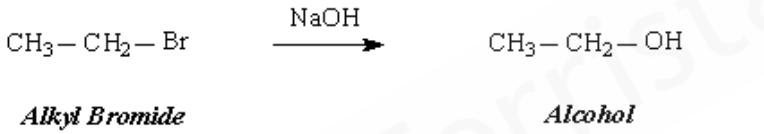
Ch 5

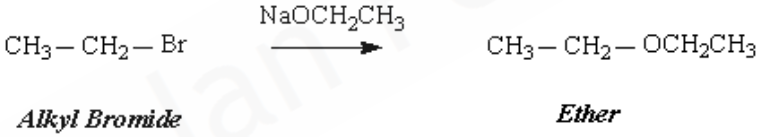
Alkyl Halides;

Substitution and Elimination reactions

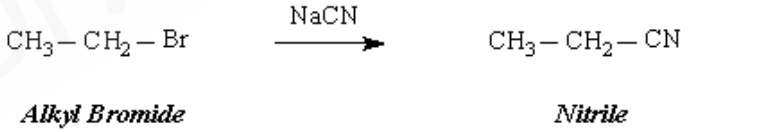
Is Organic Chemistry only based upon Memorization?



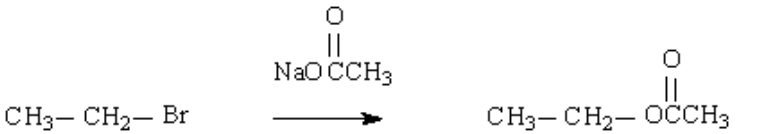
Alkyl Bromide *Alcohol*



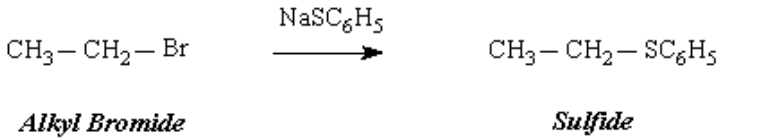
Alkyl Bromide *Ether*



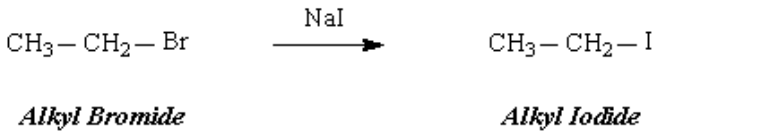
Alkyl Bromide *Nitrile*



Alkyl Bromide *Ester*

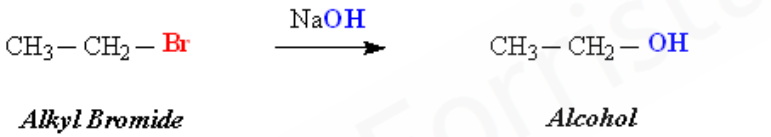


Alkyl Bromide *Sulfide*

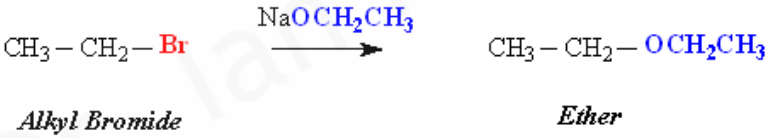


Alkyl Bromide *Alkyl Iodide*

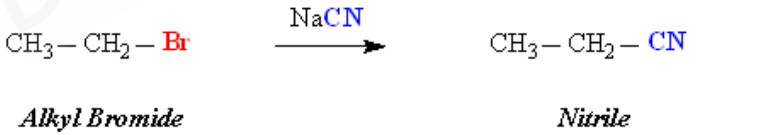
No, Organic Chemistry is based upon Understanding!



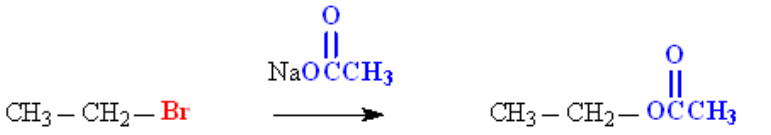
Alkyl Bromide *Alcohol*



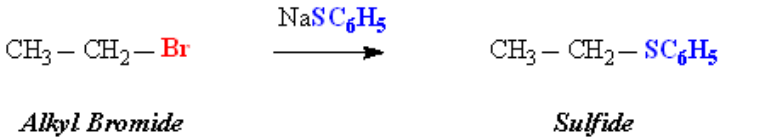
Alkyl Bromide *Ether*



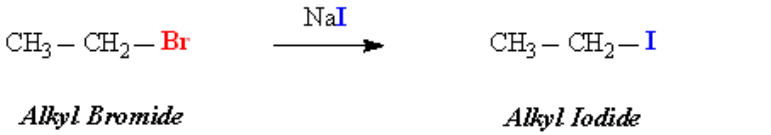
Alkyl Bromide *Nitrile*



Alkyl Bromide *Ester*

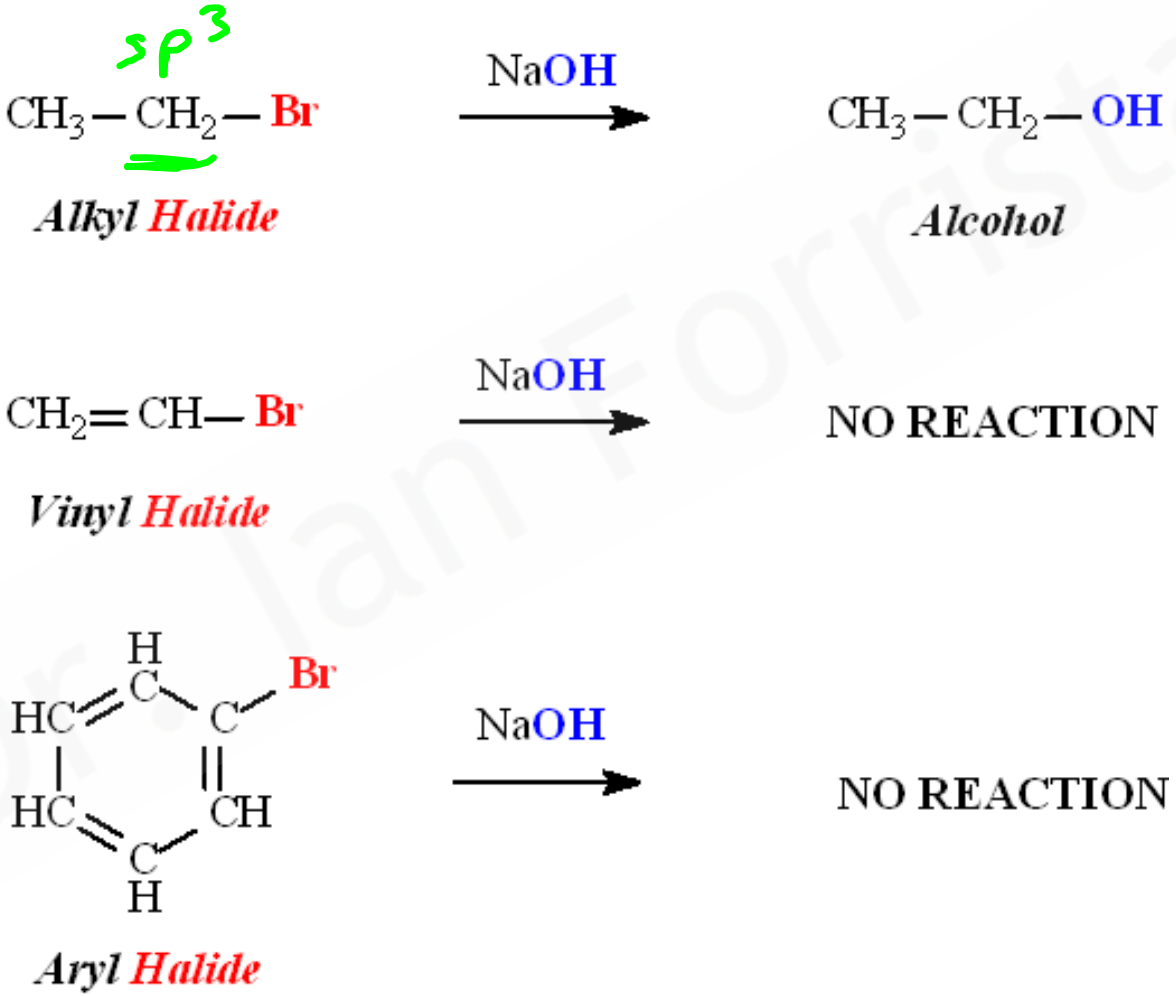


Alkyl Bromide *Sulfide*

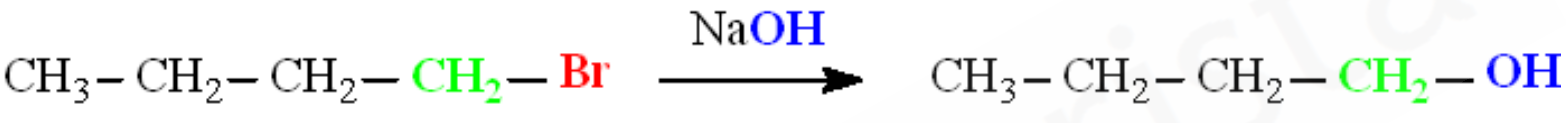


Alkyl Bromide *Alkyl Iodide*

The Relationship between STRUCTURE and REACTIVITY



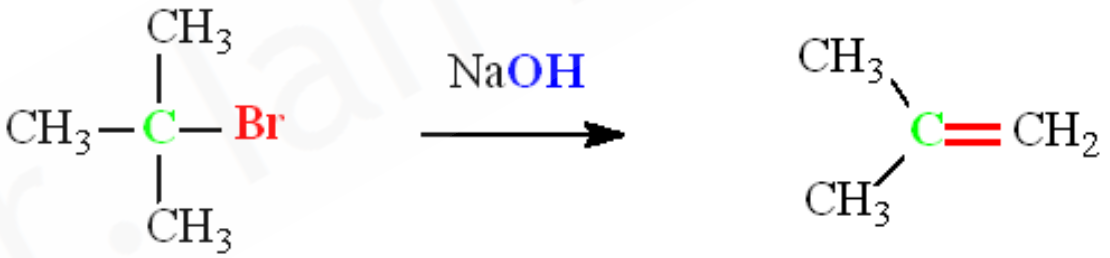
The Relationship between STRUCTURE and REACTIVITY



