

Study Notes On Curtius Rearrangement

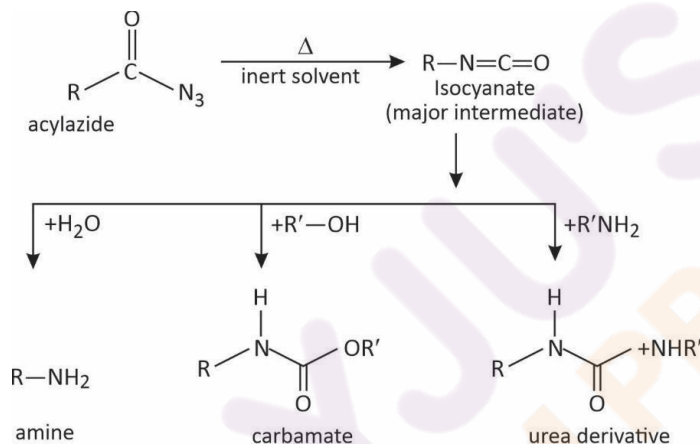


CURTIUS REARRANGEMENT

The thermal decomposition of an acyl azide in presence of an inert solvent to yield isocyanate as a major intermediate, along with nitrogen gas.

The obtained isocyanate then undergoes further reaction in presence of water, alcohols, and amines to yield primary amine, carbamate, or urea derivative, respectively.

General reaction-

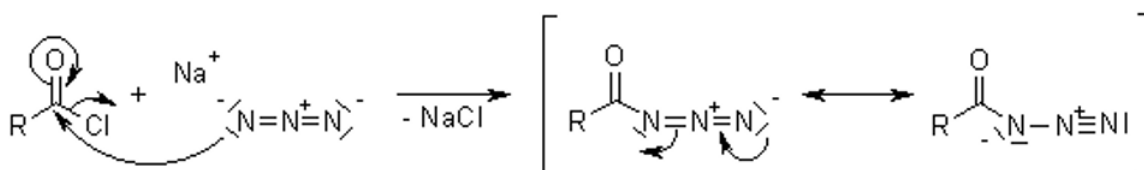


Notes:

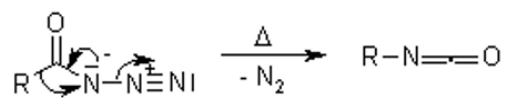
- It is a type of rearrangement reaction, also known as Curtius rearrangement or Curtius degradation.
- This thermal decomposition is a concerted process.
- The migration of R group to form isocyanate occurs with retention in configuration of R-group.
- The migratory aptitude of R-group follows the order – tertiary > secondary ~ aryl > primary
- Isocyanate undergoes hydrolysis to give primary amine. whereas, isocyanate undergoes Nucleophilic attack in presence of alcohols and amines to give carbamates and urea derivatives respectively.
- Curtius rearrangement is catalyzed by both- Bronsted acid and Lewis Acids.

Mechanism of Curtius reaction-

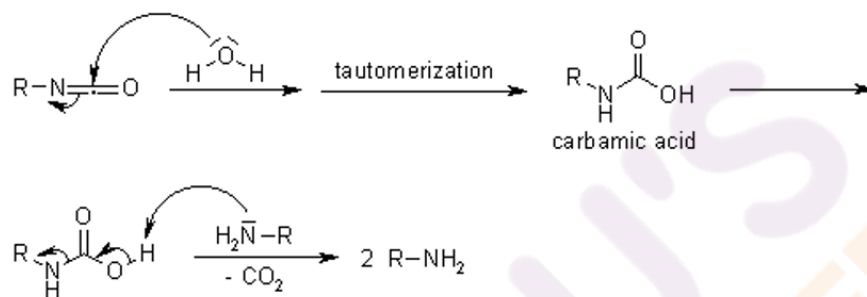
Preparation of azides:



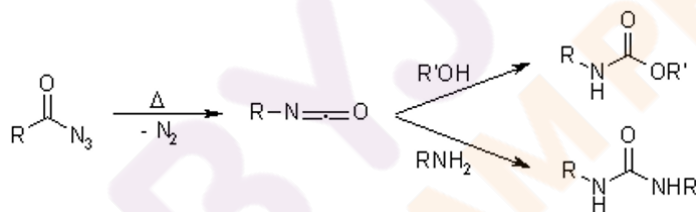
Decomposition:



Reaction with water to the unstable carbamic acid derivative which will undergo spontaneous decarboxylation-



Isocyanates are versatile starting materials:



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