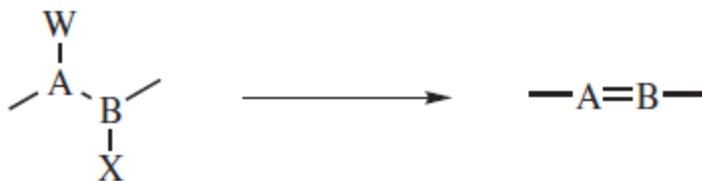


STUDY OF REACTION MECHANISM: ELIMINATION REACTIONS

- Two groups are lost without being replaced

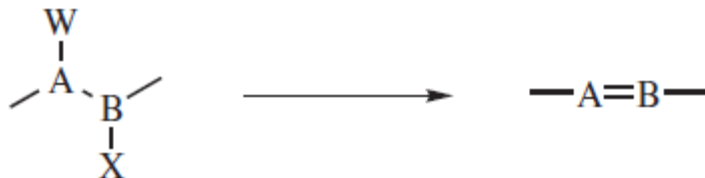


TYPES OF ELIMINATION REACTIONS

1. α -Eliminations: Both groups are lost from the same carbon to form carbene (or nitrene)



2. β -Eliminations: Both groups are lost from adjacent atoms to form a double bond



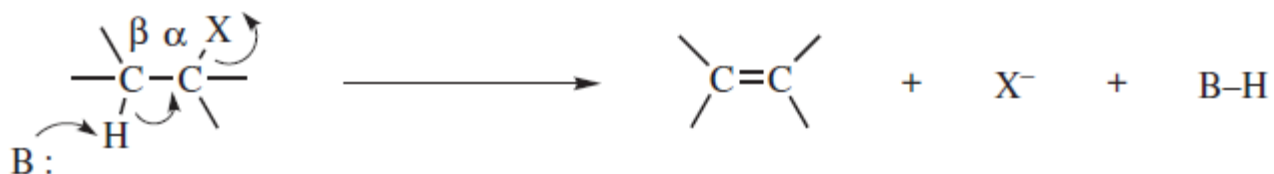
3. γ -Eliminations: One group is lost from α -carbon and other from γ -carbon to form a ring



TYPES OF ELIMINATION MECHANISMS

1. The E2 Mechanism
2. The E1 Mechanism
3. The E1cB Mechanism
4. Pyrolytic Eliminations

1. The E2 Mechanism: Elimination Bimolecular

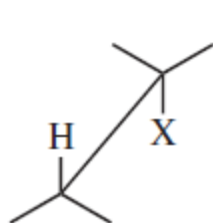


Evidences

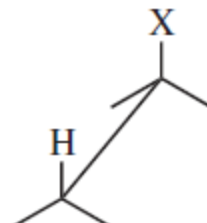
1. Kinetic Evidence

$$\text{Rate} = k [\text{substrate}][\text{Base}]$$

2. Stereochemistry



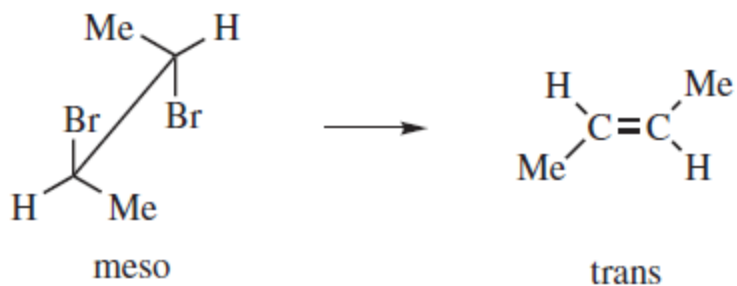
anti-Periplanar



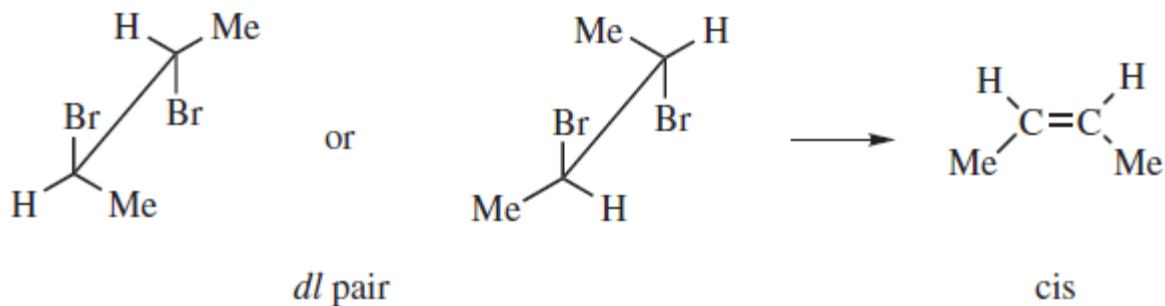
syn-Periplanar

anti-Elimination is preferred to *syn*-elimination

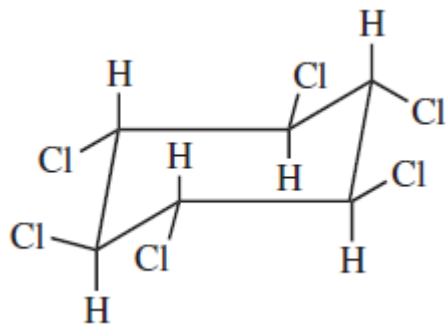
Example-1



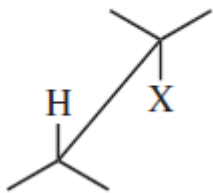
- *meso-form gives trans-isomer only*
- *Each member of dl-pair give cis-isomer only*
- *This behaviour shows that dehalogenation is taking place via anti-Elimination*



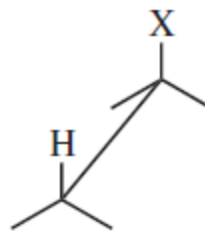
Example-2



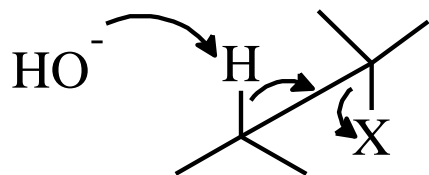
- *Hexachlorocyclohexane has 9 isomers.*
- *Out of these only one isomer has no Cl and H-atoms anti-periplanar to each other as shown in fig.*
- *This isomers shows unfavourable SYN-Elimination therefore, its rate of dehydrohalogenation is almost 7000 times slower than other isomers.*



