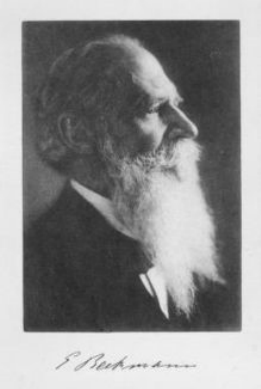
Beckmann Rearrangement



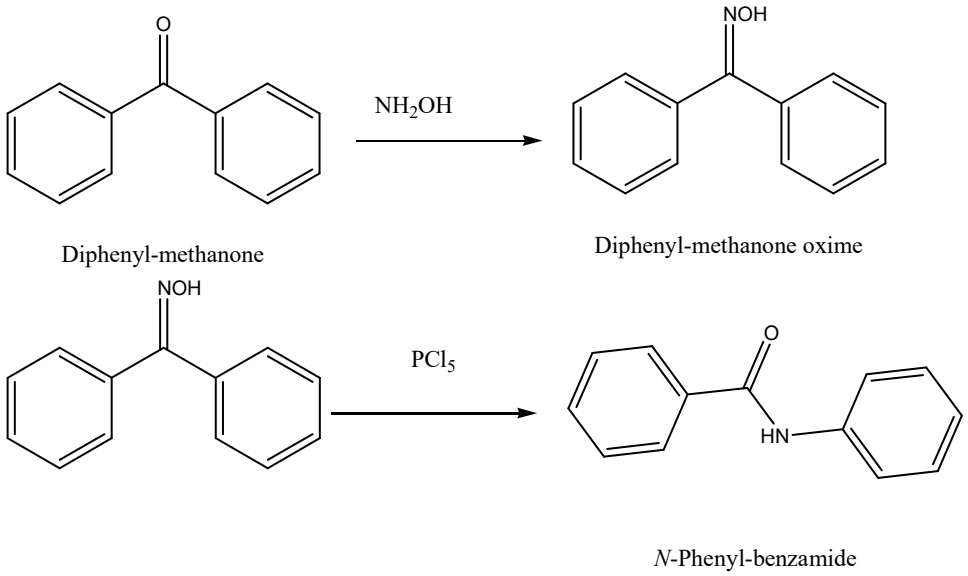
Ernst Otto Beckmann (1853-1923). Inspirational life.

Reference

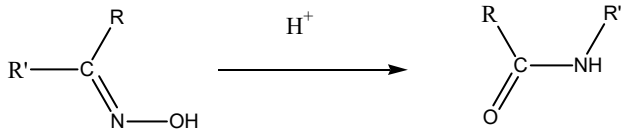
Beckmann, E. (1886) "Zur Kenntniss der Isonitrosoverbindungen" ([Contribution] to our knowledge of isonitroso compounds), Berichte der Deutschen Chemischen Gesellschaft, 19 : 988–993.

The reaction involved the use of hydroxylamine to convert benzophenone into an oxime.

Treating this oxime with phosphorus pentachloride converted it into amide.



Reaction scheme



Oxime Substituted amide

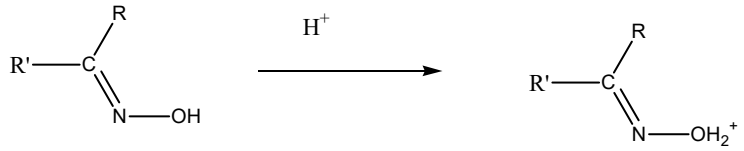
Migrating group preference

Anti to hydroxyl

Aryl or alkyl but not H

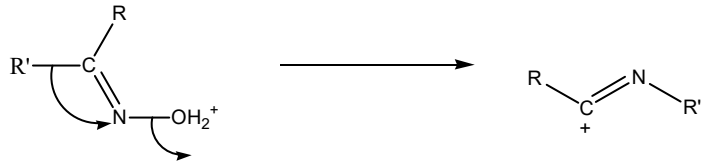
Mechanism

Step 1: Protonation



The reaction begins by protonation of the hydroxyl group forming a better leaving group.