1° Alkyl Halide

Alcohol

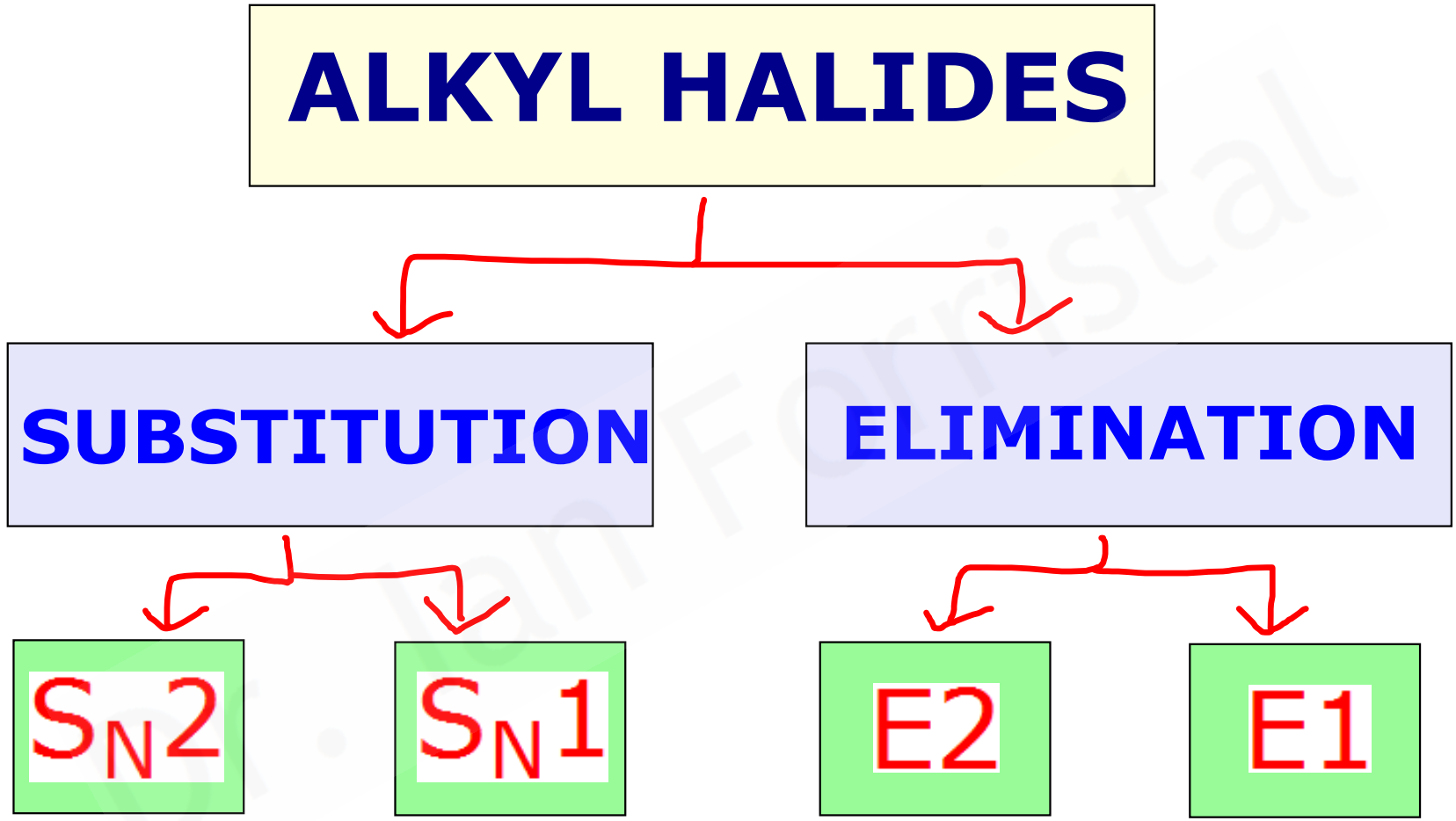
SUBSTITUTION

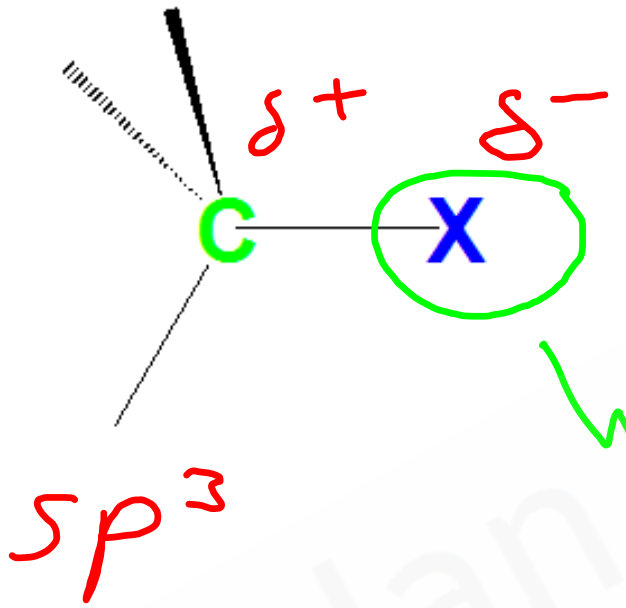


3° Alkyl Halide

Alkene

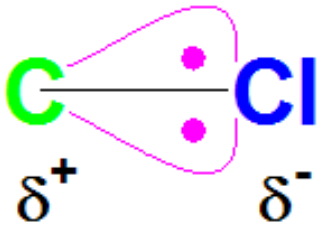
ELIMINATION


ALKYL HALIDES
SUBSTITUTION
ELIMINATION
SN2
SN1
E2
E1

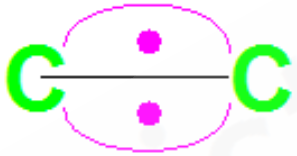


X	= Halogen (**Cl**, **Br**, **I**)
δ^-	= partially negative
δ^+	= partially postive

Leaving group



compared with

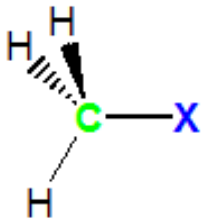
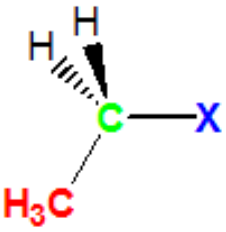
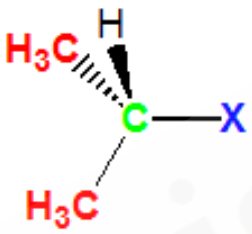
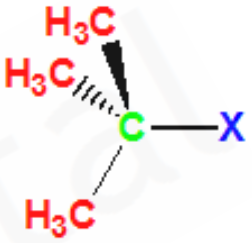


unequal
electron distribution

POLAR

equal
electron distribution

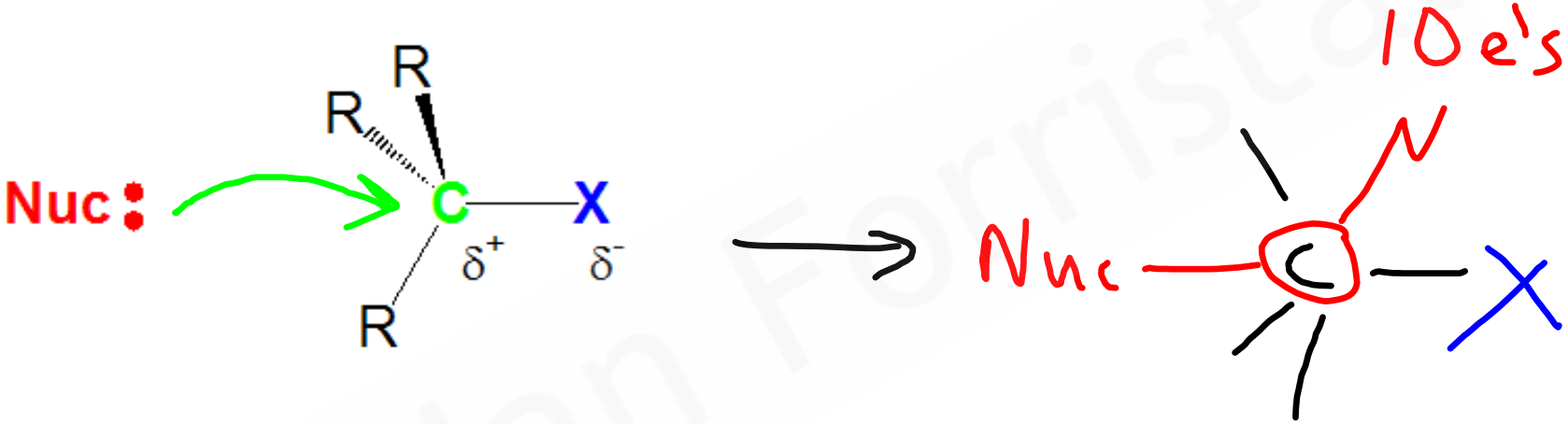
NON - POLAR

				
Number of alkyl goups	**0**	**1**	**2**	**3**
Type of Alkyl Halide	**Methyl**	**Primary (1°)**	**Secondary (2°)**	**Tertiary (3°)**

