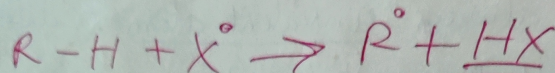
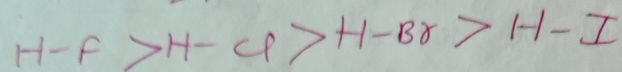
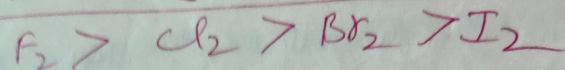
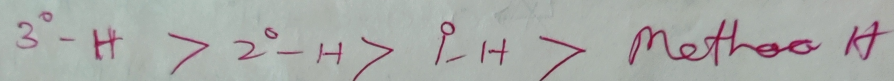


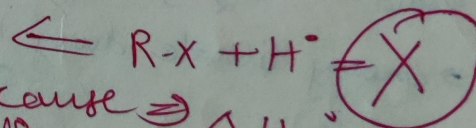
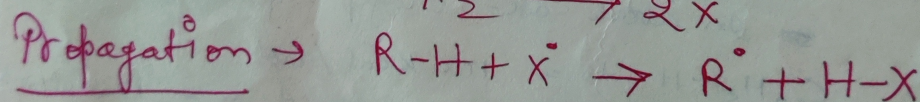
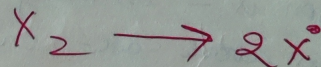
The following is the decreasing order of reactivity of halogens:



order of ease of abstraction of different kinds of H hydrogens $\rightarrow$



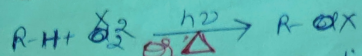
1. The reaction can also be applied to alkyl chains containing many functional groups. greater the reactivity less is the selectivity.



high for R-X formation. No because $\Rightarrow \Delta H$ is very

Free radical substitution halogenation at allyl carbons -

Temp $250-400^{\circ}\text{C}$



X = Chlorine, Bromine, Fluorine, Iodine.

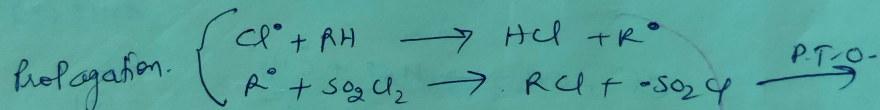
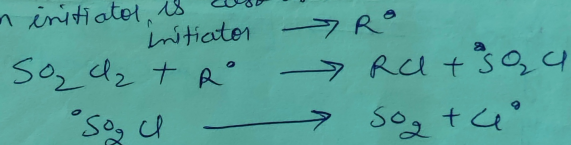
Mechanism: $\text{X}_2 \xrightarrow{\text{h}\nu \Delta} 2\text{X}^{\bullet}$
The chlorination $\text{rad}^{\bullet}$ is usually not useful for preparative purpose.

because substitution take place at every allyl carbon atom in the molecule, and also di- and Poly-Chloro substitution occur.

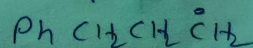
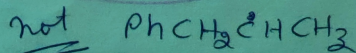
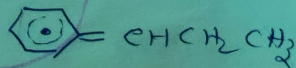
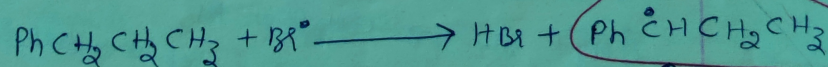
* if a mixture of chloride is wanted, the $\text{rad}^{\bullet}$ is usually quite satisfactory.

* For obtaining Pure Comp., the substrate must contain only one type of replaceable Hydrogen.
eg. ethane, cyclohexane, neopentane.

Bromination: * The bromine is much more selective than chlorine.
Mechanism: chlorination, sulphonyl chloride in the presence of an initiator, is also used -

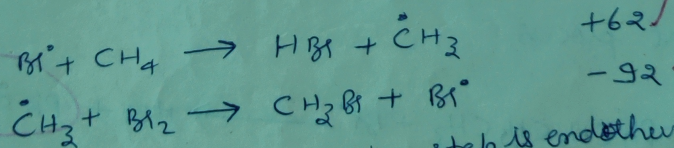
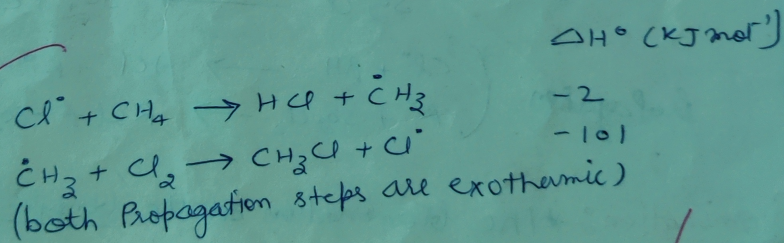
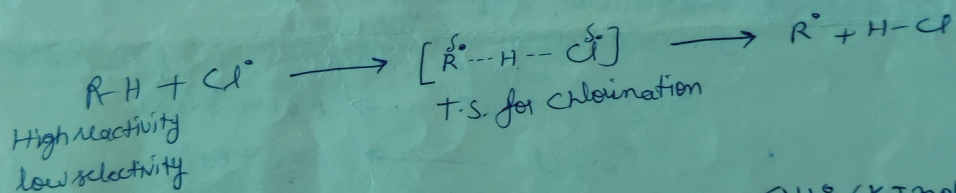
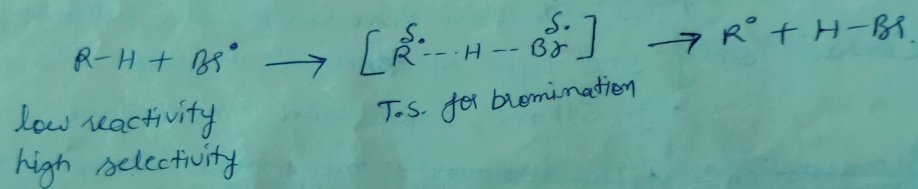


Bromination: * The bromination at the benzylic position is an efficient process.

