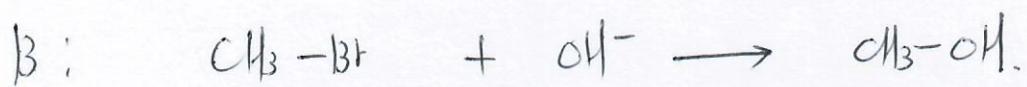
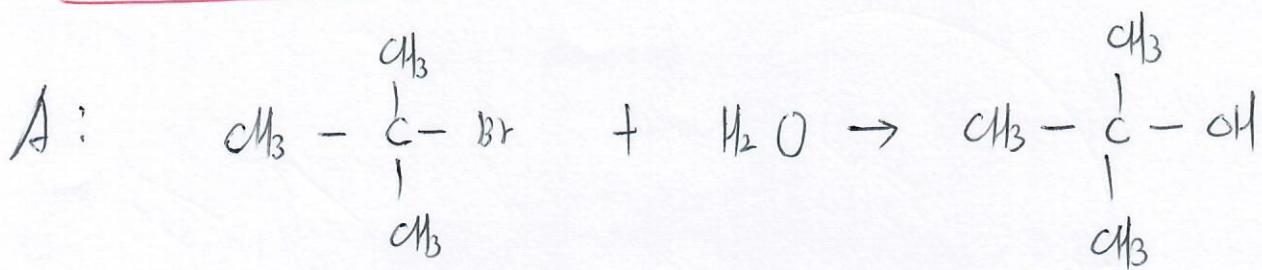


S_N1 rxn.



From S_N2 rxn.

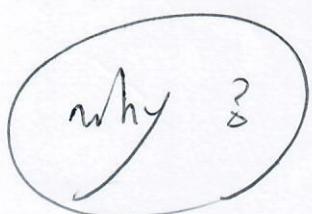
Chemical equation of A.



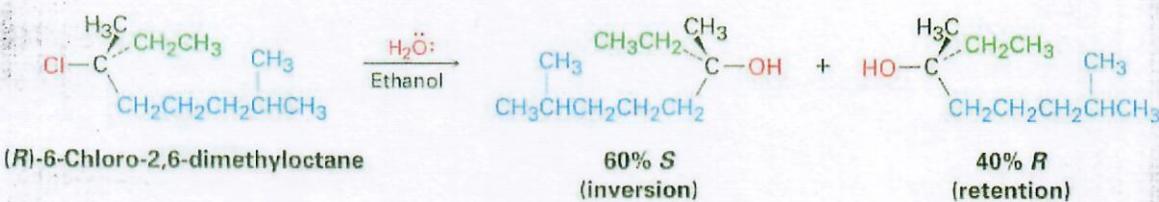
H_2O : Oxygen has two lone pair electrons
but these electrons are neutral.

So we expect chemical rxn of A is slower than B.

However, the A is 1,000,000 times faster than B.



The conclusion that S_N1 reactions on enantiomerically pure substrates should give racemic products is nearly, but not exactly, what is found. In fact, few S_N1 displacements occur with complete racemization. Most give a minor (0%–20%) excess of inversion. The reaction of (*R*)-6-chloro-2,6-dimethyloctane with H₂O, for example, leads to an alcohol product that is approximately 80% racemized and 20% inverted (80% *R,S* + 20% *S* is equivalent to 40% *R* + 60% *S*).



Saul Winstein

Saul Winstein (1912–1969) was born in Montreal, Canada, and received his Ph.D. in 1938 at the California Institute of Technology. From 1942 to 1969, he was professor of chemistry at the University of California, Los Angeles, where he devoted his scientific career to the study of organic reaction mechanisms, particularly those involving carbocations.

This lack of complete racemization in most S_N1 reactions is due to the fact that *ion pairs* are involved. According to this explanation, first proposed by Saul Winstein, dissociation of the substrate occurs to give a structure in which the two ions are still loosely associated and in which the carbocation is effectively shielded from reaction on one side by the departing anion. If a certain amount of substitution occurs before the two ions fully diffuse apart, then a net inversion of configuration will be observed (Figure 11.11).

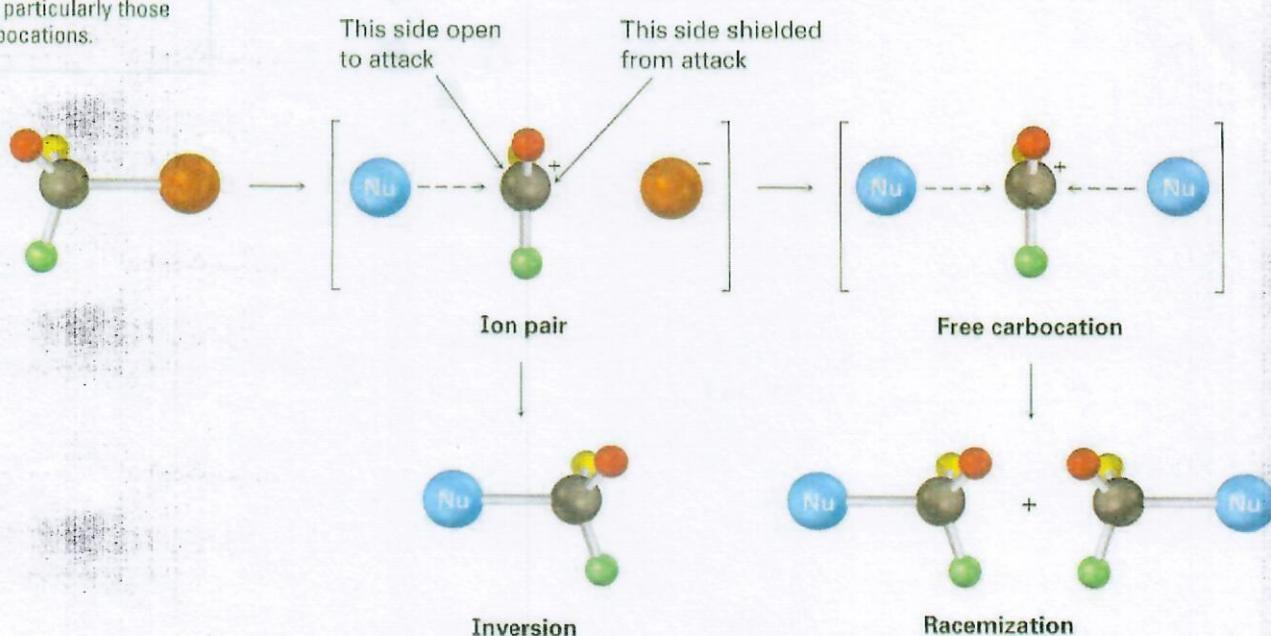


Figure 11.11 Ion pairs in an S_N1 reaction. The leaving group shields one side of the carbocation intermediate from reaction with the nucleophile, thereby leading to some inversion of configuration rather than complete racemization.

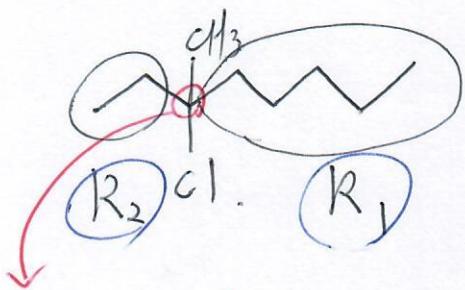
Problem 11.8

What product(s) would you expect from reaction of (*S*)-3-chloro-3-methyloctane with acetic acid? Show the stereochemistry of both reactant and product.

Problem 11.9

Among the numerous examples of S_N1 reactions that occur with incomplete racemization is one reported by Winstein in 1952. The optically pure tosylate of

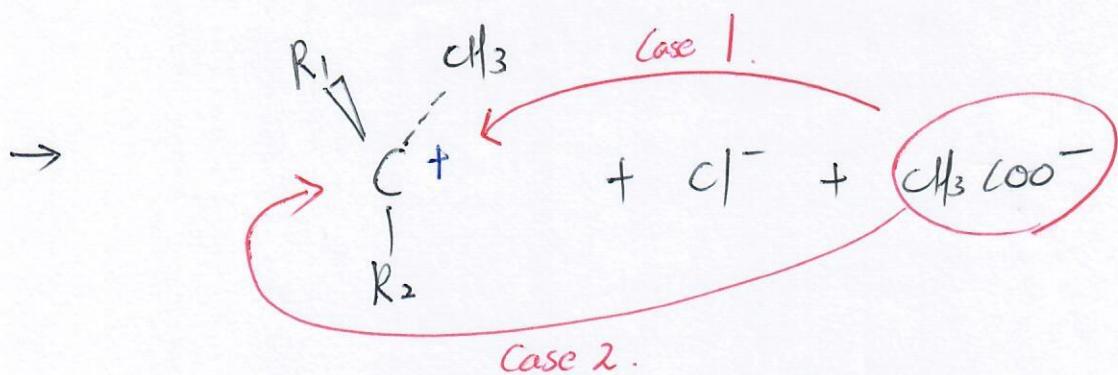
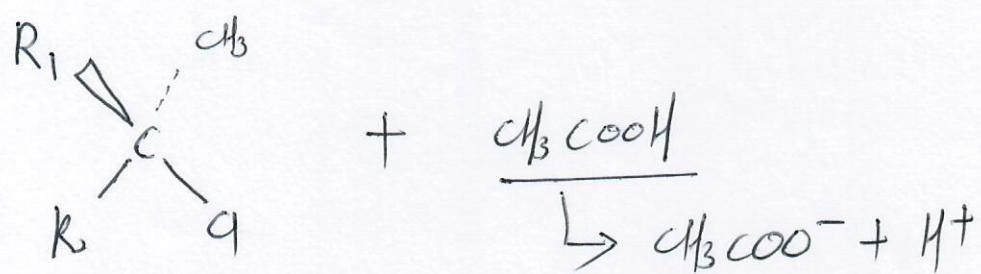
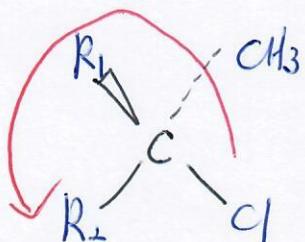
Problem 11-8 (1)



