

2020 유기화학실험 세미나

알돌 축합 엔온 합성

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강 민 기

name 1

name 2

이야기 순서

- 친핵체와 친전자체의 정의
- 알돌반응의 정의
- 간단한 분자의 알돌반응 메커니즘
- 실험에서의 알돌반응
- 실험에서의 알돌의 탈수반응
- 참고문헌

친핵체와 친전자체의 정의

A nucleophile (or nucleophilic reagent) is a reagent that forms a bond to its reaction partner (the electrophile) by donating both bonding electrons. A 'nucleophilic substitution reaction' is a heterolytic reaction in which the reagent supplying the entering group acts as a nucleophile. For example:

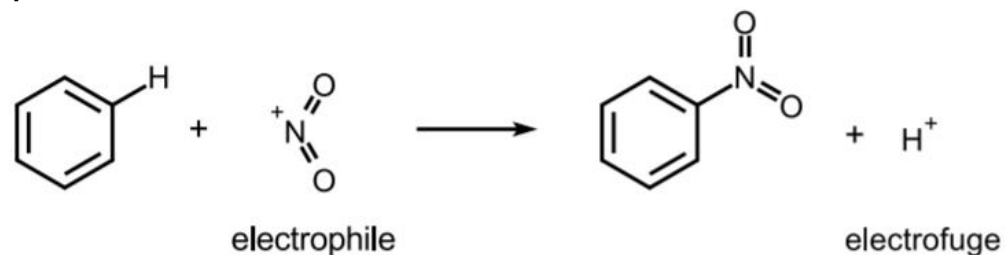


The term 'nucleophilic' is also used to designate the apparent polar character of certain radicals, as inferred from their higher relative reactivity with reaction sites of lower electron density. Nucleophilic reagents are Lewis bases.

친핵체(nucleophile) : 새로운 결합을 형성할 때 전자를 제공하는 것 ; 루이스 염기로 작용

친핵체와 친전자체의 정의

An electrophile (or electrophilic reagent) is a reagent that forms a bond to its reaction partner (the nucleophile) by accepting both bonding electrons from that reaction partner. An 'electrophilic substitution reaction' is a heterolytic reaction in which the reagent supplying the entering group acts as an electrophile. For example:

