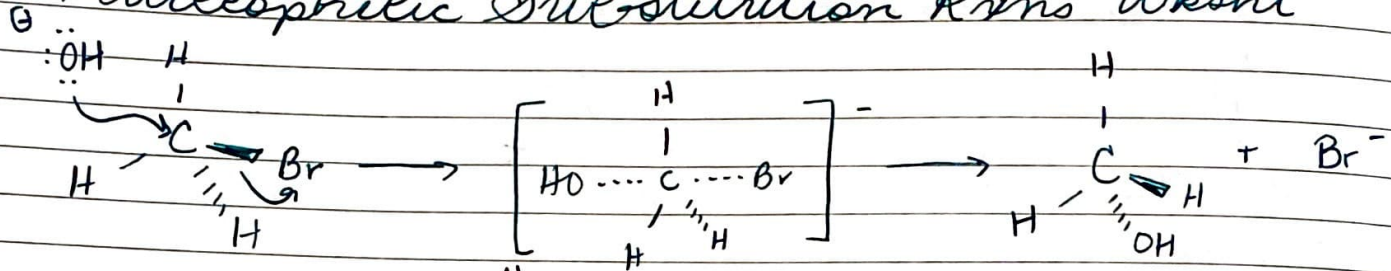
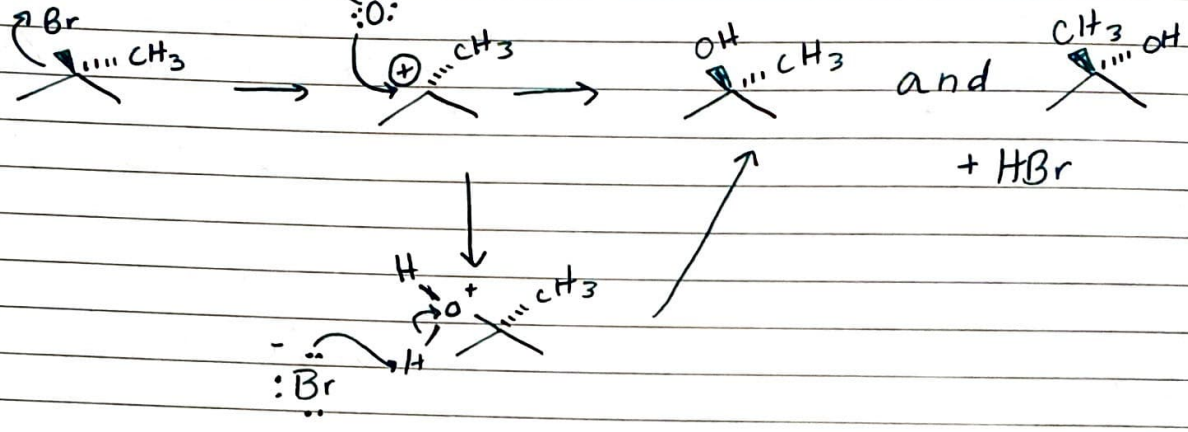
Nucleophilic Substitution Rxns Wksht

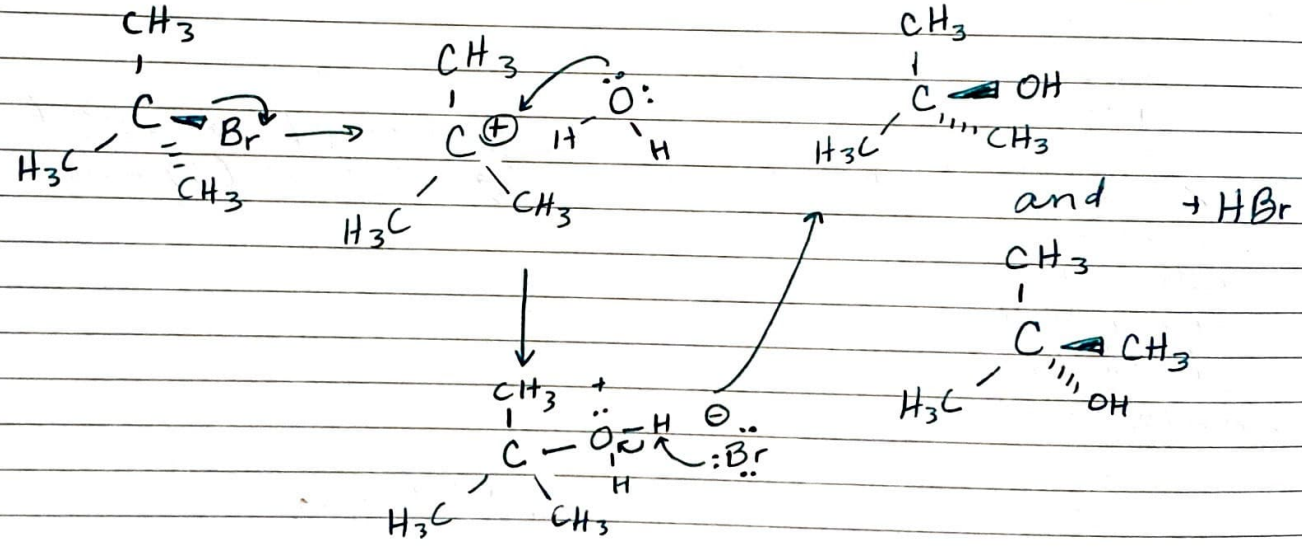
1.



