

SYNTHETIC REAGENTS 1.

D-III (H), ORGANIC CHEMISTRY, P-VII

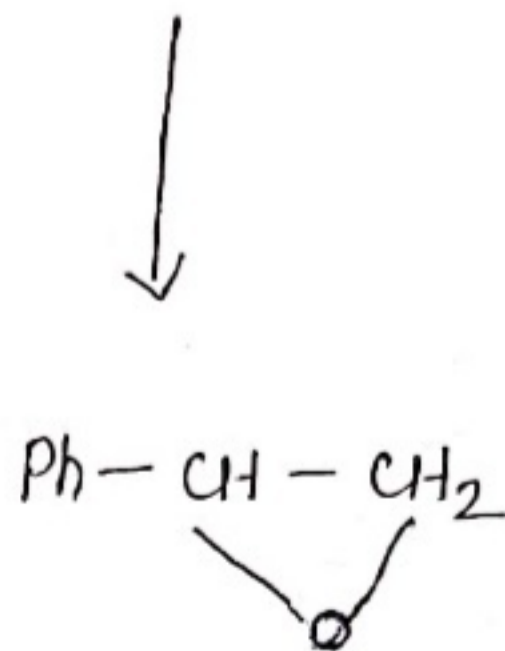
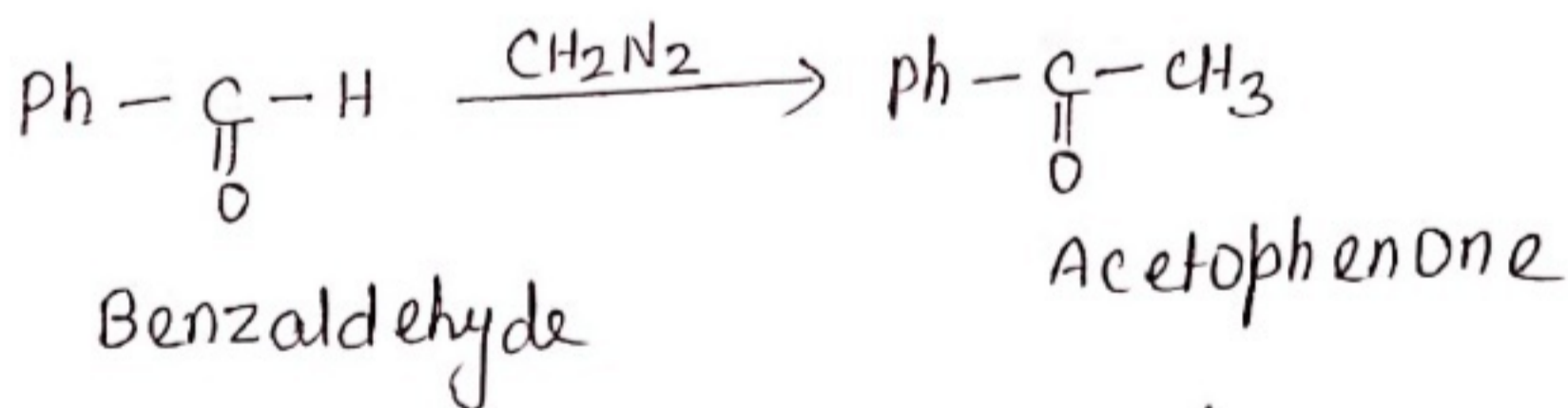
LECTURE-13, DATE 27 AUG.2020

TOPIC : DIAZOMETHANE (CONTINUED)

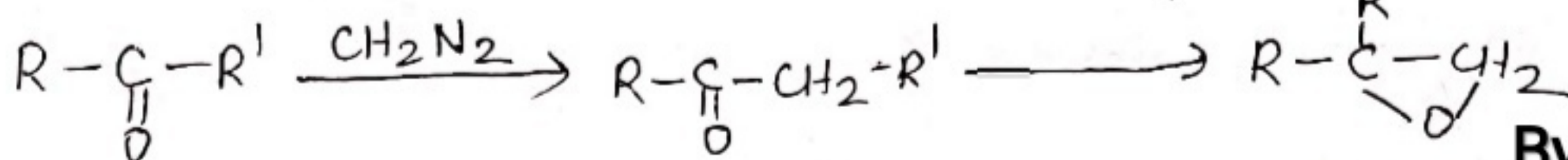
HOMOLOGATION

a) Diazomethane reacts with aldehydes to give methyl ketones, as illustrated by the conversion of benzaldehyde to acetophenone.

