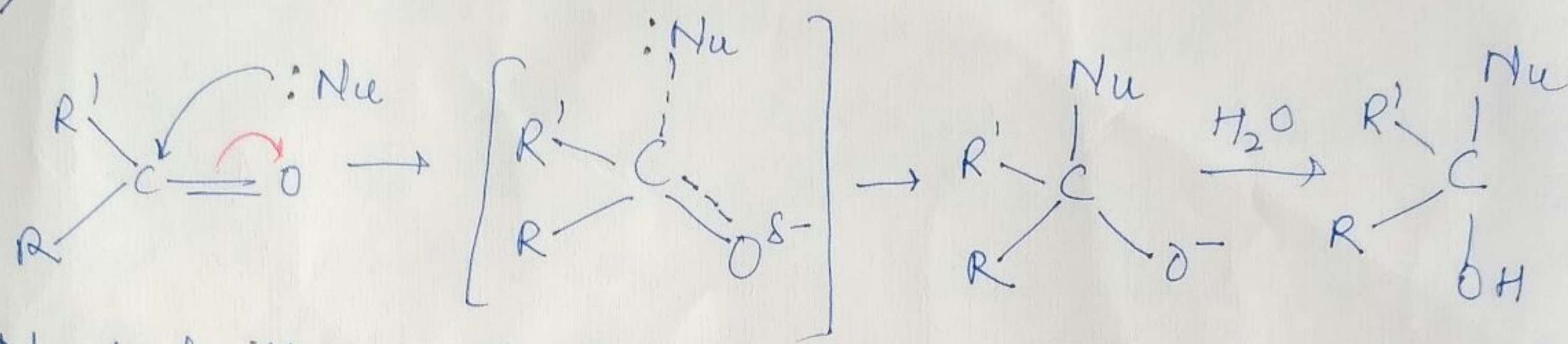


Addition Reactions: Occur in compounds containing multiple bonds, for eg $C=C$, $C\equiv C$, $C=O$, $C\equiv N$ etc. The addⁿ rxⁿ can proceed through

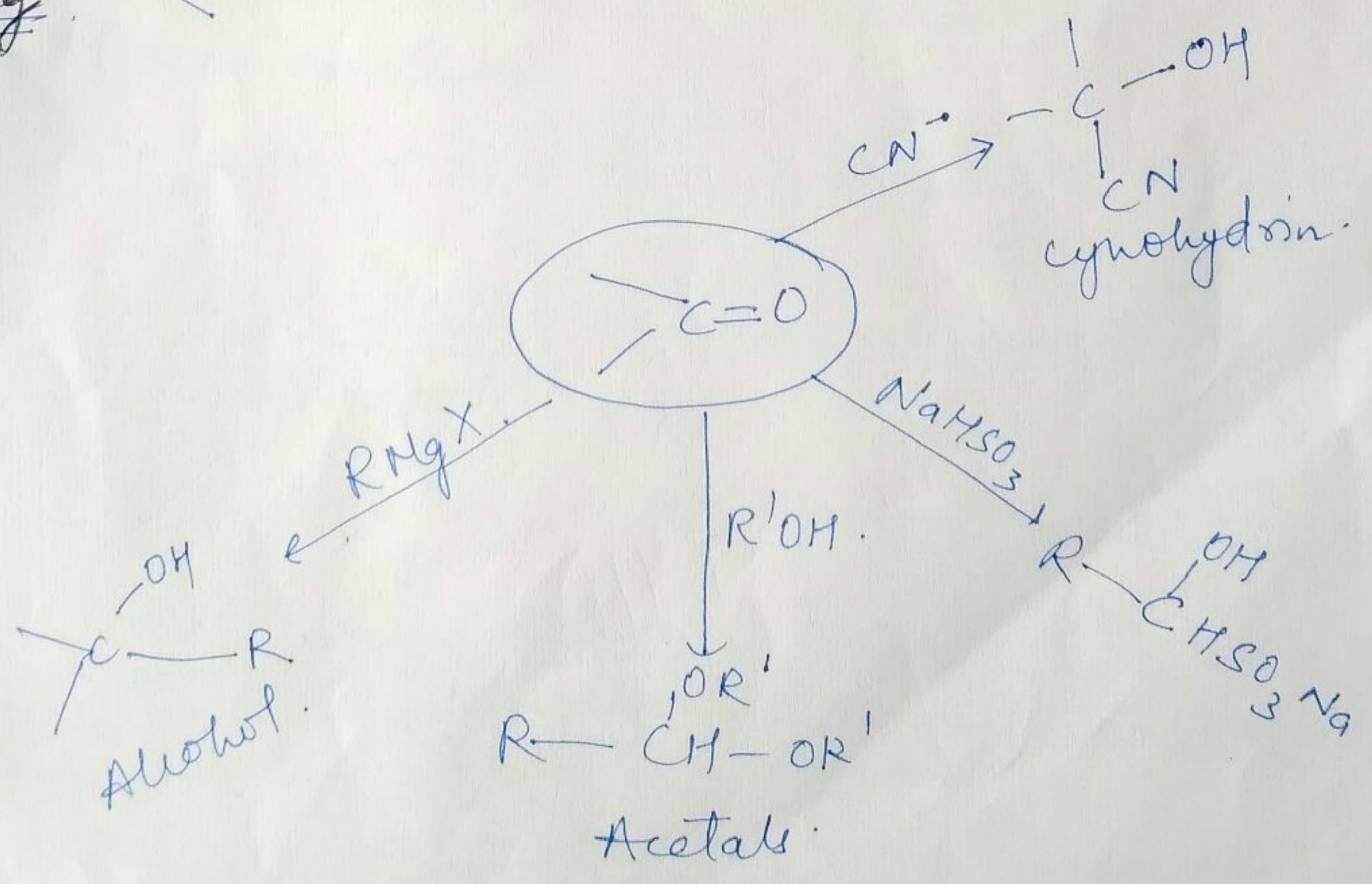
1. Nucleophilic addⁿ :- generally occurs in compounds containing polar functional g^s. for eg $C=O$, $C=N$, $C=S$ etc & most important of them being $C=O$.