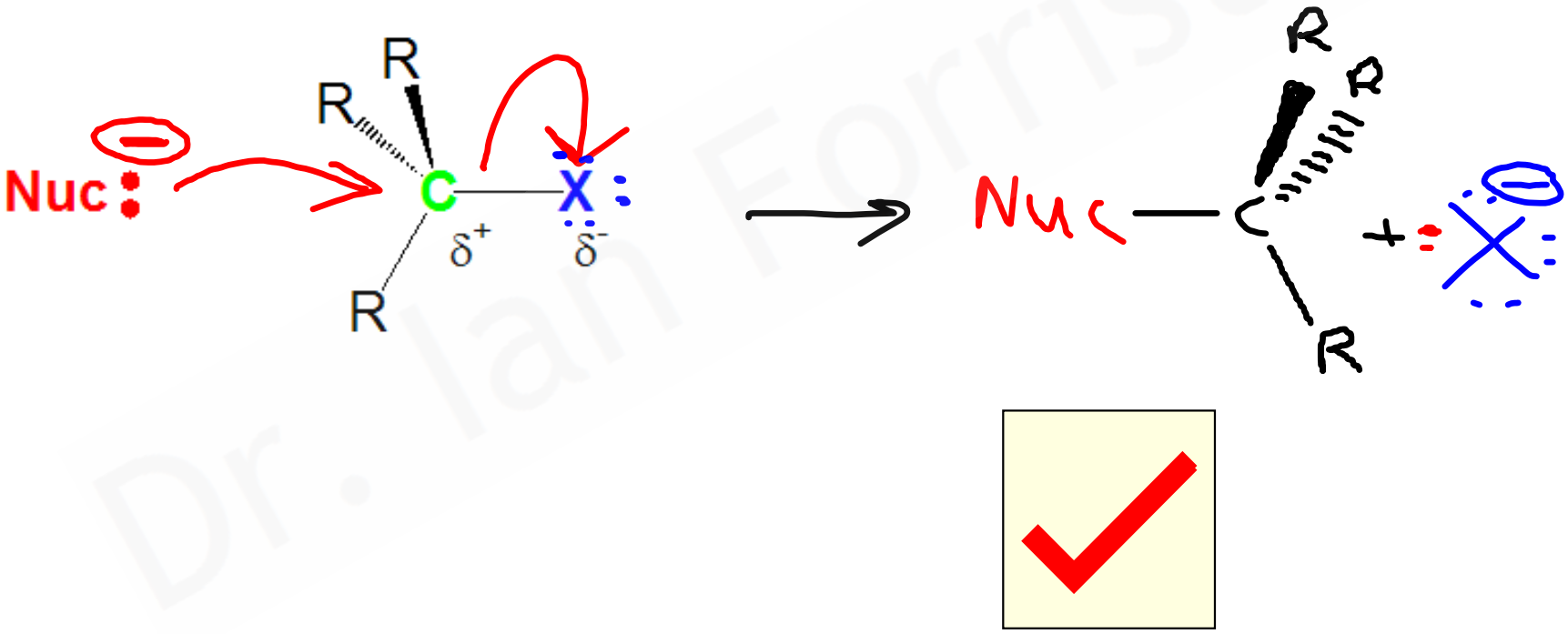
General Case

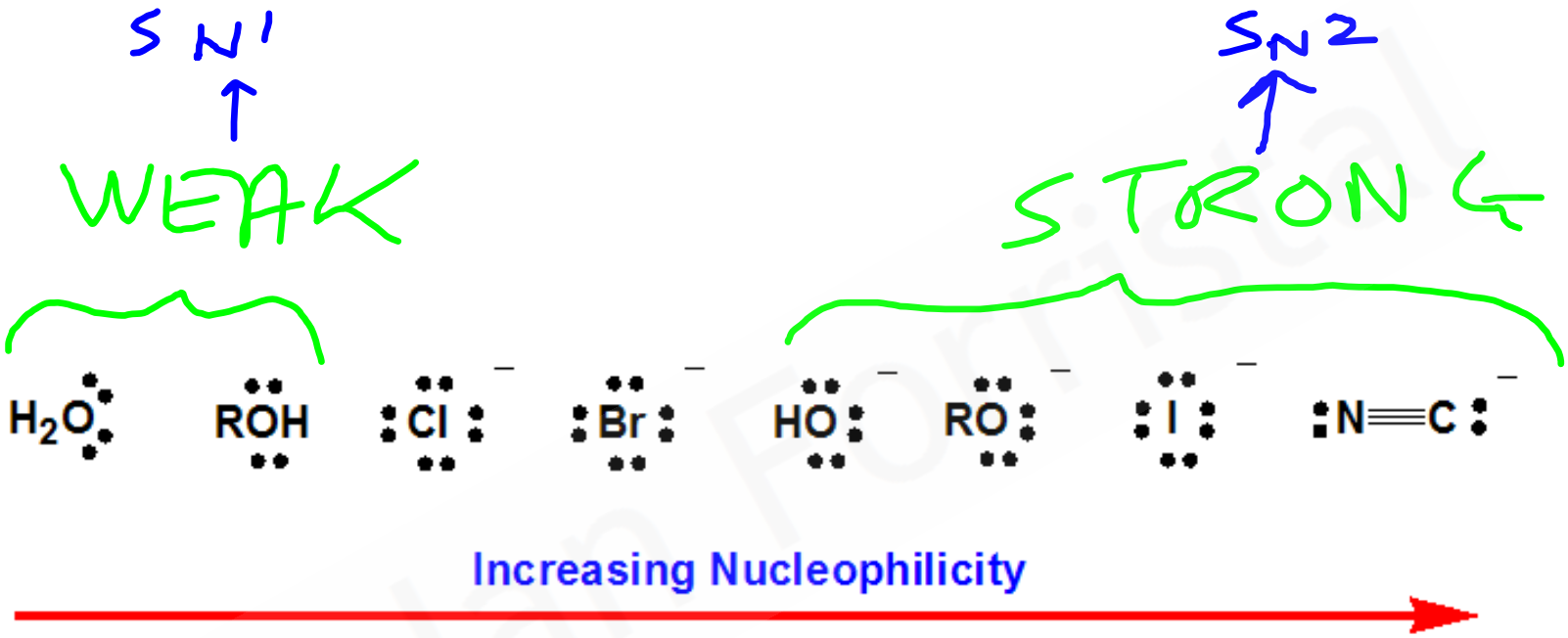
NUCLEOPHILE	ELECTROPHILE
electron rich Is attracted to positive (electron deficient) centers	electron deficient Readily attacked by nucleophiles

S_N2 reaction of a nucleophile and an alkyl halide

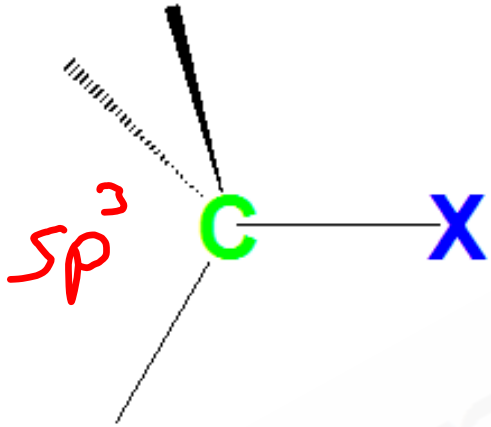


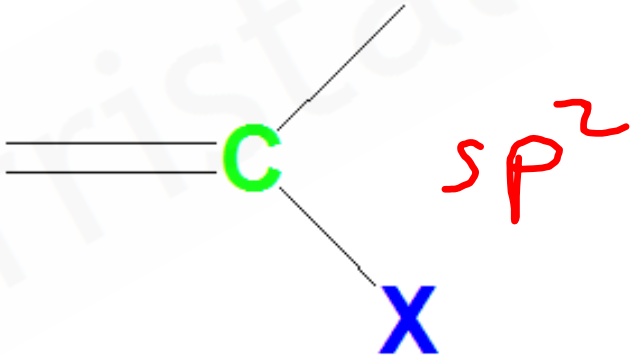
S_N2 reaction of a nucleophile and an alkyl halide

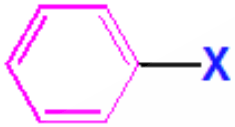


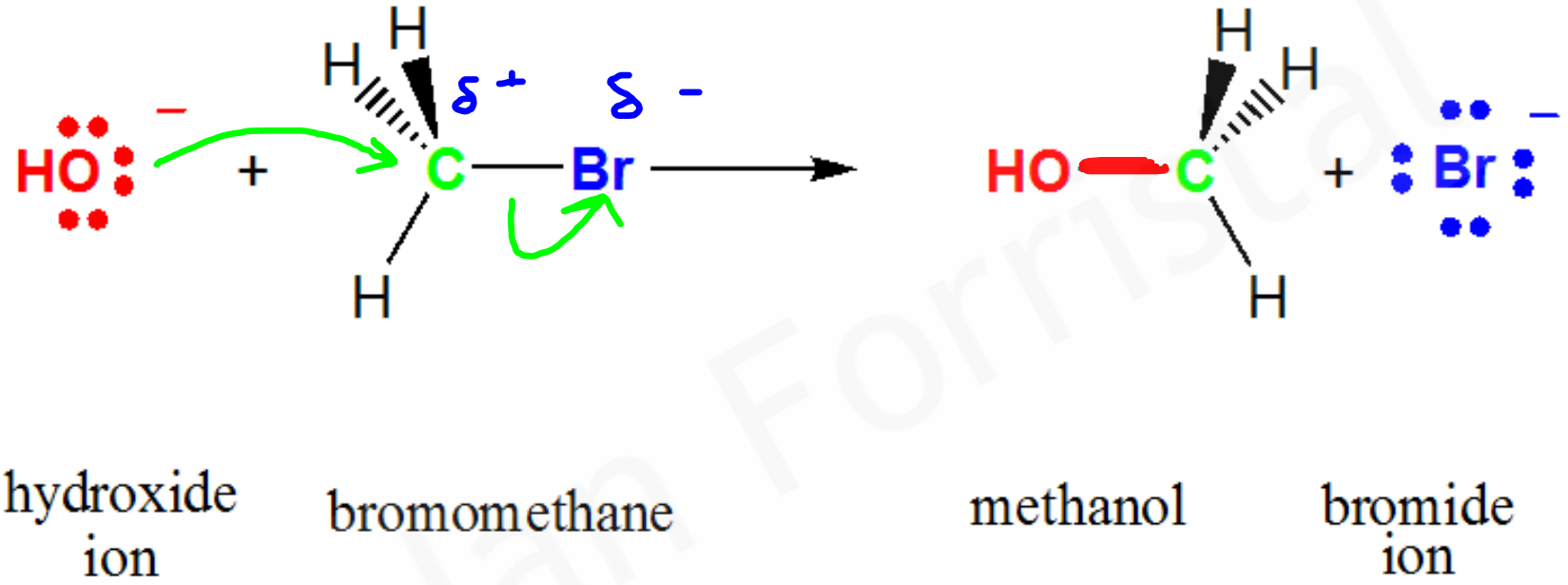


Only alkyl halides with sp3 hybridized head carbons undergo nucleophilic subsitiution reactions