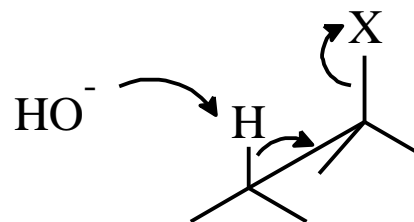
anti-Periplanar
(Low Energy Staggered Conformation)



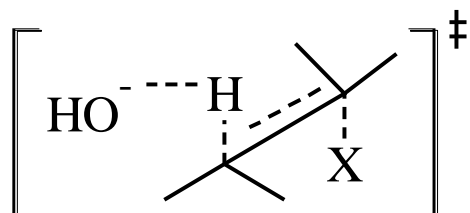
syn-Periplanar
(High Energy Eclipsed Conformation)



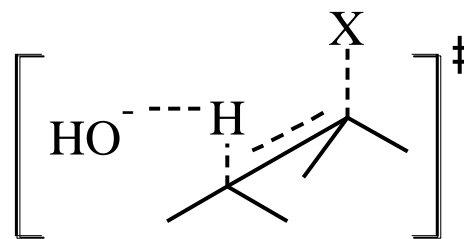
The push created by back-side attack of breaking C-H bond electrons (S_N2 type) facilitate the removal of leaving group.



The back-side push is not available since leaving group is on same side (syn-periplanar conformation)



The groups are far away from each other, therefore, less crowding, more stability.

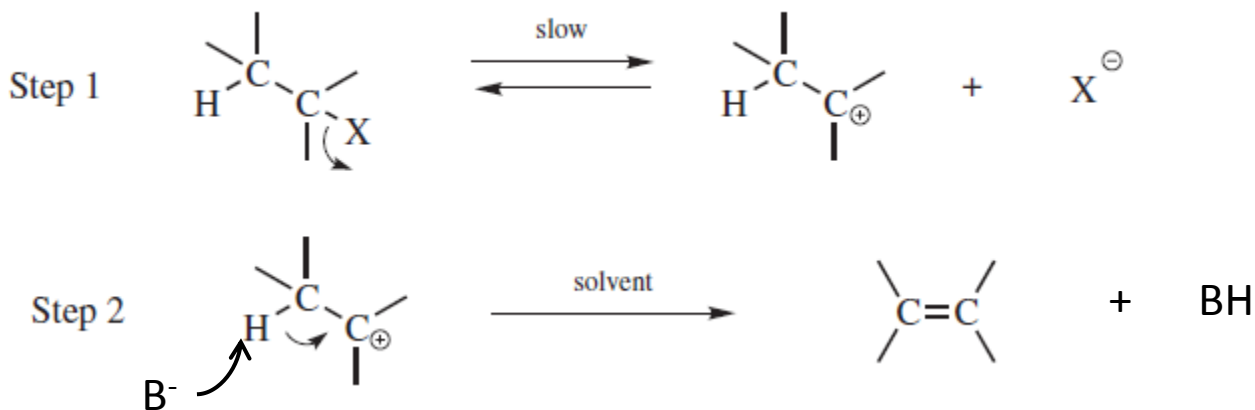


The groups are comparatively close to each other, therefore, more crowding, less stability.

3. Primary Kinetic Isotopic Effect

$$\frac{k_H}{k_D} > 1 \quad \text{Since C-H bond breaking takes place in rate determining step}$$

2. The E1 Mechanism: Elimination Unimolecular



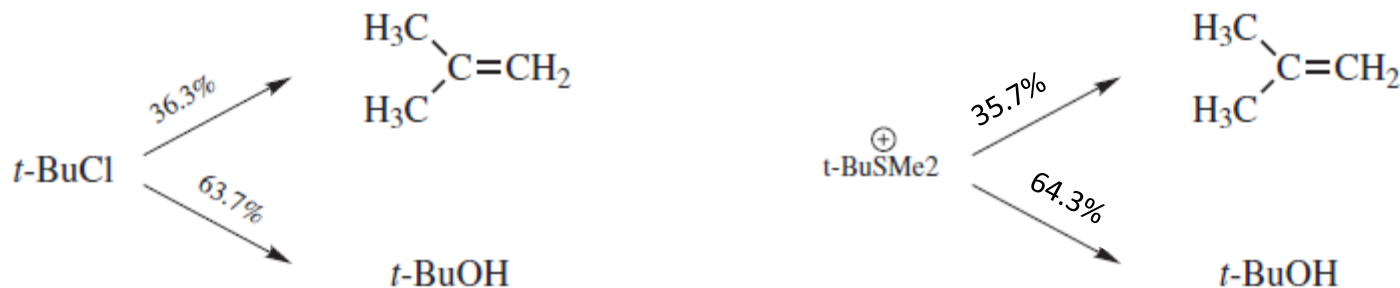
Evidences

1. Kinetic Evidence

$$\text{Rate} = k [\text{substrate}]$$

2. Effect of Leaving Group

The substitution/elimination product ratio is decided by step-II in which no leaving group is present. Therefore, changing leaving group will not affect the ratio of substitution/elimination products

