

## Carbonylation of 1-Bromo-2,6-bis(bromomethyl)benzene Catalyzed by Cobalt Carbonyl

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Dialkyl 1-bromobenzene-2,6-diacetates were easily prepared by the carbonylation of the moiety of benzylic bromide in 1-bromo-2,6-bis(bromomethyl)benzene with alcohol in the presence of NaOAc·3H<sub>2</sub>O and a catalytic amount of Co<sub>2</sub>(CO)<sub>8</sub> under the atmospheric pressure of carbon monoxide at room temperature in excellent yield. Alkyl 2,6-bis(alkoxymethyl)benzoates were obtained by the carbonylation of the moiety of aryl bromide in 1-bromo-2,6-bis(alkoxymethyl)benzene, which derived from 1-bromo-2,6-bis(bromomethyl)benzene<sup>1</sup>, alcohol, NaOR, and CH<sub>3</sub>I under the same conditions. Alkyl 2,6-bis(carboxymethyl)benzoate was also obtained in a trace amount for 24 hrs at room temperature.

### Introduction

The technology of transition metal complexes catalyzed carbonylation reaction is being currently used for the production of large volume chemicals.<sup>2</sup> Many applications were reported on the carbonylation of organic halides with carbon monoxide using cobalt,<sup>3-5</sup> iron,<sup>6,7</sup> ruthenium,<sup>8</sup> rhodium,<sup>9</sup> and palladium.<sup>10</sup>

Heck and Breslow,<sup>3</sup> or Cassar *et al.*<sup>11</sup> reported the carbonylation of benzylic halides. Foa *et al.*<sup>4,5,12</sup> reported the cobalt catalyzed carbonylation of secondary benzylic halides and aryl halides in alcohol solvent under atmospheric pressure of carbon monoxide at room temperature to give the corresponding esters in good yields.

Despite a great intensive research on the catalytic carbonylation of various organic halides, little attention has been paid to the catalytic carbonylation of poly-halides containing aryl- and benzylic moieties in a molecule.<sup>13,14</sup> It is thus desirable that we investigate their reactivity for the carbonylation of alkyl halides. In this paper, the cobalt catalyzed carbonylation of 1-bromo-2,6-bis(bromomethyl)benzene containing aryl- and benzylic moieties was reported

### Experimental

Melting point were checked by using a YAMATO melting point apparatus. FT-IR spectra were recorded on Matton Instruments 6030 using a thin film of the sample sandwiched between NaCl plates. Mass spectra were obtained on a Shimadzu-QP1000 spectrometer at 70 eV. Gas-Liquid Chromatographic analysis was performed on a Shimadzu GC-3BT gas chromatograph using 15% silicon GE SE 52 on 60-80 mesh smimalite W. <sup>1</sup>H-NMR spectra were obtained at 60 MHz on a Varian EM 360 or at 200 MHz on Bruker AC 200. All chemical shifts were measured relative to TMS ( $\delta$ =0.00). Analytical thin layer chromatography was performed using Merck silica gel 60 F<sub>254</sub>. Preparative thin layer chromatography was prepared using Merck silica gel 60 HF<sub>254</sub>, calcium sulfate and water (weight ratio=10:1:30) on 20×20 cm<sup>2</sup> glass plate. Dicobalt octacarbonyl was purchased from ST-REM chemical company. 1-Bromo-2,6-bis(bromomethyl)ben-

zene was synthesized from 2,6-dimethyl-1-bromobenzene purchased from ALDRICH chemical company.

#### Preparation of 1-bromo-2,6-bis(bromomethyl)benzene

To one necked round bottom 250 mL flask containing carbon tetrachloride (100 mL) equipped with condenser and a magnetic stirring bar were added 2,6-dimethyl-1-bromobenzene (9.25 g, 50.0 mmol), N-bromosuccinimide (17.80 g, 100.0 mmol), and benzoyl peroxide (1.00 g, 4.7 mmol). The reaction mixture was stirred at 80-90°C for 5 hr, and filtered for removing of succinimide. After the solvent was evaporated under reduced pressure, the residual solid was purified by recrystallization with *n*-hexane (8.58 g, 50%).

**1-Bromo-2,6-bis(bromomethyl)benzene.** White solid; mp. 101-102°C; <sup>1</sup>H-NMR (CDCl<sub>3</sub>)  $\delta$  4.65 (s, 4H, 2CH<sub>3</sub>), 7.45 (s, 3H, aromatic CH); mass (m/z) 340 (M<sup>+</sup>) (2), 342 (M<sup>+</sup>+2) (6), 344 (M<sup>+</sup>+4) (6), 346 (M<sup>+</sup>+6) (2), 265 (32), 263 (68), 261 (35), 184 (27), 182 (30), 103 (49), 77 (55), 51 (100).