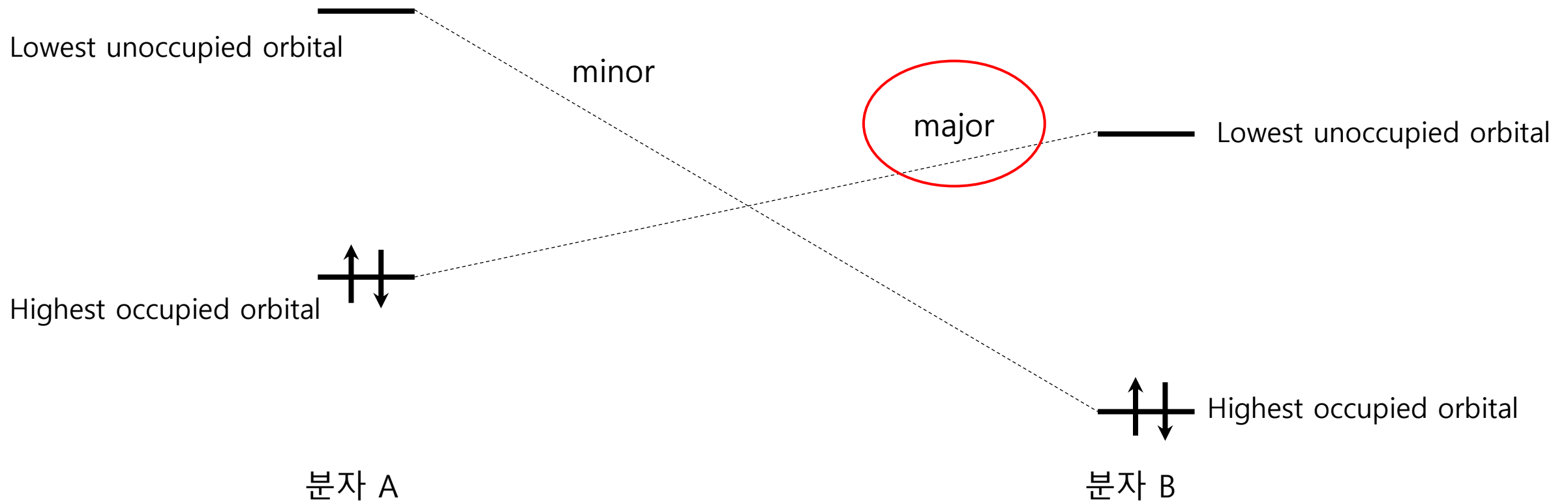


Electrophilic reagents are Lewis acids. 'Electrophilic catalysis' is catalysis by Lewis acids. The term 'electrophilic' is also used to designate the apparent polar character of certain radicals as inferred from their higher relative reactivities with reaction sites of higher electron density.

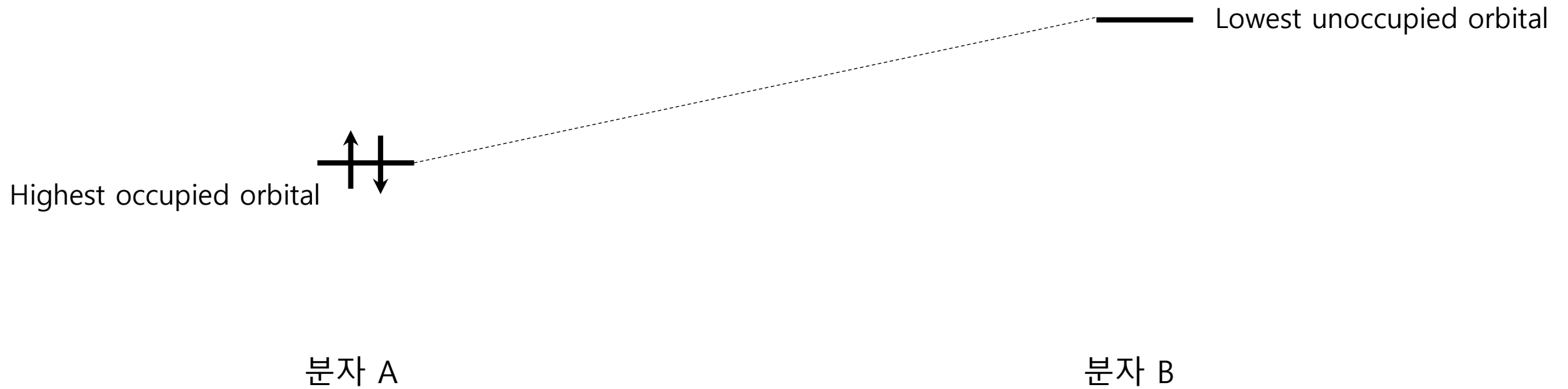
친전자체(electrophile) : 새로운 결합을 형성할 때 전자를 제공하는 것 ; 루이스 염기로 작용

친핵체와 친전자체의 정의

두개의 HOMO-LUMO interaction이 존재!



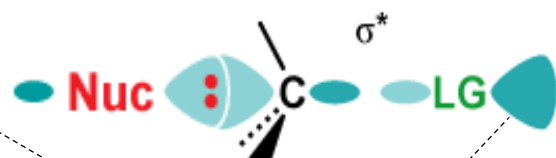
친핵체와 친전자체의 정의



친핵체와 친전자체의 정의

-친핵체
-루이스 염기

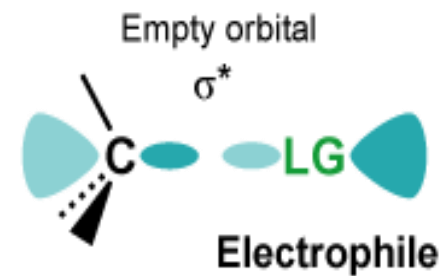
Highest occupied orbital
(HOMO)
↑↓
Filled



