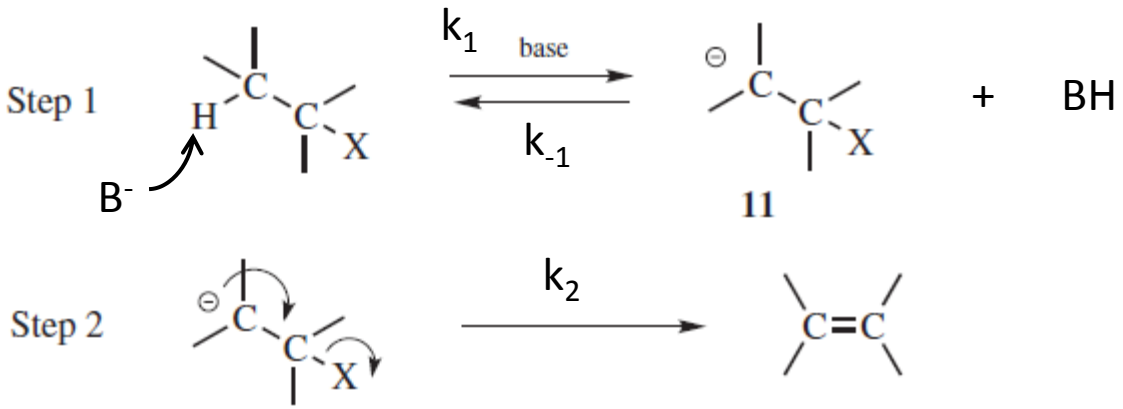
3. The E1cB Mechanism: Carbanion Mechanism