* Ketones can be converted to their higher homologues with diazomethane.

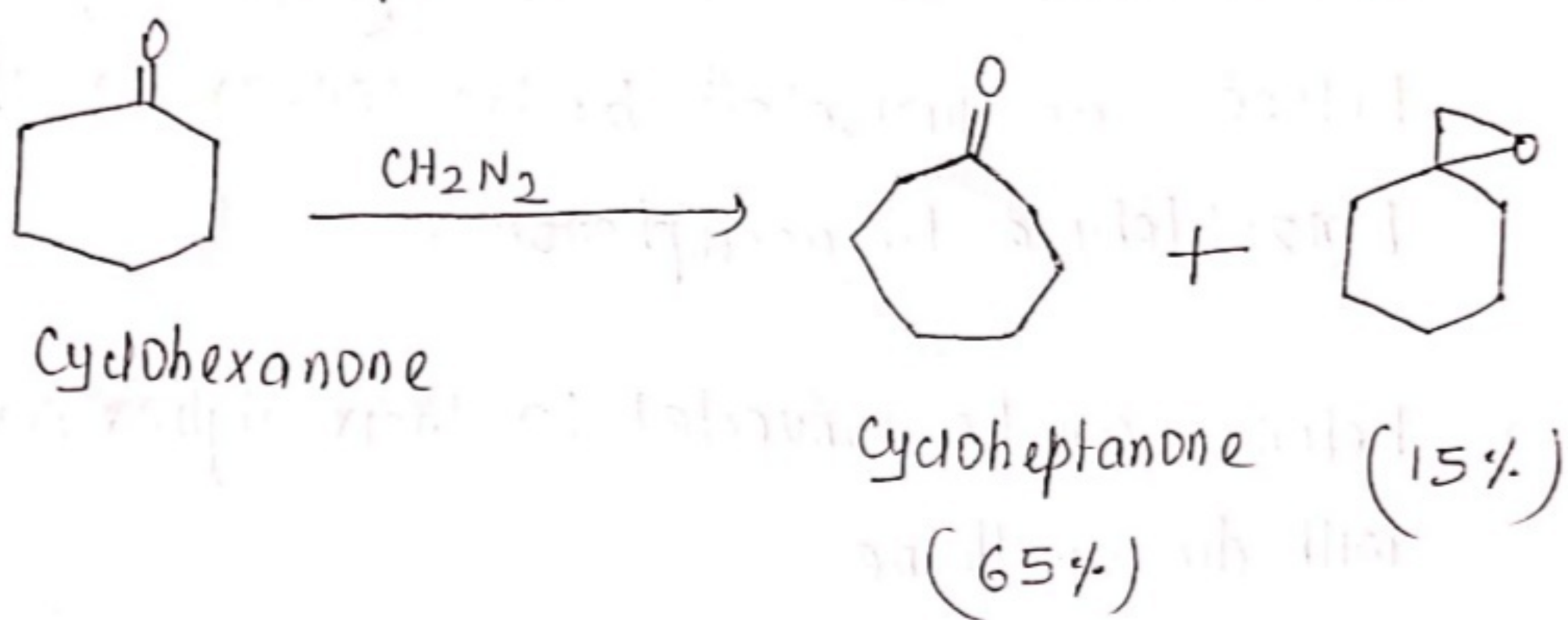


Epoxide

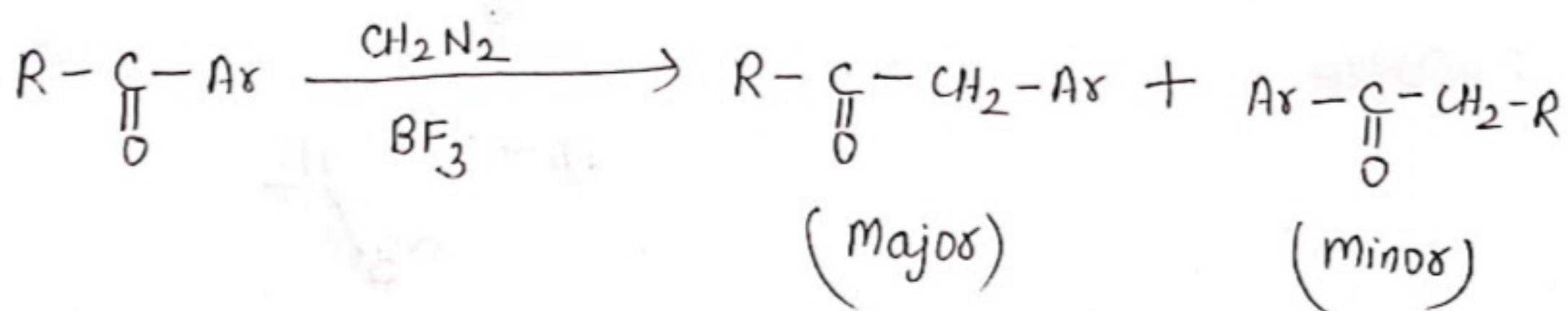


* Certain cyclic ketones undergo homologous ring enlargement when treated with CH_2N_2 in the presence of alcoholic solvents.

