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

II *. AQUEOUS SODIUM HYDROXIDE AS A BASE

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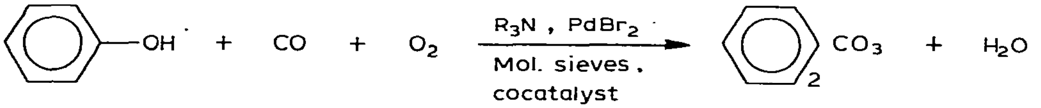
Summary

Aqueous sodium hydroxide in combination with a phase transfer catalyst was found to be an effective base for the palladium-catalyzed synthesis of diphenyl carbonate from phenol, carbon monoxide, and oxygen. Small quantities of sodium hydroxide with the phase transfer catalyst resulted in reaction rates faster than had been observed previously using a tertiary amine. The effect of anions on reaction rates is also discussed.

Introduction

Recently, we described [1] the palladium-catalyzed carbonylation of phenol to prepare diphenyl carbonate from phenol, oxygen, and carbon monoxide in the presence of a tertiary amine and an oxidation cocatalyst (eq. 1). Previous work had shown that simple tertiary alkylamines, such as triethylamine or diisopropylethylamine were subject to oxidation under the reaction conditions, resulting in side products derived from enamine intermediates [2]. Uniquely, 1,2,2,6,6-pentamethylpiperidine was found to be stable to the reaction conditions and high yields of diaryl carbonates were produced in its presence without formation of amine derived side products. The success of this amine was



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[*] For part I see ref. 1.

attributed to the combination of high basicity which resulted in substantial ionization of the phenol and low nucleophilicity which prevented coordination to palladium and subsequent oxidation. Sodium hydroxide in combination with a phase transfer catalyst has been shown to be an effective base in typical organic solvents [3—5]. We wish to report our attempts to replace the tertiary amine with sodium hydroxide and a phase transfer catalyst.

Results and discussion

Sodium hydroxide in combination with tetrabutylammonium bromide was an effective replacement for the tertiary amine previously employed for the conversion of phenols to diaryl carbonates (eq. 2). The use of solid NaOH, either as pellets or ground to a fine powder under a nitrogen atmosphere, led to erratic reaction rates. To circumvent this problem, commercial 50% aqueous sodium hydroxide was employed in combination with molecular sieves to remove the solvent water. This procedure was convenient and resulted in reproducible reaction rates. Typically, the reaction vessel was charged with phenol, tetrabutylammonium bromide, aqueous sodium hydroxide, molecular sieves, and methylene chloride, then stirred under a nitrogen atmosphere for 1.5 h. A shorter prereaction time resulted in erratic carbonylation rates, while longer prereaction times gave results indistinguishable from the 1.5 h run. During the prereaction, sodium bromide precipitated and the aqueous phase was absorbed by the sieves. Catalytic quantities of palladium(II) bromide and manganese(II) acetylacetonate then were added and carbon monoxide and oxygen bubbled slowly through the reaction mixture. A high conversion to diphenyl carbonate was obtained after 43 h (Table 1). No side products could be detected.

$$2\,\mathrm{ArOH} + \mathrm{CO} + \tfrac{1}{2}\,\mathrm{O_2} \xrightarrow[\mathrm{PdBr_2,\,Mn(acac)_2,\,Mol.sieves}]{\mathrm{CH_2Cl_2,\,NaOH,\,Bu_4NBr}} \mathrm{Ar_2CO_3} + \mathrm{H_2O} \tag{2}$$

The phase transfer catalysts varied in their effectiveness. Ammonium and phosphonium salts containing methyl substituents were unstable to the reaction conditions, resulting in the formation of anisole. The tetrabutyl and tetrahexyl salts were particularly effective. The conversions of phenol to diphenyl carbonate were in excess of those observed with 1,2,2,6,6-pentamethylpiperidine (Table 2). Similarly, initial reaction rates increased to 10 mol of diphenyl carbonate per g-atom Pd per hour (Bu_4NBr, NaOH) from 4 mol of

TABLE 1

THE CONVERSION OF PHENOL TO DIPHENYL CARBONATE [a]

Reaction time (h)	Conversion (%)
6	18
17	35
24	50
30	54
42	61

[a] Molar ratio $PdBr_2/Mn(acac)_2/NaOH/Bu_4NBr/ArOH = 1/3/20/24/500$.

TABLE 2

EFFECT OF PHASE TRANSFER CATALYST ON PHENOL CONVERSIONS AT 17 h [a]

Phase transfer catalyst	Conversion to diphenyl carbonate (%)
— [b]	0
Me_4NBr	10
Et_4NBr	16
Bu_4NBr	60
Hex_4NBr	58
Bu_4PBr	54
Ph_3PMeBr	17
18-Crown-6 (KOH)	17
(1,2,2,6,6-Pentamethylpiperidine) [c]	42

[a] Molar ratio $PdBr_2/Mn(acac)_2/NaOH/PTC/ArOH = 1/3/13/16/100$. [b] No PTC added. [c] Control experiment: $PdBr_2/Mn(acac)_2/R_3N/ArOH = 1/3/20/100$.

diphenyl carbonate per g-atom Pd hour. Crown ethers (including 18-crown-6/KOH) were found to be much less effective than tetrabutylammonium bromide with NaOH.

