CONCEPT BOOSTER

Hello! This is my immense pleasure to present this article which is completely based on some minute details of ORGANIC REAGENTS controlling the mechanism of ORGANIC CHEMISTRY. It is my long teaching experience that has enabled me to understand the necessity of the functions of these reagents as per competitive examinations are concerned. Keep practicing and all the best for the examinations.

*Arunava Sarkar

A FEW SELECTIVE REDUCING AGENTS

Maximum of these reagents we have discussed earlier. Here, we are trying to cluster all the reagents with their functions and mechanisms.

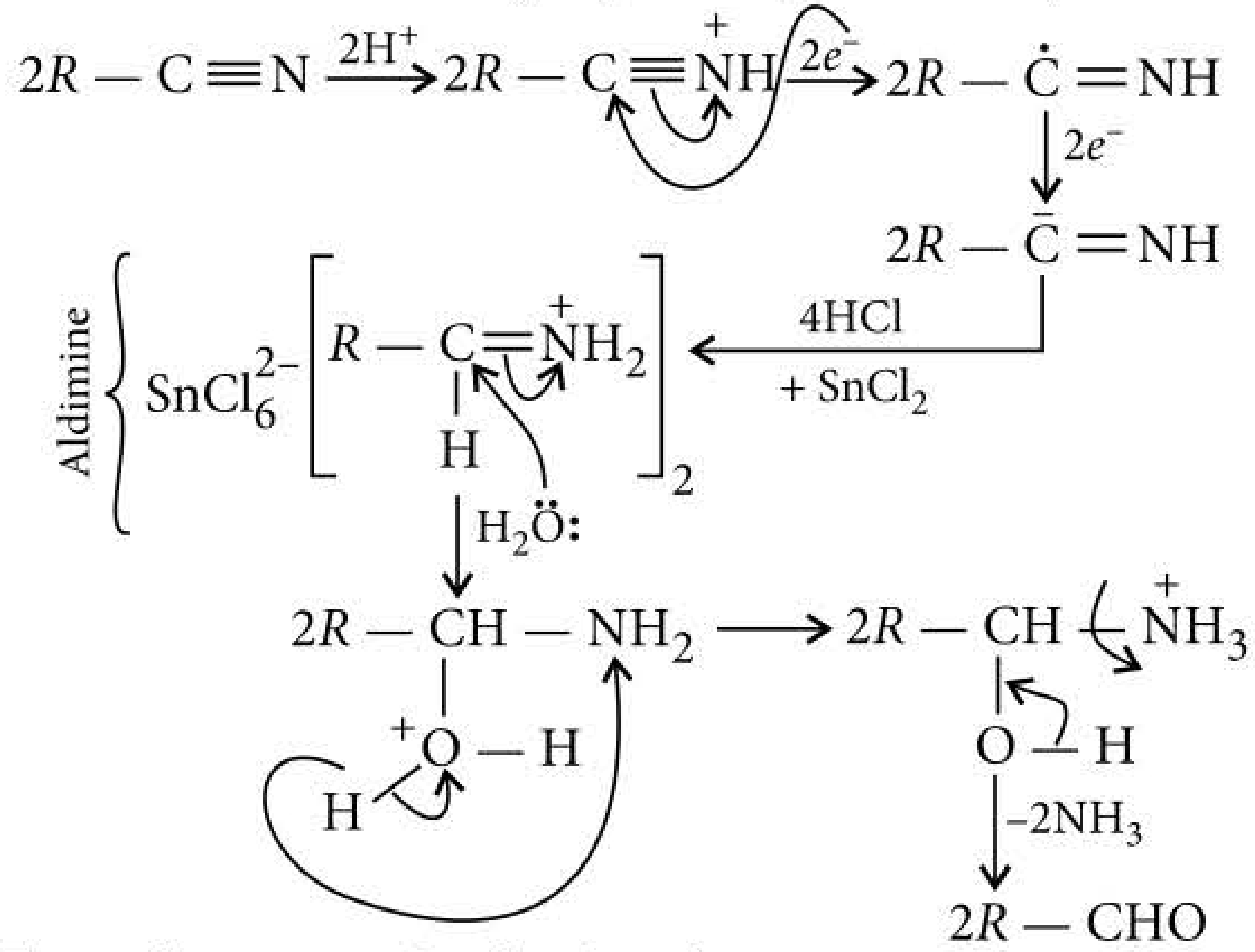
$SnCl_2 + HCl$

It is a milder reducing agent.

$$SnCl_2 + 2HCl \rightarrow SnCl_4 + 2H^+ + 2e^-$$

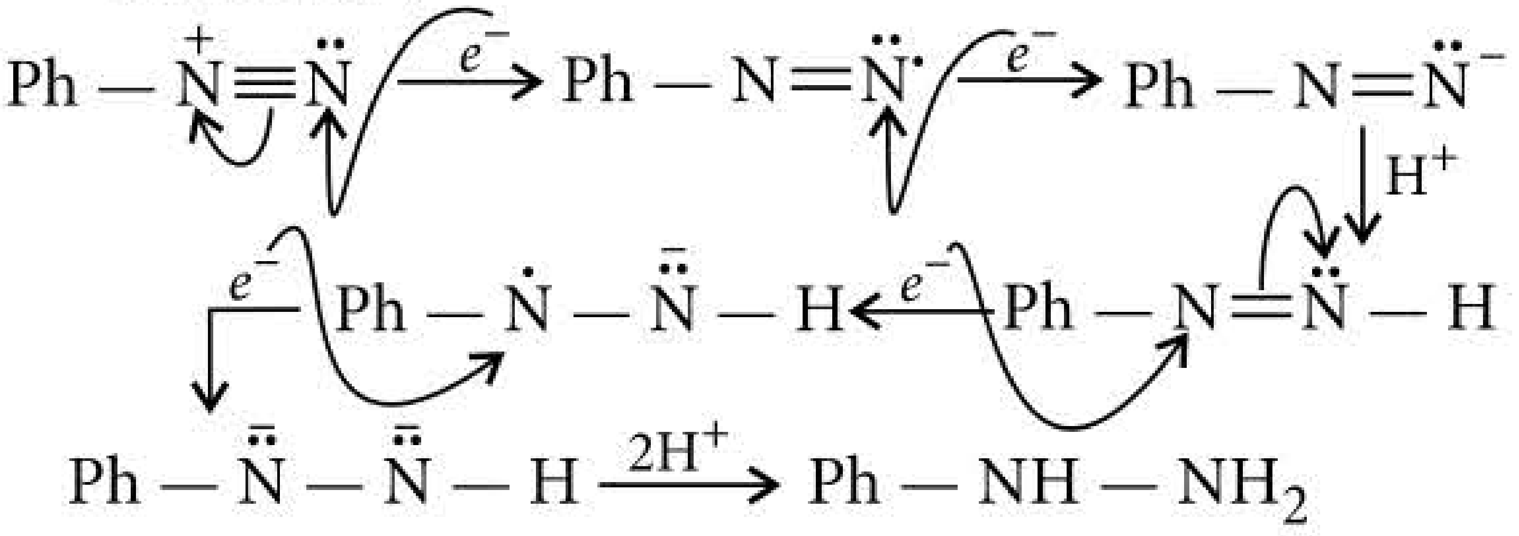
Two very important reactions under this reagent :

- **Reaction with alkyl cyanide ($R-C\equiv N$) :**



This is known as Stephen's reduction.

- **Reaction with diazonium salt (Benzene diazonium chloride) :**



$TiCl_3 + H_2O$

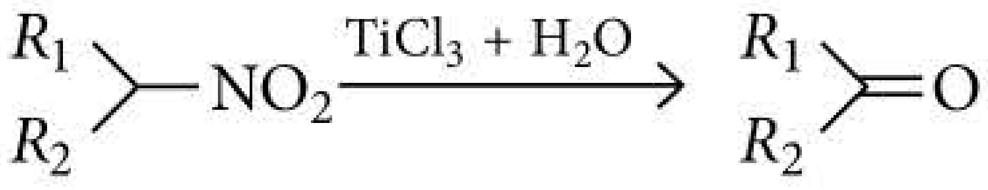
This is an electron transfer reagent.

Comparatively, milder and selective reducing agent.

