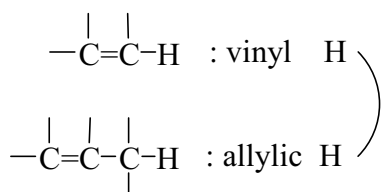
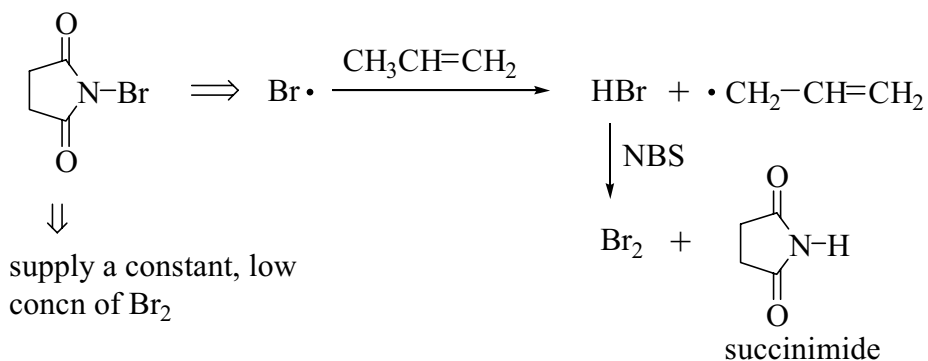


N-bromosuccinimide (NBS) : a reagent for the allylic bromination



ease of abstraction of H atom allylic $>$ 3° $>$ 2° $>$ 1° $>$ CH_4 $>$ vinylic (shorter, stronger)

ease of formation of free radical allyl $>$ 3° $>$ 2° $>$ 1° $>$ $\text{CH}_3\cdot$ $>$ vinyl

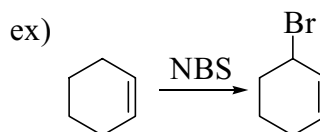
stability of free radical allyl $>$ 3° $>$ 2° $>$ 1° $>$ $\text{CH}_3\cdot$ $>$ vinyl

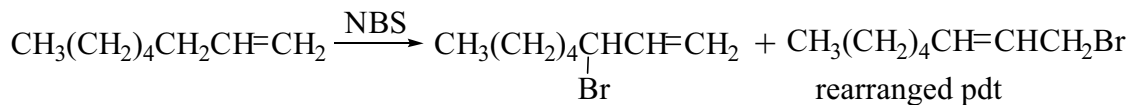
experimentally

\Downarrow

the double bond affects the stability of free radicals and of the incipient radicals in the transition state, and the rate of their formation

\Rightarrow the double bond determines the orientation of free-radical substitution

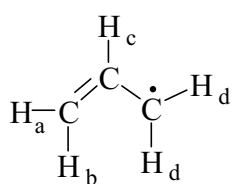




⇓

no migration of atoms or groups
migration of double bond

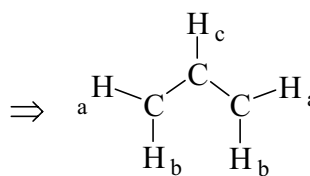
allyl radical : $\text{CH}_2=\text{CH}-\text{CH}_2 \cdot$



4 different kinds of H
are expected from the
classical structure

⇓

spectroscopically (ESR) three
different kinds of H are
observed



should be symmetrical
about the central carbon

Whenever a molecule can be represented by two or more structures (differing only in the arrangement of electrons) ⇒ there is resonance ⇒ the molecule is the hybrid of the structures

⇒ the resonance hybrid is more stable than any of the contributing structures ⇒ resonance energy ⇒ the more nearly equal their stability, the greater the resonance energy.