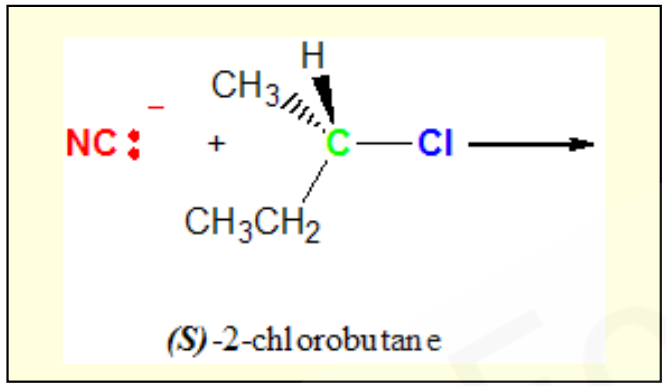




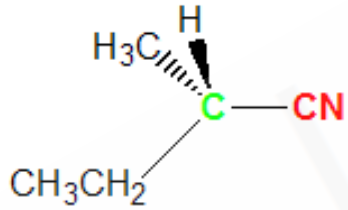
Type of Organohalide	Structure	Reactivity
Aryl	$H_2C{=}CH{-}X$	Do not undergo substitution reactions
Vinyl		
Tertiary (3°)	$(CH_3)_3C{-}X$	Undergo substitution reactions
Secondary (2°)	$(CH_3)_2CH{-}X$	
Primary (1°)	$CH_3CH_2{-}X$	
Methyl	$CH_3{-}X$	
Allylic	$H_2C{=}CHCH_2{-}X$	
Benzylic	$PhCH_2{-}X$	



What is(are) the major product(s) of the following S_N2 reaction?

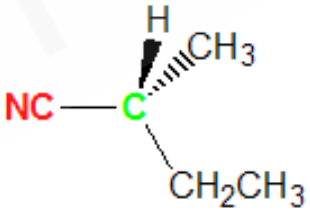


(S)-2-chlorobutane

1) 

(S)-2-methylbutanenitrile

(A)

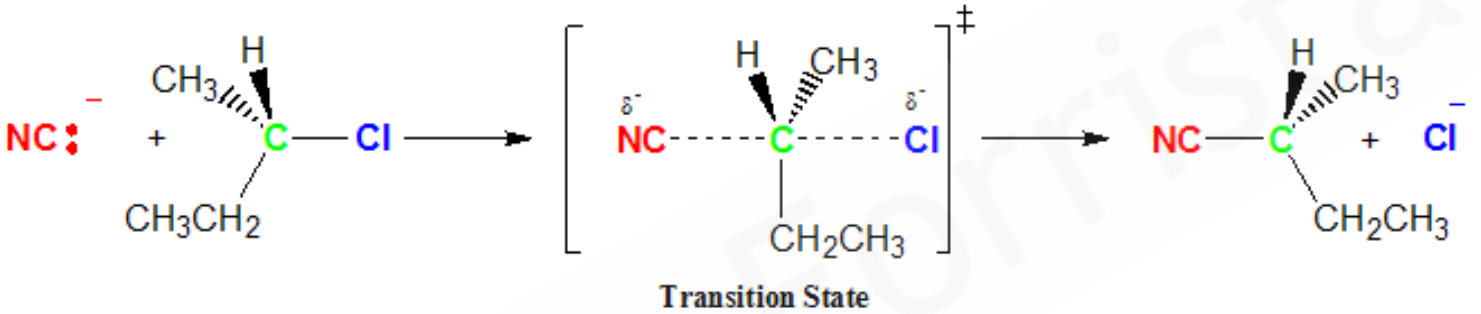
2) 

(R)-2-methylbutanenitrile

(B)