chiral carbon

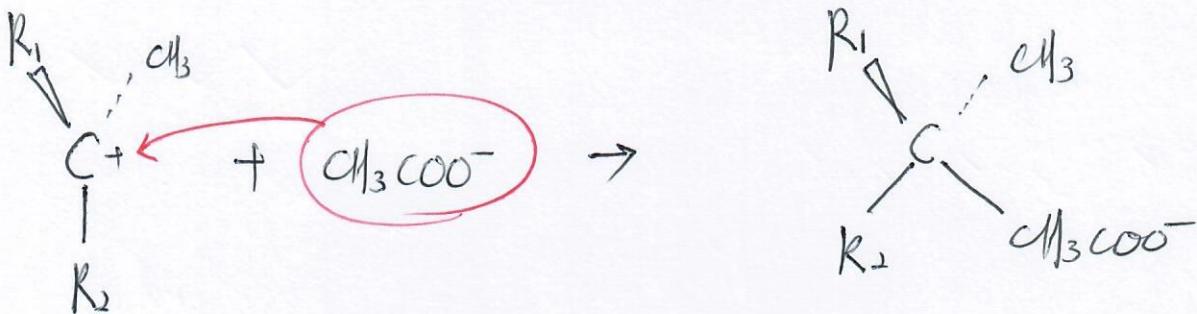
The priority of side chains
is $\text{Cl} > \text{R}_1 > \text{R}_2 > \text{CH}_3$.

The configuration of this molecule
is (S).



problem 11-8 (2)

< Case 1 >

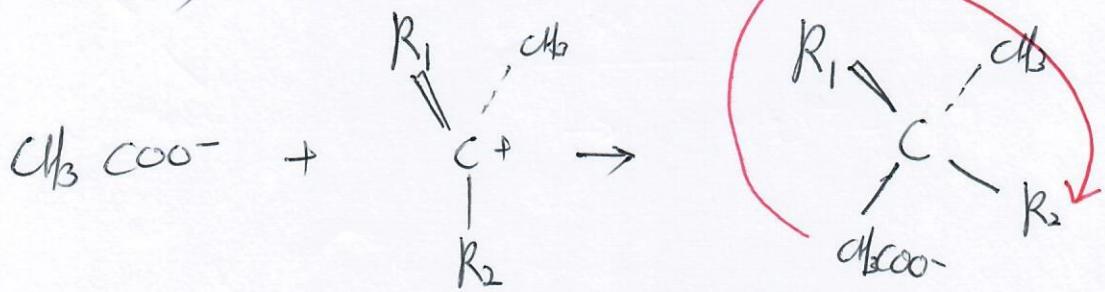


The priority of side chains. Is



so this molecule has (S) configuration.

< Case 2 >

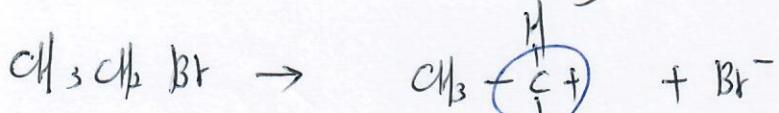
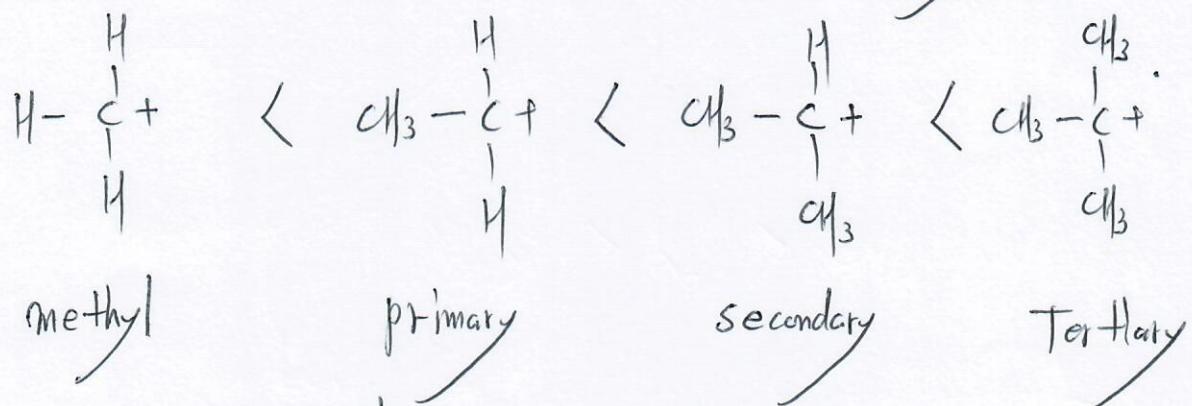


(R) configuration.

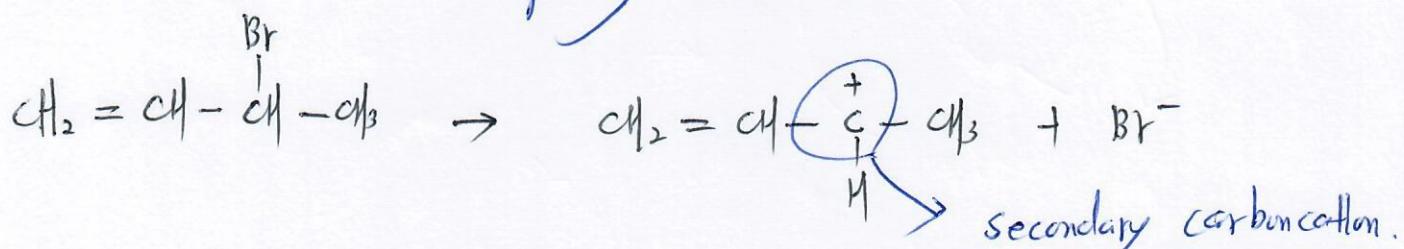
Problem 11-11 (1)

To know the S_N1 reactivity,
find the carbon cation stability.

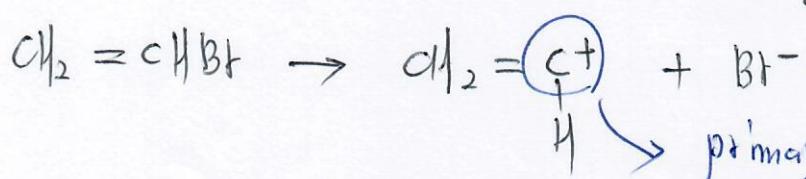
The order of alkyl carbon cation stability is



primary carbocation.

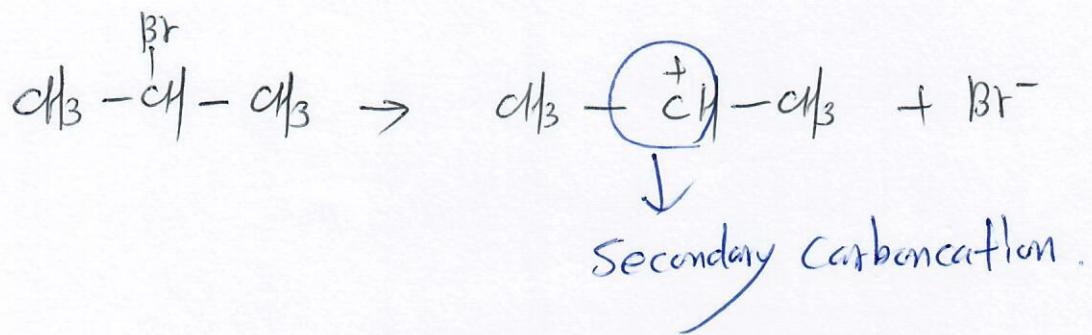


but more stable than secondary carbocation because of allyl.

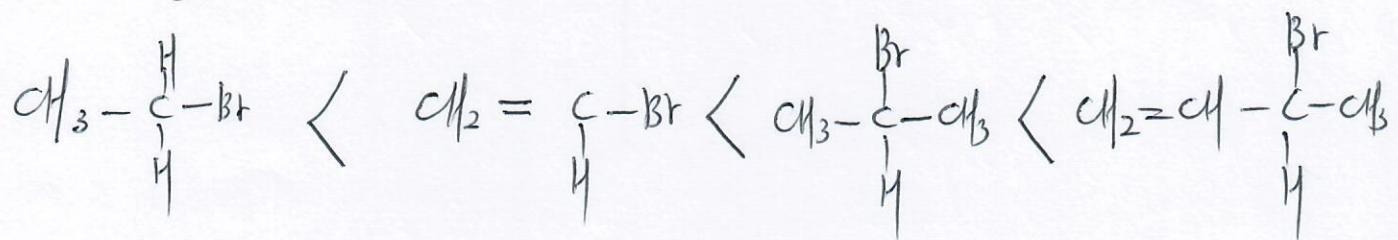


more stable than primary carbocation because of allyl group.

