Studies of 2-Oxazolidinones. (I)

A Convenient Synthesis of 3-Substituted 2-Oxazolidinones

Ryohei Oda, Masahiko Miyanoki and Masaya Okano

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A convenient synthesis of 3-substituted 2-oxazolidinones starting from three components—aliphatic or aromatic amines, phosgene and ethylene chlorhydrin—has been developed.

Studies of 2-Oxazolidinones. (II)

Products of the Pyrolysis of Some 2-Oxazolidinones

Ryohei Oda, Masahiko Miyanoki and Masaya Okano


The products obtained by the pyrolytic decarboxylation of 2-oxazolidinones have been investigated, chiefly by infrared analysis. In the case of 2-oxazolidinone, the products are 1-(β-hydroxyethyl)-2-imidazolidinone, 1-[β-(1-azilidinyl)ethyl]-2-imidazolidinone (somewhat uncertain), and poly (ethylenimine) having a 2-imidazolidinone ring at the chain end. On the other hand, the only products from 3-p-chlorophenyl- and 3-p-nitrophenyl-2-oxazolidinone are believed to be low molecular weight polymers of the corresponding ethylenimines. From 3-acetyl-2-oxazolidinone, a considerable amount of 2-methyl-2-oxazoline, which seems to arise from the rearrangement of N-acetylethylenimine, is isolated, in addition to the corresponding poly (ethylenimine). On the basis of the products obtained, a possible mechanism for the pyrolysis has been proposed.

Studies of 2-Oxazolidinones. (III)

Kinetics of the Pyrolytic Decarboxylation of 2-Oxazolidinones

Ryohei Oda, Masahiko Miyanoki and Masaya Okano


The kinetics of the pyrolytic decarboxylation of 3-substituted 2-oxazolidinones have been studied and the following results were obtained. (1) This decomposition is an autocatalytic reaction, in which the aminated formed acts as a catalyst.
(2) In the decarboxylation of 3-aryl-2-oxazolidinones, the electronic effect of the substituent on the benzene ring indicates that the fission of the N-C bond of the urethane group in the 2-oxazolidinone ring is rate-determining. (3) The initial rate of the aliphatic amine-catalyzed decarboxylation of 3-aryl-2-oxazolidinones is of the pseudo-first-order; it also depends on the concentration and structure of the amine. A mechanism has been proposed which involves a nucleophilic attack of amine on the carbonyl-carbon atom. An amine having an hydroxyl or amino group on the β-carbon shows a large rate-acceleration; this suggests the simultaneous electrophilic participation by the active hydrogen of these groups. (4) The initial rate of the decarboxylation of 2-oxazolidinone itself, catalyzed by aliphatic amine, is of the second-order in oxazolidinone and of the first-order in amine. From this a concerted mechanism has been inferred, in which the amine acts as a nucleophile and the other oxazolidinone acts as an electrophile.

New Addition Reactions. (IV)

The Addition of Schiff Bases to Diketene

Ryohei Oda, Shunichi Takashima and Masaya Okano

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Treatment of diketene with N-benzylidene-t-butylamine afforded a cyclic adduct, adduct, 1-t-butyl-6-phenyl-2,4-piperidinedione, in an excellent yield. Similar reactions with N-methylene-t-butylamine and N-methylene cyclohexylamine also gave the corresponding piperidinediones, but the yields were very low.

New Addition Reactions. (V)

Dimerization of Diketene

Ryohei Oda, Shunichi Takashima and Masaya Okano

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When diketene was treated with 5-10 mol. % of aluminum tribromide in ethylene dichloride at 10-20°C for about thirty hours, a mixture of two dimers, 2,6-dimethyl-γ-pyrone-3-carboxylic acid and dehydroacetic acid (ratio 4:7), was obtained in ca. 60% yield without any formation of a polymeric by-product. This result is contrast to other Lewis acid-catalyzed reactions (cf. Makromol. Chem., 39, 243 (1960); 43, 149 (1961)).