

Study Notes On Schmidt Reaction



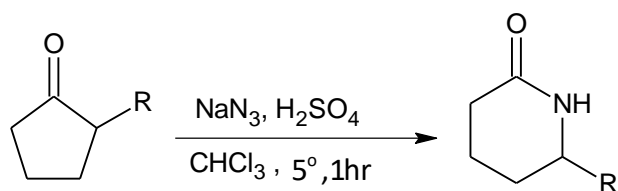
SCHMIDT REACTION

The organic reaction in which hydrogen azide (HN_3) reacts with electrophiles, such as aldehyde, ketone, carboxylic acid, tertiary alcohols, or alkenes in presence of an acid (i.e., acid catalyzed reaction) to give amines, amides, nitriles, or imines with and expulsion of Nitrogen (N_2).

In this reaction mechanism, rearrangement occurs.

Notes-

1. The Schmidt reaction is used to convert substituted ketone to amides or lactams.

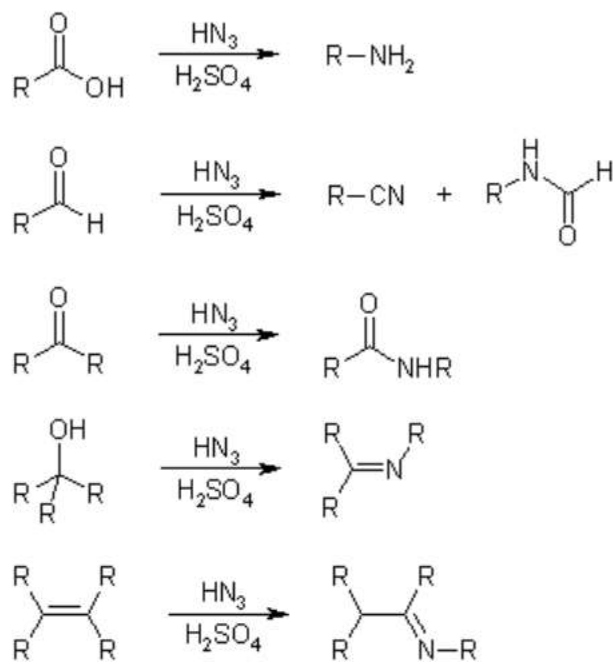


Where, R = Me or n - Pr

2. Schmidt reaction with aldehydes is not very much successful because of C - migration to form amide or H - migration to form nitrile.

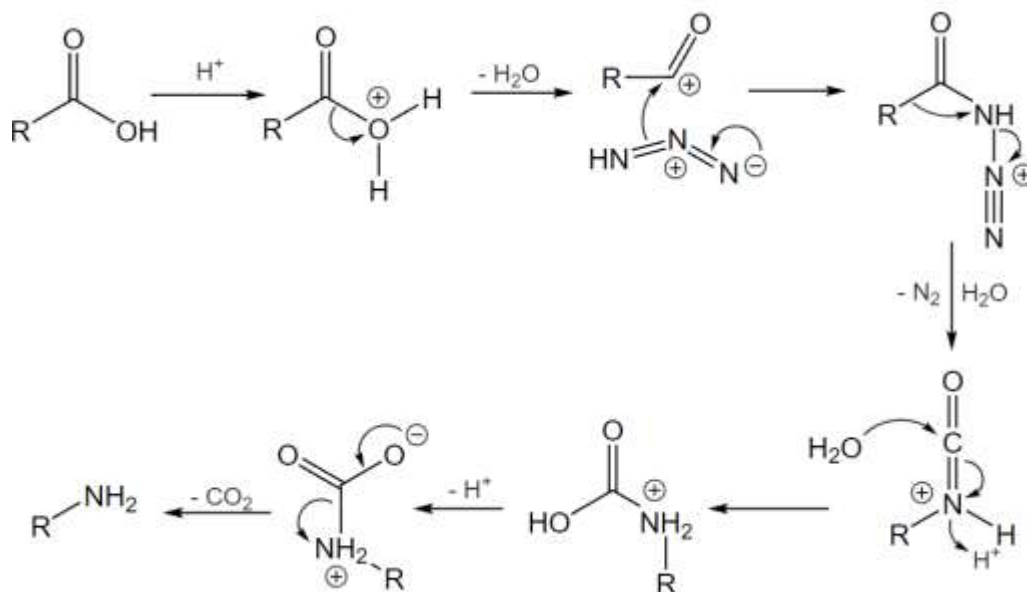
3. In case of tertiary alcohols, they give substitution by azide, via carbenium ion which gives alkyl azide that rearranges to yield an imine.

