

# ORGANIC NAMED REACTION 1.

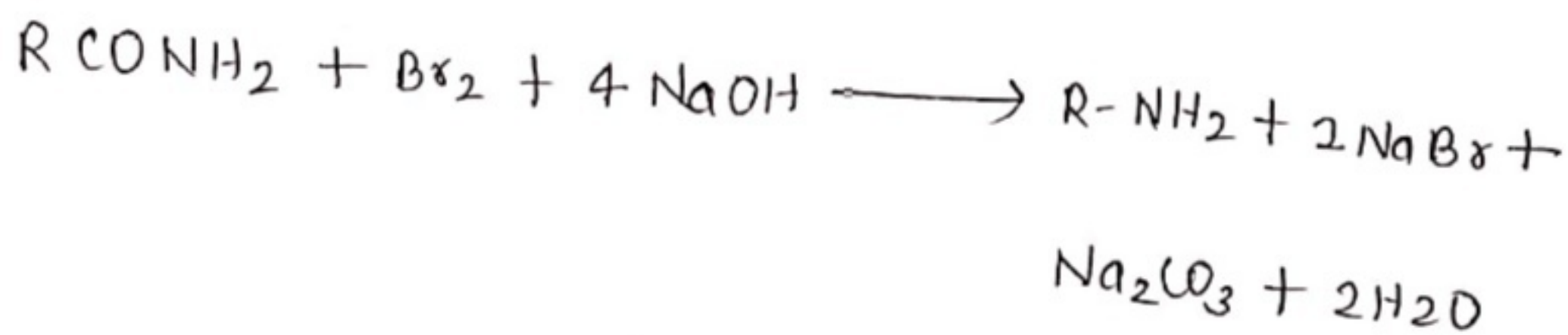
DEGREE-III (H), PAPER-VII

LECTURE-9, DATE : 23/09/2020

## HOFMANN REARRANGEMENT

\* When an amide is treated with bromine in alkali solution (or sodium hypobromite), it is converted to a primary amide that has one carbon atom less than the starting amide. This reaction is known as Hofmann degradation or Hofmann rearrangement. This is also referred to as Hofmann bromamide reaction.

\* The reaction can be used for the preparation of alkyl, aryl or heterocyclic amines.



## Mechanism

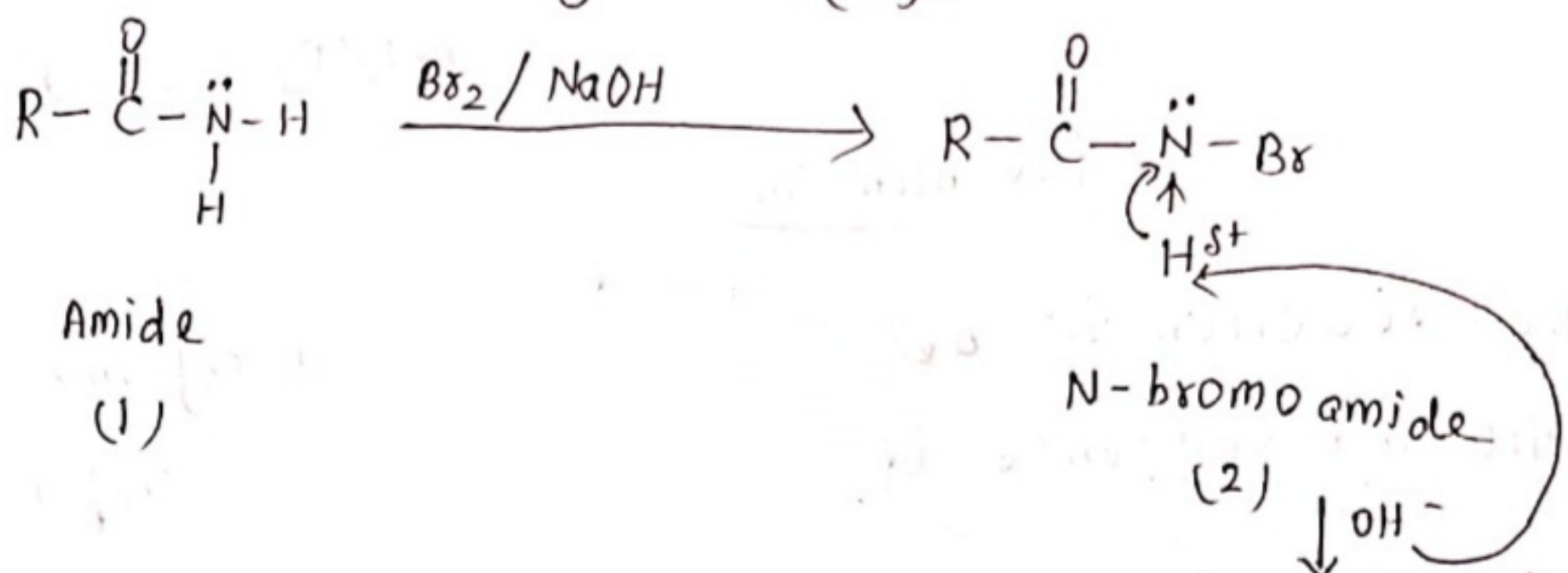
\* The reaction is believed to proceed by the following sequence of steps. In the first step,