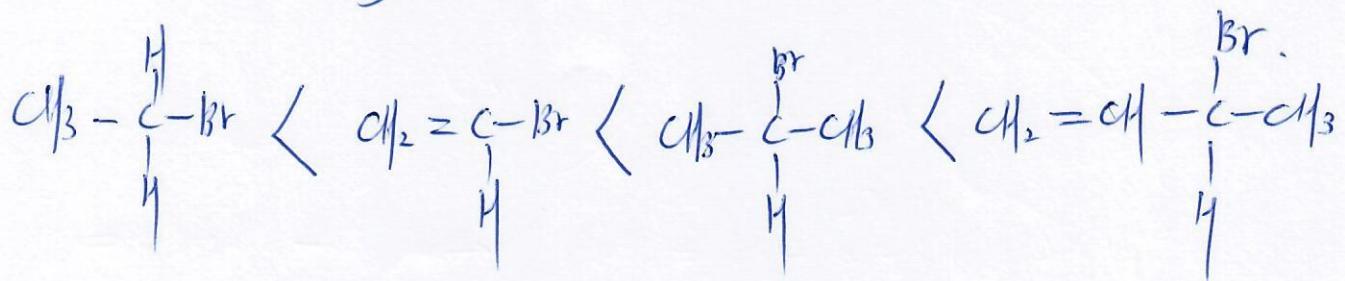
Problem 11-11 (2)



The stability of carbon cation is

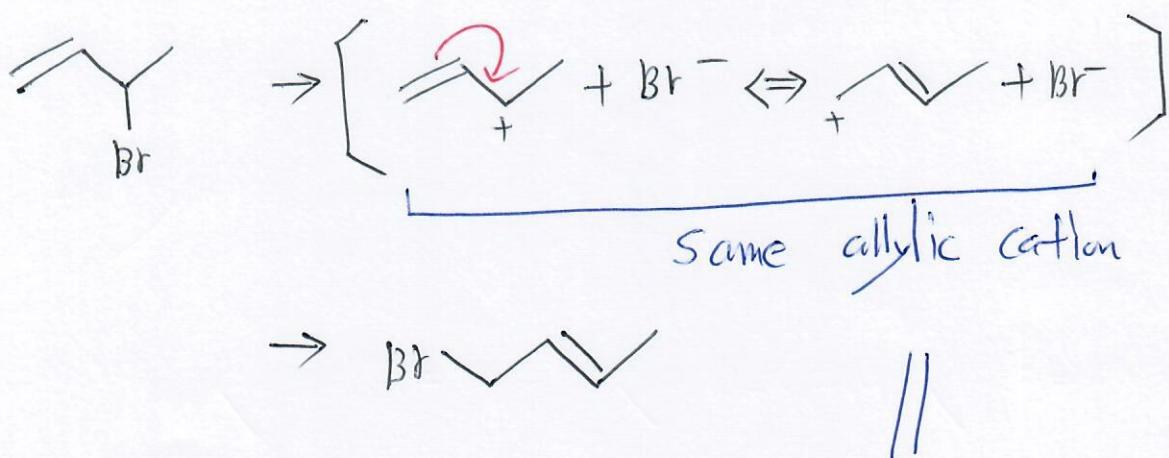


So SN1 reactivity

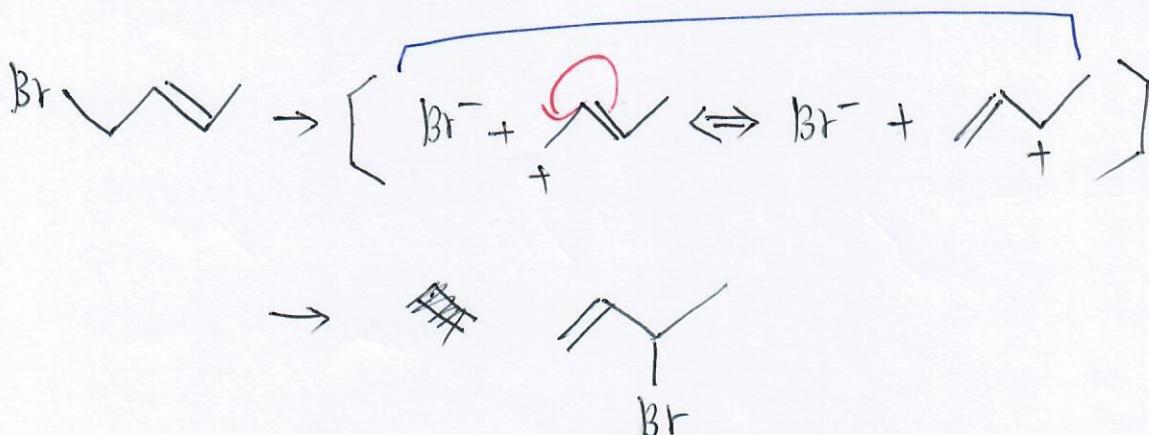


Problem 11-12.

3-Bromo-1-butene

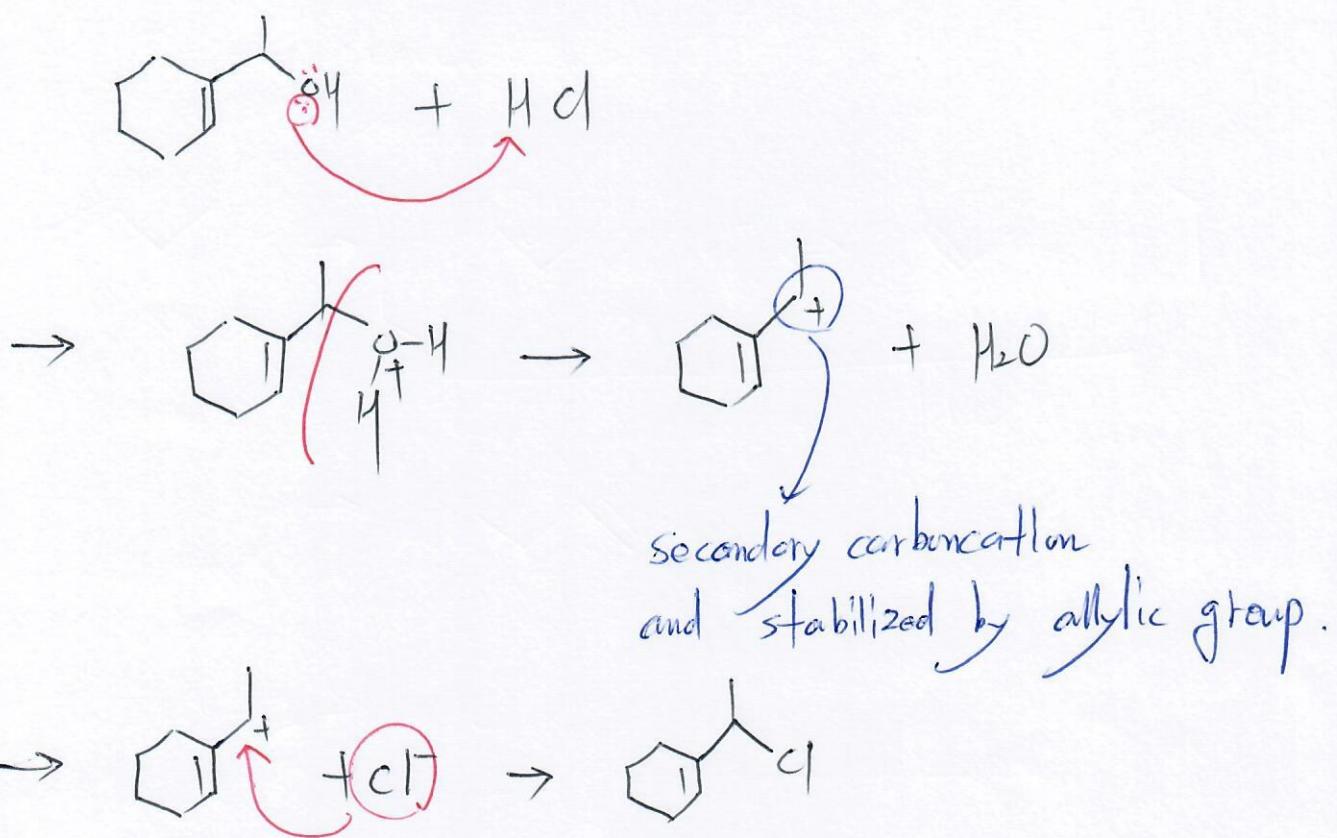


1-bromo-2-butene

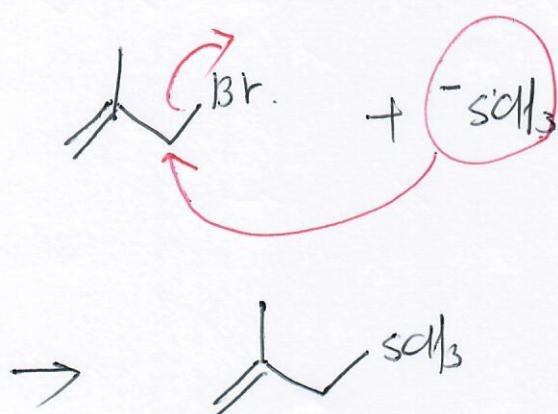


problem 11-13.

(a)



(b)



Summary

S_N1

S_N2

Substrate

tertiary carbon
related with
carbon cation

methyl.
related with
~~the~~ steric effect.

Nucleophile

same

strong nucleophile.