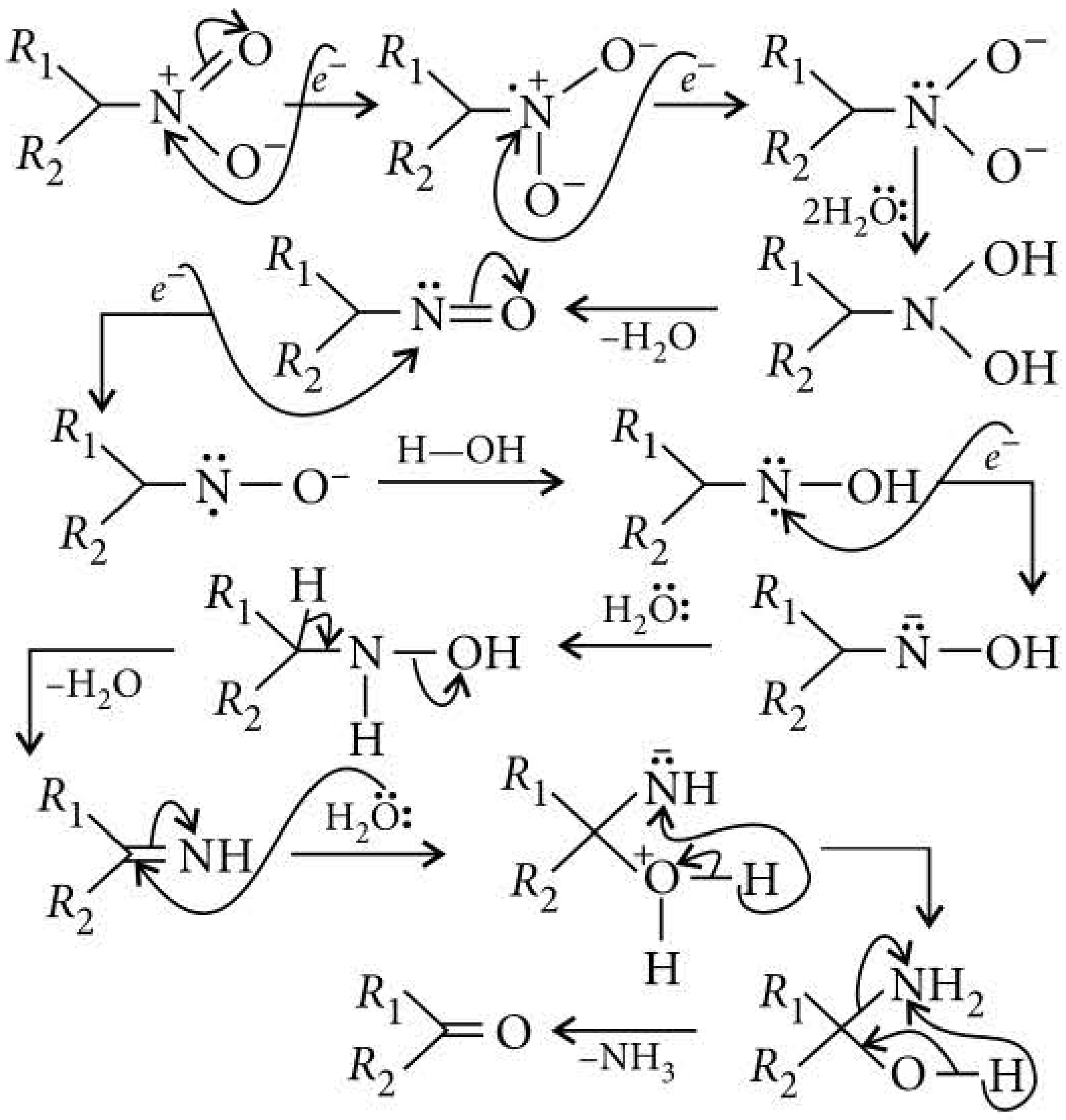
$$Ti^{3+} \rightarrow Ti^{4+} + e^-$$

Some most famous reactions shown by this reducing agent are as below :

- **Reduction of nitro group :**



Mechanism :



Overall this reaction is called to be reductive hydrolysis.

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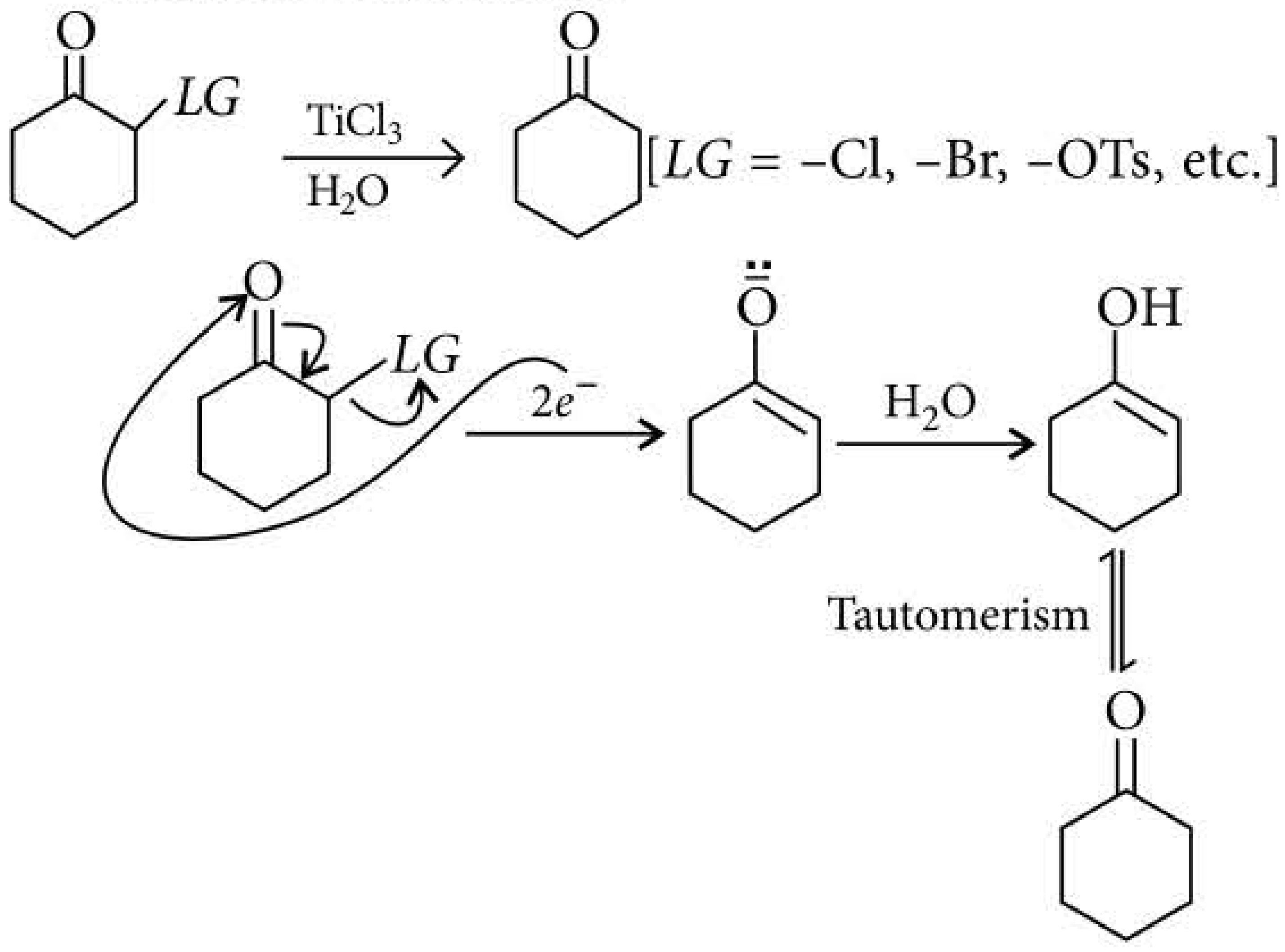
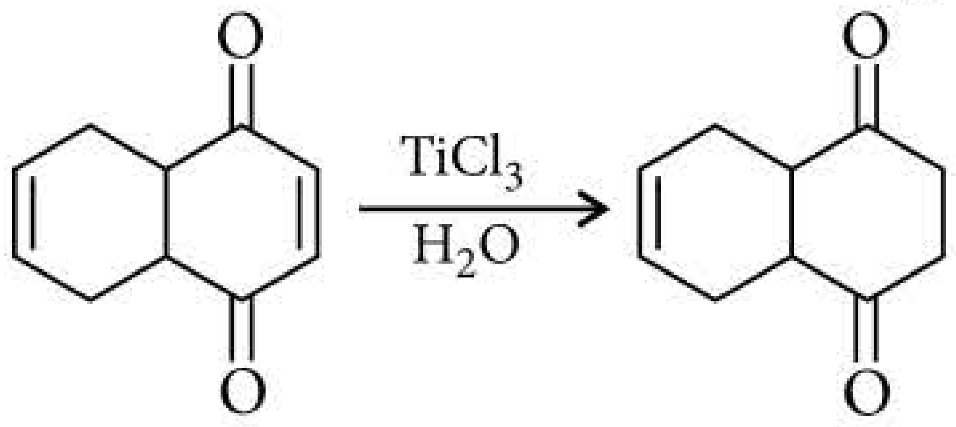
- There is another example which is known as reductive elimination.

