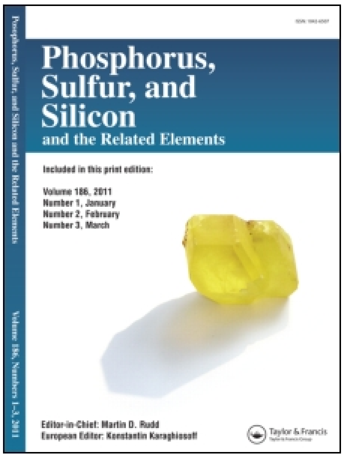

Phosphorus, Sulfur, and Silicon and the Related Elements
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

"Green" Ways of Phosphorus Compounds Preparation

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To cite this Article Budnikova, Yu. H. , Krasnov, S. A. , Graznova, T. V. , Tomilov, A. P. , Turigin, V. V. , Magdeev, I. M. and Sinyashin, O. G.(2008) '"Green" Ways of Phosphorus Compounds Preparation', Phosphorus, Sulfur, and Silicon and the Related Elements, 183: 2, 513 — 518

To link to this Article: DOI: 10.1080/10426500701761672

URL: http://dx.doi.org/10.1080/10426500701761672

Phosphorus, Sulfur, and Silicon, 183:513–518, 2008
Copyright © Taylor & Francis Group, LLC
ISSN: 1042-6507 print / 1563-5325 online
DOI: 10.1080/10426500701761672

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"Green" Ways of Phosphorus Compounds Preparation

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Essentially new approach to organophosphorus compounds (OPC) synthesis first of all with P—O, P—C or P—H bonds, resource saving and ecologically safe, from white phosphorus in electrocatalytic conditions, and effective universal technology of electrosynthesis of lines of OPC compounds were created.

Keywords Electrosynthesis; esters; organophosphorus compounds; phosphorous, phosphonic, and phosphoric acids; tertiary phosphines; white phosphorus

INTRODUCTION

The interest to direct synthesis of organophosphorus compounds from white phosphorus, escaping the traditional stages of its chlorination, is connected to the increase of the requirements of ecological safety and low-waste production.

A replacement of the present-day processes for preparation of basic organophosphorus compounds based now on reactions of phosphorus chlorides rises in importance. The existing processes are environmentally dangerous, energy consuming, and wasteful. The evolved hydrogen chloride accounting, by mass, for three quarters of initial phosphorus trichloride is their key disadvantage. This makes inaccessible a large-capacity of the organophosphorus compounds production based on the chlorine technology from the viewpoint of environmental safety. The creation of chlorine- and waste-free processes to obtain some starting compounds, namely, phosphites, phosphates, amides, tertiary phosphines, and so on, based on elemental (white) phosphorus is an alternative of the organophosphorus compounds synthesis. New technologies,

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economic and ecologically safe, are proposed in the present work.[1–3] The new general one-step way of preparation of number of OPC, such as triphenylphosphine, ethers, and amidoesters of phosphorous acids, inorganic acids was developed. These products find application as plasticizers, inhibitors of combustion, flame-retardants, insecticides, extragents of heavy metals, additives to lubricant oils and liquid fuel, herbicides, insecticides, and as precursors for synthesis of compounds with practically useful properties, as well.

This report is devoted to consideration of electrochemical methods for synthesis of the most significant types of industrially important OPC. Esters of phosphorus acids holds a particular position among these substances. The most promising approach involving a joint action of nucleophilic and electrophilic reagents on the molecule of white phosphorus was the basis for electrosynthesis of esters of phosphorus acid. The consecutive repetition of the stages of nucleophile attack on phosphorus and phosphide anion capture by electrophilic agent allows to obtain various organophosphorus products under mild conditions. Combining the advantages of usual homogeneous chemistry in solution and electrochemistry, when the reagents (both nucleophiles and electrophiles) are generated on electrodes directly in the reactions system, we succeeded in gaining high conversion of white phosphorus to desired products and choosing conditions of high selectivity of the process.[3]

The joint action of alkoxy anion and halide on the P_4 molecules results in various derivatives of phosphorus acids (phosphates, pyrophosphates, and phosphites), depending on electrolysis conditions.

