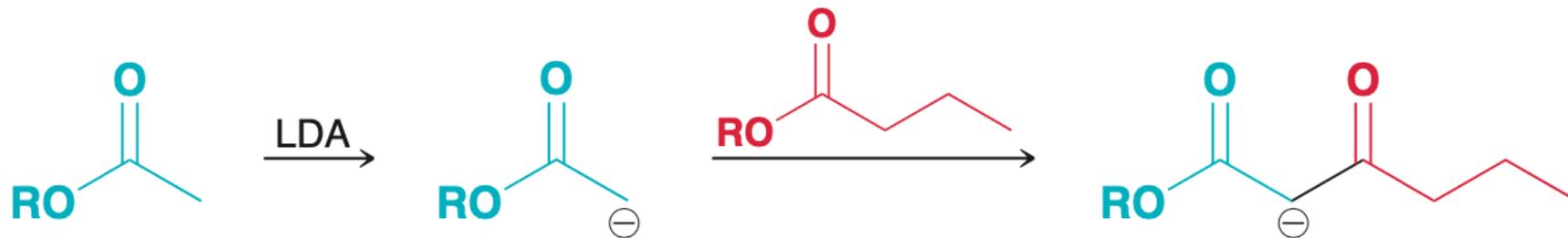
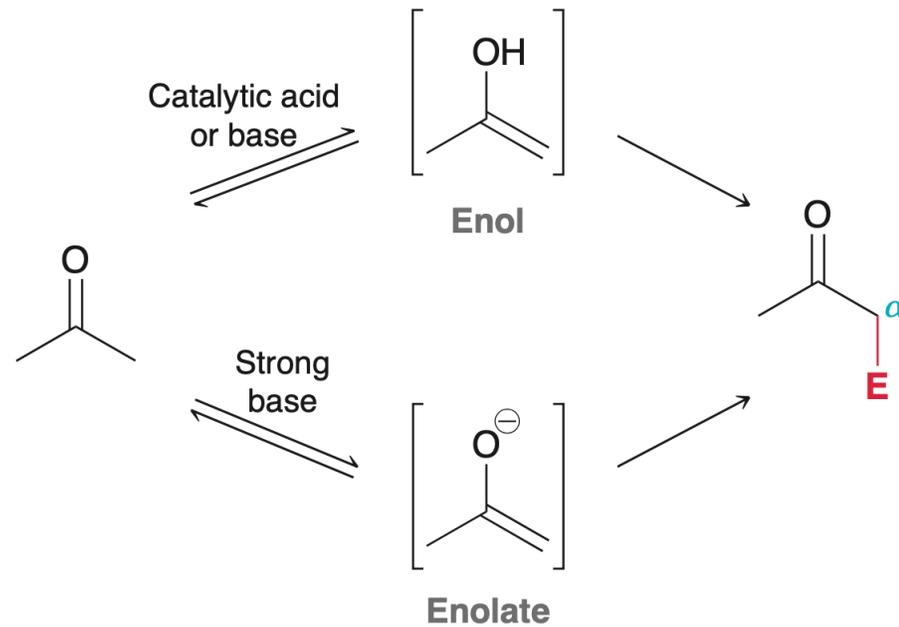
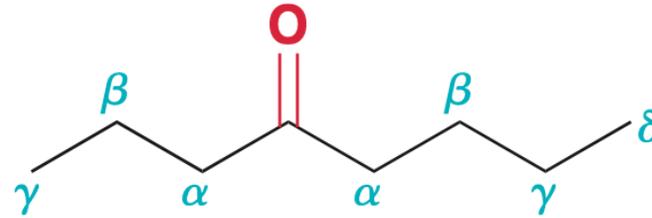


Reações de Enols e Enolatos

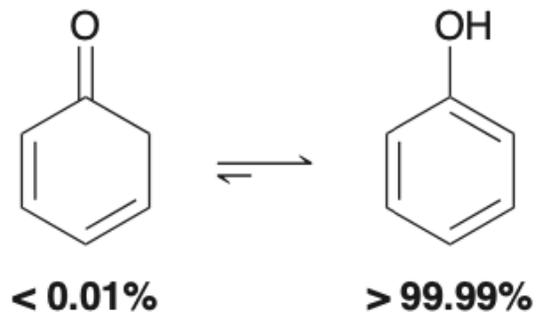
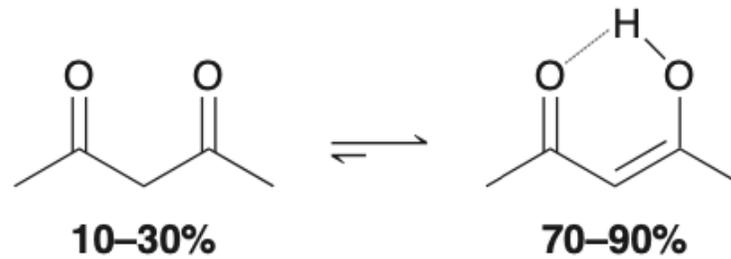
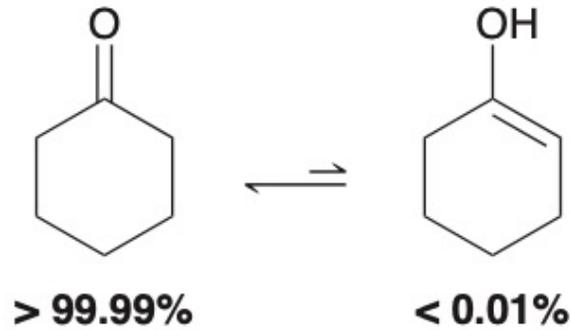
Reação de Mannich, Condensação de Claisen e Síntese dos Ésteres Malônico e Acetoacético



Relembrando...



Relembrando...

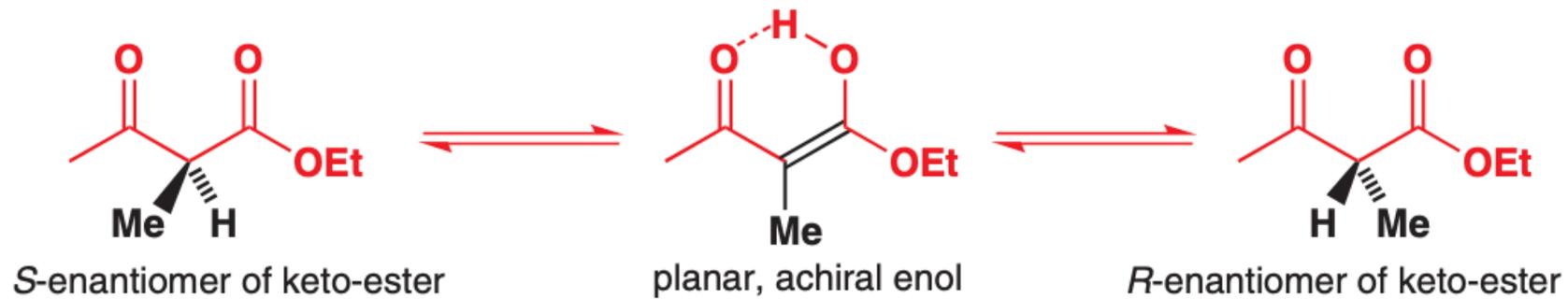
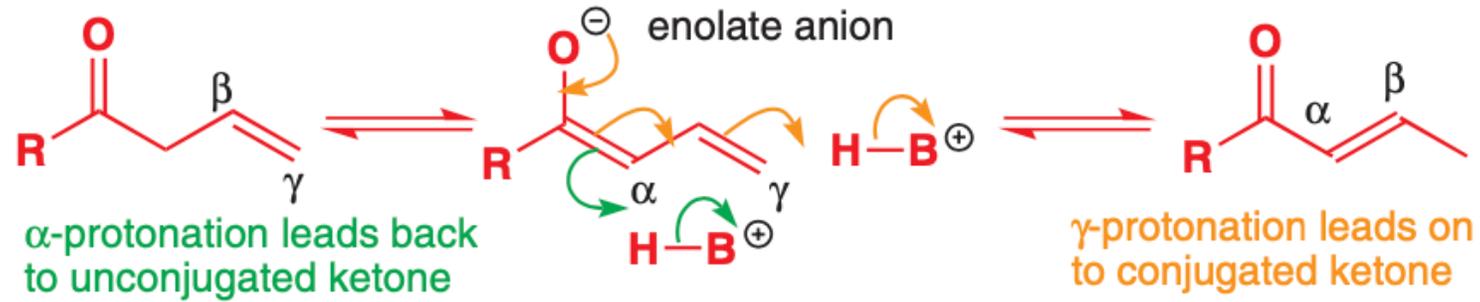


Typical bond strengths (kJ mol⁻¹) in keto and enol forms

	Bond to H	π bond	Sum
keto form	440 (C–H)	720 (C=O)	1160
enol form	500 (O–H)	620 (C=C)	1120

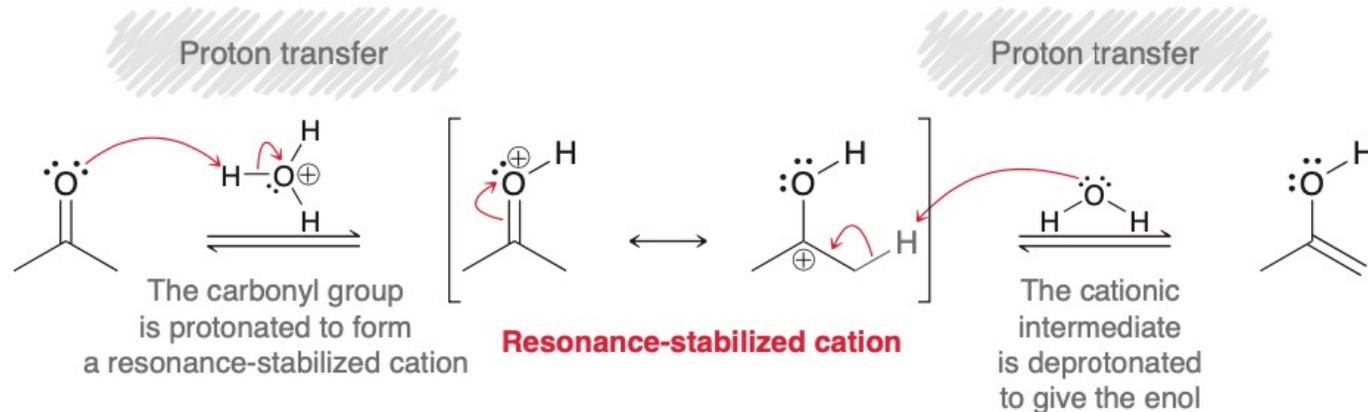
Relembrando...

