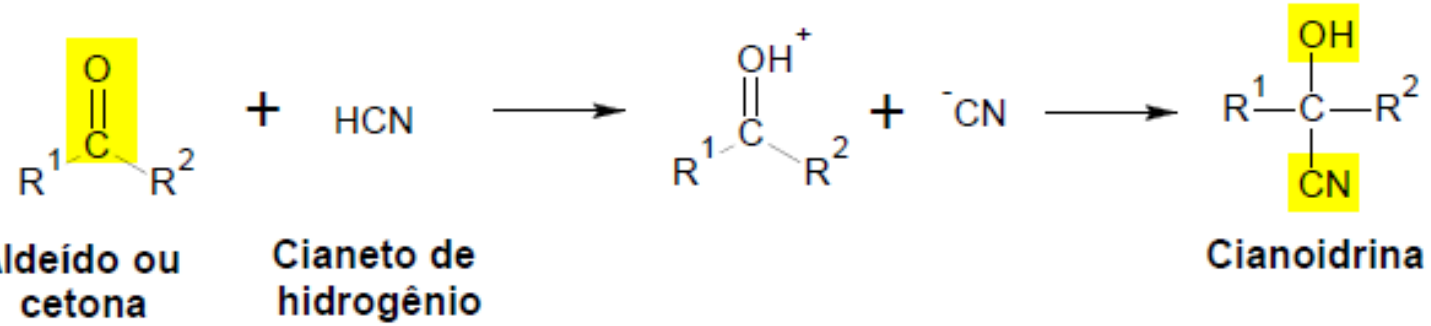
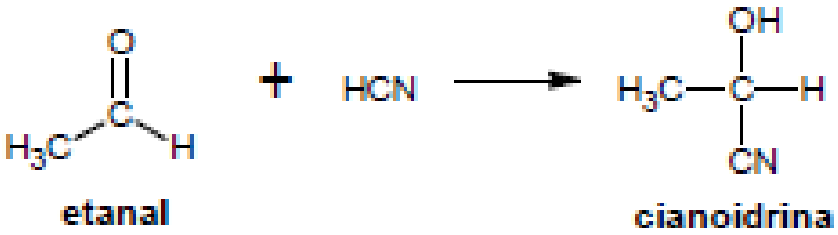
# 4- Adição de cianeto (carbono nucleofílico)



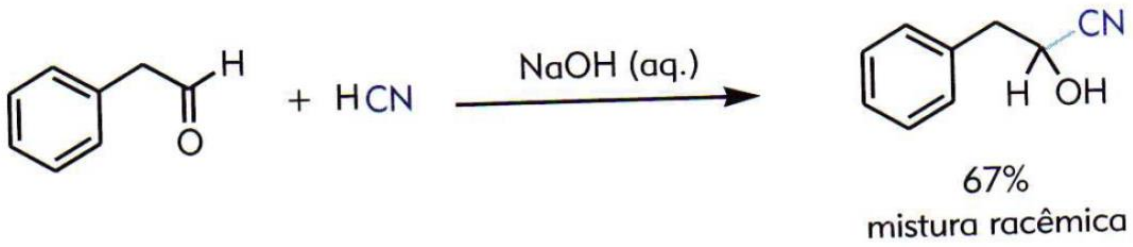

**Aldeído ou cetona** **Cianeto de hidrogênio** **Cianoidrina**

1)



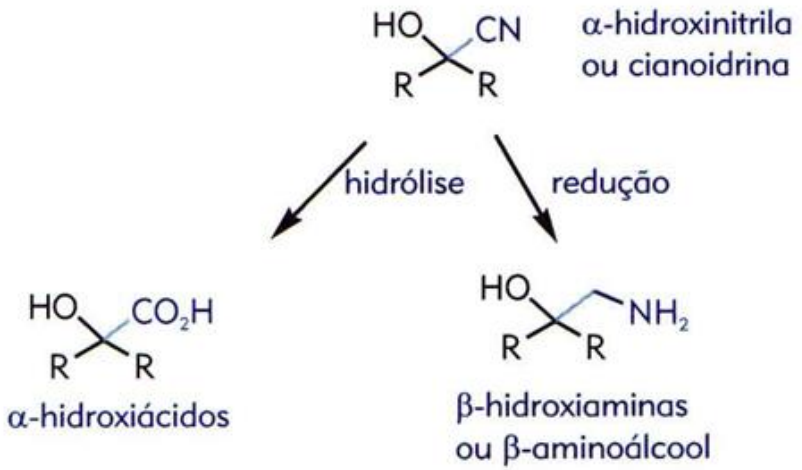

**etanal** **cianoidrina**

2)

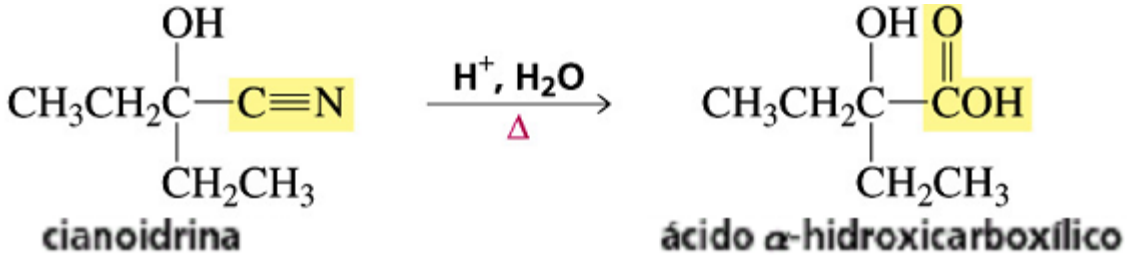



67%
mistura racêmica

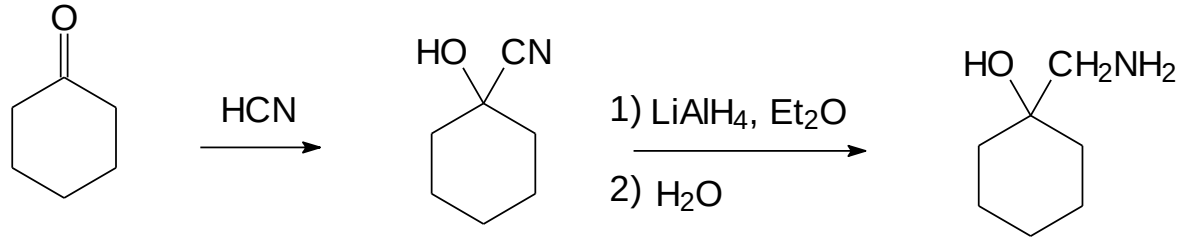
# Principais transformações de cianoidrinas




1)

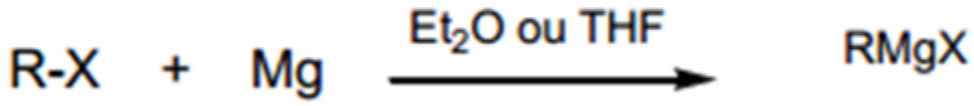



2)

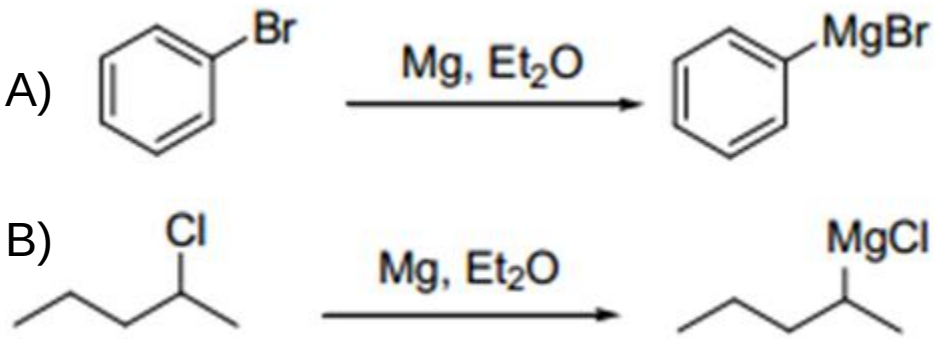


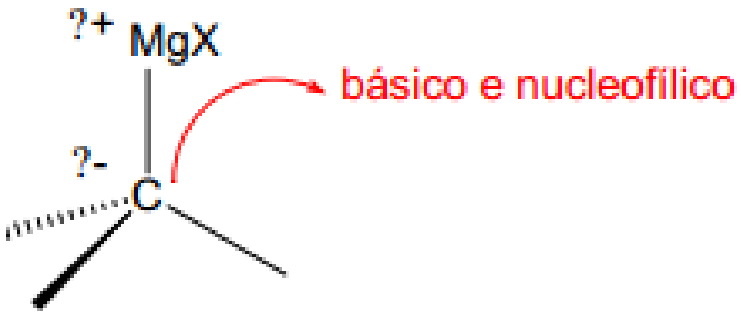
# 5- Adição de Reagentes Organometálicos