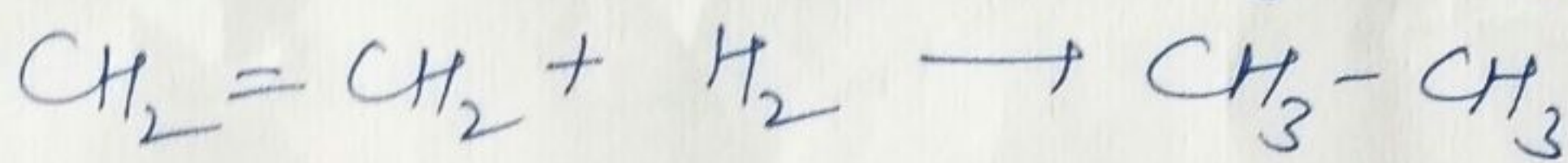
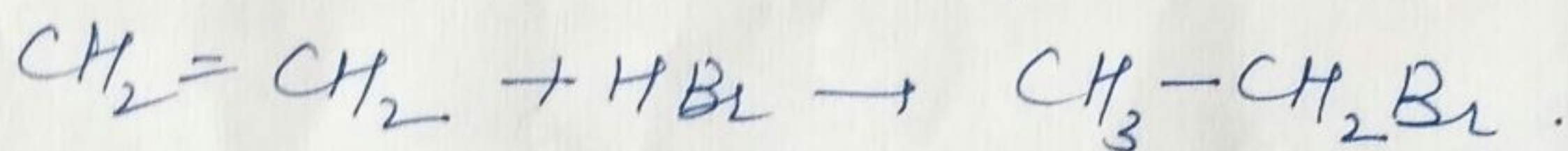
Nucleophilic addⁿ to carbonyl compds is catalysed by an acid.

Aldehydes undergo nucleophilic addⁿ more readily than ketones. As ketones contain a second alkyl or aryl gp and hence causes crowding. An alkyl gp also releases electrons and thus destabilises the transition state by intensifying the negative charge developing on oxygen.

eg.



Electrophilic addition : These rxⁿ are brought about by electrophiles and occur in compounds containing C-C double or triple bonds.

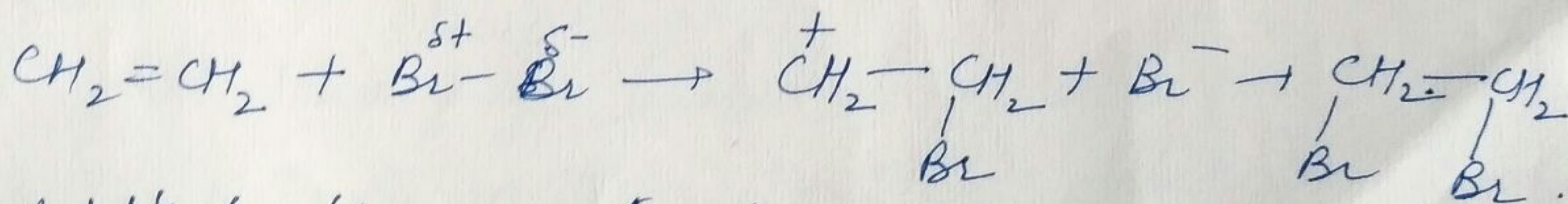


C=C is made up of

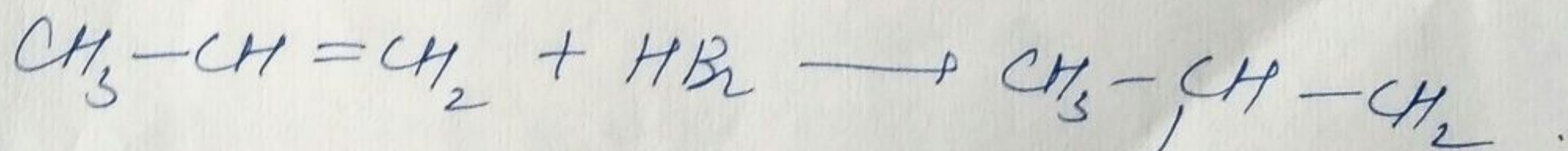
- 1) Strong σ bond $\bar{c} e'$ distribution along the line joining the two carbon nuclei and
- 2) Weaker π bond, with e' pair in orbitals perpendicular to the plane of C nuclei.

These π electrons are held less firmly by the carbon nuclei and are more readily polarizable than σ bond. Also, these $\pi e'$ attract electrophilic species and undergo electrophilic addⁿ.

