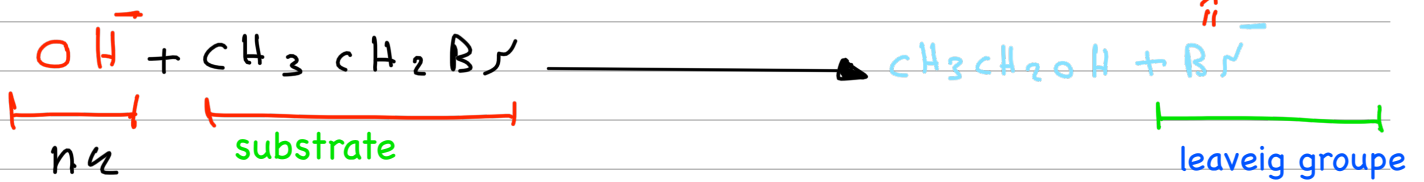


ch. 6

تأخذ ج 2 من الرابطة الجديدة .

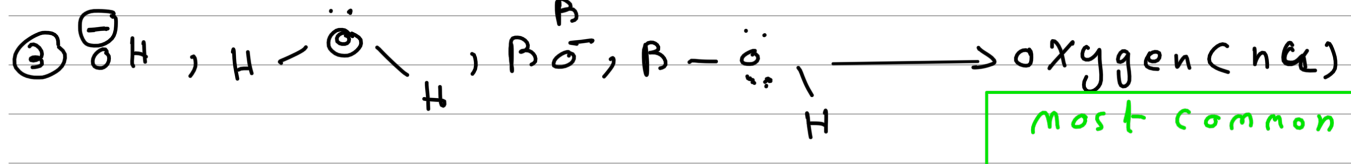
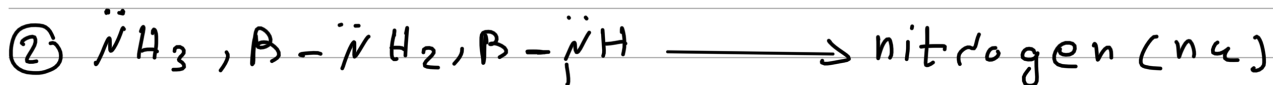
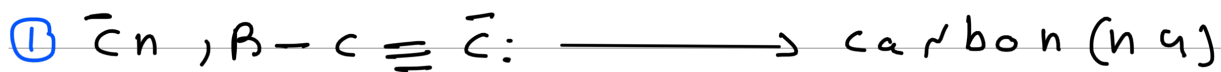


this is reaction called nucleophilic substitution Reaction .

اللي بصير هون
باختصار :

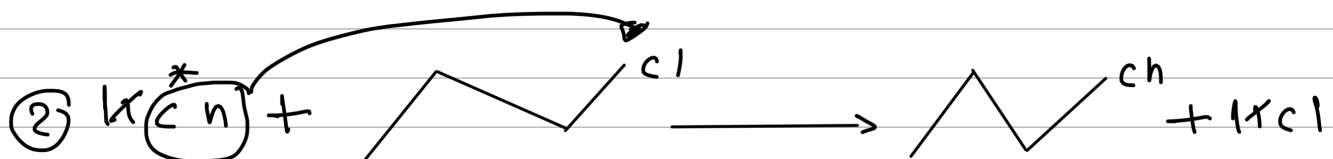
covalent bond broken and new covalent bond forming .

examples of nucleophiles :