#### Biscarbonylation of the moiety of benzylic bromide of 1-bromo-2,6-bis(bromomethyl)benzene

A mixture of 1-bromo-2,6-bis(bromomethyl)benzene (0.34 g, 1.0 mmol), sodium acetate trihydrate (0.68 g, 5.0 mmol), ethanol (20 mL), and Co<sub>2</sub>(CO)<sub>8</sub> (0.017 g, 0.05 mmol) was stirred under carbon monoxide at room temperature for 24 hours. During this reaction time, ca. 50 mL of carbon monoxide was absorbed. After the reaction flask was replenished with air, the mixture was concentrated in vacuum, and filtered with short column to remove cobalt catalyst (silica gel, 5 cm, ether). The solvent was evaporated under reduced pressure and the residue was purified by the preparative thin layer chromatography (silica gel, *n*-hexane:ethyl acetate=5:1) to give diethyl 1-bromobenzene-2,6-diacetate (0.29 g, 89%).

**Dimethyl 1-bromobenzene-2,6-diacetate.** (yield, 93 %): colorless oil: <sup>1</sup>H-NMR (CCl<sub>4</sub>)  $\delta$  3.70 (s, 6H, 2CO<sub>2</sub>CH<sub>3</sub>), 3.85 (s, 4H, 2CH<sub>2</sub>CO<sub>2</sub>), 7.25 (s, 3H, aromatic CH); mass (m/z) 300 (M<sup>+</sup>), 302 (M<sup>+</sup>+2), 271 (4), 269 (4), 243 (11), 241 (11), 221 (100).

**Diethyl 1-bromobenzene-2,6-diacetate.** (yield, 89 %): colorless oil: <sup>1</sup>H-NMR (CCl<sub>4</sub>)  $\delta$  1.25 (t, 6H, 2CO<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>), 3.70 (s, 4H, 2CH<sub>2</sub>CO<sub>2</sub>), 4.10 (q, 4H, 2CH<sub>2</sub>CH<sub>3</sub>), 7.20 (s, 3H,

aromatic CH); mass ( $m/z$ ). 255 ( $M^+ - CO_2C_2H_5$ ) (24), 257 ( $\{M^+ + 2\} - CO_2C_2H_5$ ) (24), 249 (62), 147 (90), 131 (15), 91 (21), 29 (100); IR ( $\nu_{CO}$ ) 1726  $cm^{-1}$ .

**Dipropyl 1-bromobenzene-2,6-diacetate.** (yield, 71 %): colorless oil;  $^1H$ -NMR ( $CCl_4$ )  $\delta$  0.93 (t, 6H,  $2CO_2CH_2CH_2CH_3$ ), 1.62 (m, 4H,  $2CO_2CH_2CH_2CH_3$ ), 3.85 (s, 4H,  $2CH_2CO_2$ ), 4.13 (t, 4H,  $2CO_2CH_2CH_2CH_3$ ), 7.25 (s, 3H, aromatic CH); mass ( $m/z$ ) 277 ( $M^+ - Br$ ) (19), 271 (13), 269 (13), 235 (19), 147 (37), 43 (100).

**Diisopropyl 1-bromobenzene-2,6-diacetate.** (yield, 54%): colorless oil;  $^1H$ -NMR ( $CCl_4$ )  $\delta$  1.25 (d, 12H,  $2CO_2CH(CH_3)_2$ ), 3.80 (s, 4H,  $2CH_2CO_2$ ), 4.90 (m, 2H,  $2CH(CH_3)_2$ ), 7.20 (s, 3H, aromatic CH); mass ( $m/z$ ) 277 ( $M^+ - Br$ ) (5), 271 (11), 269 (11), 43 (100).

#### Carbonylation of the moiety of aryl bromide of 1-bromo-2,6-bis-(bromomethyl)benzene to alkyl 2,6-bis(alkoxymethyl)benzoate

Sodium metal (0.46 g, 20.0 mmol) was dissolved in absolute alcohol (25 mL) to prepare sodium alkoxide solution. Then, 1-bromo-2,6-bis(bromomethyl)benzene (0.69 g, 2.0 mmol) was etherified at room temperature for 5-9 hours to give 1-bromo-2,6-bis(alkoxymethyl)benzene in quantitative yield.

**1-Bromo-2,6-bis(methoxymethyl)benzene.** colorless oil;  $^1H$ -NMR ( $CCl_4$ )  $\delta$  3.45 (s, 6H,  $2OCH_3$ ), 4.50 (s, 4H,  $2CH_2O$ ), 7.35 (s, 3H, aromatic CH); mass ( $m/z$ ) 244 ( $M^+$ ) (8), 215 (4), 213 (4), 165 (44), 100 (100), 91 (44), 45 (60).

And then,  $Co_2(CO)_8$  (0.034 g, 0.10 mmol) and iodomethane (1.420 g, 10.0 mmol) were added under carbon monoxide atmosphere. This mixture was stirred at room temperature for 24 hours. After the reaction flask was replenished with air, the reaction mixture was concentrated in vacuum, and extracted with ether ( $2 \times 20$  mL). The ether extract was dried over anhydrous magnesium sulfate. After the solvent was evaporated under reduced pressure, the residue was purified by a preparative thin layer chromatography (silica gel, ethyl ether: *n*-hexane = 1:5) to give alkyl 2,6-bis(alkoxymethyl)benzoate (80-46%).

