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# Solid-Liquid Phase Transfer and Cobalt or Palladium Complex Catalyzed Synthesis of Anhydrides from Acyl Chlorides

Jin-Xian Wang(Chin-Hsien Wang)<sup>a</sup>, Yulai Hu<sup>a</sup> & Wenfeng Cui<sup>a</sup>

<sup>a</sup> Institute of Chemistry, Department of Chemistry, Northwest Normal University, Lanzhou, 730070, China Published online: 23 Sep 2006.

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# SOLID-LIQUID PHASE TRANSFER AND COBALT OR PALLADIUM COMPLEX CATALYZED SYNTHESIS OF ANHYDRIDES FROM ACYL CHLORIDES

Jin-Xian Wang(Chin-Hsien Wang)\*, Yulai Hu and Wenfeng Cui Institute of Chemistry, Department of Chemistry, Northwest Normal University, Lanzhou 730070, China

Abstract: Acyl chloride can efficiently be converted into anhydride under solid liquid phase transfer catalysis by using bis(triphenylphosphine)cobalt dichloride or bis (triphenylphospine)palladium dichloride as catalyst.

## INTRODUCTION

It has been shown that phase transfer catalysis is a useful method in synthetic organic chemistry. In 1976, Cassar and Alper first used this technique in organometallic chemistry<sup>1,2</sup>. Now, the applications of phase transfer catalysis in organometallic chemistry have midely been developed<sup>3,4</sup>. Several reviews have appeared<sup>5-9</sup>.

Carboxylic acid anhydrides are very important reagents in organic chemistry. Anhydrides have previously been

<sup>\*</sup>To whom correspondence should be addressed.

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prepared by the reaction of acylhalides and carboxylates<sup>10</sup> or the dehydration of carboxylic acids<sup>11</sup>. Plusquellec et al., have shown that anhydrides can be obtained from corresponding acyl chloride under liquid-liquid phase transfer condition at -10°C using aqueous NaOH as base<sup>12</sup>.

## **RESULTS AND DISCUSSION**

In this paper, we wish to report that acyl chloride can be converted into corresponding anhydride under solid liquid phase transfer catalysis by using cobalt or palladium complex as catalyst. In our research, we have found that some aromatic acid anhydrides can be obtained from corresponding acyl chlorides under PTC condition.

When a mixture of acyl chloride, sodium bicarbonate, bis(triphenylphosphine)cobalt or bis(triphenylphosphine) palladium dichloride, tetrabutylammonium bromide and acetonitrile are stirred and heated for 12 hours, anhydrides can be formed in good yield (Scheme I, Table I). The effects of base and catalysts are shown in Table I.



### Scheme I

Take the reaction of benzoyl chloride for example, without tetrabutylammonium bromide, the reaction of benzoyl chloride with sodium bicarbonate catalyzed by bis( triphenylphosphine) cobalt dichloride gives benzoic acid( 59 %) and benzoic Downloaded by [University of Auckland Library] at 20:26 11 December 2014

2f:R=4-ClC <sub>6</sub> H <sub>4</sub>	2g:R=C <sub>6</sub> H <sub>5</sub> CH=CH	2h:R=4-Br-C <sub>6</sub> H <sub>4</sub>	2i:R=C <sub>15</sub> H <sub>81</sub>	2j:R=C <sub>17</sub> H <sub>85</sub>
2a;R=C <sub>e</sub> H <sub>5</sub> ;	2b:R=4-02NCeH4;	2c;R=3-O2NCeH4;	2d:R=2-O2NCeH4;	2e:R=4-CH <sub>s</sub> C <sub>6</sub> H <sub>4</sub> ;

