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

Synthesis of chiral aminocarboxylic acids containing an imide cycle and a fragment of the natural amino acid

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Abstract

In a previous work, it was shown that the imidization reaction of dystereomerically pure nitrophenylcycloalkanedicarboxylic acids with natural amino acids in acetic acid proceeds with partial racemization of the α-carbon center of the amino acid fragment. Carrying out the synthesis in DMF at room temperature allows to obtain imides with preservation of the configuration of all chiral centers. New aminocarboxylic acids were synthesized based on them, which are the starting compounds for the monomers of optically active PAI.

We used various reduction systems to produce aromatic amine compounds containing an imide cycle, such as tin or tin(II) chloride and hydrochloric acid, sodium dithionite in water and catalytic reduction with hydrogen in acetone or ethyl alcohol at various pressures and temperatures. The complete reduction of the nitroacid occurs only when using palladium on coal at a temperature of 100 °C and a hydrogen pressure of 40 atm or Raney nickel at 70 °C and a pressure of 65 atm H_2 in ethanol. Raney nickel is very sensitive to catalytic poisons, even a small amount of impurities (such as alkali) left after the catalyst has been obtained and washed leads to its complete deactivation. Therefore, synthesis using Raney nickel, although possible, is inconvenient from a practical point of view. On the contrary, the complete reduction of the nitro group occurs at lower temperatures and pressures (50 °C, 25 atm) using palladium on coal as a catalyst after its additional activation with hydrogen.

The structure of aminocarboxylic acids was confirmed by IR spectroscopy, ^{1}H NMR spectra, elemental analysis and HPLC.

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