⇓

the more stable structure,
the larger contribution

⇒ conjugation : juxtaposition of a double bond and any π or p orbital to overlap
 cf) hyperconjugation

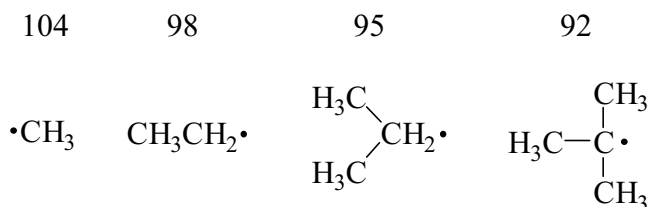
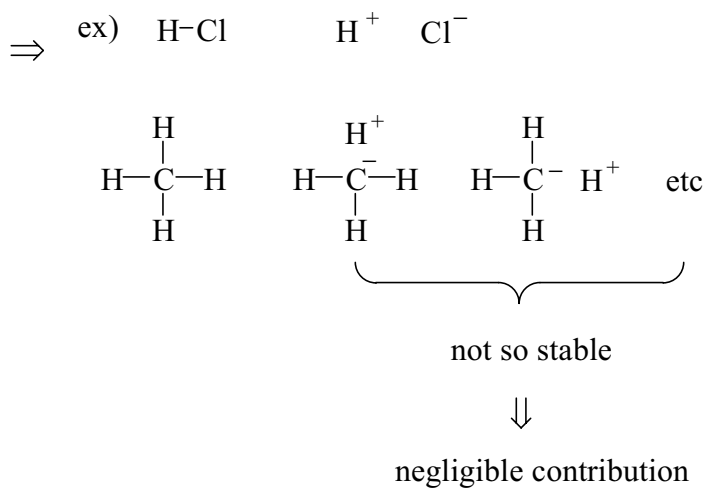
⇓

allyl radical is also a conjugated system

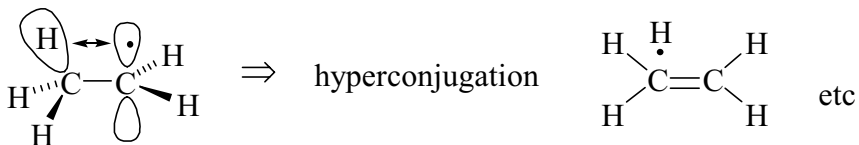
⇓

must exist as a resonance hybrid.

When drawing the resonance structures, be reasonable



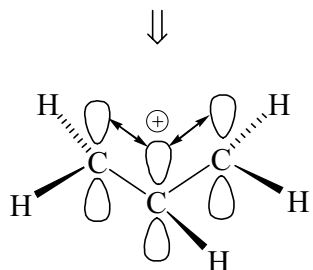
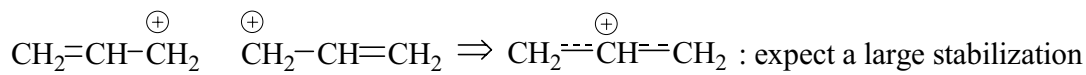
⇓