**Methyl 2,6-bis(methoxymethyl)benzoate.** (yield, 68 %): colorless oil;  $^1H$ -NMR ( $CCl_4$ )  $\delta$  3.45 (s, 6H,  $2OCH_3$ ), 3.85 (s, 3H,  $CO_2CH_3$ ), 4.50 (s, 4H,  $2CH_2O$ ), 7.35 (s, 3H, aromatic CH); mass ( $m/z$ ) 193 ( $M^+ - OCH_3$ ) (5), 176 (20), 163 (2), 161 (100), 146 (10).

**Ethyl 2,6-bis(ethoxymethyl)benzoate.** (yield, 80%): colorless oil;  $^1H$ -NMR ( $CCl_4$ )  $\delta$  1.25 (m, 9H,  $CO_2CH_2CH_3$ ,  $2OCH_2CH_3$ ), 3.43 (q, 4H,  $2OCH_2CH_3$ ), 4.30 (q, 2H,  $2CO_2CH_2CH_3$ ), 4.55 (s, 4H,  $2CH_2O$ ), 7.35 (s, 3H, aromatic CH); mass ( $m/z$ ) 221 ( $M^+ - OC_2H_5$ ) (4), 192 (17), 163 (100), 147 (10), 118 (25), 91 (29); IR ( $\nu_{CO}$ ) 1726  $cm^{-1}$ .

**Propyl 2,6-bis(propoxymethyl)benzoate.** (yield, 78 %): colorless oil;  $^1H$ -NMR ( $CCl_4$ )  $\delta$  1.00 (q, 9H,  $2OCH_2CH_2CH_3$ ), 1.63 (m, 6H,  $2OCH_2CH_2CH_3$ ,  $CO_2CH_2CH_2CH_3$ ), 3.20 (t, 4H,  $2OCH_2CH_2CH_3$ ), 4.34 (t, 2H,  $CO_2CH_2CH_2CH_3$ ), 4.50 (s, 4H,  $2CH_2O$ ), 7.30 (s, 3H, aromatic CH); mass ( $m/z$ ) 249 ( $M^+ - OC_3H_7$ ) (5), 205 (12), 163 (77), 162 (9), 146 (12), 43 (100).

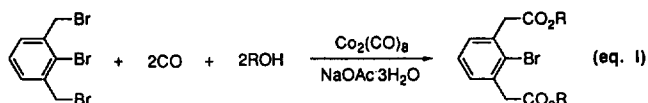
**Butyl 2,6-bis(butoxymethyl)benzoate.** (yield, 46%): colorless oil;  $^1H$ -NMR ( $CCl_4$ )  $\delta$  0.85 (t, 9H,  $2OCH_2CH_2CH_2CH_3$ ,  $CO_2CH_2CH_2CH_2CH_3$ ), 1.24 (m, 12H,  $2OCH_2CH_2CH_2CH_3$ ,  $CO_2CH_2CH_2CH_2CH_3$ ), 3.40 (t, 4H,  $2OCH_2CH_2CH_2CH_3$ ), 4.22 (t, 2H,  $CO_2CH_2CH_2CH_2CH_3$ ), 4.50 (s, 4H,  $2CH_2O$ ), 7.30 (s, 3H, aromatic CH); mass ( $m/z$ ) 277 ( $M^+ - OC_4H_9$ ) (5), 220 (20), 163 (72), 146 (12),

118 (8), 57 (100); IR ( $\nu_{CO}$ ) 1728  $cm^{-1}$ .

## Results and Discussion

### Biscarbonylation of two moieties of benzyl bromide of 1-bromo-2,6-bis(bromomethyl)benzene

Treatments of 1-bromo-2,6-bis(bromomethyl)benzene with alcohol,  $NaOAc \cdot 3H_2O$ , and  $Co_2(CO)_8$  as a catalyst under the atmospheric pressure of carbon monoxide at room temperature for 24 hours gave the corresponding dialkyl 1-bromo-benzene-2,6-diacetate in excellent yields (Eq. (1)).



The effects of base, pressure, and temperature on the biscarbonylation of the moieties of benzyl bromide were summarized in Table 1.