2.



Another way to draw it:



3. Carbocation intermediates are formed in S_N1 rxns due to the molecular geometry and tertiary carbon in the reactants. A more stable carbocation intermediate can form due to the positive inductive effects of the attached alkyl groups willing to donate some electron density to the carbocation. S_N2 rxns, on the other hand, often occur with primary carbons, which are not

geometrically favored to form a distinct carbocation intermediate. Instead, the rxn proceeds in one step through an unstable transition state, which is immediately converted into a product. The carbocation intermediate has 3 bond regions and no lone pairs, which means it has a trigonal planar (sp^2) geometry.

4. $CH_3Br > CH_3CH_2CH_2Br > (CH_3)_2CHBr > (CH_3)_3CBr$

$1° > 2° > 3°$ in terms of S_N2 rxn rates. This is because steric hindrance in tertiary structures physically prevent ~~at~~ nucleophilic attack.

5. $(CH_3)_3CBr > (CH_3)_2CHBr > CH_3CH_2CH_2Br > CH_3Br$

6. Bulky alkyl groups on tertiary carbons prevent nucleophilic attack in S_N2 rxns, but provide stabilization of the carbocation intermediate (due to positive inductive effect) in S_N1 reactions.

7.

Strong	Weak
OH^-	H_2O
CH_3O^-	CH_3OH
Br^-	NH_3

8. Strong nucleophiles are more likely to participate in S_N2 rxns due to their increased willingness to donate electrons, making them more reactive and able to attack electrophilic carbon atoms in one step. This would also make the mechanism depent on the concentration of the nucleophile (second-order kinetics). Weaker nucleophiles allow for the formation of the carbocation intermediate prior to the attack on the electrophilic carbon. Due to formation of the carbocation intermediate being the slow step, the rxn kinetics does not depend on the concentration of the nucleophile (first-order).

9. a) S_N2
NaOH is a strong nucleophile
the substrate is a secondary halogenoalkane, which can undergo S_N2 rxns with strong nucleophiles
Although EtOH is a polar, protic solvent and S_N2 rxns work best in polar, aprotic solvents, NaOH is a strong enough nucleophile to overcome EtOH.

b) S_N1
H_2O is a weak nucleophile and a polar, protic solvent

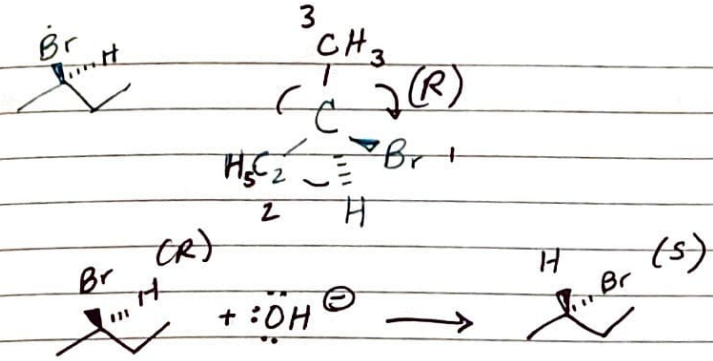
10. Polar, protic solvents have permanent dipoles and have the ability to form hydrogen bonds (usually have H covalently bonded to N or O)
ex: NH_3, H_2O, CH_3OH, CH_3COOH)
polar, aprotic solvents also have permanent dipoles, but do not form hydrogen bonds (propanone, methylene chloride, ethanenitrile)

11. a) polar, aprotic solvents favor S_N2 rxns because they are able to dissolve the ionic compounds that produce the nucleophile, but are not strong enough to inhibit the activity of the anionic nucleophile
b) polar protic solvents favor S_N1 rxns because the hydrogen bonds formed stabilize the carbocation intermediate as well as the leaving group after it leaves the substrate. The poor reactivity of the nucleophile (due in part to the solvent's ability to stabilize it), also favors the S_N1 mechanism.