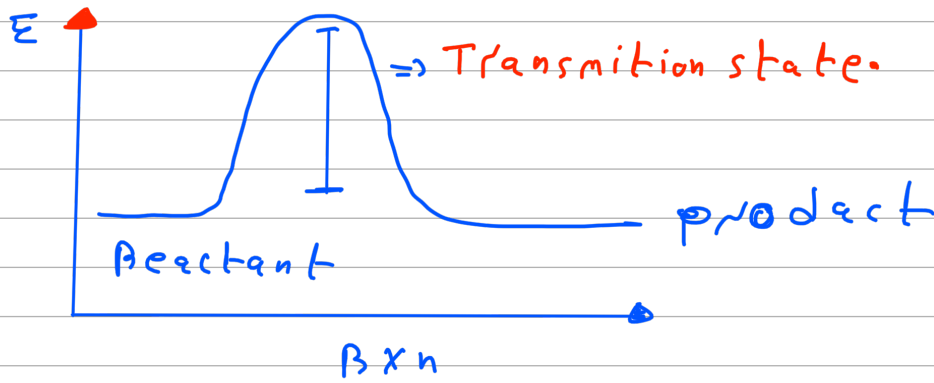
* example

الارتباط بين الذره السالبه وال C

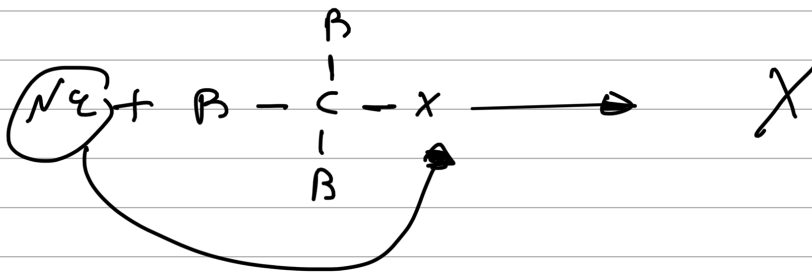
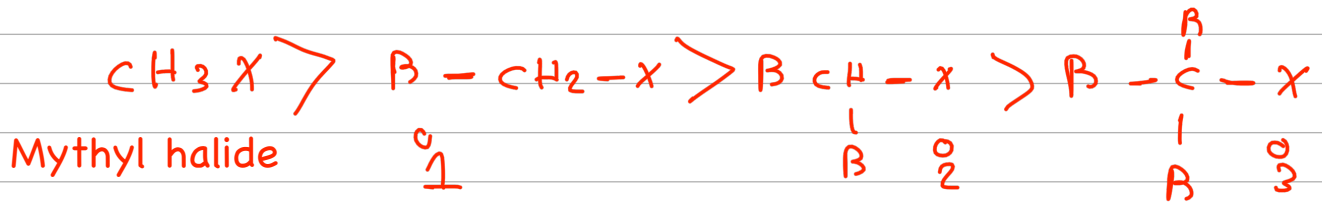


③ Reaction is occure in one step (no inter mediate).

$E = \text{energy}$



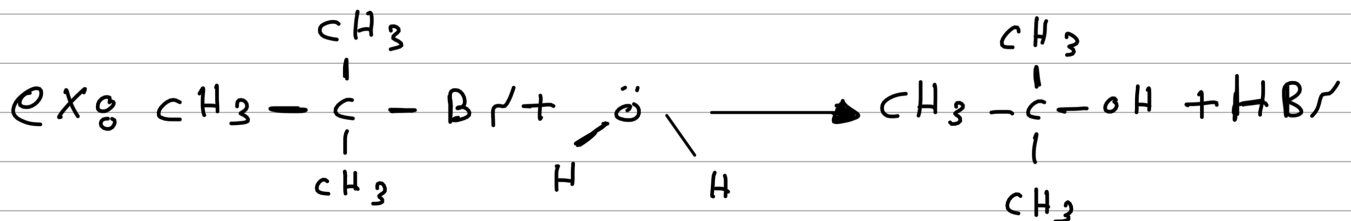
④ S_N^2 - pactions are reactive the following order.



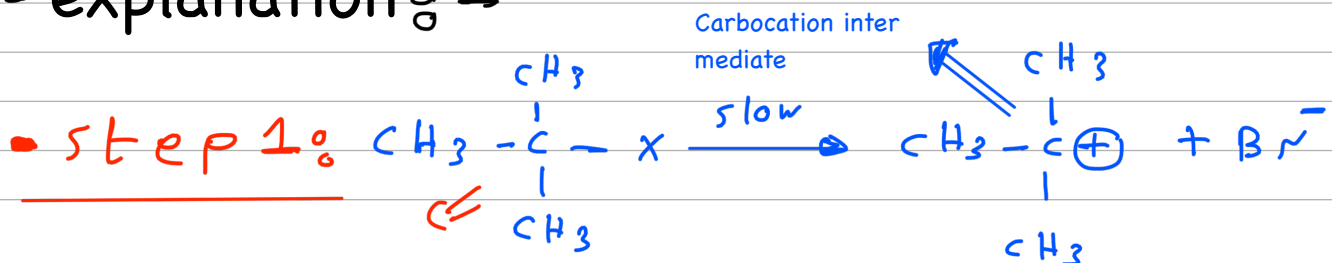
- To summarize, the S_N2 mechanism is a one-step process favored for methyl and primary halides. It occurs more slowly with secondary halides and usually not at all with tertiary halides. An S_N2 reaction occurs with inversion of configuration, and its rate depends on the concentration of both the nucleophile and the substrate (alkyl halide).