3) **(A) & (B)**

Stereochemistry of the S_N2 reaction

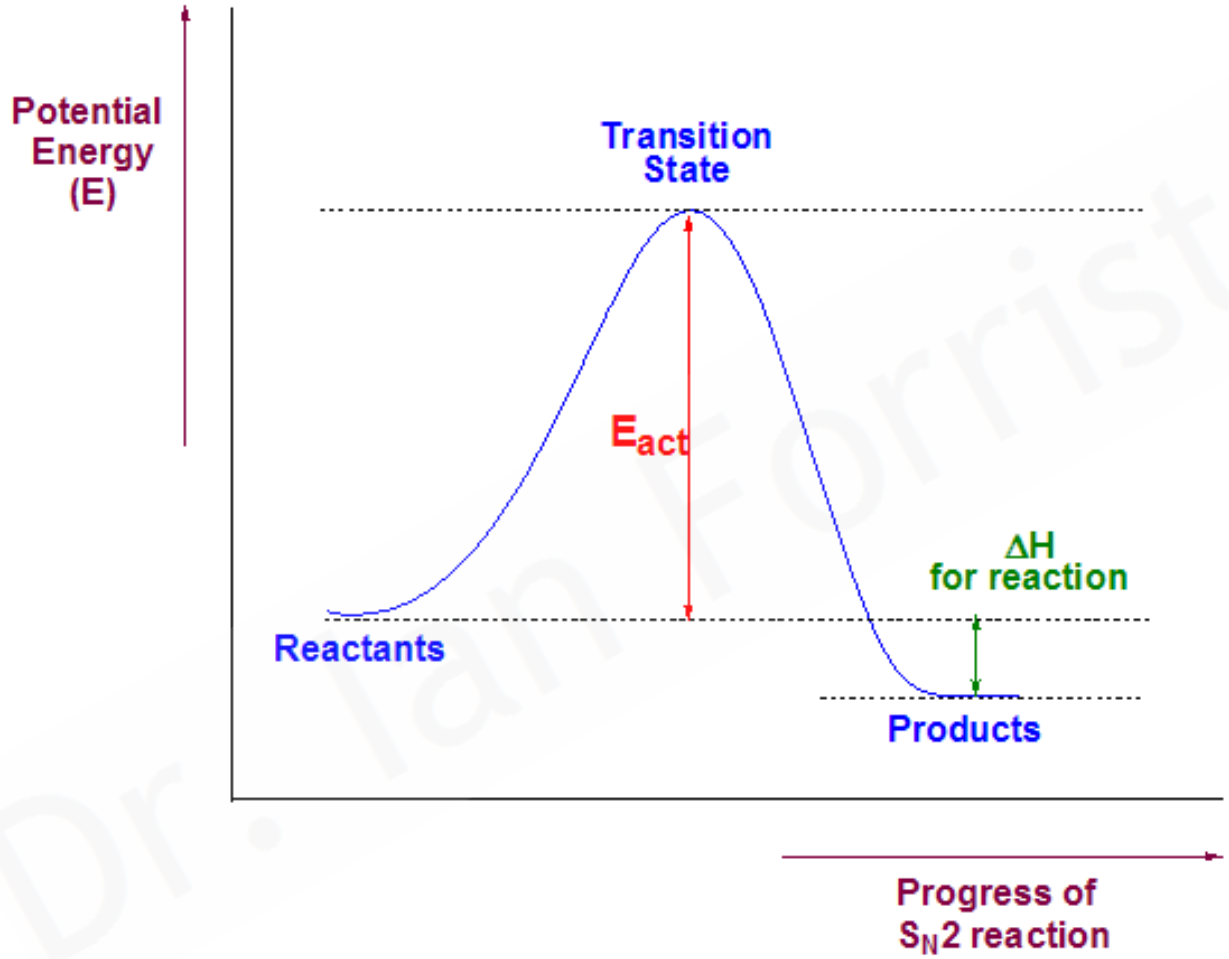


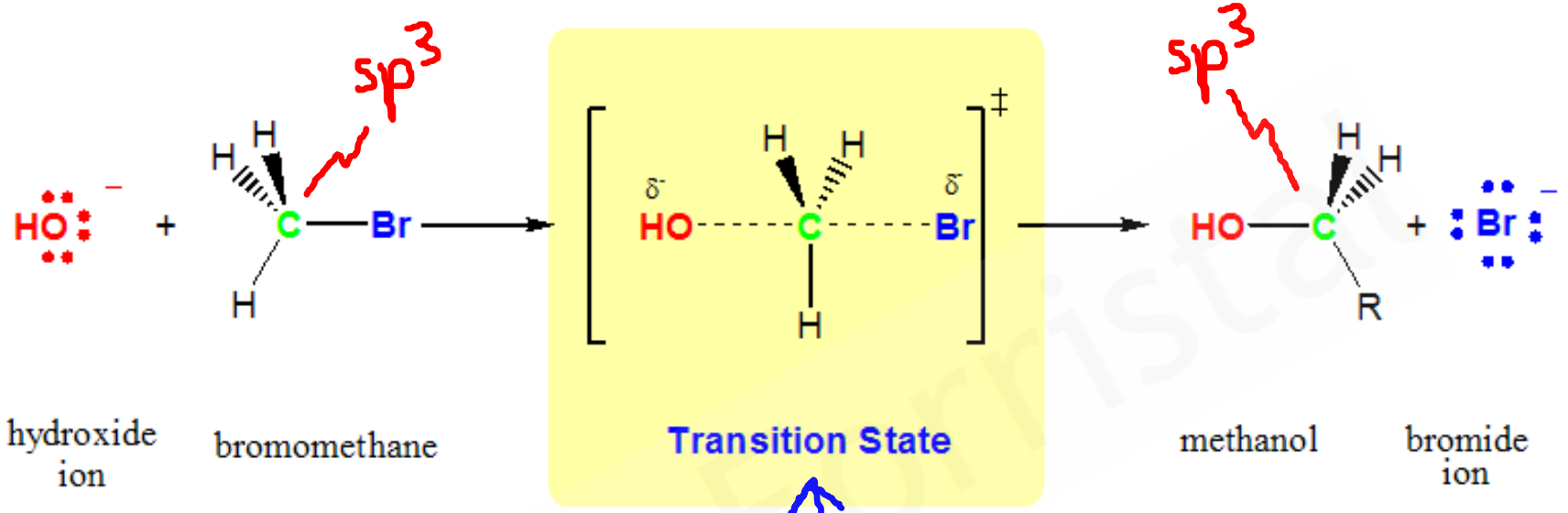
(S)-2-chlorobutane

Transition State

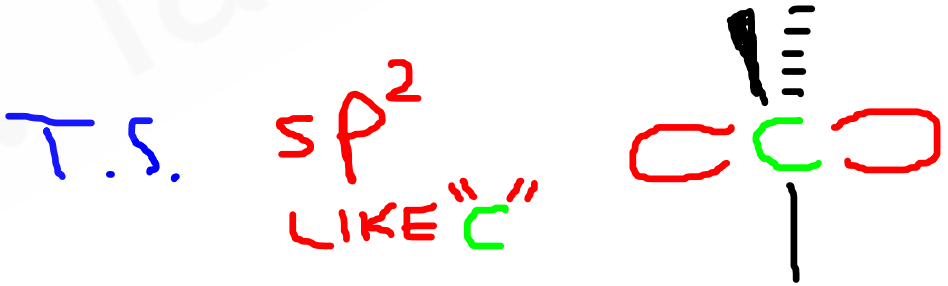
(R)-2-methylbutanenitrile

INVERSION
of stereochemistry





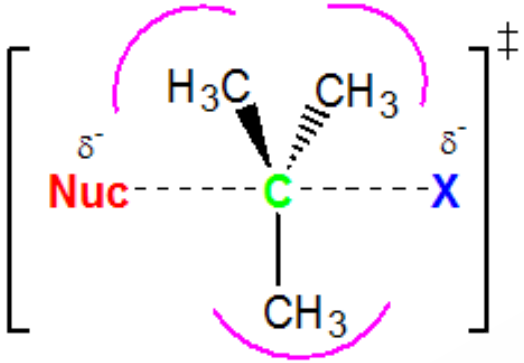
Both species are involved in the Transition State



S_N2 **reactions have 2nd order Kinetics**

Rate of Reaction = $k[Nuc][R-X]$

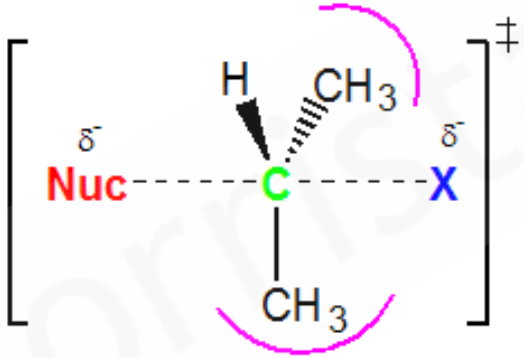
Transition States for S_N2 reactions of various alkyl halides



