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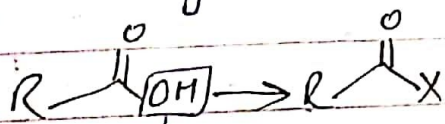
## Wolf Rearrangement:-

It is a rearrangement reaction in which a diazo ketone is converted into ketene. Takes place in the presence of light, heat or transition metal catalyst, such as  $Ag_2O$ .

### Substrate:-

Substrate is acid halide which is generated from carboxylic acid.

Ketone may also be taken as substrate.

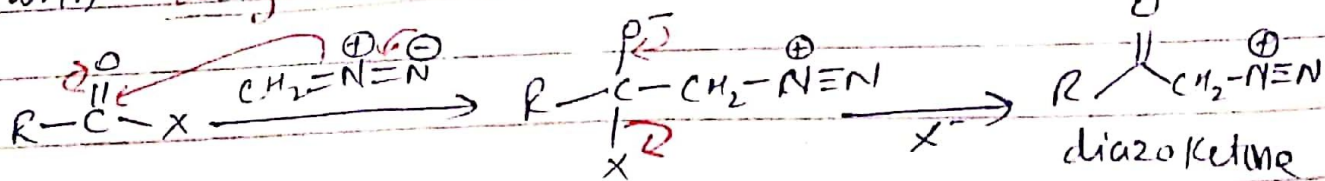


↓ decrease the electrophilic nature of carbonyl carbon, thus we make it (replace by) good nucleophile- since it leaves.

So, actually the starting material is carboxylic acid and it is halogenated to make a good leaving group. it is called activation

of carbonyl carbon (generation of good electrophile).

Reagent:- We react the acid halide or ketone with diazo methane.



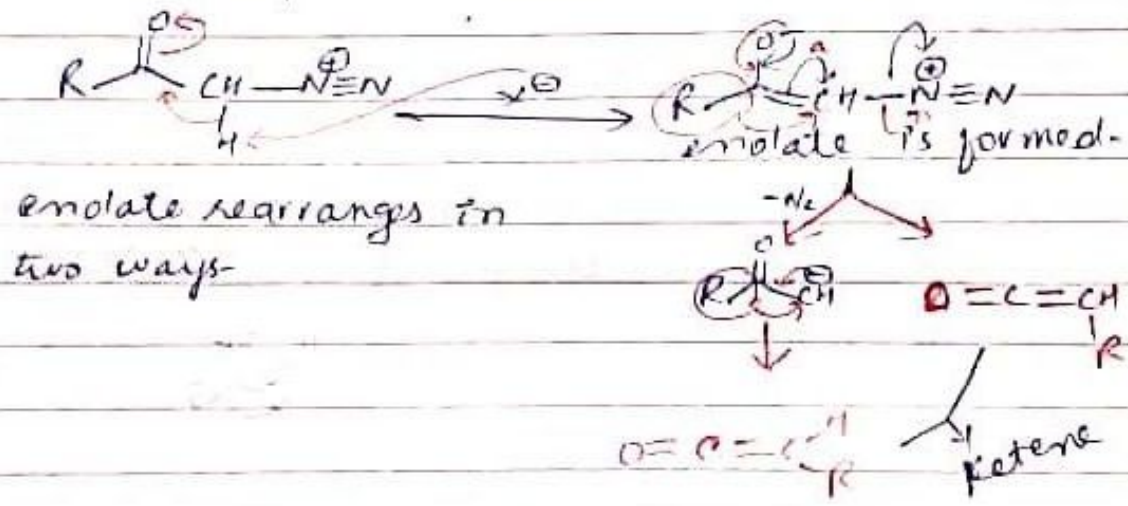
It has also good leaving group in the form of  $^+N_2C=N_2$ . All the atoms involve in reaction.  $X^-$  leaves and become good nucleophile and base (where unsaturation present the electron is electron withdrawing).

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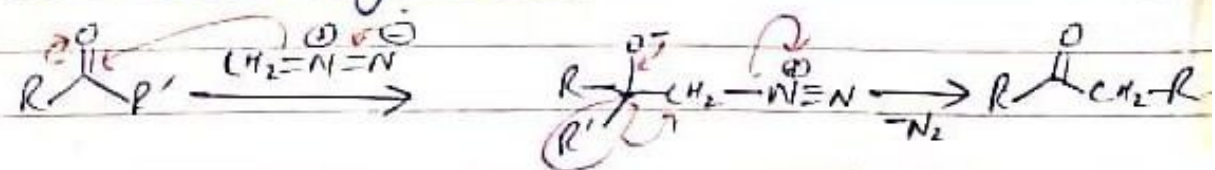
⇒ In our compound the  $\text{CH}_2$  (methylene) is bonded with two electron withdrawing groups ( $\text{C}=\text{O}$ ) and ( $\text{N}_2^+$ ). So, it becomes more polar and acidic and the H atom attached to it also become acidic.