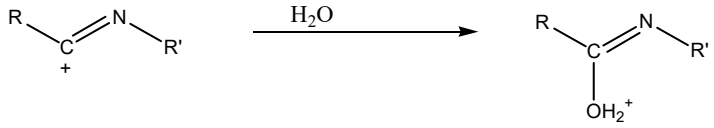
Step 2: Dehydration and migration



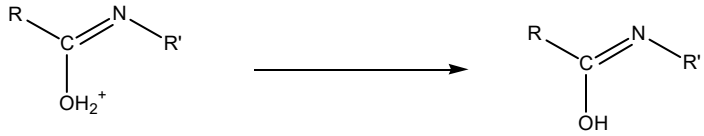
Nitrilium ion

The N-O bond is cleaved with the expulsion of waters simultaneously with N-R bond formation so that formation of a free nitrene is avoided.
trans [1-2]-shift: The R group trans to the leaving group then migrates to the nitrogen, resulting in a carbocation and the release of a water molecule.

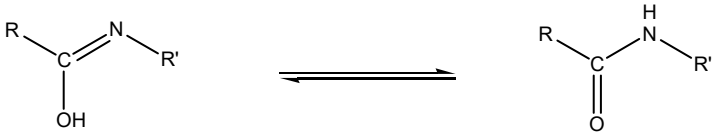
Step 3: Hydration



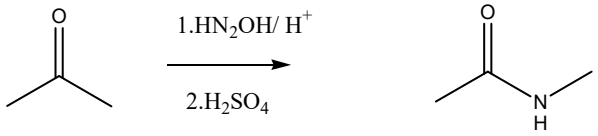
Step 4: Deprotonation



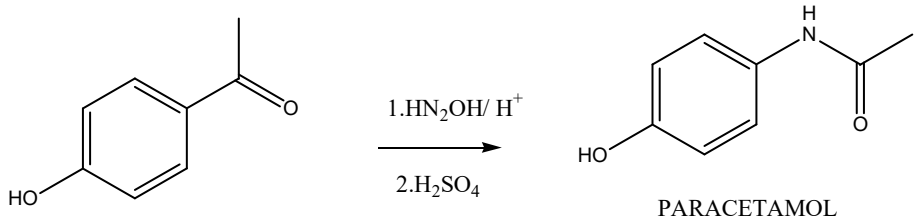
Step 5: Tautomerism



Applications

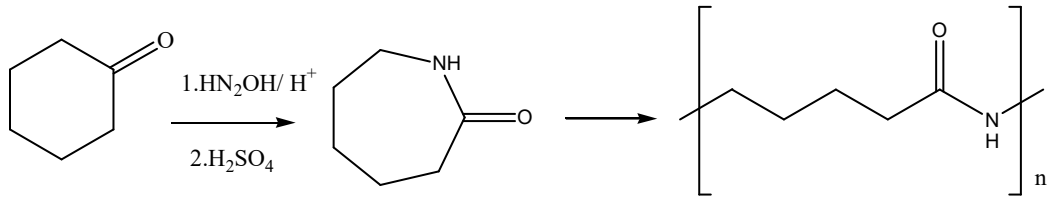


Ketone Amide



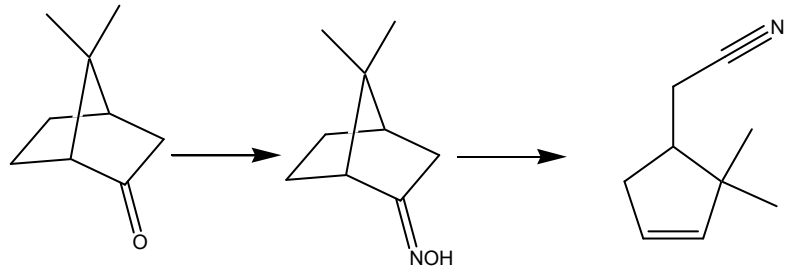
PARACETAMOL

Lactam or cyclic amide with ring enlargement



Caprolactam Nylon 6

Side reaction



Nitrile formation

Mechanism of side reaction