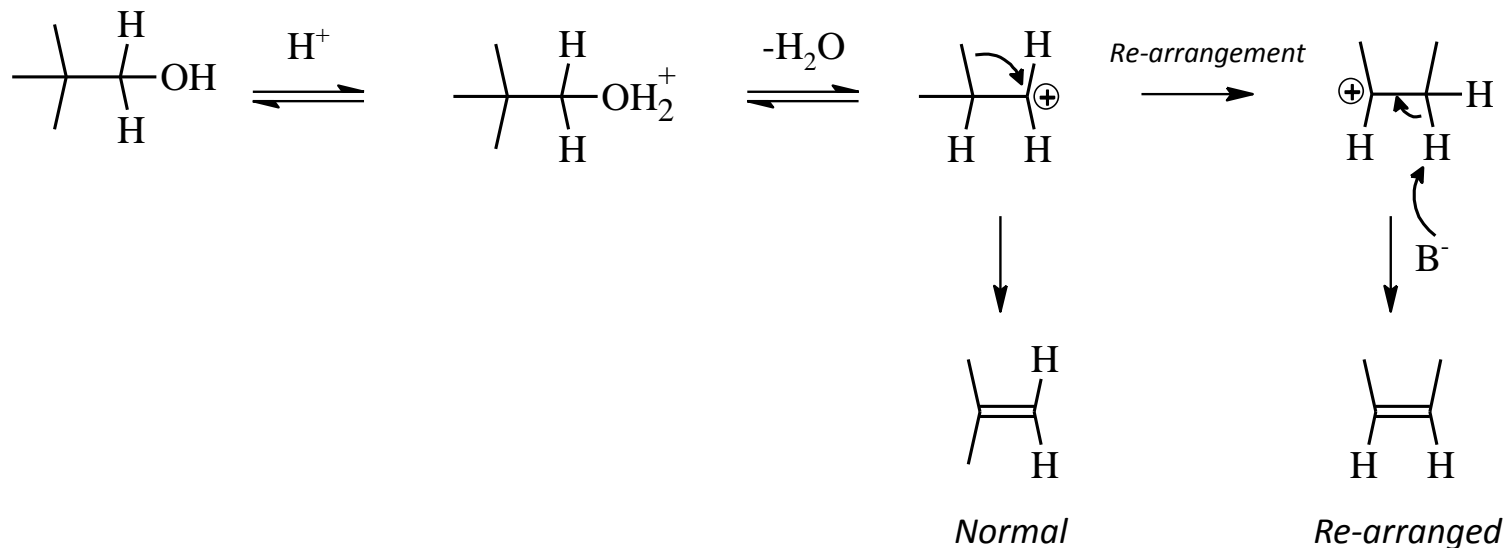


3. Primary Kinetic Isotopic Effect

$$\frac{k_H}{k_D} = 1$$

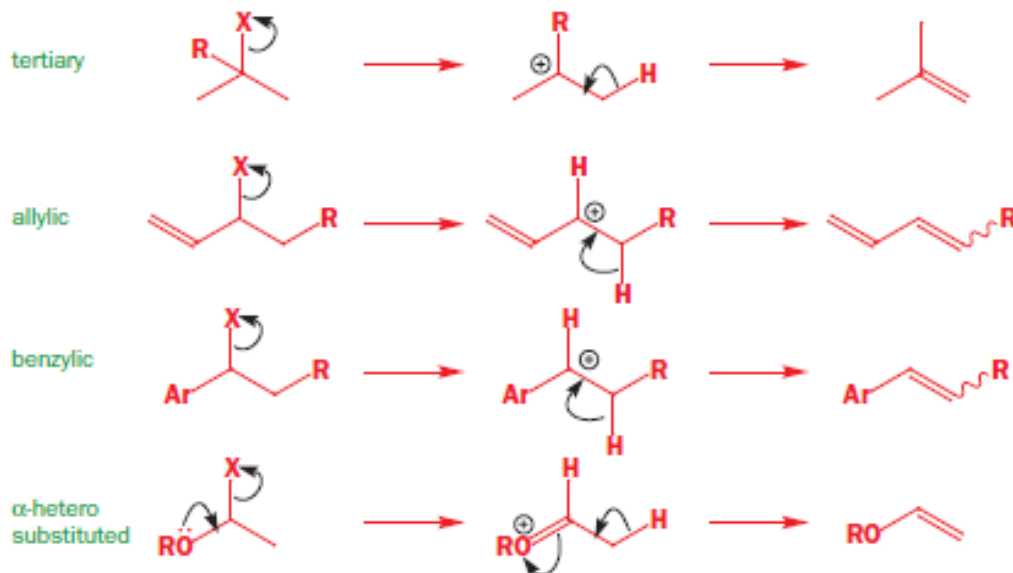
- Since C-H bond breaking does not take place in rate determining step
- This effect can distinguish between E2 and E1 mechanisms since for E2 mechanism $\frac{k_H}{k_D} > 1$

4. Rearrangements of Carbocations



substrates that readily eliminate by E1

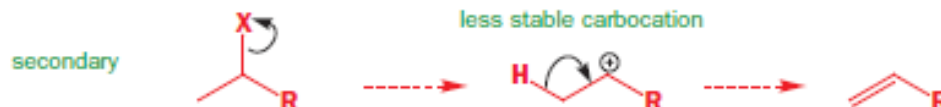
stabilized carbocations



may also eliminate by E2

substrates that may eliminate by E1

less stable carbocation

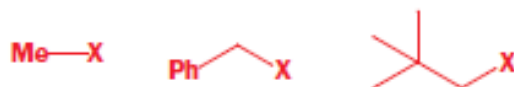


substrates that never eliminate by E1

unstable carbocation

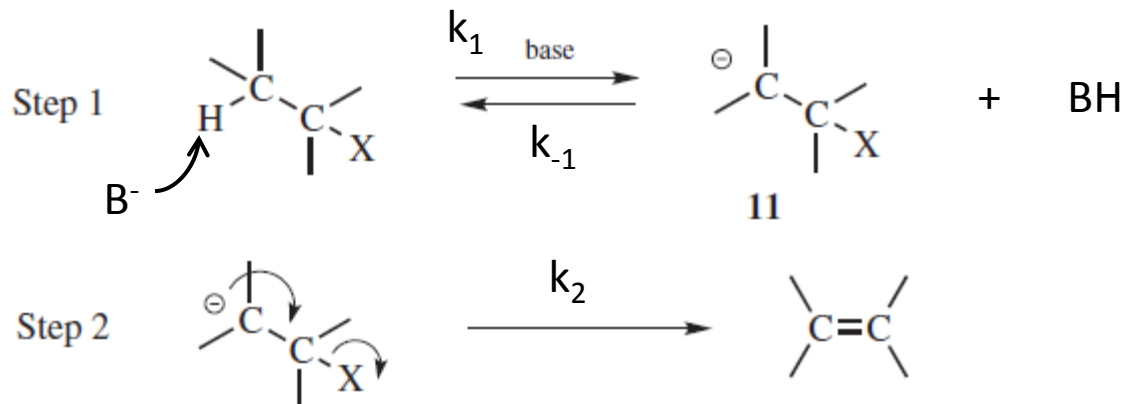


substrates that cannot eliminate by either mechanism – no appropriately placed hydrogens