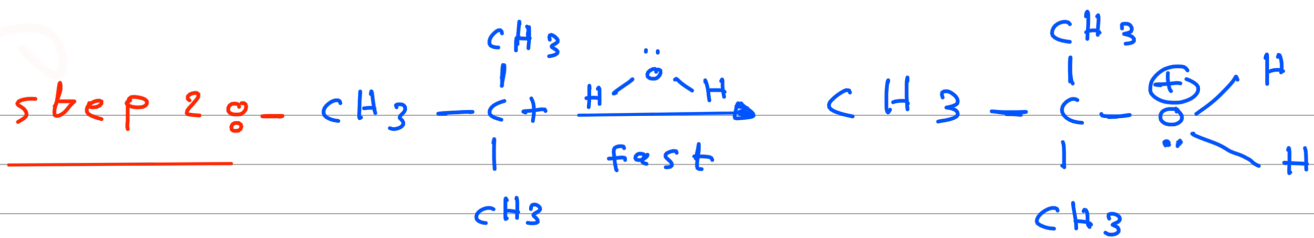
} \rightarrow SN2 مؤخر

\hookrightarrow S_N1 mechanism

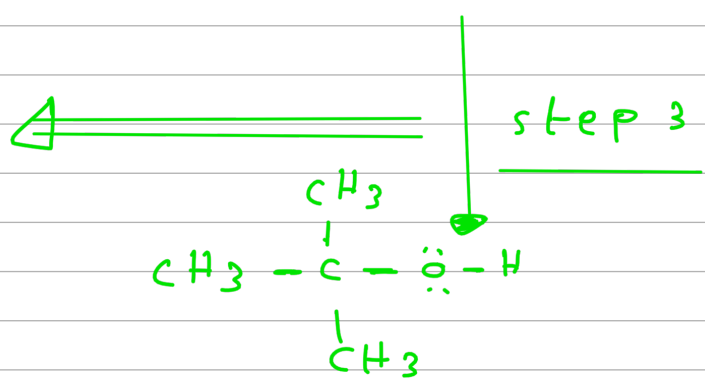


• explanation -



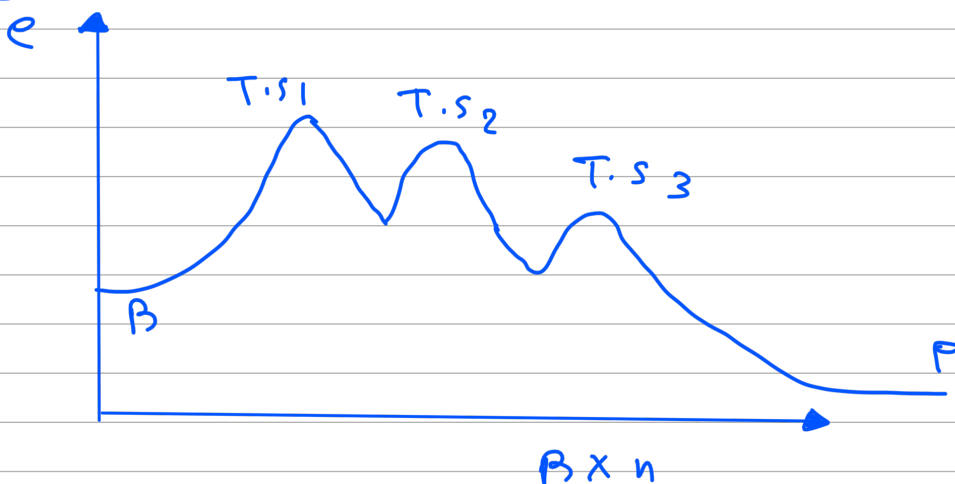


loss of H^+

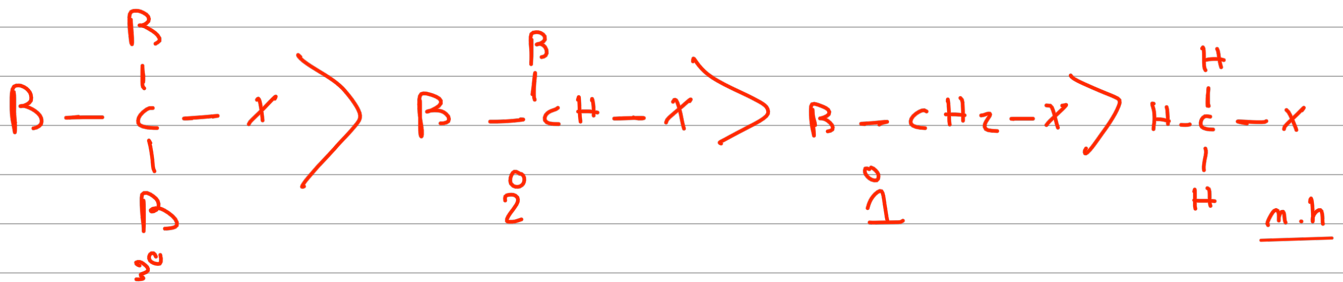


properties of $\text{S}_\text{N}1$ Reaction -

- Rate of reaction depend only on alkyl halide [unimolecular]
- Reaction is performed in more than one step.

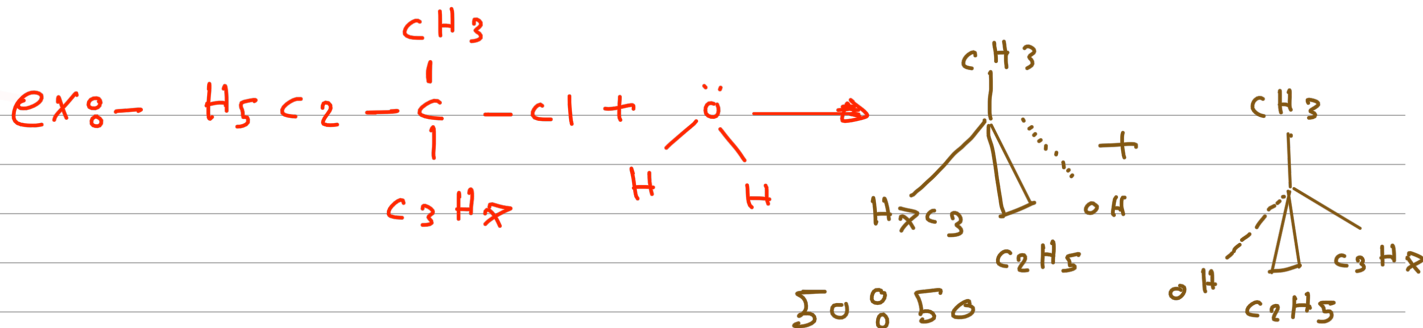


- Reactivity at reaction is ordered as -



- for stereochemistry

if reaction has a chiral center, products will be formed in a racemic mixture.



To summarize, the $\text{S}_{\text{N}}1$ mechanism is a two-step process and is favored when the alkyl halide is tertiary. Primary halides normally do not react by this mechanism. The $\text{S}_{\text{N}}1$ process occurs with racemization, and its rate is independent of the nucleophile's concentration.