Table I Synthesis of Anhydrides 2a-j

	Cataly	sts			Condition	80	
Produe	sct Metal	PTC	MHCO <sub>s</sub>	Solvent	Temp./Time (C) (b)	Yield(%)*	М. Р. (С)
28	Co(PPh <sub>8</sub> ) <sub>2</sub> Cl <sub>2</sub>	Bu₄NBr	NaHCOa	CH <sub>a</sub> CN	120/12	64	42-43
2b	Co(PPh <sub>8</sub> ) <sub>2</sub> Cl <sub>2</sub>	Bu₄NBr	NaHCO <sub>a</sub>	CH <sub>s</sub> CN	120/12	<del>6</del> 0	194-195
2c	Co(PPh <sub>3</sub> ) <sub>2</sub> Cl <sub>2</sub>	Bu₄NBr	<b>NaHCO</b> <sub>a</sub>	<b>CH</b> <sup>a</sup> CN	120/12	97	162-163
2d	Co(PPh <sub>8</sub> ) <sub>2</sub> Cl <sub>2</sub>	Bu₄NBr	NaHCO <sub>a</sub>	CH <sub>s</sub> CN	120/12	88	136-137
2e	Co(PPh <sub>8</sub> ) <sub>2</sub> Cl <sub>2</sub>	Bu₄NBr	NaHCOa	<b>CH</b> <sup>a</sup> CN	120/12	96	94-95
2f	Co(PPha) <sub>2</sub> Cl <sub>2</sub>	Bu₄NBr	<b>NaHCO</b> <sub>a</sub>	<b>CH</b> <sup>a</sup> CN	120/12	95	193-194
$2_{\rm g}$	Co(PPh <sub>3</sub> ) <sub>2</sub> Cl <sub>2</sub>	BuaNBr	NaHCO <sub>a</sub>	CH <sub>s</sub> CN	120/12	96	136-137
2h	Co(PPh <sub>8</sub> ) <sub>2</sub> Cl <sub>2</sub>	BuaNBr	NaHCO <sub>a</sub>	CHaCN	120/12	91	219-220
2;	Co(PPh <sub>8</sub> ) <sub>2</sub> Cl <sub>2</sub>	Bu₄NBr	NaHCO <sub>a</sub>	C <sub>e</sub> H <sub>e</sub>	120/12	95	63-64
2;	Co(PPha)2Cl2	Bu <sub>4</sub> NBr	NaHCOa	C <sub>e</sub> H <sub>e</sub>	120/12	94	70-71

a Yield of isolated product.

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Substrate	Catalysts Metal	PTC	Temp. (C)	Product	Yield (%)	M.P. (°)	
C <sub>a</sub> H <sub>e</sub> COCI C <sub>a</sub> H <sub>e</sub> COCI	Co(PPh <sub>a</sub> ) <sub>2</sub> Cl <sub>2</sub> Co(PPh <sub>a</sub> ) <sub>2</sub> Cl <sub>2</sub>	TBAB TBAB	120 80	(C <sub>6</sub> H <sub>6</sub> CO) <sub>2</sub> O (C <sub>6</sub> H <sub>6</sub> CO) <sub>2</sub> O	94 97	42-44 42-44	
n-02NCeH4COCI	Co(PPh <sub>3</sub> ) <sub>2</sub> Cl <sub>2</sub> Pd(PPh <sub>3</sub> ) <sub>2</sub> Cl <sub>2</sub>	TBAB TBAB	120 80	(m-0 <sub>2</sub> NC <sub>6</sub> H <sub>4</sub> C0) <sub>2</sub> O (m-0 <sub>2</sub> NC <sub>6</sub> H <sub>4</sub> C0) <sub>2</sub> O	95 97	161–163 161–163	
2 <sub>e</sub> H <sub>5</sub> CH=CHCOCI	Co(PPh <sub>a</sub> ) <sub>2</sub> Cl <sub>2</sub> Pd(PPh <sub>a</sub> ) <sub>2</sub> Cl <sub>2</sub>	TBAB TBAB	120 80	(C <sub>e</sub> H <sub>s</sub> CH=CHCO) <sub>2</sub> O (C <sub>e</sub> H <sub>s</sub> CH=CHCO) <sub>2</sub> O	96 91	134-136 134-136	
	Co(PPh <sub>8</sub> ) <sub>2</sub> Cl <sub>2</sub>	TBAB	80	( 0 <sub>2</sub> N 0 <sub>2</sub> N 0 <sub>2</sub> N	67	108–109	
	Pd(PPh <sub>s</sub> ) <sub>2</sub> Cl <sub>2</sub>	TBAB	80	N <sup>EO</sup> N <sup>EO</sup>	63	89-91	

a Mole ratio of acyl chloride, sodium bicarbonate, metal complex, tetranutyl ammomium bromide is 38:38:1:1.