새로운 분자

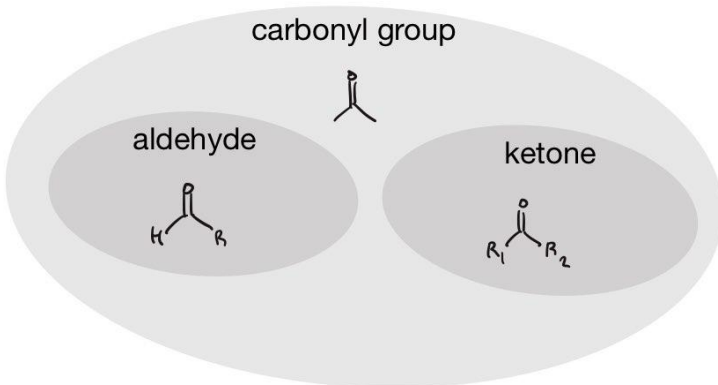
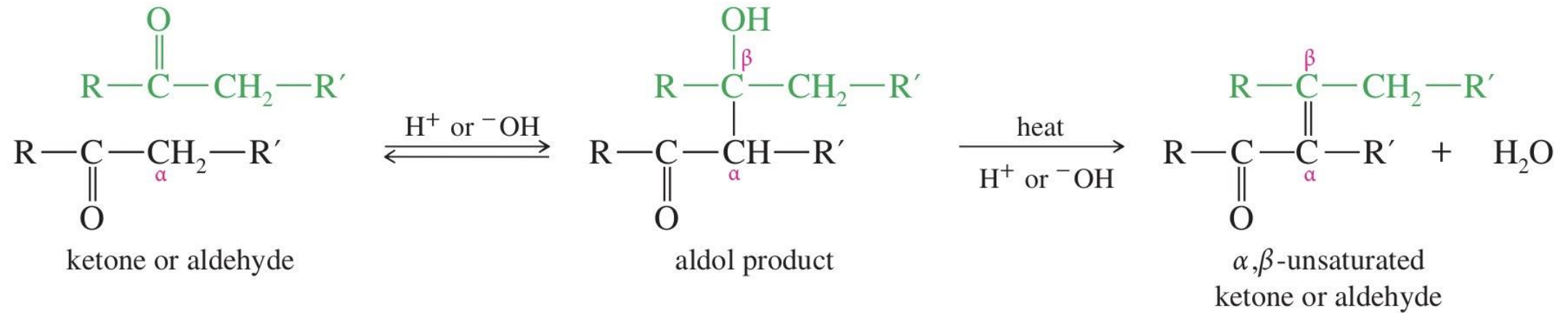
-친전자체
-루이스 산

Lowest unoccupied orbital
(LUMO)



알돌반응의 정의

The aldol condensation



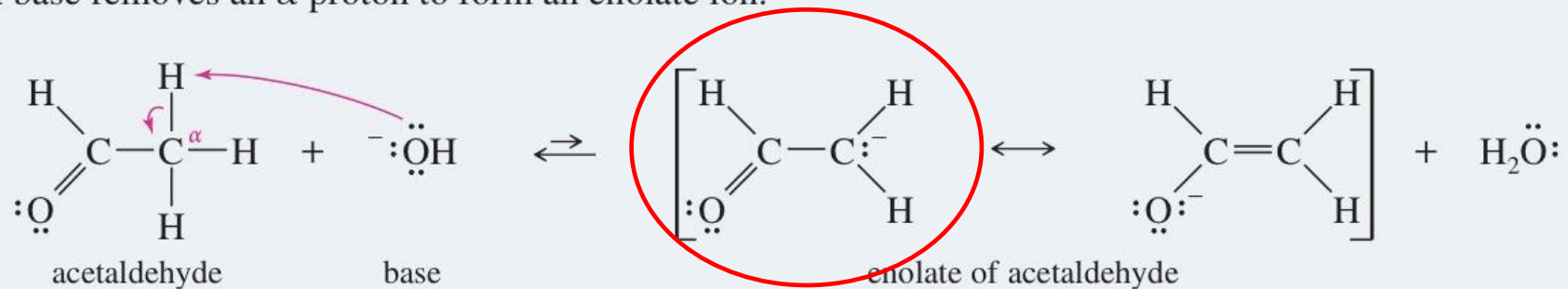
- 산 또는 염기 촉매 하에 aldehyde 또는 ketone의 alpha-탄소에서 일어나는 enolate에서 carbonyl group으로의 친핵성 첨가반응
- 반응중간체로 beta-hydroxy carbonyl이 생성
- 생성물로 대부분 alpha,beta-unsaturated carbonyl이 생성