6.6 compare between $\text{S}_{\text{N}}1$ and $\text{S}_{\text{N}}2$.

Table 6.2 Comparison of $\text{S}_{\text{N}}2$ and $\text{S}_{\text{N}}1$ Substitutions

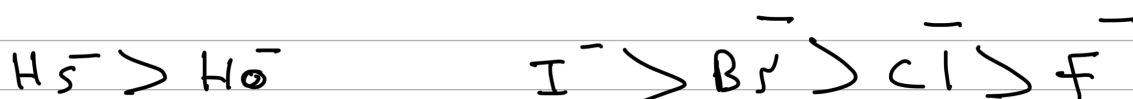
Variables	$\text{S}_{\text{N}}2$	$\text{S}_{\text{N}}1$
Halide structure		
Primary or CH_3	Common	Rarely*
Secondary	Sometimes	Sometimes
Tertiary	Rarely	Common
Stereochemistry	Inversion	Racemization
Solvent	Rate is retarded by polar protic solvents and increased by polar aprotic solvents	Because the intermediates are ions, the rate is increased by polar solvents
Nucleophile	Rate depends on nucleophile concentration; mechanism is favored when the nucleophile is an anion	Rate is independent of nucleophile concentration; mechanism is more likely with neutral nucleophiles

*Allyl and benzyl substrates are the common exceptions (see Problem 6.7b).

