

ABSTRACTS

(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

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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-methylenecyclohexylamine also gave the corresponding piperidinediones, but the yields were very low.

New Addition Reactions. (V)

Dimerization of Diketene

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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)).