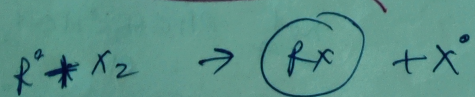


* In the case of chlorination mechanism is similar as to bromination. but selectivity in the case of chlorination is very much reduced.
 due to greater reactivity chlorine atom, abstracts primary, secondary as well as tertiary hydrogens.

↳ And all these rxns are exothermic.
 * also, the EA (activation energy) for chlorination is low as compared to bromination.

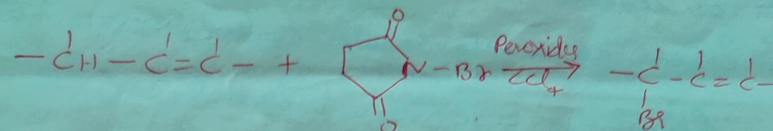


(Here, first propagation step is endothermic)



Allylic halogenation :- [by NBS] [Wohl-Ziegler bromination]

(2)

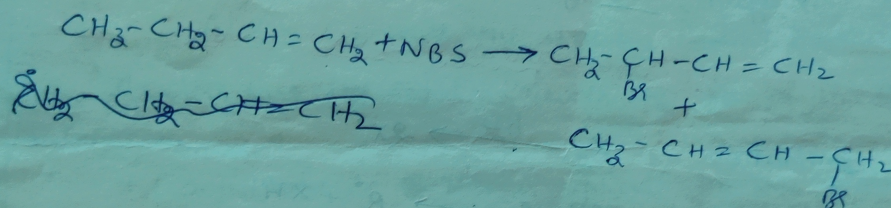


* Olefins can be halogenated in the allylic position by a number of reagents, when NBS (N-bromosuccinimide)

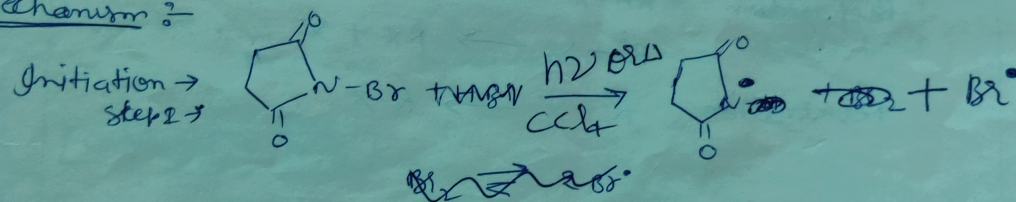
is used the rxn is known as Wohl-Ziegler bromination.

* We can also use $\rightarrow$ N-chlorosuccinimide, t-butyl hypochlorite etc.

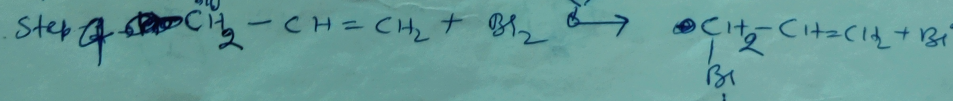
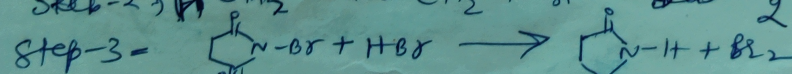
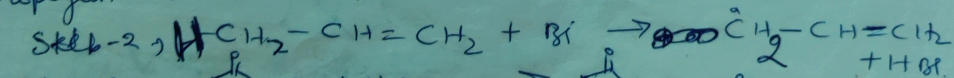
* When the allylic radical intermediate is unsymmetrical, allylic rearrangement can take place, so that the mixture of both possible products are obtained e.g.



Mechanism :-



Propagation $\rightarrow$



* The free radical formed in step 3 can then continue the chain rxn.

* The rxn is regioselective and occurs at allylic position and no addition product is formed.

* Fluorine also used for halogenation. but seldom as it is too reactive and hard to control. it often breaks carbon chains down into smaller units. [exothermic reaction]

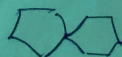
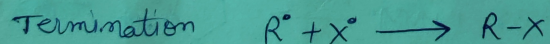
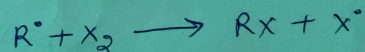
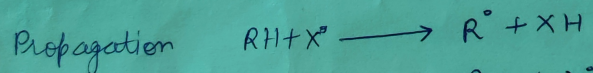
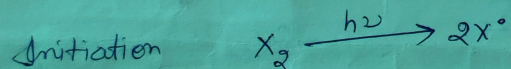
Fluorination - Chlorine trifluoride ClF_3 at -75°C

It is usually better to introduce fluorine by indirect means (electrophilic substitution)

* Radical substitution Na^+ by iodine are not practical. Since the abstraction of hydrogen from hydrocarbons by iodine - is endothermic.

* again, HI ~~from~~ forming reduces the alkyl iodide.

In almost all cases, the mechanism involves a free-radical chain



Spino