## A) Reagente de Grignard



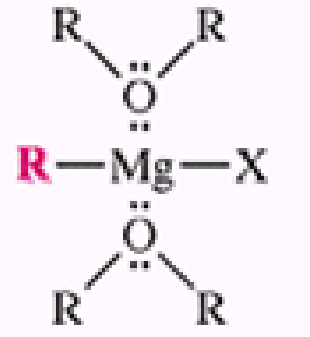

R= alquila 1º, 2º ou 3º; aril, alquenil
X= Cl, Br ou I




34% de caráter iônico

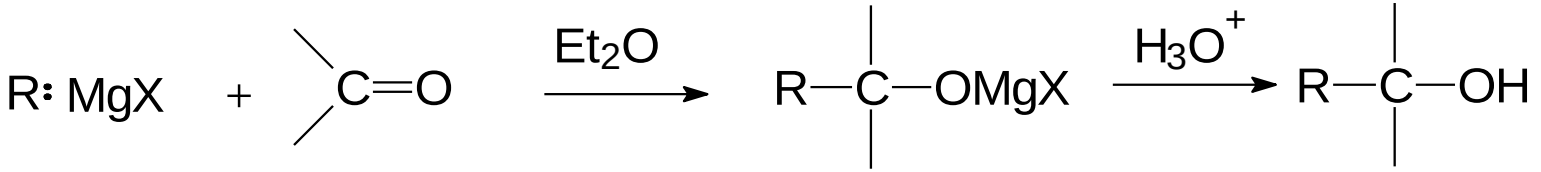
O reagente de Grignard forma complexo com o solvente etéreo (o que estabiliza): a estrutura do complexo pode ser representada como segue:



## 5.1-Adição de reagentes de Grignard a compostos carbonilados

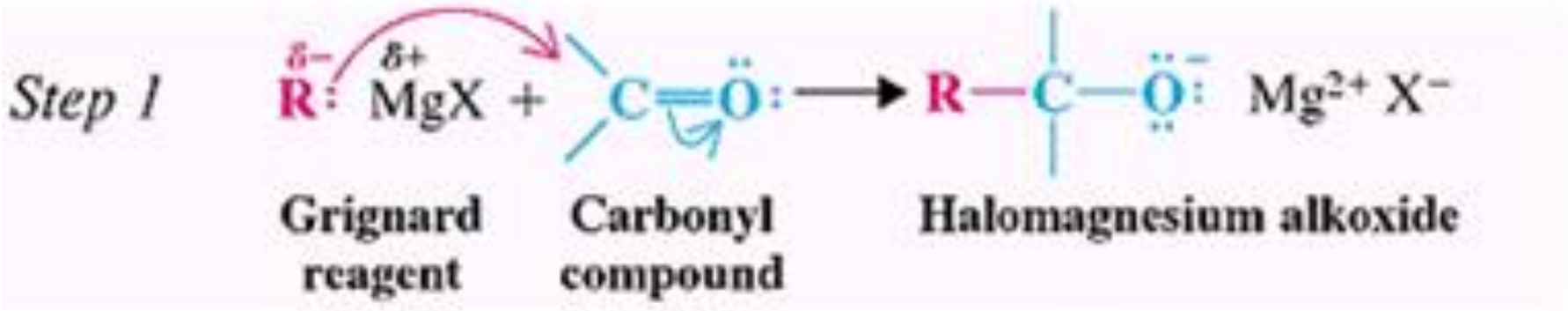
$$CH_3CH_2Br \xrightarrow[Et_2O]{Mg} CH_3CH_2MgBr$$

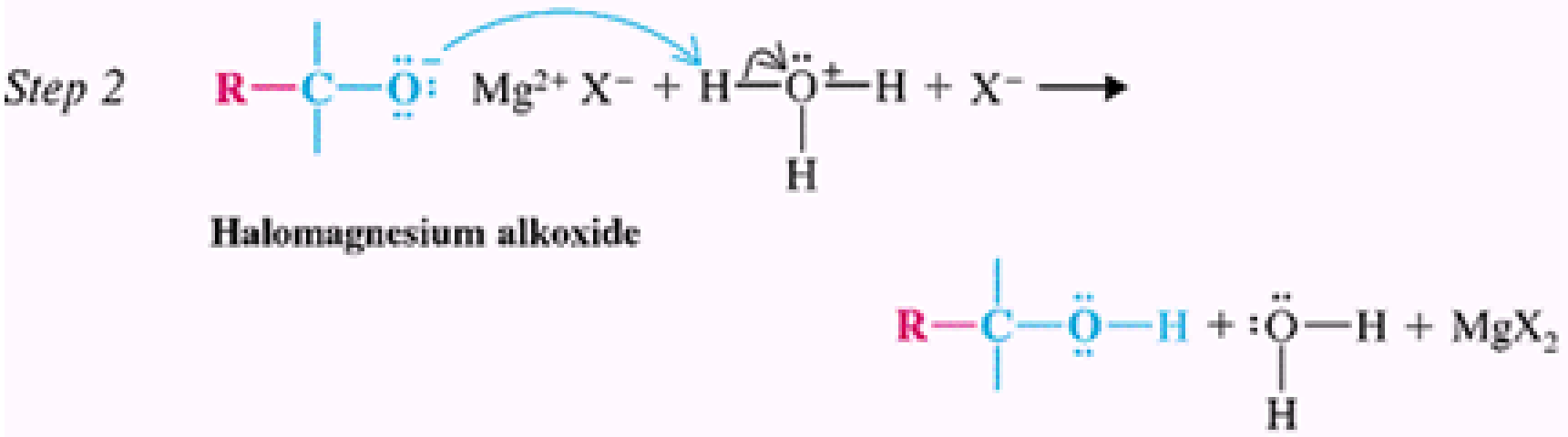
$CH_3CH_2MgBr$ **reage como se fosse** $CH_3\ddot{\underset{\cdot\cdot}{C}}H_2^{-}\ \ Mg^{+}Br$



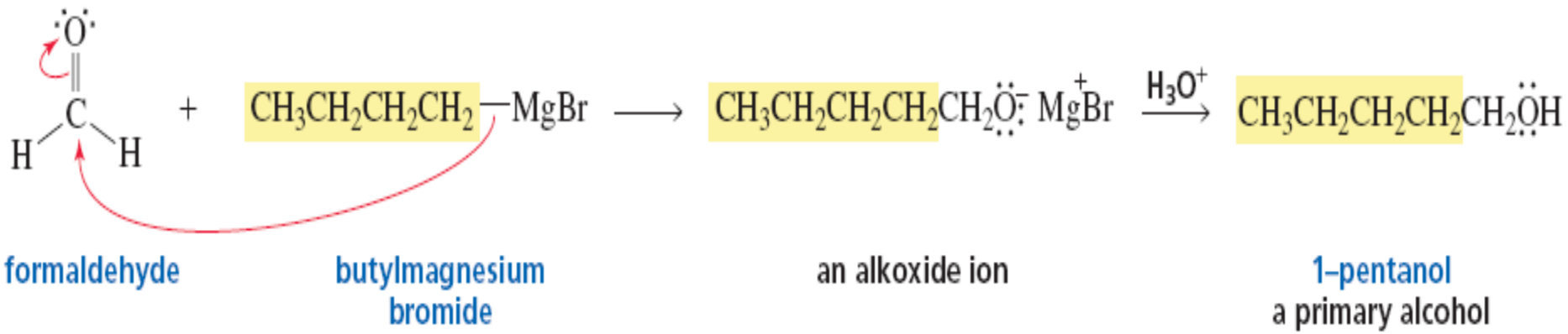

Alcóxido de halomagnesium

# Mecanismo Geral



# Exemplo



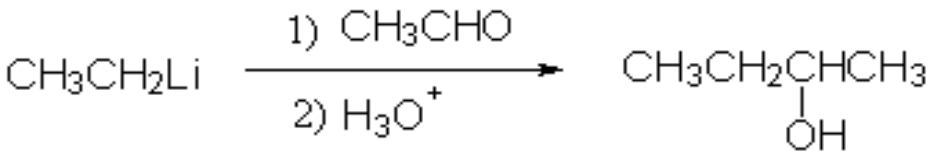

Podemos concluir que:

1- Os RG reagem com o formaldeído para dar álcool primário.

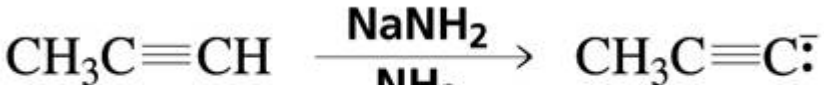
2- Os RG reagem com os outros aldeídos para dar álcoois secundários.

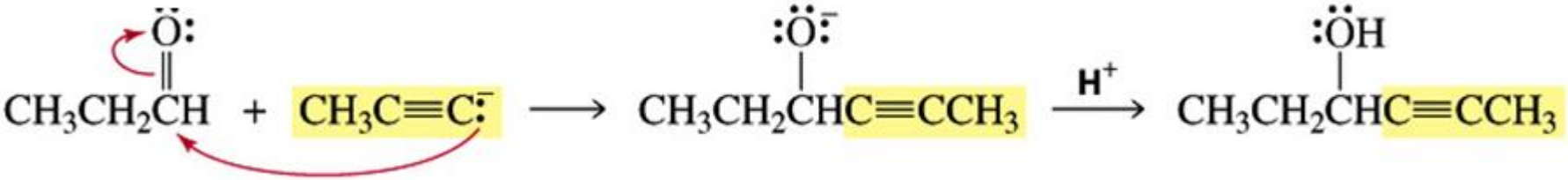
3- Os RG reagem com as cetonas para dar álcoois tericários.