cannot eliminate by E2

3. The E1cB Mechanism: Carbanion Mechanism



According to Steady State Approximation

$$\frac{d[P]}{dt} = \frac{k_1 k_2 [R-LG][B^-]}{k_{-1}[BH] + k_2}$$

Types of E1cB Mechanism

1. $(E1cB)_R$
2. $(E1cB)_{irr}$
3. $(E1cB)_{anion}$

1. (E1cB)_R

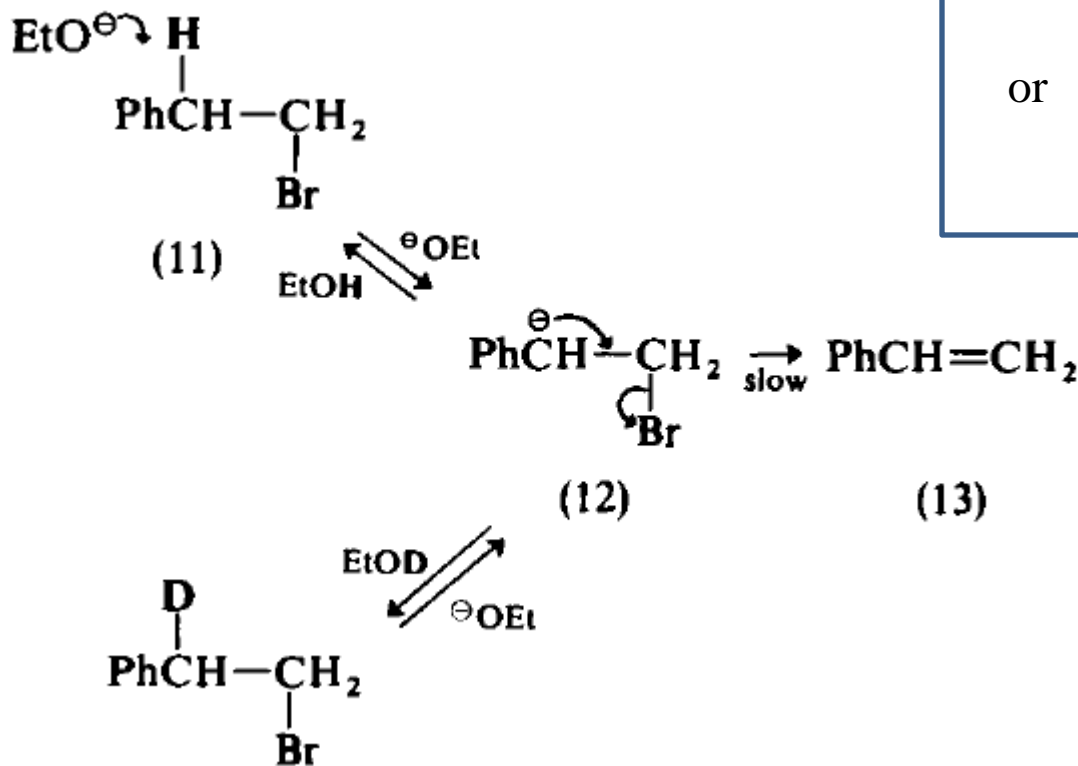
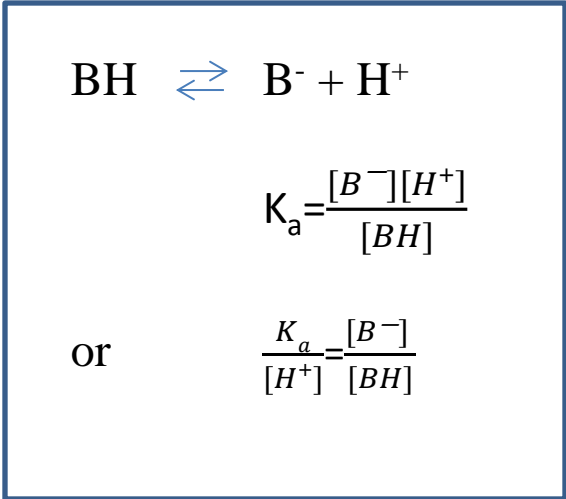
- Kinetic Evidence

$$\frac{d[P]}{dt} = \frac{k_1 k_2 [R-LG][B^-]}{k_{-1}[BH] + k_2}$$

If $k_{-1} \gg k_2$, then $\frac{d[P]}{dt} = \frac{k_1 k_2}{k_{-1}} [R-LG] \left(\frac{[B^-]}{[BH]} \right) = \frac{K_a k_1 k_2}{k_{-1} [H^+]} [R-LG]$

- Specific-acid catalyzed
- Second order

- Isotopic scrambling



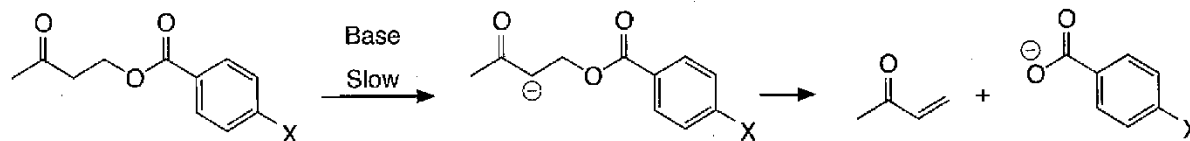
2. (E1cB)_{irr}

- Kinetic Evidence

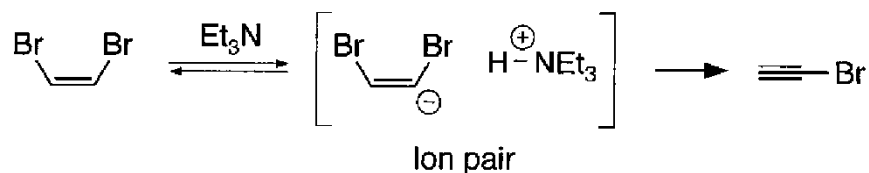
$$\frac{d[P]}{dt} = \frac{k_1 k_2 [R-LG][B^-]}{k_{-1}[BH] + k_2} \quad \text{If } k_2 \gg k_{-1} \quad \text{then} \quad \frac{d[P]}{dt} = k_1 [R-LG][B^-] \quad \bullet \text{ Second order}$$

- Leaving Group Effect

Leaving group departure does not occur in slow step. So changing leaving group will not greatly affect the rate of E1cB_{irr} reaction. However, the rate of E2 reaction is affected significantly.