3° alkyl halide

Greater
Steric Hindrance

Higher Energy

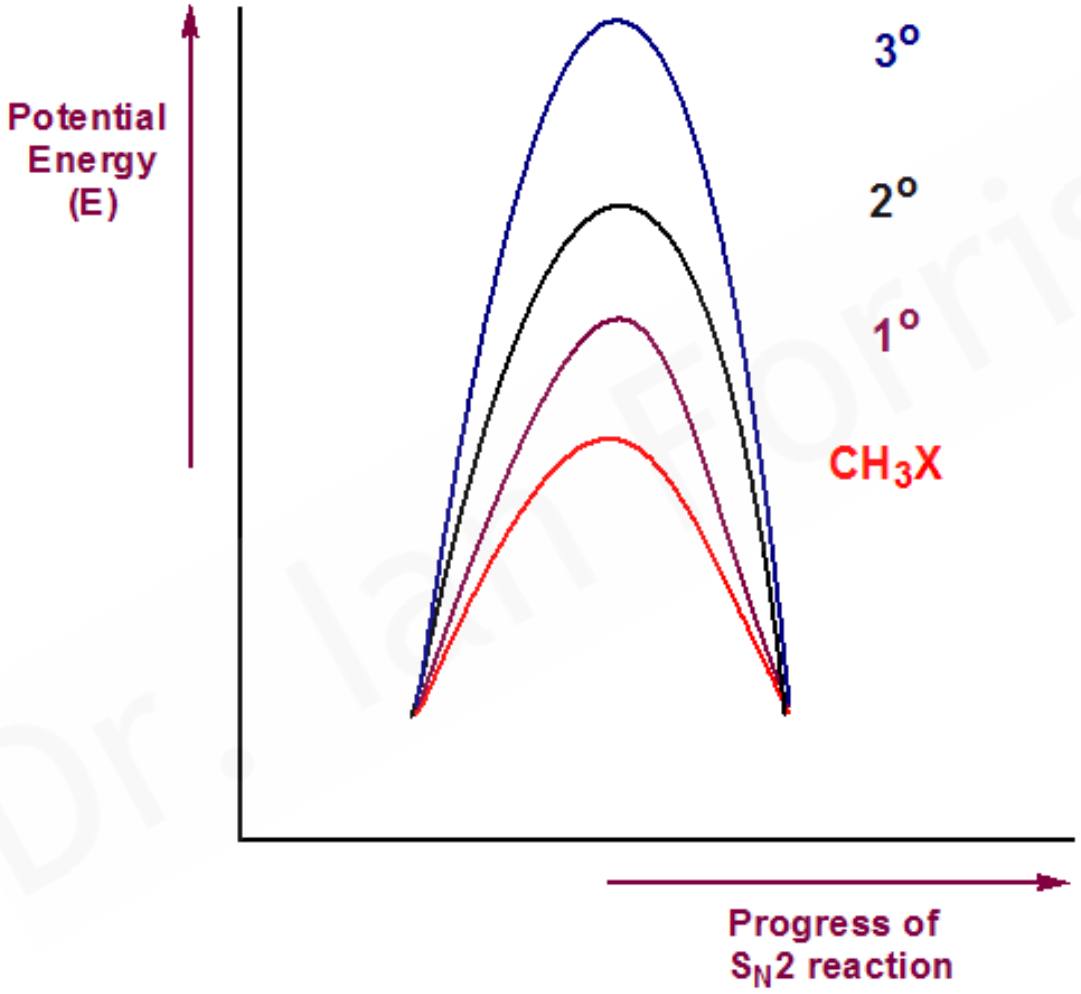


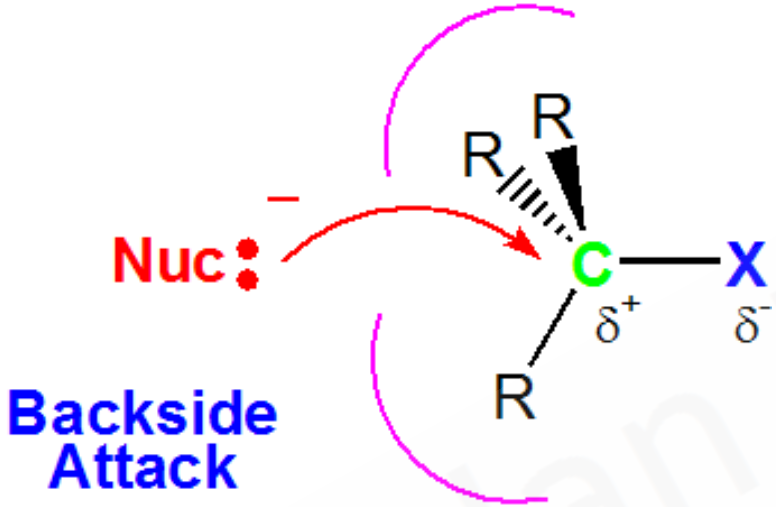
2° alkyl halide

Less
Steric Hindrance

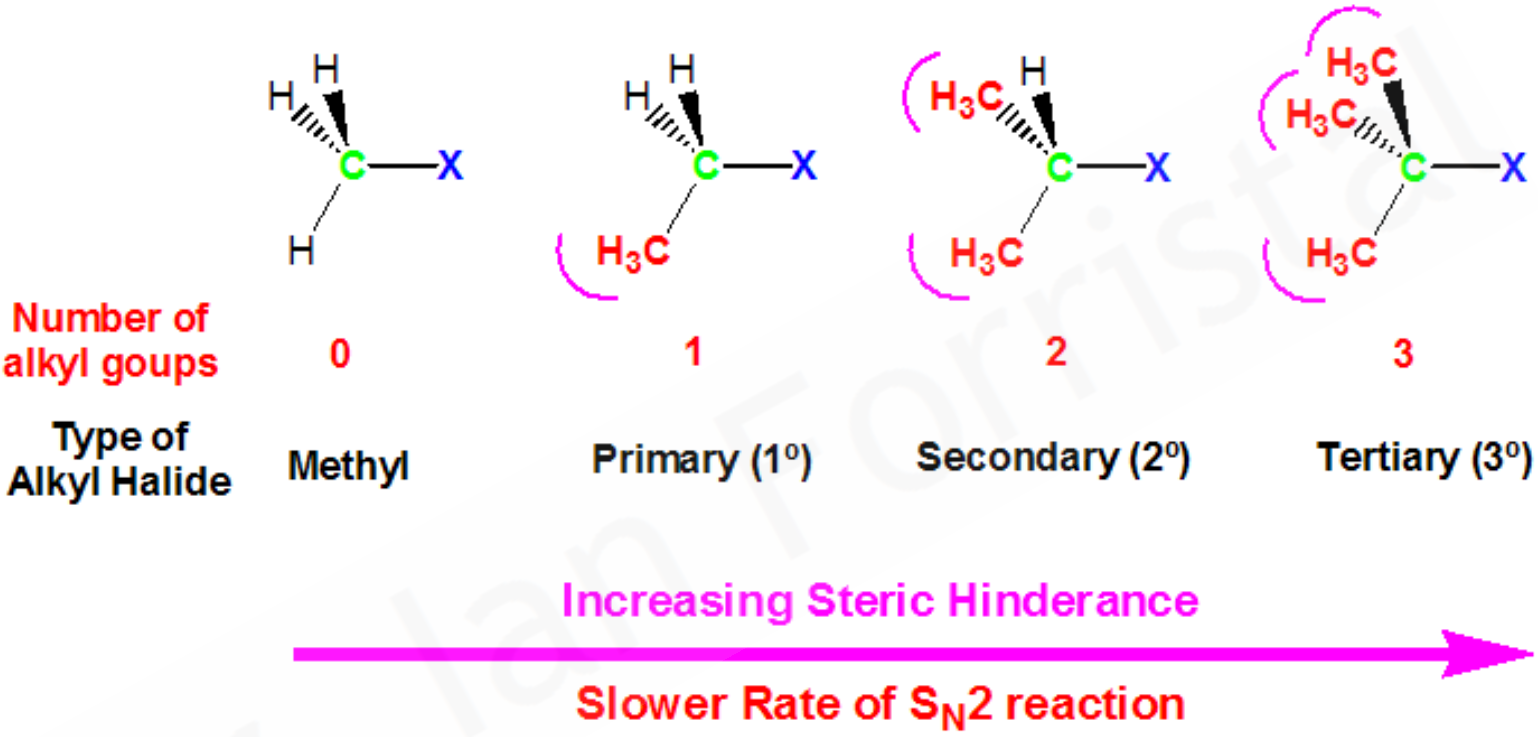
Lower Energy

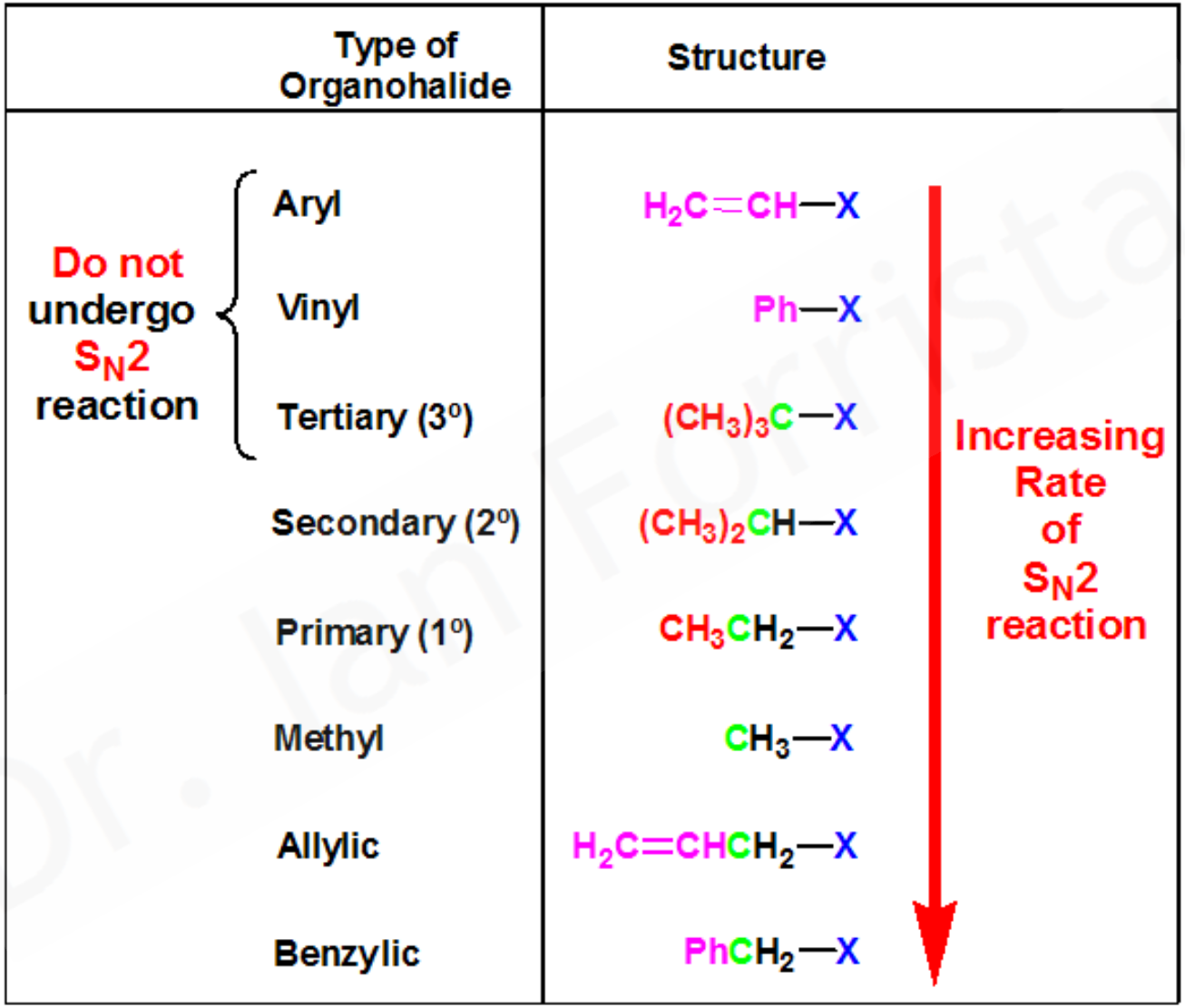
Energy diagram for S_N2 reactions of various alkyl halides



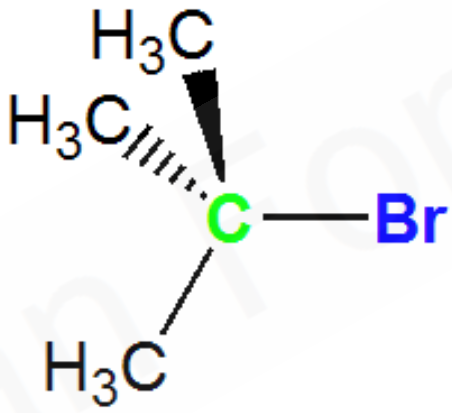


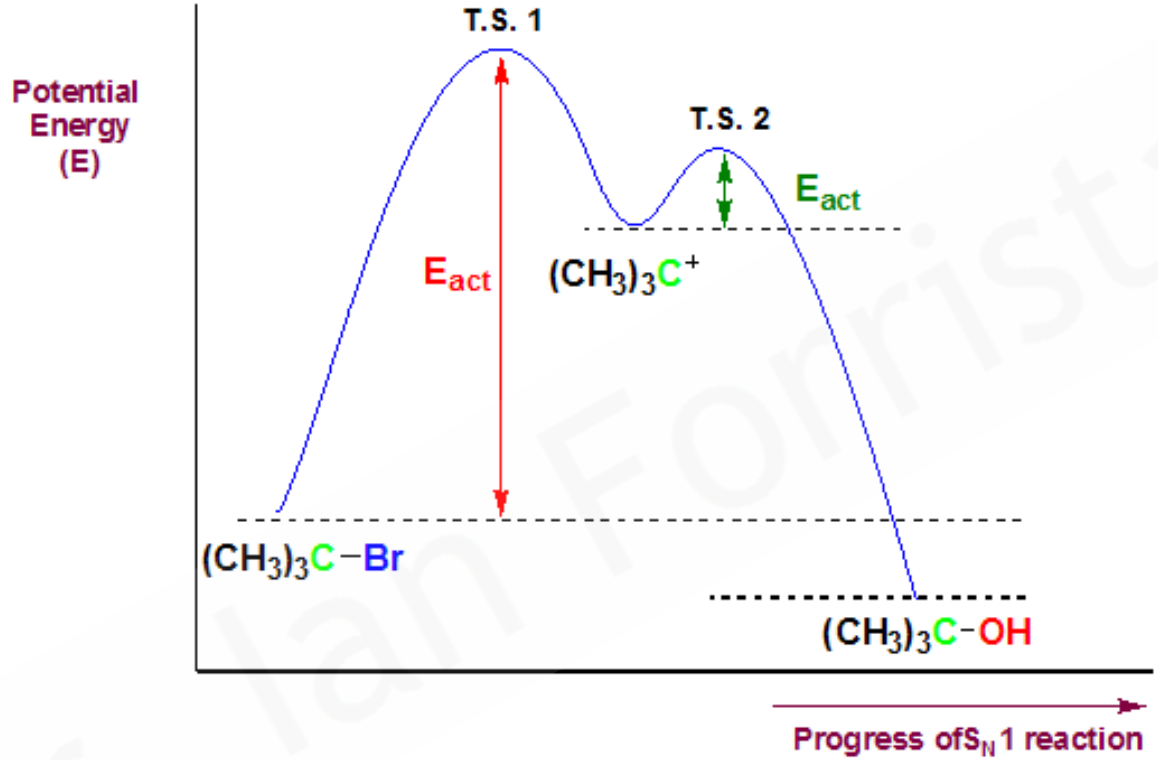
S_N2 reaction
Steric Hindeance due to groups R
(R = H or alkyl) is the key factor
which determines Rate of Reaction

