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THE PALLADIUM-CATALYZED SYNTHESIS OF DIPHENYL CARBONATE FROM PHENOL, CARBON MONOXIDE, AND OXYGEN

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Summary

Diphenyl carbonate was obtained from the reaction of carbon monoxide, phenol, and oxygen using catalytic quantities of palladium, a tertiary amine, and an oxidation cocatalyst at room temperature and atmospheric pressure. A variety of copper, vanadium, cobalt, and manganese salts were effective cocatalysts, although in many cases side products were produced. Using catalytic quantities of manganese salts, up to 100 mol of diphenylcarbonate per mol of palladium was realized.

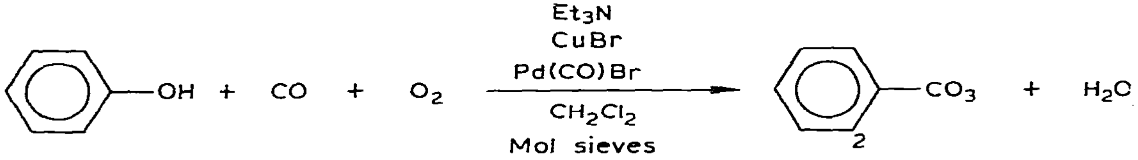
Introduction

Although dialkyl carbonates have been synthesized from alcohols, carbon monoxide, and oxygen with a variety of metal catalysts, the analogous reactions to prepare diaryl carbonates from phenols have not been reported [1—7]. Recently, we described the stoichiometric reactions of phenols with palladium carbonyl chloride in the presence of a tertiary amine to prepare diaryl carbonates [8]. Although these reactions were quite specific and high yields of diaryl carbonates were obtained, stoichiometric quantities of palladium metal were produced. To convert this reaction into a catalytic process requires oxidation of the palladium metal and regeneration of the active palladium species.

The direct reaction of palladium metal with gaseous oxygen has been reported to be slow, requiring a catalyst to achieve rapid oxidation of the metal. Typically, copper salts have been employed as oxidation cocatalysts in a variety of palladium-catalyzed transformations [9]. We wish to report our attempts to achieve a palladium-catalyzed synthesis of diphenyl carbonate.

Results and discussion

Oxygen and carbon monoxide were bubbled slowly through a mixture of phenol, palladium carbonyl bromide or chloride, and triethylamine in methylene chloride, both at room temperature and at 100°C. As anticipated, reoxidation of palladium was slow and only stoichiometric quantities of diphenyl carbonate were realized. Addition of curpous bromide and molecular sieves (to remove water coproduced during the reaction) to the reaction mixture resulted in a slow formation of diphenyl carbonate, equation 1. After 20 hours, 10 mol of diphenyl carbonate per mol of palladium was produced in addition to a host of side products, all in low yield.



Control experiments indicated that the majority of these products were phenol oxidation products such as 2,2'-biphenol which resulted from side reactions of the phenol with air in the presence of the copper salts. Attempts to increase both reaction rate and specificity by varying the copper salts were unsuccessful.

Much greater specificity was realized with bis(salicylaldehyde)ethylenediiminecobalt in place of cuprous bromide as the oxidation cocatalyst, Table 1. Reactions rates were quite slow, but diphenyl carbonate was produced in high yield, and high conversions were obtained after long reaction times. For example, after six days at a molar ratio of 1 : 3 : 100 of palladium : cobalt: phenol, an 85% conversion of phenol to diphenyl carbonate was realized. Products derived from side reactions with phenol were not observed, although small quantities of carbon dioxide could be detected in the gas phase.

Further studies demonstrated that a variety of simple manganese compounds, including manganese halides, also were effective cocatalysts, Table 2. High conversions of phenol to diphenyl carbonate have been realized with greater than 500 mol of diphenyl carbonate per mol of palladium and/or manganese at atmospheric pressure and room temperature. Side products, including carbon dioxide, could not be detected.