Leaving groups

Good leaving
group

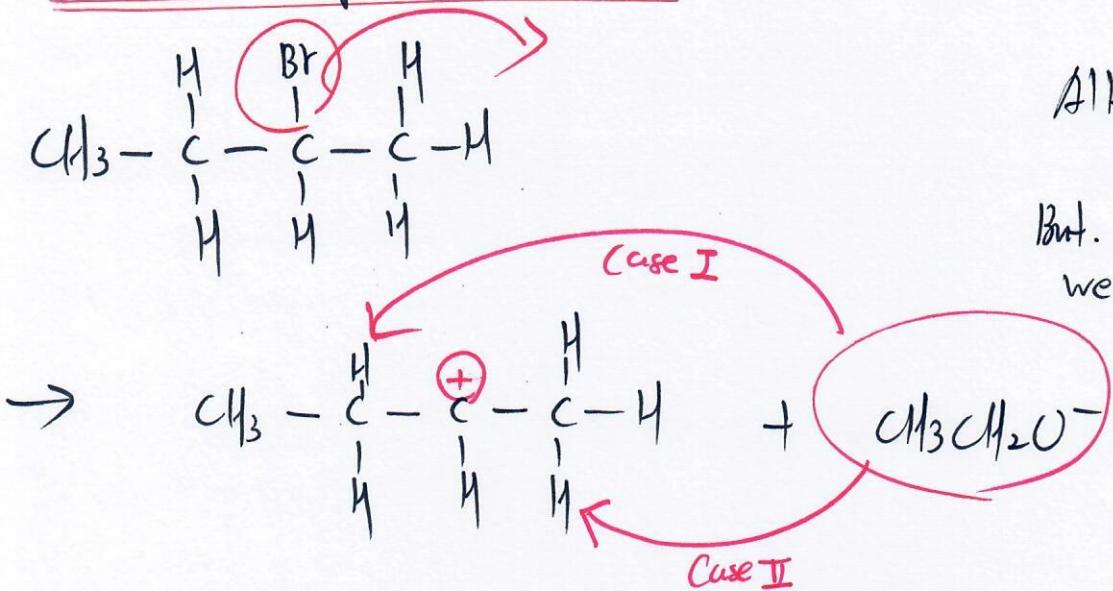
Good leaving
group

Solvent

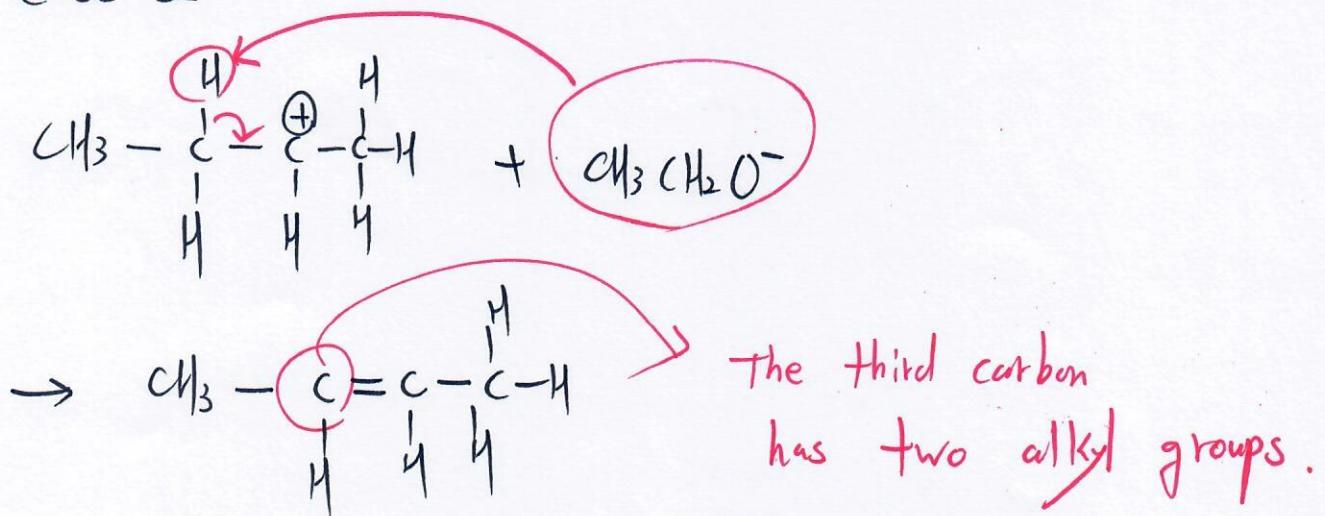
polar solvent
(H_2O).

polar solvent
(DMF, CH_3CN ,
HMPA).

