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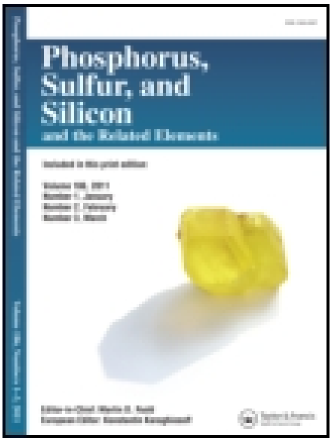

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A New Versatile Synthesis of Functionalized Phosphine Oxides—Efficient Ligands for Rare-Earth Metals Extraction

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A NEW VERSATILE SYNTHESIS OF FUNCTIONALIZED PHOSPHINE OXIDES—EFFICIENT LIGANDS FOR RARE-EARTH METALS EXTRACTION

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Abstract *A new approach to the synthesis of 2-hydroxyaryl-alkenylphosphine oxides and dialkyl (diaryl)-(2-methyl-4-oxopent-2-yl)phosphine oxides was developed that involves an interaction of Grignard reagents with available benzo[e]-1,2-oxaphosphorinines and 1,2-oxaphospholene-2-oxide. This approach allows obtaining target compounds with a high yield. The synthesized phosphine oxides proved to be highly efficient extractants in the micellar extraction of some lanthanides from the nitric acid media.*

Keywords Lanthanide; micellar extraction; organomagnesium reagents; oxaphospholene; oxaphosphorinine; phosphine oxide

A trend of modern chemistry is the development of a highly efficient and selective pathway of synthesis of the target compounds with the high potential of practice application. Phosphine oxides are widely used as the ligands for the metal complex catalysts,[1–3] extracting agents for rare-earth metals,[4–6] and for a creation of the ion-selective electrodes.[7,8] It is known that the basicity and the complexing properties of the phosphine oxide phosphoryl group are strongly influenced by the electronic effect of substituents at the phosphorus atom. The complexing properties of ligands depend on the presence of the various functional groups in the molecule. Thus, the diversity range of the substituents and functional group can increase the complexing properties of the phosphine oxide ligands and improve their selectivity.

In this work we realized a new synthetic approach to the functionally substituted phosphine oxides, which is based on the reactions of such available phosphorus heterocycles, as 4-aryl-2,6-dichlorobenzo[*e*]-[1,2]oxaphosphinine-2-oxides **1** and 2-chloro-3,3,5-trimethyl-1,2-oxaphospholene-2-oxide **2** with the organomagnesium compounds.

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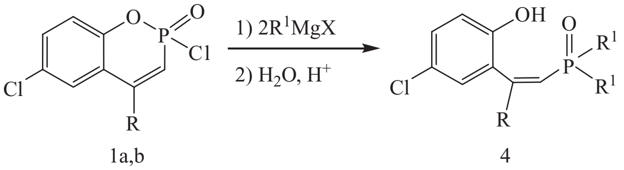
Six-membered heterocycles **1**, bearing one endocyclic phosphorus-carbon bond, are easily available from the reaction of 2,2,2-trichlorobenzo[*d*]-1,3,2-dioxaphosphole **3** with the arylacetylenes.[9] The Michaelis chloride **2** is another easily accessible heterocycle containing one endocyclic phosphorus-carbon bond.[10,11]

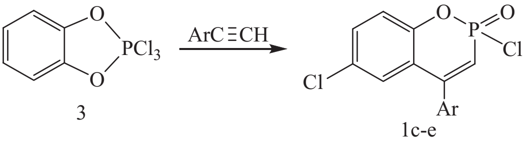


R = Ph; a) R^1 = Ph, b) Et, c) Pr; R = 1-naphthyl; d) R^1 = Ph, e) CH_2Ph

Scheme 1

Earlier we found that the interaction of the compounds **1** with Grignard reagents leads to the formation of phosphine oxides **4a–e**.[12,13] The reaction gives rise to the substitution of both exocyclic P–Cl and endocyclic P–O bonds and allows us to obtain the phosphine oxides with the hydroxy-group in δ-position to the phosphorus atom (Scheme 1). *Z*-Configuration of double bond of the alkenyl fragment is predetermined by the initial phosphorinine structure.