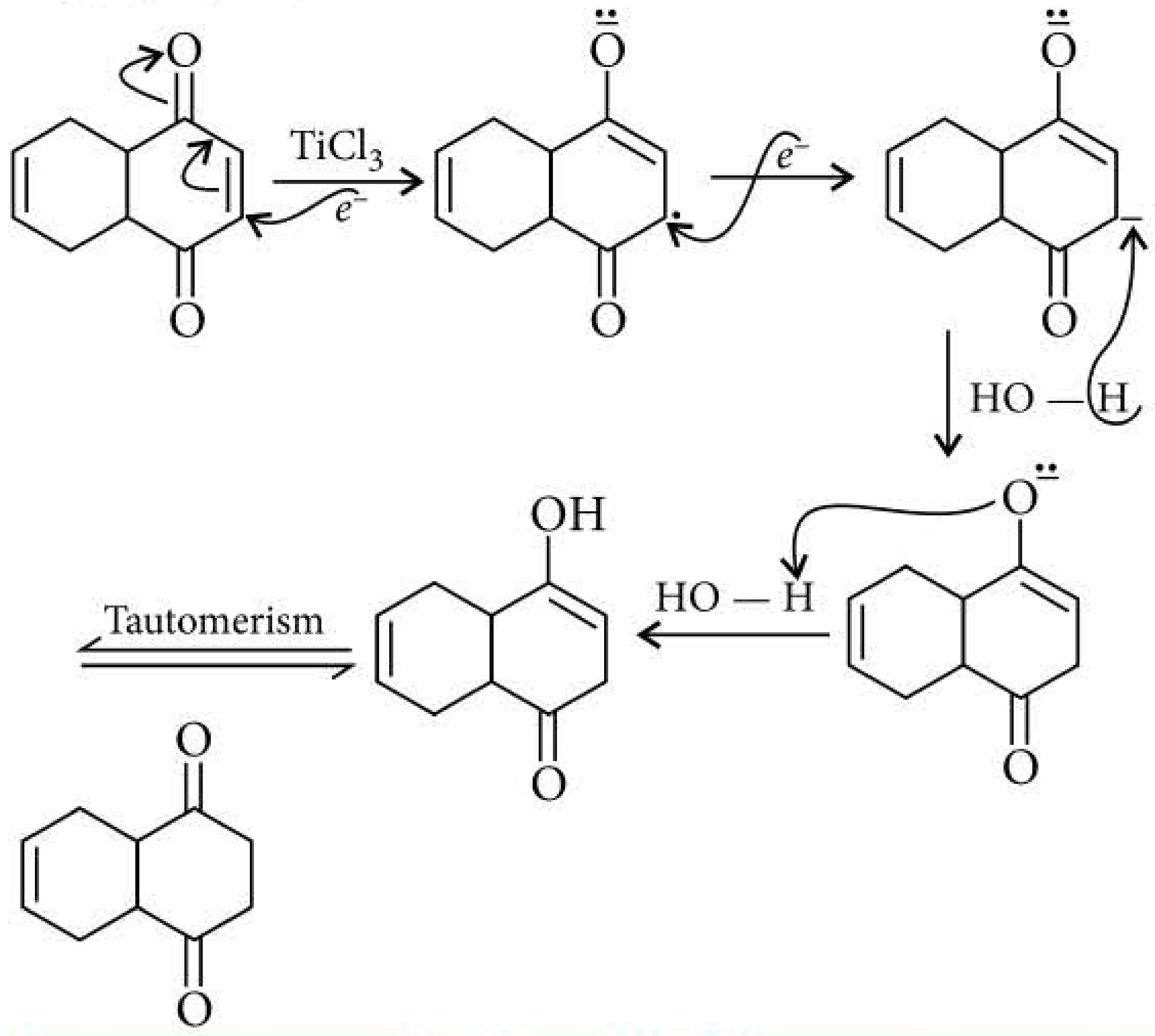


[LG = –Cl, –Br, –OTs, etc.]

- **Selective reduction :** The best example of this category is selective reduction of a particular *ene* of the diene-dione or selective reduction of *ene* of the ene-dione. Let us take the following example :



Mechanism :



$FeSO_4 + NH_4OH$

This is a milder and selective electron transfer reducing agent.

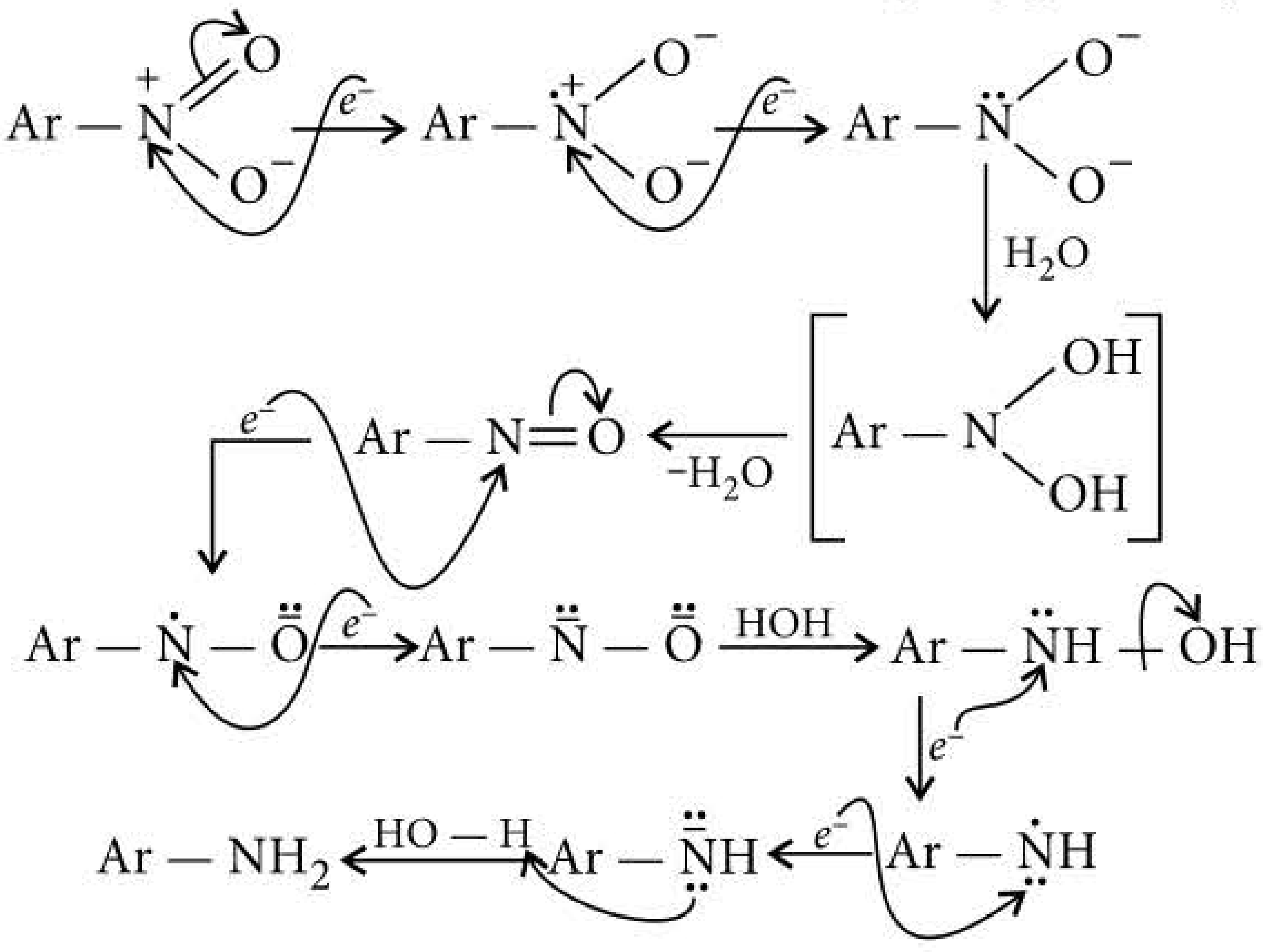
Working medium → Basic medium

- Selective reduction of aromatic nitro group to the aromatic amino group in presence of the other reducible groups.

e.g.,

$Fe^{2+} \longrightarrow Fe^{3+} + e^-$

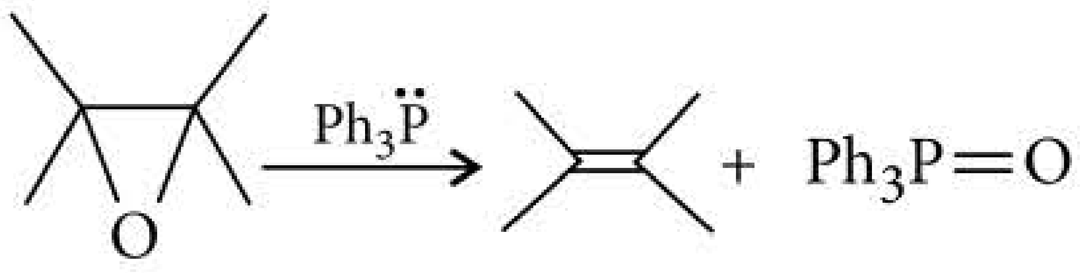
This electron transfer will reduce the nitro group preferably.