Consequências:

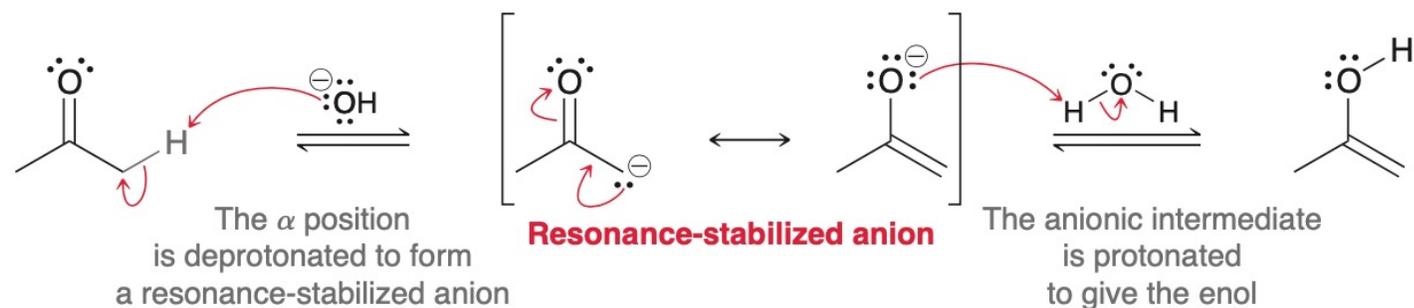


Relembando...

MECHANISM 22.1 ACID-CATALYZED TAUTOMERIZATION

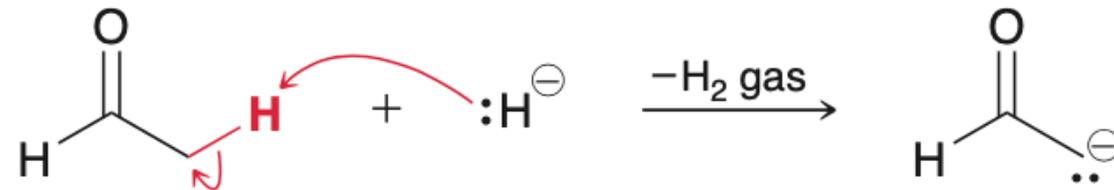
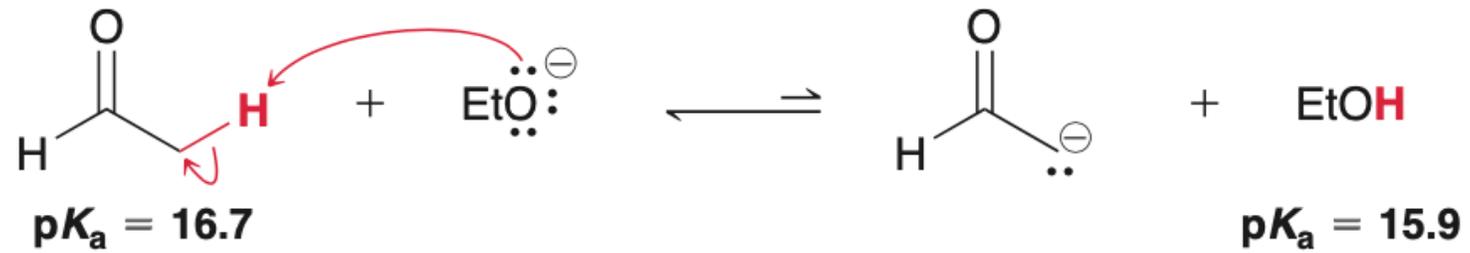


MECHANISM 22.2 BASE-CATALYZED TAUTOMERIZATION



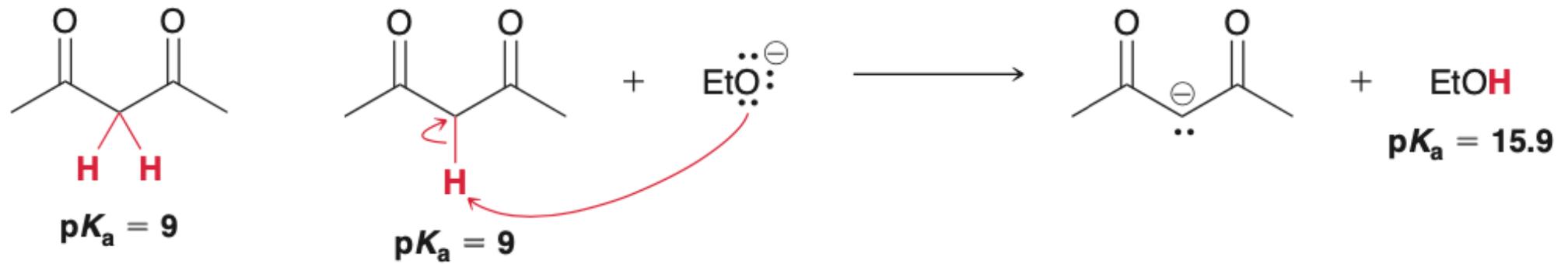
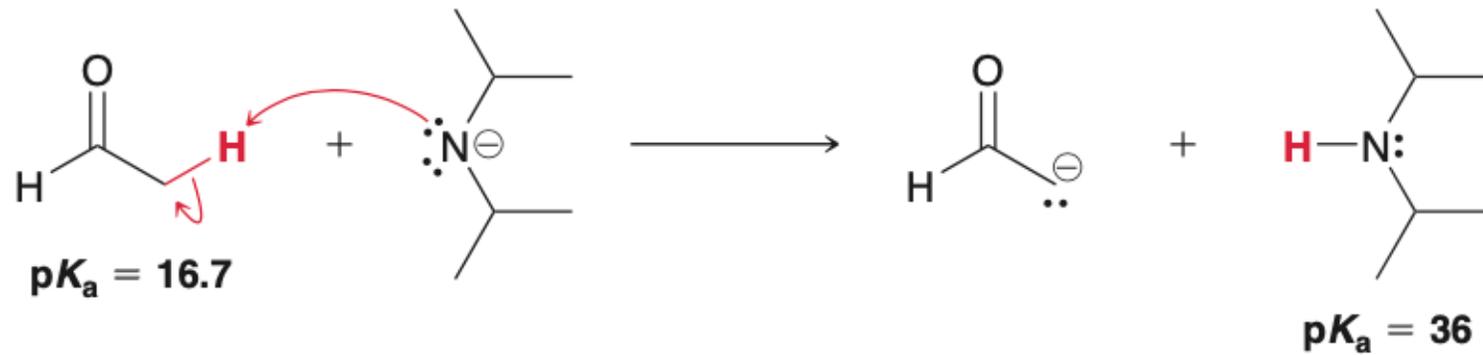
Relembrando...

A escolha da base:



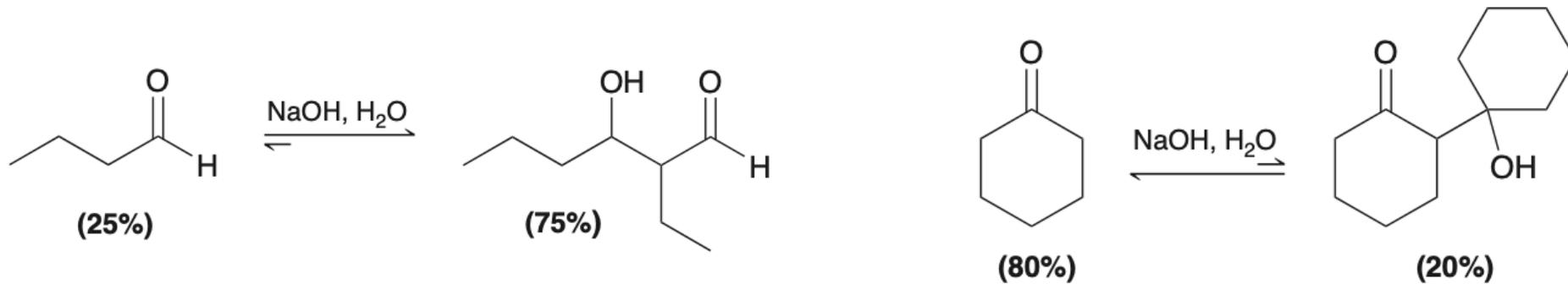
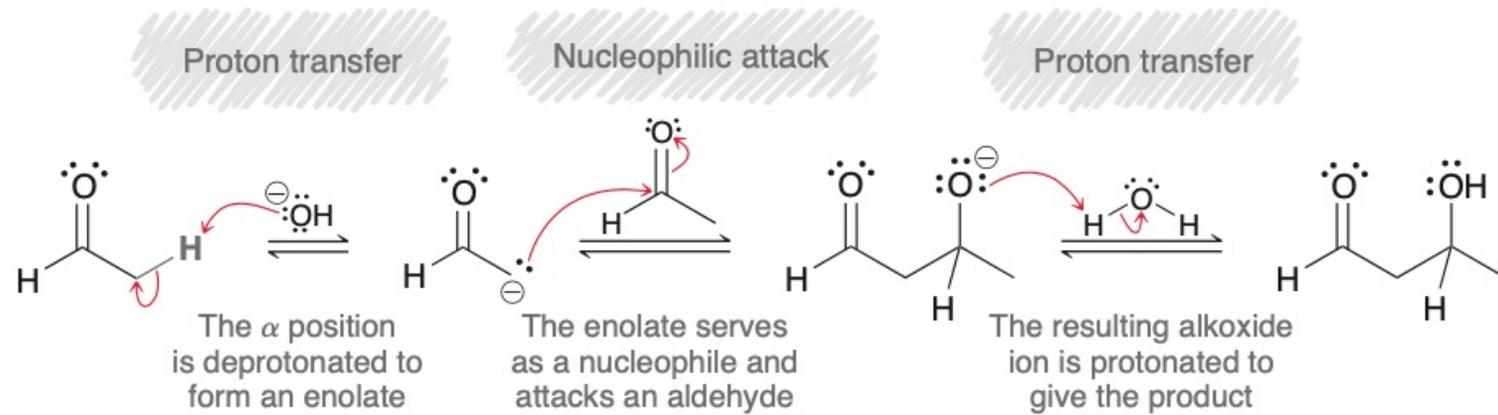
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A escolha da base:



Relembando...

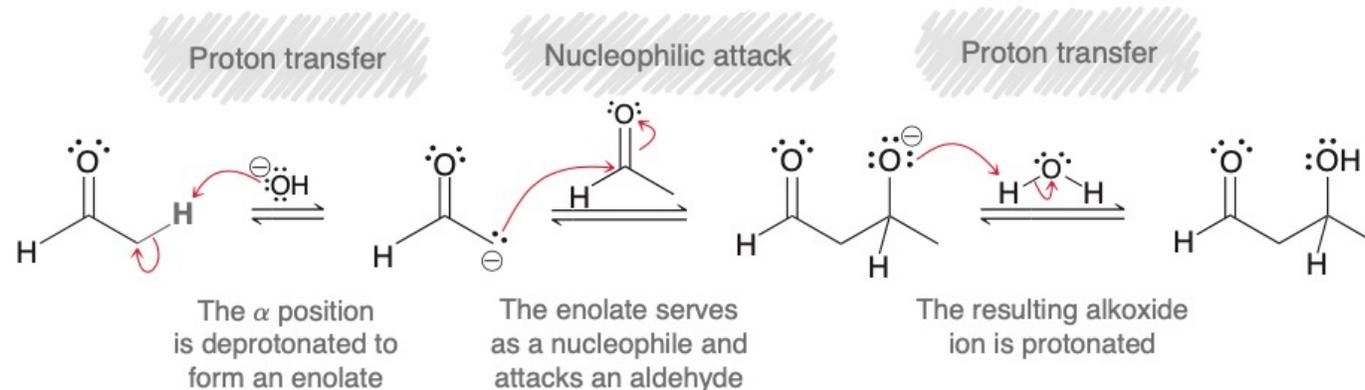
MECHANISM 22.4 ALDOL ADDITION



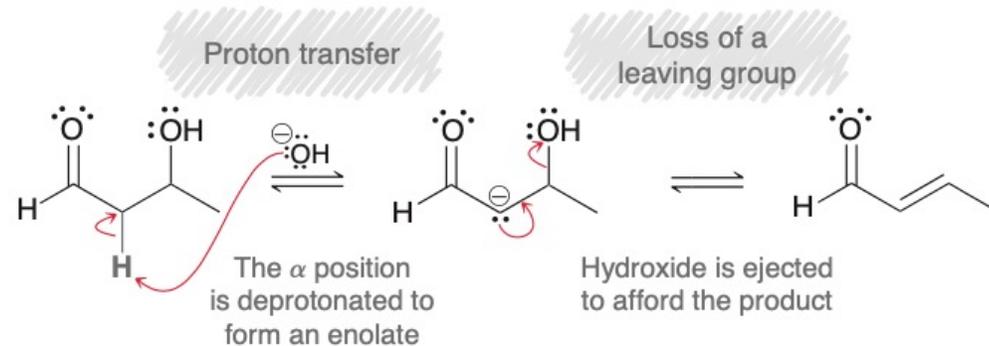
RelembRANDo...