We extended the utilization of the approach to the diversity range of the known and new oxaphosphorinines and Grignard reagents. So, 1,2-oxaphosphinines **1c–e**[9] were synthesized with this purpose for the first time. They were prepared by the reaction of dioxaphosphole **3** with various arylacetylenes (Scheme 2).



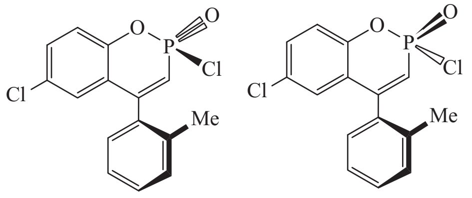
Ar = 4-*cyclo*-C_6H_{11}-C_6H_4 (c), 3-Br-C_6H_4 (d), 2-Me-C_6H_4 (e)

Scheme 2

It is interesting to note that in ^{31}P NMR spectra of compounds **1b** and **1e** we observed two signals with equal intensity. A similar picture was also observed in the proton and carbon spectra. Analysis of NMR data allows the conclusion that the doubling is caused by a diastereoisomerism of these compounds (Scheme 3), which connected with the chiral phosphorus atom and atropisomerism along C–C bond. The last phenomenon is not observed for compounds **1c** and **1d**.

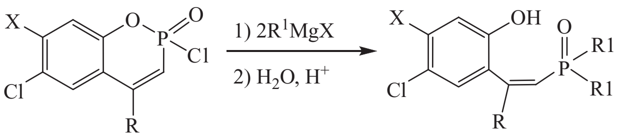
It was found that altering the nature of the substituents at the different positions of the phosphorinine's molecule and using various organomagnesium reagents, prepared from simple aryl or non-branched alkyl halides, does not influence the course of the reaction (Scheme 4). In all cases the target phosphine oxides **4** were obtained with a high yield (85–95%).

Due to their structural peculiarities, the phosphine oxides **4**, bearing phosphoryl and hydroxyl groups at the one side of the double bond can, be effective ligands for the extraction of ions of various metals. This proposition was confirmed by the effective



1e

Scheme 3



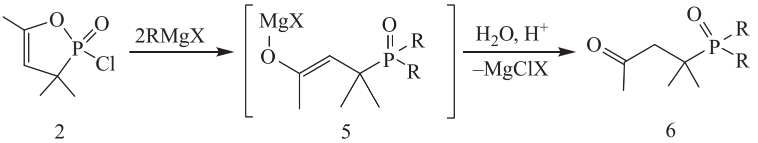
1 4

R^1 = Aryl, Alkyl; R = Aryl; X = H, Me

Scheme 4

micellar extraction of the range lanthanides ions by the some of the obtained phosphine oxides. They exhibit a high extraction degree in the nitric acid media (pH ∼ 1), which reaches about 100% in some cases.[14]

We also extend our approach to other phosphorus heterocycles. Recently it was found that the reaction of 2-chloro-3,3,5-trimethyl-1,2-oxaphospholene-2-oxide **2** with benzyl- and hexylmagnesium halides gives rise to the formation of dialkyl(2-methyl-4-oxopent-2-yl)-phosphine oxides.[15] The reactions of the various alkyl- and arylmagnesium halides turned out to give dialkyl(diaryl)-(2-methyl-4-oxopent-2-yl)-phosphine oxides **5** with a high yield (>90%) in all cases (Scheme 5). The formation of 3-oxoalkylphosphine oxides **6** occurs through the intermediate magnesium salt **5**, which further was converted into the **6** as the result of hydrolysis.



2 5 6

R = alkyl, aryl

Scheme 5

CONCLUSIONS

A new synthetic approach to the functionalized phosphine oxides that is based on the reactions of available phosphorus heterocycles bearing one endocyclic P–C bond was developed. The extracting properties of the obtained phosphine oxides were tested and showed a high efficiency for the micellar extraction from the acid media.

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