## 5.2) Adição de organolítio



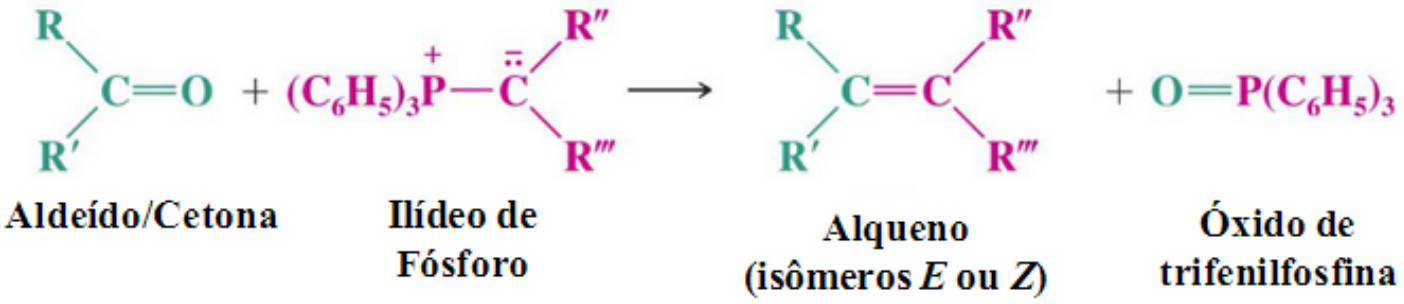

## 5.3) Adição de alquinetos de sódio

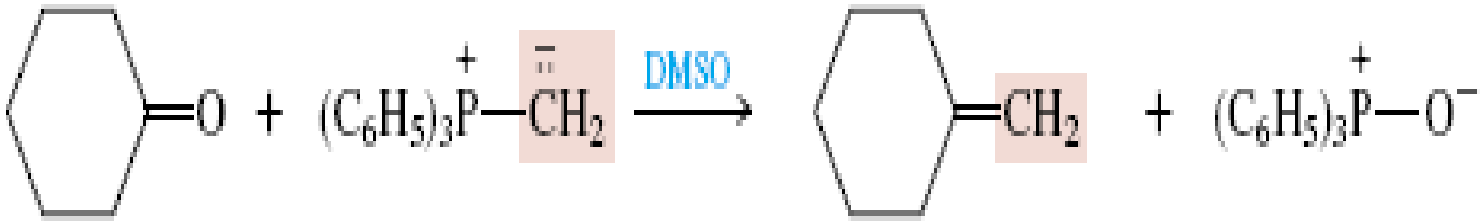


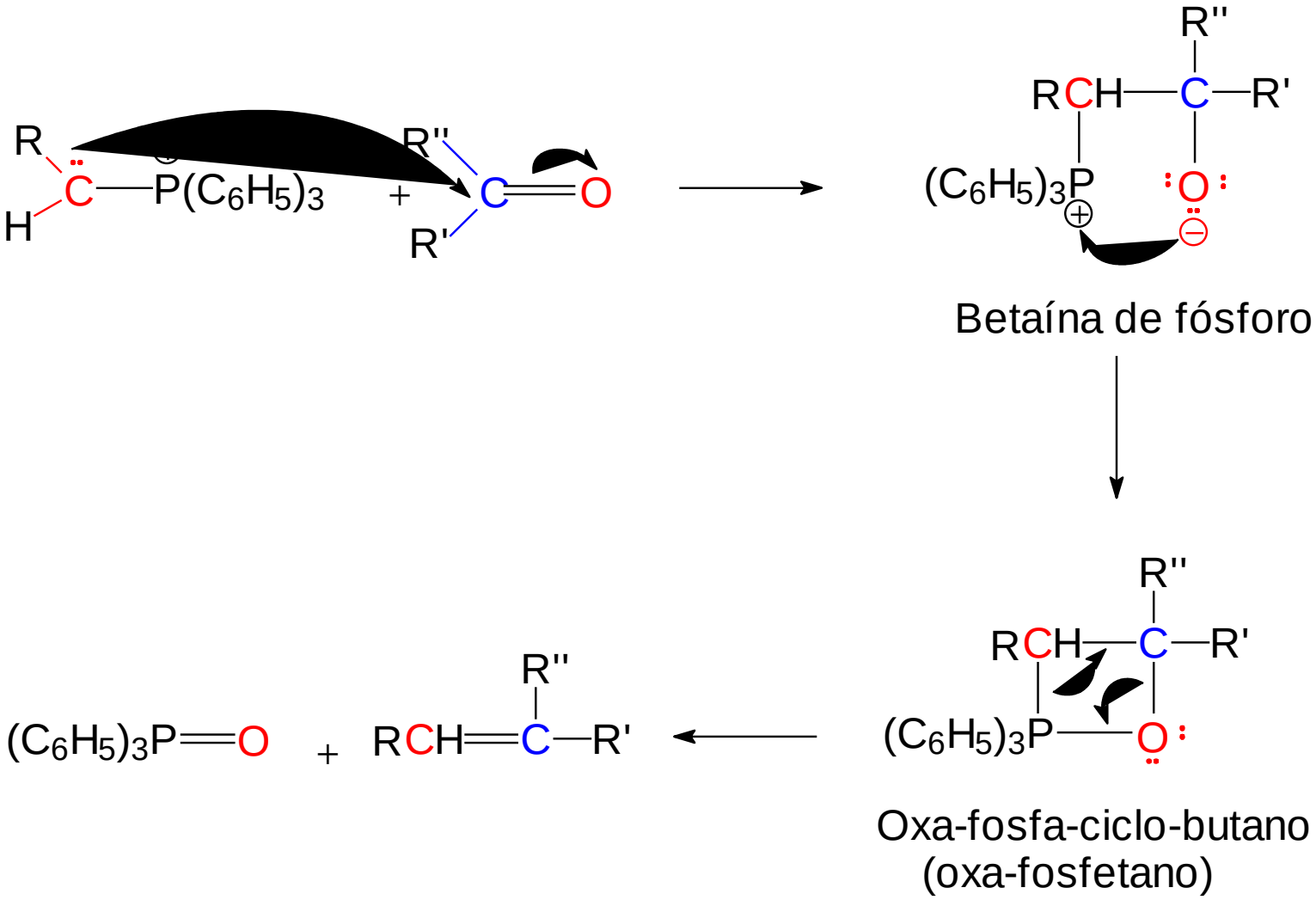
# 6- Adição de ilídeo de fósforo: Reação de Witting

-Síntese seletiva de alquenos (reação regioespecífica)

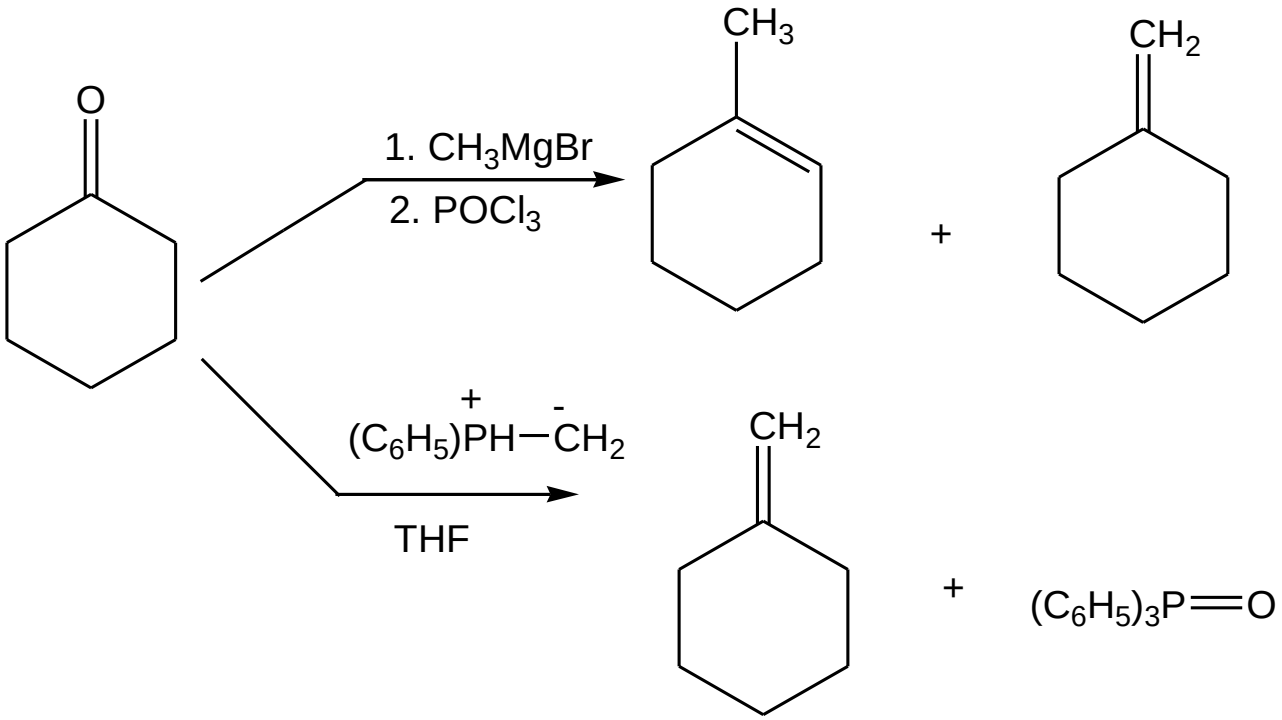


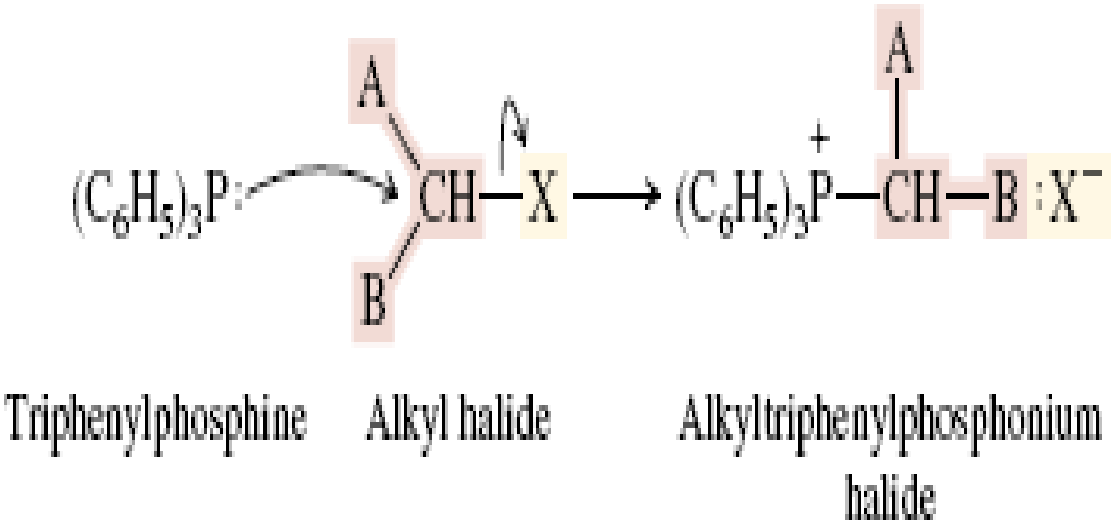
## Mecanismo Geral:

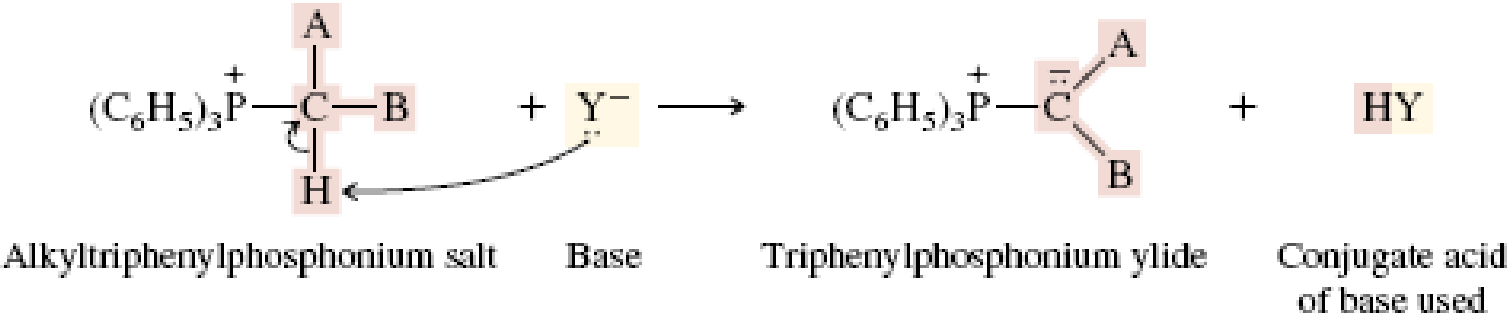


A reação de Wittig produz alquenos puros e de estrutura conhecida. A ligação dupla do alqueno ocupa sempre o mesmo lugar do grupo carbonila no precursor, e não se obtêm misturas de produtos (exceto os isômeros *E,Z*).

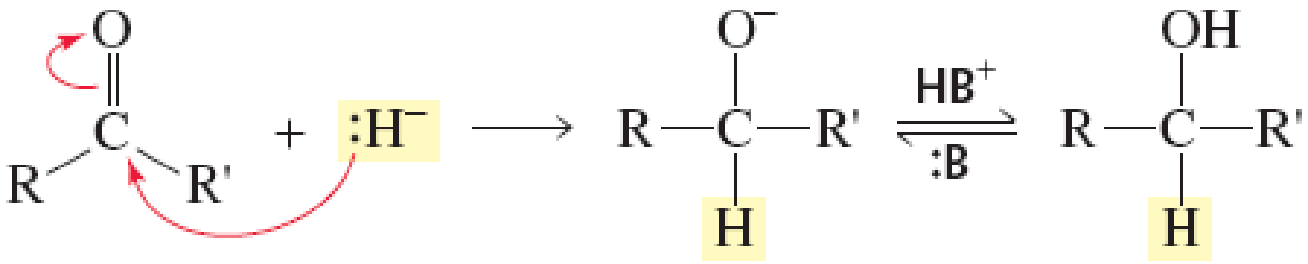


# Obtenção de ilídeo de fósforo

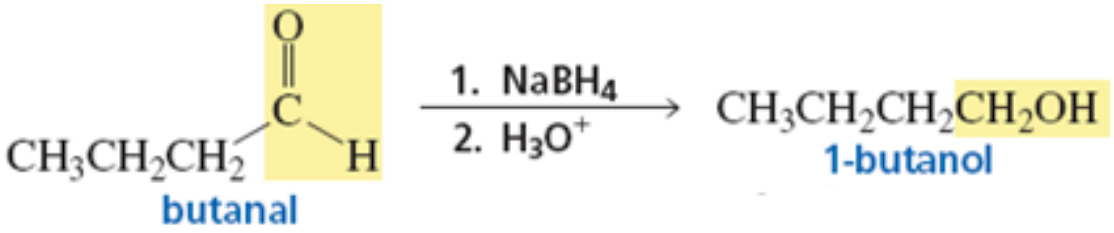


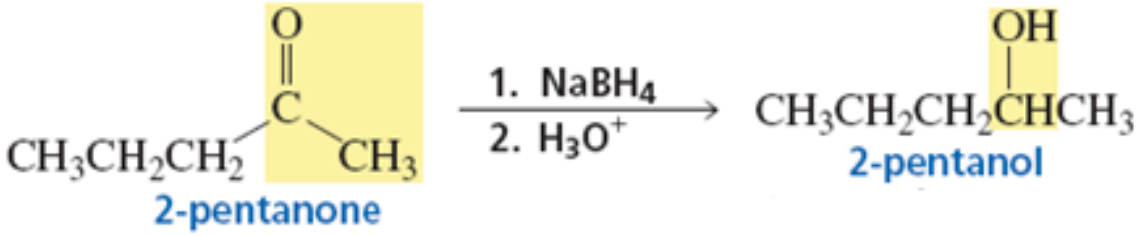
# 7) Adição de Hidreto- Reações de Redução




A)

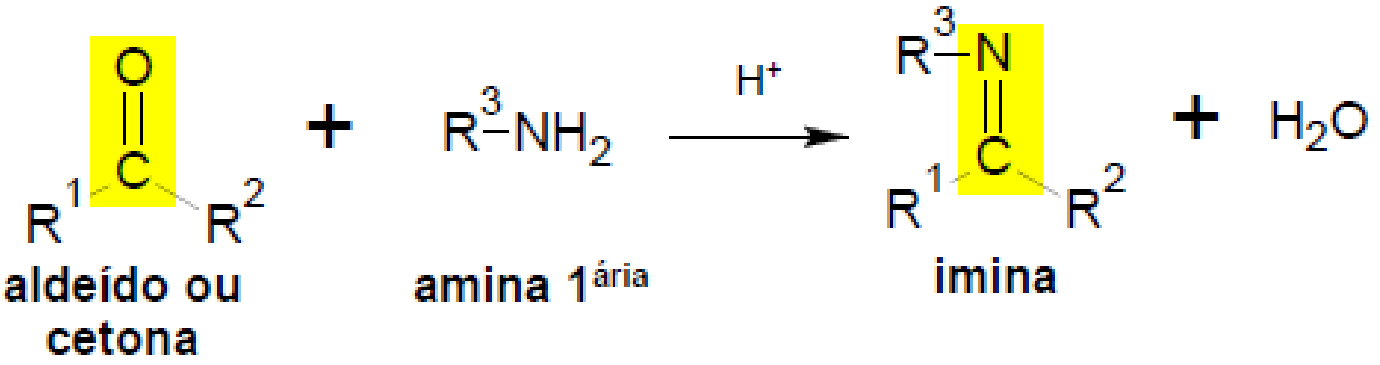



B)