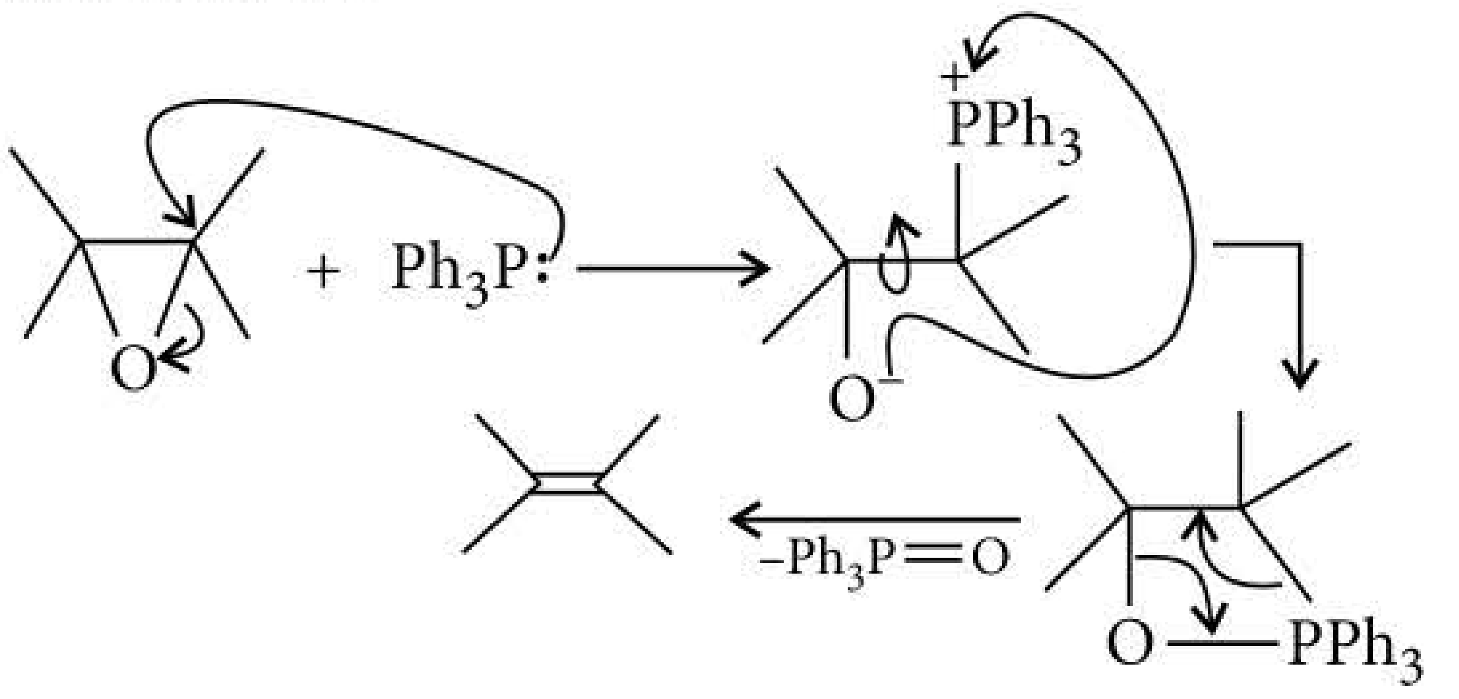
Phosphine Derivatives : Ph_3P and $(EtO)_3P$

We have seen the better use of Ph_3P : In Wittig reaction. It converts the carbonyl group into an alkene moiety. Some of the important reactions are as below :

