Palladium-catalyzed arylation of hydrophosphoryl compounds under conditions of phase transfer catalysis

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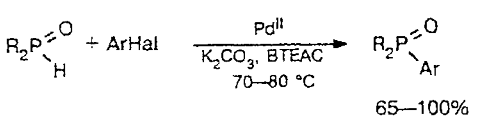
A simple and efficient method for the synthesis of derivatives of arylphosphonic and phosphinic acids and phosphine oxides was developed. The method is based on palladium-catalyzed arylation of hydrophosphoryl compounds under conditions of phase transfer catalysis.



R = Alk, Ph, AlkO, Et_2N;
Hal = I, Br;
Ar = Ph, p-MeC_6H_4, p-$MeOC_6H_4$, p-$NO_2C_6H_4$, p-NCC_6H_4, p-ClC_6H_4, p-$EtOOCC_6H_4$, p-$HOOCC_6H_4$

The reactions of esters of phosphoric (phosphonic) acids and diphenylphosphinic acid with iodo- or bromoarenes readily occur at 70—80 °C in the presence of 2 mol.% of a palladium catalyst, potassium carbonate, and benzyltriethylammonium chloride (BTEAC) without a solvent for liquid aryl halides or in acetonitrile in the case of solid aryl halides. Derivatives of the corresponding acids with tetracoordinated phosphorus and phosphine oxides were obtained in 65—100% yields.[1,2]

The palladium-catalyzed arylation of dialkyl phospites with iodo- and bromoarenes was accomplished using palladium(II) acetate as the precursor of the catalyst, *i.e.*, without a phosphine ligand. The use of $Pd(OAc)_2$—2L (L = Ph_3P, $(2\text{-furyl})_3P$) as the precursor of the catalyst markedly increases the rate of the reaction of dialkyl phosphites with aryl bromides but has no significant effect on the reaction with aryl iodides.

Based on the palladium-catalyzed arylation of dimethyl phosphite with bromoarenes under conditions of phase transfer catalysis, we developed a versatile preparative procedure for the synthesis of arylphosphonic acids containing various substituents in the aromatic ring, which had been difficult to obtain previously.[3]

Potassium carbonate (9 mmol) was added with stirring to a hydrophosphoryl compound (9 mmol) placed in a Schlenk vessel pre-filled with argon. The mixture was stirred for 15 min, and then BTEAC (0.9 mmol) and aryl halide (11 mmol) were successively added (in the case of solid aryl halide, 0.5 mL of MeCN was also added). The reaction mixture was stirred for 5 min, and a phosphine ligand (triphenylphosphine or tris(2-furyl)phosphine) (0.36 mmol) and palladium(II) acetate (0.18 mmol) were added. The mixture was kept at 70—80 °C for 6—10 h in the case of aryl iodides and for 20—22 h in the case of aryl bromides. After that, 3 mL of 2 *M* HCl was added to the reaction mixture, and the resulting solution was filtered. The organic layer was separated, and the aqueous layer was extracted with ether (5×5 mL). The ethereal extracts were combined with the organic layer, the solvent was evaporated, and the residue was distilled *in vacuo*. The yields of phosphonates, phosphinates, and phosphine oxides were 65—100%. Physicochemical characteristics of the resulting compounds correspond completely to published values.[4]

References

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