General reaction-

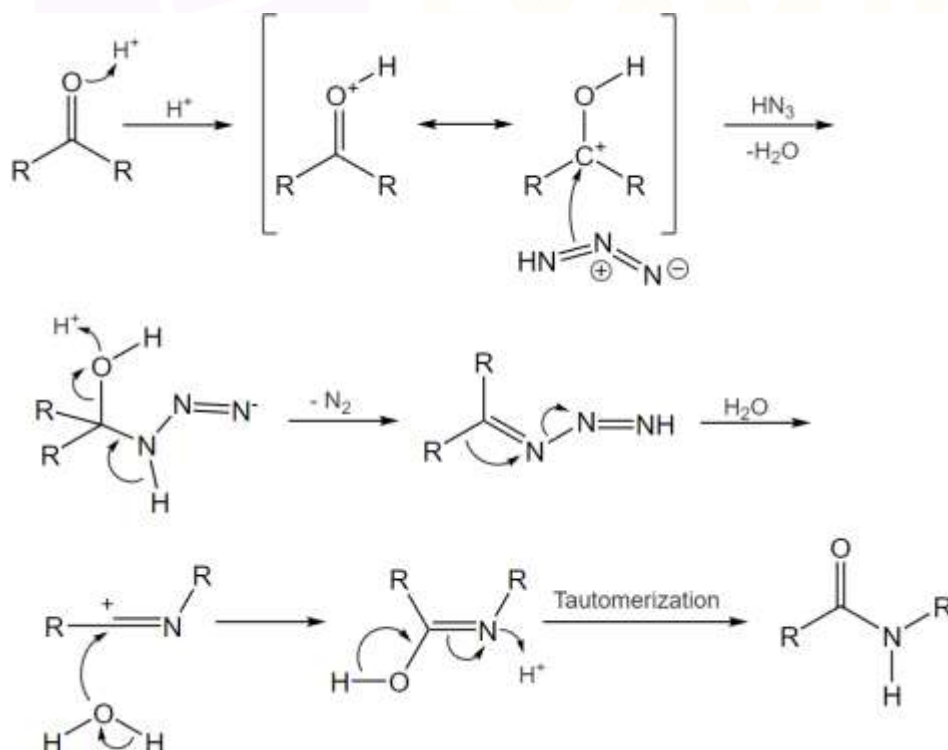


Reaction mechanism-

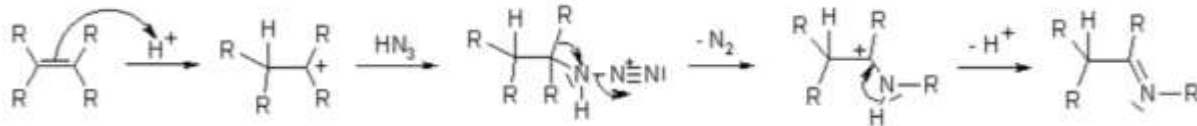
For an acid: The reaction with carboxylic acid produces acyl azides, which rearranges to form isocyanates, which is further either solvolized to carbamates or hydrolyzed to carbamic acid; decarboxylation of which successfully gives amines with carboxylic acids.



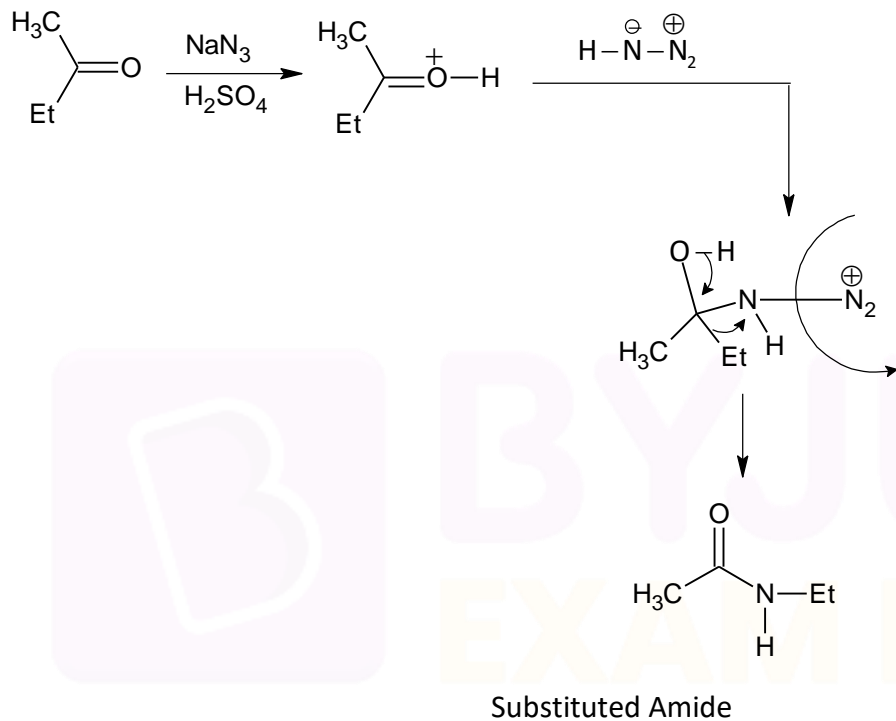
For a ketone: The reaction produces azido hydrin intermediate which thereafter successfully gives amides with ketones.



For an alkene: Addition of HN_3 gives alkyl azide which rearranges to produce imine.



Example-



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