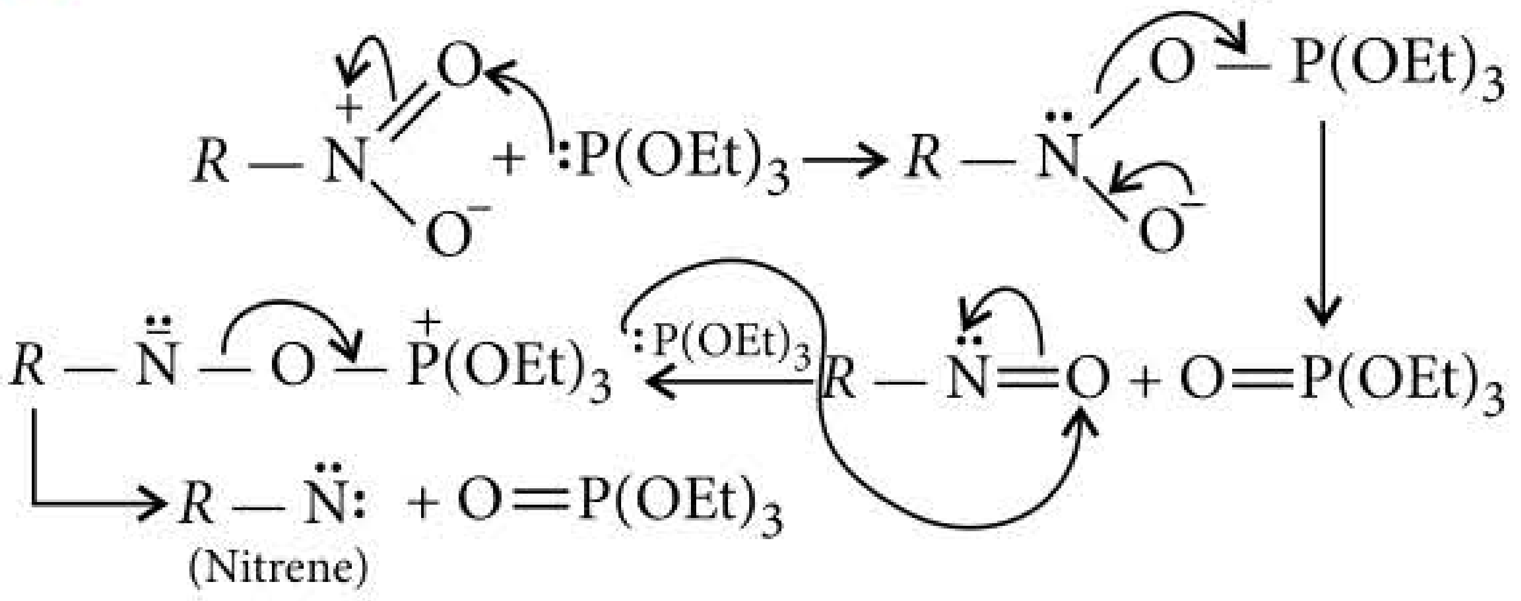
- **Conversion of epoxide to alkene :**



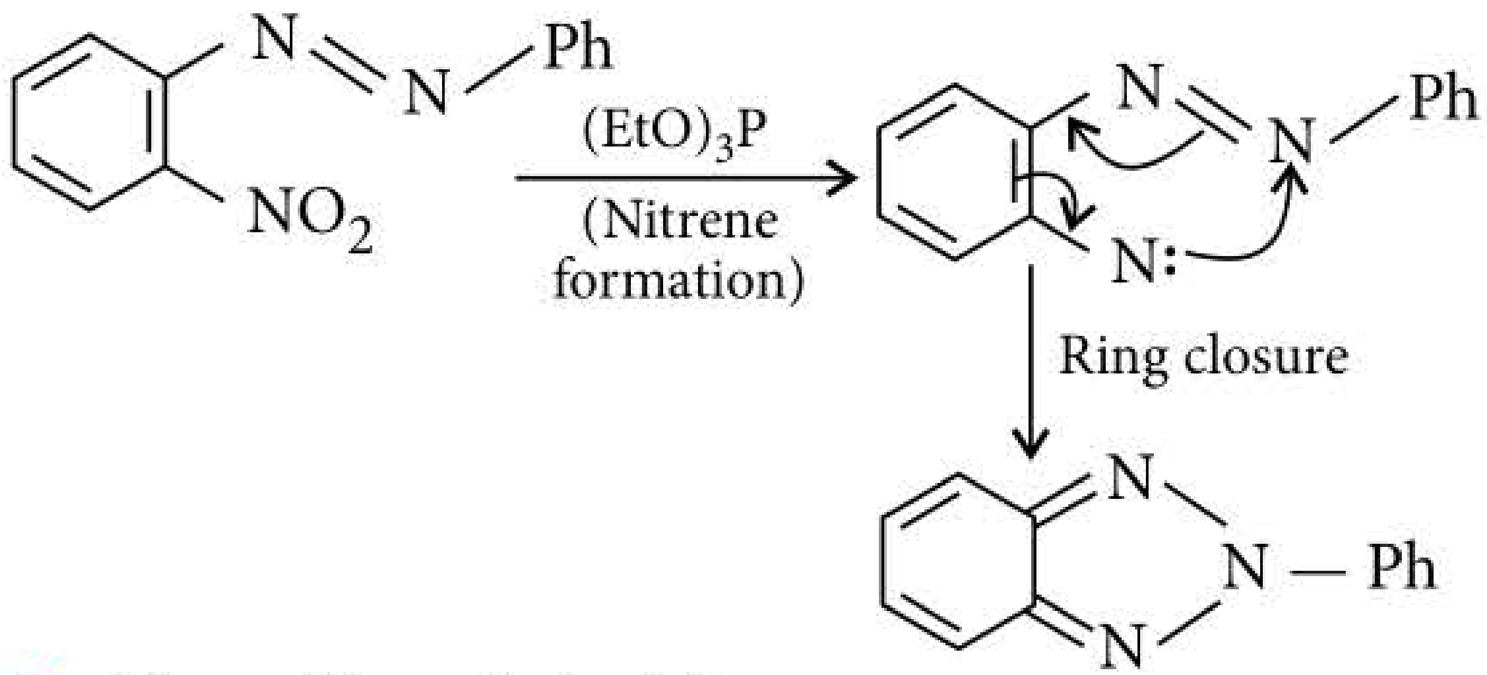
Mechanism :



- **Formation of Nitrene :** From nitro compound.

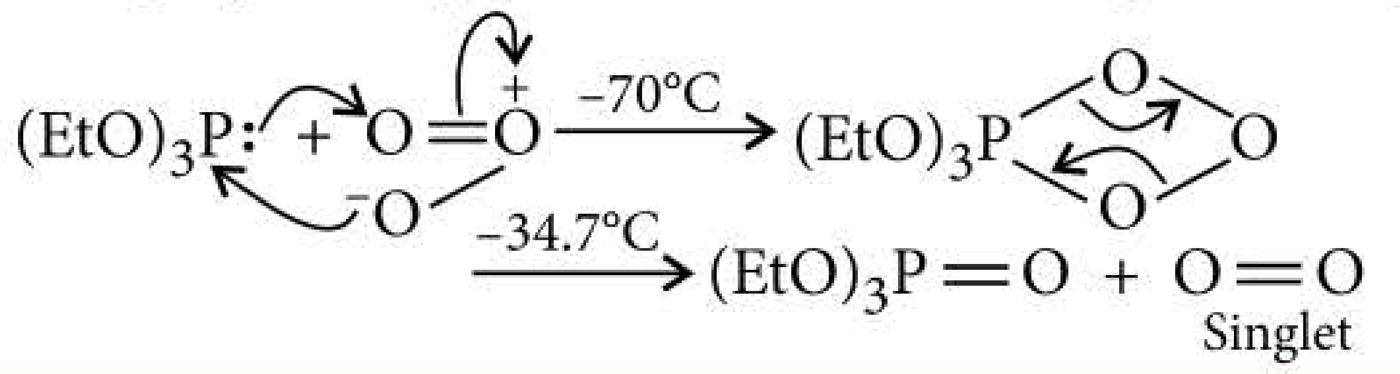


Now, this nitrene can be used for ring closure purposes in many cases. For example :



❍ **Formation of singlet oxygen :**

Triplet oxygen is $\cdot\ddot{O}-\ddot{O}\cdot$ represented by $^3O_2$. Singlet oxygen is $\ddot{O}=\ddot{O}$ represented by $^1O_2$. Singlet oxygen (which is required in Diels-Alder and other reactions) can be prepared by the treatment of $(EtO)_3P$ with O_3.