간단한 분자의 알돌반응 메커니즘

Base catalyzed aldol condensation of acetaldehyde

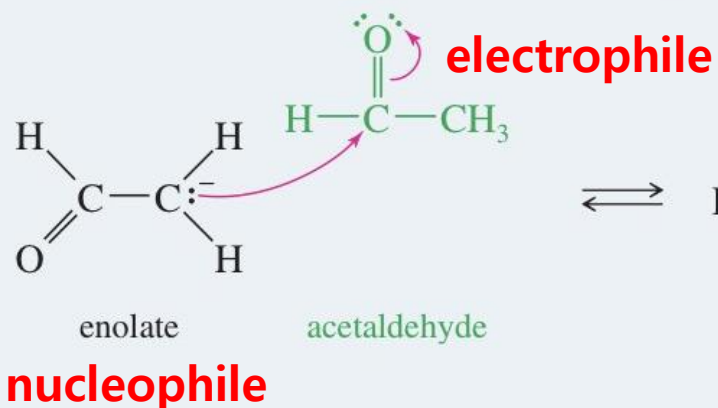
The enolate ion of acetaldehyde attacks the carbonyl group of another acetaldehyde molecule. Protonation gives the aldol product.

Step 1: A base removes an α proton to form an enolate ion.

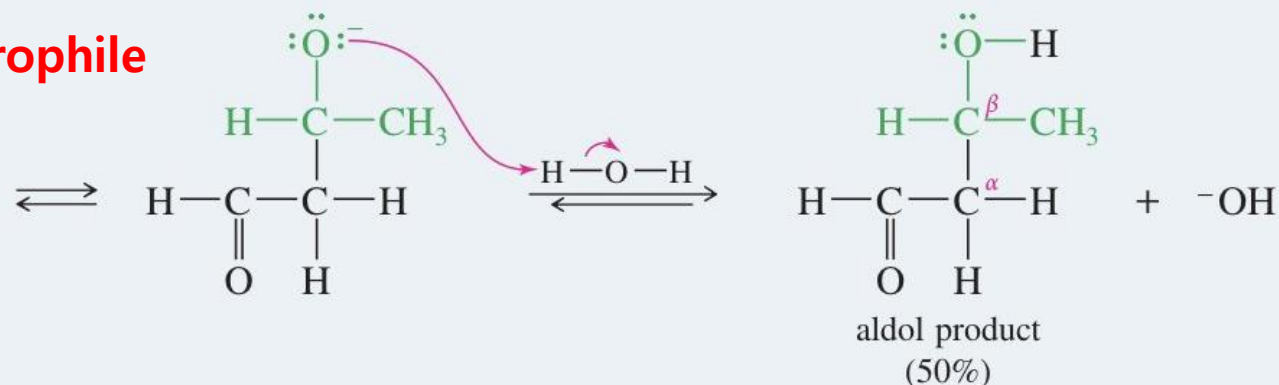


간단한 분자의 알돌반응 메커니즘

Step 2: The enolate ion adds to the carbonyl group.



Step 3: Protonation of the alkoxide gives the aldol product.



Review

친핵체(nucleophile) : 새로운 결합을 형성할 때 전자를 제공하는 것 ; 루이스 염기로 작용

친전자체(electrophile) : 새로운 결합을 형성할 때 전자를 제공하는 것 ; 루이스 염기로 작용

알돌반응 : 염기 촉매 하에 aldehyde 또는 ketone의 alpha-탄소에서 일어나는 enolate에서 carbonyl group으로의 친핵성 첨가반응