MECHANISM 22.6 ALDOL CONDENSATION

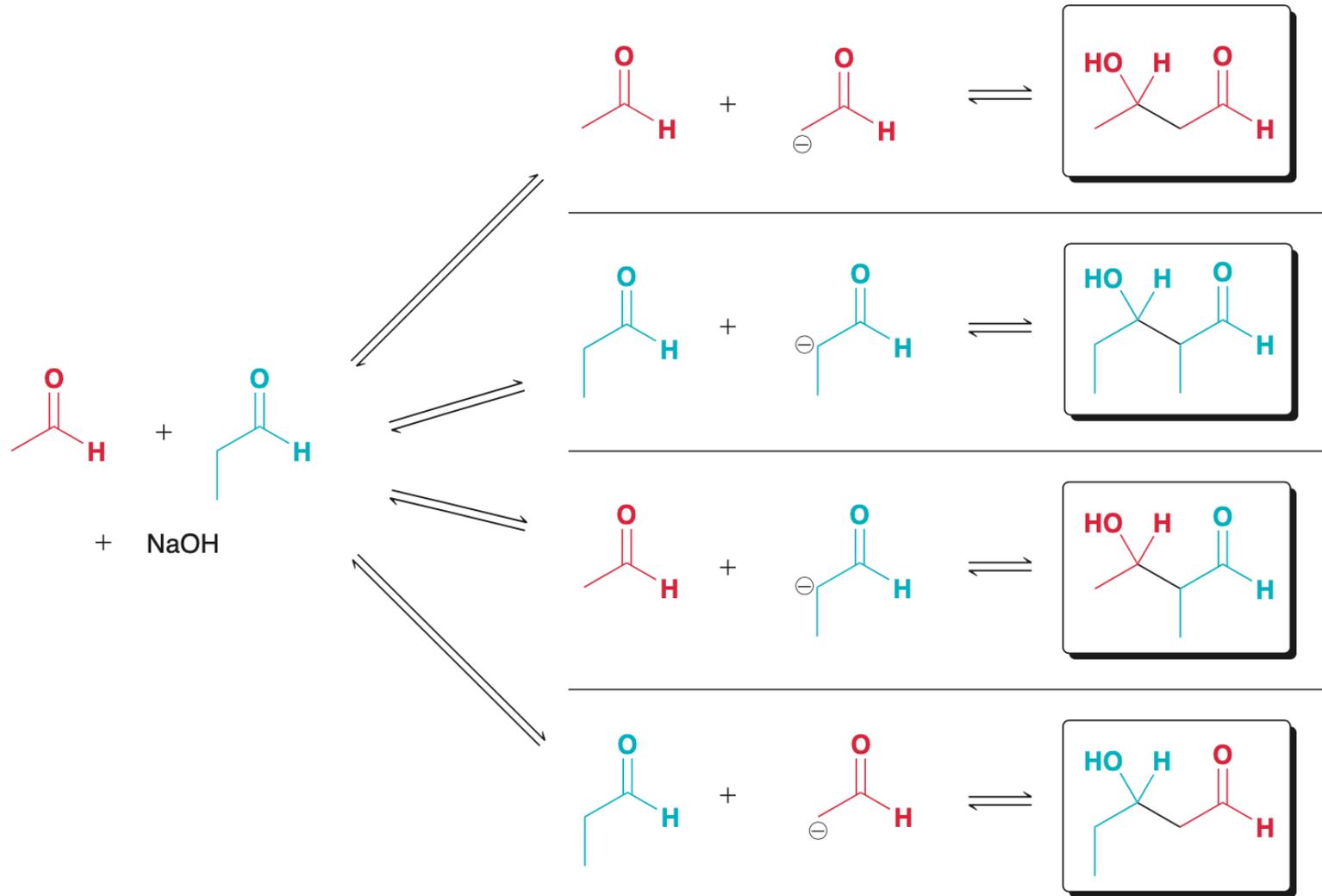
PART 1: ALDOL ADDITION



PART 2: ELIMINATION OF H₂O

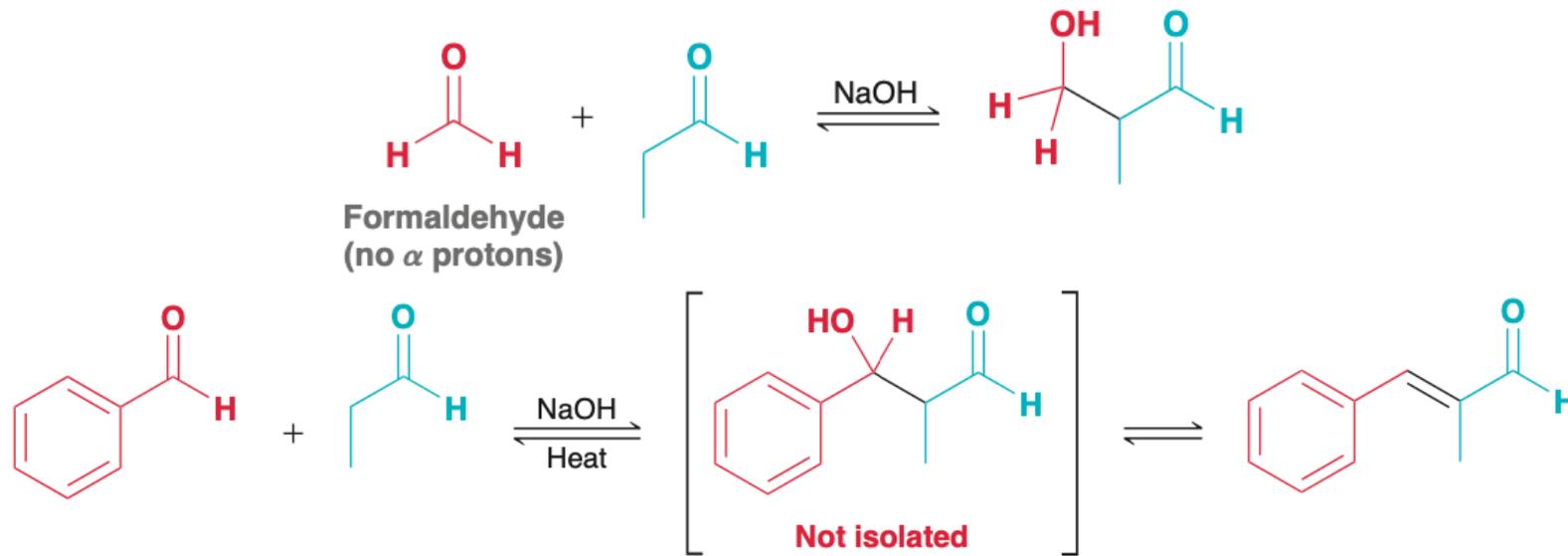


Relembrando...

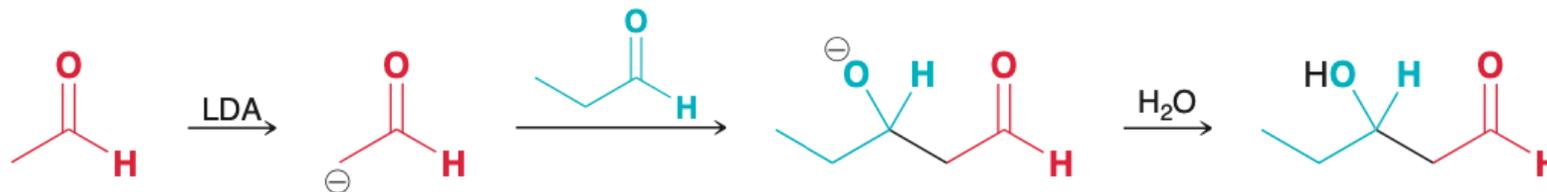


Relembando...

1.



2.



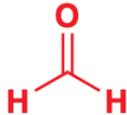
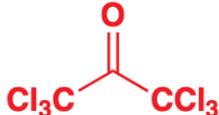
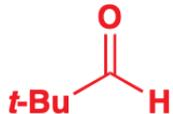
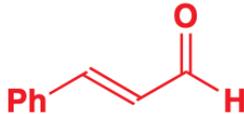
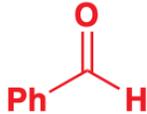
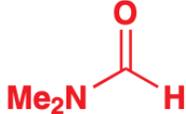
● Successful crossed aldol reactions

For this kind of crossed aldol reaction to work well we must have two conditions:

- One partner only must be capable of enolization.
- The other partner must be incapable of enolization and be *more electrophilic than the enolizable partner*.

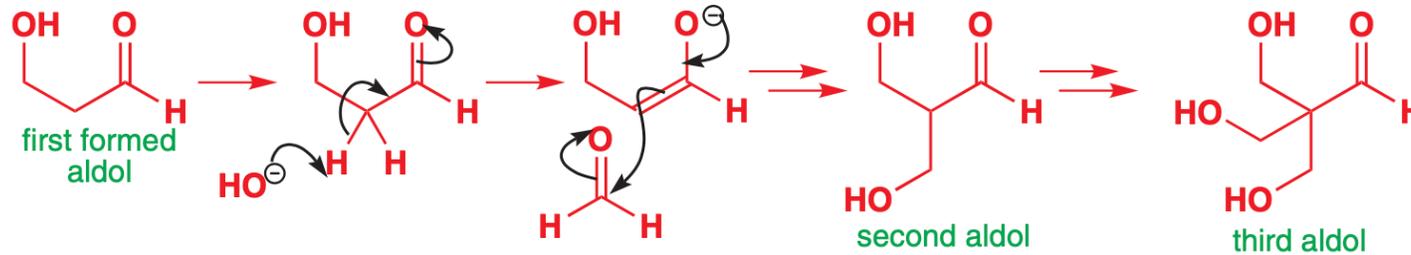
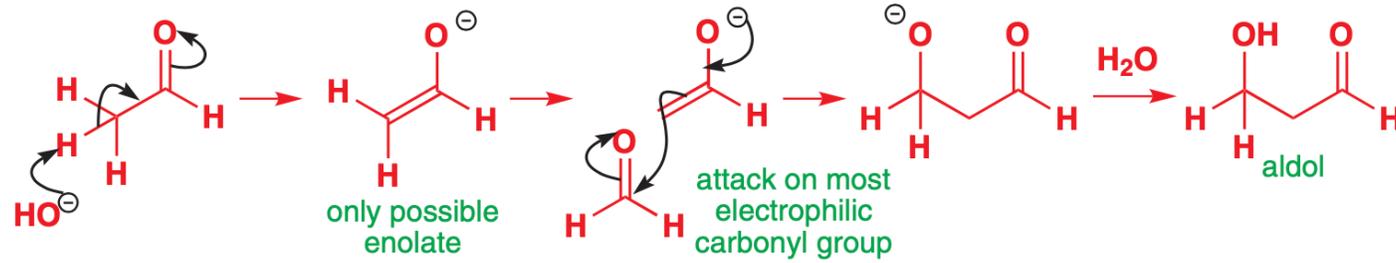
RelembRANDo...

Carbonyl substituents that block enolization

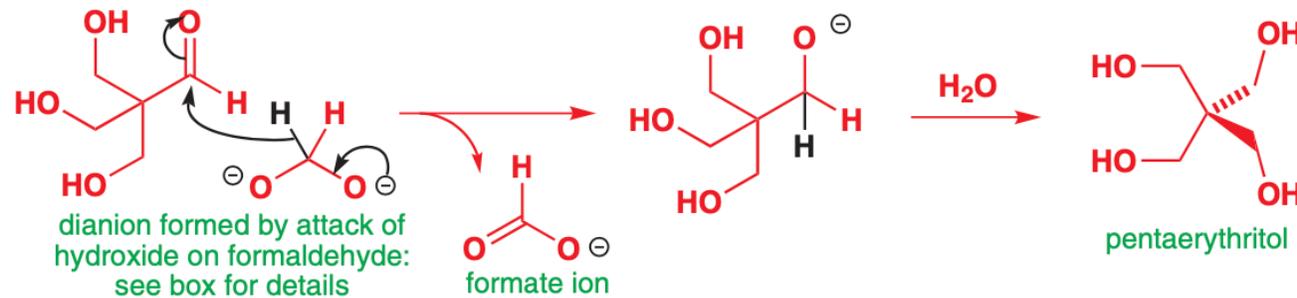
	Substituent	Typical compounds	Comments
most electrophilic	H		needs special methods: see Mannich reaction
	CF ₃ , CCl ₃		made by halogenation of enols (Chapter 20)
	<i>t</i> -alkyl		many other <i>t</i> -alkyl groups
	alkenyl		nucleophile may attack alkene: see Chapter 25
	aryl		many other aromatic rings, e.g. heterocycles
	OR		formate esters and carbonates
least electrophilic	NR ₂		this is DMF: other amides unreactive

Formaldeído – o problema

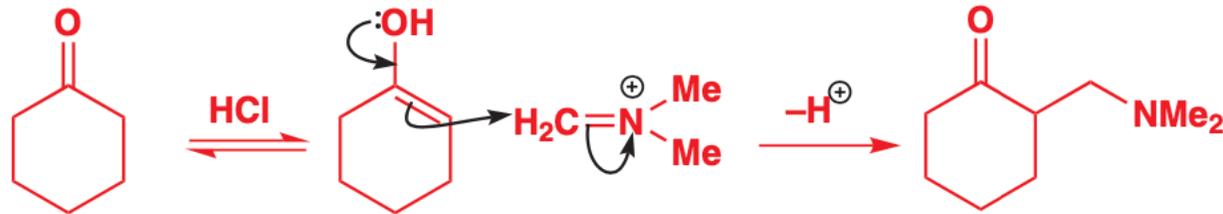
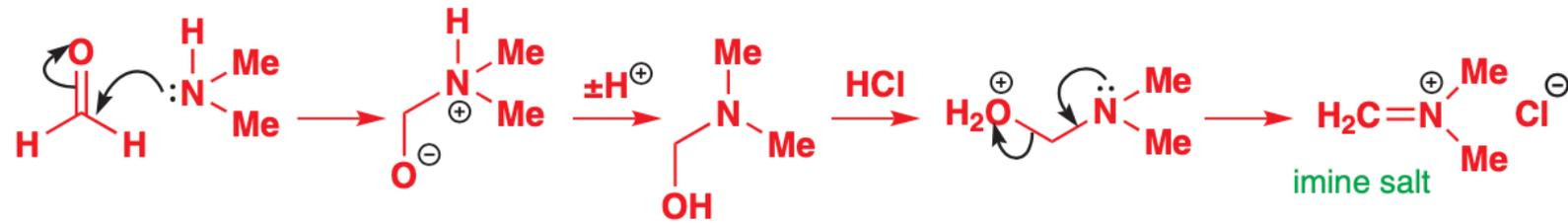
crossed aldol reaction between acetaldehyde and formaldehyde