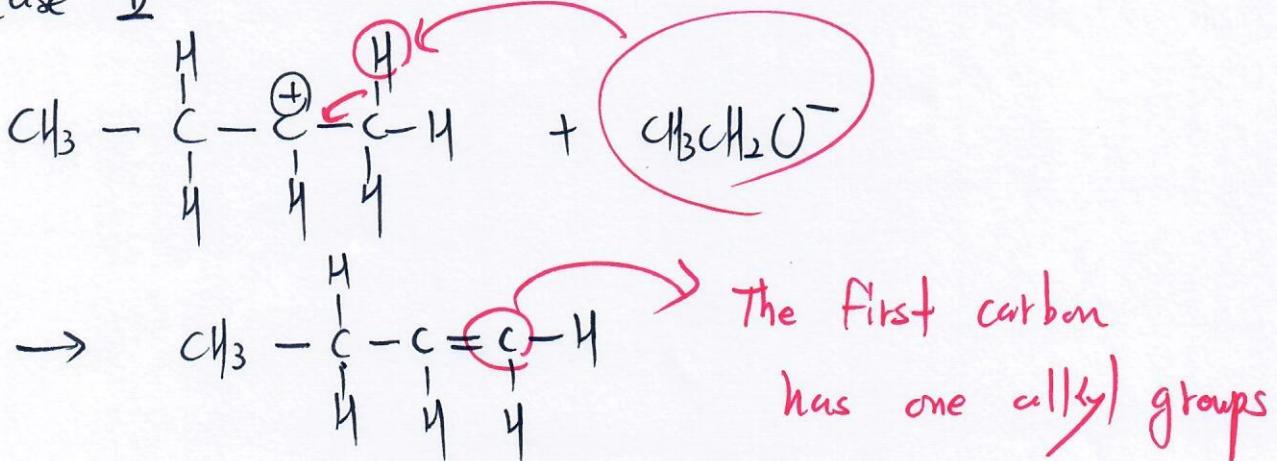
Lecture ppt p59-1



Case I

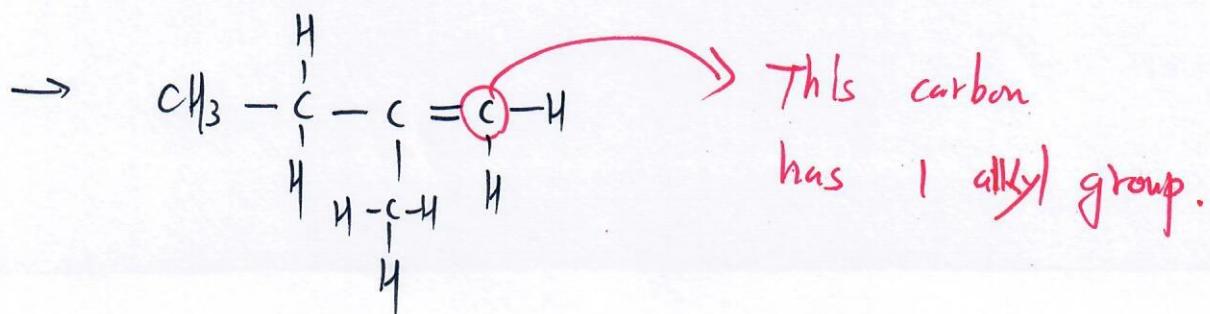
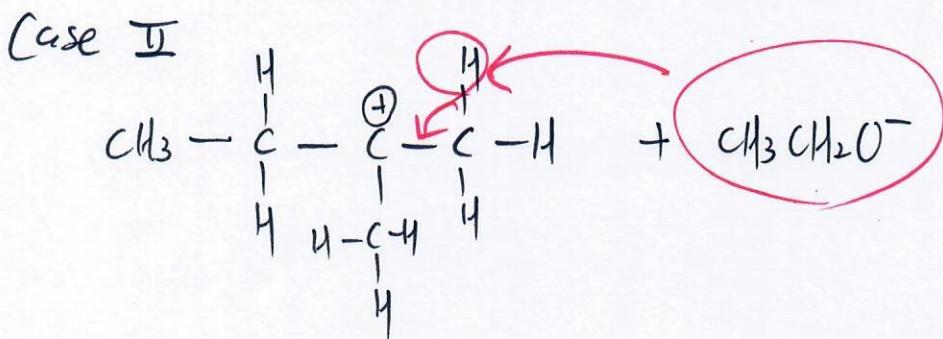
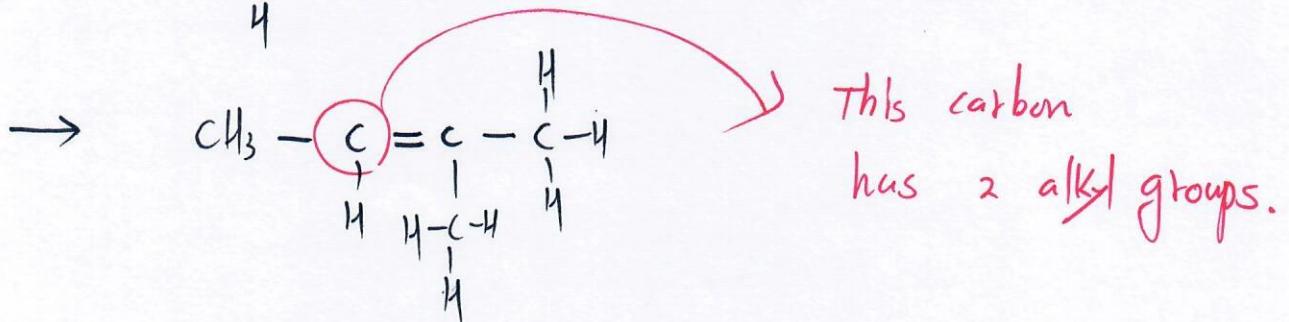
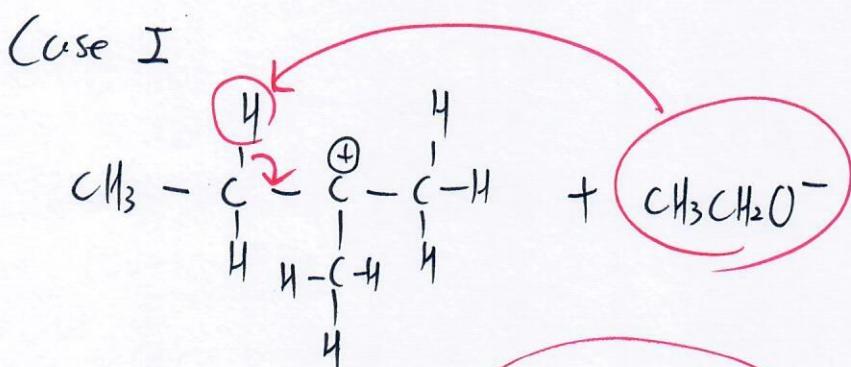
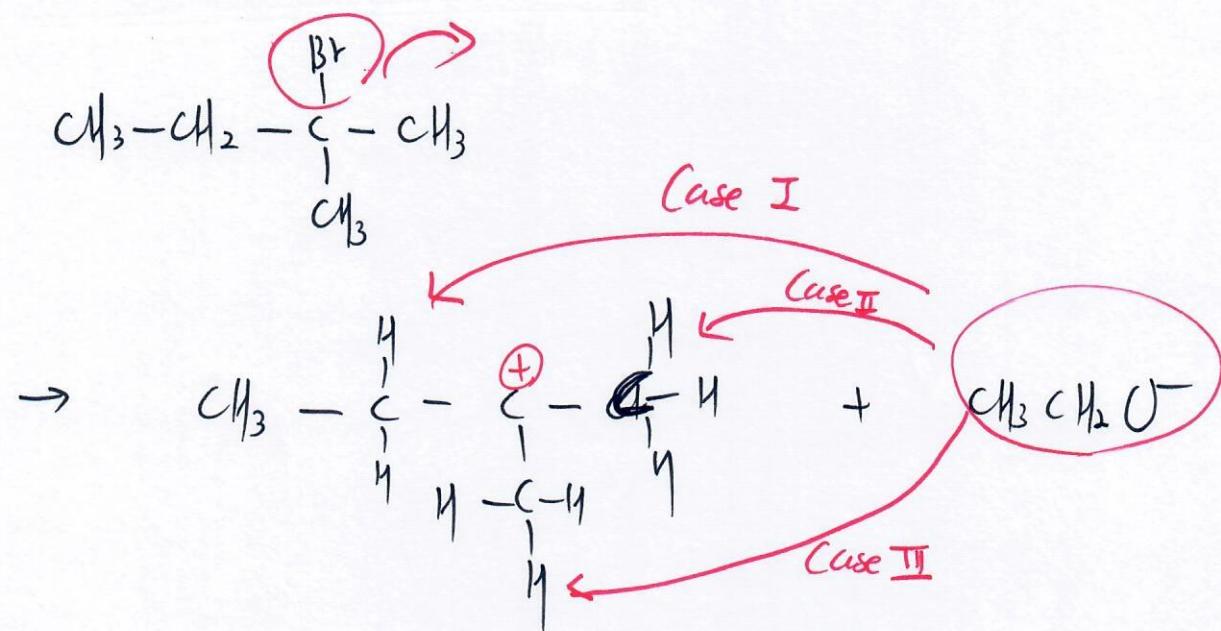


Case II



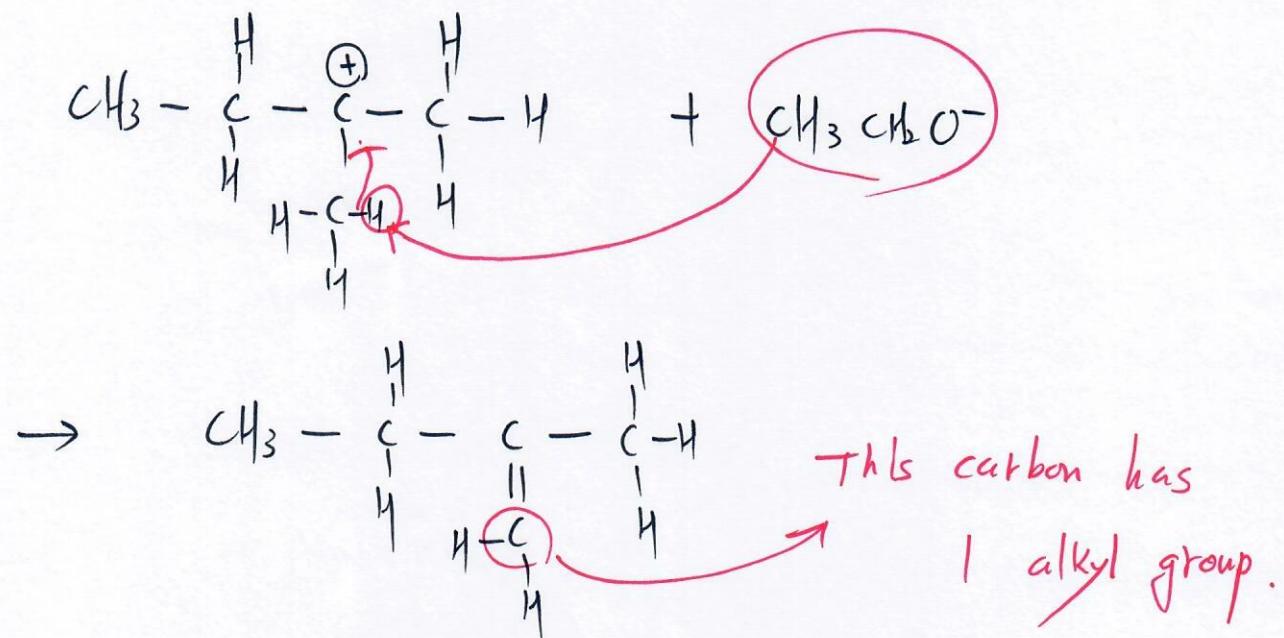
From Zaitsev's rule, α -butene is major product.

