

## Synthesis of Diphenyl Carbonate from CO<sub>2</sub>, Phenoxide, and CCl<sub>4</sub> with ZnCl<sub>2</sub> as Catalyst

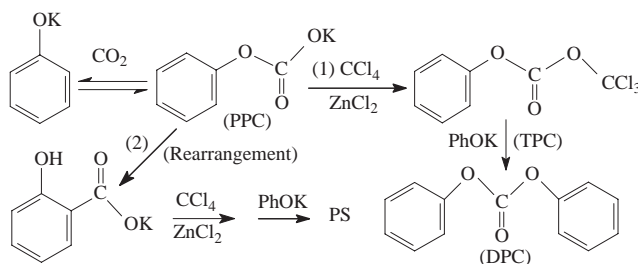
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Direct synthesis of diphenyl carbonate (DPC) from phenoxide, CO<sub>2</sub> and CCl<sub>4</sub> in one pot was realized with ZnCl<sub>2</sub> as catalyst. Trichloromethyl cation may act on potassium phenyl carbonate, which brings the carbonyl more easily attached on by the phenoxide. Onium salts promote the reaction greatly, especially with phenol and potassium carbonate instead of phenoxide as reactants. Moreover, the substituent on the aromatic ring has significant effects on the selectivity and yield of carbonate.



**Scheme 1.** The possible reaction mechanism.

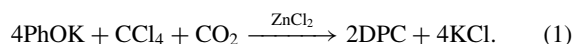
Diphenyl carbonate (DPC) is a key raw material for the production of aromatic polycarbonates. As yet, it can be obtained through the phosgenation of phenol,<sup>1</sup> oxidative carbonylation of phenol,<sup>2</sup> transesterification of dimethyl carbonate (DMC),<sup>3</sup> or dimethyl oxalate (DMO) with phenol.<sup>4</sup> All those methods have certain disadvantages, for example, the phosgenation process uses severely toxic phosgene as raw material,<sup>5</sup> oxidative carbonylation method needs noble metal catalyst and costly procedures, and transesterification demands intricate multistage procedures with a critical thermodynamic limitation,<sup>6</sup> which results in very low DPC yield and selectivity. It will be undoubtedly a much more economical option if DPC can be synthesized directly from phenol and CO<sub>2</sub>.

In this work, the direct synthesis of DPC from phenoxide, CO<sub>2</sub>, and CCl<sub>4</sub> in one pot was realized with ZnCl<sub>2</sub> as catalyst. The effects of reaction temperature, promoter, and substituent attached to the aromatic ring on the carbonate yield were investigated.

The reaction results are summarized in Table 1. In the presence of an inert atmosphere N<sub>2</sub>, no reaction was observed at 100 °C (Entry 1). With the introduction of CO<sub>2</sub>, DPC is detected even at 80 °C (Entry 2). As the temperature is elevated to 100 °C, phenyl salicylate (PS) appears as the main by-product (Entry 3). It seems that with the increase of reaction temperature, the yields of both DPC and PS increase, but the selectivity to

DPC decreases slightly. At 120 °C, the yields of DPC and PS come up to 3.6% and 4.6%, respectively (Entry 4).

According to the above described results, it is found that the presence of CO<sub>2</sub> is an important factor for synthesis DPC. One possible reaction process is started with the nucleophilic attack of the potassium phenoxide to CO<sub>2</sub> and it produces potassium phenyl carbonate (PPC).<sup>7</sup> During the reaction, trichloromethyl cation CCl<sub>3</sub><sup>δ+</sup> is formed on the catalyst surface, which is similar to the destruction of carbon tetrachloride over lanthanide oxide-based catalyst.<sup>8</sup> Thus, potassium phenyl carbonate may either form trichloromethyl phenyl carbonate (TPC) through binding with CCl<sub>3</sub><sup>δ+</sup> (Scheme 1, pathway 1) or be rearranged into salicylate<sup>7</sup> (Scheme 1, pathway 2). After transesterification with phenoxide, TPC changes into DPC, KCl, and phosgene. The phosgene, produces in situ during the reaction, reacts with phenoxide to produce another molecular DPC. In one word, one molecular CO<sub>2</sub> couples with one molecular CCl<sub>4</sub> to produce two molecular DPC.



Further tests proved that the yield and selectivity of DPC can be improved significantly by using the reactants of phenol + K<sub>2</sub>CO<sub>3</sub> as a substitute for potassium phenoxide with certain co-catalysts like onium salts. As listed in Table 2, with potassium phenoxide as reactant, the main product is PS (Entries 1–5). With tetramethylammonium bromide (Me<sub>4</sub>NBr) as co-catalyst, the formation of DPC and especially PS is suppressed in comparison with the reaction without co-catalyst (Entry 2). Using tetrabutylammonium bromide (Bu<sub>4</sub>NBr) as co-catalyst, the yield of PS increases moderately and a small amount of phenyl *p*-hydroxybenzoate (PPB) is detected even at such a low temperature (Entry 3). With cetyltrimethylammonium bromide (CeMe<sub>3</sub>NBr) as co-catalyst, DPC yield was also suppressed (Entry 4). These results suggested that onium salt with large organic group (Bu<sub>4</sub>NBr) can enhance the conversion of phenoxide obviously, while the onium salt with small organic group (Me<sub>4</sub>NBr) is facile to enhance the selectivity to DPC. This may be related to their difference in the steric hindrance. The reaction at 120 °C exhibits high selectivity to PS (Entry 5), which proved further that higher