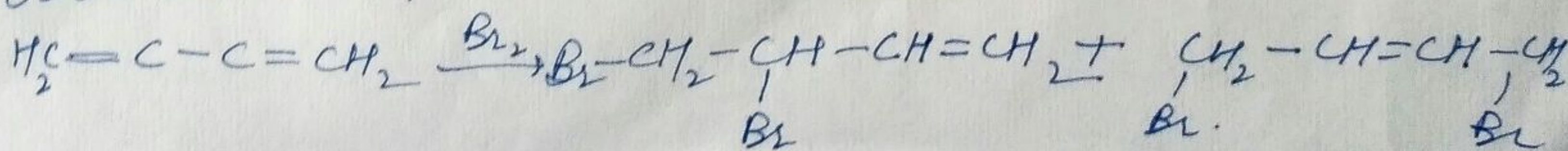
1. Addⁿ to symmetrical alkenes:- When Br_2 gets in proximity of an alkene, it gets polarized due to π electrons of the alkene. The two ends of the polarized bromine gets attached to $\pi e'$ cloud of the alkene leading to the formation of a π complex which further react to form dibromomethane.



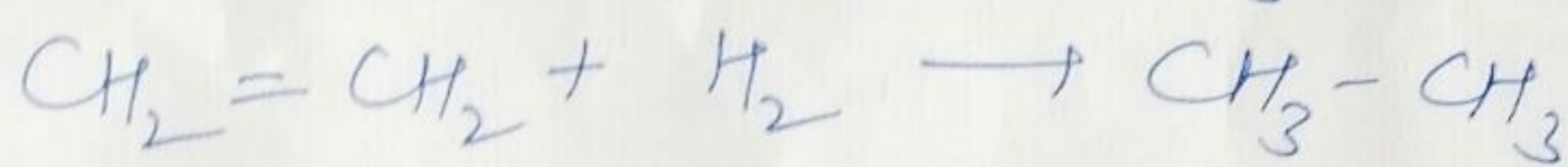
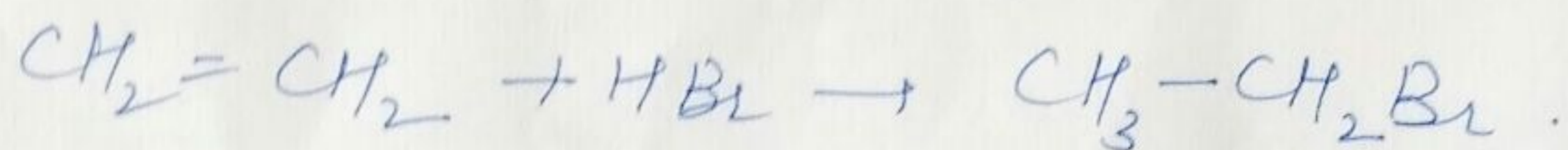
2. Addⁿ to unsymmetrical alkenes : Occur by Markownikoff's rule.



- 3) Addⁿ to conjugated diene:- When conjugated diene like 1,3-butadiene reacts with bromine, the major product obtained is 1,4-dibromo-2-butene.



2. Electrophillic addition : These rxⁿ are brought about by electrophiles and occur in compounds containing C-C double or triple bonds.

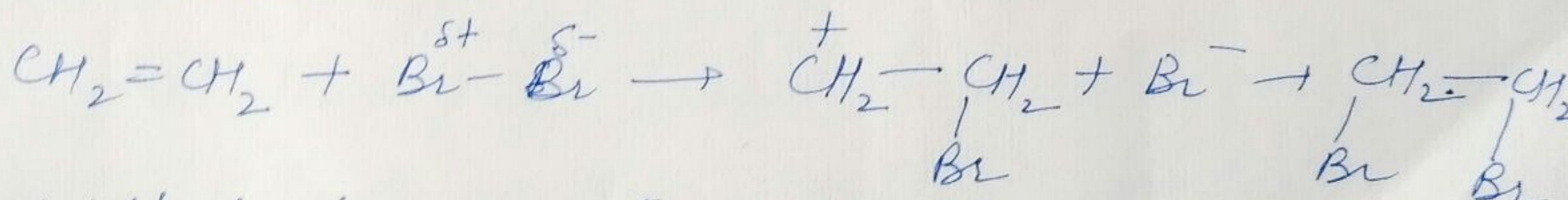


C=C is made up of .

