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# FRIEDEL-CRAFTS REACTION OF BIS(TRICHLOROMETHYL)CARBONATE FOR THE PREPARATION OF BENZOPHENONES

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# FRIEDEL-CRAFTS REACTION OF BIS(TRICHLOROMETHYL)CARBONATE FOR THE PREPARATION OF BENZOPHENONES

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# ABSTRACT

Benzophenones ( $RC_6H_4COC_6H_4R$ , R=H, Cl, CH<sub>3</sub> or (CH<sub>3</sub>)<sub>2</sub>N) have been prepared by the Friedel-Crafts reactions of aromatic compounds  $C_6H_5R$  with *bis*(trichloromethyl)carbonate (BTC) instead of toxic phosgene. ACl<sub>3</sub>, FeCl<sub>3</sub> or ZnCl<sub>2</sub> were used as Lewis acids in the reaction. The preparation is safe, convenient and in higher yields than phosgene-processes.

*Key Words:* Benzophenone; bis(Trichloromethyl)carbonate; Triphosgene; Phosgene; Friedel-Crafts reactions

Benzophenones are a class of very useful fine chemicals such as UV absorbents and dye intermediates. They are usually prepared by toxic phos-

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gene-processes with poisoning danger and in low yields. Recently, *bis*(trichloromethyl)carbonate (BTC) (1), a stable and safe crystalline is developed into a new substitute of phosgene.<sup>[1,2]</sup> Since BTC is easy to be transported, stored, and handled, it has been used in the convenient phosgenation of various amines,<sup>[3]</sup> alcohols,<sup>[4,5]</sup> carboxylic acids,<sup>[6]</sup> and amino acids.<sup>[7]</sup> However, no report is on the reaction of BTC with aromatic compounds for preparation of benzophenones. In this paper, we disclose our first study of a convenient method for the preparation of benzophenones (3) by Friedel-Crafts reaction of BTC with related aromatic hydrocarbons (2) using AlCl<sub>3</sub>, FeCl<sub>3</sub>, or ZnCl<sub>2</sub> as Lewis acids (Scheme 1).

# **EXPERIMENTAL**

Infra red spectra were recorded on a Nicolet FTIR-20 spectrophotometer. The <sup>1</sup>H-NMR spectra were obtained on a JEOL FX-90Q. GC and GC/MS spectra were carried out using HP 5890 and Finnigan MAT 312/SS200 combined system.

Anhydrous aluminum trichloride and anhydrous ferric trichloride were from Dalian Dyestuff Company and purified by sublimation in vacuum. Zinc chloride was from Shenyang Chemical Company (China). *Bis*(trichloromethyl)carbonate (BTC) was prepared from the per-chlorination of dimethyl carbonate according to the method of Eckerr and Forster<sup>[1]</sup> and purified by recrystallization from hexane.

#### Benzophenone (3a)

To a solution of anhydrous aluminum chloride (4.0 g, 30.0 mmol) in benzene (10 mL), BTC (2.0 g, 6.74 mmol) in benzene (10 mL) was added dropwise over 1 h under nitrogen atmosphere at 2–4°C with stirring. The

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reaction was maintained for 10 h. Then the reaction mixture was poured into an ice—concentrated hydrochloride acid solution. The organic layer was separated, washed successively with water, 5% sodium carbonate, and water, and dried over anhydrous sodium sulfate. Evaporation of the unreacted benzene from the solution and distillation of the residue in water steam, afforded **3a** as a white solid (2.84 g, 77% yield) with mp 47–48°C (purity: 99.2% by GC). IR v (KBr, cm<sup>-1</sup>): 3030 (C–H), 1665(C=O), 1596, 1576, 1492 (benzene ring). <sup>1</sup>H-NMR  $\delta$  (ppm): 7.48 (t, J=7.6 Hz, 4H), 7.59 (t, J=7.4 Hz, 2H), 7.81 (d, J=8.0 Hz, 4H). MS m/z: 182 (M<sup>+</sup>).