Among several bases employed for biscarbonylation, sodium acetate trihydrate was the most effective one in the formation of diethyl 1-bromobenzene-2,6-diacetate in 89% yield (Exp. No. 1). In the case of anhydrous sodium acetate, the product was obtained in lower yield (79%, Exp. No. 8) than the one obtained in the case of  $NaOAc \cdot 3H_2O$ . On the other hand, in the case of other bases such as triethyl amine, potassium bicarbonate, and sodium carbonate, the product was obtained in 82, 67, and 35% yields, respectively (Exp. Nos. 9-11). But sodium bicarbonate and calcium hydroxide were not effective for this biscarbonylation of benzyl moieties (Exp. Nos. 12, 13). When strong base such as sodium hydroxide or sodium ethoxide was used, Williamson ethers were formed in considerable amounts and also ethyl 2,6-bis(ethoxymethyl)benzoate was formed (Exp. Nos. 14, 15). It is noteworthy that the latter product has not been reported in similar carbonylation reaction. From investigation of base effect, it was found that the base played a decisive role in the selectivity and in the yield of product. Also the pressure of carbon monoxide has an effect on the reaction. The higher pressure of carbon monoxide gave the higher yield of product (Exp. Nos. 2, 3). These results are presumably due to the increase of insertion ability of CO into benzyl-cobalt complex. In the case of different temperatures such as 0°C, 60°C, and reflux temperature, the yields were lower than that of room temperature (Exp. Nos. 5-7). At 60°C and reflux temperature, esterification of the moiety of the benzyl bromide with acetate anion occurred (Exp. Nos. 6, 7). The optimum temperature for the biscarbonylation of 1-bromo-2,6-bis(bromomethyl)benzene has room temperature.

Table 2 shows solvent dependence for the yield of biscarbonylation. Methanol was found to be the best solvent among alcohols employed (Exp. No. 16), higher alcohols having ethyl-, *n*- or *iso*-propyl-, and *n*- or *t*-butyl group gave lower yields (Exp. Nos. 1, 17-19) because of the low solubilities of bases in higher alcohol. In the case of butanol, monocarbonylated product was generated in a noticeable amount (40 %) to reduce the biscarbonylated product drastically (20%, Exp. No. 19) and longer reaction time gave only slightly increased product (35%, Exp. No. 20). In the case of *n*-butanol, biscarbonylation was not successful because of the high steric hindrance of *n*-butoxy group in monocarbonylated product.

**Table 1.** Base, Pressure, and Temperature Effect on the Carbonylation of 1-Bromo-2,6-bis(bromomethyl)benzene Catalyzed by Cobalt<sup>a</sup>

