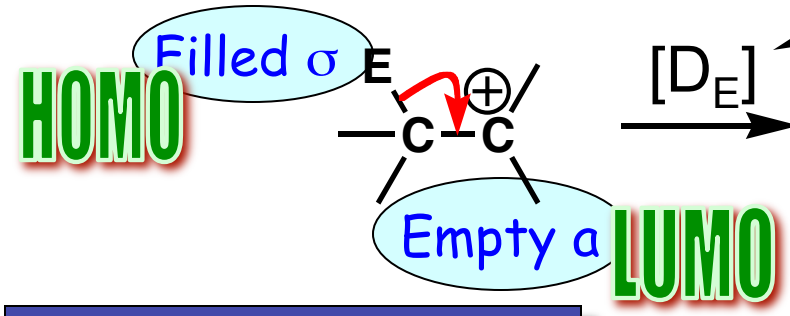
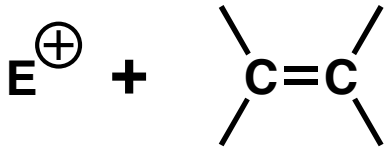
Elimination Mechanisms Require New Elementary Steps: Electrophile Dissociation From an Adjacent Carbocation

-E is the electrophile
(-E is often an -H, hydrogen)

This symbol means dissociation of an electrophile



$[D_E]$



$[D_E]$ involves σ-bond breaking, π-bond making

$[D_E]$ is a $\sigma \rightarrow a$ *π-type* interaction

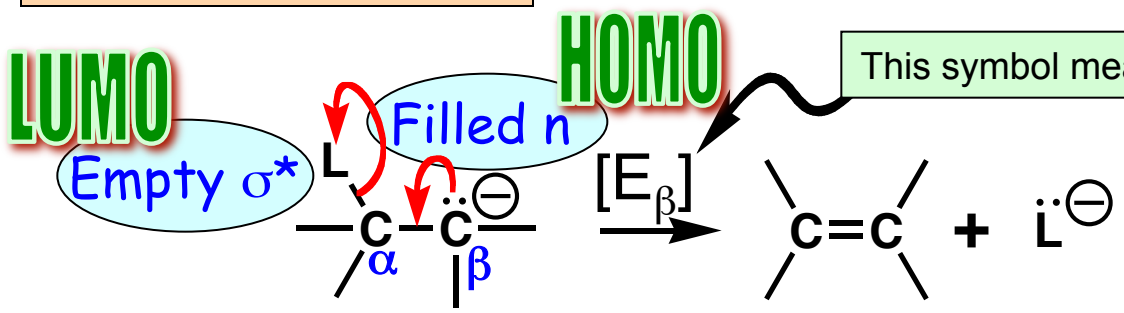
empty / filled	σ*	a	π*
σ	σ→σ*	σ→a	σ→π*
n	n→σ*	n→a	n→π*
π	π→σ*	π→a	π→π*

Curved Arrows Imply the Frontier Orbitals

Curved arrows indicate the HOMO-LUMO pair (Frontier Orbitals) involved in the elementary step. The tail of the arrow implies the filled orbital (HOMO) is an electron pair in a σ-bond. The head of the arrow points between two carbon atoms and suggests a new π-bond. An empty orbital on the carbocation is available to accommodate this electron pair implying that the LUMO is an atom-centered, empty orbital (*a*). The HOMO (σ-orbital) is beside (and nearly parallel to) the LUMO (*a*) allowing for a π-type interaction.

Elimination Mechanisms Require New Elementary Steps: Beta Elimination [E_β]

-L is a leaving group



This symbol means beta elimination

[E_β] involves
π-bond making
σ-bond breaking

The alpha carbon (C_α) is defined as the carbon bearing the leaving group, -L. **Many leaving groups (-L) participate in [E_β], even poor ones (e.g., -OH).** The new π-bond is formed across the C_α-C_β bond.