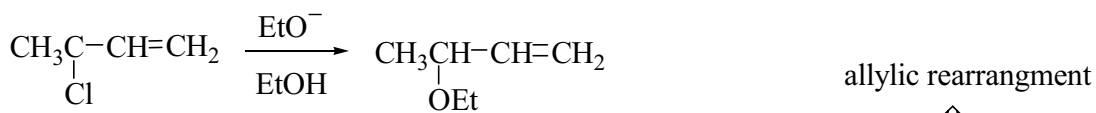
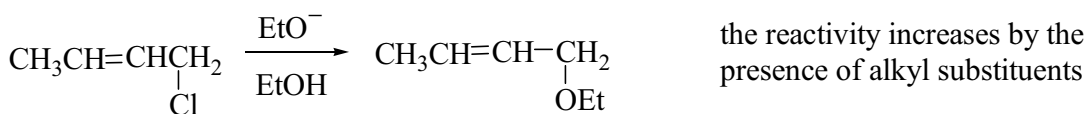
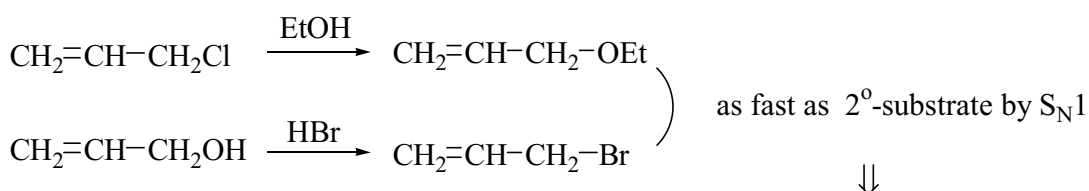
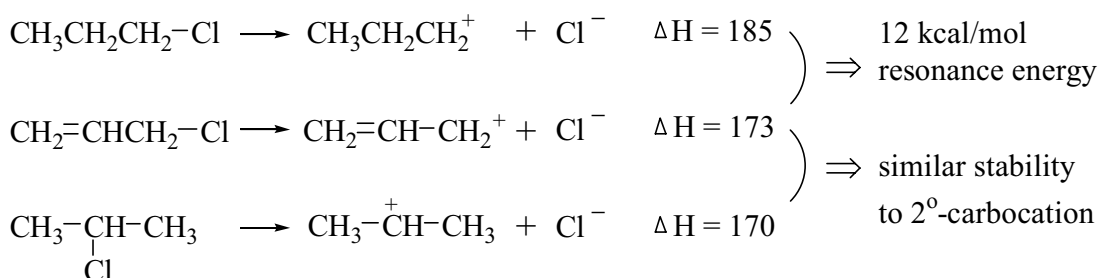
⇓

6 kcal/mole resonance energy

allyl cation



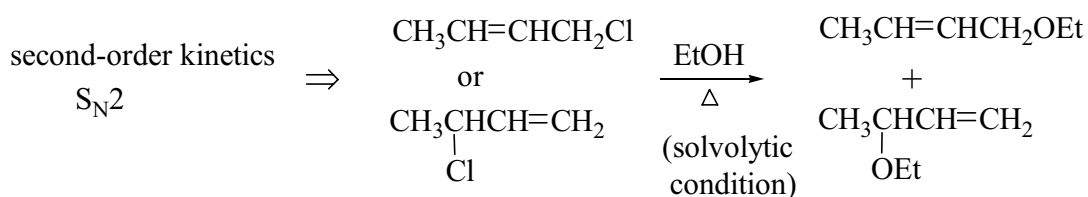
spectroscopically
one kind of C-C bond



↓

↑↑
S_N1 mechanism

↑



The stability of carbocation \Rightarrow depend on dispersal of charge

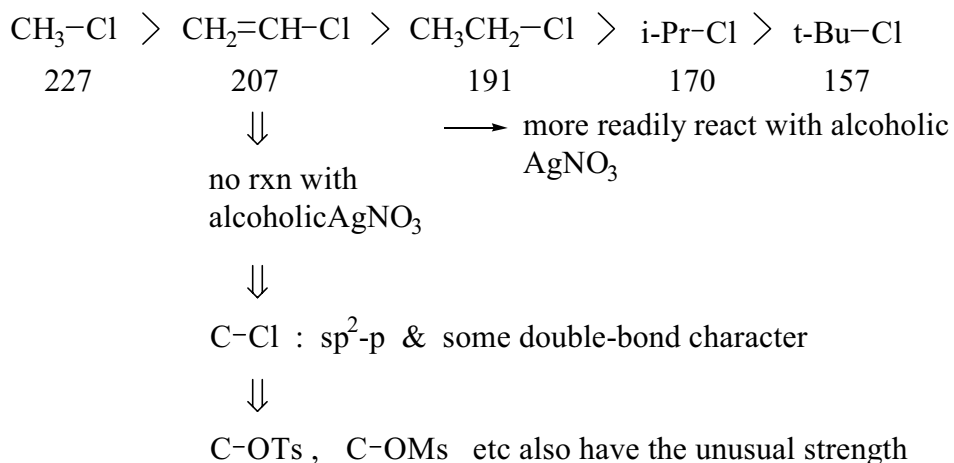


due to overlap between certain orbitals (called conjugation) \Leftarrow resonance effect \Leftarrow inductive effect (the strength depends on distance)