No.	Base	Temp.	Pressure (atm)	Product	Yield (%) <sup>b</sup>
1	NaOAc·3H <sub>2</sub> O	r.t.	1	1-BrC <sub>6</sub> H <sub>3</sub> -2,6-(CH <sub>2</sub> CO <sub>2</sub> CH <sub>2</sub> CH <sub>3</sub> ) <sub>2</sub>	89
2	NaOAc·3H <sub>2</sub> O	r.t.	10	1-BrC <sub>6</sub> H <sub>3</sub> -2,6-(CH <sub>2</sub> CO <sub>2</sub> CH <sub>2</sub> CH <sub>3</sub> ) <sub>2</sub>	92
3	NaOAc·3H <sub>2</sub> O	r.t.	20	1-BrC <sub>6</sub> H <sub>3</sub> -2,6-(CH <sub>2</sub> CO <sub>2</sub> CH <sub>2</sub> CH <sub>3</sub> ) <sub>2</sub>	94
4	NaOAc·3H <sub>2</sub> O	r.t.	40	1-BrC <sub>6</sub> H <sub>3</sub> -2,6-(CH <sub>2</sub> CO <sub>2</sub> CH <sub>2</sub> CH <sub>3</sub> ) <sub>2</sub>	97
5	NaOAc·3H <sub>2</sub> O	0	1	1-BrC <sub>6</sub> H <sub>3</sub> -2,6-(CH <sub>2</sub> CO <sub>2</sub> CH <sub>2</sub> CH <sub>3</sub> ) <sub>2</sub>	73
6	NaOAc·3H <sub>2</sub> O	60	1	1-BrC <sub>6</sub> H <sub>3</sub> -2,6-(CH <sub>2</sub> CO <sub>2</sub> CH <sub>2</sub> CH <sub>3</sub> ) <sub>2</sub>	38
			1	1-BrC <sub>6</sub> H <sub>3</sub> -2,6-(CH <sub>2</sub> OCOCH <sub>2</sub> CH <sub>3</sub> ) <sub>2</sub>	19
7	NaOAc·3H <sub>2</sub> O	reflux	1	1-BrC <sub>6</sub> H <sub>3</sub> -2,6-(CH <sub>2</sub> CO <sub>2</sub> CH <sub>2</sub> CH <sub>3</sub> ) <sub>2</sub>	tr
			1	1-BrC <sub>6</sub> H <sub>3</sub> -2,6-(CH <sub>2</sub> OCOCH <sub>2</sub> CH <sub>3</sub> ) <sub>2</sub>	42
8	NaOAc	r.t.	1	1-BrC <sub>6</sub> H <sub>3</sub> -2,6-(CH <sub>2</sub> CO <sub>2</sub> CH <sub>2</sub> CH <sub>3</sub> ) <sub>2</sub>	79
9	NEt <sub>3</sub>	r.t.	1	1-BrC <sub>6</sub> H <sub>3</sub> -2,6-(CH <sub>2</sub> CO <sub>2</sub> CH <sub>2</sub> CH <sub>3</sub> ) <sub>2</sub>	82
10	KHCO <sub>3</sub>	r.t.	1	1-BrC <sub>6</sub> H <sub>3</sub> -2,6-(CH <sub>2</sub> CO <sub>2</sub> CH <sub>2</sub> CH <sub>3</sub> ) <sub>2</sub>	67
11	Na <sub>2</sub> CO <sub>3</sub>	r.t.	1	1-BrC <sub>6</sub> H <sub>3</sub> -2,6-(CH <sub>2</sub> CO <sub>2</sub> CH <sub>2</sub> CH <sub>3</sub> ) <sub>2</sub>	35
12	NaHCO <sub>3</sub> O	r.t.	1	1-BrC <sub>6</sub> H <sub>3</sub> -2,6-(CH <sub>2</sub> CO <sub>2</sub> CH <sub>2</sub> CH <sub>3</sub> ) <sub>2</sub>	tr
13	Ca(OH) <sub>2</sub>	r.t.	1	1-BrC <sub>6</sub> H <sub>3</sub> -2,6-(CH <sub>2</sub> CO <sub>2</sub> CH <sub>2</sub> CH <sub>3</sub> ) <sub>2</sub>	tr
14	NaOAc·3H <sub>2</sub> O	r.t.	1	1-BrC <sub>6</sub> H <sub>3</sub> -2,6-(CH <sub>2</sub> CO <sub>2</sub> CH <sub>2</sub> CH <sub>3</sub> ) <sub>2</sub>	0
				1-CH <sub>3</sub> CH <sub>2</sub> O <sub>2</sub> CC <sub>6</sub> H <sub>3</sub> -2,6-(CH <sub>2</sub> OCH <sub>2</sub> CH <sub>3</sub> ) <sub>2</sub>	33
				1-BrC <sub>6</sub> H <sub>3</sub> -2,6-(CH <sub>2</sub> OCH <sub>2</sub> CH <sub>3</sub> ) <sub>2</sub>	47
				1-HO <sub>2</sub> CC <sub>6</sub> H <sub>3</sub> -2,6-(CH <sub>2</sub> OCH <sub>2</sub> CH <sub>3</sub> ) <sub>2</sub>	tr
15	NaOEt	r.t.	1	1-BrC <sub>6</sub> H <sub>3</sub> -2,6-(CH <sub>2</sub> CO <sub>2</sub> CH <sub>2</sub> CH <sub>3</sub> ) <sub>2</sub>	0
				1-CH <sub>3</sub> CH <sub>2</sub> O <sub>2</sub> CC <sub>6</sub> H <sub>3</sub> -2,6-(CH <sub>2</sub> OCH <sub>2</sub> CH <sub>3</sub> ) <sub>2</sub>	46
				1-BrC <sub>6</sub> H <sub>3</sub> -2,6-(CH <sub>2</sub> OCH <sub>2</sub> CH <sub>3</sub> ) <sub>2</sub>	50

<sup>a</sup> 1-Bromo-2,6-bis(bromomethyl)benzene (0.343 g, 1.0 mmol), base (5.0 mmol), EtOH (20 mL), and Co<sub>2</sub>(CO)<sub>8</sub> (0.017 g, 0.05 mmol) were stirred under CO (1 atm) at r.t. for 24 hrs. <sup>b</sup> Isolated yield.

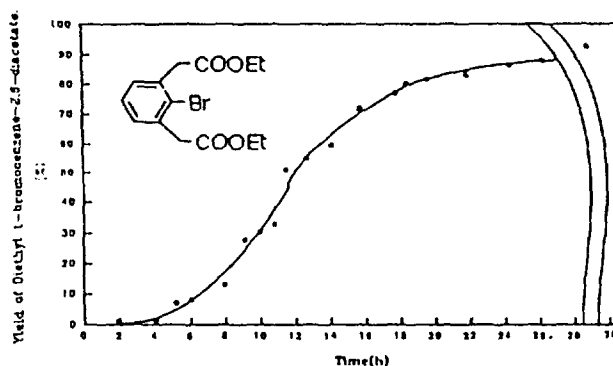
**Table 2.** Alcohol Effect on the Carbonylation of 1-Bromo-2,6-bis(bromomethyl)benzene Catalyzed by Cobalt<sup>a</sup>