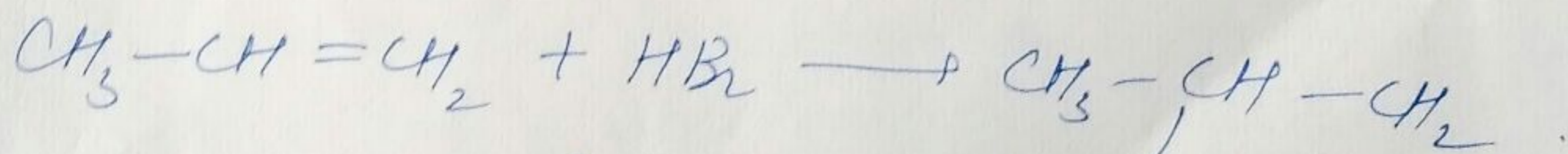
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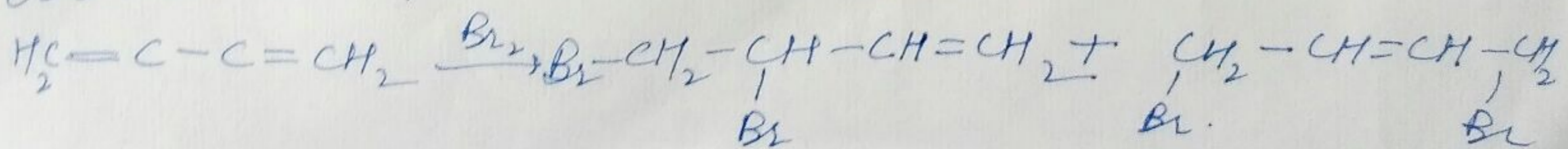
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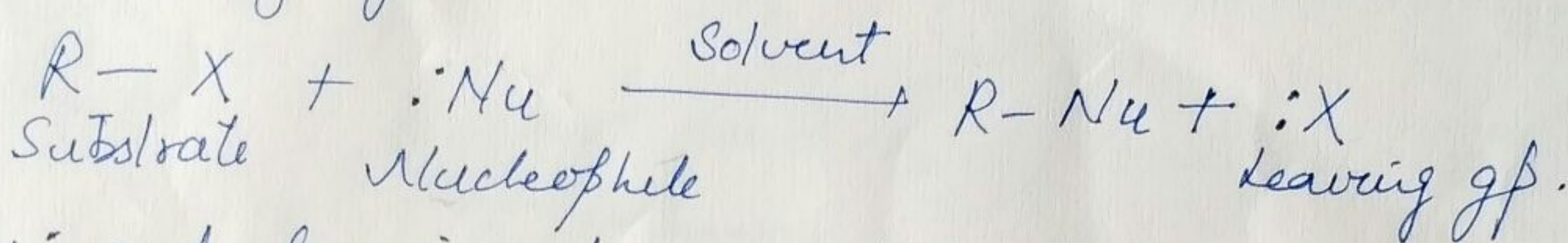


Substitution Reactions

(3)

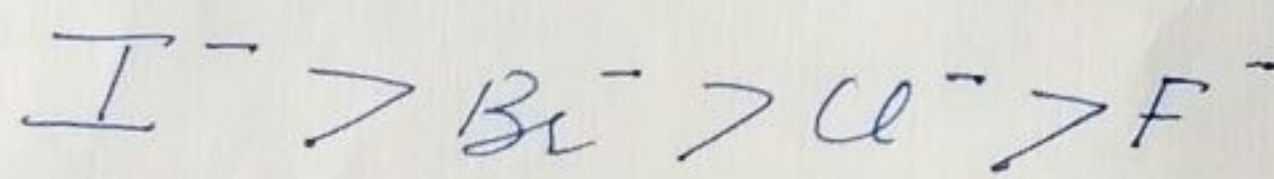
In these types of reactions, an atom or gp replaces another atom or gp present in a compound, without causing a change in the structure of that compound. Free radicals, E^+ , Nu^- , ~~NS~~ may be involved in these rxⁿ.

① Nucleophilic Substitution (S_N): These rxⁿ occur in presence of Nu^- . Apart from Nu^- , NS rxⁿ requires substrates (which contain an alkyl gp and a leaving gp) and solvent.



Both Nu^- and leaving gps are bases, but one of the two, the leaving gp is weaker base.

Nucleophilicity :- large attacking atom, high polarizability and should be weakly solvated.



leaving group :- leaves with the electrons of the σ bond. Better the leaving group, faster is the rxⁿ.
leaving ability of leaving gp (X) depends on three factors:

- strength of the R-X bond.
- polarizability of R-X bond.
- Stability of X^- .

A good leaving gp should be a weak base.

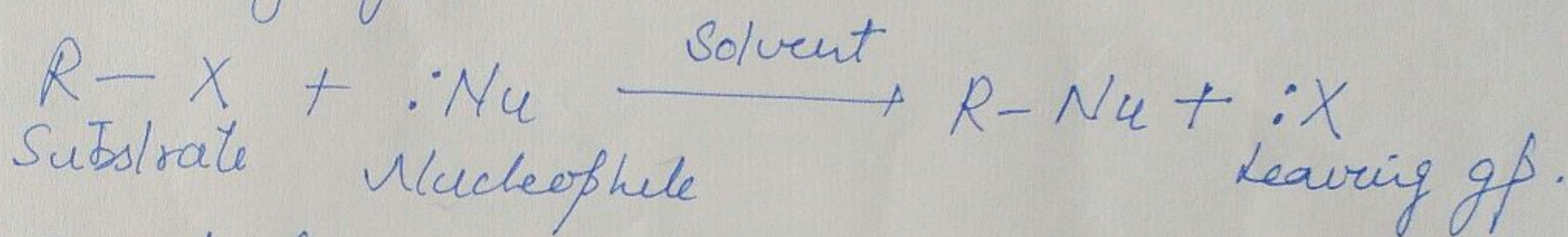
② Electrophilic Substitution :- This substitution rxⁿ occurs in presence of E^+ . Aromatic system with high e^- density generally undergo substitution by this mechanism. For eg benzene has delocalized π electrons and there is concentration of negative charge above and below the plane of the ring-carbon atoms. This promotes the attack of electrophile E^+ .

The examples of ES include nitration, halogenation, sulphonation of aromatic system, Friedel Crafts alkylation, acidification etc.

