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LETTERS TO THE EDITOR

Synthesis of Optically Active α-Aminophosphine Oxides and Enantioselective Membrane Transport of Acids with Their Participation

R. A. Cherkasov, A. R. Garifzyanov, and S. A. Koshkin

Kazan (Volga Region) Federal University, ul. Kremlevskaya 18, Kazan, 420008 Russia
e-mail: scioris@yandex.ru

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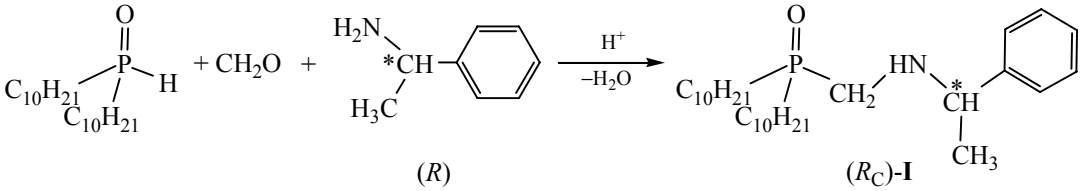
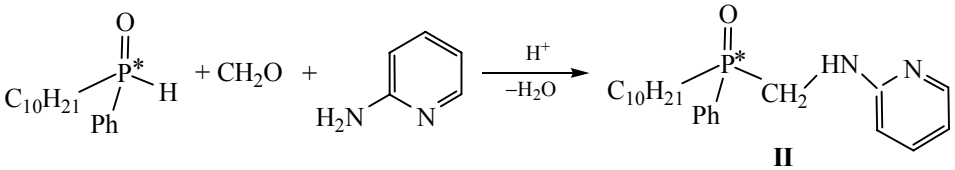
Previously, we have shown the prospect of using lipophilic α-aminophosphine oxides in the processes of membrane extraction for efficient and selective extraction of substrates of different nature, including mineral and organic acids [1]. We first attempted to carry out the enantioselective membrane transport of chiral carboxylic acids with optically active α-aminophosphine oxides. For their synthesis we used the Kabachnik–Fields reaction in the three-component system phosphinous acid–formaldehyde–amine. The stereogenic carbon atom was introduced into the structure of α-aminophosphine oxides by using the (*R*)-enantiomer of α-methylbenzylamine. The chiral center on the phosphorus atom was introduced by the reaction of racemic decylphenylphosphinous acid followed by the separation of stereoisomers mixture. The reactions were carried out in the boiling toluene, using a small (4%) excess of formaldehyde and catalyzing with *p*-toluenesulfonic acid.

Optically pure α-aminophosphine oxides **I** were prepared in 94% yield by reacting didecylphosphinite with formaldehyde and (*R*)-α-methylbenzylamine for 3 h and were purified by recrystallization from hexane.



(*R*) (R_C)-**I**

The longer heating (5 h) was required in the case of the reaction of decylphenylphosphinous acid with formaldehyde and 2-aminopyridine, which gave rise to aminophosphine oxide **II**.



II

The formation of aminophosphine oxide **II** as a racemic mixture is characterized by the appearance in the $^{31}P\{H\}$ NMR spectrum of the signals of two enantiomeric products (38.7 and 39.5 ppm); a singlet at 40.5 ppm corresponds to them in chloroform solution that may testify to the diastereomeric associates formation [2].

For the racemate resolution, the aminophosphine oxide **II** was converted into the tartrate salt via the

reaction with an equimolar amount of *D*-tartaric acid in ethanol. Further fractional crystallization of the resulting tartrate and the conversion of α-aminophosphine oxide into the basic form by the action of sodium carbonate resulted in the isolation of (–)-stereoisomer. The attempts to isolate (+)-enantiomer have not been successful.

The study of membrane transport of *D*- and *L*-tartaric acids with aminophosphine oxide **I** under the conditions given in [1] showed that the rate of transfer of the *L*-form (40×10^{-6} mol min^{-1} m^{-2}) through an impregnated membrane is 4.4 times higher compared with the corresponding *D*-form (9.1×10^{-6} mol min^{-1} m^{-2}). The results obtained indicate suitability of the enantiomeric aminophosphine oxide for the enantioselective membrane transport of acidic chiral substrates.

(*R*)-Didecyl-(*N*-1-phenylethyl)aminomethylphosphine oxide (I). Yield 94%. White crystals, mp 47°C, pK_{BH^+} 4.13 (isopropanol–water, 1:1). $^{31}P\{H\}$ NMR spectrum ($C_6H_5CH_3$), δ_P, ppm: 43.87. ^1H NMR spectrum ($CDCl_3$), δ, ppm: 0.85–1.7 m (15H, $2C_6H_{11}$, CH_3), 2.66 d.d.d (2H, CH_2P, $^2J_{HH}$ 15, $^2J_{PH}$ 64.5 Hz), 3.69 q (H, CH, $^3J_{HH}$ 6 Hz), 7.27 m (5H, C_6H_5). IR spectrum, ν, cm^{-1}: 3367 s (NH), 1156 s (P=O), 1458 m, 1465 s (CH_{Ar}).

(–)-Didecylphenyl-(*N*-2-pyridinyl)aminomethylphosphine oxide (II). Yellow amorphous substance. $[\alpha_D^{23}]$ –4.95° (*c* 2, $C_6H_5CH_3$), pK_{BH^+} 4.65 (isopropanol–water, 1:1). $^{31}P\{H\}$ NMR spectrum ($C_6H_5CH_3$), δ_P, ppm: 38.7, 39.5. $^{31}P\{H\}$ NMR spectrum ($CHCl_3$), δ_P, ppm: 40.5. ^1H NMR spectrum ($CDCl_3$), δ, ppm: 0.89–2.09 m (24H, $C_{10}H_{21}$, CH_3), 4.08 m (2H, PCH_2N), 4.37 s (1H, NH), 6.5–6.6, 8.06 m (3H, C_5H_3N), 7.37–7.81 m (5H, C_6H_5). IR spectrum, ν, cm^{-1}: 3385 s (NH), 1130 s (P=O), 1653 m, 1561 br.s (CH, pyridine), 1443 m, 1530 br.s (CH_{Ar}).

The ^1H and $^{31}P\{H\}$ NMR spectra were registered on a Varian XL-300 spectrometer operating at 300 and 122.4 MHz respectively. The IR spectra were Registered on a Fourier-spectrometer Tensor 27 (Bruker) in mineral oil.

ACKNOWLEDGMENTS

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