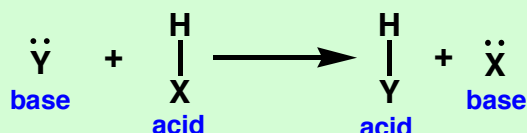


# Nucleophilic Addition Reactions - Adding XY Across Unsaturated C=Z and C=C Bonds

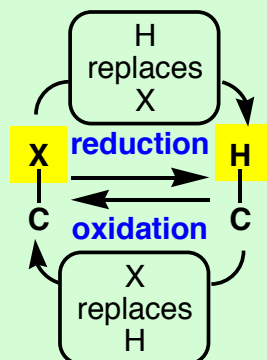
We previously studied the **electrophilic addition** of "XY" across carbon-carbon multiple bonds. Here we examine the **nucleophilic** variations of addition. We will consider C=C and C=Z  $\pi$ -bonds (where Z is a heteroatom such as O or N).

## 1) Acid-Base - hydrogen swap

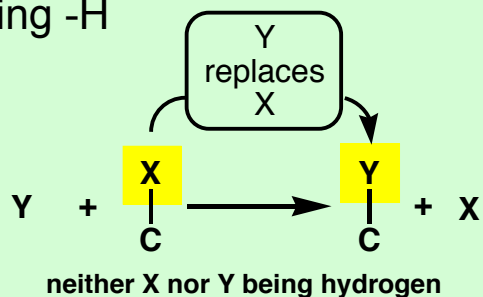


## 2 & 3) Oxidation & Reduction

change in the number of C-H bonds in relation to the number of C-X bonds

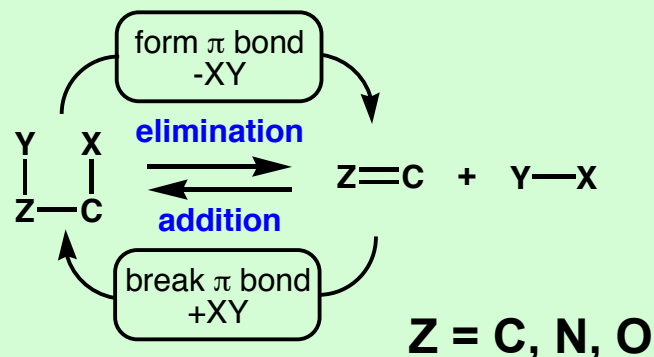


**4) Substitution** - replace C's substituent (-X) with another (-Y), neither being -H

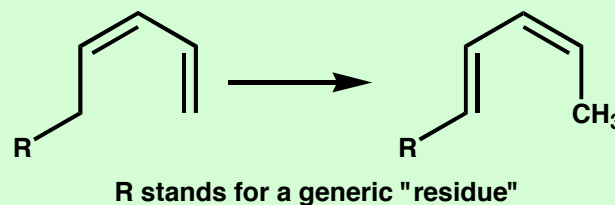


**5) Elimination** - loss of XY elements with concomitant pi bond formation

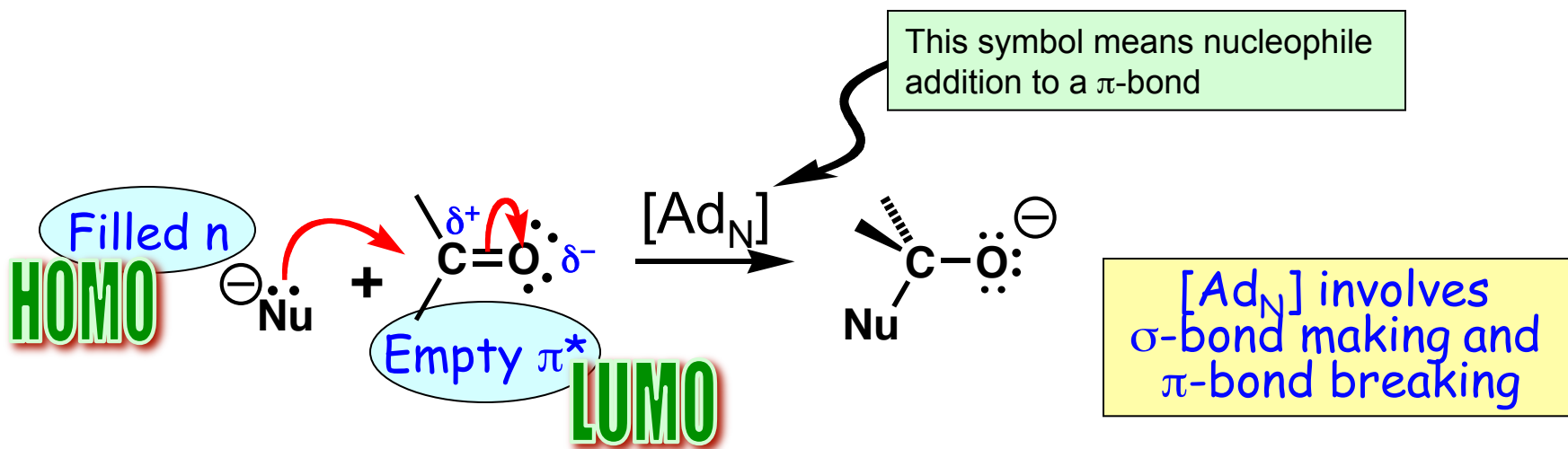
**6) Addition** - gain of XY elements with concomitant loss of pi bond



**7) Rearrangement** - isomerization process (no atoms lost or gained); results in new bonding connectivity (one of many examples shown as there is no generic representation).