According to Steady State Approximation

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

Types of E1cB Mehcanism

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

1. $(E1cB)_R$

- Kinetic Evidence

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

If $k_{-1} >> k_2$, then

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

- *Specific-acid catalyzed*
- *Second order*

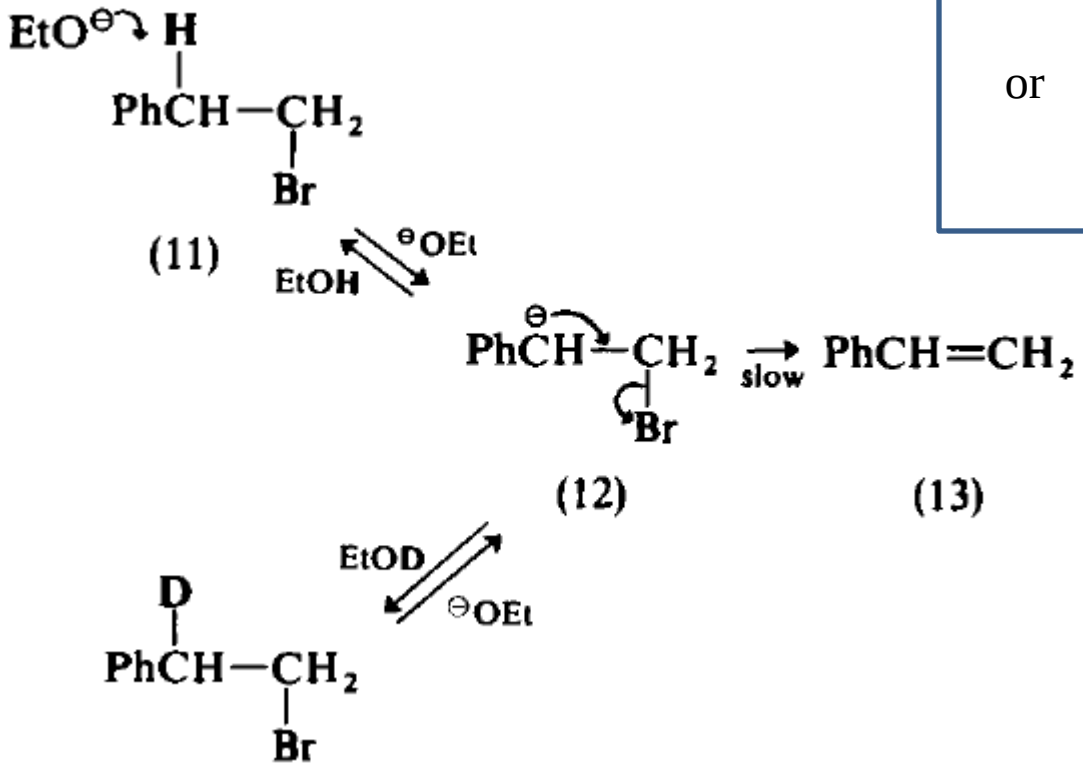
$$BH \rightleftharpoons B^- + H^+$$

$$K_a = \frac{[B^-][H^+]}{[BH]}$$

or

$$\frac{K_a}{[H^+]} = \frac{[B^-]}{[BH]}$$

- Isotopic scrambling



2. $(E1cB)_{irr}$

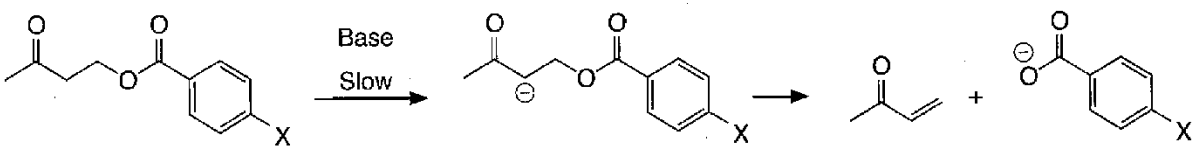
- Kinetic Evidence

$$\frac{d[P]}{dt} = \frac{k_1 k_2 [R\text{–}LG][B^-]}{k_{-1}[BH] + k_2} \qquad \text{If} \quad k_2 >> k_{-1} \qquad \text{then} \quad \frac{d[P]}{dt} = k_1 [R\text{–}LG][B^-]$$

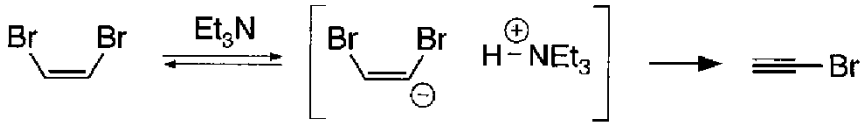
- *Second order*

- 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. $(E1cB)_{ip}$



Ion pair

Generally $k_{-1} >> k_2$ *therefore second order like E2*

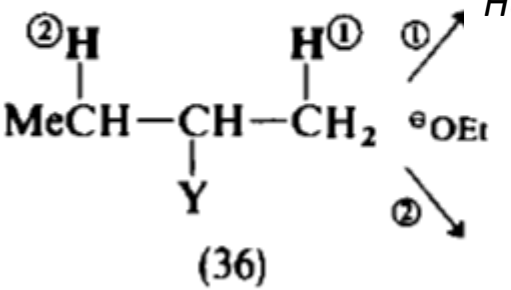
However, primary kinetic isotopic effect is much less than that of E2 mechanism

ORIENTATION OF DOUBLE BOND: REGIOSELECTIVITY

Saytzev vs Hoffmann Elimination

1. Effect of Leaving group

Strong electron-withdrawing groups favour Hoffmann elimination over Saytzev elimination



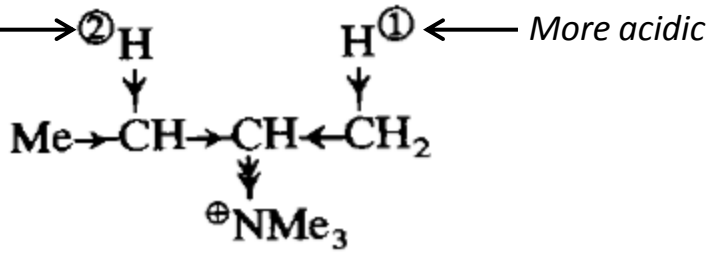
(36)

	Y = Br	⊕SMe2	⊕NMe3
$MeCH_2CH{=}CH_2$	19%	74%	95%
$MeCH{=}CHCH_3$	81%	26%	5%

Hoffmann Product

Saytzev Product

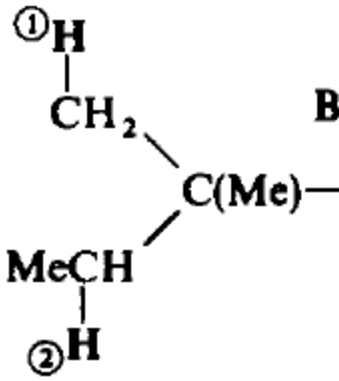
Less acidic due to electron donating effect of methyl group



More acidic

2. Effect of Size of Base

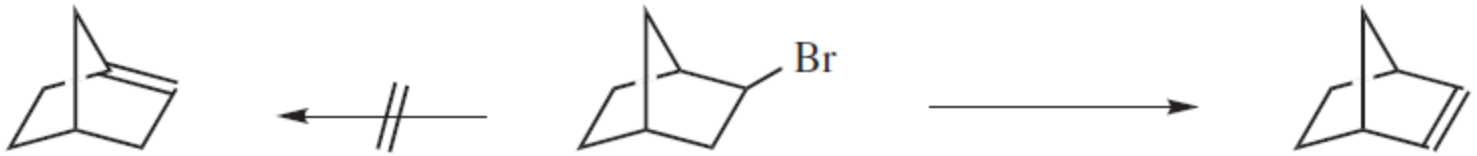
Increase in size of base favour Hoffmann elimination over Saytzev elimination due to steric hinderance