간단한 분자의 알돌반응 메커니즘

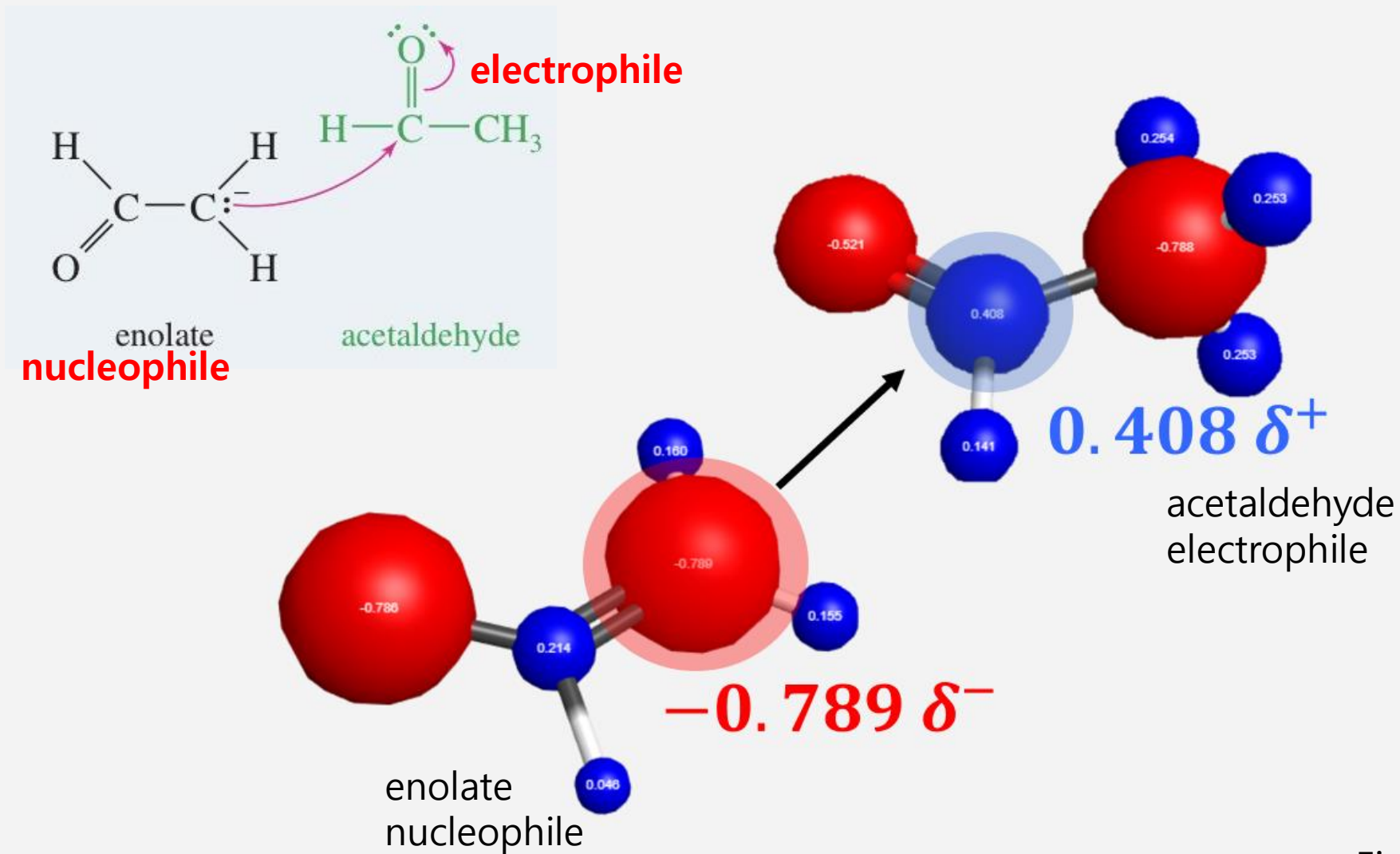