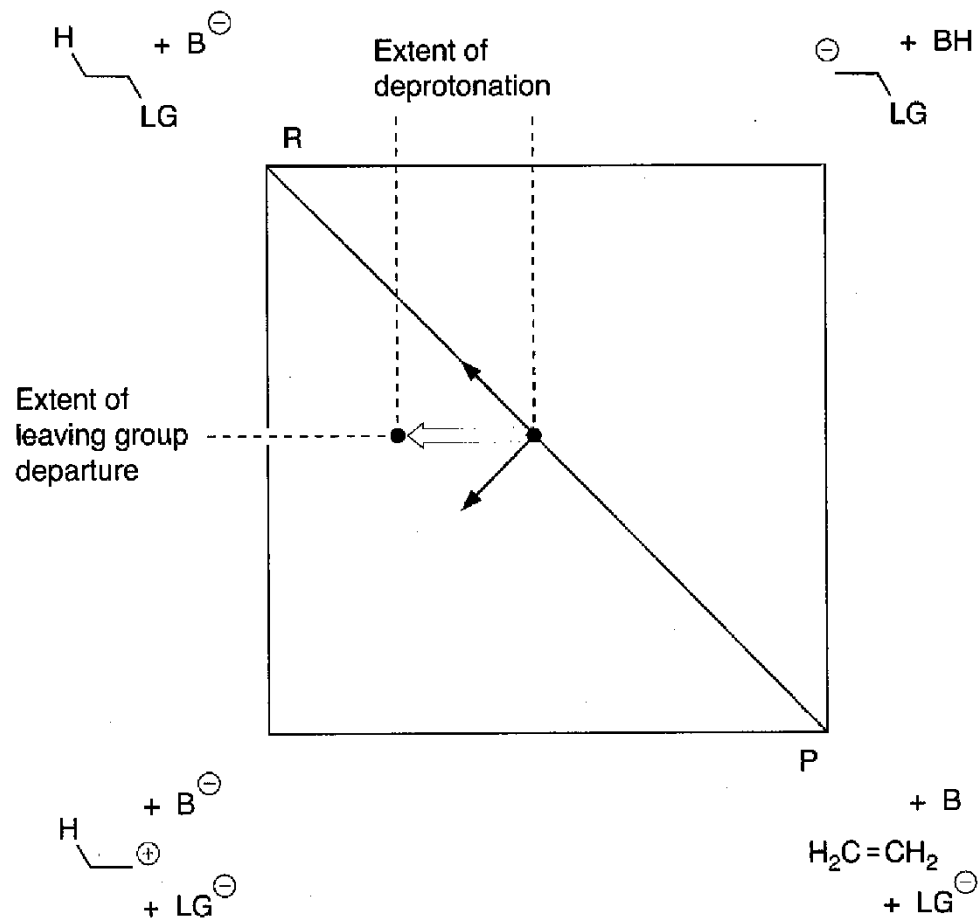
3. (E1cB)_{ip}



Generally $k_{-1} \gg k_2$, therefore second order like E2

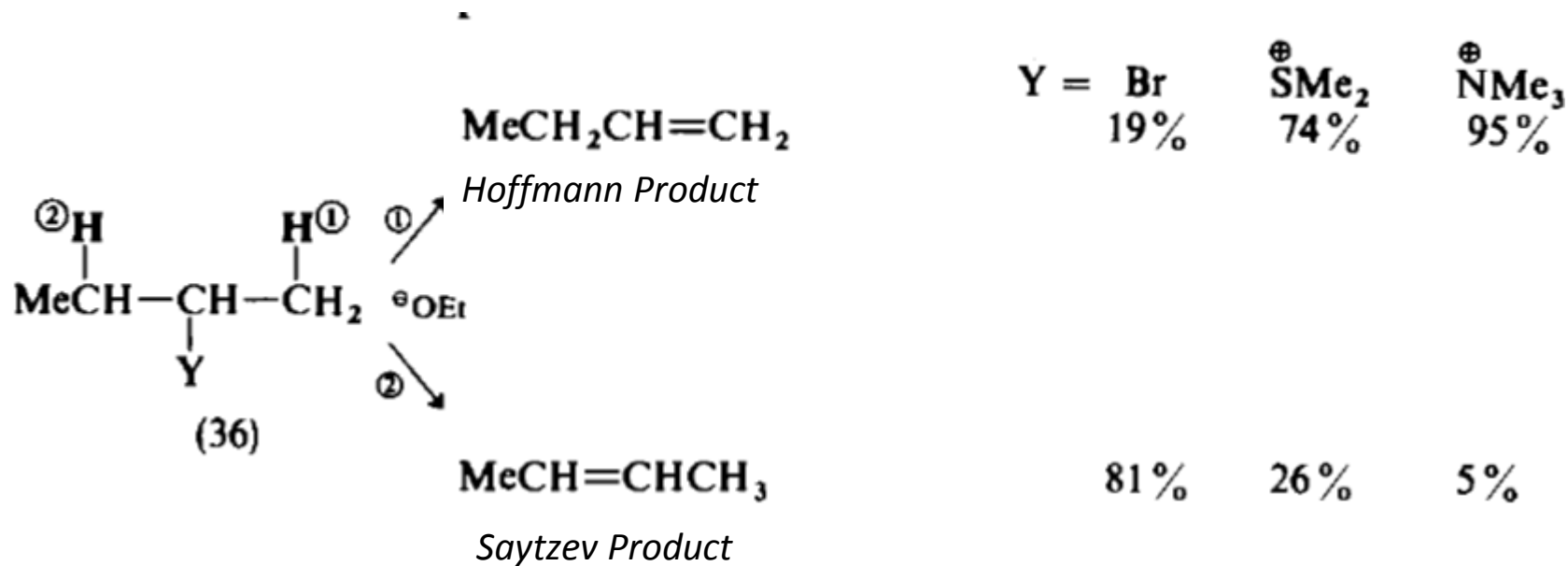
However, primary kinetic isotopic effect is much less than that of E2 mechanism