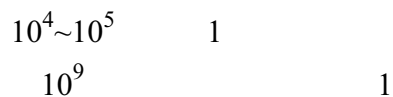
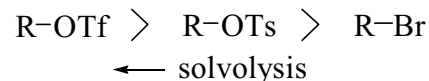
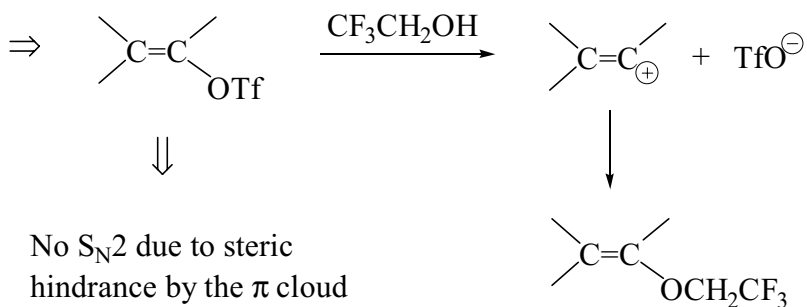


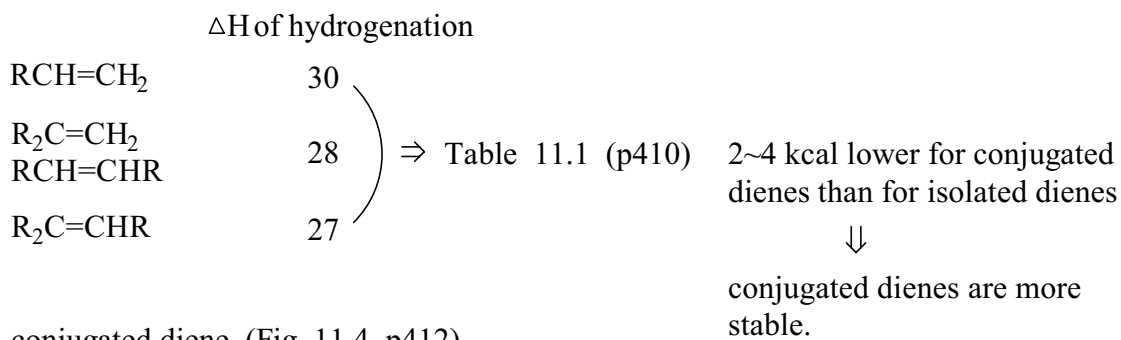
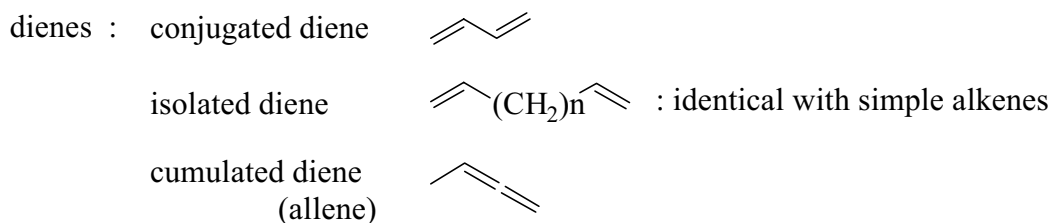
the empty p orbital and π - (group), σ -bond (C-H bond) or other filled p(d) orbitals (atom) \Rightarrow should be flat \Rightarrow a carbanion also can be stabilized by resonance effect.

allyl substrates are as reactive as saturated primary substrates in S_N2 due to the similar steric environment.