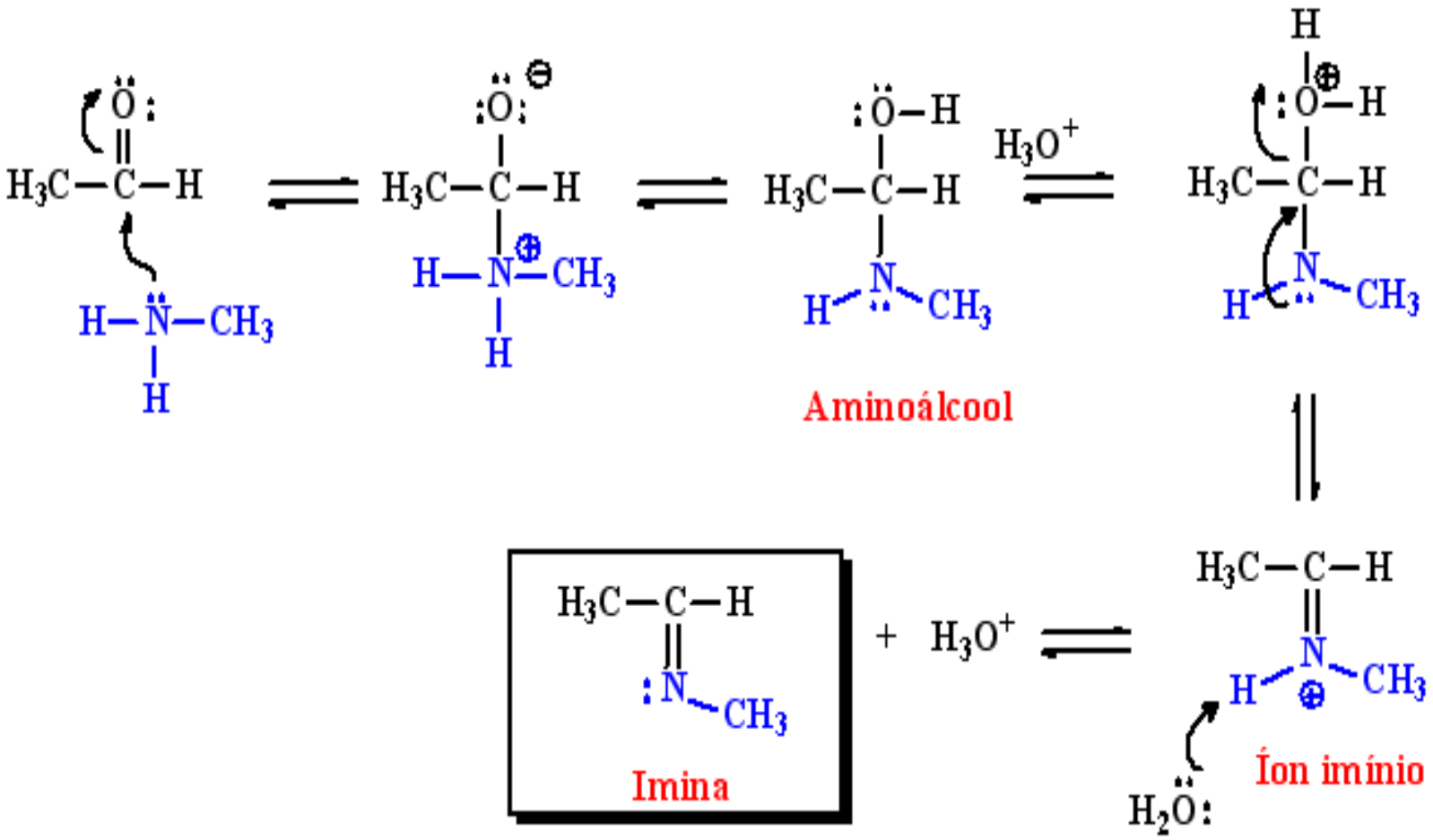
## 8) Adição de nitrogênio nucleofílico

### A) Adição de aminas primárias ou amônia: iminas (bases de Schiff)

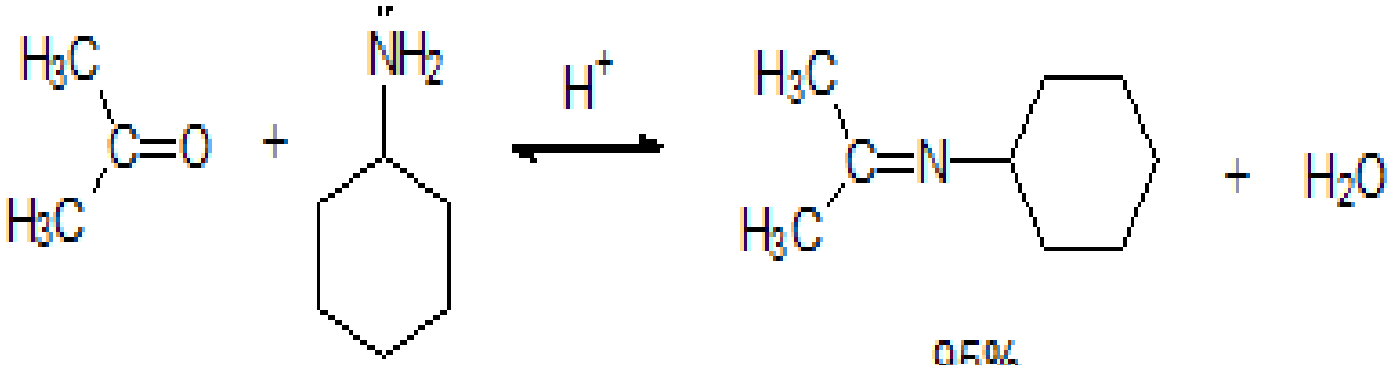



O pH no qual é conduzida a formação da imina deve ser cuidadosamente controlado: Condição ideal de pH : pH 4 a 5.

# Proposta de Mecanismo



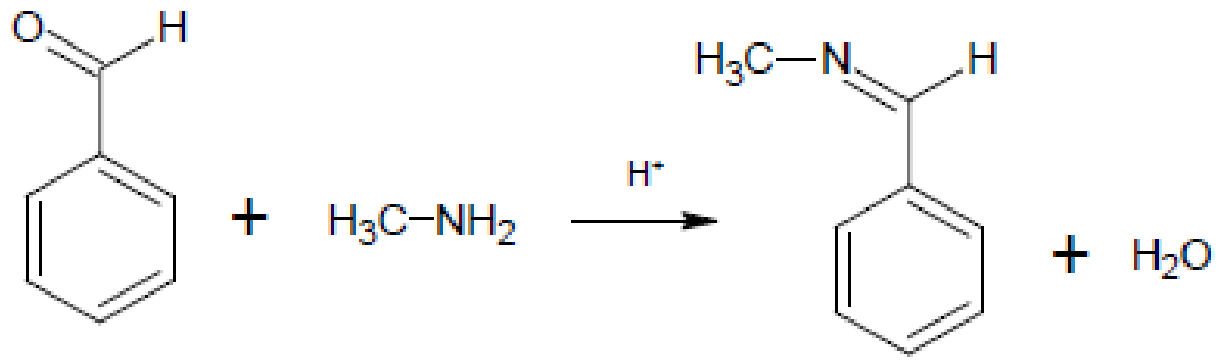
A)




95%

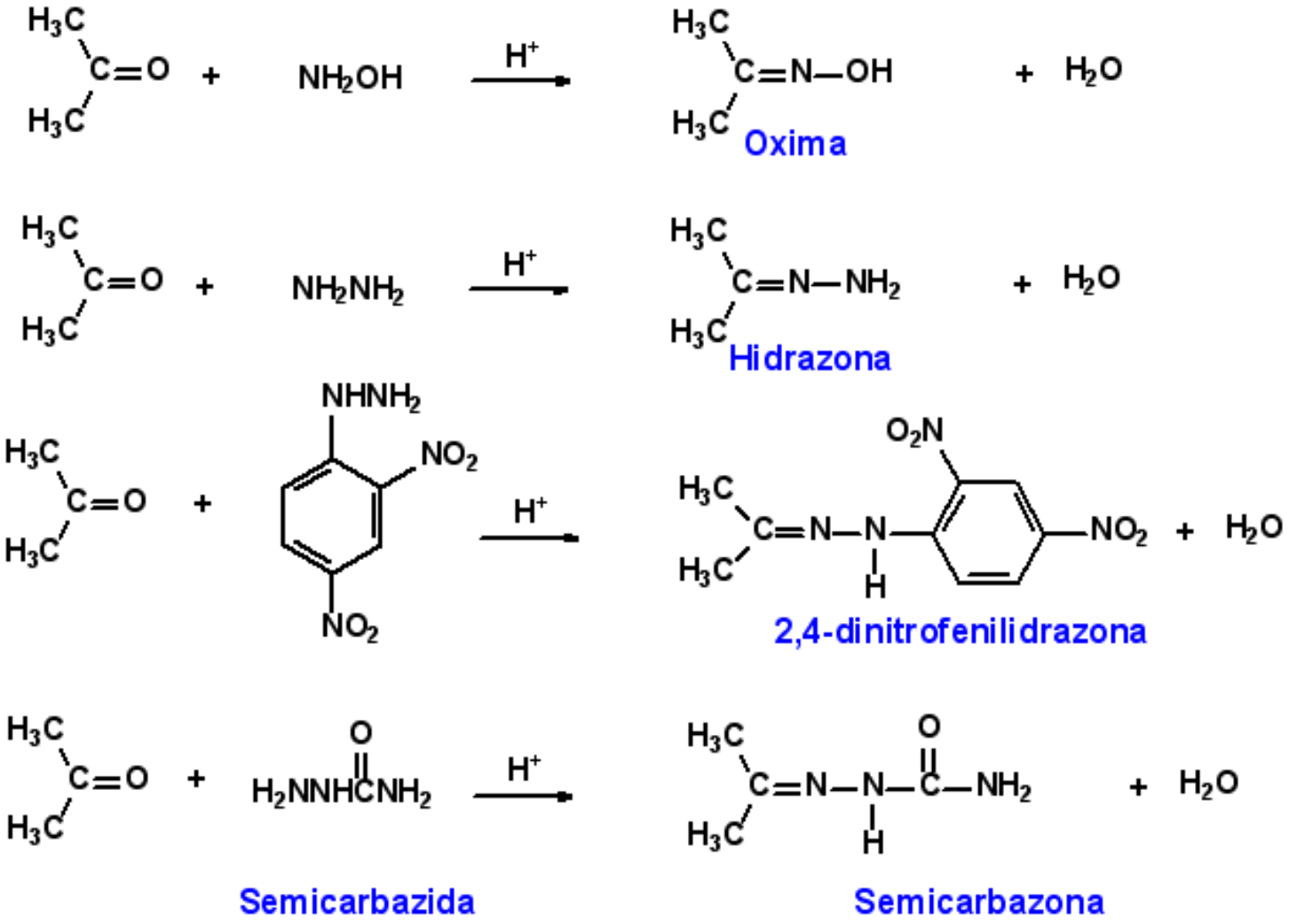
Imina substituída

B)