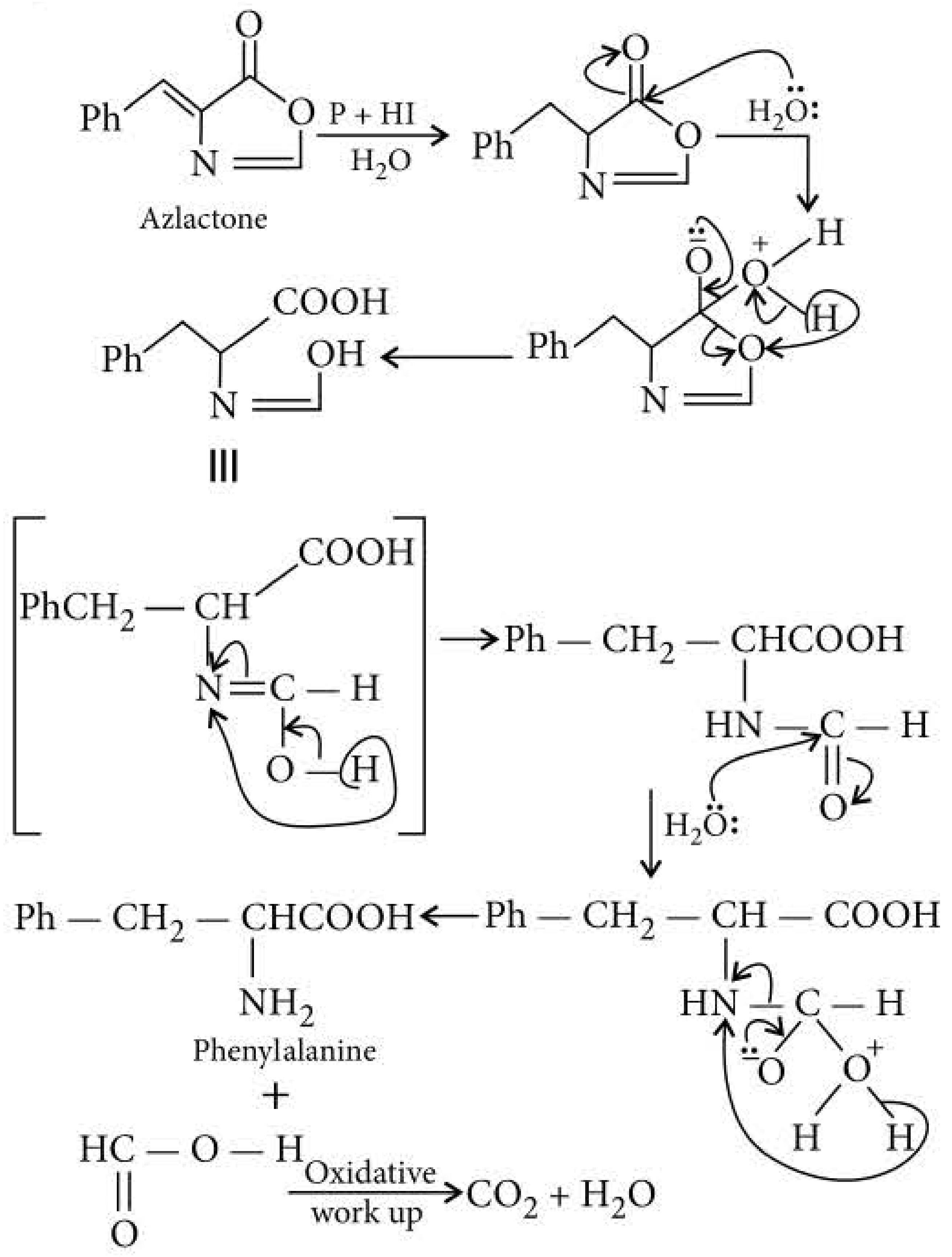


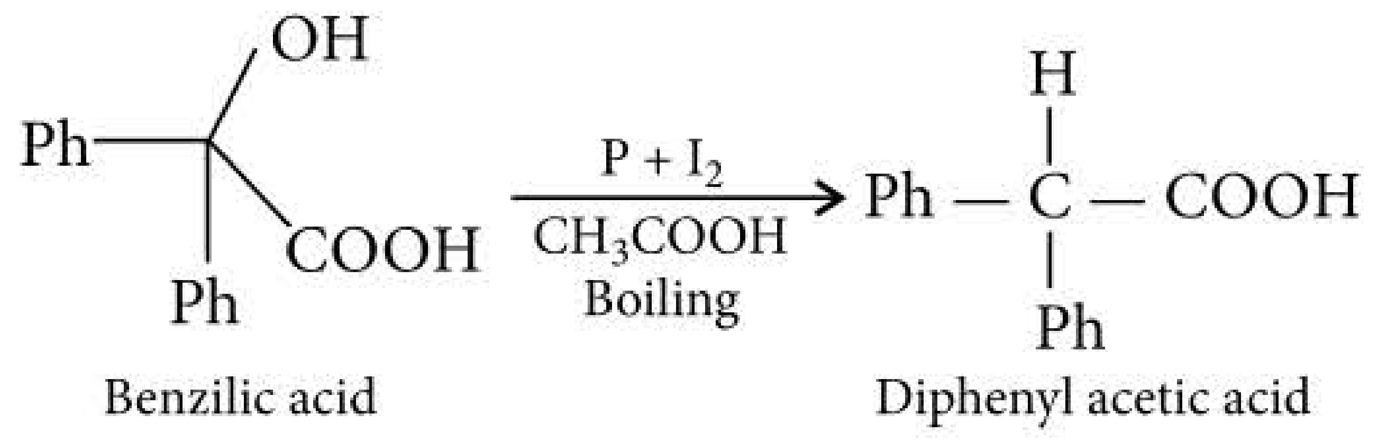
P + HI + H_2O and P + I_2 + CH_3COOH

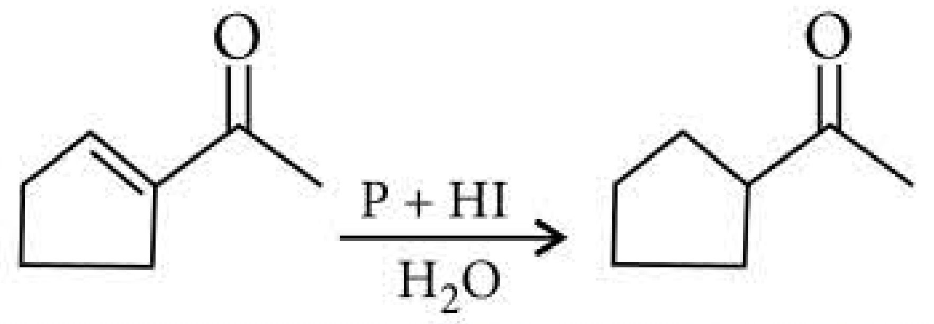
It is a very useful reagent usually used for the following purposes :

(1) Hydrogenolysis of alcoholic hydroxyl group.

(2) Hydrogenation of $>C=C<$ which is α(alpha) to the carbonyl group. This is one of the best methods for the preparation of α-amino acids. Some common examples are :







$LiAlH_4$ and $NaBH_4$

$LiAlH_4$ and $NaBH_4$ and their comparative study :

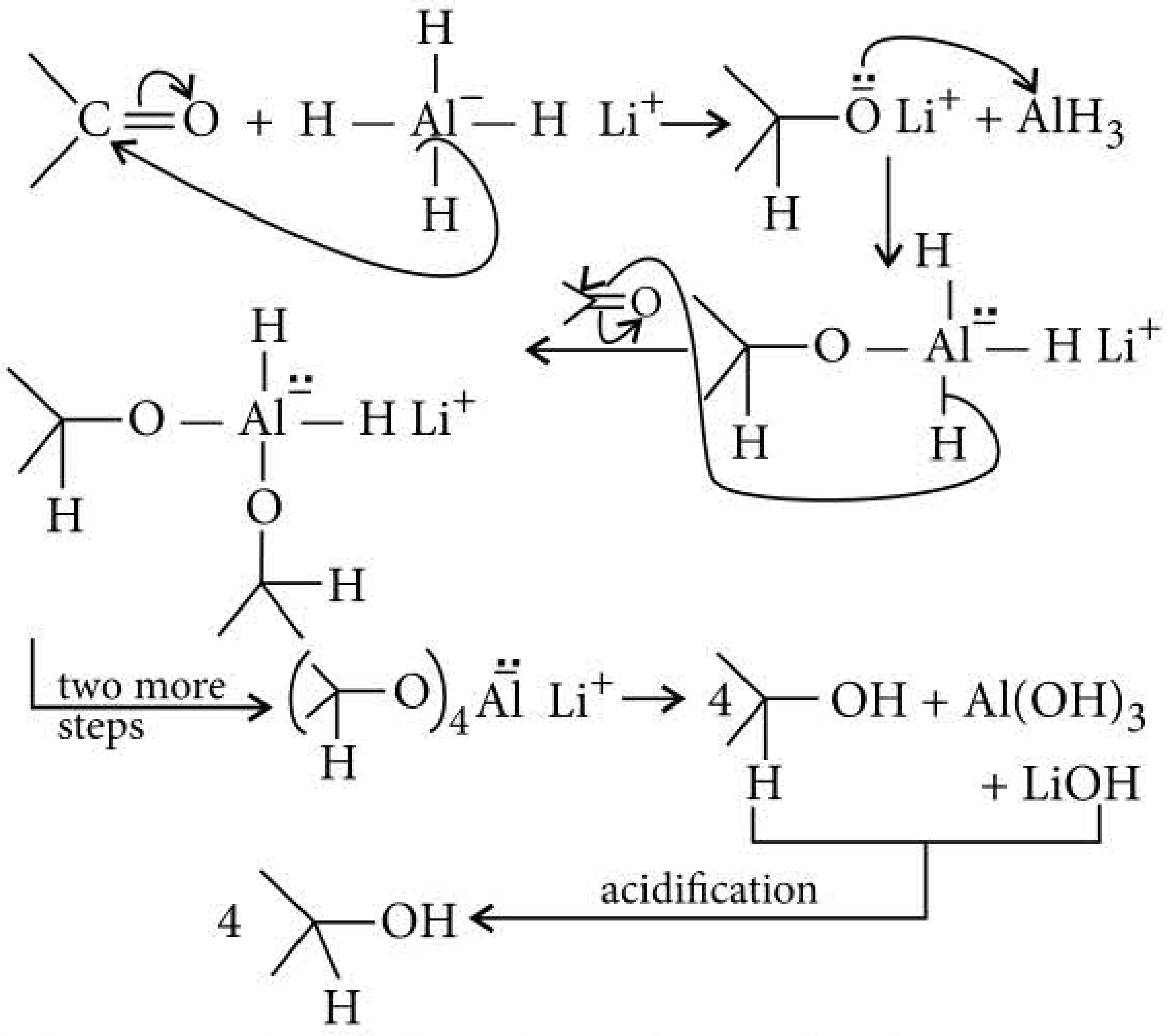
Both these reagents follow similar mechanism for reduction and that is 'hydride' transfer mode of preparation of both the reagents is also similar.

$$LiH + AlH_3 \longrightarrow \overset{+}{Li}\overset{-}{Al}H_4$$

$$NaH + BH_3 \longrightarrow \overset{+}{Na}\overset{-}{B}H_4$$

Reduction is carried out by the anionic part and therefore it is understandable that these attacking parts are nucleophilic and hence the attack is usually carried out to the polarised multiple bonds like $>C=O$, $-C\equiv O$, $-N=O$, $-C=N-$, etc. The funda is hydride transfer takes place to the more positive atom. This is the sole reason why $LiAlH_4$ and $NaBH_4$ cannot reduce non-polarised multiple bond.

Now, though I have discussed the mechanism of hydride transfer several times earlier, but let us take the glimpse of reduction by $LiAlH_4$ once to understand a few things :



Now, some key points about the mechanism :

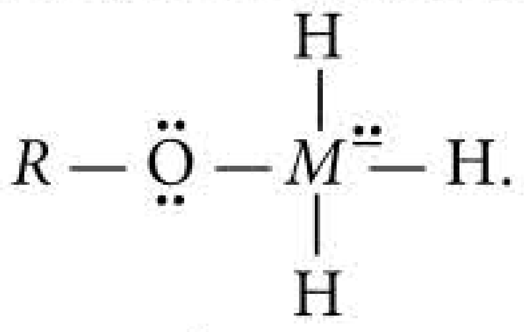
(1) The first step here is the fastest step and with the

progress, rate of reaction decreases because –*I* effect of alkoxy groups oppose the loss of H^- ion. So, obviously the last step is the rate determining step.