# Addition Mechanisms Require a New Elementary Step: Nucleophile Addition to a C=O $\pi$ -bond [Ad<sub>N</sub>]



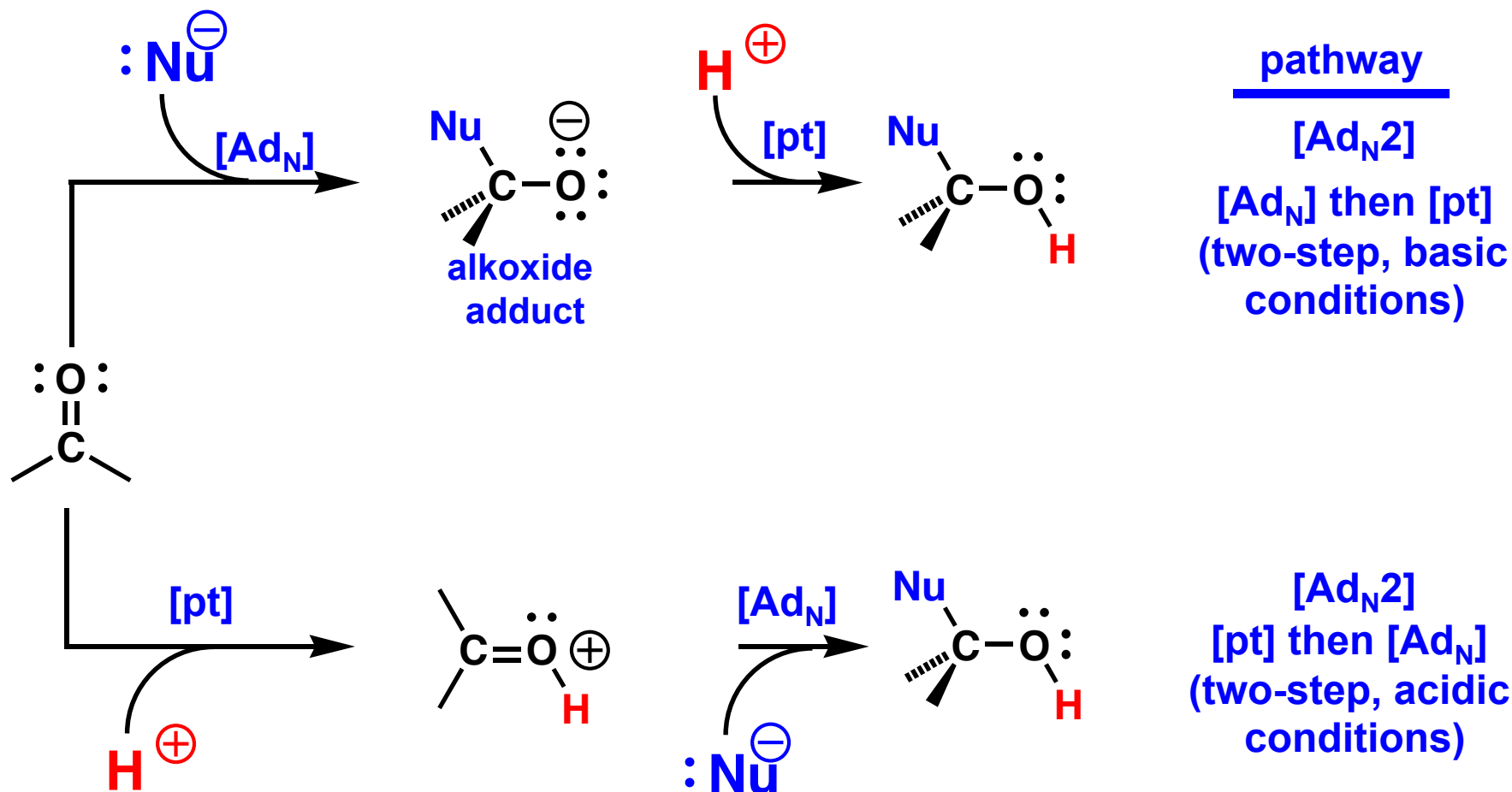
[Ad<sub>N</sub>] is a  $n \rightarrow \pi^*$   
 $\sigma$ -type interaction

## Curved Arrows Imply the Frontier Orbitals

Curved arrows indicate the HOMO-LUMO pair (Frontier Orbitals) involved in an elementary step. The tail of the first arrow implies the filled orbital (HOMO) is non-bonded electron pair. The head of the arrow points between Nu<sup>-</sup> and a carbon atom from the  $\pi$ -bond. The tail of the second arrow shows that a  $\pi$ -bond breaks suggesting that  $\pi^*$  accepts the electron pair via  $\sigma$ -type orbital interaction.

empty filled	$\sigma^*$	a	$\pi^*$
$\sigma$	$\sigma \rightarrow \sigma^*$	$\sigma \rightarrow a$	$\sigma \rightarrow \pi^*$
n	$n \rightarrow \sigma^*$	$n \rightarrow a$	$n \rightarrow \pi^*$
$\pi$	$\pi \rightarrow \sigma^*$	$\pi \rightarrow a$	$\pi \rightarrow \pi^*$

## There are Two Mechanistic Pathways for Nu Addition



The two addition pathways differ in the timing of the proton transfer and nucleophile addition. Both are two-step mechanisms and both are called  $[\text{Ad}_\text{N}2]$  (**bimolecular nucleophilic addition to a polarized  $\pi$ -bond**). The bimolecular  $[\text{Ad}_\text{N}]$  step is rate-determining for both. In the top case, the two steps are often actually performed sequentially (i.e., in the laboratory, a proton source is subsequently introduced to “quench” the initially formed adduct). For the top case nucleophilic addition is under basic conditions and an acid then neutralizes the initially formed alkoxide adduct. In the bottom case, reversible proton transfer takes place followed by  $[\text{Ad}_\text{N}]$ . Unlike the top case, this two-step process occurs without changing conditions (no intervention on the part of the chemist is needed).