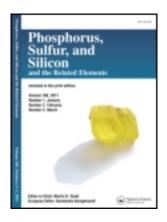
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## Phosphorus, Sulfur, and Silicon and the Related Elements

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# Synthesis of a-Aminophosphine Oxides with Chiral Phosphorus and Carbon Atoms

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## SYNTHESIS OF $\alpha$ -AMINOPHOSPHINE OXIDES WITH CHIRAL PHOSPHORUS AND CARBON ATOMS

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Lipophilic  $\alpha$ -aminophosphine oxides are good extractants for liquid and membrane extraction. Optically active  $\alpha$ -aminophosphine oxides, containing chiral centers in their structure, can provide selective means for transfer of stereoisomers through supported liquid membranes. We have developed a method for synthesis of such carrier compounds based on a three-component Kabachnik–Fields reaction.

**Keywords**  $\alpha$ -Aminophosphine oxide; chiral phosphorus atom; Kabachnik–Fields reaction; membrane extraction; stereoselective membrane transport

### INTRODUCTION

The increased interest in  $\alpha$ -aminophosphine oxides is caused by their well-defined complexation abilities. These properties and hydrolytic stability of  $\alpha$ -aminophosphine oxides allow them to be used in the processes of liquid and membrane extraction of both inorganic and organic substrates. Supported liquid membranes containing chiral  $\alpha$ -aminophosphine oxides can provide stereoselective transport of optically active organic substrates.

## **RESULTS AND DISCUSSION**

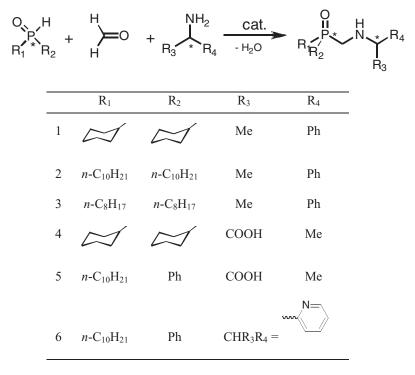
We have developed a technique for synthesizing of  $\alpha$ -aminophosphine oxides and derivatives containing chiral phosphorus and carbon atoms, based on the three-component Kabachnik–Fields reaction of formaldehyde, phosphinic acids, and amines or amino acids (Scheme 1). Formaldehyde was used in excess of 5%.

The introduction of chiral centers in the resulting  $\alpha$ -aminophosphine oxides was achieved by application of reagents that contained asymmetric phosphorus and carbon atoms: (*R*)-, (*S*)-1-phenylethylamines, (*S*)-alanine, and racemic phenyldecylphosphinic acid (only for compounds **5** and **6**) in the Kabachnik–Fields reaction.

Syntheses were performed in suitable solvents (toluene for amines and acetonitrile for the amino acid) under reflux and were catalyzed by *p*-toluenesulfonic acid. These conditions

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Scheme	1
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allowed us to obtain  $\alpha$ -aminophosphine oxides in high yield. The structure of the products was confirmed by <sup>1</sup>H and <sup>31</sup>P NMR spectroscopy. The yield and selected physicochemical data of final  $\alpha$ -aminophosphine oxides are presented in Table 1.

Separation of an enantiomer of *P*-phenyl-*P*-decyl-*N*-2-pyridineaminometylphosphine oxide (compound **6**) was performed by crystallization of its diastereoisomeric salt with *D*-tartaric acid. As the result, laevorotatory scalemic aminophosphine oxide **6** was obtained.

Compound	Yield [%]	$^{31}$ P NMR [ppm] $\delta^a$	Mp [°C]	$R_{\rm f}{}^b$	$pK_{BH}^{+c}$
(R)-1	93	50.9 (chloroform)	99	0.46	4.35
(S)- <b>1</b>	92	50.8 (chloroform)	99	0.47	4.35
(R)-2	94	43.9 (toluene)	47	0.64	4.13
(S)-2	95	43.9 (toluene)	47	0.65	4.13
(S)- <b>3</b>	95	49.1 (toluene)	_	0.58	
(S)-4	51	52.4 (acetonitrile)	172	0.26	
(S)- <b>5</b>	64	32.1 (metanol)	_	0.41	
(–)-6	88	40.5 (chloroform)	—	0.47	4.65

Table 1 Yields and properties of  $\alpha$ -aminophosphine oxides

<sup>a</sup>External reference 85% H<sub>3</sub>PO4.

<sup>b</sup>Eluent chloroform/acetone/methanol (3.6:3.7:0.7), Silufol UV-254.

 ${}^{c}pK_{BH}^{+}$  was determined in the propanol-2 water system (1:1).

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Membrane extraction of tartaric acids through supported liquid membranes (teflon porous matrix with a pore diameter of 0.6 mkm saturated, 0.1 M solution of carrier  $\alpha$ -aminophosphine oxide in phenylcyclohexane) was studied for (*R*)-didecyl-*N*-1phenylethylaminometylphosphine oxide (compound (*R*)-2). The difference between flow rate transfer of *L*-tartaric acid (40.40 × 10<sup>6</sup> mol/min × m<sup>2</sup>) versus the *D*-form (13.95 × 10<sup>6</sup> mol/min × m<sup>2</sup>) through the membrane demonstrates the stereoselectivity of transport. Such stereoselectivity is probably a consequence of formation of diastereomeric complexes of  $\alpha$ -aminophosphine oxide with substrates of different stability. The results indicate that (*R*)-didecyl-*N*-1-phenylethylaminometylphosphine oxide can be used for stereo enrichment of tartaric acid.