N-bromamide (2) is formed by the action of alkaline hypobromite on the amide (1). The N-hydrogen atom of N-bromamide (2) becomes acidic because it has electron withdrawing acyl and electronegative halogen functions.

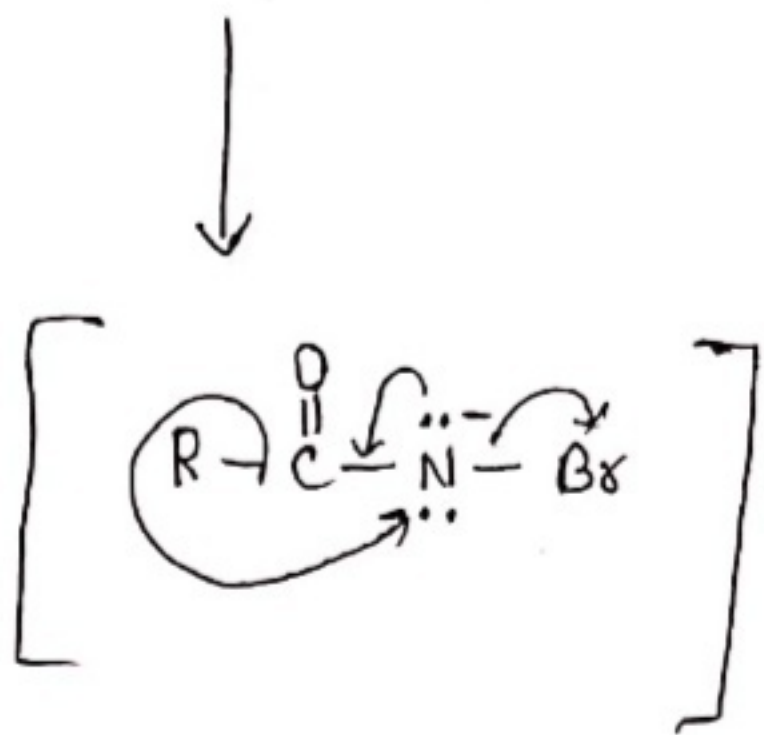
The second step in the reaction involves removal of the acidic hydrogen from the N-haloamide (2) by the basic hydroxide ion. Removal of this proton by base gives the transit nitrogen anionic species (3), which is unstable and loses bromide ion with the simultaneous migration of acyl or alkyl group from the adjacent carbon atom to the nitrogen.

The resulting isocyanate (4) is hydrolysed under the reaction conditions to N-substituted carbamic acid (5) which is unstable and finally decarboxylates into the primary amine (6).

