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Thematic course: Synthesis of monomers for the preparation of optically active poly(amido-imide)s. Part 1.

Synthesis of chiral imides containing a fragment of the natural amino acid based on nitrophenylcycloalkanedicarboxylic acids

© **Anna A. Koverda**,[1]* **Mikhail N. Koverda**,[2+] **Alexandra I. Korshunova**[1] and **Evgeny N. Sechin**[2]
[1] *Organic and Analitical Chemistry Division. Yaroslavl State Technical University. Moscovsky Ave., 88. Yaroslavl, 150023. Russia. Phone: +7 (4852) 44-05-29. E-mail: a.koverda@pm.me*
[2] *Yaroslavl State Institute of Raw Materials and Food Quality. Moscovsky Ave., 76a. Yaroslavl, 150030. Russia. Phone: +7 (4852) 47-86-86. E-mail: m.kov@pm.me*

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*Supervising author; +Corresponding author

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Abstract

Previously it was shown that the stereochemical result of the alkylation reaction of benzene with cycloalkanedicarboxylic acids depends on the order of mixing the reagents. The resulting diastereomerically pure derivatives can be used as precursors of monomers for the synthesis of optically active poly(amido-imide)s, which are basic materials in chiral chromatographic separation. Their potential for use in chiral catalytic systems, liquid crystals in ferroelectric and nonlinear optics, in the manufacture of electrodes for enantioselective recognition during bioelectrosynthesis, membrane separation technology, etc. is shown.

Nitration reactions of alkyl derivatives were carried out with their subsequent imidization with natural amino acids. The resulting diastereomerically pure dicarboxylic acids are nitrated with low selectivity, unlike their anhydrides, so the nitro derivatives were synthesized by nitrating the anhydrides with anhydrous nitric acid in chloroform solution. The racemization of the α-carbon center of the amino acid fragment occurs during the imidization reaction in glacial acetic acid. Using of DMF as a solvent under mild conditions is preferable, as it eliminates the possibility of racemization of the chiral center of the amino acid fragment. It was also found that during the preparation of imides, the configuration of the chiral centers of the cycloalkane dicarboxylic acid fragment is preserved. Nitrophenylnorbornanedicarboxylic acid forms an anhydride directly during synthesis in acetic acid, unlike cyclohexanedicarboxylic acids, due to its spatial structure. Nitrophenylnorbornanedicarboxylic acid is also characterized by easier imidization.

The structure was determined using ^{1}H, ^{13}C NMR, ^{1}H-^{1}H NOESY, ^{1}H-^{1}H COSY, HPLC, capillary electrophoresis.

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