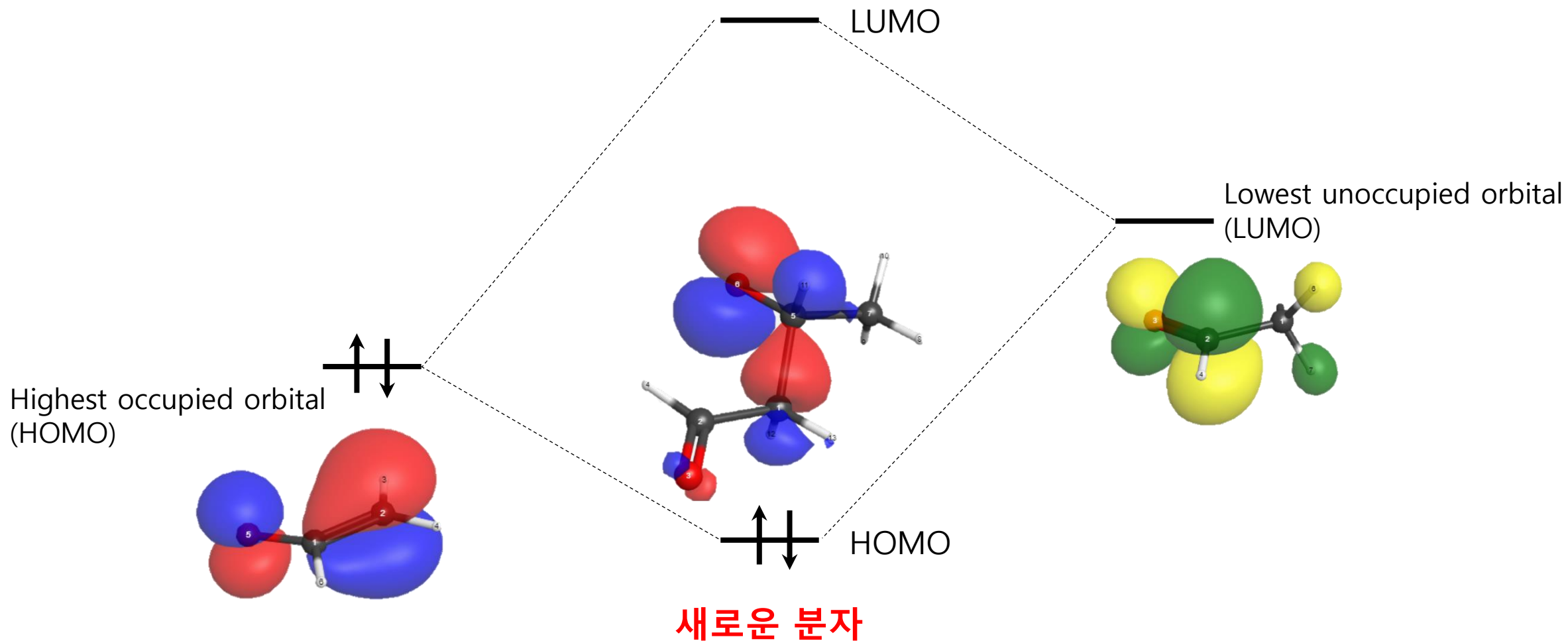