Table I Effects of different metallic catalyst

anhydrede (25 %). If the tetrabutylammonium bromide is added, benzoic anhydride can be obtained in yield of 94 %. This shows that the exsistence of tetrabutylammonium bromide in reaction mixture is essential to produce anhydride in high yield. When bis(triphenylphosphine)cobalt dichloride is taken away from the reaction mixture, the yield of benzoic anhydride is only 44 %, but the corresponding acid is the only product for three other acyl chlorides. Without sodium bicarbo nate and tetrabutylammonium bromide, benzoyl chloride is heated at 120%in the presence of bis(triphenephosphine)cobalt dichloride, both benzoic anhydride and benzoic acid can not be observed. All this shows that bis(triphenylphosphine)cobalt dichloride and sodium bicarbonate take part in the reaction and indicates that sodium carboxylate may be the intermediate. However, the replacement of benzoyl chloride with benzoic acid allows the reaction of the acid with sodium bicarbonate and bis(triphenylphosphine)cobalt dichloride and tetrabutylammonium bromide at 120 °C to give no benzoic anhydride.Without sodlum bicarbonate and tetrabutylammonium bromide, the reaction is replaced with benzoic acid by using bis(triphenylphosphine)cobalt dichloride as catalyst, benzoic anhydride is not also formed. In the light of these facts, we tentatively propose the mechanism in scheme I.

We have also found that the mixture of benzoyl chloride (20 mmol), benzoic acid (20 mmol), sodium bicarbonate (20 mmol), bis(triphenylphosphine)cobalt dichloride (10 mmol), tetrabutylammonium bromide (0.9 mmol) and acetonitrile are stirred and heated for 12 hours, benzoic anhydride can be obtained in yield of 88%. When the same reaction is carried



out without the bis(triphenylphosphine)cobalt dichloride the yield of benzoic anhydride is only 40%.

On the besis of these experiments <sup>12,13,15</sup>, we tentatively propose the mechanism shown in Scheme I. Initial interaction of acyl chloride 1 with  $Co(PPh_B)_2Cl_2$  2 would give a complex 3 <sup>17</sup>. Reaction of second molecule 1 with Q<sup>+</sup>HCO<sub>B</sub> forms R-C-O-C-OH 4 which elimination of CO<sub>2</sub>, generates R-C-OH 5. The latter is then converted to R-C-O-Q<sup>+</sup> 6 <sup>16</sup> by reaction with the Q<sup>+</sup>HCO<sub>B</sub>. O The complex 3 reacts with the 6 rapidly to afford the product R-C-O-C-R 7 and Co(PPH<sub>B</sub>)<sub>2</sub>Cl<sub>2</sub> 2 is regenerated.

#### EXPERIMENTAL

IR spectra were measured for KBr discs using a Alpha Centauri FT-IP spectrophotometer. 'HNMR spectra (80 MHz) were recorded in CDCl<sub>3</sub> using a FT- 80 spectrometer. Microanalyses were measured using a Carlo Elba 1106 microelemental analyser.

General Procedure for the Preparation of Anhydrides: Sodium bicarbonate, tetrabutlammonium bromide and acetonitrile are placed in a three flask eguiped with stirrer and condenser. Acyl chloride and bis(triphenylphosphine)cobalt dichloride or bis(triphenylphosphine)palladium dichloride are added. The mixture is stirred at 120° for 12 hours. The reaction mixture is cooled and poured into cold watre. The deposit is collected by filtration and washed with agueous NaOH dilute HCl, water. After dried, the products can be obtained.

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