① Negative ions are more nucleophilic, or better electron suppliers, than the corresponding neutral molecules



② Elements low in the periodic table tend to be more nucleophilic than elements above them in the same column

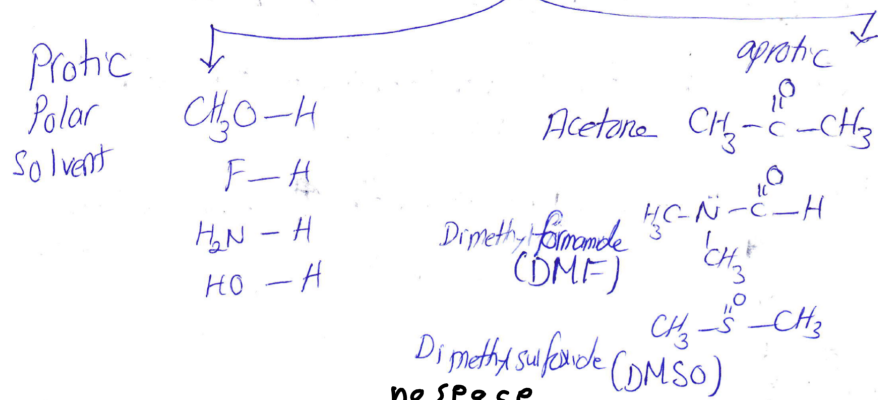


in protic solvents

③ Across a row in the periodic table, more electronegative elements (that is, the more tightly an element holds electrons to itself) tend to be less nucleophilic.



④ Organic solvents may include non-polar and polar solvents. For polar solvents, there are:



S_{N}^2 rxns prefer aprotic polar solvents, while S_{N}^1 : protic polar solvents.