Fig. NAO의 charge map

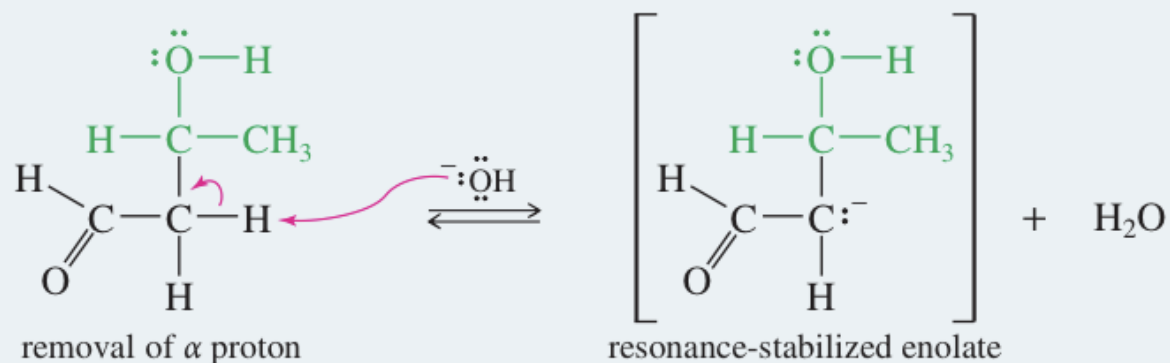
간단한 분자의 알돌반응 메커니즘



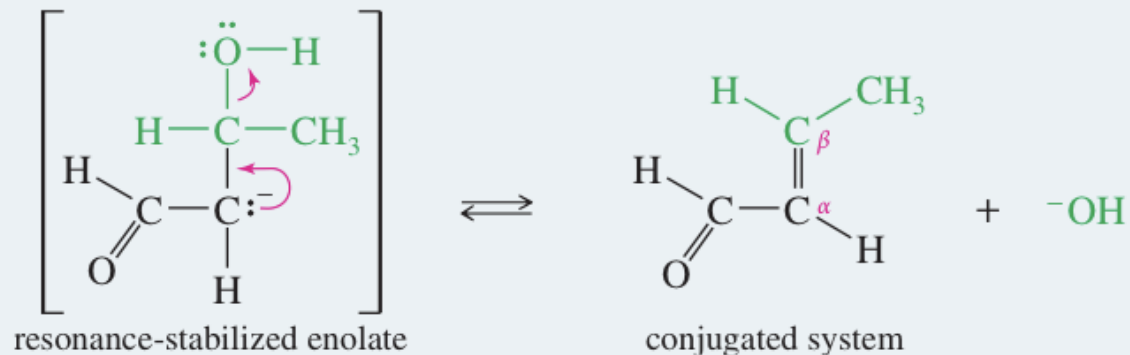
간단한 분자의 알돌반응 메커니즘

Unlike most alcohols, aldols undergo dehydration in base. Abstraction of an α proton gives an enolate that can expel hydroxide ion to give a conjugated product.

Step 1: Formation of the enolate ion.

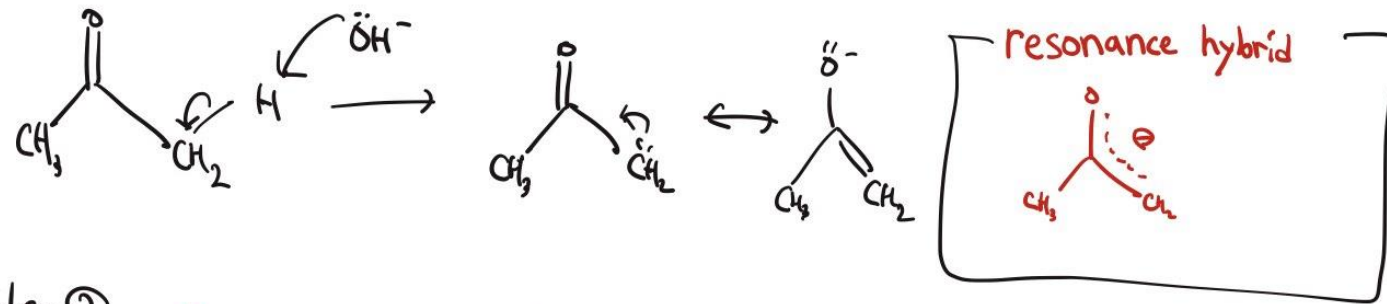


Step 2: Elimination of hydroxide.