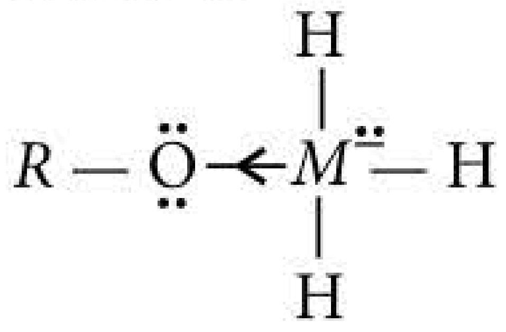
(2) Steric hindrance is also a key factor for the subsequent decrease in the rate of the reaction.

(3) For every mole of $LiAlH_4$, 4 moles of ketones are required.

Now, if you go through the mechanism of $NaBH_4$ reduction, then you will find that the basic scheme of the mechanism is exactly same but the twist is while using $NaBH_4$, the first step is found to be the rate determining step.

Well, now we would try to explain this scenario. Suppose the metal hydride is MH_3. It is a Lewis acid which gives $\ddot{M}H_4$. After the reaction with first carbonyl group, it gives  $R-\underset{\cdot\cdot}{\ddot{O}}-\overset{H}{\underset{H}{\ddot{M}}}-H$. Now, two types of effects can be seen here :

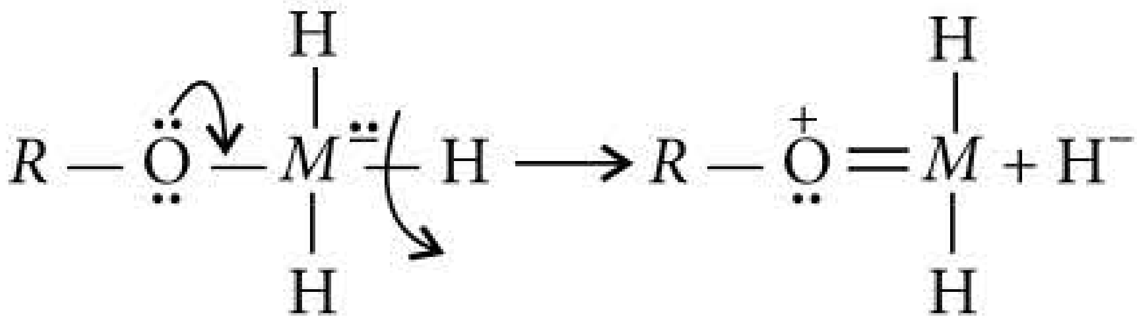
Effect 1 :



$R-\underset{\cdot\cdot}{\ddot{O}}\leftarrow\overset{H}{\underset{H}{\ddot{M}}}-H$

It is the electron withdrawing effect of the oxygen atom and this effect lessens the hydride transfer.

Effect 2 :



It is the mesomeric effect which helps in the release of H^-. Now, in case of $LiAlH_4$ effect 1 operates and in case of $NaBH_4$ effect 2 operates. Reason is simple, due to the smaller size of boron, overlapping takes place effectively and mesomeric effect prevails strongly. But, due to comparatively larger size of Al, effective overlapping does not take place and —*I* effect strongly prevails here.

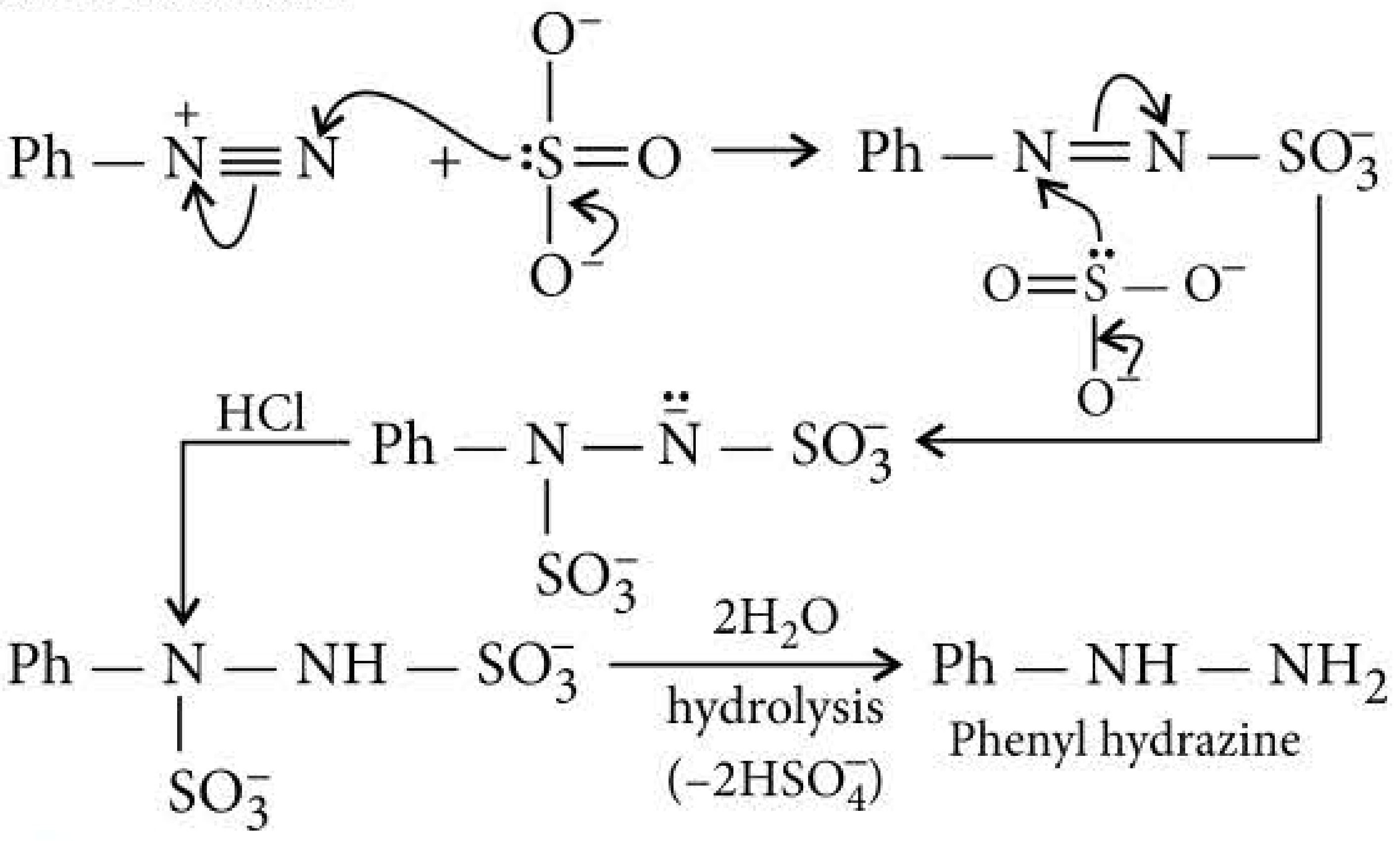
Na$_2$SO$_3$ and H$_2$SO$_3$

It is a comparatively less used reducing agent. Reduction through electron pair donation get initiated by sulphur atom.