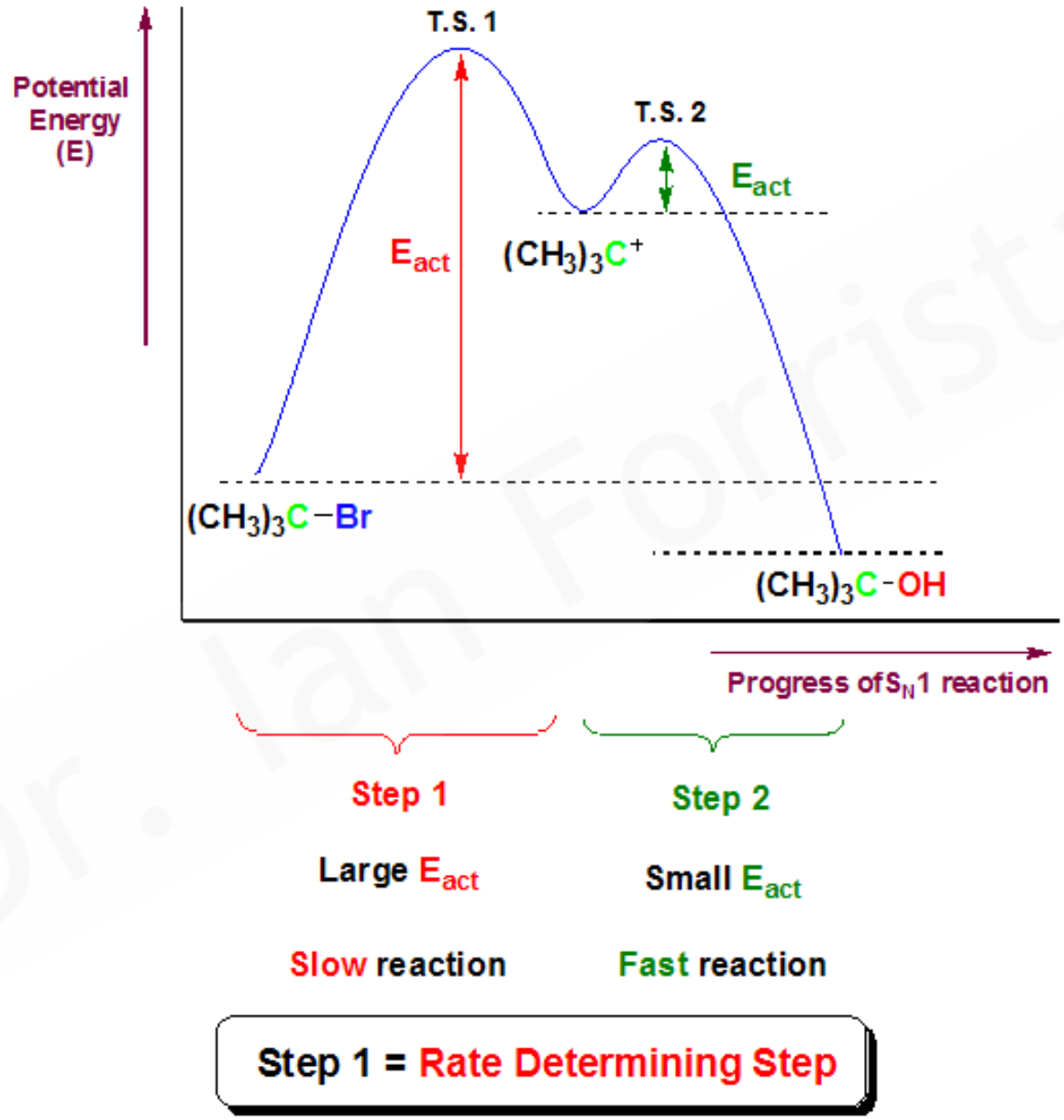


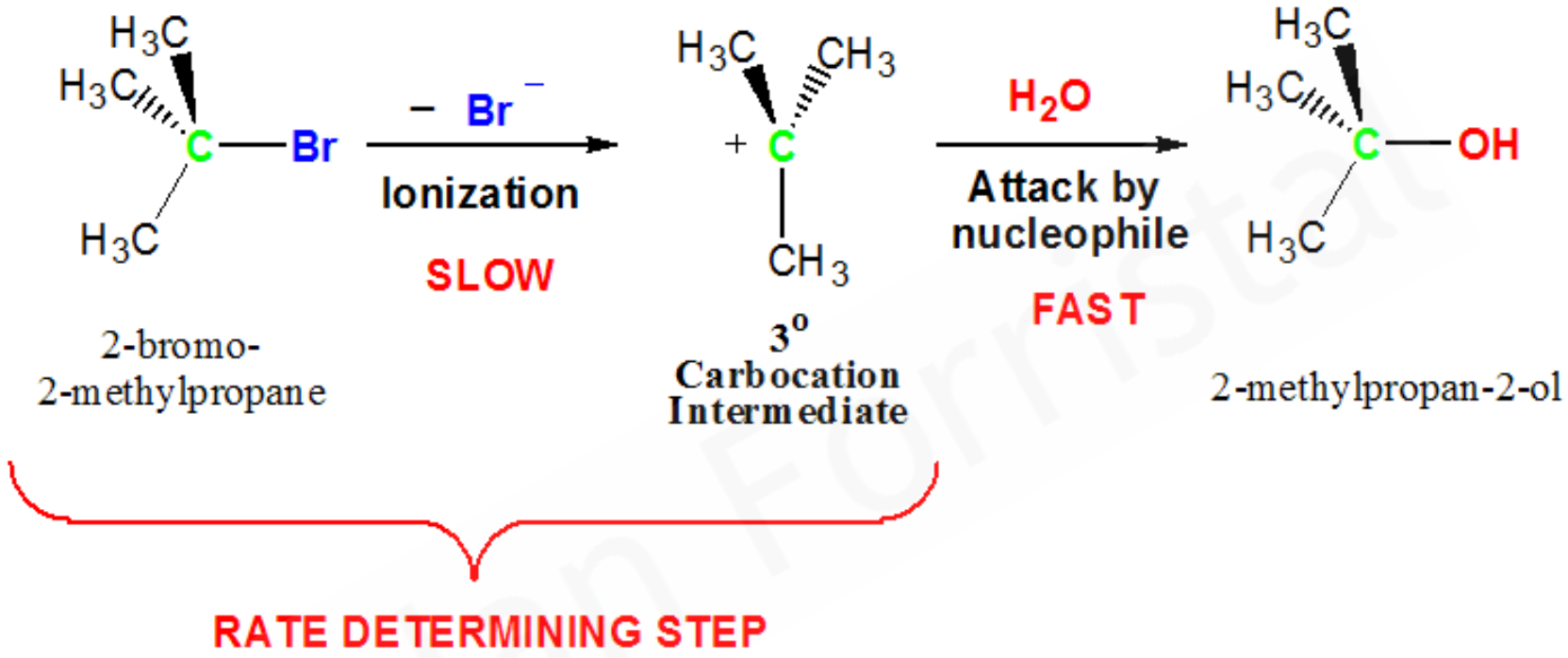

Type of Organohalide
Structure
Do not undergo S_N2 reaction
Aryl
Vinyl
Tertiary (3°)
Secondary (2°)
Primary (1°)
Methyl
Allylic
Benzylic
$H_2C{=}CH{-}X$
$Ph{-}X$
$(CH_3)_3C{-}X$
$(CH_3)_2CH{-}X$
$CH_3CH_2{-}X$
$CH_3{-}X$
$H_2C{=}CHCH_2{-}X$
$PhCH_2{-}X$
Increasing Rate of S_N2 reaction

Tertiary alkyl halides **DO NOT** undergo S_N2 reactions





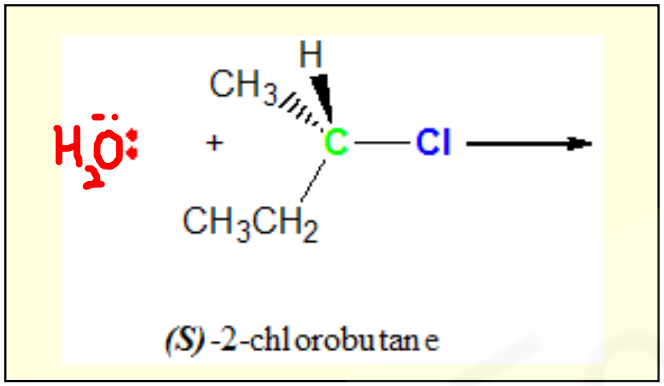


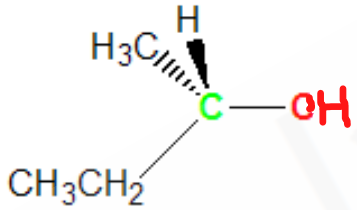


reactions have 1st order Kinetics

Rate of Reaction = $k[R-X]$

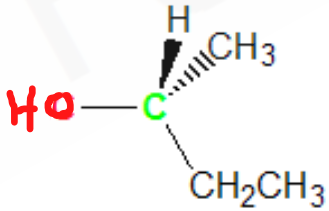
What is(are) the major product(s) of the following S_N1 reaction?



1) 

(S)-2-methylbutanol

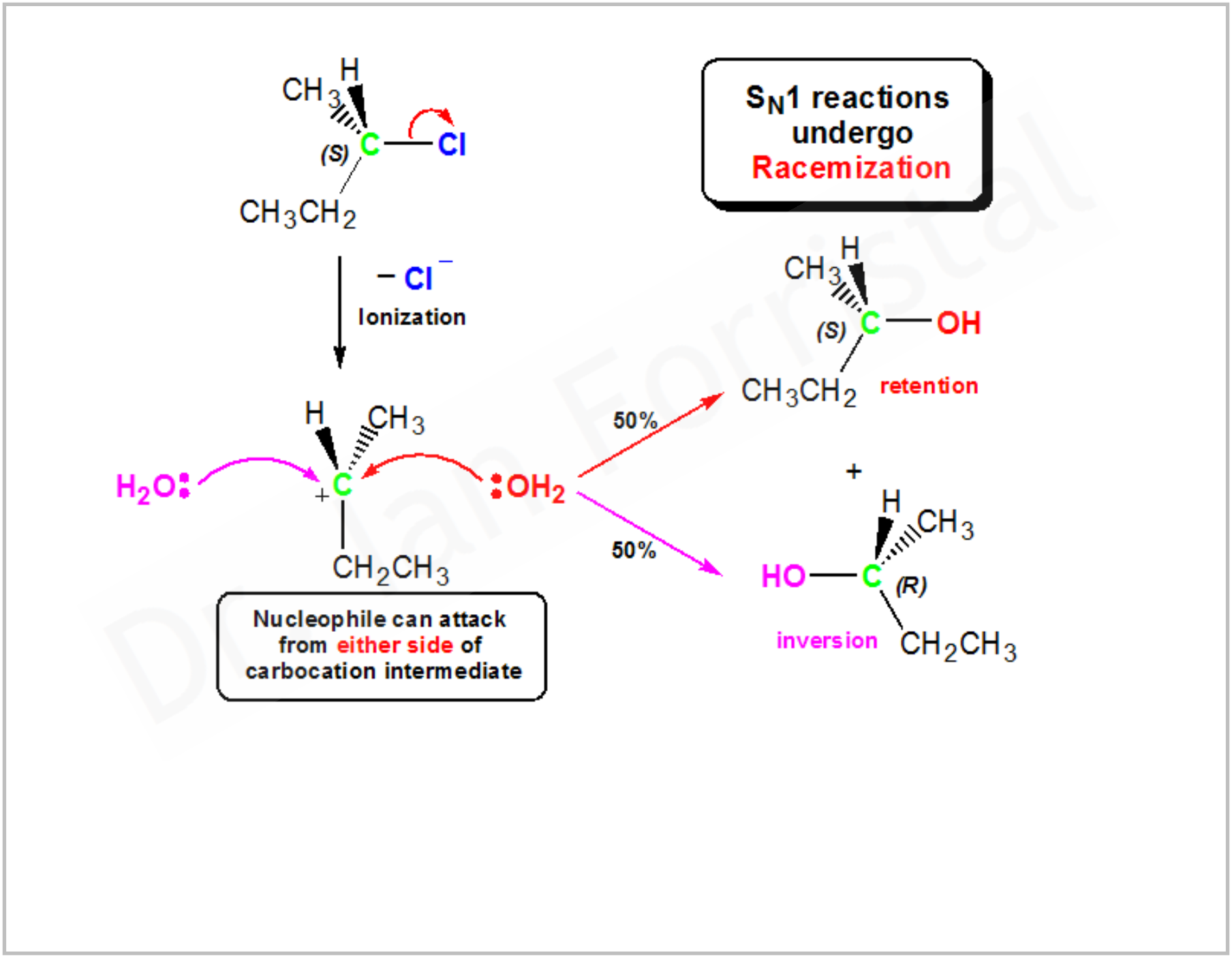
(A)