Base =	$EtO^{\ominus}$	$Me_3CO^{\ominus}$	$Me_2EtCO^{\ominus}$	$Et_3CO^{\ominus}$	
	30	72	77	78	% Hofmann (i.e. ①)

3. Effect of Bridgehead

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

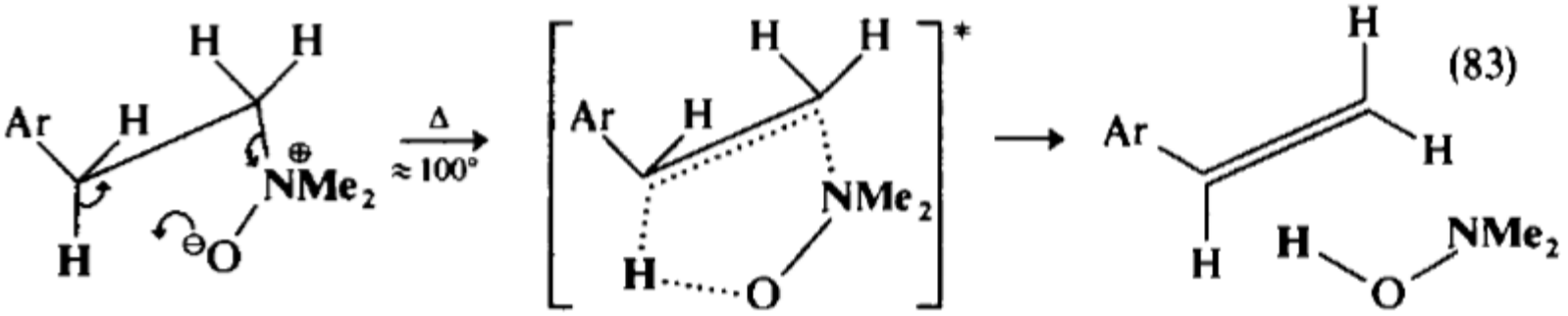


Saytzev Product *Hoffmann Product*

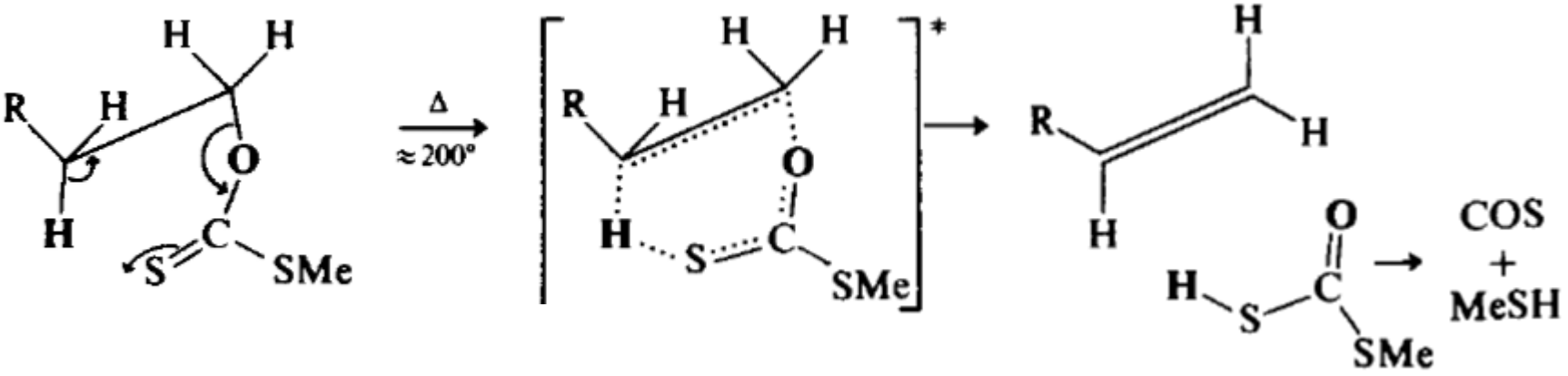
4. The Pyrolytic SYN Eliminations

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

(i) The Cope Reaction: Pyrolysis of Amine Oxide



(ii) The Chugaeve Reaction: Pyrolysis of Xanthate Ester



(iii) Pyrolysis of Carboxylate Ester