No.	Alcohol	Product	Yield (%) <sup>b</sup>
1	EtOH	1-BrC <sub>6</sub> H <sub>3</sub> -2,6-(CH <sub>2</sub> CO <sub>2</sub> C <sub>2</sub> H <sub>5</sub> ) <sub>2</sub>	89
16	MeOH	1-BrC <sub>6</sub> H <sub>3</sub> -2,6-(CH <sub>2</sub> CO <sub>2</sub> CH <sub>3</sub> ) <sub>2</sub>	93
17	<sup>n</sup> PrOH	1-BrC <sub>6</sub> H <sub>3</sub> -2,6-(CH <sub>2</sub> CO <sub>2</sub> C <sub>3</sub> H <sub>7</sub> ) <sub>2</sub>	71
18	<sup>i</sup> PrOH	1-BrC <sub>6</sub> H <sub>3</sub> -2,6-(CH <sub>2</sub> CO <sub>2</sub> C <sub>3</sub> H <sub>7</sub> ) <sub>2</sub>	54
19	<sup>n</sup> BuOH	1-BrC <sub>6</sub> H <sub>3</sub> -2,6-(CH <sub>2</sub> CO <sub>2</sub> C <sub>4</sub> H <sub>9</sub> ) <sub>2</sub>	20
		1,2-Br <sub>2</sub> C <sub>6</sub> H <sub>3</sub> -6-CH <sub>2</sub> CO <sub>2</sub> C <sub>4</sub> H <sub>9</sub>	40
20	<sup>n</sup> BuOH	1-BrC <sub>6</sub> H <sub>3</sub> -2,6-(CH <sub>2</sub> CO <sub>2</sub> C <sub>4</sub> H <sub>9</sub> ) <sub>2</sub>	35
21	<sup>i</sup> BuOH	1-BrC <sub>6</sub> H <sub>3</sub> -2,6-(CH <sub>2</sub> CO <sub>2</sub> C <sub>4</sub> H <sub>9</sub> ) <sub>2</sub>	tr

<sup>a</sup> 1-Bromo-2,6-bis(bromomethyl)benzene (0.343 g, 1.0 mmol), NaOAc·3H<sub>2</sub>O (0.680 g, 5.0 mmol), Co<sub>2</sub>(CO)<sub>8</sub> (0.017 g, 0.05 mmol) and Alcohol (20 mL) were stirred under CO (1 atm) at r.t. for 24 hrs. <sup>b</sup> Isolated yield.

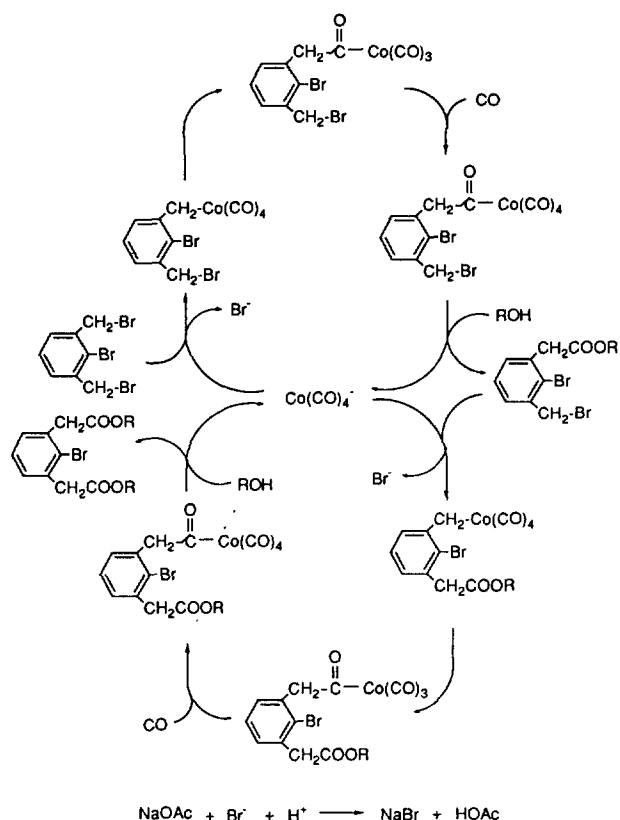
Tertiary butanol gave the corresponding product in a trace amount, because of its bulkiness as well as its very low solubility of base.

As shown in Figure 1, the rate of product formation was very slow for early 4 hours. After 4 hours, the product was formed fast and this reaction was almost completed after 24 hour. The slow reaction rate during the first several hours may be due to the cleavage time of dicobalt octacarbonyl, Co<sub>2</sub>(CO)<sub>8</sub>, to cobalt tetracarbonyl anion, Co(CO)<sub>4</sub><sup>-</sup>, as a true catalyst.

**Figure 1.** Plot of the percent generation of diethyl 1-bromobenzene-2,6-diacetate with time. [1-bromo-2,6-bis(bromomethyl)benzene (1 mmol); Co<sub>2</sub>(CO)<sub>8</sub> (0.05 mmol); NaOAc·3H<sub>2</sub>O (5 mmol); CLOH (20 mL)].

As shown in Scheme 2, the mechanism of carbonylation was proposed by several authors.<sup>3,15-17</sup> Nucleophilic attack of Co(CO)<sub>4</sub><sup>-</sup> to benzyl carbon of 1-bromo-2,6-bis(bromomethyl)benzene results in (1-bromo-2-bromomethylbenzyl) cobalt tetracarbonyl species. Generated alkyl cobalt complex equilibrates with 1-bromo-2-(bromomethyl)phenylacetyl cobalt tetracarbonyl absorbing a carbon monoxide. Acyl cobalt complex is cleaved by alcohol to give alkyl 1-bromo-2-(bromomethyl)phenyl-6-acetate and cobalt tetracarbonyl anion.