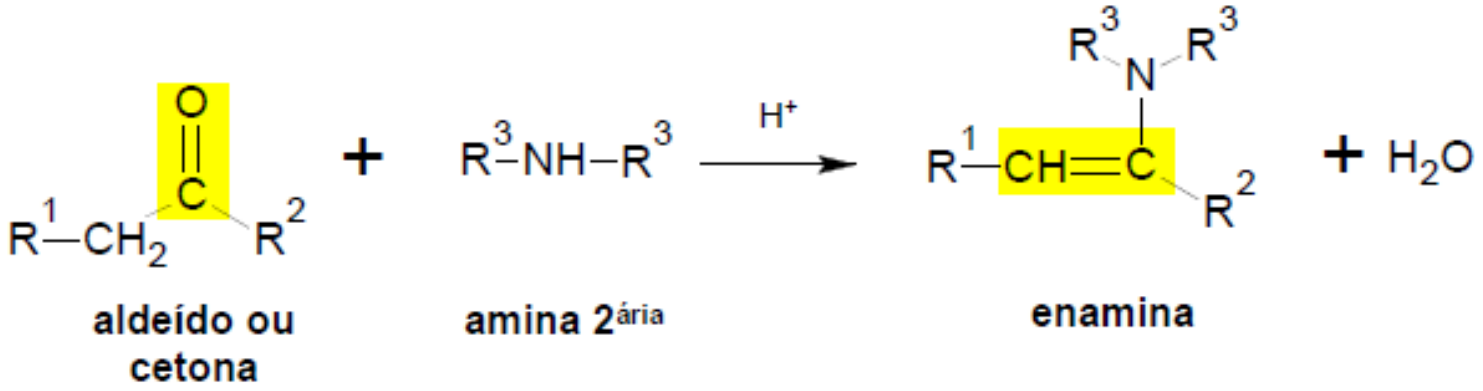



**benzaldeído** **metanamina (amina 1ária)** **Imina**

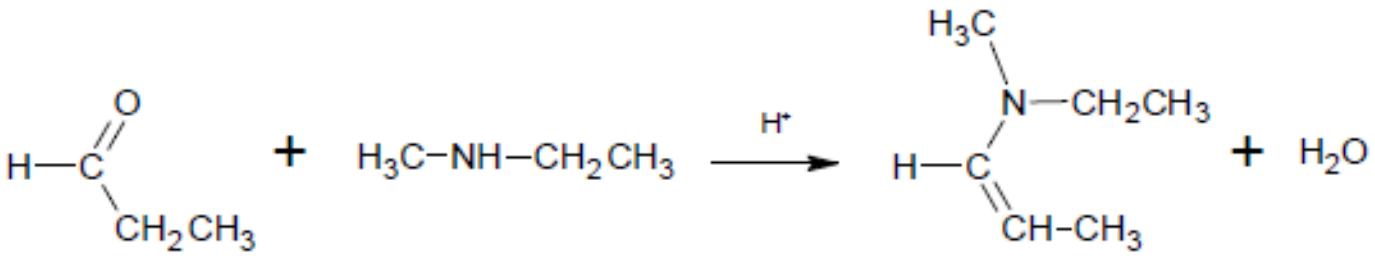
# ADIÇÃO DE OUTROS DERIVADOS DA AMÔNIA



# B) Adição de aminas secundárias: enaminas




**aldeído ou cetona** | **amina 2ária** | **enamina**




**propanal** | **N-metiletanamina (amina 2ária)** | **enamina**

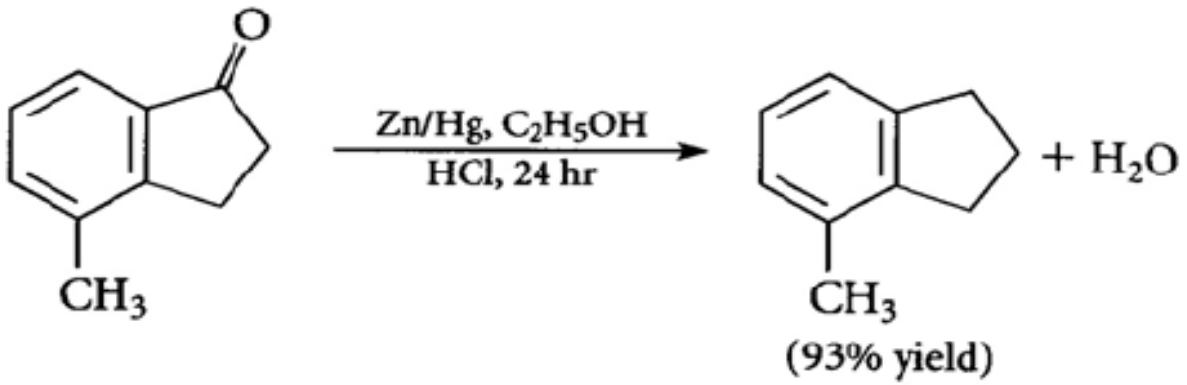
Proposta Mecanística:

# 9) Desoxigenação do Grupo Carbonila

Permite a redução de um grupo carbonílico de um aldeído ou de uma cetona a um grupo metilênico.

Esta transformação de grupo funcional pode ser efetuada de três maneiras diferentes:

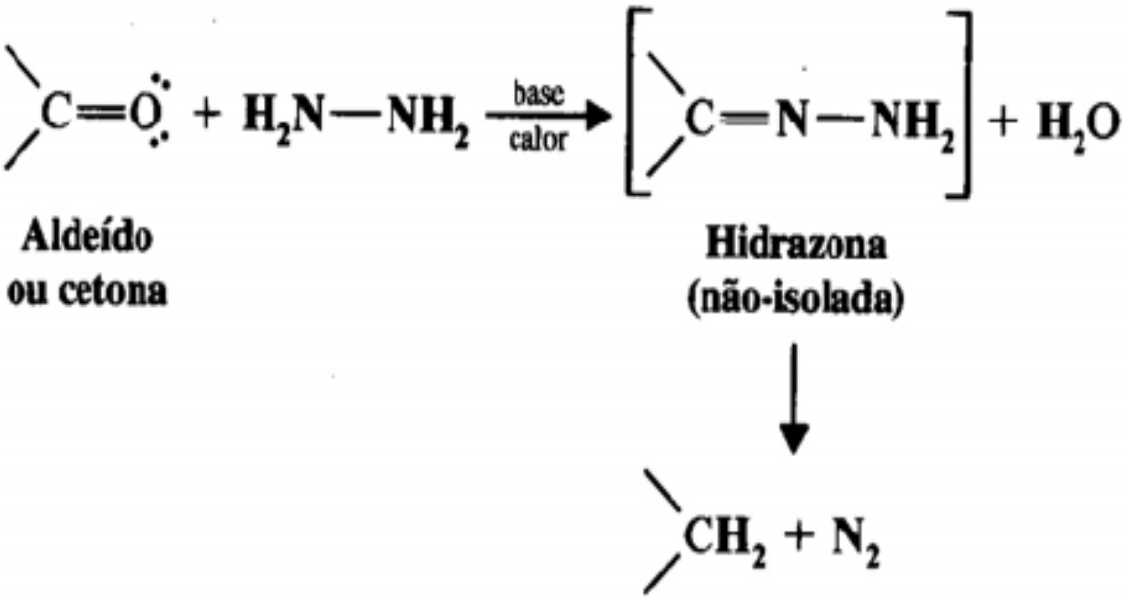
**1) Redução de Clemmensen**



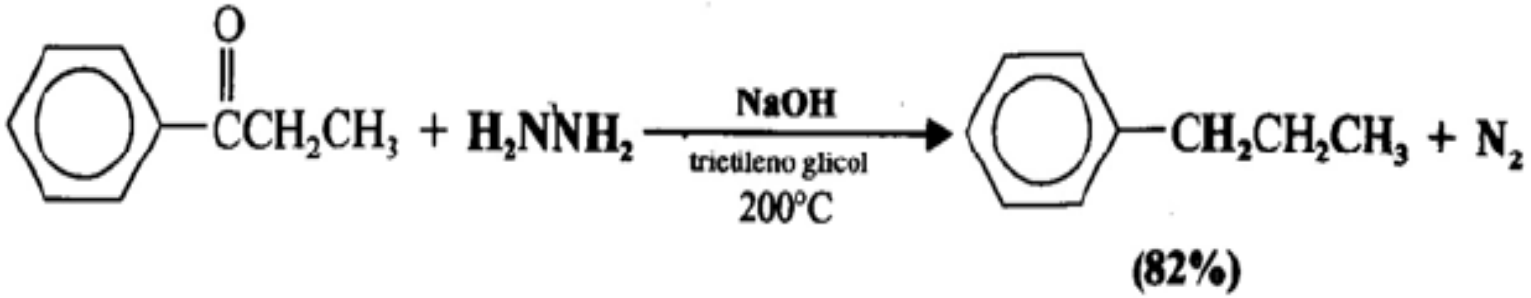

$$CH_3(CH_2)_5CH{=}O \xrightarrow[25\%\ HCl]{Zn/Hg} CH_3(CH_2)_5CH_3$$

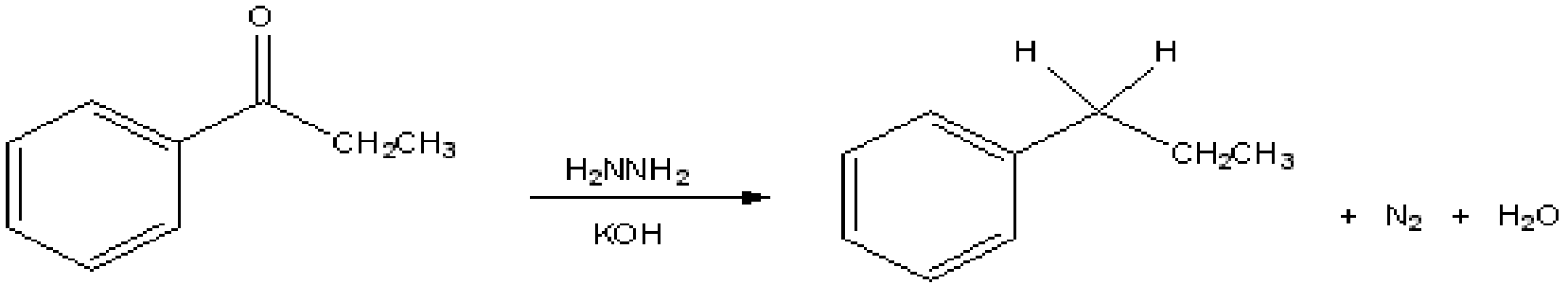
**heptanal** — **heptane** (87% yield)