Contrasting E2, E1, and E1cB

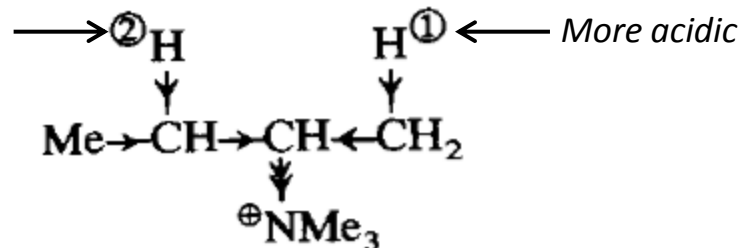


1. Effect of Leaving group

Strong electron-withdrawing groups favour Hoffmann elimination over Saytzev elimination

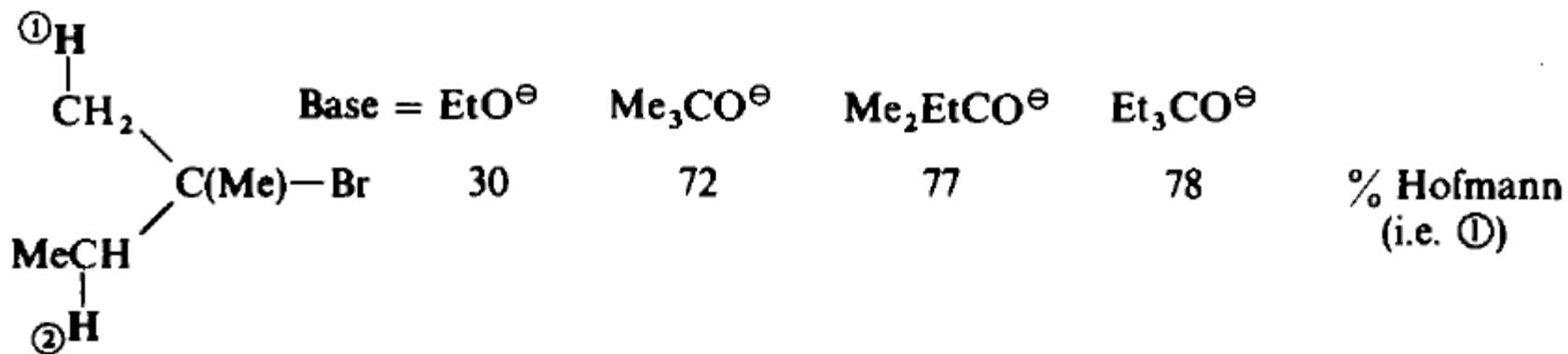


Less acidic due to electron donating effect of methyl group



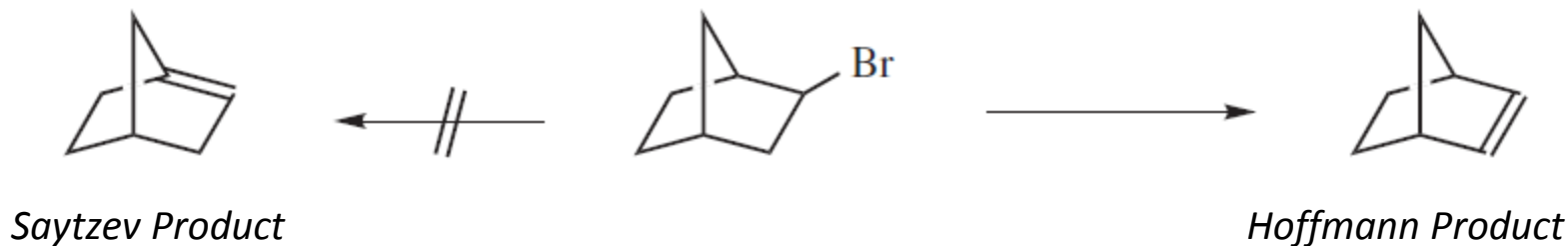
2. Effect of Size of Base

Increase in size of base favour Hoffmann elimination over Saytzev elimination due to steric hinderance



3. Effect of Bridgehead

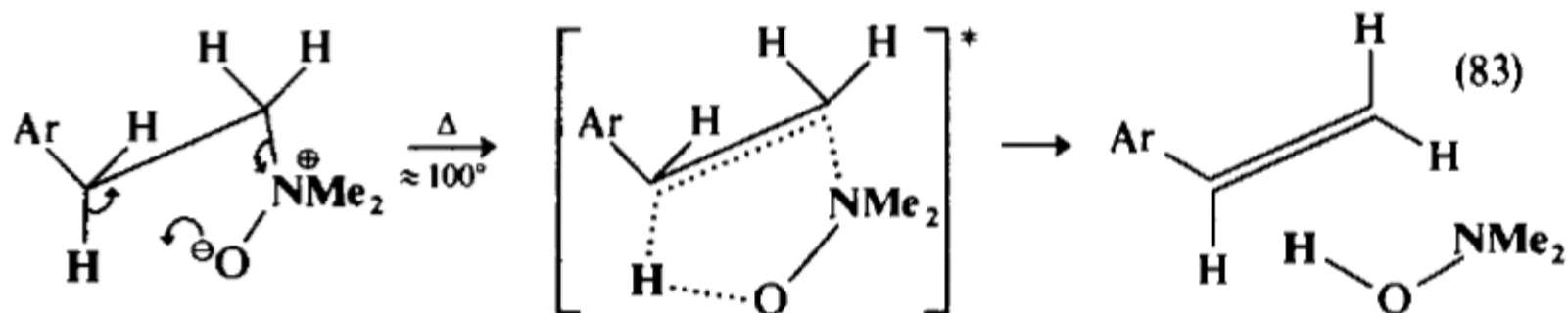
Double bond is not created at bridgehead because planarity cannot be achieved so Hoffmann elimination dominates over Saytzev elimination