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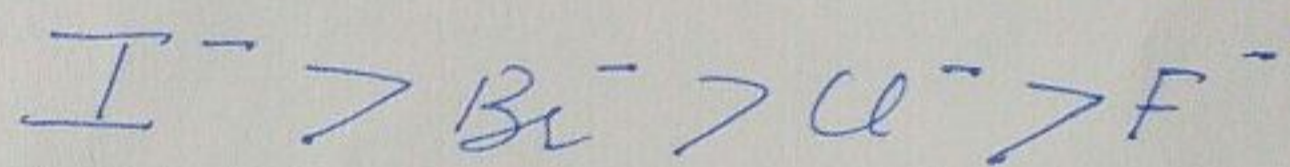
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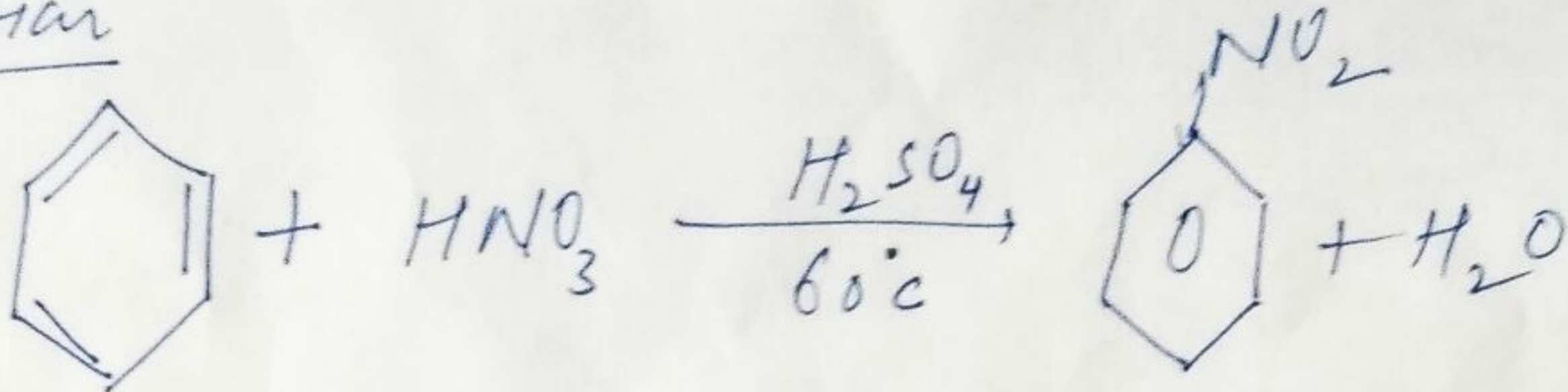
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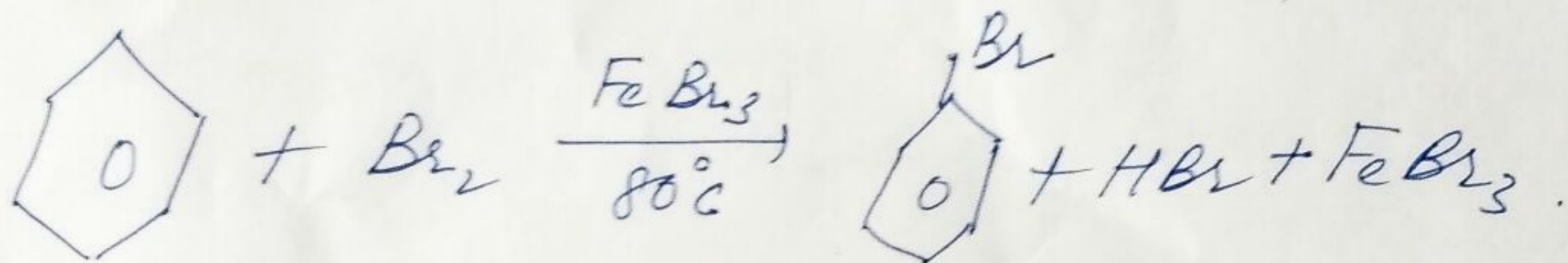
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Nitration

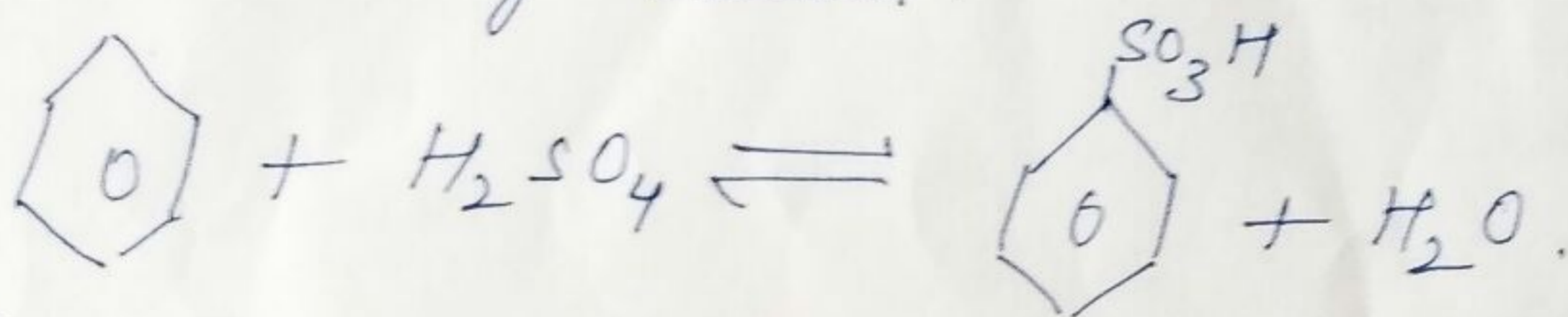
(4)



(2) Halogenation :- Benzene can be halogenated with Cl_2 or Br_2 in the presence of Lewis acids, such as FeBr_3 , FeCl_3 , AlCl_3 etc.



