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EFFECT OF VARIOUS PHOSPHINES ON SELECTIVITY IN THE CARBONYLATION OF AMINES

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Considering the current interest in the activation of carbon monoxide by coordination catalysts, we would like to report some results of the remarkable effect of various phosphines on selectivity in the carbonylation of amines catalyzed by rhodium complexes.

In this reaction, primary aliphatic amines are converted into substituted formamides and disubstituted ureas according to

$$RNH_2 + CO \longrightarrow RNHCHO$$

$$2\ RNH_2 + CO \longrightarrow RNHCONHR + H_2$$

It is known that the selectivity depends largely on the metal used. Copper gives rise to disubstituted formamides alone (1), manganese to disubstituted ureas (2), palladium to both of these compounds plus oxamide RNHCOCONHR (3).

Till now, very few results have been published concerning the influence of the ligand on the selectivity in a carbonylation reaction.

Our results obtained with tri.n.butyl amine are shown in Table 1.

TABLE 1

	P/Rh ratio	Conversion	Selectivity	
			amide	urea
$Rh_2Cl_2(CO)_4$ (I)	-	92	35	65
(I) + $P(CH_3)_3$	1	74.5	62	38
"	2	94.5	94	6
"	4	98.5	98	2
"	6	100	100	-
(I) + dmpe*	2	100	100	-
(I) + $P(C_6H_5)_3$	2	46.5	70	30
(I) + $P(C_2H_4CN)_3$	2	65	57.5	42.5
"	4	93	78	22
(I) + dpe*	2	51	83.5	16.5
(I) + $P(OC_2H_5)_3$	2	0	-	-

* dmpe : $(CH_3)_2\ P.C_2H_4.P(CH_3)_2$; dpe : $(C_6H_5)_2\ P.C_2H_4.P(C_6H_5)_2$

The catalytic system is prepared independently in a benzene solution and introduced with the amine into the autoclave (500 ml). In a typical experiment, 0.370 g of $P(CH_3)_3$ (5.3 mM) in 8 ml of benzene is introduced into a benzene solution (10 ml) of $Rh_2Cl_2(CO)_4$ (0.245 g = 1.26 mM). A rapid evolution of carbon monoxide occurs and this catalytic solution is introduced into 56 ml of n.butylamine. Carbon monoxide is introduced (60 kg/cm^2) and the reaction is carried out at 160 °C for 4 hours with shaking. After the usual work-up, 54.3 g of N.butylformamide and 0.5 g of N.N'.dibutylurea are obtained. Conversion = 98.5 %, Selectivity in N.butylformamide = 98 %. Aniline and tertiary amines failed to react, and secondary amines gave little conversion over a long reaction time.

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