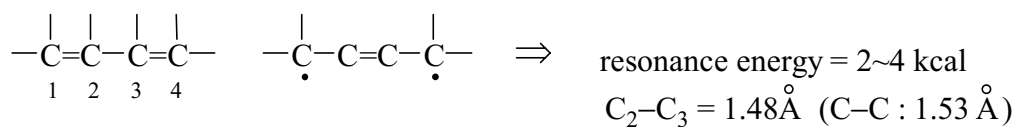


vinyl substrates may undergo S_N1 when the leaving group is extremely good and it contains electron-releasing substituents

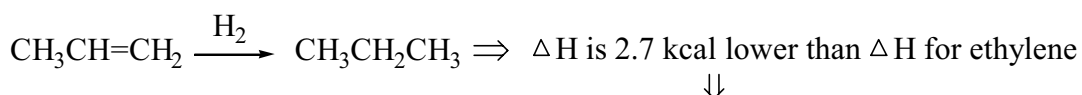
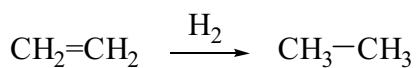




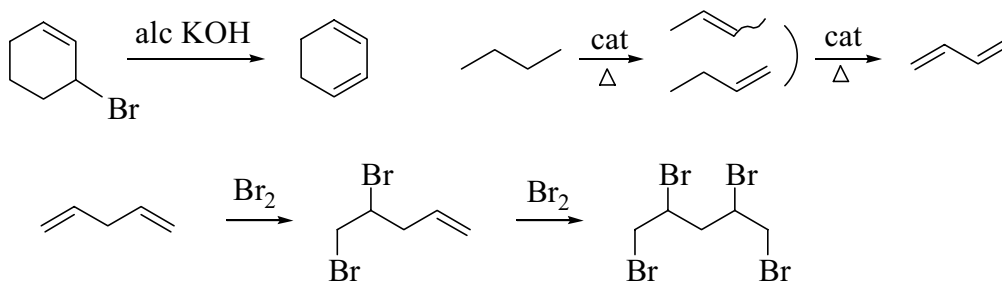
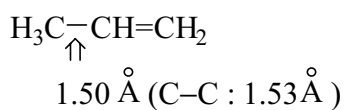
conjugated diene (Fig 11.4, p412)

