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Author	柳沢, 宏明(Yanagisawa, Hiroaki)
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A New Synthesis of Cyclic α -Amino Acids

Hiroaki YANAGISAWA*

Cyclic α -amino acids were previously prepared from the corresponding cyclic ketones by Strecker synthesis or Bucherer-hydantoin synthesis.

A new synthesis of cyclic α -amino acids from α,β -unsaturated α -nitroesters has been explored. It has been found that the Diels-Alder reaction between α,β -unsaturated nitroesters and dienes forms the cyclic α -nitroesters which were led to cyclic α -amino acids by reduction followed by hydrolysis.

Ethyl α -nitrocrotonate (I), ethyl 2-nitro-5-methyl-2-hexenoate (II) and ethyl α -nitrocinnamate (III) were used as the dienophiles; cyclopentadiene and butadiene were used as the dienes. From these compounds, 2-amino-3-methylbicyclo [2. 2. 1]-heptane-2-carboxylic acid (IV), 1-amino-2-methylcyclohexane-1-carboxylic acid (V), 2-amino-3-isobutylbicyclo [2. 2. 1] heptane-2-carboxylic acid (VI) and 2-amino-3-phenylbicyclo [2. 2. 1] heptane-2 carboxylic acid (VII) were prepared in this paper. The Diels-Alder reaction of (I) with furan gave only a small quantity of ethyl 1-nitro-2-methyl-3,6-endoxo- Δ^4 -tetrahydrobenzoate (VIII).

It has been proved, by chemical method, gas chromatography and n. m. r. spectral study, that these diene synthesis products were the mixtures of the diastereomers.

*柳 沢 宏 明