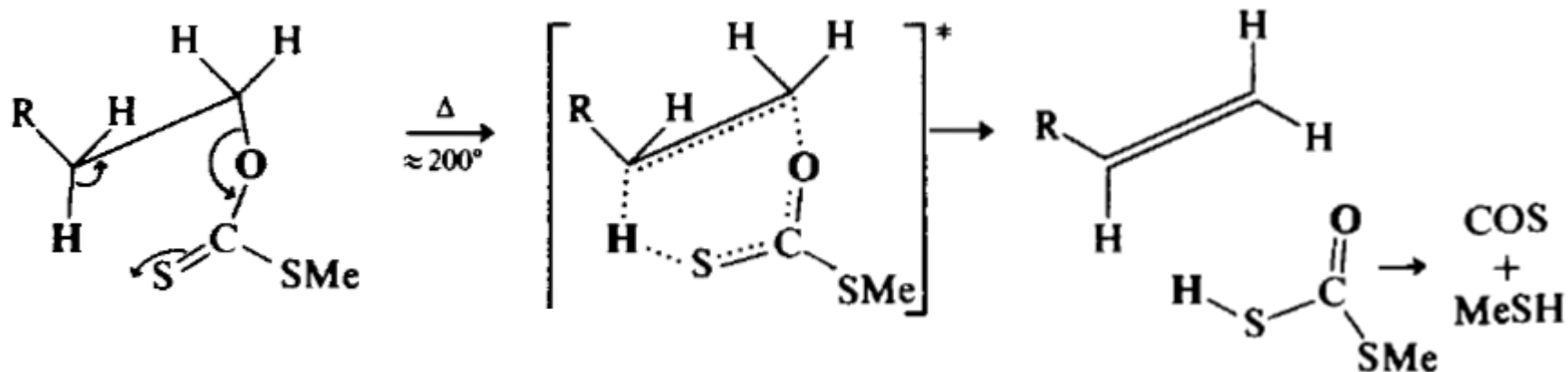
4. The Pyrolytic SYN Eliminations

- Rate = k [Substrate]
- Distinguished from E1 reactions by SYN Stereoselectivity
- Cyclic Transition State

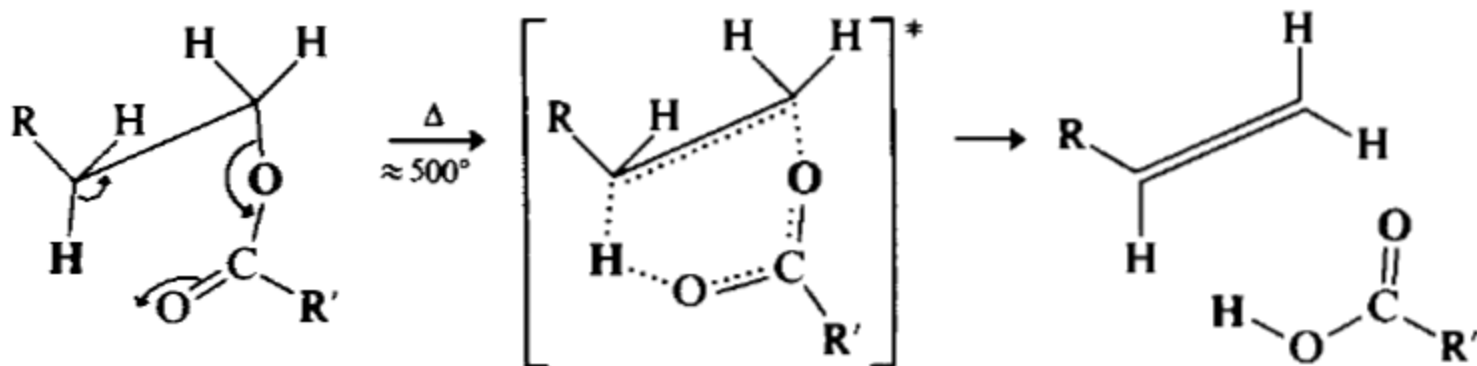
(i) The Cope Reaction: Pyrolysis of Amine Oxide



(ii) The Chugaev Reaction: Pyrolysis of Xanthate Ester

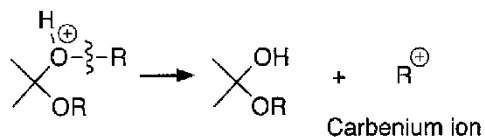
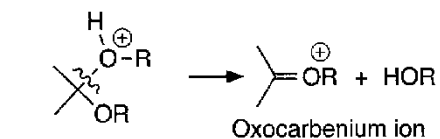
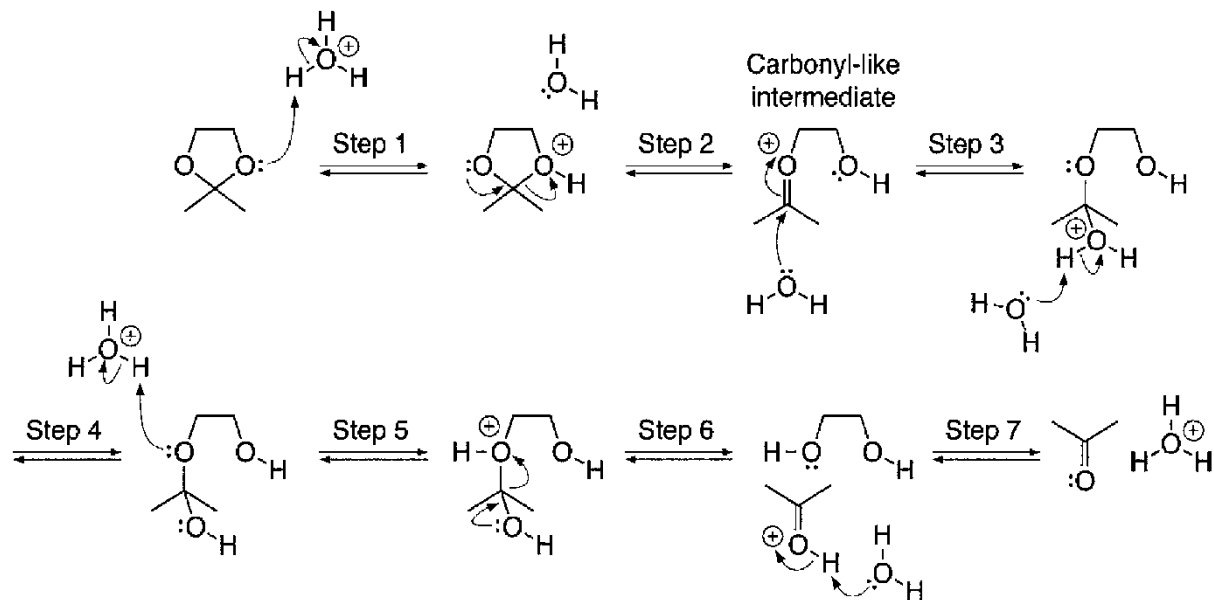