• Elimination or dehydrohalogenation

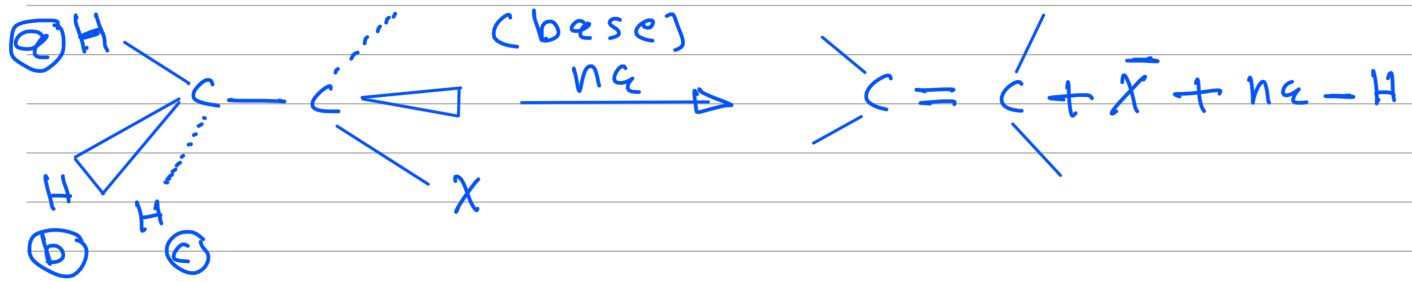


• Pi bond is formed in the product

2 mechanisms



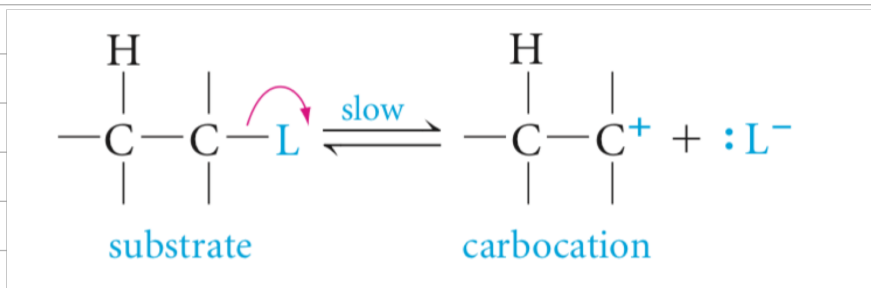
① E2-Mechanism



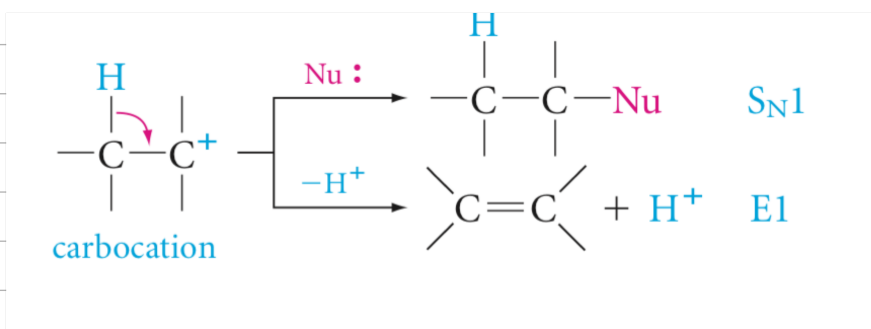
the E2 mechanism is a one-step process. The nucleophile, acting as a base, removes the proton (hydrogen) on a carbon atom adjacent to the one that bears the leaving group. At the same time, the leaving group departs and a double bond is formed. The bond breaking and bond making that occurs during an E2

② E1-Mechanism

- The E1 mechanism is a two-step process and has the same first step as the SN1 mechanism, the slow and rate-determining ionization of the substrate to give a carbocation

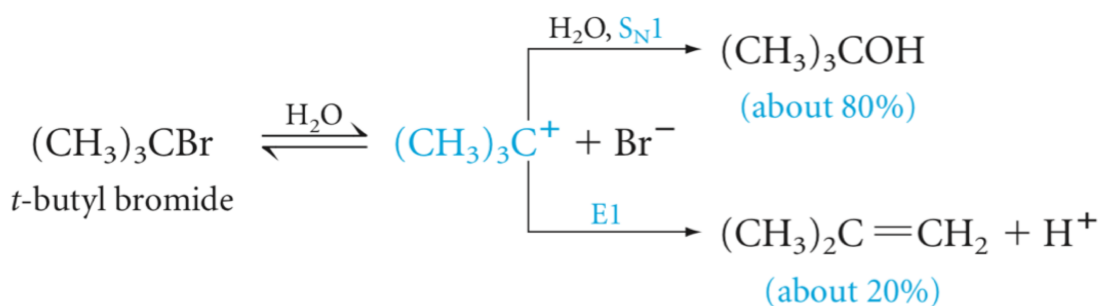


- Two reactions are then possible for the carbocation. It may combine with a nucleophile (the SN1 process), or it may lose a proton from a carbon atom adjacent to the positive carbon, as shown by the curved arrow, to give an alkene (the E1 process)

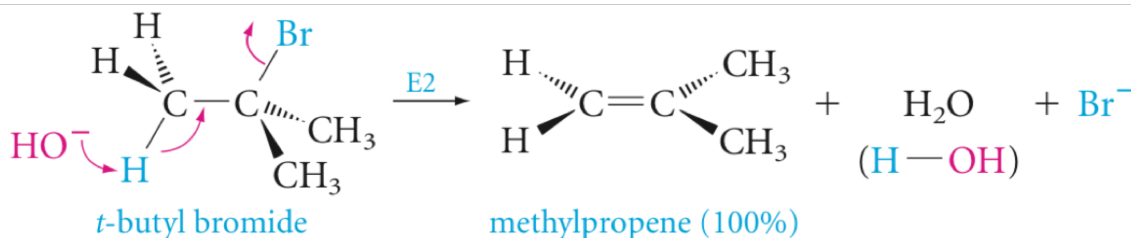


6.8 → Tertiary halide

- Substitution can only occur by the SN1 mechanism, but elimination can occur by either the E1 or the E2 mechanism. With weak nucleophiles and polar solvents, the SN1 and E1 mechanisms compete with each other. For example:

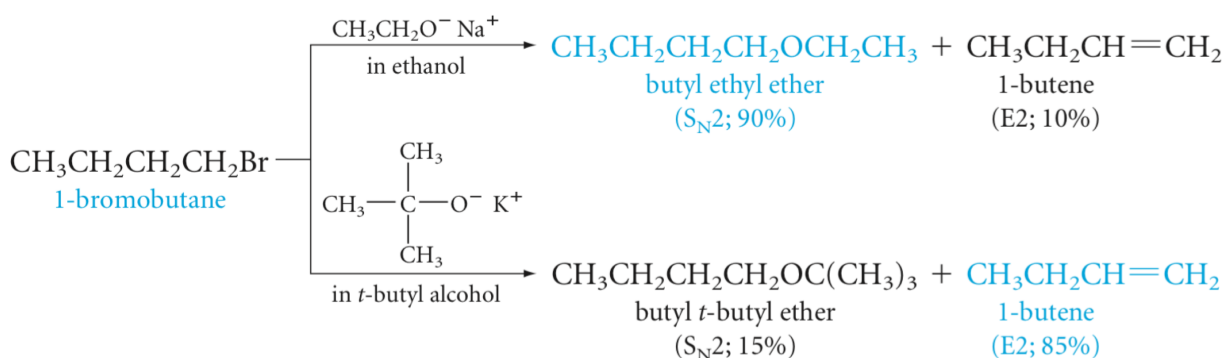


- If we use a strong nucleophile (which can act as a base) instead of a weak one, and if we use a less polar solvent, we favor elimination by the E2 mechanism. Thus, with OH⁻ or CN⁻ as nucleophiles, only elimination occurs (eqs. 6.5 and 6.7), and the exclusive product is the alkene



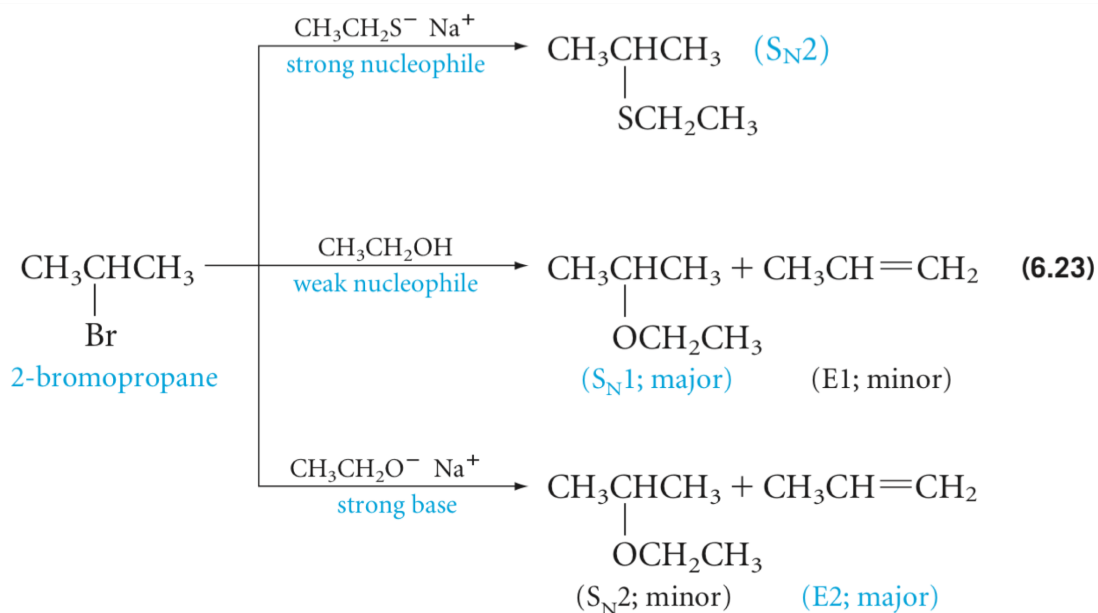
→ Primary halides

- Only the SN2 and E2 mechanisms are possible, because ionization to a primary carbocation, the first step required for the SN1 or E1 mechanisms, does not occur. With most nucleophiles, primary halides give mainly substitution products (SN2). Only with very bulky, strongly basic nucleophiles do we see that the E2 process is favored. For example