The electrolysis carrying out in water-alcohol solutions under optimal conditions and reagents ratio indicated on the slide allows us to obtain trialkyl phosphates practically with quantitative yields both based on phosphorus and as a function of current.[1,3] Preliminary economic calculation of triethylphosphate manufacture by traditional method (alkoholyze of phosphorus oxychloride) and by electrochemical way has shown, that in the latter case the cost price of a product is reduced in ~1.5 times. For the first time the technology of electrosynthesis of trialkylphosphates from white phosphorus in mild non-polluting conditions with a high yields was developed and the economic solvency of this method was shown. When water and alcohol content in the electrolyte against white phosphorus decreases, a general direction of electrochemical process changes, and tetraalkyl pyrophosphate becomes the main product, and its yield depends on the aliphatic alcohol structure. The yield reaches 80% in the case of iso-alcohols.

Thus, it is clearly demonstrated—using a simple system including white phosphorus, alcohol and water as examples—that electrochemistry is a powerful synthetic method offering few advantages over some classical methods of organophosphorus chemistry. These include mild conditions of the process; its high rate and selectivity; environmental safety (electrophilic component is cyclically regenerated on the anode); and purposeful synthesis of desired products due to variation of electrosynthesis conditions. Comparative characteristics of offered and existing production engineering for $(EtO)_3PO$, for example, are demonstrated the number of advantages, such as, one-step process, low-waste generation, and economic and ecological purity of electrochemical production.

The ways of selective synthesis for compounds with P—C bonds starting from white phosphorus at room temperature with high rate are not described. However, compounds with the phosphorus-carbon bond are most important in phosphorus chemistry, for example, tertiary phosphines are the most widespread ligands in metallocomplex catalysts, including the industrial ones, and used widely as extractants of heavy metal ions. We have developed essentially new approach to PPh_3 preparation from P_4, using not divided electrolyzer and activation of white phosphorus under the action of zinc compounds. Cyclic regeneration of Zn-catalyst takes place at the cathode, reactive sigma-complex forms in the bulk of the solution. The σ-complex attacks the P_4 molecule resulting in tertiary phosphines as target product.[2,3]

The base to realization of the developed processes of organophosphorus compounds preparation from elemental phosphorus at the technological level was incorporated as a result. Scaling process was carried out in chosen conditions on the parameter of production yield from unit of volume. Electrochemical synthesis of PPh_3 in integrated electrolyzer was carried out. The block diagram of synthesis and separation of a target product was made. The technological instruction of process was developed.

The rough cost price of PPh_3 prepared electrochemically from white phosphorus, which shows an economic solvency of our way was designed. In addition, the cost price of the electric power spent for process makes a scanty part from all expenses. The production schedules are developed.

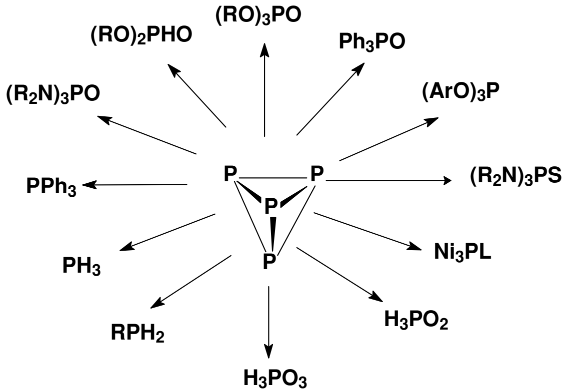
Suggested new ways of synthesis of basic organophosphorus compounds have a number of advantages. Electrochemical generation of reagents allows to supervise in most cases speed and a direction of process and finally will allow to develop new highly effective methods of electrosynthesis of various OPC with P—C or P—O bonds and regeneration of the catalyst. There are two different efficient electrochemical systems allowing to prepare the phosphorus compounds from white phosphorus.