3. Sulphonation :- by hot conc H_2SO_4 but rapidly by oleum.

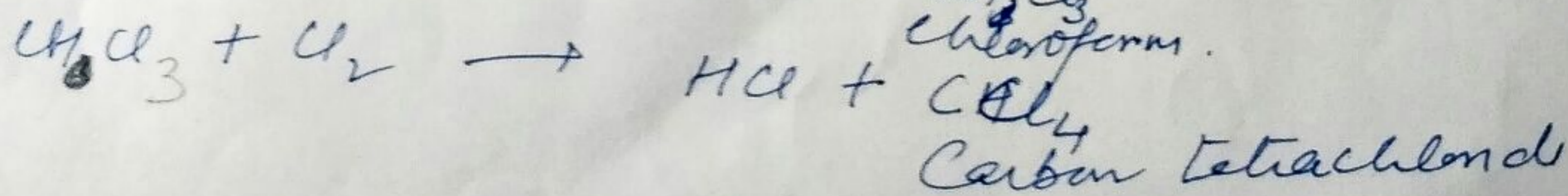
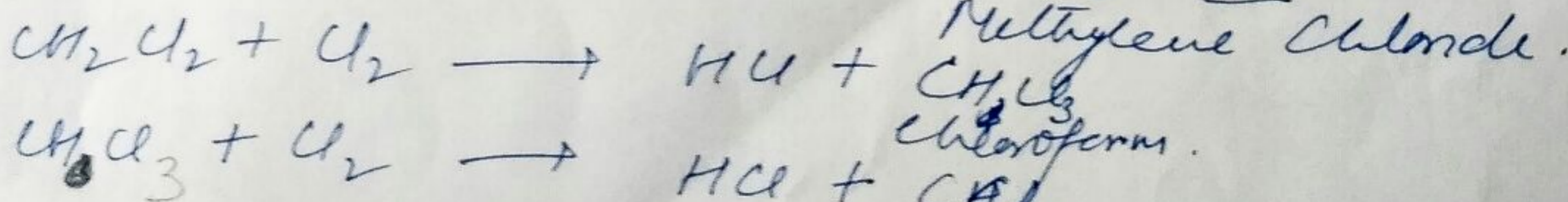
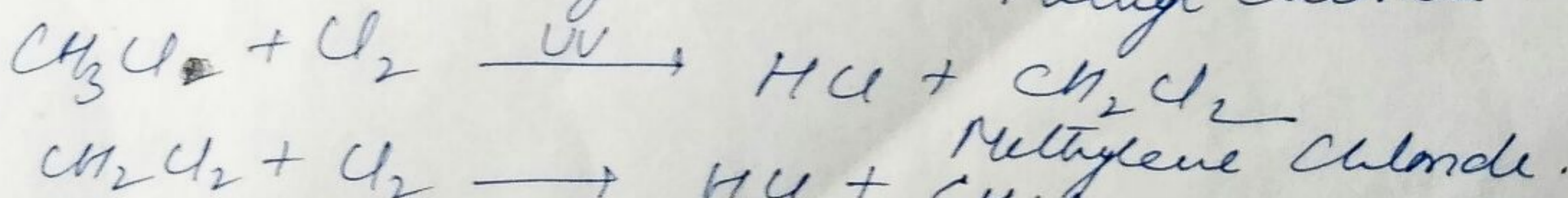
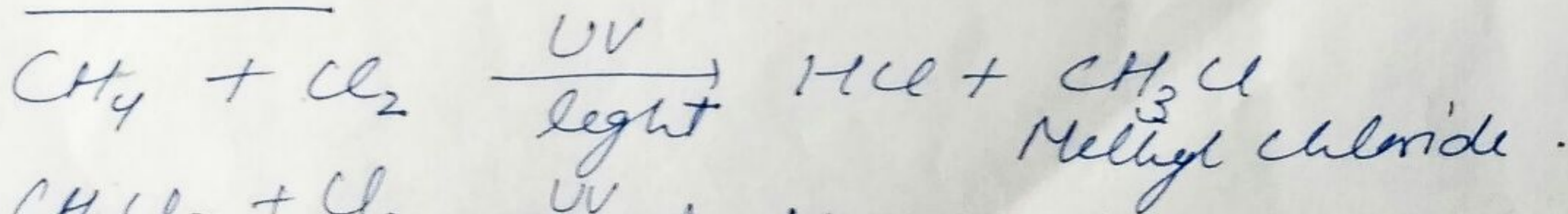


- #
- (1) electron donating gp activate the ring towards ES because of +R and +I effects.
 - (2) electron withdrawing gp deactivate the ring towards ES because of -R & -I effects.

Orientation of ES

R, -OH, NH_2 , OR are o-p directing.
otherwise meta directing.