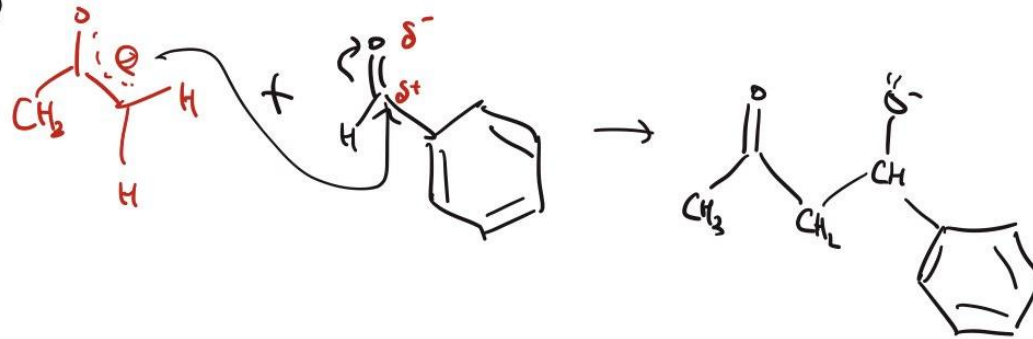
실험에서의 알돌반응

Step ①



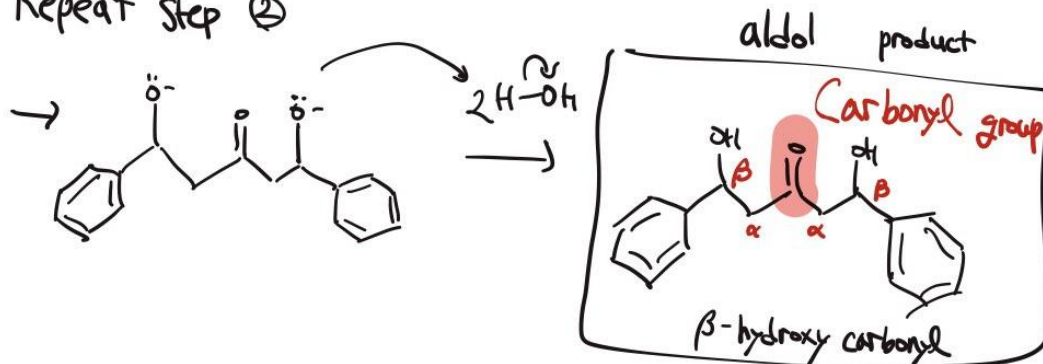
Enolate 생성

Step ②



Enolate와 benzaldehyde와 aldol 반응
→ aldolate의 생성

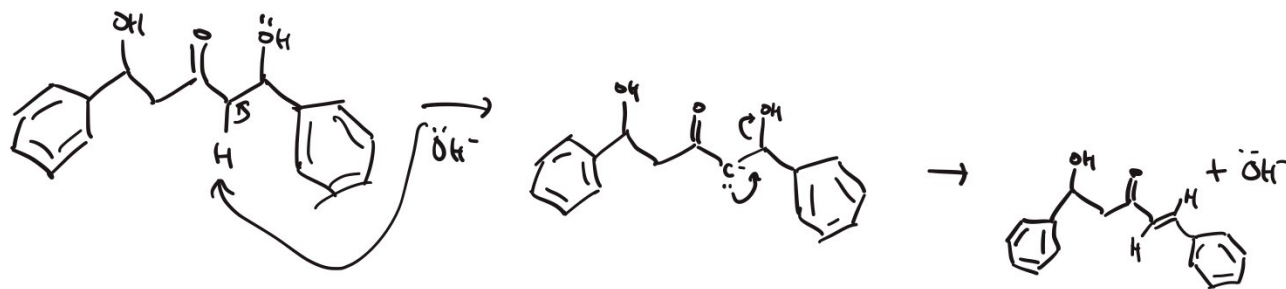
Step ③ : Repeat step ②



Aldol product 생성

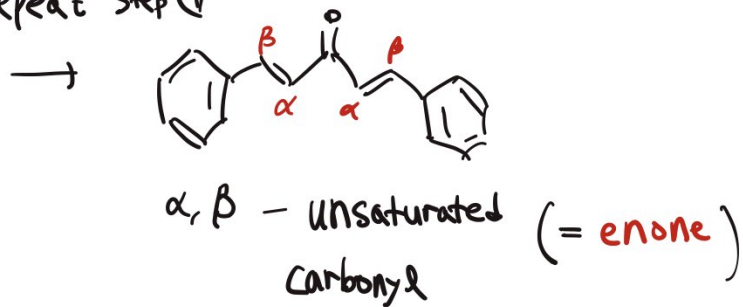
실험에서의 알돌의 탈수반응

Step ④



Aldol의 탈수반응

Step ⑤ : repeat step ④



enone의 생성

참고 문헌

[1] IUPAC. Compendium of Chemical Terminology, 2nd ed., Oxford (1997)

[2] L.G. Wade, Organic chemistry, 8e, Person, 2013, 1061-1064