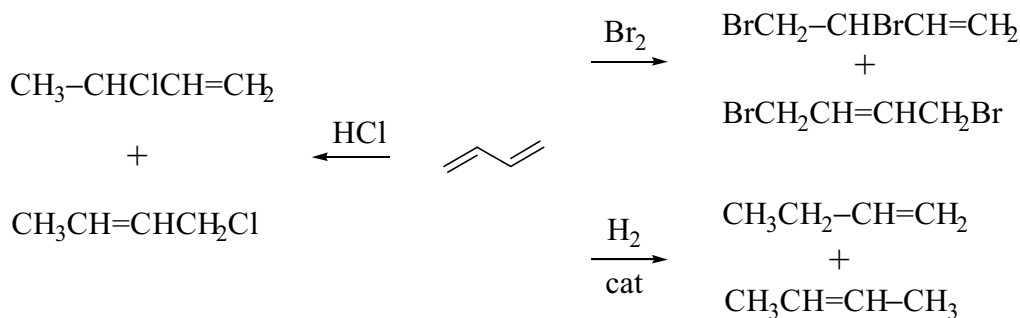


more stable
 \Downarrow
more contribution

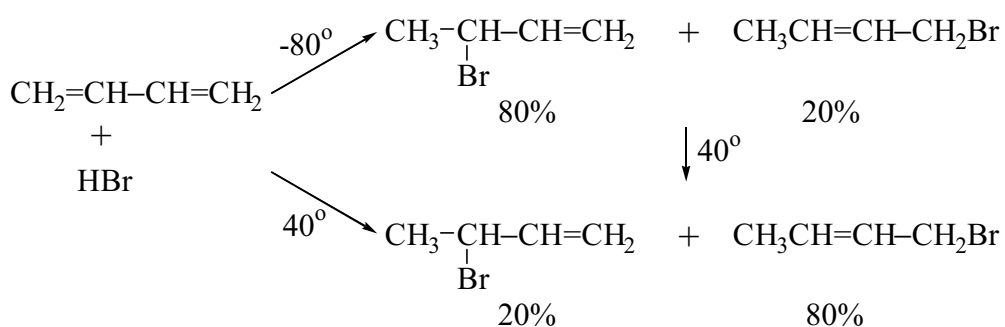
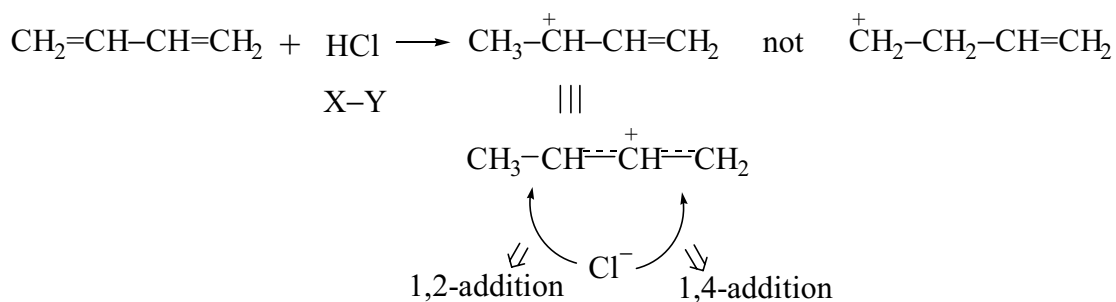


due to hyperconjugation \Leftarrow propylene is 2.7 kcal more stable than ethylene





⇒ 1,2-addition & 1,4-addition



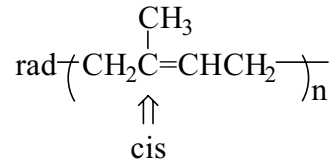
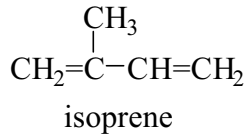
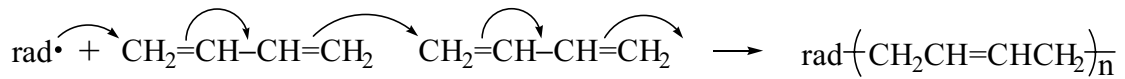
either compd is converted into the same composition of the two compds by heating. ⇒ the result of equilibrium
 ↓
 1,4-adduct is predominant and more stable.

1,2-product is formed more at -80° ⇒ no equilibrium at -80° ⇒ 1,2-product is formed faster than 1,4-product.

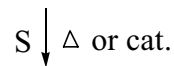
at low T : the ratio of pdts is determined by the rates of addition ⇒ should be no conversion after their formation
 at high T : the ratio of pdts is determined by the equilibrium of pdts

↓
 Fig 11.6 (p418)

↓
 the more stable pdt is not always formed faster



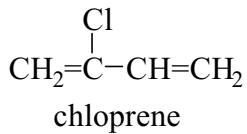
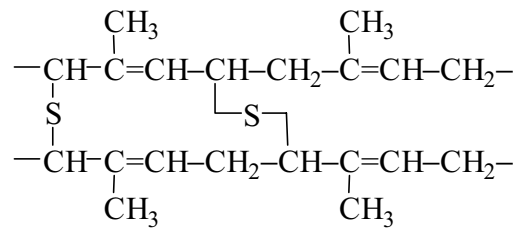
natural rubber



make rubber
harder and
stronger.
remove tackiness
of rubber.



vulcanization
(cross-link
chains by S)



polychloroprene (Neoprene, Duprene)

terpenes (from the essential oils of many plants) are made up of isoprene units joined in a regular way : isoprene rule \Rightarrow p421