⇒ While the  $\text{CH}_2$  present on other side of carbonyl group is not much acidic because of absence of  $\text{N}_2^+$  group at that side.

⇒ Thus  $\ominus \text{X}$  captures more acidic proton.

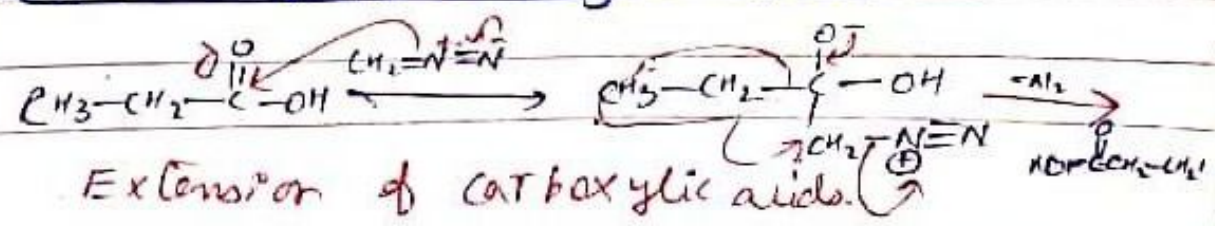


⇒ Reaction using Retone:-



It is the Extension of ketone. The ketonic product has one more extra carbon than in substrate ketone.

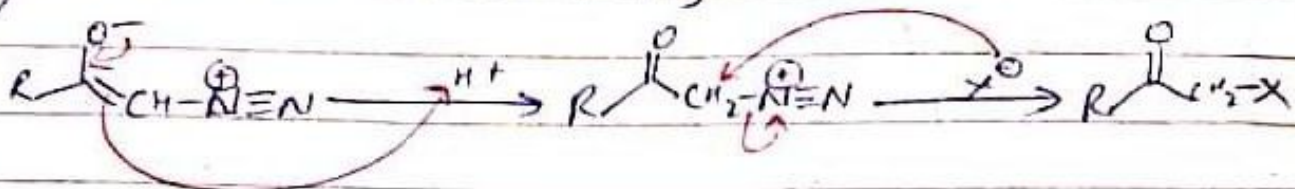
⇒ Reaction with carboxylic acids:-



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## Side product Mechanism

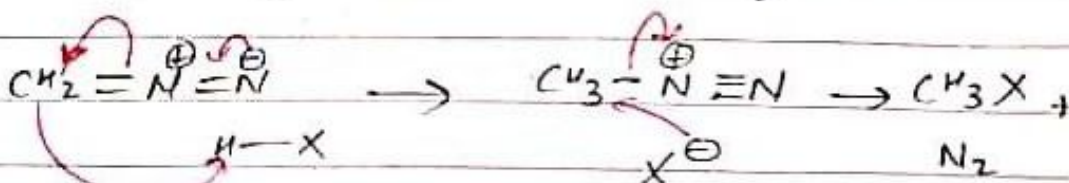
As  $H-X$  is formed and it is acidic in nature. So, it can protonate the carbanion (enolate) formed in the reaction- AS,



It is the extension of acid halide and it is side chain reaction and is called "Alndt-Fischer synthesis".

### Control of Reaction

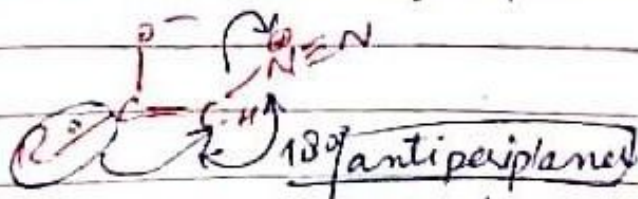
We can control the reaction by consuming  $H-X$ . We use diazomethane in excess. It act as base and quench the  $H^+$  of  $H-X$ .



Alkyl halide is formed which can easily be removed.

The reaction is just like the concerted mechanism. Thus, it is just like  $SN_1$ ,  $SN_2$  mechanism. Hence <sup>correct</sup> position is required.

The coming (attacking)  $N^+$  and leaving group must be at antiperiplanar with each other.



It is also called  $\alpha$ -enolate because