(iii) Pyrolysis of Carboxylate Ester

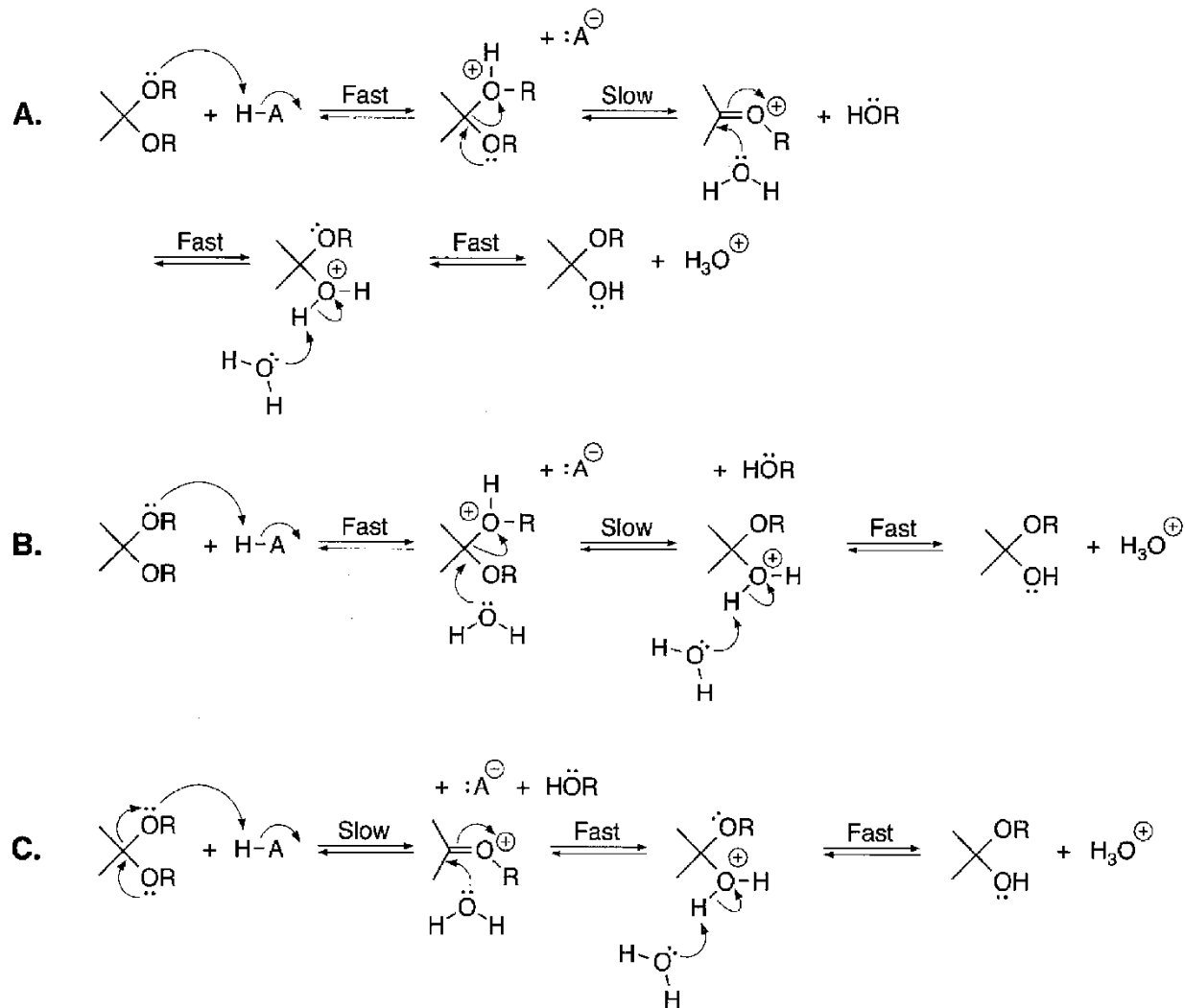


STUDY OF REACTION MECHANISM OF ELIMINATION REACTIONS

Eliminations to Form Carbonyls or "Carbonyl-Like" Intermediates

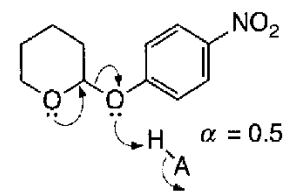
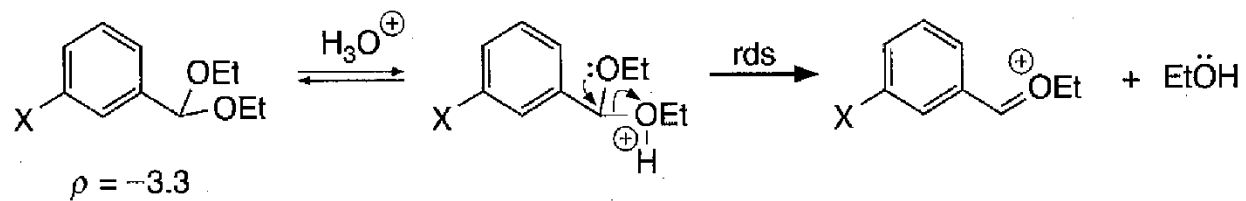


POSSIBLE MECHANISMS



Figure

A. Specific-acid-catalyzed pathway for acetal hydrolysis that occurs with poor leaving groups. B. A pathway seldom if ever seen. C. General-acid-catalyzed pathway that occurs with good leaving groups.



General-acid catalysis

Stereoelectronic Effects