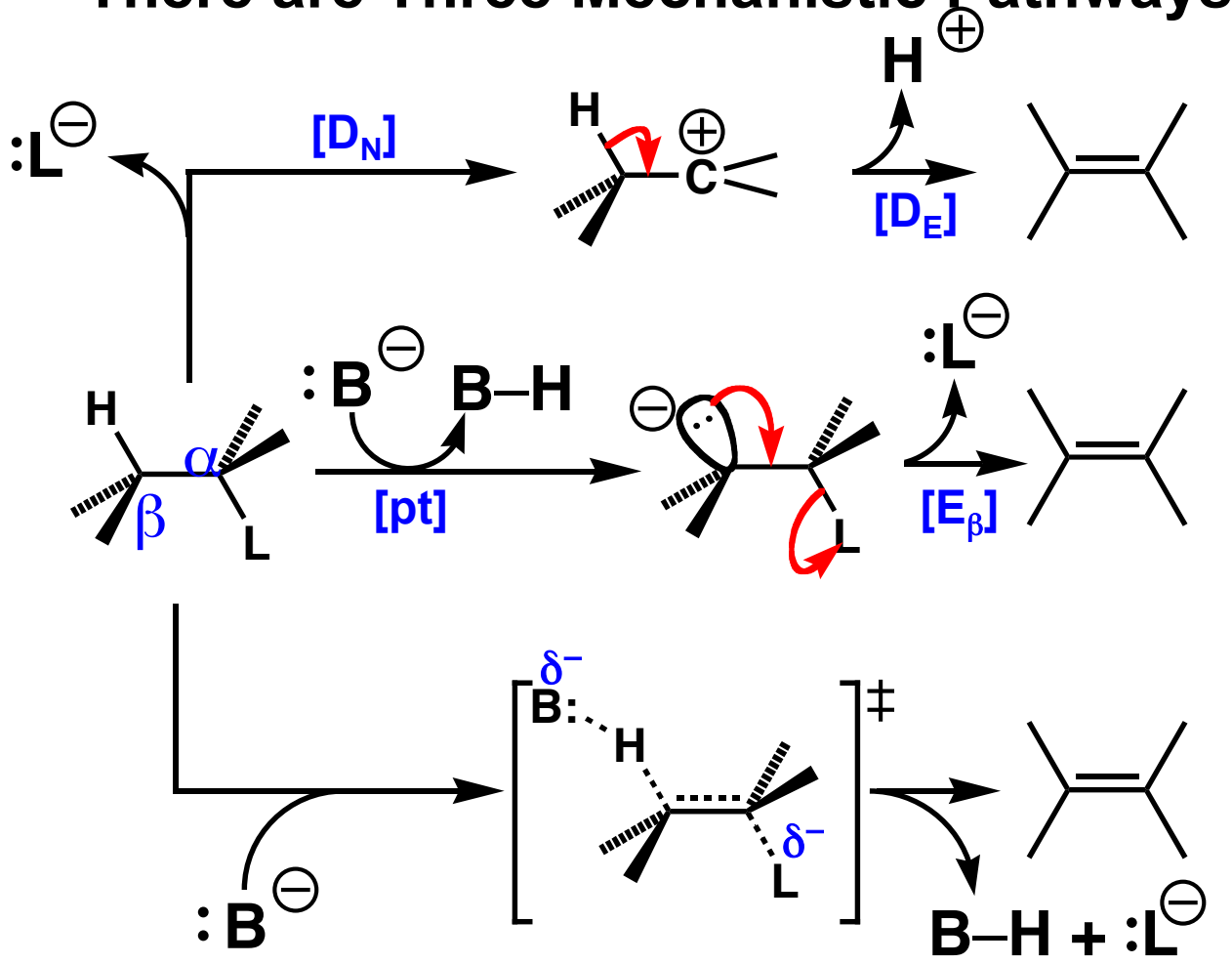
[E_β] is an n → σ* *π-type* interaction

Curved Arrows Imply the Frontier Orbitals

Curved arrows indicate the HOMO-LUMO pair (Frontier Orbitals) involved in this elementary step. The tail of the first arrow implies that the filled orbital (HOMO) is a nonbonded electron pair, *n*. The head of the first arrow points between two carbon atoms suggesting in a new π-bond. An empty, low-lying σ*-orbital from the adjacent C-L bond is available to accommodate this electron pair suggesting the LUMO is σ*. The HOMO, *n*, is beside (and nearly parallel to) the LUMO, σ*, allowing for a π-type interaction.

empty / filled	σ*	a	π*
σ	σ→σ*	σ→a	σ→π*
n	n→σ*	n→a	n→π*
π	π→σ*	π→a	π→π*

There are Three Mechanistic Pathways for Elimination



pathway

[E1]
[D_N] then [D_E]
(two-step)

[E1cb]
[pt] then [E_β]
(two-step)

[E2]
[pt] + [D_N]
(concerted)

The three elimination pathways differ in the timing of the leaving group's departure. In the unimolecular elimination, [E1], the leaving groups departs in the first step via a [D_N] process. In the [E1cb] (**conjugate base variant of the unimolecular elimination**), the leaving group departs in the second step via a [E_β]. In the [E1cb] mechanism, a strong base must be present, the leaving group will generally be poor, and the beta hydrogen must be acidic. In the bimolecular elimination pathway, [E2], the leaving group leaves at the same time as the beta hydrogen is loss. This is a one-step, concerted process with [pt] + [D_N] happening in unison.