reduction by the Cannizzaro reaction

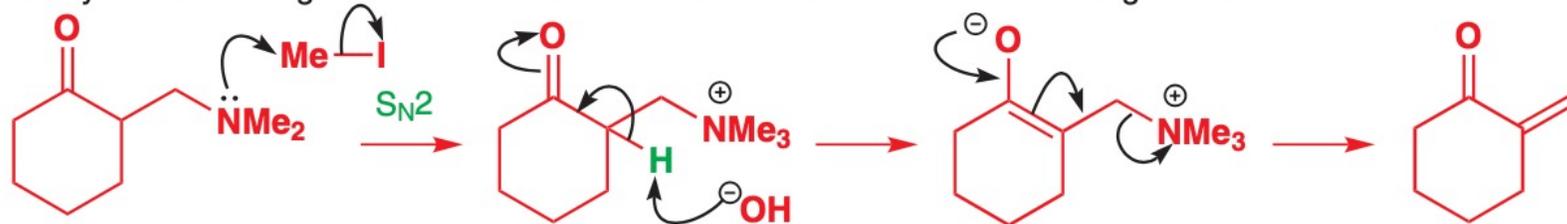


Reação de Mannich

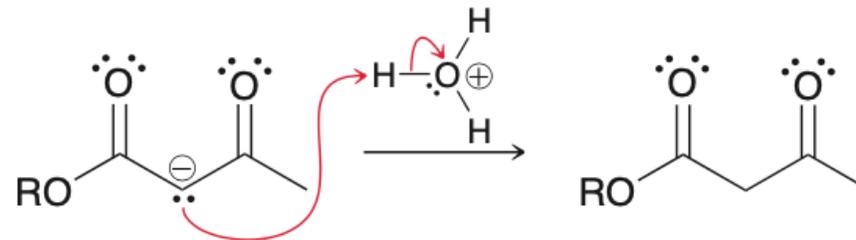
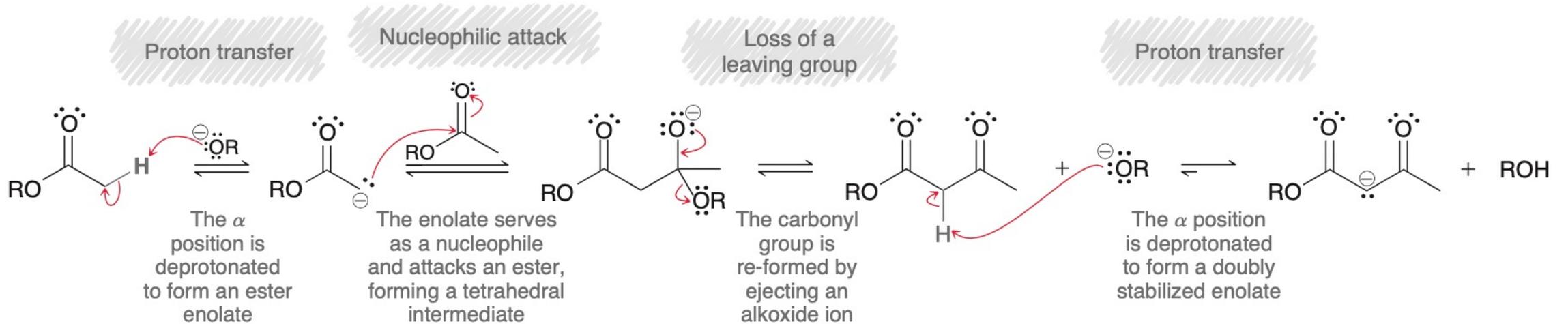
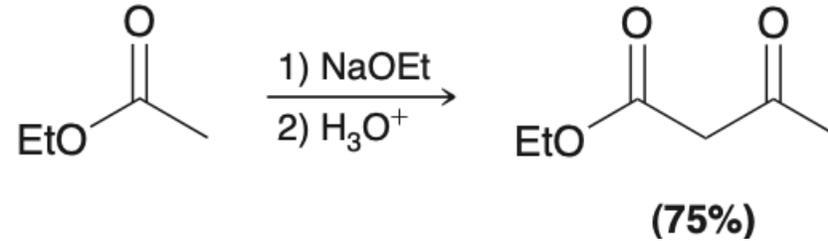


1. alkylate amine to give ammonium salt

2. treat with base: elimination gives enone

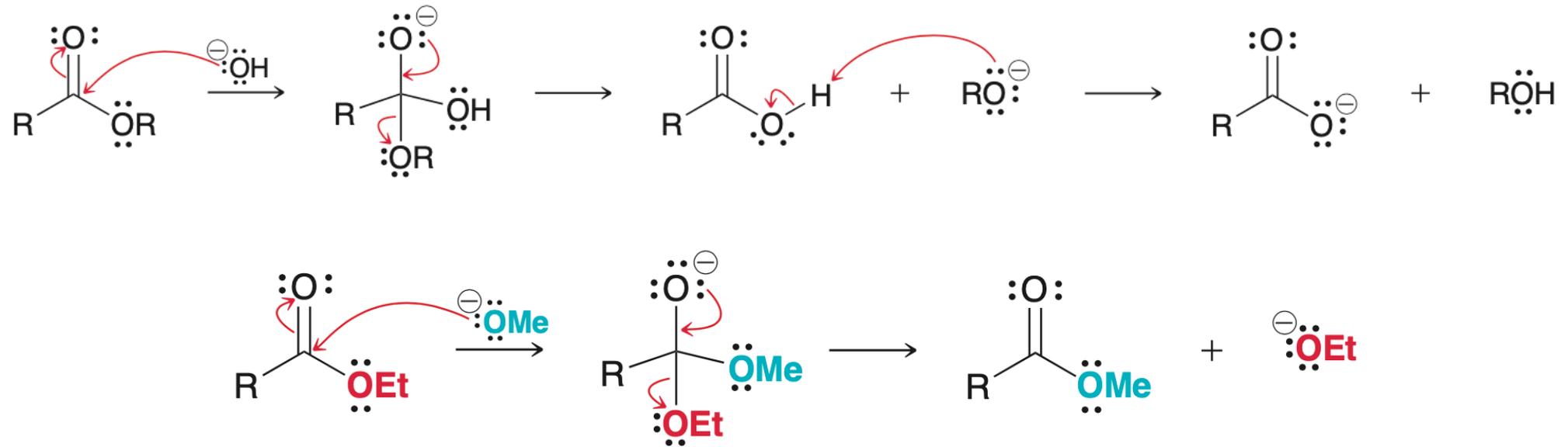


Condensação de Claisen



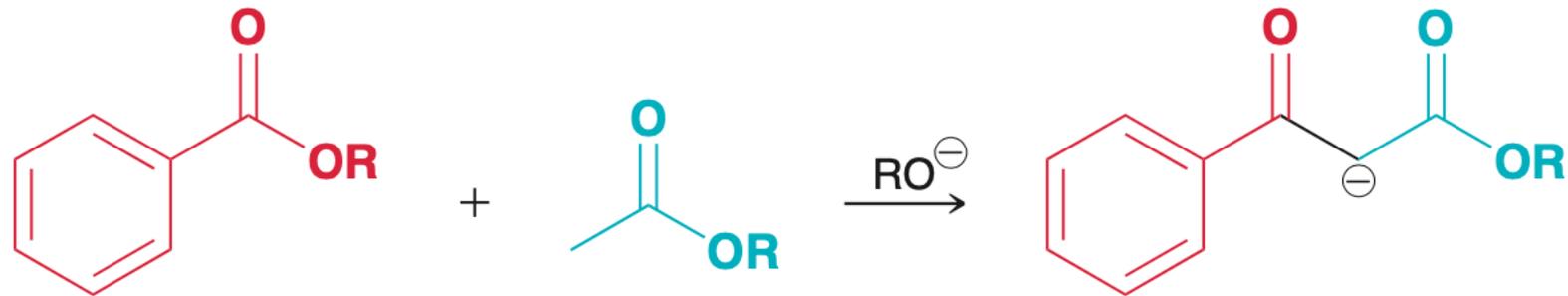
Condensação de Claisen

A escolha da base:

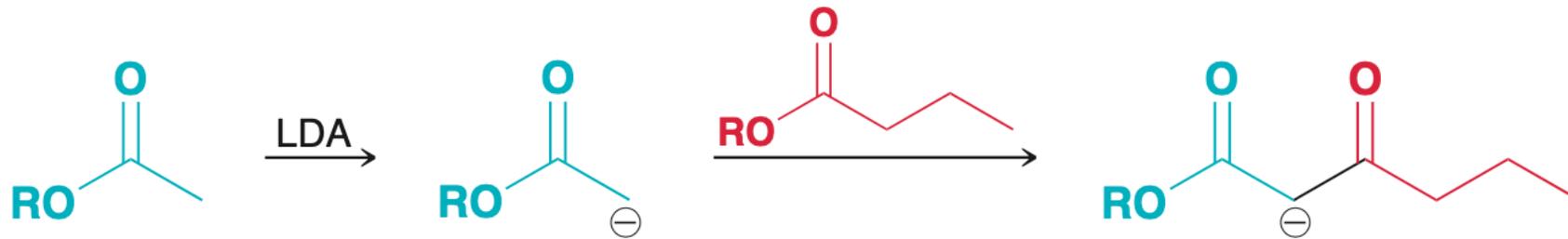


Condensação de Claisen Cruzada

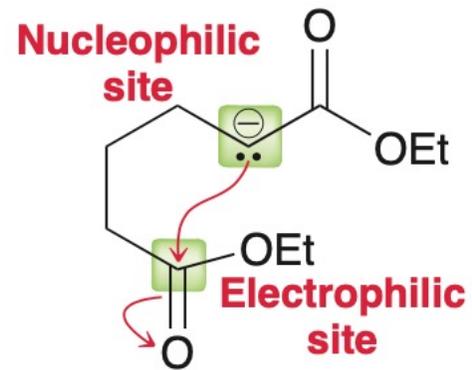
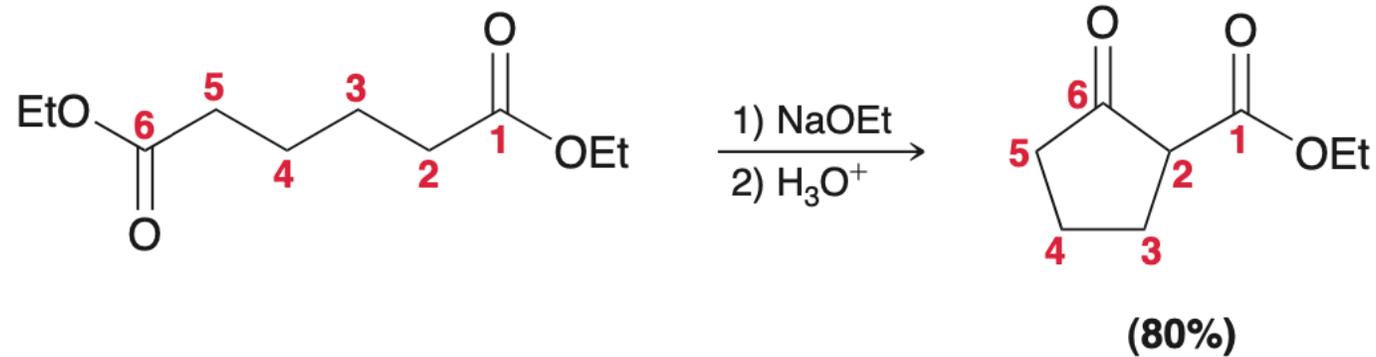
1.



2.

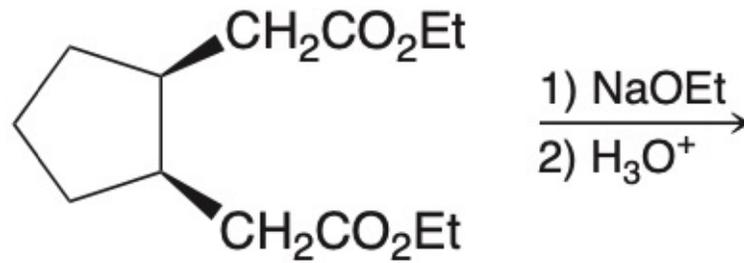


Condensação de Claisen Intramolecular: Ciclização de Dieckmann

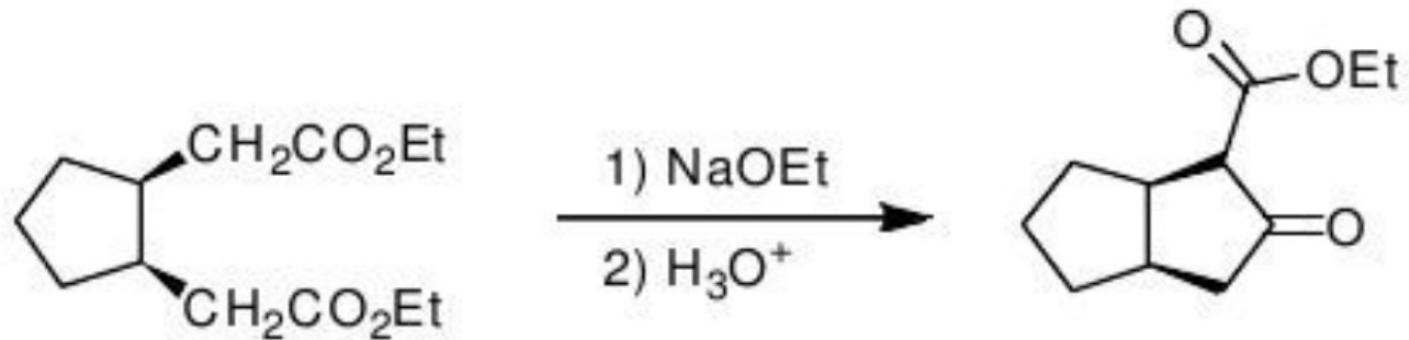


Desafio!

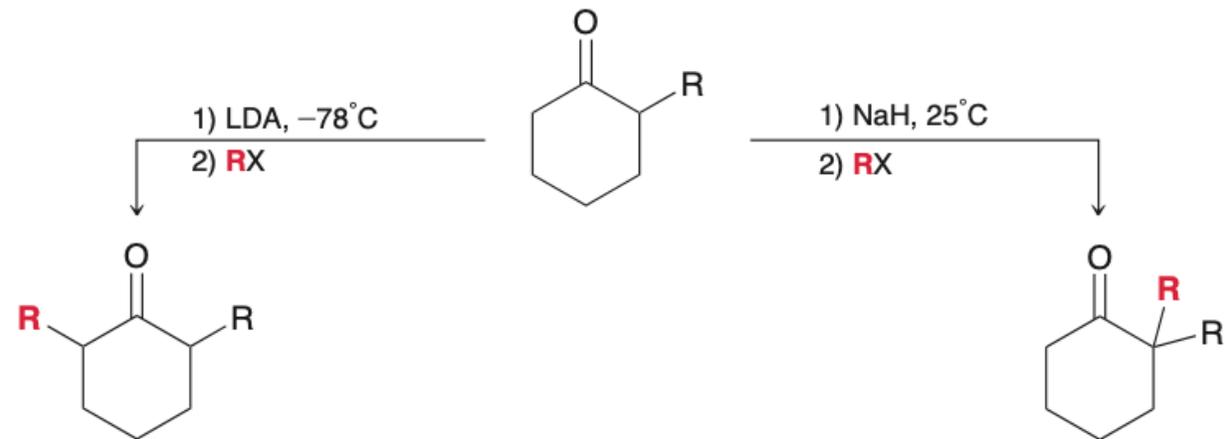
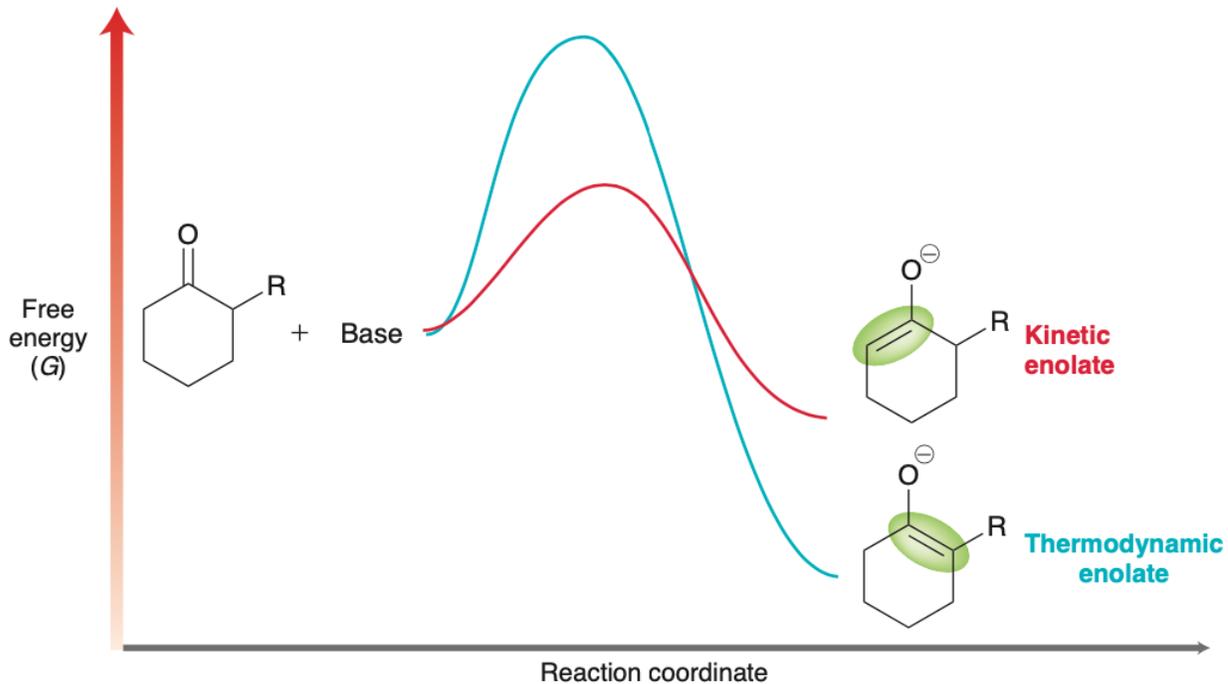
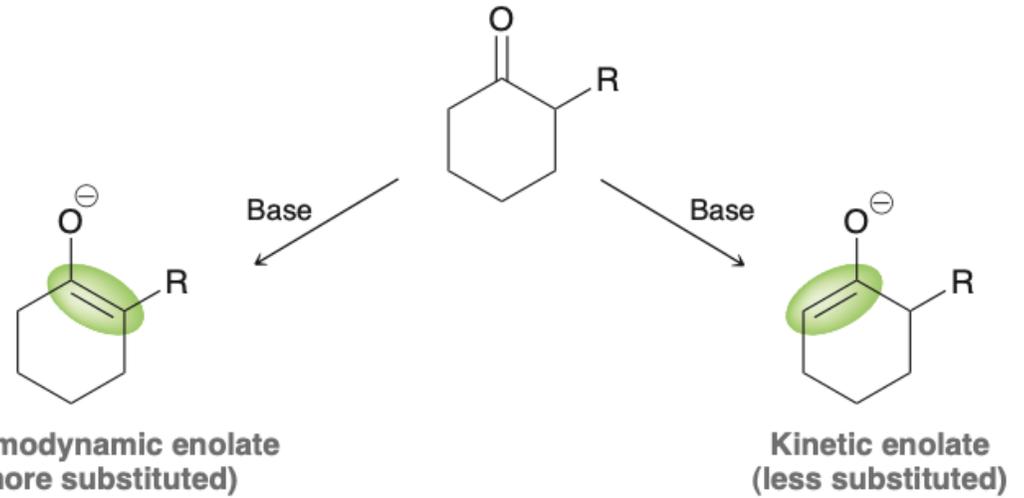
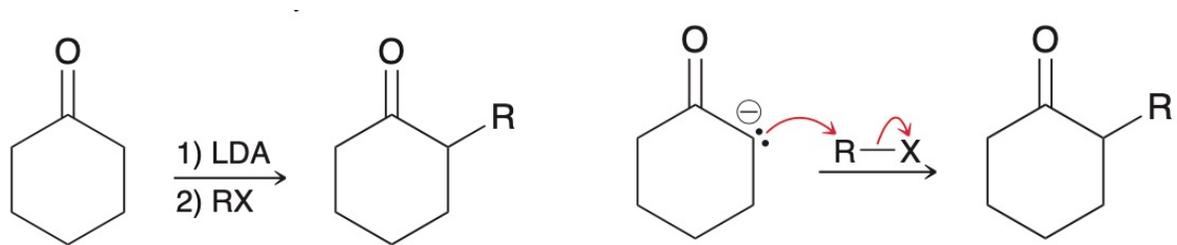
Preveja o produto formado:



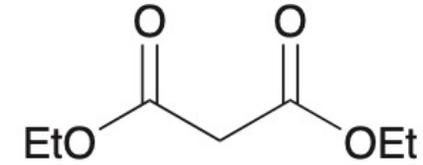
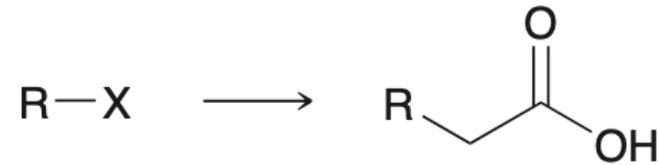
Resposta:



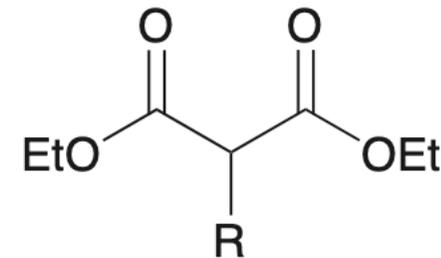
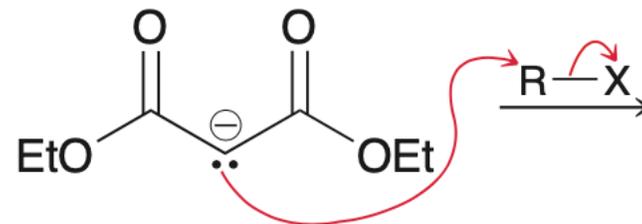
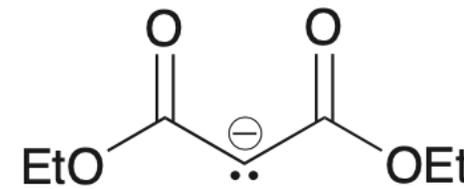
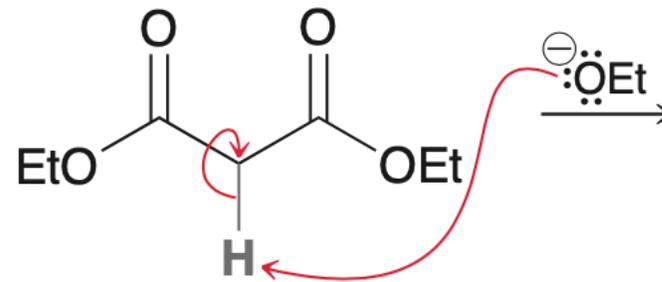
RelembRANDo...



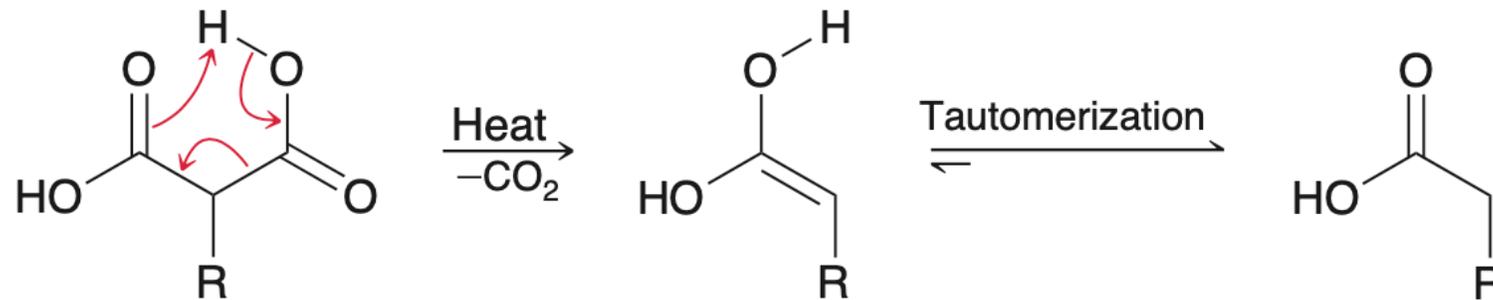
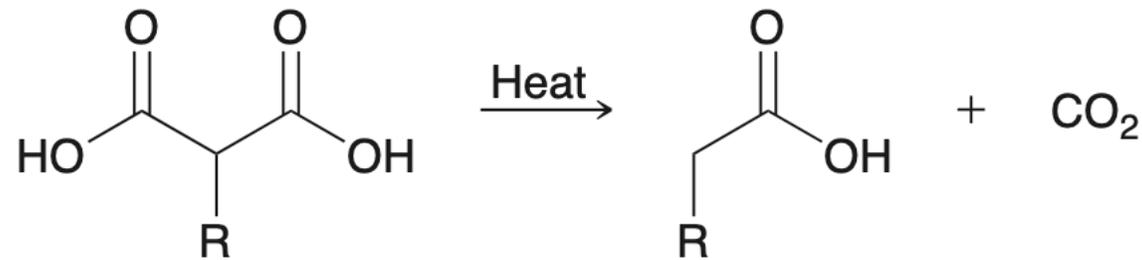
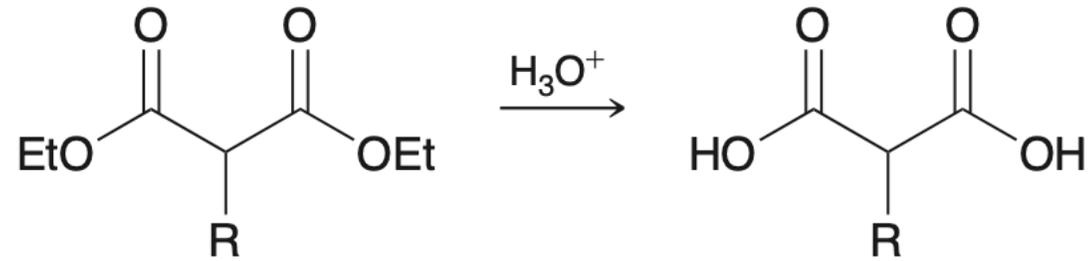
Síntese do Éster Malônico