The second mechanistic circulation of the generated mo-



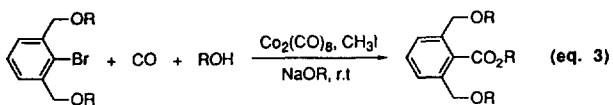
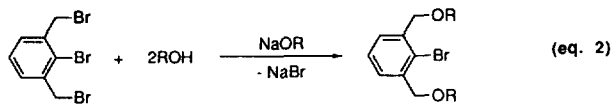
**Scheme 1.** Mechanism of Benzylic Carbonylation of 1-Bromo-2,6-bis(bromomethyl)benzene catalyzed by Cobalt.

nocarbonylated species results in the biscarbonylated final product.

#### Carbonylation of the moiety of aryl bromide of 1-bromo-2,6-bis(bromomethyl)benzene

A method for the transformation of alkyl 2,6-bis(alkoxymethyl)benzoate from 1-bromo-2,6-bis(bromomethyl)benzene is described in Eq. (3).

In the first step, the moiety of benzyl bromides were etherified with sodium alkoxide by Williamson ether process quantitatively under the condition described in Eq. (2). In the second step, the moiety of aryl bromide was carbonylated in the presence of  $\text{CH}_3\text{I}$  as a catalyst promoter<sup>4,11</sup> to give 1-alkyl-2,6-bis(alkoxymethyl)benzoate in good yields (Eq. (3)). These results are summarized in Table 3.



In these reactions, sodium alkoxides were fixed as the bases. It is more nucleophilic than hydroxide ion (Exp. No. 14). Of various alcohols employed, ethanol shows the best yield of carbonylation of the moiety of aryl bromide (Exp. No. 23). On the other hand, in the absence of  $\text{CH}_3\text{I}$  leads to the low yield of carbonylated product indicating its effect

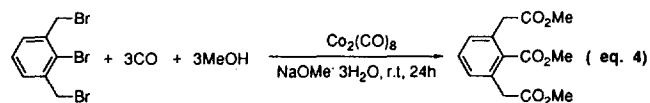
**Table 3.** Effect of Alcohol and Pressure of CO on the Carbonylation of 1-Bromo-2,6-bis(bromomethyl)benzene to alkyl 2,6-bis(alkoxymethyl)benzoate<sup>a</sup>

No.	Base	Alcohol	CO	Product	Yield (%) <sup>b</sup>
15 <sup>c</sup>	NaOEt	EtOH	1	1-C <sub>2</sub> H <sub>5</sub> O <sub>2</sub> CC <sub>6</sub> H <sub>3</sub> -2,6-(CH <sub>2</sub> OC <sub>2</sub> H <sub>5</sub> ) <sub>2</sub>	46
22	NaOMe	MeOH	1	1-CH <sub>3</sub> O <sub>2</sub> CC <sub>6</sub> H <sub>3</sub> -2,6-(CH <sub>2</sub> OCH <sub>3</sub> ) <sub>2</sub>	68
23	NaOEt	EtOH	1	1-C <sub>2</sub> H <sub>5</sub> O <sub>2</sub> CC <sub>6</sub> H <sub>3</sub> -2,6-(CH <sub>2</sub> OC <sub>2</sub> H <sub>5</sub> ) <sub>2</sub>	80
24	NaO <sup>n</sup> Pr	<sup>n</sup> PrOH	1	1-C <sub>3</sub> H <sub>7</sub> O <sub>2</sub> CC <sub>6</sub> H <sub>3</sub> -2,6-(CH <sub>2</sub> OC <sub>3</sub> H <sub>7</sub> ) <sub>2</sub>	78
25	NaO <sup>n</sup> Bu	<sup>n</sup> BuOH	1	1-C <sub>4</sub> H <sub>9</sub> O <sub>2</sub> CC <sub>6</sub> H <sub>3</sub> -2,6-(CH <sub>2</sub> OC <sub>4</sub> H <sub>9</sub> ) <sub>2</sub>	46
26	NaOEt	EtOH	10	1-C <sub>2</sub> H <sub>5</sub> O <sub>2</sub> CC <sub>6</sub> H <sub>3</sub> -2,6-(CH <sub>2</sub> OC <sub>2</sub> H <sub>5</sub> ) <sub>2</sub>	59
27	NaOEt	EtOH	20	1-C <sub>2</sub> H <sub>5</sub> O <sub>2</sub> CC <sub>6</sub> H <sub>3</sub> -2,6-(CH <sub>2</sub> OC <sub>2</sub> H <sub>5</sub> ) <sub>2</sub>	46
28	NaOEt	EtOH	30	1-C <sub>2</sub> H <sub>5</sub> O <sub>2</sub> CC <sub>6</sub> H <sub>3</sub> -2,6-(CH <sub>2</sub> OC <sub>2</sub> H <sub>5</sub> ) <sub>2</sub>	46
29	NaOMe	MeOH	20	1-CH <sub>3</sub> O <sub>2</sub> CC <sub>6</sub> H <sub>3</sub> -2,6-(CH <sub>2</sub> OCH <sub>3</sub> ) <sub>2</sub>	43