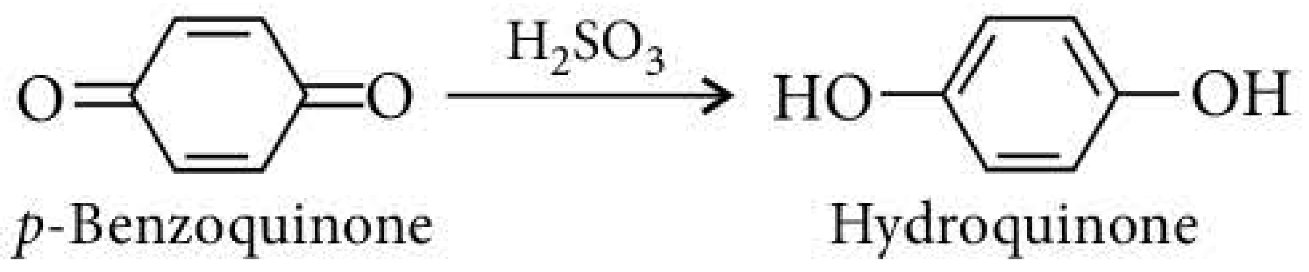
- **Reduction of benzene diazonium salt :**

$$Ph-\overset{+}{N}\equiv N \xrightarrow{Na_2SO_3} \text{Adduct} \xrightarrow{\text{conc. HCl}} \xrightarrow{H_2O} Ph-NH-NH_2$$

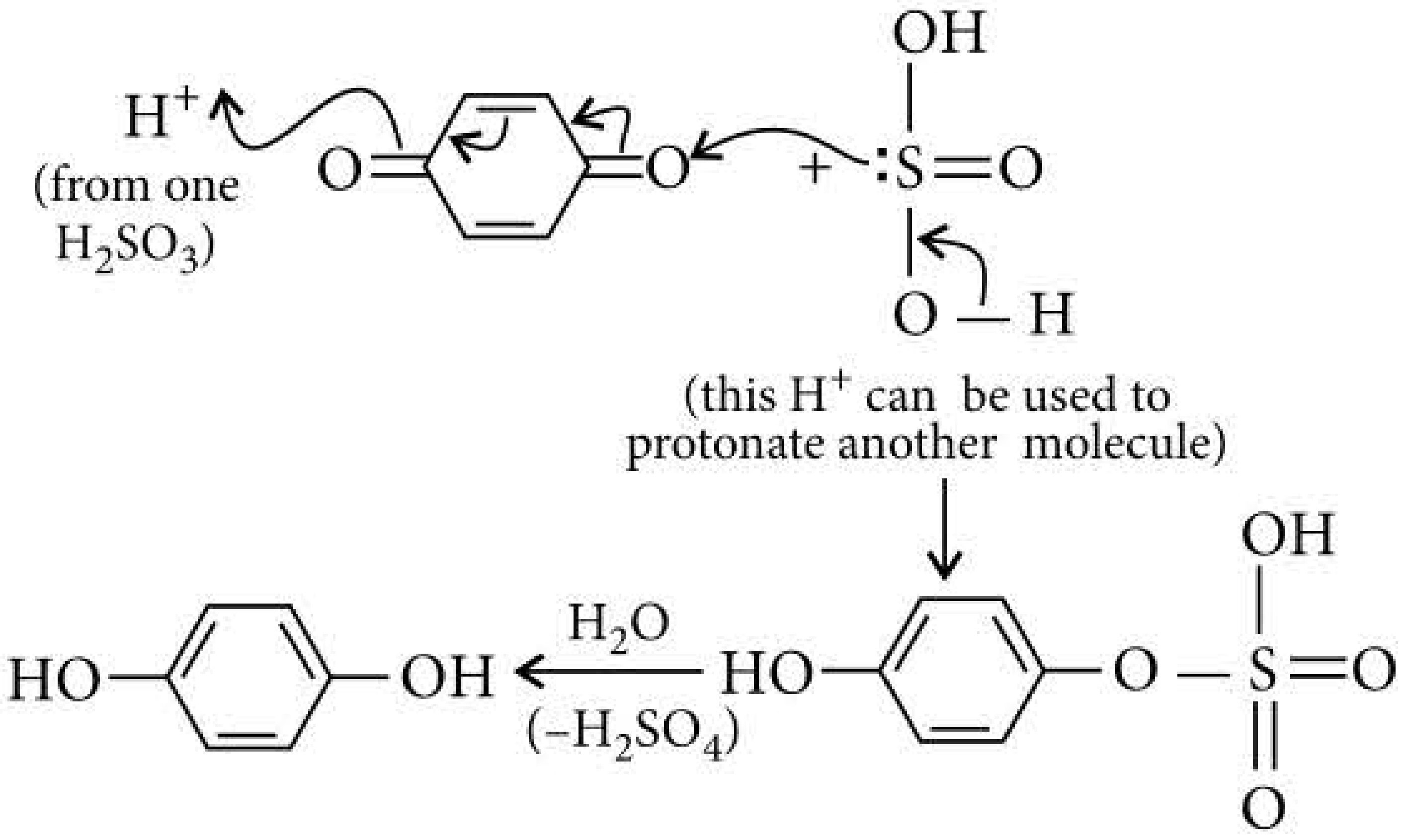
Mechanism :



- **Reduction of *p*-benzoquinone :** A famous one :



Mechanism :

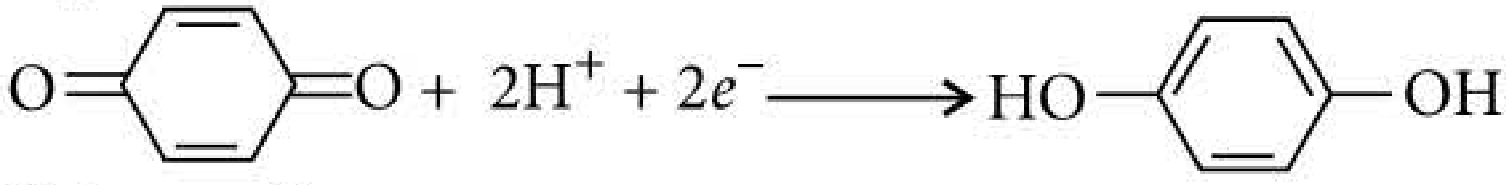


Equation wise this reduction can be shown as below :

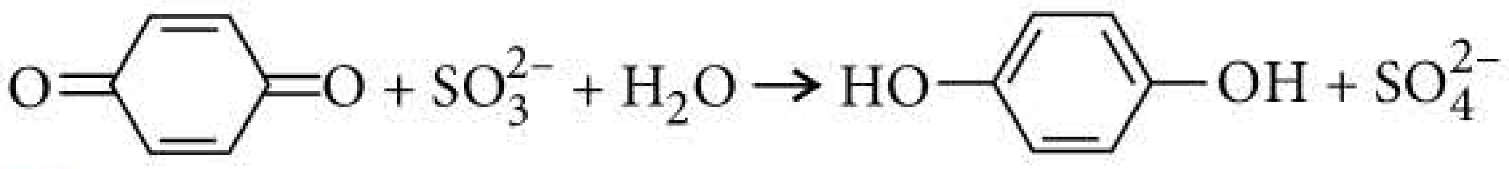
Equation 1 :

$$SO_3^{2-} + H_2O \longrightarrow SO_4^{2-} + 2H^+ + 2e^-$$

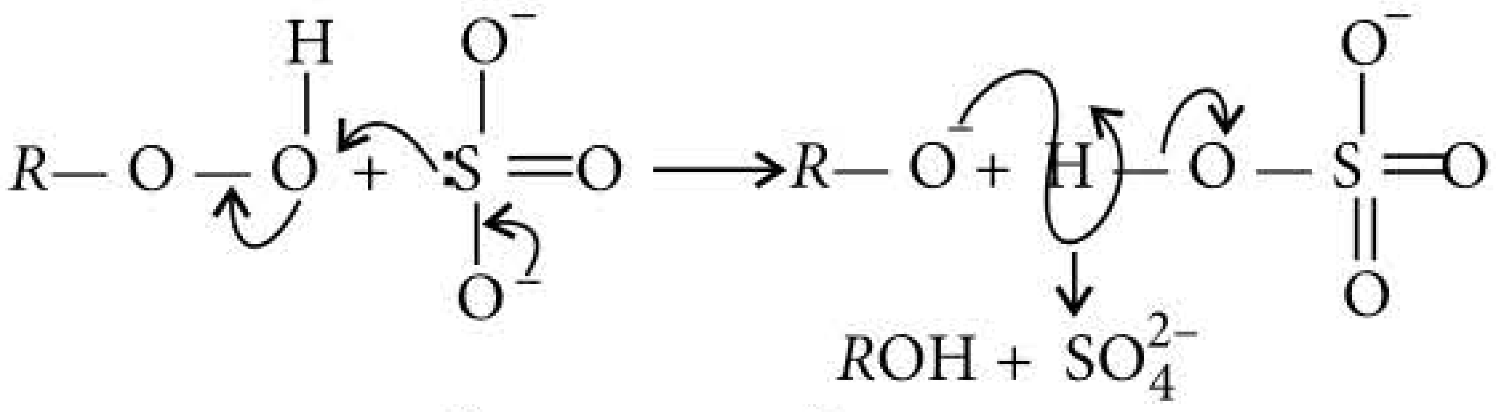
Equation 2 :

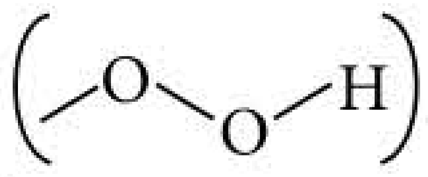


Net equation :



- SO_3^{2-} is also capable of reducing peroxide compounds. Mechanism of the reaction can be shown as below :



So, the funda is  group will be converted to —OH group.

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