12. a) 1° substrate, strong nucleophile : S_N2
b) 3° substrate, weak nucleophile : S_N1

13.

a)

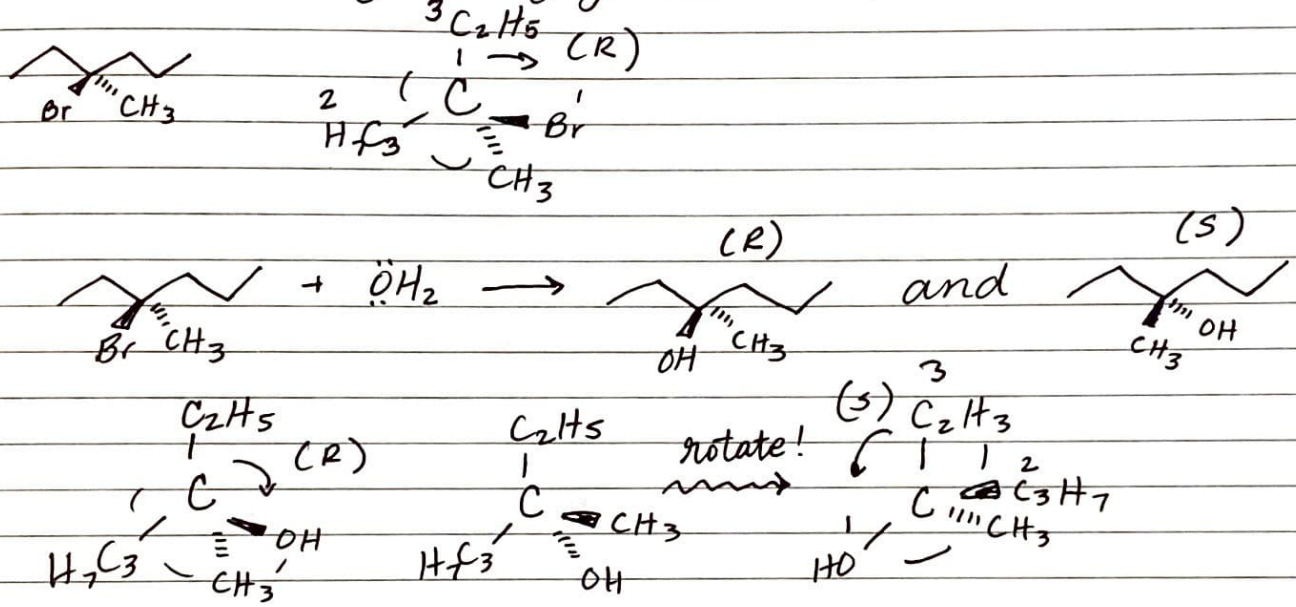


S_N2 mechanism favored due to 2° carbon and strong configuration

b) inversion of configuration occurs due to the nucleophile attacking on the opposite side of the leaving group, so as the carbon forms a bond with the nucleophile, the bond with the leaving group breaks, leading to an inversion of configuration.

14.

a)



b) racemization occurs because the carbocation intermediate has a trigonal planar geometry, meaning the nucleophile can attack from either side of the carbon with equal probability. This leads to a mixture of stereoisomers as products.

c) You would not expect exactly a 50:50 mix of enantiomers. This is because the attack from the opposite side of the leaving group is partially favored due to the departed leaving group blocking access to the nucleophile. It's more 60% inverted configuration, 40% retained.

15. S_N1 rxns result in a racemic mixture (both retention and inversion of stereochemistry due to the ability of the nucleophile to attack from both sides of the carbocation. S_N2 rxns result in an inversion of stereochemistry due to the preference of the nucleophile to attack from the backside of the carbon in the substrate. This also occurs because the nucleophile attacks as the leaving group leaves, resulting in a stereospecific nucleophilic attack (in S_N2 rxns).

16. a) rate = $k[RX]$
    b) rate = $k[RX][Nu]$

17. a) S_N1 rxn so doubling the concentration of the reactant doubles the rxn rate
    b) no change
    c) the formation of the carbocation intermediate is the rate-determining step. This step is not dependent on the concentration of the nucleophile

18. a) rate triples because S_N2 rxn depends on both substrate & nucleophile; tripling substrate triples rxn rate
    b) rate increases by a factor of 4 since rate is dependent upon both substrate and nucleophile

19.

	S_N1	S_N2
# steps	2	1
rate law	1st	2nd order
substrate pref.	3°	1°
nucleo. strength	weak	strong
solvent type	polar protic	polar, aprotic
stereochem	racemic	inversion
int. formed	carbocat	none
transition state	no	yes

20. I would use polarimetry to determine stereochemistry of products. S_N2 would result in bending of light the opposite of the reactant. S_N1 rxns product would not bend light due to presence of racemic mixture
    ↳ aka optically inactive