Tertiary halides

All four mechanisms, SN2 and E2 as well as SN1 and E1, are possible. The product composition is sensitive to the nucleophile (its strength as a nucleophile and as a base) and to the reaction conditions (solvent, temperature). In general, substitution is favored with stronger nucleophiles that are not strong bases (SN2) or by weaker nucleophiles in polar solvents (SN1), but elimination is favored by strong bases (E2).



* Finally \implies ملخص خفيف لطيف

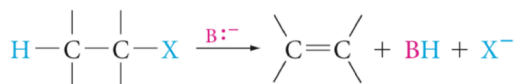
1. Nucleophilic Substitutions (S_N1 and S_N2)

Alkyl halides react with a variety of nucleophiles to give alcohols, ethers, alkyl halides, alkynes, and other families of compounds. Examples are shown in Table 6.1 and Section 6.2.



2. Elimination Reactions (E1 and E2)

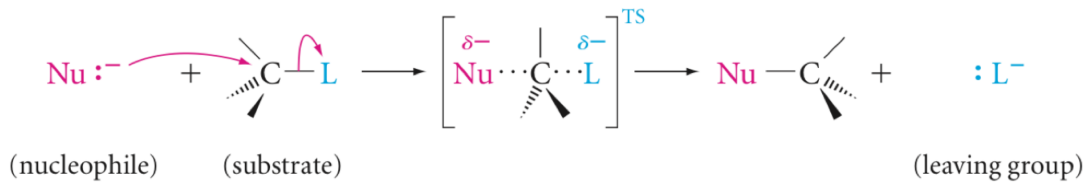
Alkyl halides react with bases to give alkenes (Sec. 6.7).



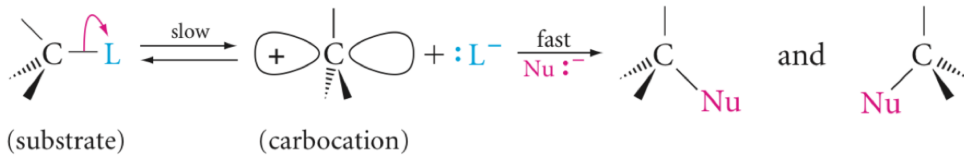
Summary reactions

Summary mechanisms

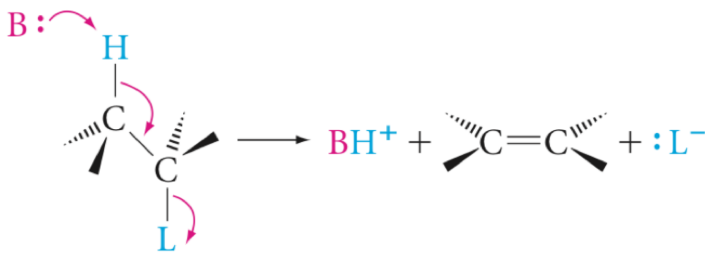
1. S_N2: Bimolecular Nucleophilic Substitution (Sec. 6.4)



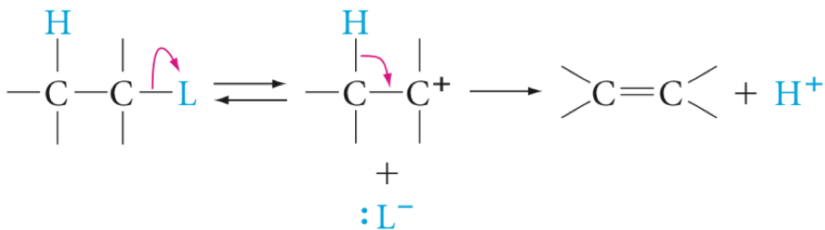
2. S_N1: Unimolecular Nucleophilic Substitution (Sec. 6.5)



3. E2: Bimolecular Elimination (Sec. 6.7)



4. E1: Unimolecular Elimination (Sec. 6.7)



قاوم ما تكره ، لتصل



إلى ما تحب