eg, cycloheptanone is prepared from cyclohexanone on reaction with CH_2N_2 in 65% yield, along with 15% of epoxide.



* Aliphatic and aryl alkyl ketones react similarly but generally require an acid catalyst. The reaction is catalysed by BF_3 and there is a preference for aryl migration.



Mechanism

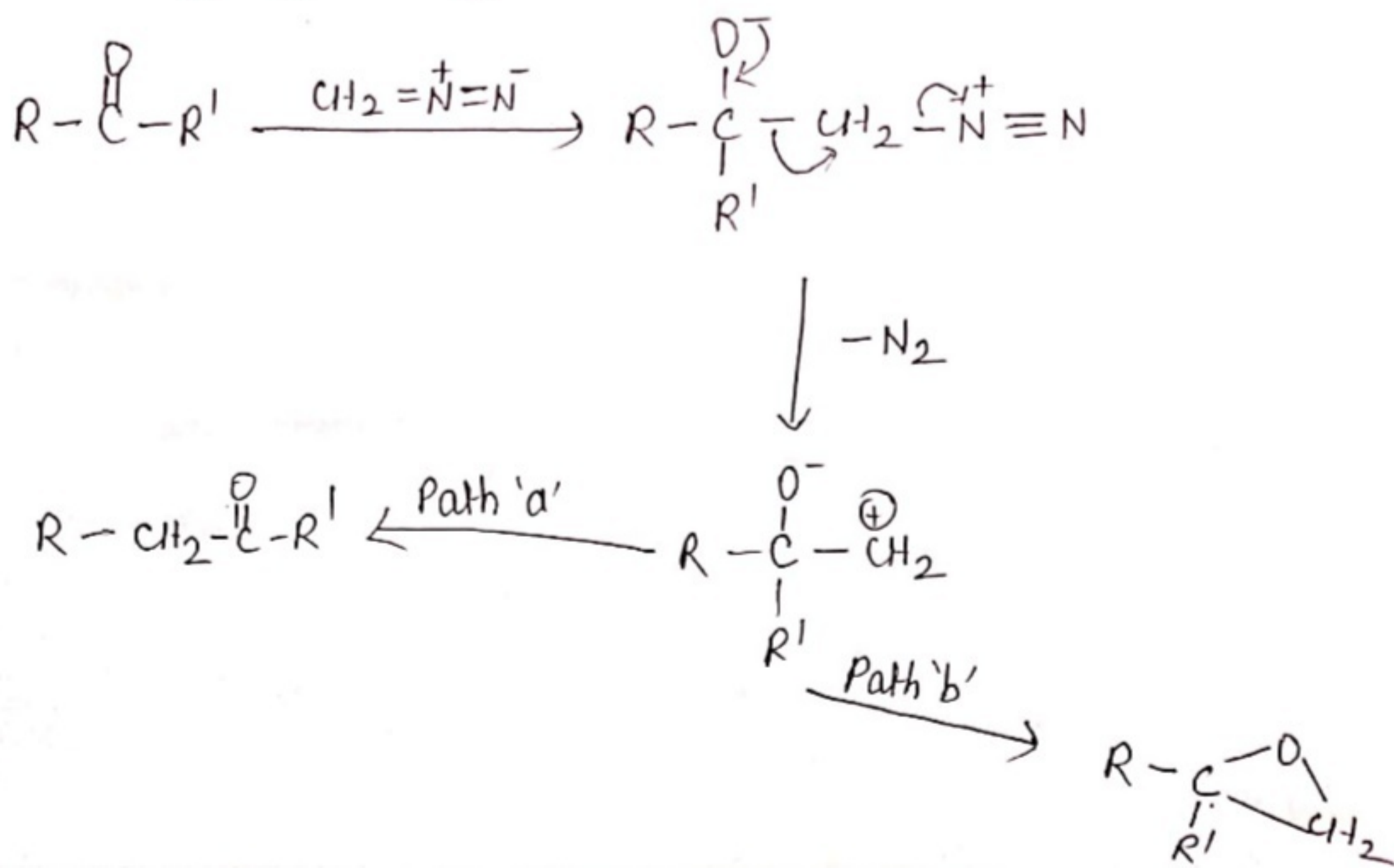
3.

* The reaction involves rearrangement and no free carbene is involved.

First step is the addition of diazomethane to the carbonyl group of the aldehyde or ketone.

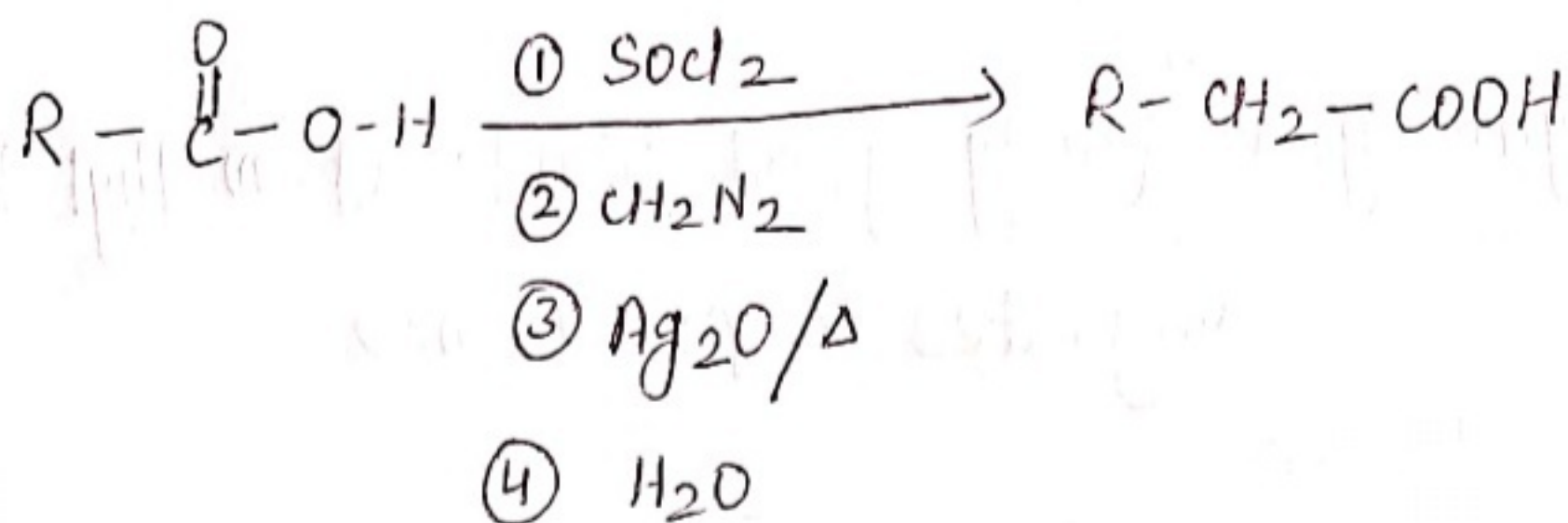
* The resulting betain loses nitrogen to give intermediate which undergoes rearrangement to yield higher ketones (Path 'a') or can also cyclise to give epoxide (Path 'b').

* Aldehyde give fairly good yields of methyl ketones i.e; hydrogen migrates in preference to alkyl.



b. Arndt-Eistert Reaction :

- * This reaction is used for converting a carboxylic acid into its next higher homologue.
- * Acid chloride reacts with diazomethane to give α -diazoketone, which rearranges with loss of nitrogen in the presence of colloidal silver to give ketene.
- * The ketene is subsequently converted to carboxylic acid or its derivatives.



To be continued in next lecture..

By: Dr. Rinky

Dept. of Chemistry.

J.N. College, Madhubani.