**Table 1.** Synthesis of DPC from potassium phenoxide in liquid CCl<sub>4</sub> at different temperatures<sup>a</sup>

Entry	Temperature /°C	Catalyst	Yield/% <sup>b</sup>	
			DPC	PS
In the presence of N <sub>2</sub> (1 MPa)				
1	100	ZnCl <sub>2</sub>	—	—
In the presence of CO <sub>2</sub> (1 MPa)				
2	80	ZnCl <sub>2</sub>	0.1	—
3	100	ZnCl <sub>2</sub>	1.4	1.7
4	120	ZnCl <sub>2</sub>	3.6	4.6

<sup>a</sup>Reaction conditions: PhOK 30 mmol, catalyst 2.0 g, CCl<sub>4</sub> 40 mL, reaction duration 6 h. <sup>b</sup>Yield based on phenoxide was determined by GC analysis.

**Table 2.** Effect of co-catalyst onium salts on the reaction behavior

Entry	Temperature /°C	Co-catalyst	Yield/% <sup>c</sup>	
			DPC	PS
With PhOK as reactant <sup>a</sup>				
1	110	—	6.6	17.9
2	110	Me <sub>4</sub> NBr	4.6	4.2
3	110	Bu <sub>4</sub> NBr	6.2	21.1
4	110	CeMe <sub>3</sub> NBr	3.6	15.3
5	120	Me <sub>4</sub> NBr	2.9	23.0
With phenol + K <sub>2</sub> CO <sub>3</sub> as reactants <sup>b</sup>				
6	120	—	15.8	2.9
7	120	Me <sub>4</sub> NBr	14.1	3.7
8	120	Bu <sub>4</sub> NBr	29.7	2.2
9	120	CeMe <sub>3</sub> NBr	20.4	2.7

<sup>a</sup>Reaction conditions: PhOK 30 mmol, ZnCl<sub>2</sub> 2.0 g, co-catalyst 0.5 g, CCl<sub>4</sub> 40 mL, CO<sub>2</sub> 3.0 MPa, reaction duration 6 h.

<sup>b</sup>Phenol 30 mmol and K<sub>2</sub>CO<sub>3</sub> 15 mmol was used instead of PhOK. <sup>c</sup>Yield based on phenoxide was determined by GC analysis.

temperature is favorable for the formation of PS. Using phenol + K<sub>2</sub>CO<sub>3</sub> instead of PhOK as reactants, DPC turns out to be the main product. In this case, PhOK may be formed in situ during the reaction. DPC yield reaches 15.8% at 120 °C (Table 2, Entry 6). It further increases to 29.7% with Bu<sub>4</sub>NBr as co-catalyst (Entry 8), while the selectivity to PS is kept at a low level (2.2%).

The carbonate yield also depends on the substituent attached to the aromatic ring of phenoxide as listed in Table 3. With methyl as the substituent, the conversion of R-PhOK as well as the yield of carbonate is much lower than those of reaction without substituent attached to the aromatic ring. This suggests that methyl substituent, especially at the *para*-position, is unfavorable for the carbonate formation (Entries 3–6). However, the steric hindrance due to the methyl substitution at the *ortho*-position may suppress the rearrangement of potassium *o*-methylphenyl carbonate (PPC) into salicylate, which results in the high carbonate selectivity (Entries 3 and 4).

With chlorine as substituent, either at *ortho*- or *para*-position, however, gives high selectivity to carbonate, because chlorine as an electron-withdrawing group makes the rearrangement of PPC more difficult. Like the methyl substituent, the steric hindrance of *o*-chlorine substituent can enhance the selectivity to DPC (Entries 7 and 8). Especially, with chlorine as a substituent at *para*-position (Entries 9 and 10), high yield of carbonate (45.6% at 120 °C) was obtained also with high selectivity (98.0%). These proved that electron-withdrawing group as substituent attached to the aromatic ring can enhance the formation of carbonate.

In summary, this work demonstrates that DPC can be obtained from phenoxide, CCl<sub>4</sub>, and CO<sub>2</sub> in one pot with ZnCl<sub>2</sub>

**Table 3.** Effects of substituents attached to the aromatic ring on the carbonate selectivity and yield<sup>a</sup>

Entry	R	Temperature /°C	Selectivity /%	Yield /%
2	H	120	63.0	7.0
3	<i>o</i> -Me	100	100	3.1
4	<i>o</i> -Me	120	86.0	3.3
5	<i>p</i> -Me	100	—	—
6	<i>p</i> -Me	120	40.0	1.8
7	<i>o</i> -Cl	100	100	5.7
8	<i>o</i> -Cl	120	100	6.2
9	<i>p</i> -Cl	100	100	20.5
10	<i>p</i> -Cl	120	98.0	45.6

<sup>a</sup>Reaction conditions: R-PhOK 30 mmol, ZnCl<sub>2</sub>/MCM-41 (loading = 4 mmol/g) 1.0 g, CCl<sub>4</sub> 40 mL, CO<sub>2</sub> 1.0 MPa, reaction duration 6 h.

as catalyst. Onium salt with large organic group promotes the reaction greatly, especially with phenol and potassium carbonate as reactants. Moreover, the substituent attached to the aromatic ring on the carbonate yield has significant effects on the selectivity and yield of carbonate.

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