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ELECTROCHEMICAL SYNTHESIS OF TERTIARY PHOSPHINES FROM ORGANIC HALIDES AND CHLOROPHOSPHINES

J.C. FOLEST, J.Y. NEDELEC and J. PERICHON
Laboratoire d'Electrochimie, Catalyse et Synthèse Organique (U.M. n° 28)
C.N.R.S., 2, rue Henri-Dunant 94320 THIAIS (France)

Abstract : The electrochemical synthesis of a wide range of tertiary mono- and diphosphines has been achieved in very simple and mild conditions, in an undivided electrolytic cell with a sacrificial anode of magnesium.

We have recently reported that the electrochemical reduction of organic halides in the presence of Mg(II) ions produced by oxidation of a sacrificial magnesium anode permits the generation in very mild conditions of various nucleophilic species which react efficiently with many electrophiles such as CO_2 (1), aldehydes or ketones (2) or anhydrides (3). We have now extended the process to the preparation of trisubstituted phosphines, whose interest has been especially emphasized in homogeneous catalysis, and which are usually prepared by reaction of an organometallic compound with mono- or dihalogenophosphines (4).

The electrochemical reduction of Ph_2PCl in N,N-dimethylformamide (DMF), at its reduction potential (- 1V/sce) (5), performed in a two compartment electrolytic cell with ammonium salts as electrolyte, mainly gave Ph_2PH. Oppositely in an undivided cell with an Mg-anode, Ph_2P-PPh_2 was obtained in high chemical and faradic yield. The formation of the dimer is consistent with the generation of the Ph_2P^- ion which, in the presence of Mg(II) ions, would react efficiently with Ph_2PCl. So we could expect, in those conditions, similar SN_2 reactions with alkyl halides, provided that they are reducible at more negative potential than Ph_2PCl, according to the mechanism :

$$Ph_2PCl + 2e \longrightarrow Ph_2P^- + Cl^-$$

$$Ph_2P^- + RX \longrightarrow Ph_2P\text{-}R + X^-$$

The electrochemical reactions reported here have been carried out in a glass vessel fitted with a magnesium bar as anode and a cylindrical stainless steel grid as cathode, at constant current with a current density of $2A/dm^2$. Runs have been performed at room temperature, under argon, in aprotic solvents, DMF or NMP (N-methylpyrrolidone) with small amounts of supporting electrolyte (NBu_4BF_4 $2\ 10^{-2}$ M and NBu_4I $2\ 10^{-2}$ M). The obtained phosphines have been isolated by extraction with diethyl ether, or in some cases, precipitated by hydrolysis of the reaction mixture, and purified by crystallisation in n-butanol.

Table I summarizes the results of the reaction of Ph_2PCl with various alkyl mono- and dihalides (6). In the preparation of monophosphines, RX has been used in slight excess (1 M of RX and 0,7 M of Ph_2PCl) in order to minimize the formation of the dimer Ph_2P-PPh_2, whereas concentrations of 0,4 M of dihalides and 0,8 M of Ph_2PCl have been used to prepare diphosphines. Electrolysis have been stopped after over 2,2 moles of electron per mole of Ph_2PCl have been passed. Yield of Ph_2P-PPh_2 has been found to depend on the type of RX, ranging from less than 3 % with alkylbromides to around 20 % with $PhCH_2Cl$. NMP proves to be better than DMF as solvent for this reaction in contrast to what we have observed in the electrochemical synthesis of carboxylic acids, alcools or anhydrides using the same procedure. The electrosynthesis of phosphines can also be conducted with Zinc in place of Magnesium as anode, but yields of phosphines are lower. For example coupling of Ph_2PCl with $ClCH_2CO_2Et$ in DMF in presence of Zn yielded only 30 % of phosphine instead of 45 % with Mg. Sofar solvent or anode effects on this process are not clearly understood.

We have also investigated the coupling of $PhPCl_2$ with alkylhalides (Table II). The reduction of this dichlorophosphine was found to occur in two steps at -1 and -1,4 V/sce, in agreement with reported data (7). Runs have been carried out only in DMF, with concentrations of respectively 1 M for RX and 0,3 M for $PhPCl_2$. Yields are still good considering the length of the sequence leading to the product.

TABLE I : Reactions of Ph_2PCl with organic halides

RX	Solvent	Tertiaryphosphine	Isolated yield % relative to Ph_2PCl
$PhCH_2Cl$	DMF	Ph_2PCH_2Ph	30
$PhCH_2Cl$	NMP	Ph_2PCH_2Ph	45
$CH_3(CH_2)_2CH_2Br$	DMF	$Ph_2P(CH_2)_3CH_3$	80
$CH_3(CH_2)_2CH_2Br$	NMP	$Ph_2P(CH_2)_3CH_3$	90
$ClCH_2CO_2Et$	DMF	$Ph_2PCH_2CO_2Et$	45
$ClCH_2CO_2Et$	NMP	$PH_2PCH_2CO_2Et$	55
$CH_3CHBrCO_2Et$	DMF	$Ph_2PCHCH_3CO_2Et$	25
$Br(CH_2)_4Br$	DMF	$Ph_2P(CH_2)_4PPh_2$	60
$Br(CH_2)_4Br$	NMP	$Ph_2P(CH_2)_4PPh_2$	85
$Br(CH_2)_2Br$	NMP	$Ph_2P(CH_2)_2PPh_2$	40
$Cl(CH_2)_2Cl$	NMP	$Ph_2P(CH_2)_2PPh_2$	65

TABLE II : Reactions of $PhPCl_2$ with organic halides

RX	Tertiaryphosphine	Isolated yield % relative to $PhPCl_2$
$CH_3(CH_2)_2CH_2Br$	$PhP(C_4H_9)_2$	55
$CH_3(CH_2)_5CH_2Br$	$PhP(C_7H_{15})_2$	40
$ClCH_2CO_2Et$	$PhP(CH_2CO_2Et)_2$	20
$PhCH_2Br$	$PhP(CH_2Ph)_2$	20

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