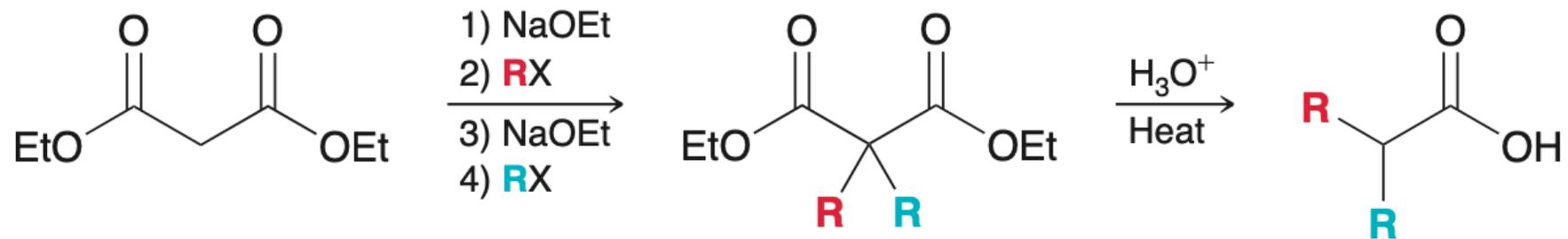
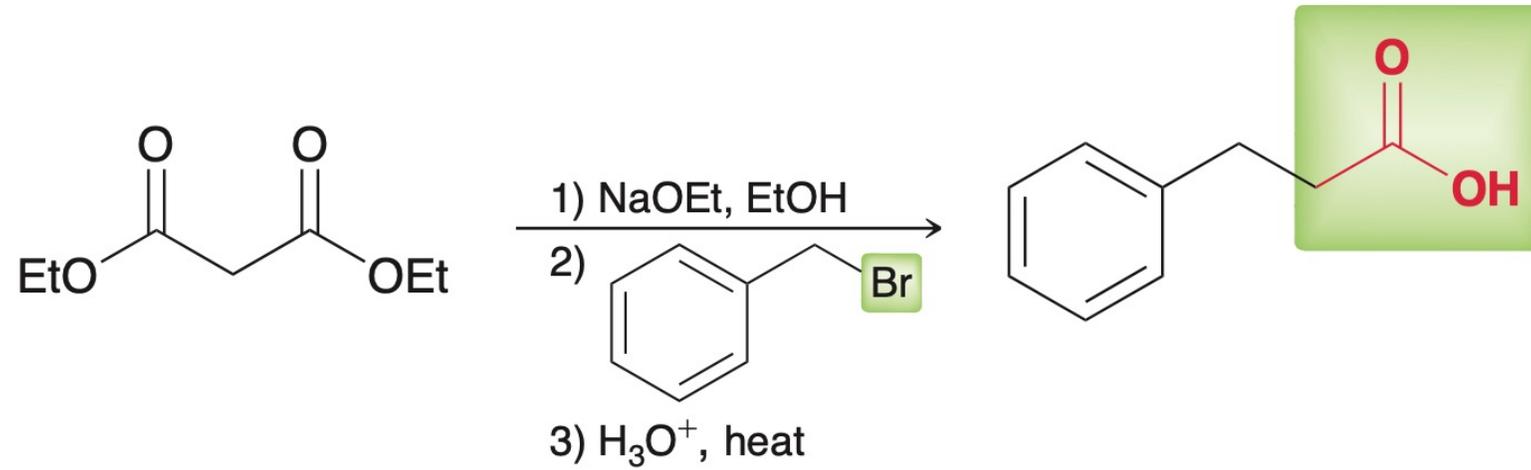
Diethyl malonate



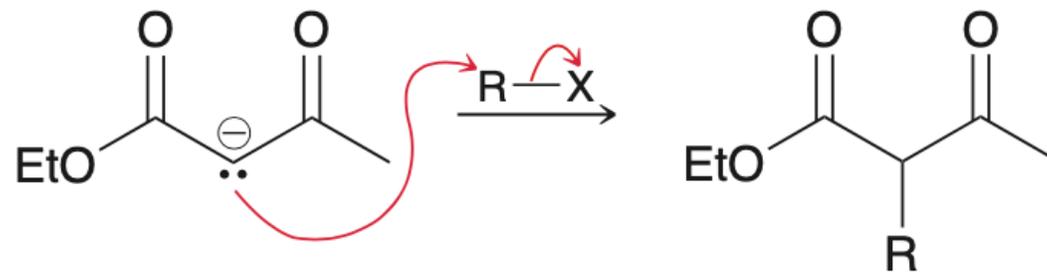
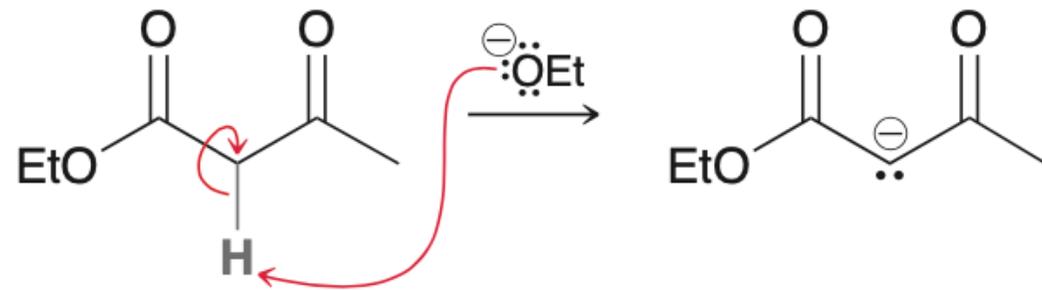
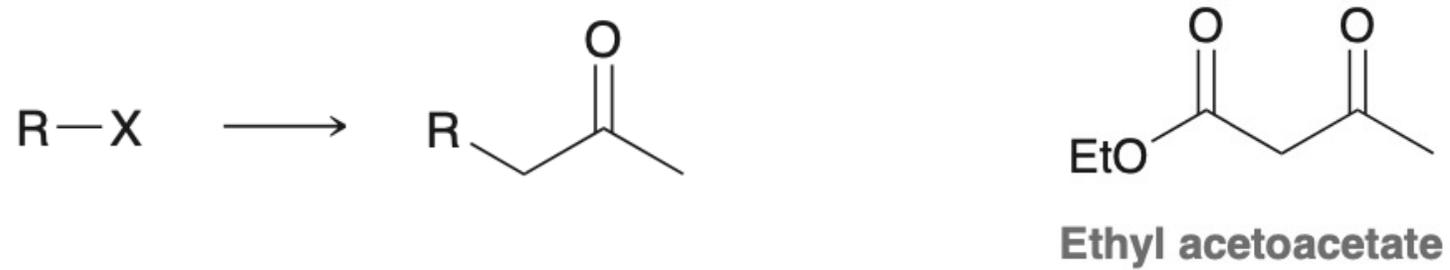
Síntese do Éster Malônico



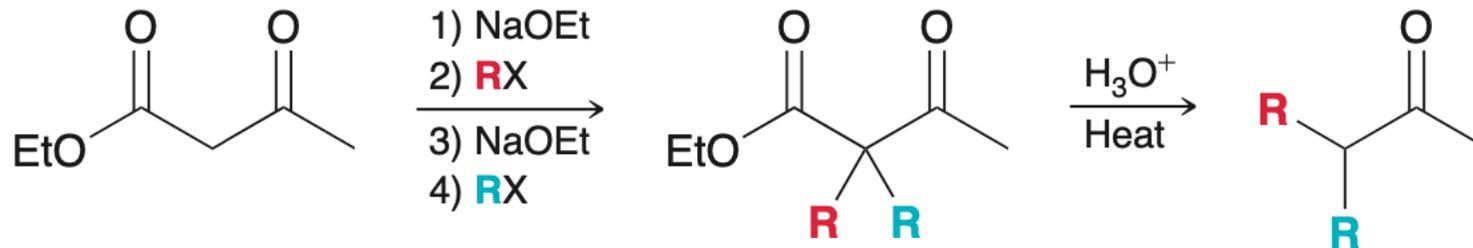
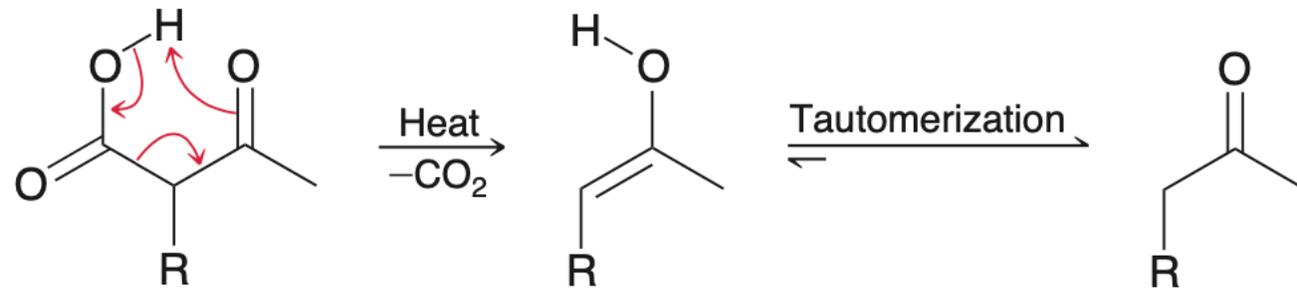
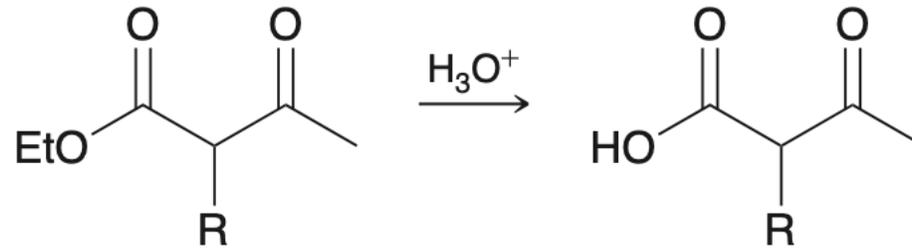
Síntese do Éster Malônico



Síntese do Éster Acetoacético

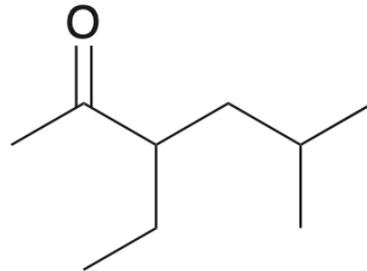


Síntese do Éster Acetoacético



Desafio!

Mostre como você usaria a síntese do éster acetoacético para preparar o seguinte composto:



Resposta:

