26 AUG 2020

SYNTHETIC REAGENTS

DEGREE-III (H) ,LECTURE-12

ORGANIC CHEMISTRY , PAPER-VII

TOPIC : DIAZOMETHANE Continue..

Methylation

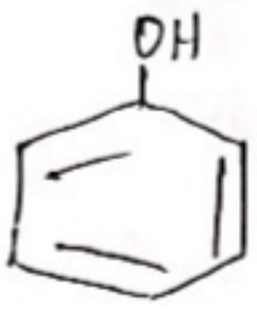
* Diazomethane methylates acidic hydroxy groups, Carboxylic acids, Sulphonic acids, phenols and enols.

* Conditions are mild and high yields are obtained. It reacts with carboxylic acid to liberate nitrogen and form methyl ester.

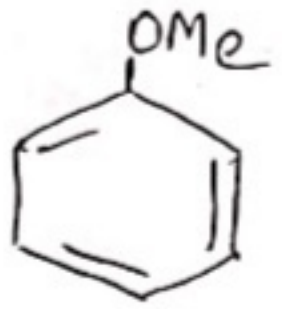
* Typical examples of methylation with diazomethane are preparation of methyl ester of cinnamic acid from cinnamic acid anisole from phenol.

$$C_6H_5 - CH = CH - COOH \xrightarrow{CH_2N_2} C_6H_5 - CH = CH - COOCH_3$$

Cinnamic Acid — Methyl Cinnamate



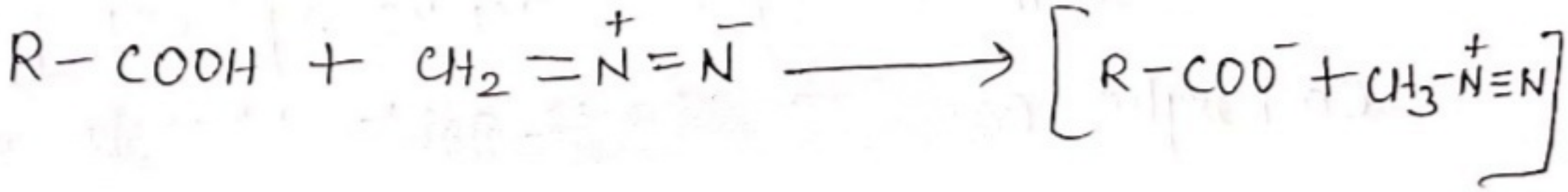
+ CH_2N_2 ⟶



Phenol — Anisole

* Methyl esters are prepared by treating a solution or suspension of the carboxylic acid with an ether solution of diazomethane.

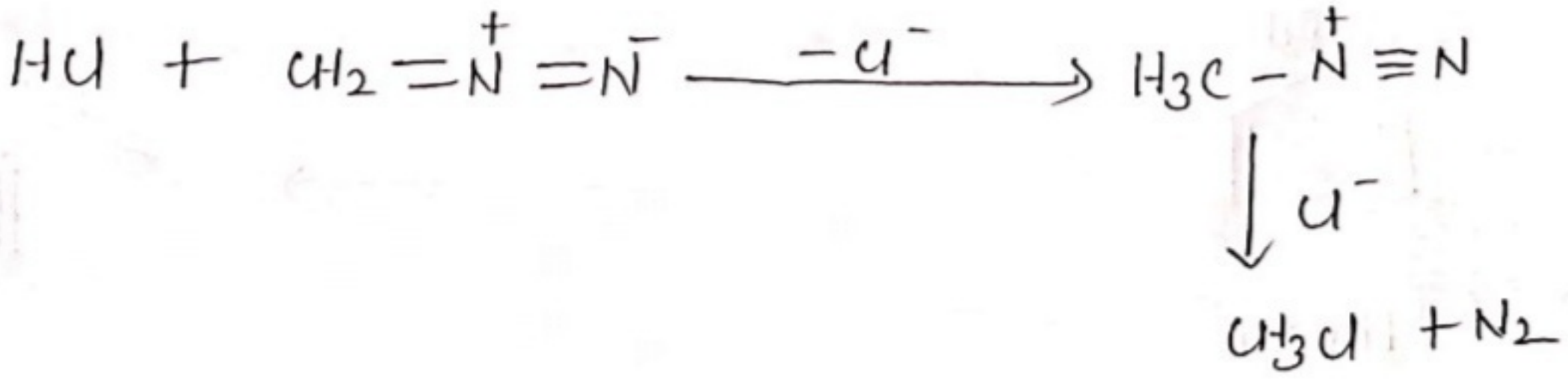
* The mechanism of the reaction is given below:-



* Diazomethane deprotonates the acid forming methyl diazonium ion and weak nucleophile, $R-COO^-$.

* Although $R-COO^-$ is a weak nucleophile, it can displace the excellent leaving group, nitrogen (N_2)

* Similarly, halogen acids react with CH_2N_2 to form methyl halides.



* Ordinary alcohols and amines because of the low acidity of the hydroxyl hydrogen, react with CH_2N_2 in the presence of catalyst

* Aluminium chloride, boron trifluoxide etherate and fluoroboric acid are employed as catalyst.

$$CH_2N_2 + R\text{-}OH \xrightarrow{BF_3\text{-}Ether} CH_3\text{-}O\text{-}R + N_2$$

$$R\text{-}OH + CH_2{=}\overset{+}{N}{=}\bar{N} \longrightarrow \left[R\bar{O} + CH_3\text{-}\overset{+}{N}{\equiv}N\right]$$

$$\downarrow S_N2$$

$$\boxed{R\text{-}O\text{-}CH_3} + N_2$$

* $CH_2N_2 + R_2NH \xrightarrow{BF_3\text{-}Ether} CH_3NR_2 + N_2$

To be continued in next lecture