The catalytic manganese species involved in these systems are unknown. Both oxygen and the cocatalyst were required: neither $(Bu_4N)_2MnBr_4$ nor $Mn(acac)_3$ oxidized palladium metal under the reaction conditions in the absence of

TABLE 1

COMPARISON OF COBALT COMPOUNDS AS OXIDATION COCATALYSTS

Cocatalyst	Pd : CO : ArOH : R_3N [b]	% Conversion	Time (h)
$CoBr_2 \cdot 6\ H_2O$	1 : 3 : 100 : 15	1	70
Co(salen) · py [b]	1 : 3 : 100 : 15	13	20
Co(salen) · py	1 : 3 : 100 : 15	85	150
Co(salen) · H_2O	1 : 3 : 100 : 15	5	20
Co(salen) · H_2O	1 : 3 : 100 : 15	22	66

[a] Molar ratio. [b] H_2 salen = bis(salicylaldehyde)ethylene diimine.

TABLE 2

COMPARISON OF Mn COMPOUNDS AS OXIDATION COCATALYSTS

Cocatalyst	Pd : Mn : ArOH : R_3N [a]	% Conversion	Time (h)
$MnCl_2 \cdot 4\ H_2O$	1 : 10 : 100 : 100	20	165
$MnBr_2 \cdot 4\ H_2O$	1 : 10 : 100 : 100	35	145
$(Bu_4N)_2MnBr_4$	1 : 3.6 : 100 : 35	20	18
$Mn(acac)_3$ [b]	1 : 3 : 100 : 15	45	18
$Mn(acac)_3$	1 : 3 : 100 : 15	56	31
$Mn(acac)_3$	1 : 3 : 100 : 15	72	70
$Mn(acac)_3$	1 : 3 : 100 : 15	75	96

[a] Molar ratio. [b] Hacac = 2,4-pentanedione.

oxygen. Furthermore, analysis of the reaction mixtures suggested that the manganese halides were not stable to the reaction conditions. For example, when $(Bu_4N)_2MnBr_4$ was employed as the cocatalyst, the concentration of soluble manganese decreased rapidly to less than 10% of the initial value after 72 hours. In contrast, with manganese tris(acetylacetonate) in place of $(Bu_4N)_2$-$MnBr_4$, the concentration of soluble manganese decreased by less than 20% over the same time period. Currently, we favor a manganese(III) (or IV) oxide as the active species for the oxidation of palladium. Attempts to isolate and characterize such a species have not been successful, although freshly prepared manganese dioxide was found to reoxidize palladium metal readily under the reaction conditions in the absence of oxygen.

In principle, the palladium metal formed during these reactions could be oxidized to either a palladium(I) or a palladium(II) species. Previous work has shown that reaction of palladium(I) carbonyl halides with phenol produced diphenyl carbonate while palladium(II) compounds produced phenyl salicylate [8]. Only diphenyl carbonate was observed from any of the catalytic reactions, suggesting that a palladium(I) species and not a palladium(II) species may be involved. When palladium(II) bromide was employed as the palladium source, only traces (less than one mol per mol of palladium) of phenyl salicylate were observed. Furthermore, the salicylate was produced within the initial five minutes of the reaction and not thereafter. Palladium(I) carbonyl bromide [10] in place of palladium bromide eliminated phenyl salicylate entirely.

Experimental

In a typical reaction, a 100 ml 3-neck flask equipped with a spin bar, subsurface CO and air inlets, and a gas exit tube was charged with 0.94 g (10.0 mmol) of phenol, 0.232 g (1.8 mmol) of diisopropylethylamine, 0.025 g (0.1 mmol) palladium(II) bromide, 0.105 g (0.3 mmol) of $Mn(acac)_3$, 5 g of 3A molecular sieves which had been dried at 250°C in a stream of dry nitrogen for 24 hours, 0.10 g of bibenzyl as internal standard and 50 ml of methylene chloride. Carbon monoxide (0.01 SCFH) and air (0.03 SCFH) were bubbled slowly through the stirred mixture at room temperature. Aliquots were withdrawn periodically, evaporated to dryness in a stream of nitrogen, extracted with 1 : 1 hexane : methylene chloride, and filtered. The filtrate was analyzed by HPLC using a Waters Associates μ-Bondapak-CN column with a hexane-THF solvent gradient as eluent.

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