## 2) Redução de Wolff-Kishner: conversão de hidrazonas em hidrocarbonetos

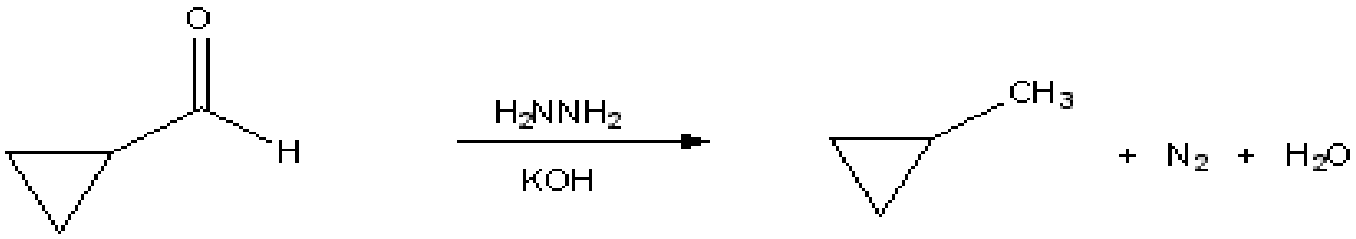



Exemplo:



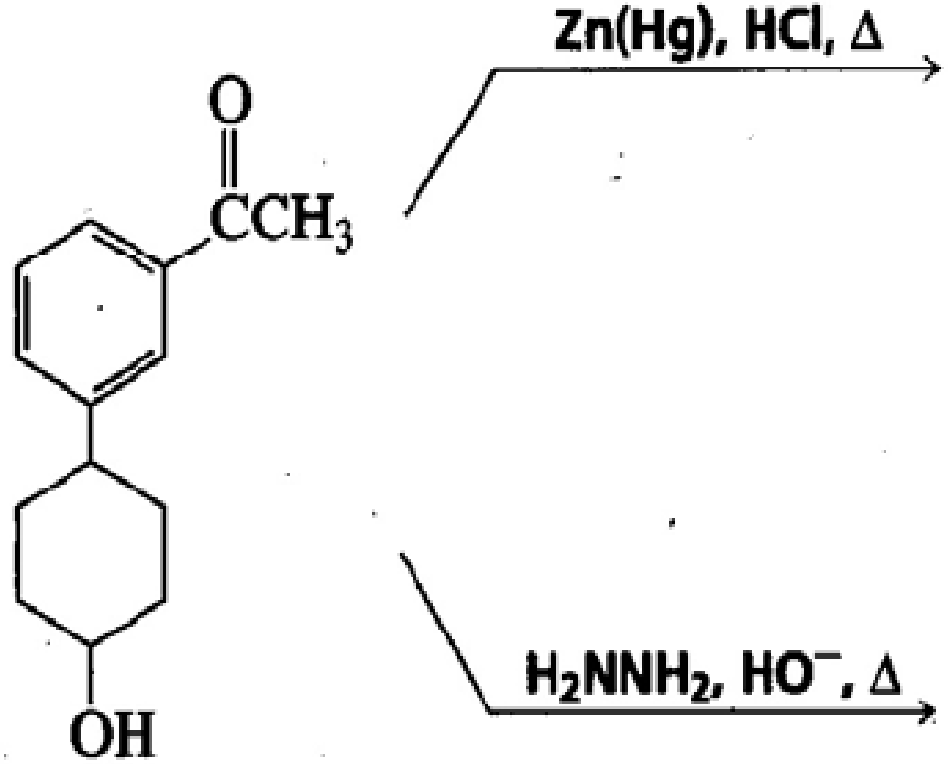



**Propiofenona** **Propilbenzeno (82%)**

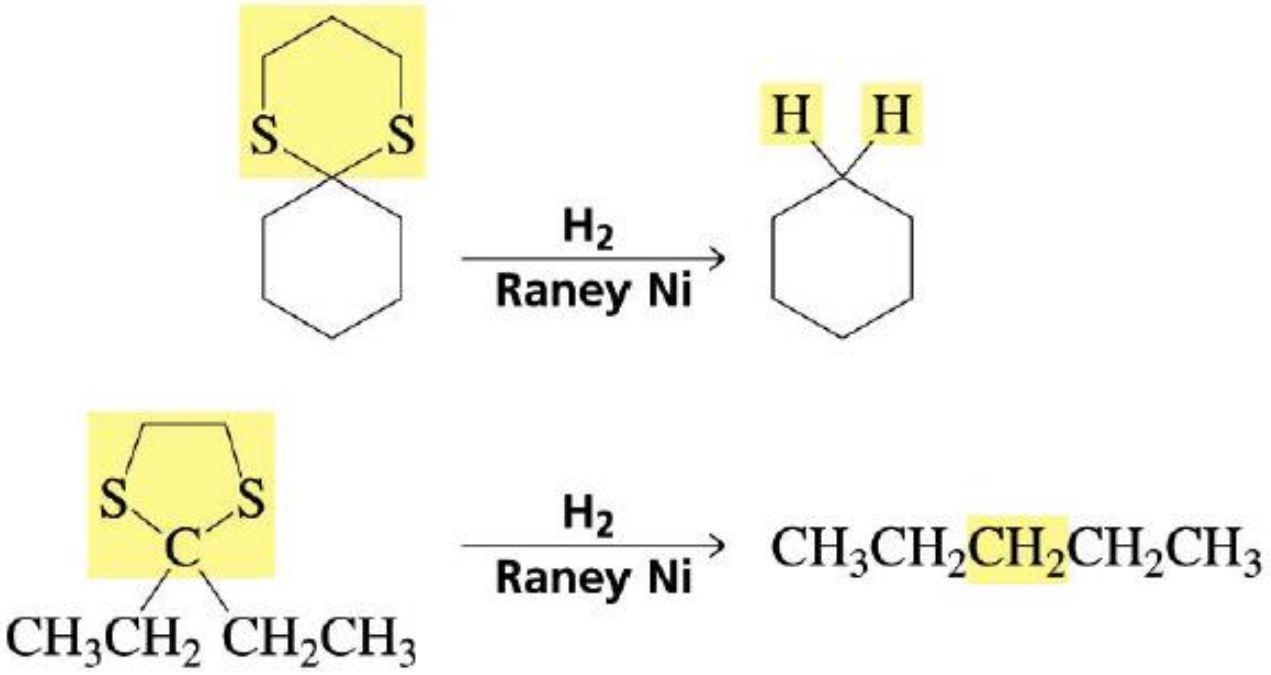


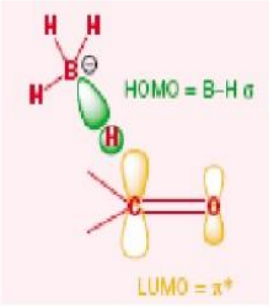

**Ciclopropanocarbaldeído** **Metilciclopropano (72%)**

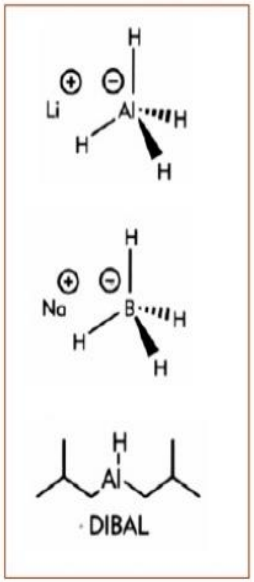
Comparação entre Clemmensen e Wolff-Kishner.
Qual o produto principal de cada uma das reações abaixo?



