 Hz, CH_3), 1.60 (m, 4H, $CH_2)_2$), 3.95 (s, 2H, CH_2), 3.90 (t, 2H, J=6 Hz, CH_2), 4.17 (t, 2H, J=6 Hz, CH_2), 7.30 (m, 3H, aromatic H-3, 4, 5), 7.90 (m, 1H, aromatic H-6).

^{n}Butyl 2-carbo-^{n}butoxyphenylacetate. colorless oil; ^{1}H-NMR (CCl_4) δ 0.98 (m, 6H, $(CH_3)_2$), 1.55 (m, 8H, $(CH_2)_4$), 3.93 (s, 2H, CH_2), 4.10 (m, 4H, $(CH_2)_2$), 7.30 (m, 3H, aromatic H-3, 4, 5), 7.90 (m, 1H, aromatic H-6).

Methyl 3-carbomethoxyphenylacetate. colorless oil; ^{1}H-NMR (CCl_4) δ 3.60 (s, 2H, CH_2), 3.63 (s, 3H, CH_3), 3.85 (s, 3H, CH_3), 7.44 (m, 2H, aromatic H-4, 5), 7.91 (m, 2H, aromatic H-2, 6); Mass (m/e) 209 (4), 208 (M^+, 34), 178 (4), 177 (47), 164 (6), 151 (9), 149 (100), 119 (17), 105 (15), 91 (21), 90 (21), 80 (28); IR (ν_{CO}) 1724 cm^{-1}.

Ethyl 3-carboethoxyphenylacetate. colorless oil; ^{1}H-NMR (CCl_4) δ 1.23 (t, 3H, J=7 Hz, CH_3), 1.37 (t, 3H, J=7 Hz, CH_3), 3.57 (s, 2H, CH_2), 4.12 (q, 2H, J=7 Hz, CH_2), 4.37 (q, 2H, J=7 Hz, CH_2), 7.47 (m, 2H, aromatic H-4, 5), 7.90 (m, 2H, aromatic H-2, 6); Mass (m/e) 237 (2), 236 (M^+, 17), 218 (11), 192 (5), 191 (36), 164 (26), 165 (100), 136 (23), 135 (36), 119 (47), 91 (30), 89 (30), 32 (74); IR (ν_{CO}) 1721 cm^{-1}.

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Deoxygenation of β-Aryl-α,β-Epoxy Silanes to Vinylsilanes by Magnesium-Magnesium Halide

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The reactions of β-aryl-α,β-epoxy silanes with magnesium bromide or magnesium iodide in the presence of excess magnesium in ether at room temperature afforded vinylsilanes in 18-100% yields. E-Vinylsilanes were predominant over Z-isomers (>80%) regardless of the stereochemistry of α,β-epoxy silanes.

Introduction

The deoxygenation of epoxides to olefins has been studied and numerous reagents have been developed.[1] The deoxygenation of α,β-epoxy silanes was largely ignored in spite of its synthetic interest.[2] This reaction could provide a good route to vinylsilanes which have received increasing attention as a highly versatile synthon in organic synthesis.[3] Y. Ito and coworkers have reported that coppper-catalyzed Grignard reagent caused deoxygenation of α,β-epoxy silanes having one or two alkoxy groups on silicon.[4] However, the reaction with α,β-epoxy trimethylsilanes gave a normal ring-opening product. No deoxygenation was observed. Recently, we found that lithium was more effective than copper-catalyzed Grignard reagent for the deoxygenation of α,β-epoxy silanes; α,β-epoxy trimethylsilanes, which are more readily