<sup>a</sup> 1-Bromo-2,6-bis(bromomethyl)benzene (0.686 g, 2.0 mmol), Base (20.0 mmol), Alcohol (25 mL),  $\text{Co}_2(\text{CO})_8$  (0.034 g, 0.1 mmol), and  $\text{CH}_3\text{I}$  (1.420 g, 10.0 mmol) at r.t. for 24 hrs. <sup>b</sup> Isolated yield. <sup>c</sup>  $\text{CH}_3\text{I}$  is not added.

as a catalyst promoter. When the pressure of carbon monoxide is elevated up to 30 atm (Exp. Nos. 26-29), the yields of alkyl 2,6-bis(alkoxymethyl)benzoate were lower than 1 atm (Exp. No. 15).

These results are compared with those of 2,6-dimethyl-1-bromobenzene. Under the same condition or more drastic conditions, carbonylation of 2,6-dimethyl-1-bromobenzene did not occur. Although 1-bromo-2,6-bis(alkoxymethyl)benzene is more sterically hindered than 2,6-dimethyl-1-bromobenzene, aryl bromide of 1-bromo-2,6-bis(alkoxymethyl)benzene can be carbonylated. This reaction mechanism is far not clearly understood, but we think that nonbonding electron of oxygen probably coordinates to cobalt atom, resulting in carbonylation of aryl bromide. When reactant was treated with methanol and NaOMe in the presence of a catalytic amount of  $\text{Co}_2(\text{CO})_8$  under CO (1 atm) at room temperature without first etherification of benzylic bromide, trisubstituted methyl 2,6-bis(carbomethoxymethyl)benzoate was obtained in a trace amount (Eq. (4)) along with 1-bromo-2,6-bis(methoxymethyl)benzene (62%) and methyl 2,6-bis(methoxymethyl)benzoate (20%).



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## Generalization of the Curie-Weiss Model to the $D$ -dimensional Spin System

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The critical behavior of the classical  $D$ -dimensional spin model ( $D \geq 2$ ), which is the intermediate model that link up the Ising ( $D=1$ ) and the spherical model ( $D=\infty$ ), is studied for the case of constant coupling interaction independent of the spin-spin distance (Curie-Weiss model). Analytical results show that the critical behavior of the present model is in quantitative agreement with the prediction of the phenomenological mean-field theory independent of  $D$ . Critical temperature is calculated to be  $T_c = k/JD$ . This gives a quantitative explanation of the relationship between the spin degree of freedom and the critical temperature.

### Introduction

As the most symplified model of the long-range interacting spin system, meanfield theory has been used as a guide to the more realistic models<sup>1,2</sup>. A macroscopic hamiltonian can be made to get the thermodynamic properties that exactly match the predictions of the phenomenological mean-field theory. This so-called "Curie-Weiss Model" has been solved and discussed in the Ising case<sup>2</sup>, in which each spin interacts with all others equally, and the spin variable can take the values of  $\pm 1$  only.

In this paper, the spin model is generalized to the  $D$ -dimensional case, in which each spin variable is a  $D$ -dimensional unit vector. This classical spin model is a realistic approximation to the quantum mechanical Heisenberg model for  $D=3$  case near the critical temperature. The phase transition for  $D \geq 2$  spin system is known to be given by the long-range fluctuations, whereas for the Ising case, it is done by the local defects. However, our result shows that such a difference is not reflected on the critical behavior for the present

system in which each spin interacts with all others equally, which confirms the predictions of the phenomenological mean-field theory.

### Thermodynamic Properties

Our derivation of the thermodynamic properties is a direct generalization of Kac's argument<sup>2</sup>. But our analysis covers the case of nonzero magnetic field, without which the critical exponents  $\beta$ ,  $\gamma$  and  $\delta$  cannot be obtained. let us define the hamiltonian for the Curie-Weiss model in  $D$ -dimension as

$$H = -h \cdot \sum_i \mathbf{x}_i - \frac{J}{N} \sum_i \sum_{j < i} \mathbf{x}_i \cdot \mathbf{x}_j, \quad (1)$$

wher  $h$  is the external field vector and  $\mathbf{x}_i$  is the spin vector which satisfies  $|\mathbf{x}_i| = 1$ . One of the great virtues of the model is that the hamiltonian can be transformed to the following form.

$$H = -\frac{J}{2N} \left| \sum_i \mathbf{x}_i \right|^2 - h \cdot \sum_i \mathbf{x}_i + J/2$$

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