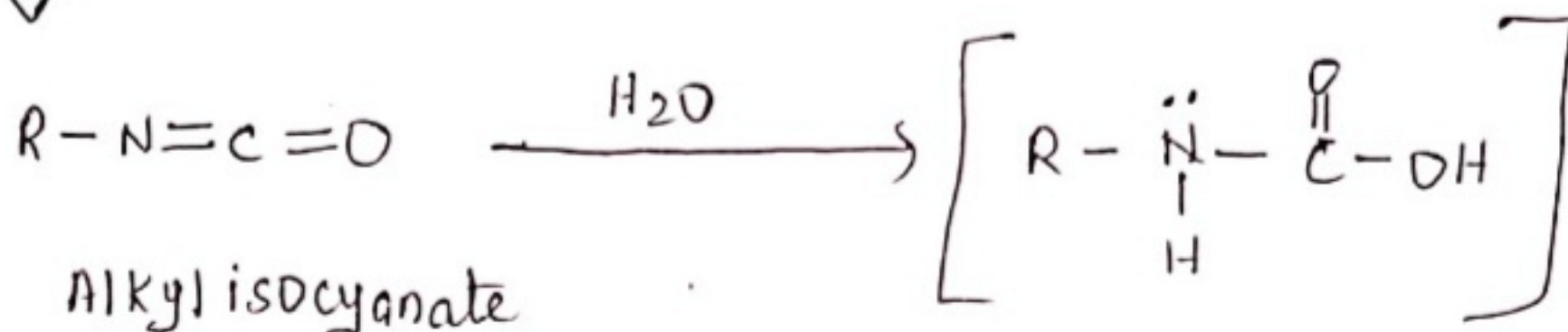
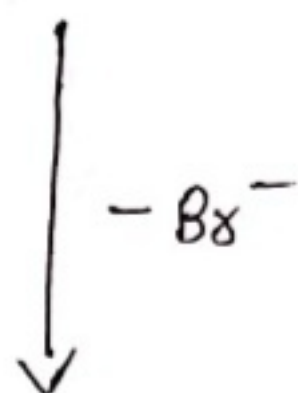


\*\* continued

3.



(3)



Alkyl isocyanate

(4)

N-alkyl carbamic acid

(5)



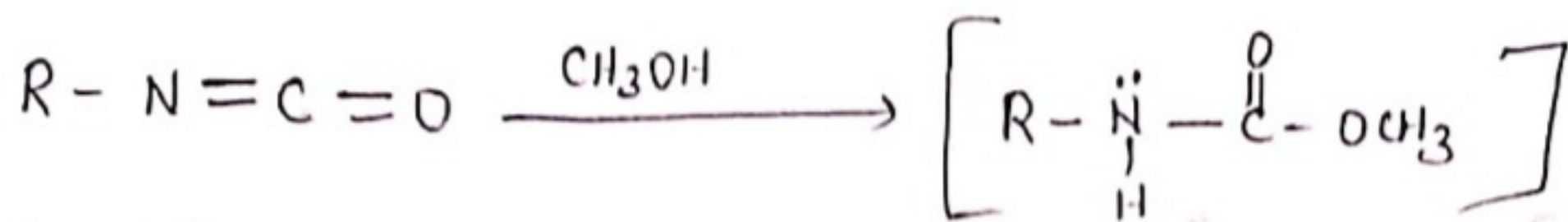
$R-NH_2$

Amine (6)

\* When the reaction is carried out in methanol, the intermediate isocyanate is converted into methyl carbamate (7), which may be isolated and hydrolysed subsequently.

Hydrolysis of methyl carbamate yield amine.





Alkyl isocyanate

(4)

Methyl carbamate

(7)

R-NH<sub>2</sub>

Amine (6)

- \* It is believed that the loss of halogen ion and the shift of alkyl or aryl group occurs simultaneously. Migrating group does not break away from the carbon till it has started to bind itself with nitrogen. Hence, the reaction must proceed through a transition state in which the migrating group is partially bonded to both the migrating origin and the migration terminus.

**To be continued in next lecture..**

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