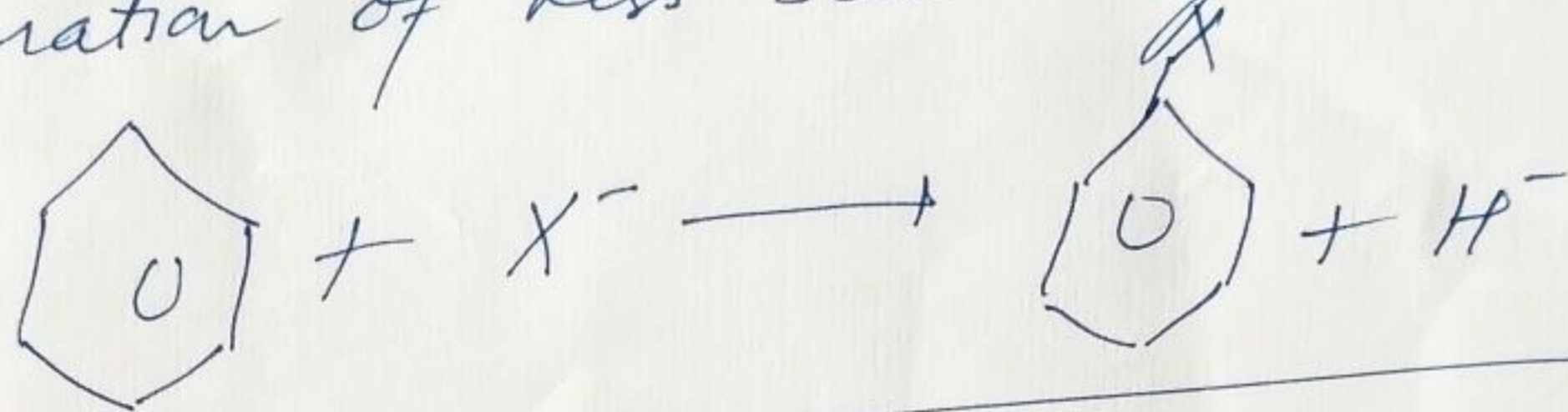
(3) Free Radical Substitution :- eg halogenation of alkanes in the presence of light or at a temp 300-400°C



