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Preliminary communication

THE USE OF PHASE-TRANSFER CATALYSIS IN PALLADIUM-CATALYZED CARBONYLATION OF ORGANIC HALIDES

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Summary

Aryl, benzyl, vinyl and heterocyclic halides RX have been converted in high yields into the corresponding acids RCOOH by adding the RX with a little PPh_3 slowly to a rapidly stirred mixture of aqueous NaOH, $[Pd(PPh_3)_2Cl_2]$, and n-Bu_4NI in toluene under a CO atmosphere.

We report briefly below on our studies of the application of the phase-transfer technique [1] to the palladium-catalyzed carbonylation of organic halides [2].

The carbonylation reaction 1 can be carried out by mixing an aqueous solution of NaOH with a xylene solution of the palladium triphenylphosphine complex in the presence of a salt such as $[C_6H_5CH_2N(C_2H_5)_3]Cl$.

$$RX + CO + 2\,NaOH \xrightarrow[Pd[P(C_6H_5)_3]_4,\ NR'_4X]{\text{NaOH aqueous/xylene}} RCOONa + NaX + H_2O \qquad (1)$$

The organic halide (benzyl, aryl, vinyl or heterocyclic) is slowly added to the reaction mixture under carbon monoxide to give the sodium salts of the organic acid. For example, benzyl chloride (50 g) and $P(C_6H_5)_3$ (0.2 g) were added during 4 h to a rapidly stirred mixture of aqueous (30%) NaOH (220 ml) $Pd[P(C_6H_5)_3]_2Cl_2$ (0.18 g) and NBu_4I (0.6 g) in *p*-xylene (50 ml) under CO pressure (5 atm) at 95°C. The mixture was kept at 95°C for an additional hour. Separation and acidification of the aqueous phase gave 45 g of phenylacetic acid (yield 83%). The xylene solution containing the catalyst may be recycled many times in the carbonylation process with no loss in catalytic activity. Addition of a small quantity of $P(C_6H_5)_3$ is necessary to avoid precipitation of palladium metal**. Phenylacetic acid has thus been obtained to the extent of more than 4000 moles per mole of palladium, and 400 moles per mole of $P(C_6H_5)_3$ taken.

Another important advantage of this system is the possibility of achieving

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**$P(C_6H_5)_3$ is partially transformed into a phosphonium salt.

selective carbonylation of polyhalogenated aromatic compounds when the reactivities of the halogens are very similar. Thus *p*-dibromobenzene can be transformed into *p*-bromobenzoic acid with a selectivity as high as 95% at 90% conversion. This is possible because conversion of the first C—X group into C—COO⁻ causes the molecule to go from the organic to the aqueous phase, thus removing it from further reaction.

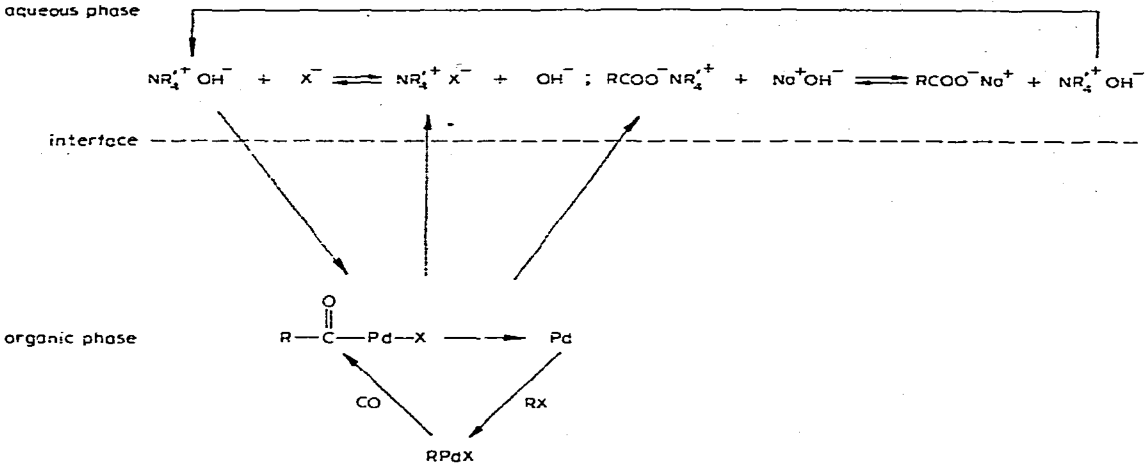

Fig. 1. Phase transfer catalysis in palladium-catalyzed carbonylation of organic halides. Pd denotes palladium with its associated phosphine.

Figure 1 shows the probable reactions involved in carbonylation of organic halides (R—X), following the general scheme applicable to phase-transfer catalysis [1].

An important practical aspect of this process is the continuous separation of the products from the catalyst, which in effect heterogenizes the homogeneous catalyst. This point accounts for the high catalyst turnover, the selectivity encountered in the carbonylation of polyhalogenated compounds, and the high activity of the catalyst.

References

1 M. Makosza, Pure Appl. Chem., 43 (1975) 439; E.V. Delmon, Angew. Chem. Internat. Edit., 13 (1974) 170; J. Dockx, Synthesis, (1973) 441.

2 A. Schoenberg, I. Bartoletti and R.F. Heck, J. Org. Chem., 39 (1974) 3318; J.K. Stille, L.F. Hines, R.W. Friess, P.K. Wong, D.E. Tanees and K. Lau in Advances in Chemistry Series No. 132, Amer. Chem. Soc., 1974, p. 90; M. Hidai and Y. Uchida in Y. Ishii and M. Tsutsui, Organotransition-Metal Chemistry, Plenum Press, New York - London, 1975, p. 265; J.K. Stille, P.W. Wong, J. Org. Chem., 40 (1975) 532; M. Hidai, T. Hikita, Y. Wada, Y. Fujikura and Y. Uchida, Bull. Chem. Soc. Japan, 48 (1975) 2075.