In the alcohol system under study, a nucleophile generated on cathode acts as an initiator for disclosure of white phosphorus tetrahedron, and a product of iodide ion oxidation promotes the process complection being regenerated during the electrolysis. The high selectivity and rate of electrosynthesis allowed us to carry out this process with high conversion of white phosphorus to target organophosphorus products. The use of electrochemical approach to generate Zn(0) and σ-organozinc complexes appears to have considerable promise.[2]

Until now, one failed to elaborate an approach to synthesize from P_4 phosphine derivatives with one or two P-H bonds, e.g. primary or secondary phosphines R_2PH, RPH_2, tertiary phosphines other than triphenylphosphine, phosphorus acids such as phosphonic acid H_3PO_3, phosphinic acid H_3PO_2 and others, being important precursors in phosphorus chemistry. The main problem of all known reactions concerns either low yield of a product due to the formation of nonreactive polyphosphides and consequently low phosphorus conversion, or the use of expensive reagents, such as rhodium complexes. We were attracted by rather old publications on phosphine electrolytic production, which were carried out already in the 60th and for some reason did not receive further progression. Thus, the cathodic reduction of white phosphorus in aqueous solutions on metals with high hydrogen overvoltage was shown to result in the formation of PH_3 with high yield. We have reinvestigated the electrochemical reduction of white phosphorus in water systems on the different electrodes. In that way, the loss of white phosphorus in a solution occurs much faster than it is required for three-electron process. Phosphorus one-electron reduction results in the formation of phosphorus hydride P_4H_4. A. P. Tomilov has demonstrated the good possibility of PH_3 preparation from white phosphorus with high yield up to 95% at the room temperature in alcohol solution (the best ones are ethanol and $CH_3OC_2H_4OH$ in HCl) on the lead cathode. It is worth noting that the direction of white phosphorus conversion into phosphine is sufficiently well worked out by patents. The present task consists in creation of conditions, allowing instant conversion of PH_3 and other phosphine intermediates into the derivatives with P—H bonds, e.g., organic phosphines. This will allow avoiding the accumulation of intermediate toxic and dangerously explosive phosphine, converting it into undetectable "conventional intermediate." Joint electrolysis of white phosphorus emulsion and alkene in the aqueous acetic buffer solution results in the formation of just primary phosphine in these conditions. The mechanism of phosphine with P—C bond formation is not quite clear. In the case of divinyl benzene or divinylpyridine the phosphorus containing polymers with high phosphorus concentration were formed. These polymers are inflammables. In pure inorganic medium, the selective formation of inorganic acids is possible.

The important problem for successful realization of electrosynthesis process of concrete phosphoric products is a correct choice of a material of electrodes and electrolyzer designs. We have generalized the supervision in the form of the table. On the basis of the experimental facts the design universal the electrolyzer—installations-combines has been developed, allowing to receive a wide spectrum of phosphorous compounds, changing nozzles—electrodes and entering or removing a diaphragm.

Thus, scientific bases of effective, resource saving and ecologically safe technology of electrosynthesis of the major classes of OPC were created. The electrosynthesis ways have been patented. The optimal modes of electrosynthesis were picked up for each concrete product, laws of process were investigated, the choice of the most effective reagents for selective disclosing of P—P bonds was carried out, the design special integrated electrolyzer was developed and created. Electrolyzers are designed to produce phosphorus derivatives by means of white phosphorus electrocatalytic transformation. Depending the electrolysis purposes electrolyzer includes the following set of substituted electrodes Pt, Ni, Ti, glass carbon, Pb, dioxides of ruhenium and titanium ($RuO_2/TiO_2/Ti$), carbon, and so on. Electrolyzer comprises apparatus, assembled with bipolar elements (bipolars), interchanging with diaphragm frames. The diaphragm is made from polytetrafluoroethylene. The spectrum of prepared products is rather wide:



To summarize, there are many interesting promising synthetic applications combining electrochemistry with homogeneous catalysis. Electrosynthesis of the organophosphorus compounds on the basis of white phosphorus has a number of advantages in comparison with common production methods. The most essential ones are: no additional chemicals; a possibility to carry out the reaction in practically closed system with minimum amount of cyclically regenerated reagents; greater product selectivity a yield, reduced or no disposal cost, recovery, recycling of wastes/pollutants, low capital costs/low operating costs. Essentially new approach to OPC synthesis, having practical value, from white phosphorus in electrocatalytic conditions, first of all with P—O, P—C or P—H bonds based of effective universal technology of electrosynthesis of lines of OPC compounds were created. The economic estimation of technological process shows a solvency of the developed approaches. Electrochemistry is a powerful synthetic method for preparing a wide range of phosphorus compounds.

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