### **Dimethylbenzophenone (3b)**

With the similar procedure as **3a**, the reaction of toluene with BTC gave dimethylbenzophenone, **3b**, in 72% yield. GC (capillary column: OV101) and GC/MS analyses showed that **3b** was a mixture of two isomers with a ratio of 1:3.86. By preparative TLC (silica as absorbent, benzene: hexane: acetone 1:1:1 in volume as eluent), the isomers were separated. The first isomer was confirmed to be 2,4'-dimethylbenzophenone: oil, bp: 181–182°C/2999.5Pa. IR v (KBr, cm<sup>-1</sup>): 3030 (Ar–H), 2920 (CH<sub>3</sub>), 1645 (C=O), 1605 (benzene ring). <sup>1</sup>H-NMR  $\delta$  (ppm): 2.30 (s, 3H), 2.37 (s, 3H), 7.2–7.7 (m, 8H). MS *m/z*: 210 (M<sup>+</sup>); the second isomer was 4,4'-dimethylbenzophenone: mp 94–95°C, IR v (KBr, cm<sup>-1</sup>): 3030 (Ar–H), 2919 (CH<sub>3</sub>), 1645 (C=O), 1602 (benzene ring). <sup>1</sup>H-NMR  $\delta$  (ppm): 2.40 (s, 6H), 7.22 (dd, *J*=8.4, 1.7 Hz, 4H), 7.70 (dd, *J*=8.4, 1.7 Hz, 4H). MS *m/z*: 210 (M<sup>+</sup>).

#### **Dichlorobenzophenone (3c)**

Similarly, the reaction of chlorobenzene with BTC afforded dichlorobenzophenone, **3c**. The gas chromatography of the reaction mixture showed it comprised 4 compounds (I–IV) whose retention times (and contents: were: 0.69 (7.6%); 3.15 (35.7%); 3.38 (7.5%); 3.56 (34.0%) respectively. GC/MS of I gave an m/z of 174 [M<sup>+</sup>] and 139 [M-35]<sup>+</sup> (base peak) and identified to be chlorobenzoyl chloride. The next three compounds, II, III, IV, exhibited similar mass spectra in GC/MS with the same m/z of [M<sup>+</sup>]: 250. They were confirmed to be three isomers of dichlorobenzophenones. Separated by preparative TLC (silica, benzene/hexane/acetone 1:1:1 in volume) as the case in dimethylbenzophenone, II and IV were obtained. II: 2,4'-dichlorobenzophenone: m.p. 66–67°C, IR v (KBr, cm<sup>-1</sup>): 3060 (Ar–H), 1662 (C=O), 1580, 1482 (benzene ring). NMR  $\delta_{\rm H}$  (ppm): 7.20–7.40 (m, 6H), 7.50–7.70 (m, 2H).

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MS m/z: 250 (M<sup>-</sup>). IV: 4,4'-dichlorobenzophenone: m.p. 145–147°C, IR v (KBr, cm<sup>-1</sup>): 3030 (Ar–H), 1666 (C=O), 1588, 1570, 1482 (benzene ring). NMR  $\delta_{\rm H}$  (ppm): 7.47 (dd, J = 8.3, 1.1 Hz, 4H), 7.71 (dd, J = 8.3, 1.1 Hz, 4H). MS m/z: 250 (M<sup>+</sup>).

# N,N,N',N'-tetramethyl Michler's Ketone (3d)

To a solution of *N*,*N*-dimethylaniline (2.4 g, 19.8 mmol) in ethylene dichloride (20 mL), BTC (1.0 g, 3.38 mmol) in ethylene dichloride (10 mL) was added dropwise over 1 h at 3–5°C with stirring. The reaction was carried out at 15–20°C for 6 h without Lewis acid, then at 35–40°C for 14 h with anhydrous zinc chloride (1.5 g). The mixture was cooled, washed successively with diluted hydrochloric acid, water, 5% of sodium carbonate, and water, dried over sodium sulfate. Evaporation of the solvent and recrystallization of the residue solid from alcohol gave 1.7 g of bluish crystal of *N*,*N*,*N'*,*N'*-tetramethyl Michler's ketone in 64% yield based on dimethylaniline. Mp: 175–177°C. IR v (KBr, cm<sup>-1</sup>): 2901, 2820 (CH<sub>3</sub>), 1608 (C=O). NMR  $\delta_{\rm H}$  (ppm): 3.01 (s, 12H), 6.67 (d, *J*=8.2 Hz, 4H), 7.75 (d, *J*=8.2 Hz, 4H), MS *m/z*: 268 (M<sup>+</sup>).