Lecture ppt P59-2

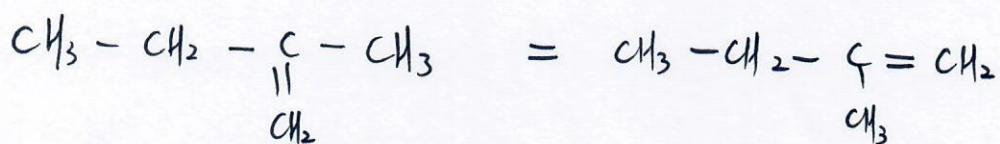


Lecture ppt p59-3

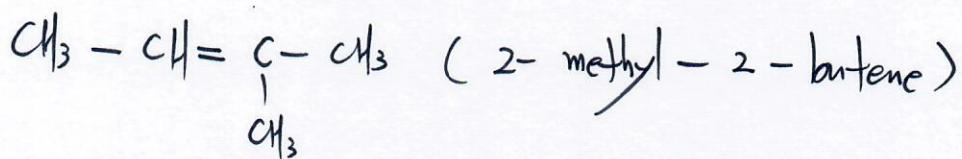
Case III



In Case III and IV,

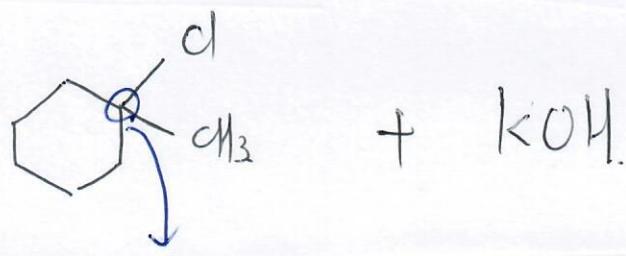


From the Zaitsev's rule,

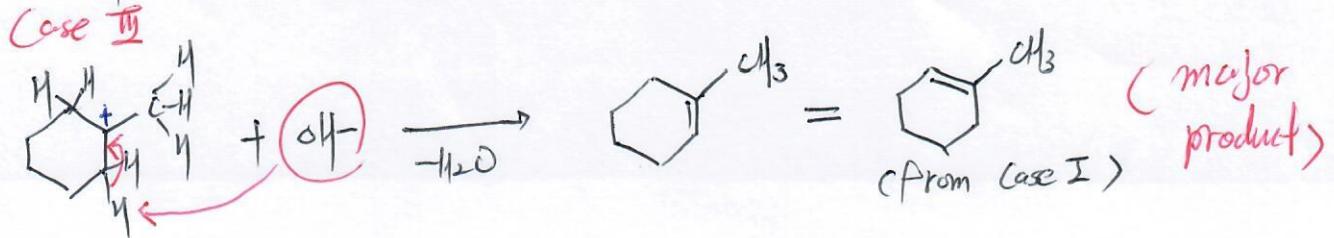
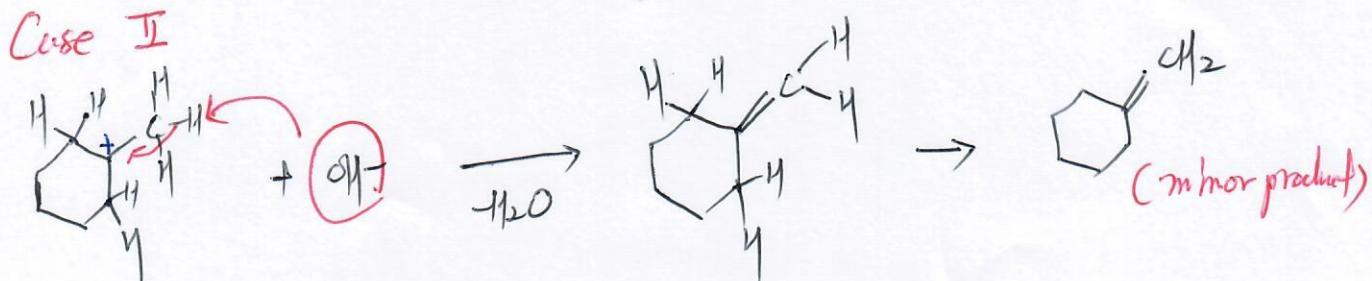
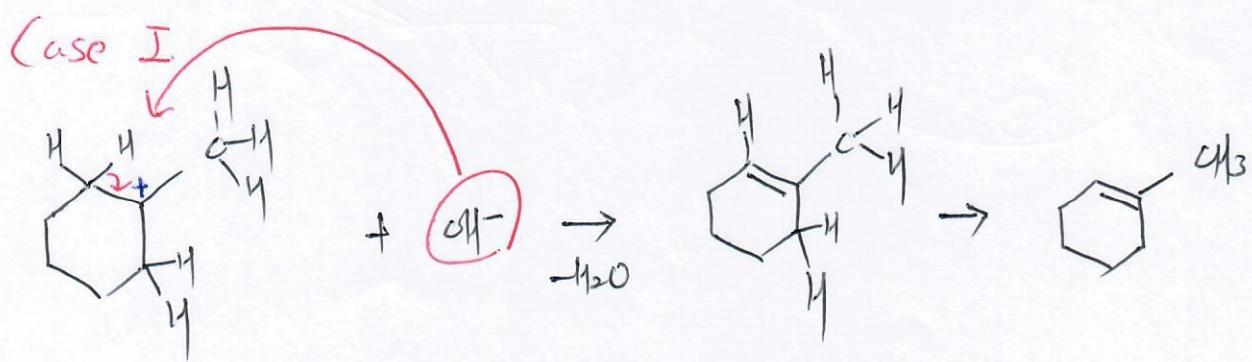
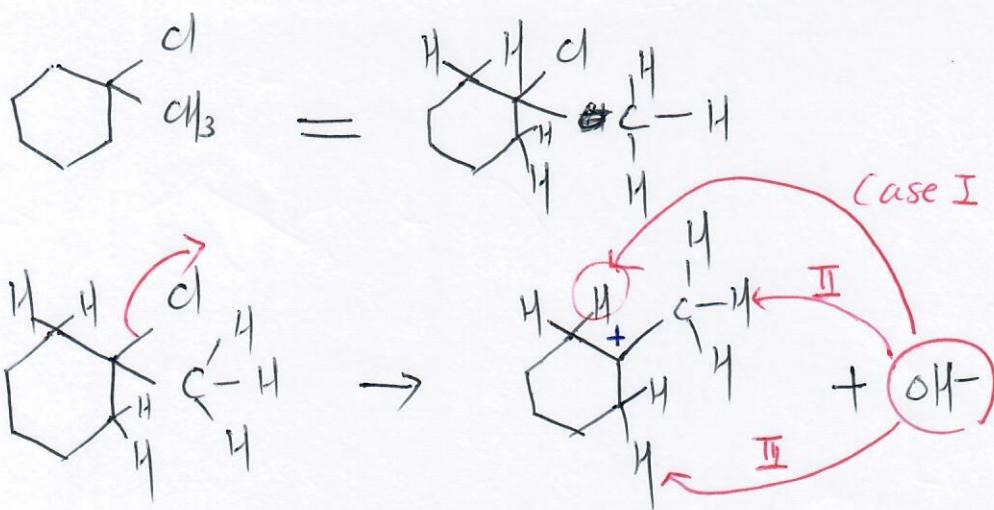


is major product.

work Example 11-3. (1)

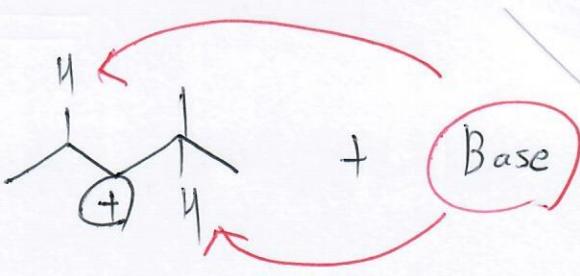
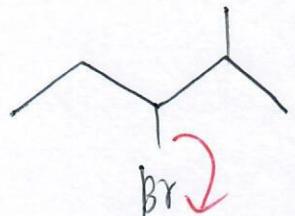


This carbon is tertiary carbon. ~~So E2 rxn~~ ^{This rxn is E2 because of the tertiary C and strong base.}
But we assume this rxn is E1.



Problem 11-15.c1)

(a)



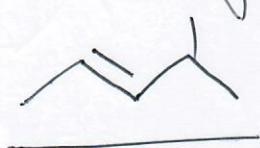
or



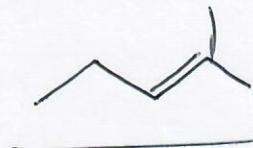
(two alkyl group)

(three alkyl group)

According to Zaitsev's rule,

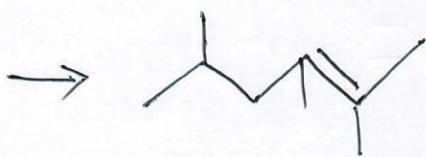
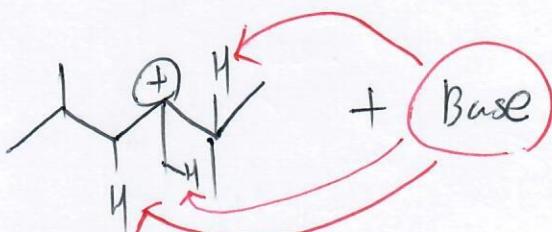
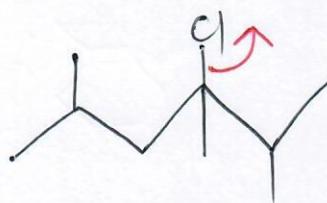


minor

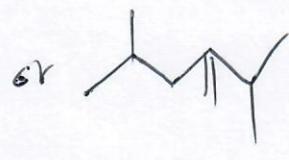
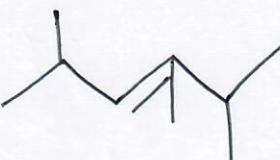


major

(b)



or



4 alkyl group

major

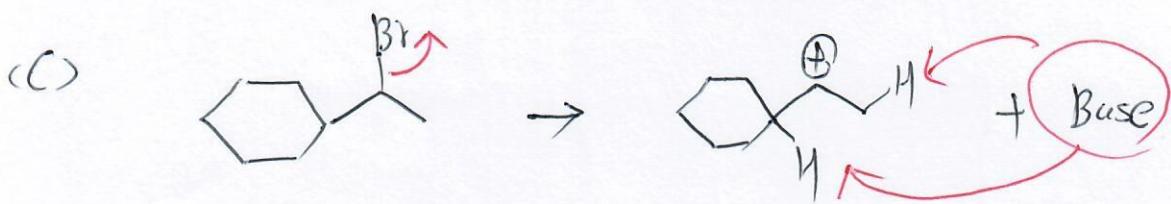
3 alkyl group

minor.

2 alkyl group

minor.

Problem 11-15 (2)

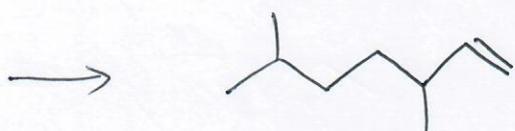
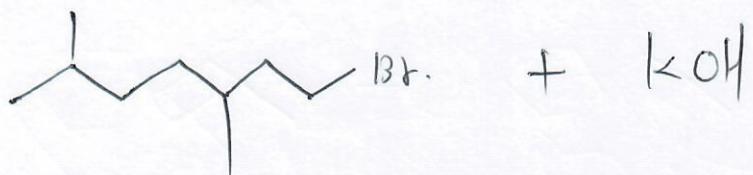


three alkyl groups
Major product

one alkyl group
Minor product.

problem 11-16(c)

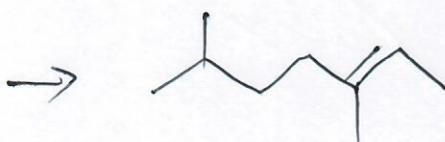
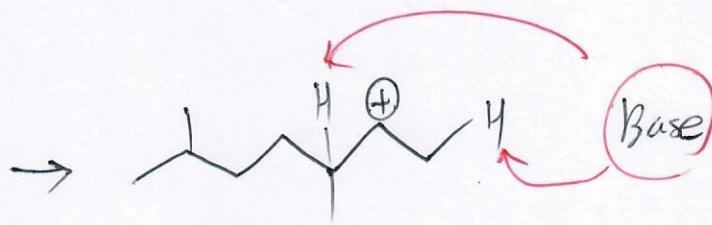
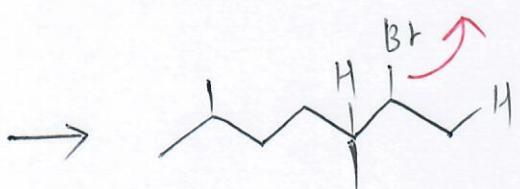
(a)



or.



