



Salahaddin University – Erbil
College of Science
Chemistry Department

Practical Organic chemistry
3rd Stage

Experiment (2):

Hofmann rearrangement (degradation)

of Benzamide

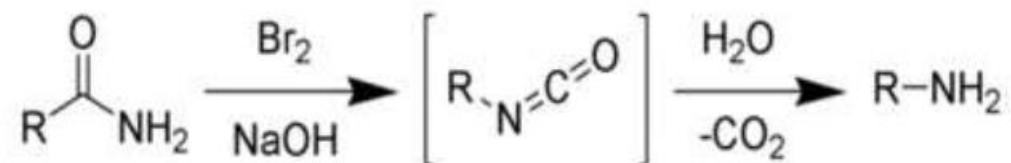
2023- 2024

Rearrangement reaction is a broad class of organic reactions where the carbon skeleton of a molecule is rearranged to give a structural isomer of the original molecule. Often a substituent move from one atom to another atom in the same molecule

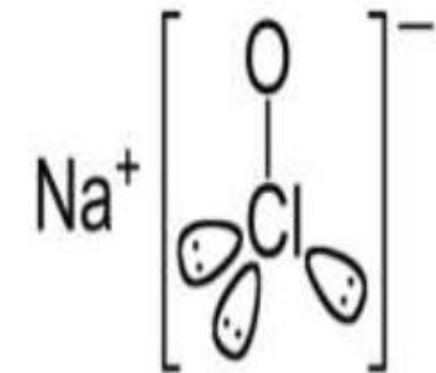


The Hofmann rearrangement of an amide to form an amine with carbon dioxide loss is an example of reaction where alkyl or aryl groups migrate to electron-deficient nitrogen atoms. First published 1881 Hofmann, A. W. Chem.

Hofmann Bromide Reaction is the conversion of an Amide to a 1° Amine containing one less carbon atom than the original amide. Thus, it is also known as Hofmann Degradation of Amide. The reaction is achieved by heating the amide with in presence of an alkali (NaOH or KOH).

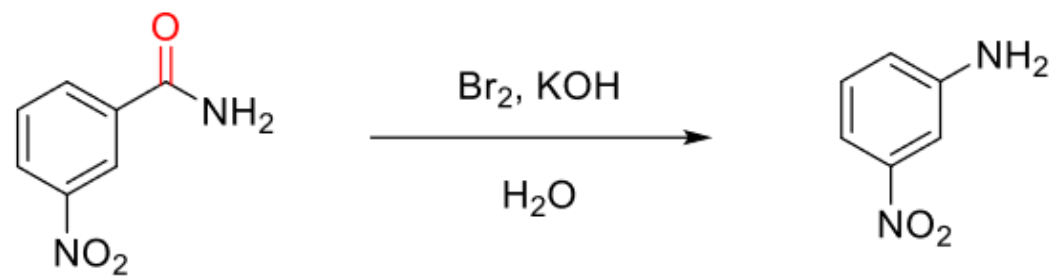
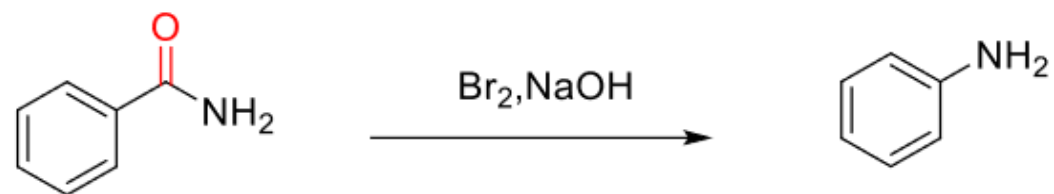
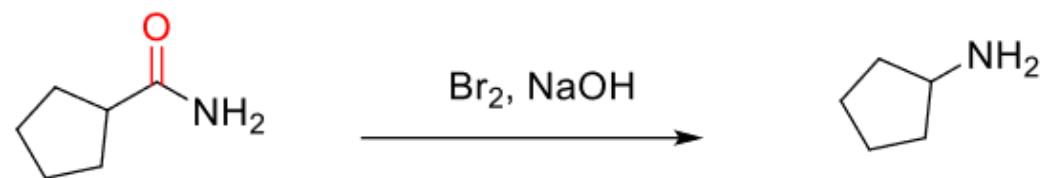