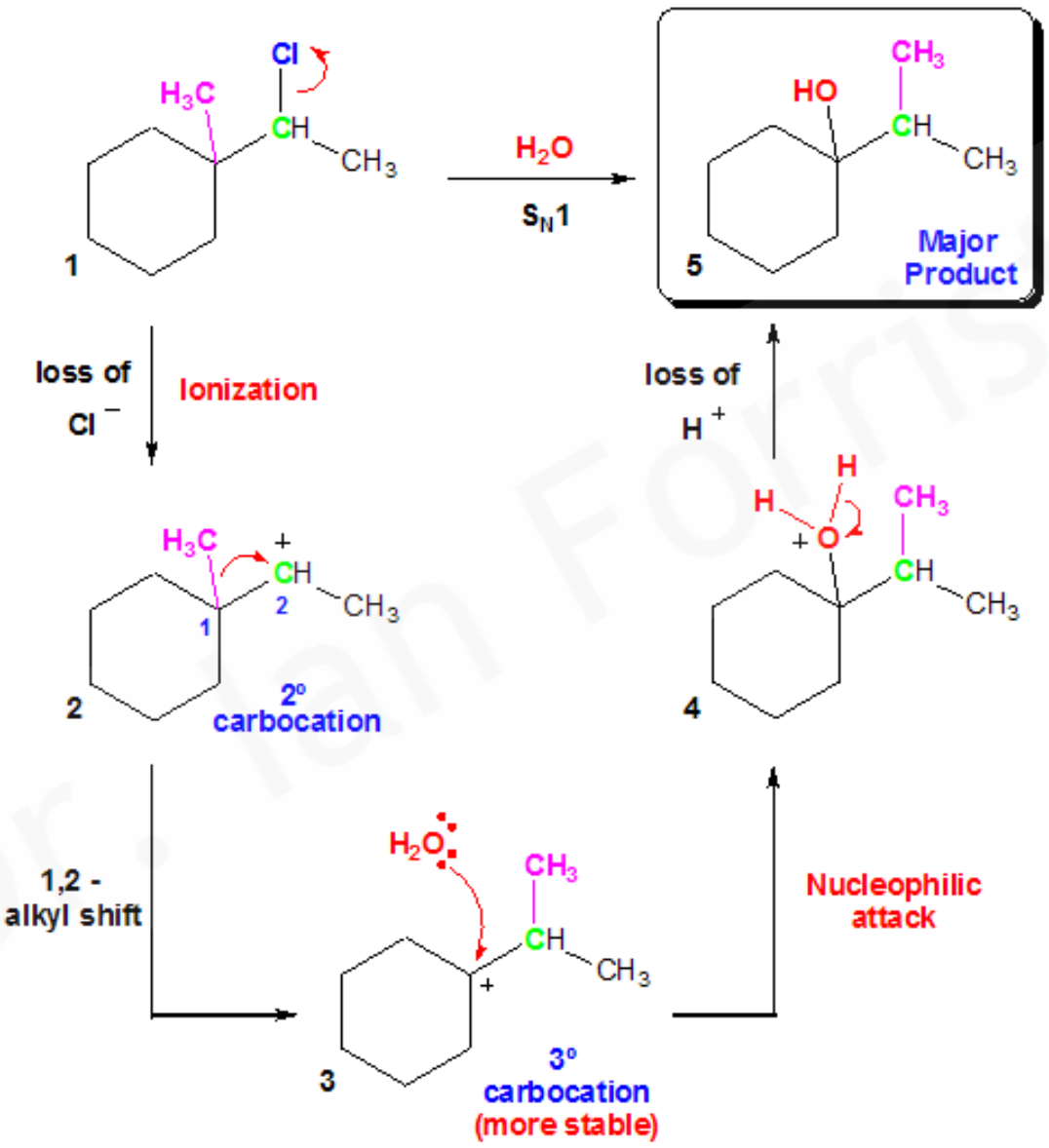
2) 

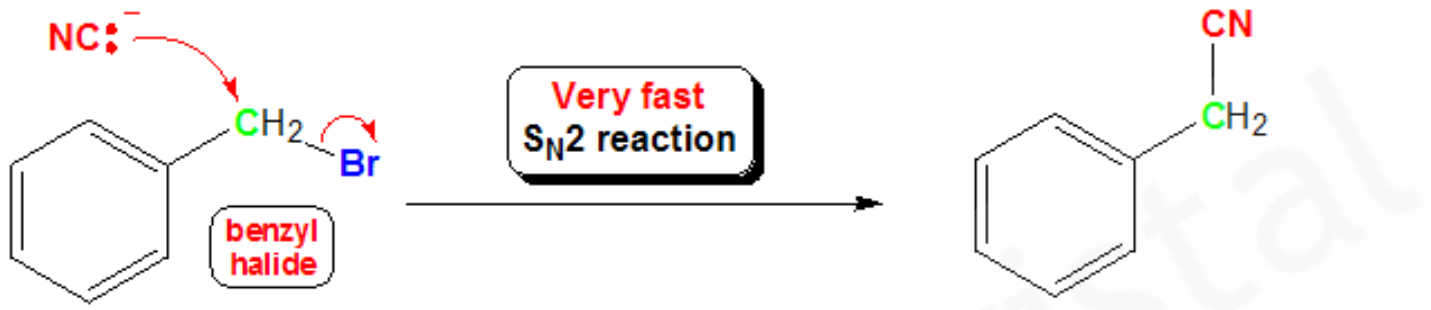
(R)-2-methylbutanol

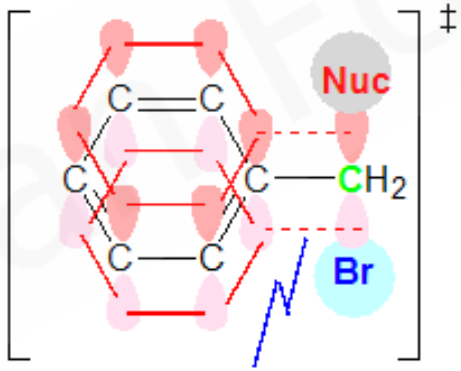
(B)

3) **(A) & (B)**

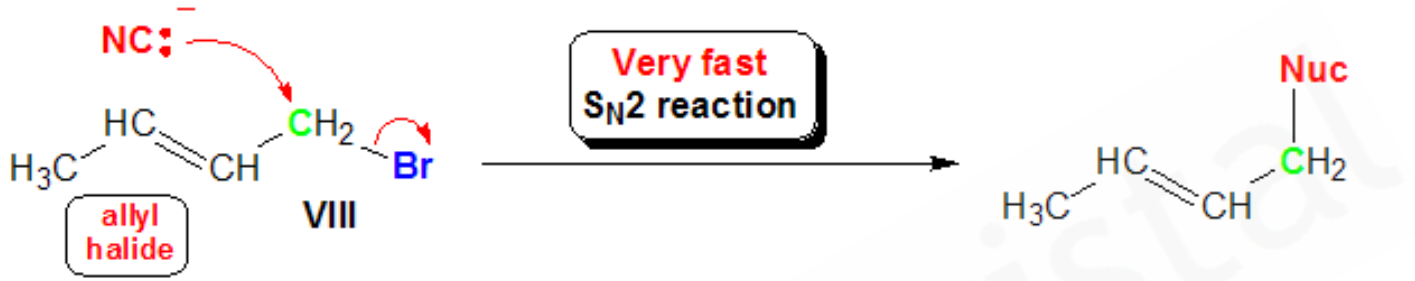

S_N1 reactions undergo Racemization
H
CH_3
(S)
C
Cl
CH_3CH_2
$-Cl^-$
Ionization
H
CH_3
C
+
CH_2CH_3
H_2O:
:OH_2
Nucleophile can attack from either side of carbocation intermediate
50%
50%
H
CH_3
(S)
C
OH
CH_3CH_2
retention
+
H
CH_3
HO
C
(R)
inversion
CH_2CH_3

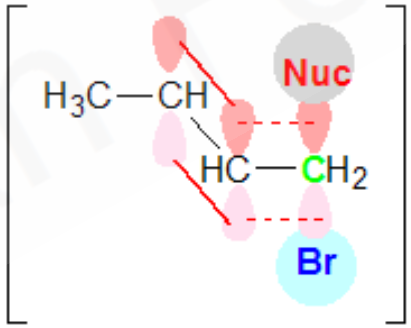






transition state stabilised by p orbials from benzene ring





transition state stabilised by
p orbials from double bond