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Modified Alkaloids as Organocatalysts for the Asymmetric Synthesis of Organophosphorus Compounds

Anastasia O. Kolodiazhna^a; Valery P. Kukhar^a; Oleg I. Kolodiazhnyi^a

^a Institute of Bioorganic Chemistry and Petrochemistry, National Academy of Sciences of Ukraine, Kiev, Ukraine

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Modified Alkaloids as Organocatalysts for the **Asymmetric Synthesis of Organophosphorus** Compounds

Anastasia O. Kolodiazhna, Valery P. Kukhar, and Oleg I. Kolodiazhnyi

Institute of Bioorganic Chemistry and Petrochemistry, National Academy of Sciences of Ukraine, Kiev, Ukraine

Modified alkaloids as organocatalysts for phospho-aldol reaction were studied.

Keywords Cinchona alkaloids; organocatalysis; phospho-aldol reaction

Organocatalysis is the acceleration of chemical reactions with a substoichiometric amount of an organic compound that does not contain a metal atom.

As an important subset of the larger field of organocatalysts, interest in amino acid and peptide-based catalysts has increased over the past decade. Important progress has been made in the development of asymmetric reactions with amino acid (proline) and peptide-based catalysts.

Cinchona alkaloids 1 (cinchonine, cinchonidine, quinine, etc.) are accessible and effective reagents for the asymmetric synthesis and are widely in organic chemistry.¹

In this article we studied the modified alkaloids **1–3** as organocatalysts for phospho-aldol reaction. We found that the bifunctional cinchona derivatives 1-3 act as asymmetric catalysts in the phosphoaldol reaction. By means of these catalysts both optical antipods of hydroxyalkylphosphonic acids have been obtained. Good enantiomeric excesses were achieved with activated aromatic aldehydes.

Stereoselectivity of catalysts in case of a single asymmetric induction (R = Et) was good and high in case of a double and triple asymmetric induction. Products 4, 5 were purified by crystallization and were isolated as chemically and optically pure compounds. The optical purity of these

Address correspondence to Anastasia O. Kolodiazhna, Institute of Bioorganic Chemistry and Petrochemistry, National Academy of Sciences of Ukraine, Murmanskaya str. 1, Kiev, 02094 Ukraine. E-mail: oikol123@rambler.ru

$$(RO)_{2}P(O) \xrightarrow{R'} H OH \xrightarrow{R'CH=O} (RO)_{2}P(O)H \xrightarrow{R'CH=O} (RO)_{2}P(O) \xrightarrow{R'} H$$

compounds was studied by means of NMR chiral solvating reagents.² The absolute configuration of the new stereogenic center in **4** and **5** was also assigned by analogy with other hydroxyphosphonates using the method of chemical correlation.

The most effective were catalysts obtained on the base of quinine and cinchonidine $(R=H,\,R'=PhCH_2)$

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