Sodium hypochlorite is a strong oxidizing agent in liquid form and is greenish or yellowish in color. It is commonly referred to as bleach because it is the active ingredient in bleach. Its chemical formula is NaClO, composed of one sodium (Na) atom, one chlorine (Cl) atom and one oxygen (O) atom



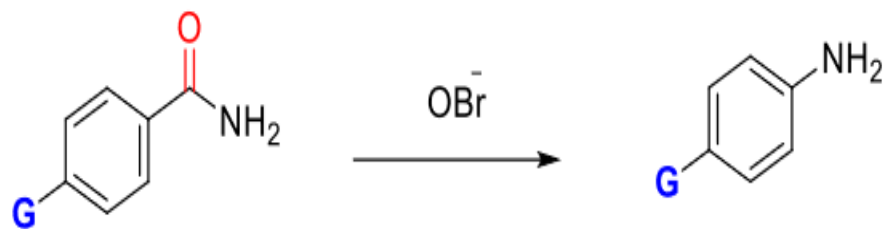
Sodium Hypochlorite Chemical Structure

Example:

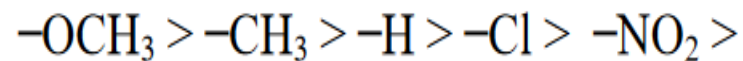


Further, in arylamide, i.e., when the migrating group is aryl, then the rate of Hofmann reaction gets increased by presence of electron-releasing (donating) substituents in the aromatic rings.

For instance, in the case of substituted benzamide as:

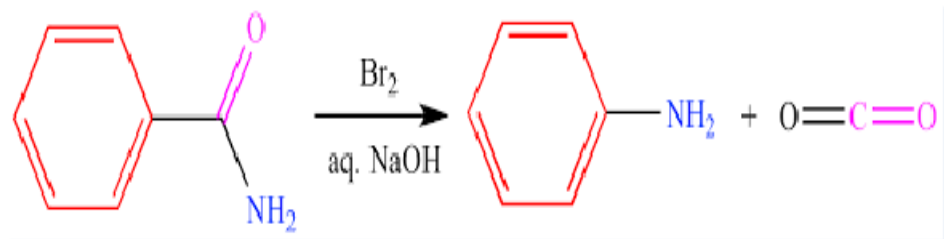


The reactivity of **G** is of the following order:



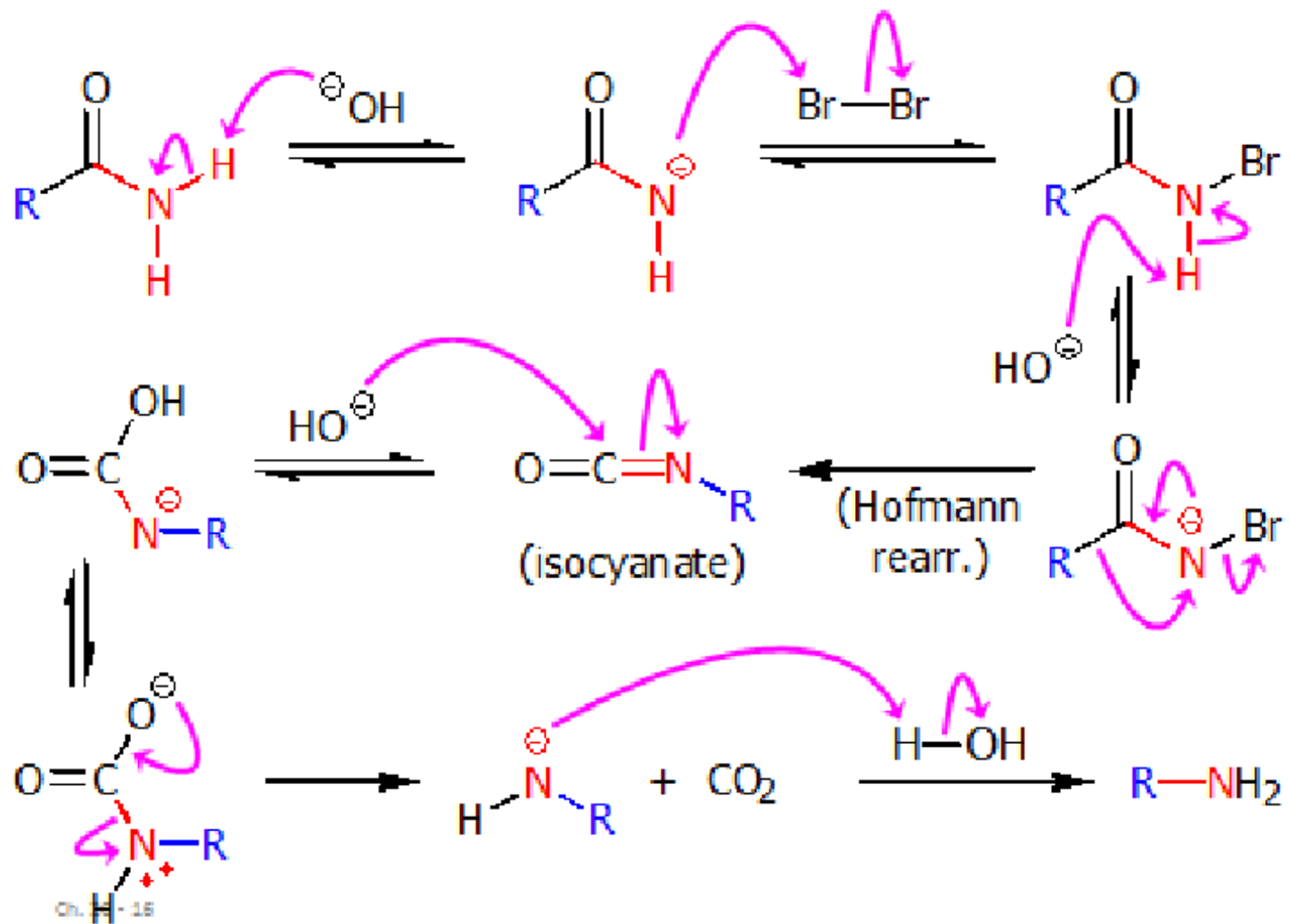
Mechanism of the Hofmann Rearrangement

Treatment of an amide with sodium hypobromite or sodium hypochlorite (or with the halogen and alkali), results in the amine of one less carbon atom being produced. The net result being the elimination of the carbonyl group.



The Hofmann rearrangement involves 6 steps in 3 stages:

- 1) formation of an N-bromo amide (2 steps)
- 2) conversion of the N-bromo amide to an isocyanate (2 steps)
- 3) hydrolysis of the isocyanate (2 steps)

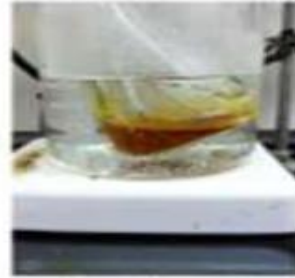


Procedure:

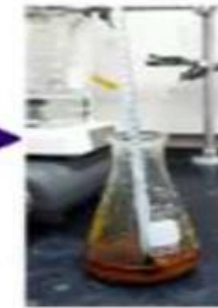
Add 1g of m-nitrobenzamide to Erlenmeyer flask then add 10 mL (1M) NaOH and 10 mL of household bleach. the well-stirred mixture was heated at 80 °C in water bath for 30 min. The mixture was cooled to 50 °C and then 10% aqueous NaHSO₃ (10 mL) was add then filtrate the ppt.



After 10 minutes of stirring, the mixture turned a bright orange color.



After 30 minutes of stirring, the mixture turned a dark brown color.



The mixture was then cooled to 50 °C and 10% aqueous NaHSO₃ (10 mL) was added. The mixture turned a lighter orange color.



The solution was cooled to a temperature of 50 °C for 15 minutes.



The product was then collected with a Buchner funnel and washed with cold water.