

Proceeding Paper

3R-Substituted and Norbornane-Annulated 1H-Phospholanoxides: Synthesis and Structure †

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Abstract: A method for the synthesis of 3R-substituted and norbornane-annulated 1H-phospholan oxides has been developed. The method is based on the in situ substitution of the Al atom by the P atom in five-membered cyclic alumolanes using phosphorus trichloride. Substituted alumolanes were prepared by the reaction of cycloaluminum of aliphatic and aromatic α -olefins and norbornene derivatives with triethylaluminum in the presence of *bis*(cyclopentadienyl)zirconium(IV) dichloride catalyst.

Keywords: phospholanes; heterocyclic compounds; organoaluminum compounds; zirconocene dichloride; cycloaluminum; metal complex catalysis



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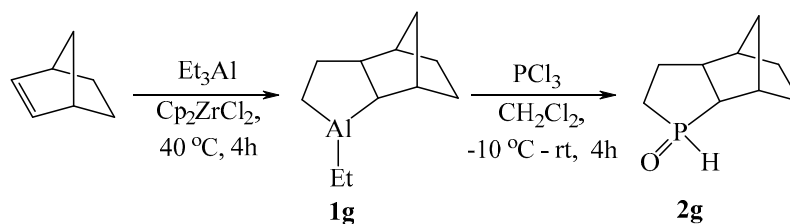
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1. Introduction

The development of new methods for the synthesis of five-membered cyclic organophosphorus compounds due to practical demands is an important area of the chemistry of organoelement compounds [1]. The topic is relevant and arouses constant interest among researchers due to the practical importance of the derivatives of phospholanes, phospholenes, and phosphols, which are widely used in asymmetric catalysis [2], in organic and organoelement chemistry as effective reagents, synthons for fine organic synthesis, and as precursors of biologically active compounds.

Some of the new and promising directions for the synthesis of cyclic organophosphorus compounds include methods based on the direct conversion of metallocarbycles into the corresponding phospholenes and phosphols. This is a direct transformation of zirconacyclopentenes [3,4], zirconacyclopentadienes [5–9], and titanacyclopentadienes [10].

Recently, we have developed a universal method for the synthesis of phospholanes and phospholenes of various structures, promising for their practical application, based on the use of the reaction of catalytic cycloaluminum of unsaturated compounds (alkenes, alkynes, α,ω -diolefins, and norbornenes) through the stage of formation of alumolanes (aluminacyclopentanes and aluminacyclopentenes) based on the substitution of aluminum atoms in alumolanes with phosphorus atoms using alkyl(aryl) phosphorodichlorides (III) [11–13]. However, the replacement of the aluminum atom in substituted alumolanes with a phosphorus atom using $\text{P}(\text{HAl}_3)$ has hardly been studied. Therefore, in the development of ongoing research on the development of effective methods for the synthesis of cyclic organophosphorus compounds, and in order to develop the synthesis of new practically important cyclic organophosphorus compounds, we studied the reaction of alumolanes with phosphorus trichloride.



Scheme 3. The synthesis of (3aR,4R,7S,7aS)-octahydro-4,7-methanophosphindole 1-oxide **2g**.

The structure of the synthesized cyclic organophosphorus compounds was proved by mass spectrometry and ^1H , ^{13}C , ^{31}P NMR spectroscopy, as well as homo- and heteronuclear 2D correlation experiments (COSY ^1H - ^1H , HSQC, HMBC).

3. Conclusions

An original one-pot method for the synthesis of 3R-substituted and norbornane-annulated 1H-phospholane oxides by the reaction of substituted alumolanes with phosphorus trichloride is proposed. The obtained cyclic 1H-phosphine oxides are of practical interest as key monomers for the synthesis of new catalysts for homogeneous catalysis.

4. Experimental Part

The ^1H , ^{13}C , and ^{31}P NMR spectra were acquired on a Bruker Avance-400 instrument (400, 100, and 162 MHz, respectively) in CDCl_3 . The two-dimensional homonuclear (COSY) and heteronuclear (^1H - ^{13}C HSQC and ^1H - ^{13}C HMBC) NMR spectra were acquired according to the standard procedures of Bruker. The mass spectra (GC-MS) were recorded on a Shimadzu GC-2010 instrument equipped with a GCMSQP2010 Ultra mass selective detector and a Supelco 5 ms capillary column (60 m \times 0.25 mm \times 0.25 μm); the carrier gas was helium; the injector temperature was 260 $^\circ\text{C}$; the interface temperature was 260 $^\circ\text{C}$; and the ion source temperature was 200 $^\circ\text{C}$. Chromatographic analysis was performed on a Shimadzu GC-9A gas chromatograph using a 2000 \times 2 mm column; the stationary phase consisted of silicone SE-30 (5%) on a Chromaton N-AW-HMDS carrier (0.125–0.160 mm); the carrier gas was helium (30 mL/min); and the temperature program from 50 to 300 $^\circ\text{C}$ at the rate of 8 $^\circ\text{C}/\text{min}$. The reactions with organometallic compounds were accomplished under dry argon flow. The solvents were dried and distilled immediately prior to use. Commercially available Cp_2ZrCl_2 , phosphines (Acros), and 92% AlEt_3 (from Redkinsk Experimental Factory) were used.

3-Substituted 1H-phospholane oxides 2a–g. General procedure. A round-bottomed flask was charged at 0 $^\circ\text{C}$ with Cp_2ZrCl_2 (0.073 g, 0.25 mmol), alkene or norbornene (5 mmol), and Et_3Al (0.75 mL, 5 mmol) in a dry argon atmosphere. The temperature was brought to 40 $^\circ\text{C}$, and the mixture was stirred for 4 h. Then, the reaction mixture was cooled to $-(5\text{--}10)^\circ\text{C}$, and CH_2Cl_2 (7 mL) with phosphorus trichloride (15 mmol, 3 equiv) was added. The mixture was stirred at room temperature for 4–6 h until the solution became discolored. The mixture was then hydrolyzed with water; the reaction products were extracted with CH_2Cl_2 ; and the organic phase was dried with MgSO_4 . The solvent was evaporated, and the residue was vacuum-distilled to give 1H-phospholane oxides **2a–g** as colorless oils.

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Conflicts of Interest: The authors declare no conflict of interest.

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