# **RESULTS AND DISCUSSION**

Phosgene is considered as "gold block" in organic synthesis and related with a large amount of chemicals. However, it is one of the most toxic gases. BTC, a white crystal, has been developed as a safe substitute for phosgene. For the Fridel-Crafts reaction, the conditions were very mild and convenient: BTC in **2** was dropped into the cold solution of Lewis acid, benzophenones were produced with no releasing of toxic phosgene. The reaction conditions and yields of the products are listed in Table 1. Generally, in a phosgene reaction, a part of phosgene releases from the reaction system when phosgene is introduced. So 4 or 5 times excess of phosgene are always needed for the phosgenation, and the yield base on phosgene is very low. For BTC, however, theoretical amount or a very little excess is enough.

For the preparation of benzophenone, the reaction was monitored by GC and GC/MS. In the case of AlCl<sub>3</sub> as Lewis acid, an intermediate, benzoyl chloride was detected by GC at the beginning of reaction, reached its maximal amount in 1 h, and then gradually converted to benzophenone. The reaction finished in 10 h. after steam distillation, 77% yield (based on the

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			Table 1.	Friedel-Cra	fts Reaction of BTC		
	R	Lewis Acid	Temp. (°C)	Time (h)	Solvent	3	Yield (%)
a	Н	AlCl <sub>3</sub>	0-5	10	Benzene		77 <sup>b</sup>
		FeCl <sub>3</sub>	$5{-}10$	10	Benzene		37 <sup>b</sup>
		$ZnCl_2$	5-10	10	Benzene		19 <sup>b</sup>
q	CH <sub>3</sub>	AICI <sub>3</sub>	0-5	9	Toluene		72 <sup>b</sup>
J	CI	AICI <sub>3</sub>	0-5	17	Chlorobenzene		$77^{\rm b}$
p	N(CH <sub>3</sub> ) <sub>2</sub>	$ZnCl_2^a$	10-40 <sup>b</sup>	20	Ethylene dichloride		64 <sup>c</sup>
athe	reaction proc	eeded in two stag	es: firstly at 15-20	0°C for 6 h wi	th no Lewis acid and ther	n at 40–45°C for 14 h with 2	zinc chloride

as Lewis acid; <sup>b</sup>based on BTC; <sup>c</sup>based on 2.

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BTC) was obtained with purity of 99.2%. This yield is much higher than with phosgene which gave only 38% yield based on phosgene in our contrasting experiments. When reaction temperature was above  $15^{\circ}$ C, however, some by-products might produced. When ZnCl<sub>2</sub> or FeCl<sub>3</sub> was used as Lewis acid the reaction speed was very slow so that only 19% and 37% of theoretical amount of benzophenone was formed respectively after reactions proceeded for 10 h.

Toluene reacted with BTC, producing two isomers of dimethyl-benzophenone with total yield of 72%. After separated by preparative TLC, the isomers were confirmed to be the corresponding 4,4'-(m.p.  $94-95^{\circ}$ C) and 2,4'-isomer (oil, bp:  $181-182^{\circ}$ C/2999.5 Pa). GC showed their mole ratio was 3.86:1.

The products of chlorobenzene were more complex. Chlorobenzoyl chloride (compound I) and three isomers of dichlorobenzophenone (compound II, III, IV) were detected as main products by GC and GC/MS. The relative contents of the isomers are: II 46.2%, III 9.7% and IV 44.1%. Separated by preparative TLC, II and IV were obtained and identified. II was 2,4'-dichlorobenzophenone; IV was 4,4'-dichlorobenzophenone. The identification of isomer III and other two by-products (<2% by GC) was unsuccessful due to the little contents.

For the reaction of *N*,*N*-dimethylaniline with BTC, when CS<sub>2</sub> used as solvent and AlCl<sub>3</sub> as Lewis acid, only a trace of aimed product was obtained. The main product was a triarylmethane-type blue compound which was formed from the condensation of the aimed product, N,N,N',N'-tetra alkyl Michler's ketone with unreacted N,N-dialkylaniline. This blue compound also appears in the commercial manufacturing processes for the Michler's ketone from phosgene. In order to improve the yield, the reaction was carried out in ethylene dichloride and in two steps: firstly at 15–20°C for 6 h without Lewis acid, and then at 40–45°C for 14–19 h with ZnCl<sub>2</sub> as Lewis acid. In this way, with only a little excess (2%) of BTC, pure Michler's ketone were obtained in 64% yield based on N,N-dimethylaniline, much higher than 46%, the yield of a commercial phosgene-process in which 400 to 500% excess of phosgene and much longer reaction time (2 to 3 days) are required.

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