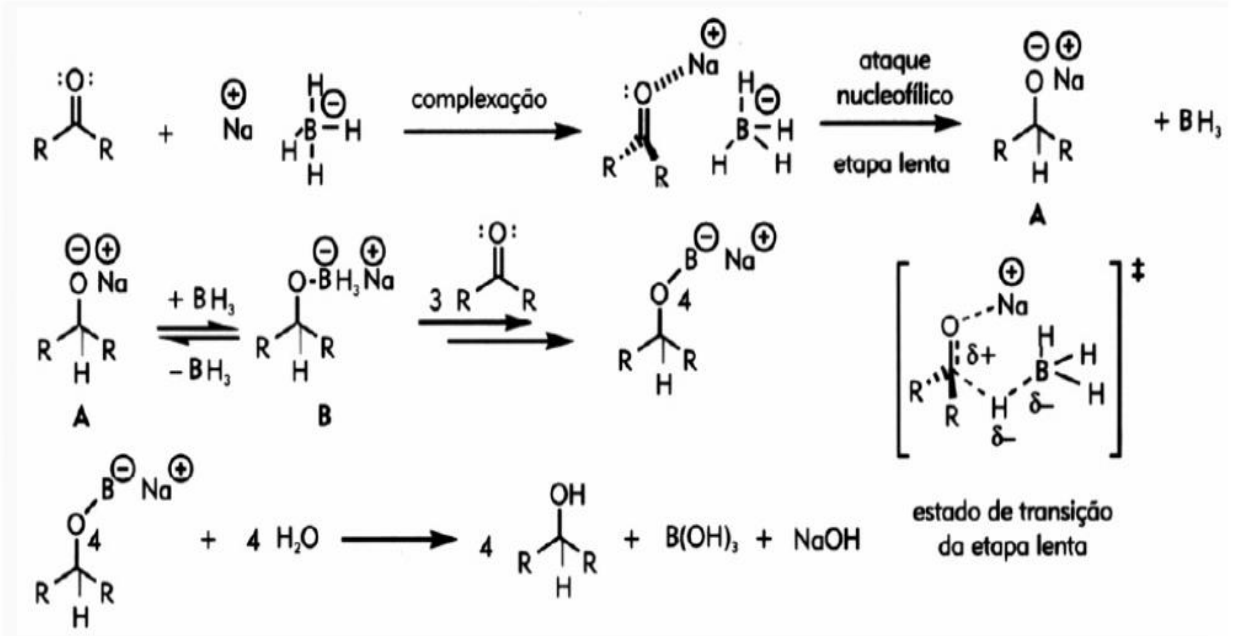
## 3) Dessulfurização de Tioacetais



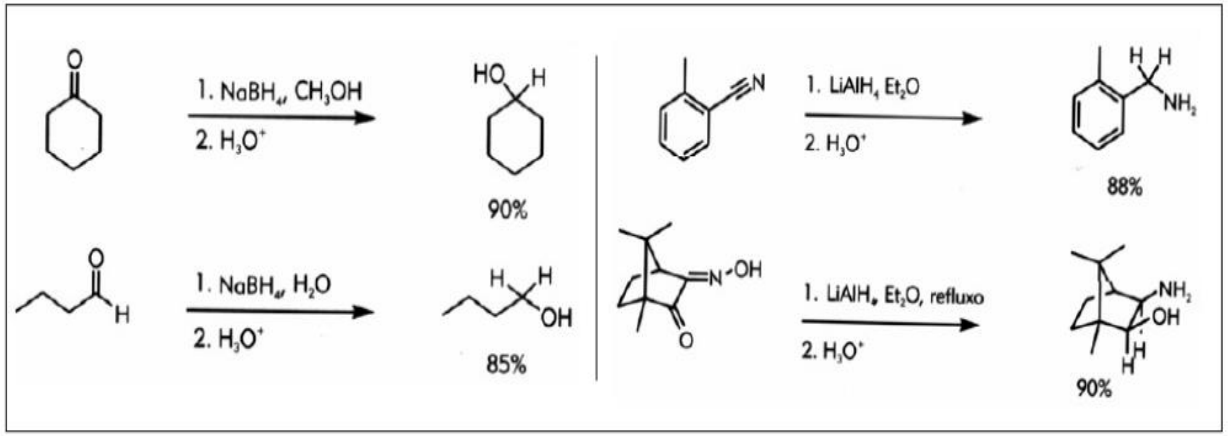


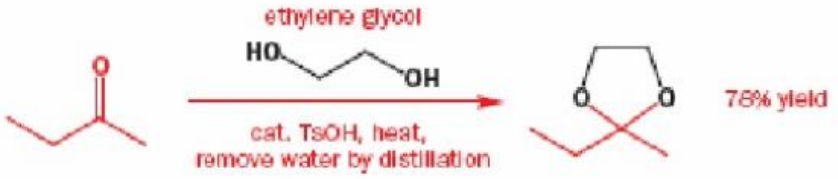

## Mecanismo da adição de hidreto



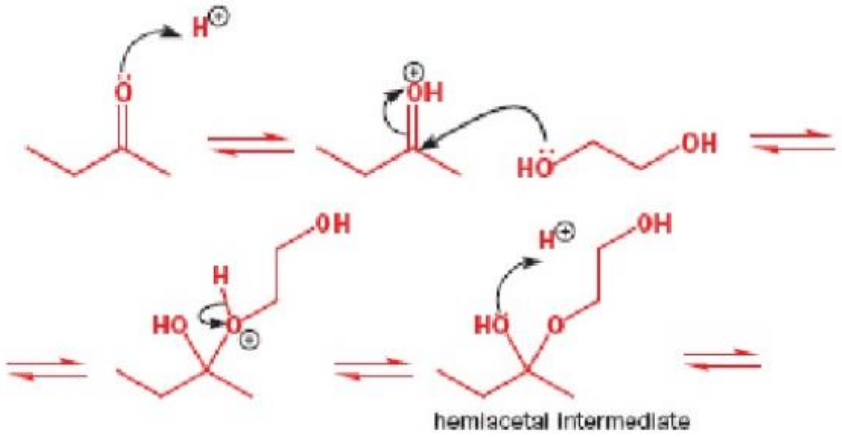

## Exemplos



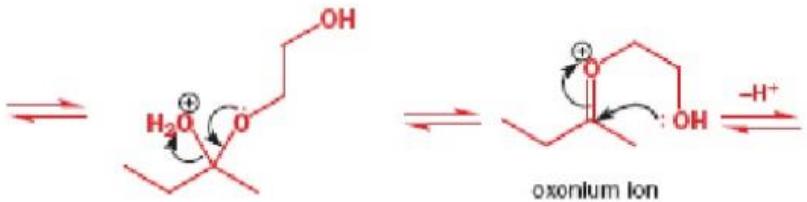
## Acetais cilcicos



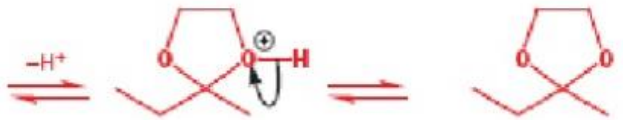

acid-catalysed dioxolane formation




hemiacetal intermediate

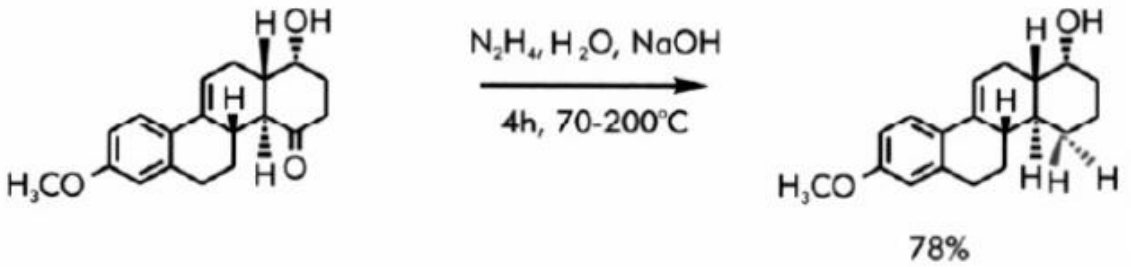


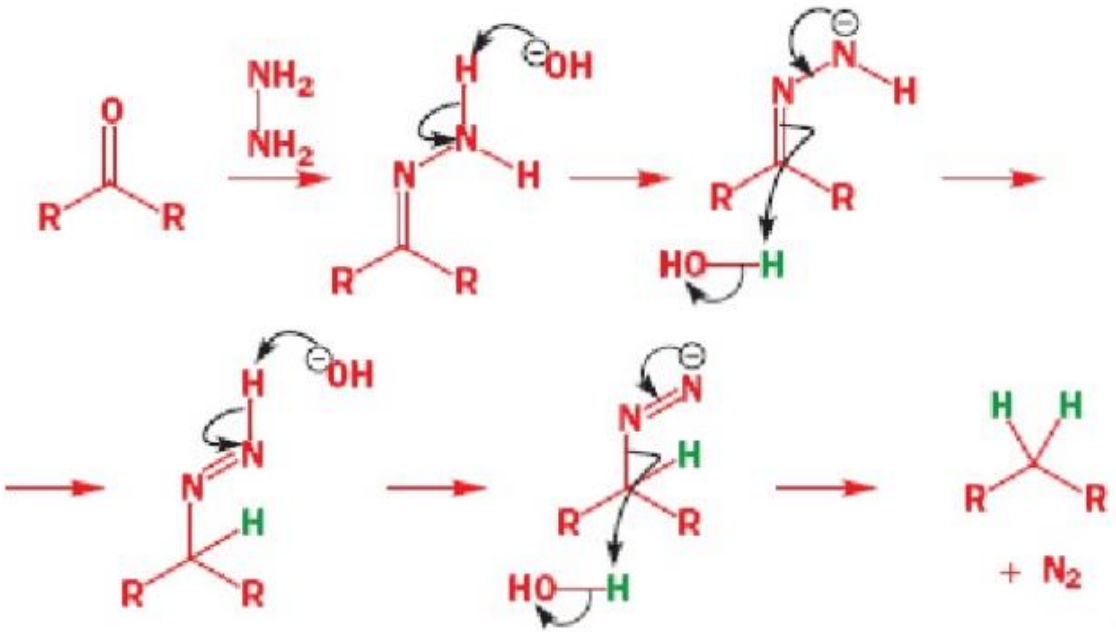

oxonium ion




the dioxolane

## Redução de Wolff-Kishner




## Mecanismo da redução de Wolff-Kishner