+ Base



or



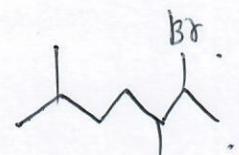
three alkyl groups

Major

one alkyl group

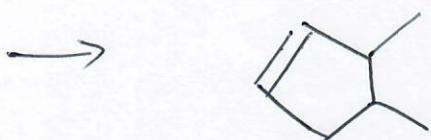
Minor.

we can get it from

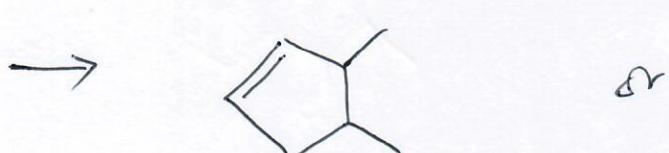
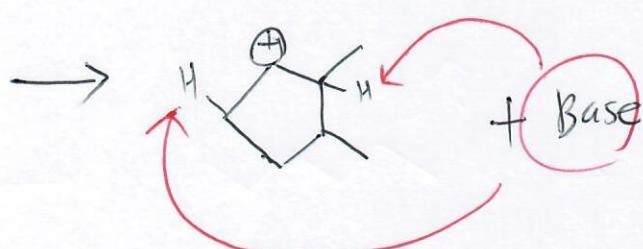


Problem 11-16 (2)

(b)



or



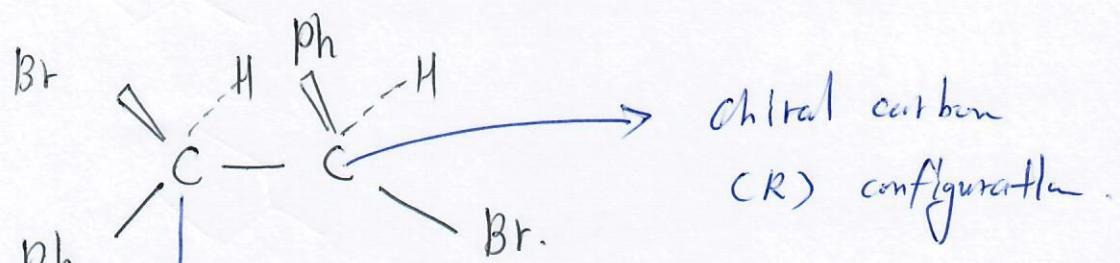
two alkyl groups
minor

3 alkyl groups
major.

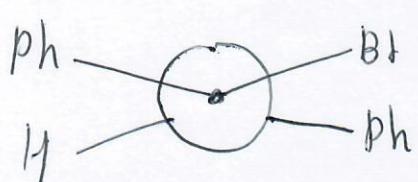
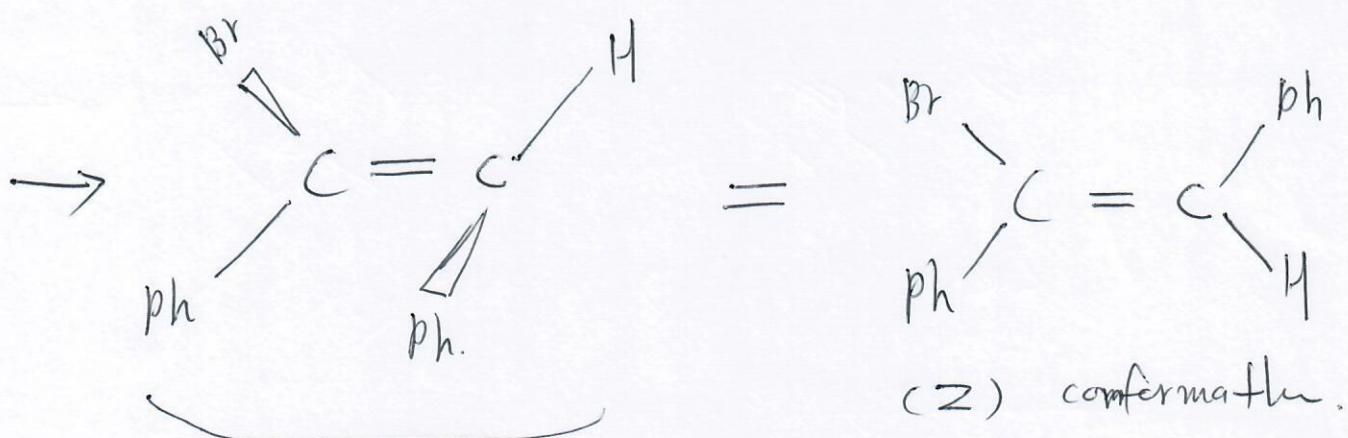
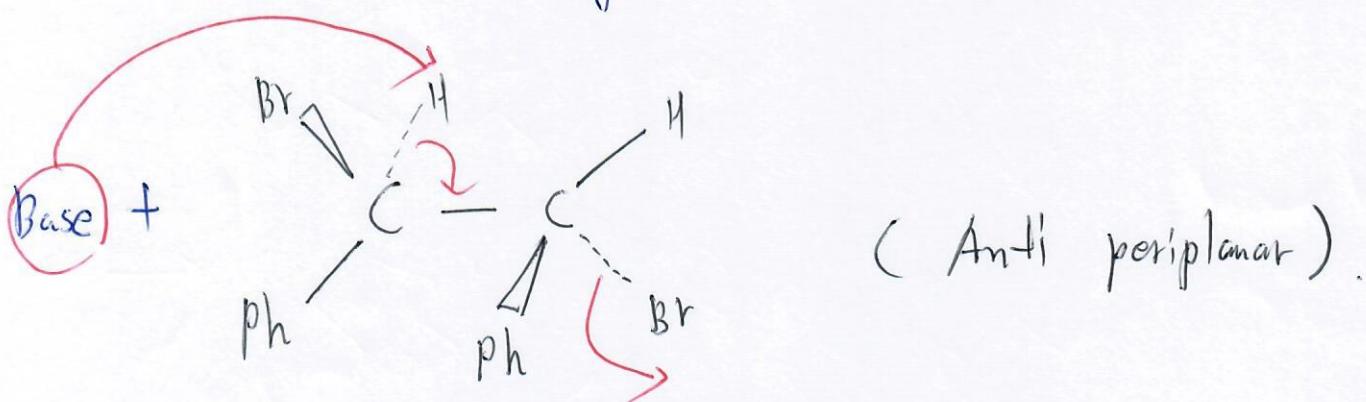
Answer .

Problem 11-17.

(1R, 2R)-1,2-dibromo-1,2-diphenylethane.

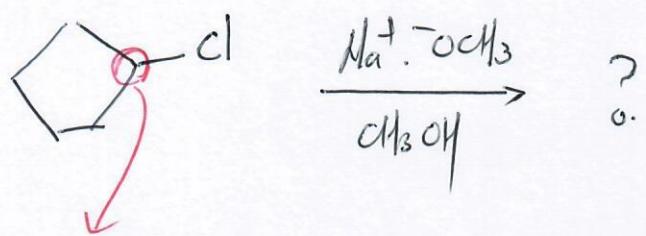


chiral carbon → (syn periplanar)
(R) configuration.



Worked Example 11.5. -1

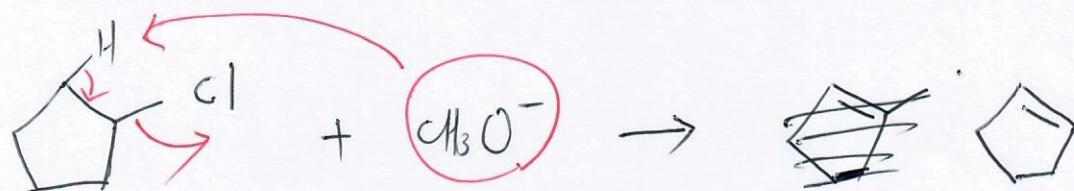
(a)



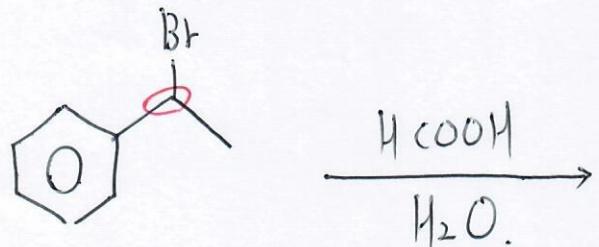
This carbon is secondary carbon.

and methoxide (CH_3O^-) is strong base.

So this rxn is E2.



