

ELECTROCHEMICAL SYNTHESIS OF TERTIARY PHOSPHINES
FROM ORGANIC HALIDES AND CHLOROPHOSPHINES

J.C. FOLEST, J.Y. NEDELEC and J. PERICHON

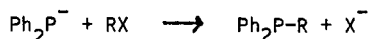
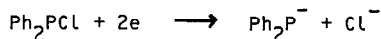
Laboratoire d'Electrochimie, Catalyse et Synthèse Organique (U.M. n° 23)

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 CO₂ (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 Ph₂PCL 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 Ph₂PH. Oppositely in an undivided cell with an Mg-anode, Ph₂P-PPh₂ was obtained in high chemical and faradic yield. The formation of the dimer is consistent with the generation of the Ph₂P⁻ ion which, in the presence of Mg(II) ions, would react efficiently with Ph₂PCL. So we could expect, in those conditions, similar S_N2 reactions with alkyl halides, provided that they are reducible at more negative potential than Ph₂PCL, according to the mechanism :



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/dm². Runs have been performed at room temperature, under argon, in aprotic solvents, DMF or NMP (N-methylpyrrolidone) with small amounts of supporting electrolyte (NBu₄BF₄ 2 · 10⁻² M and NBu₄I 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 Ph₂PCL 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 Ph₂PCL) in order to minimize the formation of the dimer Ph₂P-PPh₂, whereas concentrations of 0,4 M of dihalides and 0,8 M of Ph₂PCL have been used to prepare diphosphines. Electrolysis have been stopped after over 2,2 moles of electron per mole of Ph₂PCL have been passed. Yield of Ph₂P-PPh₂ has been found to depend on the type of RX, ranging from less than 3 % with alkylbromides to around 20 % with PhCH₂Cl. 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, alcohols 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 Ph₂PCL with ClCH₂CO₂Et in DMF in presence of Zn yielded only 30 % of phosphine instead of 45 % with Mg. So far solvent or anode effects on this process are not clearly understood.

We have also investigated the coupling of PhPCL₂ 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	$\text{Ph}_2\text{PCH}_2\text{Ph}$	30
PhCH_2Cl	NMP	$\text{Ph}_2\text{PCH}_2\text{Ph}$	45
$\text{CH}_3(\text{CH}_2)_2\text{CH}_2\text{Br}$	DMF	$\text{Ph}_2\text{P}(\text{CH}_2)_3\text{CH}_3$	80
$\text{CH}_3(\text{CH}_2)_2\text{CH}_2\text{Br}$	NMP	$\text{Ph}_2\text{P}(\text{CH}_2)_3\text{CH}_3$	90
$\text{ClCH}_2\text{CO}_2\text{Et}$	DMF	$\text{Ph}_2\text{PCH}_2\text{CO}_2\text{Et}$	45
$\text{ClCH}_2\text{CO}_2\text{Et}$	NMP	$\text{Ph}_2\text{PCH}_2\text{CO}_2\text{Et}$	55
$\text{CH}_3\text{CHBrCO}_2\text{Et}$	DMF	$\text{Ph}_2\text{PCHCH}_3\text{CO}_2\text{Et}$	25
$\text{Br}(\text{CH}_2)_4\text{Br}$	DMF	$\text{Ph}_2\text{P}(\text{CH}_2)_4\text{PPh}_2$	60
$\text{Br}(\text{CH}_2)_4\text{Br}$	NMP	$\text{Ph}_2\text{P}(\text{CH}_2)_4\text{PPh}_2$	85
$\text{Br}(\text{CH}_2)_2\text{Br}$	NMP	$\text{Ph}_2\text{P}(\text{CH}_2)_2\text{PPh}_2$	40
$\text{Cl}(\text{CH}_2)_2\text{Cl}$	NMP	$\text{Ph}_2\text{P}(\text{CH}_2)_2\text{PPh}_2$	65

TABLE II : Reactions of PhPCL_2 with organic halides

RX	Tertiaryphosphine	Isolated yield % relative to PhPCL_2
$\text{CH}_3(\text{CH}_2)_2\text{CH}_2\text{Br}$	$\text{PhP}(\text{C}_4\text{H}_9)_2$	55
$\text{CH}_3(\text{CH}_2)_5\text{CH}_2\text{Br}$	$\text{PhP}(\text{C}_7\text{H}_{15})_2$	40
$\text{ClCH}_2\text{CO}_2\text{Et}$	$\text{PhP}(\text{CH}_2\text{CO}_2\text{Et})_2$	20
PhCH_2Br	$\text{PhP}(\text{CH}_2\text{Ph})_2$	20

REFERENCES

- O. SOCK, M. TROUPEL, J. PERICHON.
French patent N° 8409787 (1984)
- S. SIBILLE, E. D'INCAN, L. LEPORT, J. PERICHON.
Tetrahedron Lett. (1986) 27, 3129.
S. SIBILLE, E. D'INCAN, L. LEPORT, M.C. MASSEBIAU, J. PERICHON.
Tetrahedron Lett. (1987), 28, 55.
- E. D'INCAN, S. SIBILLE, J. PERICHON.
Tetrahedron Lett. (1986), 27, 4175.
- G.M. KOSOLAPOFF, L. MAIER.
"Organic phosphorus compounds" Volume 1 - Wiley Interscience New-York, 1972.
- T.J. HALL, J.H. HARGIS.
J. Org. Chem. (1986), 51, 4185.
- J.C. FOLEST, J. PERICHON.
French patent n° 8615630 (1986).
- H. MATSHINER, H. TANNEDERG.
Z. Chem. (1980), 20, 218.