Arylation and alkylation of white phosphorus in the presence of electrochemically generated nickel(0) complexes

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White phosphorus yields arylation (or alkylation) products with organic halides in the presence of electrochemically generated Ni^0 complexes.

The problem of selective opening of the white phosphorus P_4 tetrahedron and its direct functionalization has assumed a growing significance in the discovery of novel ecologically pure syntheses of organophosphorus compounds. The methods previously proposed by us were based on the joint action of nucleophilic and electrophilic agents on white phosphorus in an undivided electrochemical cell and allowed us to solely obtain esters of phosphorus acids[1–4] but not compounds with P–C bonds. To the best of our knowledge, the pathways for selective synthesis of compounds with P–C bonds from white phosphorus have not been reported. A mixture of phenyl phosphines and organopolyphosphines was obtained (5–40% yields) from the reaction of P_4 and phenyllithium or phenylmagnesium bromide in ether followed by hydrolysis.[5] Using a combination of carbanions from organometallic reagents and alkyl halide electrophiles, the overall yield of the organophosphorus products was increased.[5] Russian investigators achieved the cleavage of P–P bonds in red phosphorus by performing a sequence of alternating treatments with sodium in liquid ammonia and addition of alkyl halides, and ultimately obtained tertiary phosphines (isolated as phosphine sulfides) in low to moderate yields.[6] Cleavage of P–P bonds in red phosphorus can be achieved by adding *tert*-butyl alcohol to a mixture of phosphorus, lithium and liquid ammonia at –30 °C.[7] However, the practicalities of this reaction with white phosphorus were limited as brown partial cleavage products were constantly deposited on the wall of the flask.

A novel synthesis based on P_4 in mild conditions using cheap and accessible reagents like organic halides, metal salts is of potential use. The aim of the present study is to synthesize compounds with P–C bonds from white phosphorus and organic halides using electrochemically generated Ni^0 complexes. Besides the theoretical interest which the study of reactivity of Ni^0 and organonickel compounds relative to white phosphorus represents, this problem has a practical goal because the direct synthesis of organophosphorus compounds from P_4 has advantages over classical methods based on phosphorus chlorides, synthesized from P_4, because of its potential environmentally friendly processing. This is caused by the fact that direct synthesis from P_4 avoids the stage of phosphorus chlorination and chlorine-containing waste when the chlorine atom is substituted for various functional groups.

According to our data, white phosphorus in an aprotic solvent such as MeCN is reduced at a glassy carbon electrode at high negative potentials.

We have suggested that white phosphorus can be involved in a reaction leading to phosphorus cage disruption and P–C bonds formation in conditions where the reagent is generated reversably *in situ* in the presence of P_4. With this in mind we selected Ni^0 complexes of dipy generated electrochemically from Ni^{II} which yield organonickel compounds which react quickly with organic halides.[8]

The electrolyses were carried out in an electrolyser without a diaphragm in acetonitrile without adding a supporting electrolyte.[†] The complex of $NiCl_2$ and 2,2'-dipiridyl were used both as a mediator and as a catalyst. Electroconductivity was provided by $NiCl_2$ (5×10^{-3} M). However, its concentration may be diminished to 10^{-4} M when $LiBF_4$ was added as a supporting electrolyte. The process efficiency is not influenced because of it. The results of these experiments show that arylation or alkylation of white phosphorus in the presence of electrochemically generated Ni^0 complexes and halides RX (see Table 1) can be carried out (method A).

Table 1 Products of electrochemical functionalization of white phosphorus in the presence of Ni^0 complexes of 2,2'-dipy.

R–X	Products	Yield (%)
PhBr	Ph_3P	10
	Ph_3PO	79
PhI	Ph_3P	11
	Ph_3PO	75
Pr^iI	Pr^i_3PO	73
BuBr	Bu_3PO	78
$C_6H_{13}I$	$(C_6H_{13})_3PO$	77

Cathode: $Ni^{II}L_3 + 2e^- \rightleftharpoons Ni^0L_2 + L$, L= dipy, E = –1.68 V
Anode: $Al - 3e^- \longrightarrow Al^{3+}$

$$P_4 + RX \xrightarrow[-X^-]{Ni^0L_2} >P–R$$

The cleavage of P–P bonds in the white phosphorus tetrahedron and phosphorus oligomers under these experimental conditions leads to formation of triorganylphosphorus derivatives R_3PO and R_3P. A key stage in the reaction of P–C bond formation is assumed to be the interaction between the organonickel compound $Ni^{II}RXL_2$ and white phosphorus:

$$Ni^0L_m + RBr \longrightarrow Ni^{II}RBrL_m \xrightarrow{P_4} >P–R + Ni^{II}L_m$$

The nickel(II) complex is regenerated during electrolysis.

In order to confirm the white phosphorus pathway, the organonickel compound $Ni^{II}RXL_m$ formation and the functionalization of white phosphorus by this nickel complex were separated (method B). It was found that white phosphorus under the action of a small excess of $Ni^{II}PhXL_m$ (obtained electrochemically from PhBr, $NiCl_2$ and dipy in the cathodic

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[†] The electrolysis was carried on a preparative scale in a three-electrode cell (150ml) with the platinum cylinder as the cathode and an aluminum anode. A solution of $NiCl_2$ (5×10^{-3} M) in the presence of 2,2'-dipy (1.5×10^{-2} M) and organic halide (8×10^{-2} M) in MeCN with white phosphorus (2×10^{-2} M, method A) or without white phosphorus (method B) was electrolysed at 50°C. 2.2 F mol^{-1} of $NiCl_2$ (method B) or 6.2 F mol^{-1} of P_w (method A) were passed through the electrolyte solution (cathodic current density 0.5 A dm^{-2}). The saturated solution of Et_4NCl in MeCN was used as anolyte, the membrane was made from paper (method B). In method B, after the electrolysis was complete white phosphorus (2×10^{-2} M) was added to the electrolyte with continuous argon bubbling. The mixture was further stirred for 3 h. The solvent was then distilled off and the residue was extracted with benzene. The benzene extract was evaporated and analysed by ^{31}PNMR. The product physical data were compared with literature values.

compartment of the electrolyser after 2 F mol^{-1} $NiCl_2$ passage) in the presence of PhBr also yielded products of phosphorus arylation. A mixture of Ph_3P and Ph_3PO (1 : 1) was obtained after stirring for 1h at room temperature (80% yield). The oxidation of Ph_3P to Ph_3PO probably proceeds at the product isolation stage because no special precautions were taken and nickel salts are known to promote this reaction.[9] It was shown previously that the autocatalytic transformation of phosphines to phosphine oxides under the influence of Ni^0 complexes and molecular oxygen at room temperature takes place. To avoid this reaction, syntheses should be carried out in the absence of oxygen at all stages using the so-called argon line or at below –5 °C. This makes the process experimentally difficult. Nevertheless, the synthesis of tertiary phosphines from white phosphorus without their subsequent oxidation is very attractive and will be studied further. The mechanism of P_4 functionalization is still not completely understood. Probably, the P=O bond is also formed in the intermediate phosphorus oligomers. The differences between the final transformation products may be associated with the fact that white phosphorus reacts both with Ni^{II} complexes (giving rise to triphosphorus cycles δ-P_3[10] in inner sphere) and, probably, with reduced Ni^0 complex (where P_4 may also serve as ligand), and its reactivity in processes of P–P bond rupture is bound to change.

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