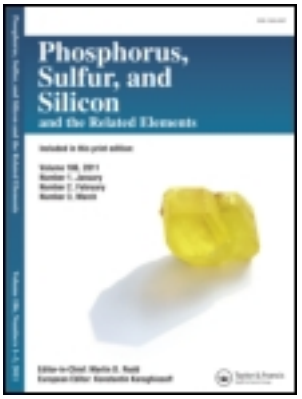

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Synthesis of α-Aminophosphine Oxides with Chiral Phosphorus and Carbon Atoms

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SYNTHESIS OF α-AMINOPHOSPHINE OXIDES WITH CHIRAL PHOSPHORUS AND CARBON ATOMS

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Lipophilic α-aminophosphine oxides are good extractants for liquid and membrane extraction. Optically active α-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 α-Aminophosphine oxide; chiral phosphorus atom; Kabachnik–Fields reaction; membrane extraction; stereoselective membrane transport

INTRODUCTION

The increased interest in α-aminophosphine oxides is caused by their well-defined complexation abilities. These properties and hydrolytic stability of α-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 α-aminophosphine oxides can provide stereoselective transport of optically active organic substrates.

RESULTS AND DISCUSSION

We have developed a technique for synthesizing of α-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 α-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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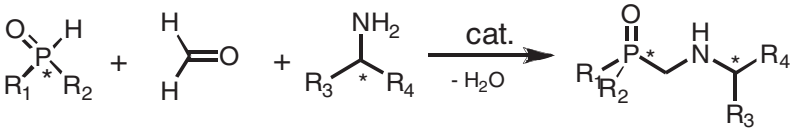
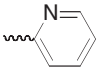


	R_1	R_2	R_3	R_4
1			Me	Ph
2	*n*-$C_{10}H_{21}$	*n*-$C_{10}H_{21}$	Me	Ph
3	*n*-C_8H_{17}	*n*-C_8H_{17}	Me	Ph
4			COOH	Me
5	*n*-$C_{10}H_{21}$	Ph	COOH	Me
6	*n*-$C_{10}H_{21}$	Ph	CHR_3R_4 =	

Scheme 1

allowed us to obtain α-aminophosphine oxides in high yield. The structure of the products was confirmed by ^{1}H and ^{31}P NMR spectroscopy. The yield and selected physicochemical data of final α-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.

Table 1 Yields and properties of α-aminophosphine oxides

Compound	Yield [%]	^{31}P NMR [ppm] δ^a	Mp [°C]	$R_f{}^b$	$pK_{BH}{}^{+c}$
(*R*)-**1**	93	50.9 (chloroform)	99	0.46	4.35
(*S*)-**1**	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*)-**3**	95	49.1 (toluene)	—	0.58	
(*S*)-**4**	51	52.4 (acetonitrile)	172	0.26	
(*S*)-**5**	64	32.1 (metanol)	—	0.41	
(−)-**6**	88	40.5 (chloroform)	—	0.47	4.65

[a]External reference 85% H_3PO4.
[b]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).

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 α-aminophosphine oxide in phenylcyclohexane) was studied for (*R*)-didecyl-*N*-1-phenylethylaminometylphosphine oxide (compound (*R*)**-2**). The difference between flow rate transfer of *L*-tartaric acid (40.40×10^6 mol/min $\times$ m^2) versus the *D*-form (13.95×10^6 mol/min $\times$ m^2) through the membrane demonstrates the stereoselectivity of transport. Such stereoselectivity is probably a consequence of formation of diastereomeric complexes of α-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.