Quaternary phosphonium salts have been reported to be more stable to concentrated alkali than the analogous ammonium salts [6]. In this system, Bu_4PBr and Bu_4NBr exhibited similar reactivity. Small quantities of Bu_3P, which could be formed via Hofmann degradation of Bu_4P^+ or from nucleophilic attack of phenoxide or hydroxides on Bu_4P^+, were found to inhibit the reaction. This strongly suggests that Bu_4PBr was stable to the reaction conditions. The similar reactivity of Bu_4NBr implies similar stability under these reaction conditions.

The role of the anions in this system is not well understood. With palladium bromide as the palladium source, differences in reaction rates were observed as a function of phase transfer anion.

With palladium acetate [7] in place of palladium bromide (i.e., no halide other than that introduced by the phase transfer catalyst), only the chloride- and bromide-containing phase transfer catalysts were effective (Table 3). *Apparently chloride or bromide ion is required for reoxidation of palladium* under the basic reaction conditions.

Neither sodium nor potassium phenoxide was an effective base when used in place of sodium hydroxide. This is particularly puzzling since sodium phenox-

TABLE 3

EFFECT OF PHASE TRANSFER CATALYST COUNTERION OR CONVERSION OF PHENOL TO DIPHENYL CARBONATE AFTER 17 h [a]

PTC	Conversion ($PdBr_2$) (%)	Conversion ($Pd(OAc)_2$) (%)
Bu_4NCl	46	42
Bu_4NBr	60	61
Bu_4NI	0 [b]	0
Bu_4NF	36	1
Bu_4NOH	35	1

[a] Molar ratio $PdX_2/Mn(acac)_2/NaOH/PTC/ArOH = 1/3/13/16/100$. [b] Reaction mixture turned red-brown due to I_2 formation.

ide is a probable intermediate when sodium hydroxide is employed (eq. 3 and 4).

$$NaOH + PhOH \longrightarrow NaOPh + H_2O \tag{3}$$

$$NaOPh + Bu_4NBr \rightarrow Bu_4NOPh + NaBr \tag{4}$$

Increased quantities of sodium phenoxide did not lead to carbonate, but rather to diphenyl formal and no trace of carbonate (eq. 5). It can only be concluded that reactions 6 and 7 dominate.

$$2\ NaOPh + CH_2Cl_2 \xrightarrow{PTC} (PhO)_2CH_2 + 2\ NaCl \tag{5}$$

$$Bu_4NBr + NaOH \longrightarrow Bu_4NOH + NaBr \tag{6}$$

$$Bu_4NOH + PhOH \longrightarrow Bu_4NOPh + H_2O \tag{7}$$

Furthermore, Et_4NOH functioned as both base and phase transfer catalyst, producing carbonate at a reasonable rate (32% conversion after 17 h).

Experimental

The 3A molecular sieves were purchased from Linde and were activated prior to use by heating to 200°C in vacuo for 72 h. The phase transfer catalysts, Me_4NBr (Eastman), Et_4NBr (Baker), Bu_4NBr (RSA), Hex_4NBr (Eastman), Bu_4PBr (Aldrich), Ph_3PMeBr (Aldrich), Bu_4NCl (Eastman), Bu_4NI (Aldrich), Bu_4NF (Eastman), Bu_4NOH (Southwestern), and 18-crown-6 (Aldrich) were used as received. Solid sodium hydroxide pellets (Baker) were used as received or ground under nitrogen in a dry box to a fine powder. Aqueous sodium hydroxide (Baker 50%) was standardized by titration. Palladium bromide was prepared by the literature procedure, then ground to a fine powder. Manganese(II) bis(acetylacetonate) (Alfa) was light tan in color and used without purification.

Analyses were performed by liquid chromatography using a Waters Associates Model 244 ALC-GPC and a Waters Associates μ-Bondapak CN column with hexane/THF mixtures as eluent.

Carbonylation of phenol

In a typical experiment, a 50 ml 3-neck flask equipped with subsurface carbon monoxide and air inlets, a gas exit and a spin bar was charged with 0.94 g (10.0 mol) of phenol, 3.0 g of 3A molecular sieves, 0.805 g (2.5 mmol) of Bu_4NBr, 0.160 g (2.0 mmol) of 50% aqueous sodium hydroxide, and 30 ml of methylene chloride. The resulting mixture was stirred for 1.5 h. During this time, a white precipitate (NaBr) was formed. To this mixture was added 0.050 g of bibenzyl (internal standard), 0.027 g (0.10 mmol) of $PdBr_2$ and 0.076 g (0.3 mmol) of $Mn(acac)_2$. Carbon monoxide and air were then bubbled slowly through the mixture for 17 h at room temperature. An aliquot was removed, diluted with an equal volume of hexane, filtered through a 0.47 μ teflon filter and analyzed by LC.

References

1 J.E. Hallgren, G.M. Lucas and R.O. Matthews, J. Organometal. Chem., 204 (1981) 135.
2 J.E. Hallgren and R.O. Matthews, J. Organometal. Chem., 192 (1980) C12.
3 W.P. Weber and G.W. Goekel, Phase Transfer Catalysis in Organic Synthesis, Springer-Verlag, New York, 1977.
4 C.M. Starks and C. Liotta, Phase Transfer Catalysis, Academic Press, New York, 1978.
5 H. Alper and J.K. Currie, Tetrahedron Lett., (1979) 2665.
6 E.V. Dehmlow, M. Slopianka and J. Heider, Tetrahedron Lett., (1977) 2361.
7 Palladium acetate was found to be as effective as palladium bromide for the stoichiometric reactions. See J.E. Hallgren and R.O. Matthews, J. Organometal. Chem., 175 (1979) 135.