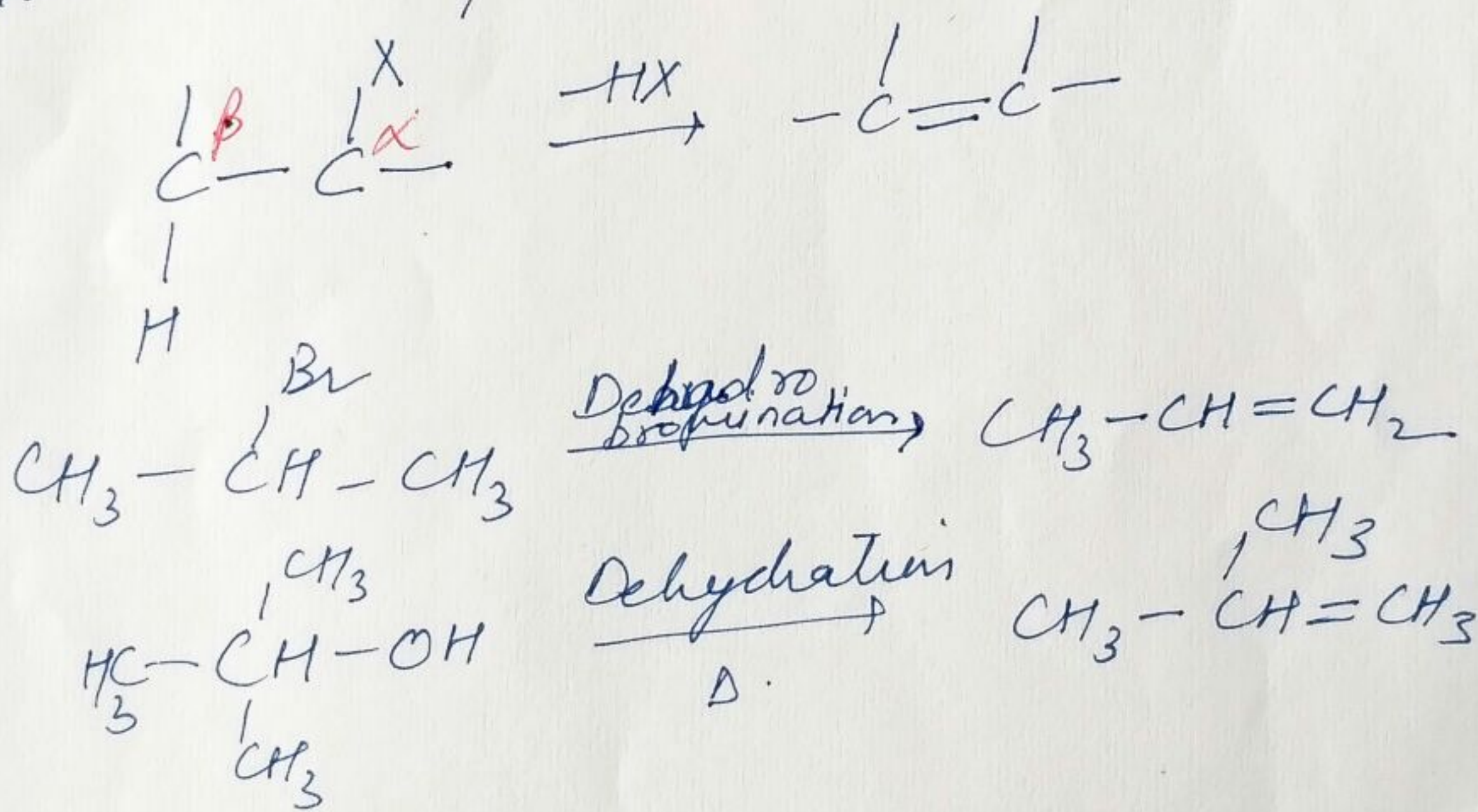
Nucleophilic Aromatic Substitution :-

When either Hydrogen or any other substituent is replaced by nucleophilic agent in an aromatic ring, significantly, the substitution does not take place with benzene but with substituted benzene derivatives and naphthalene. Benzene does not undergo NS due to:

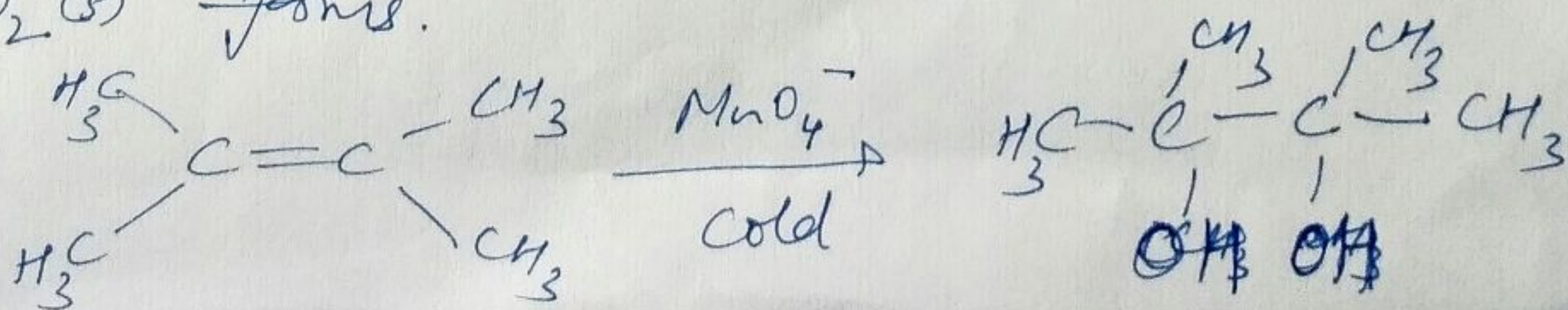
- ① Presence of $-ve$ charge above and below the plane of C atom of the ring.
- ② The formation of less stable hydride ion.

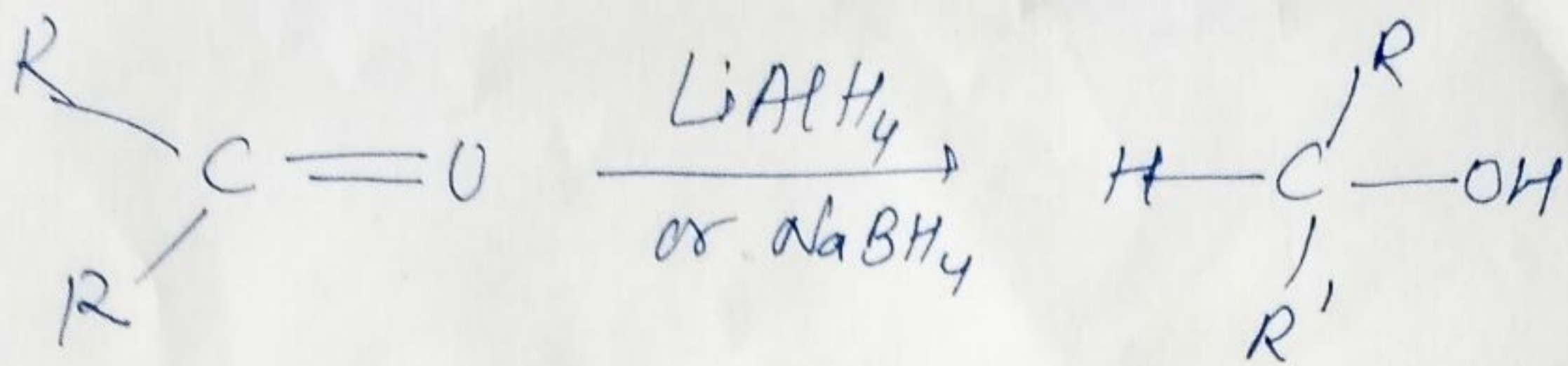


Elimination Reactions: It involves removal of two atoms/gps. In these rxⁿ, an atom/gp from α C atom and a proton from the β C are eliminated.



Oxidation: Alkenes react readily with no. of oxidising agents. A simple test for the presence of olefin gp is the rxⁿ in an aqueous solⁿ of permanganate ion. The purple colour of permanganate ion disappears as olefin is oxidized and brown $\text{MnO}_2(s)$ forms.





These examples show that reduction of an aldehyde yields a primary alcohol, while redⁿ of a ketone produces a secondary alcohol. These are the same interrelationships we encountered in oxidizing alcohols to form aldehydes and ketones. $NaBH_4$ is more selective reducing agent than $LiAlH_4$, it cannot reduce acids or esters to their corresponding alcohols as can $LiAlH_4$.