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Studies of 2-Oxazolidinones. (I)

A Convenient Synthesis of 3-Substituted 2-Oxazolidinones

Ryohei ODA, Masahiko MIYANOKI and Masaya OKANO

Bulletin of the Chemical Society of Japan, **35**, 1309 (1962)

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

Studies of 2-Oxazolidinones. (II)

Products of the Pyrolysis of Some 2-Oxazolidinones

Ryohei ODA, Masahiko MIYANOKI and Masaya OKANO

Bulletin of the Chemical Society of Japan, **35**, 1910 (1962)

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-azolidinyl)-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

Bulletin of the Chemical Society of Japan, **35**, 1915 (1962)

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 amine formed acts as a catalyst.

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(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

Bulletin of the Chemical Society of Japan, **35**, 1843 (1962)

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-methylenecyclohexylamine 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

Bulletin of the Chemical Society of Japan, **36**, 476 (1963)

When diketene was treated with 5-10mol. % 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)).