(b)

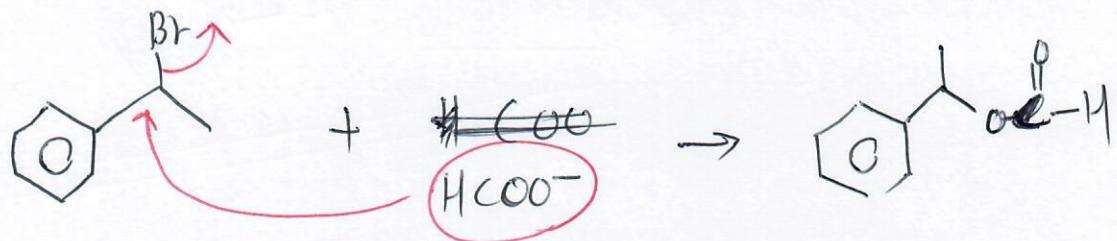


This carbon is secondary carbon.

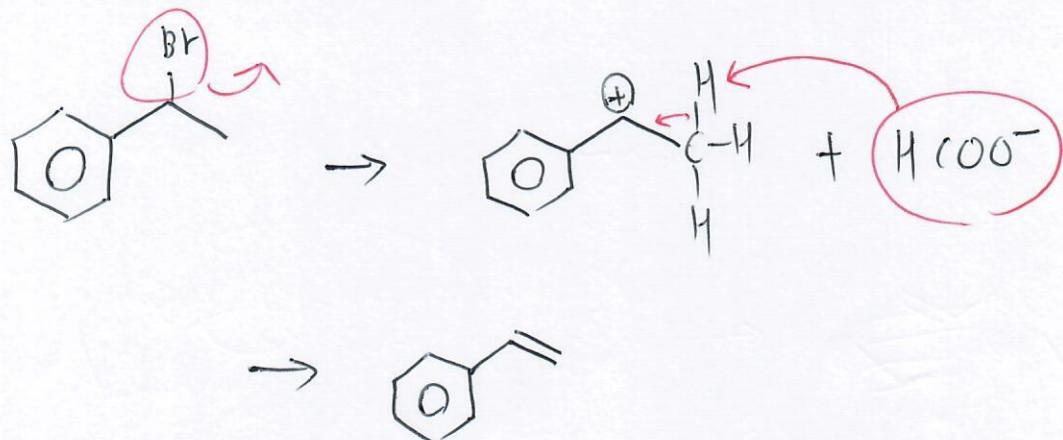
Weak base,
protic solvent. $\Rightarrow \text{SNI}$.
 Br is good leaving group $\Rightarrow \text{E1}$.

Worked Example 11.5-2

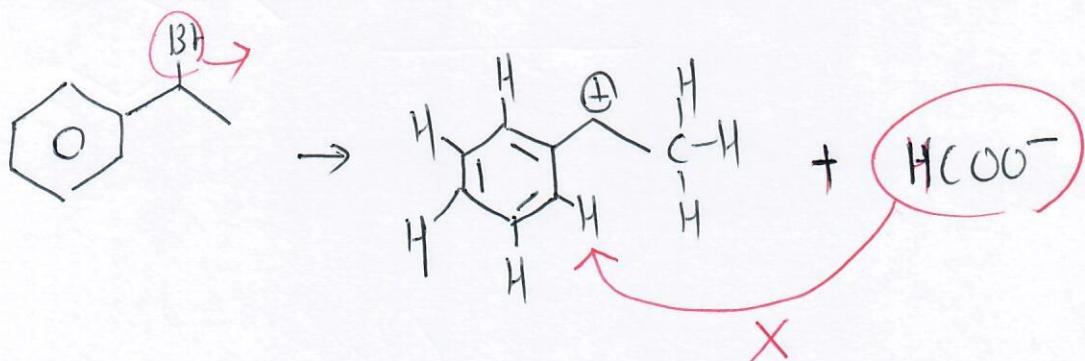
In S_N1 rxn.



In $E1$ rxn



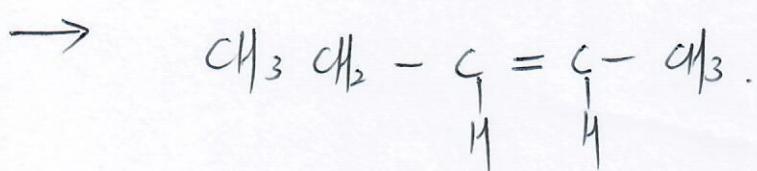
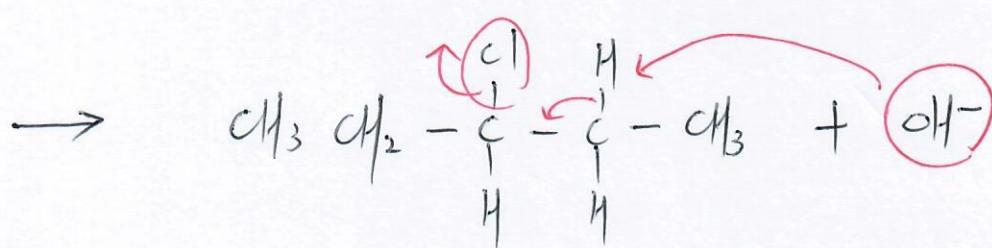
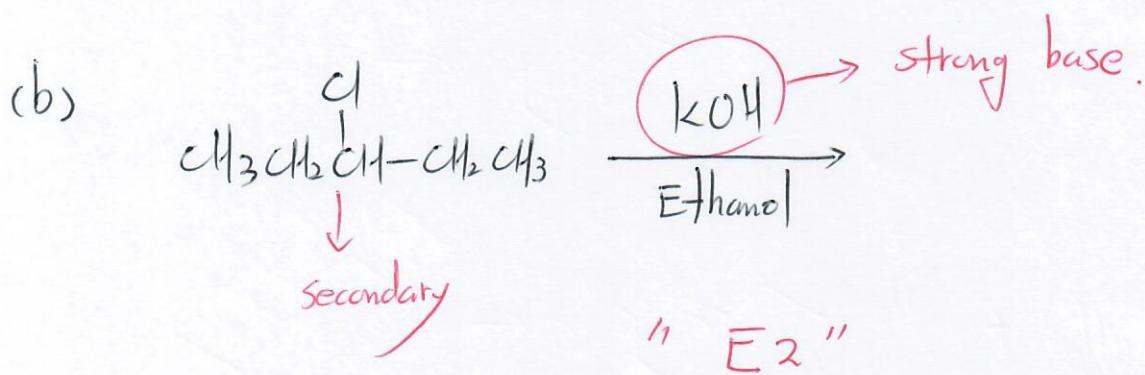
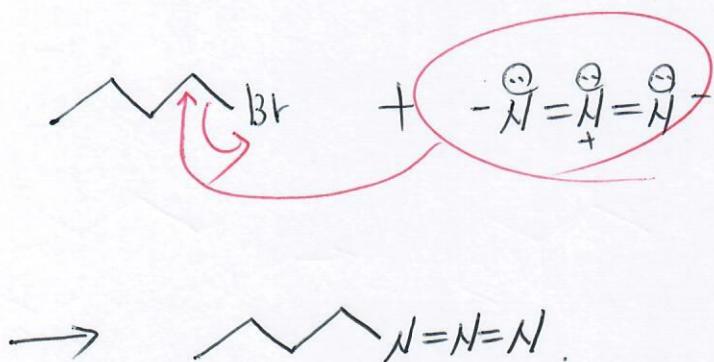
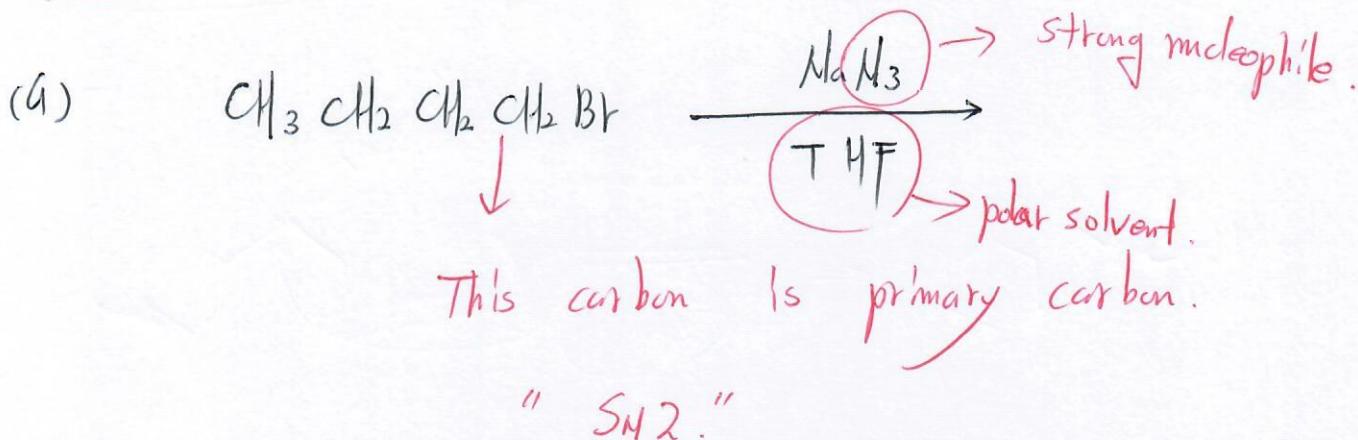
Another $E1$ rxn



Benzene is very stable.

So the base can not take the proton from benzene.

problem 11. 20 . - 1



problem II. 20 - 2

