

COMPOSTOS CARBONÍLICOS: ALDEÍDOS E CETONAS

Estrutura, Nomenclatura, ocorrência natural,
aplicação, propriedades físicas e preparação

PARTE I

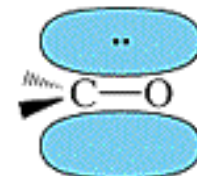
CURSO DE FARMÁCIA/ TURMA 22/QUI 215
Profa. Tânia Márcia S. Melo
1º Semestre/2017

1-Tipos de compostos carbonilados

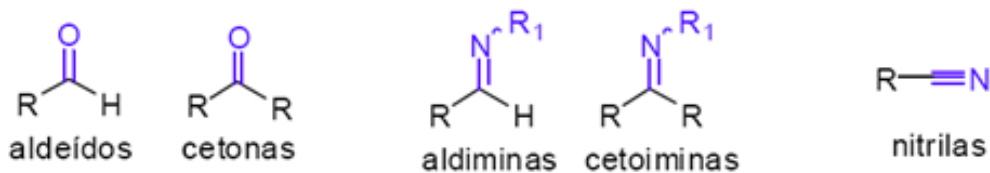
- O grupo carbonila é um dos mais importantes grupos funcionais (reações sintéticas e biológicas).

I - CARBONILAS E GRUPOS RELACIONADOS – Adição Nucleofílica

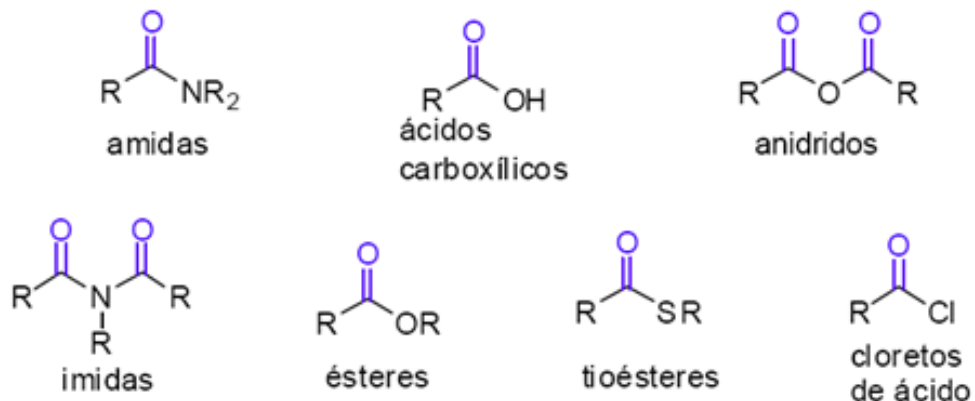
II - CARBONILAS E GRUPOS RELACIONADOS – Substituição Nucleofílica



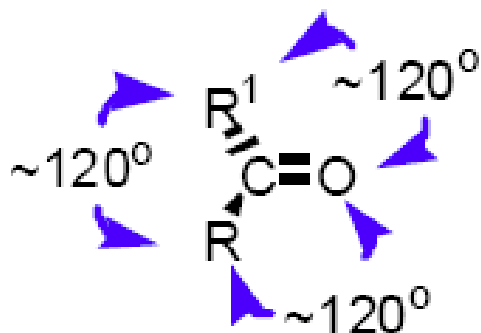
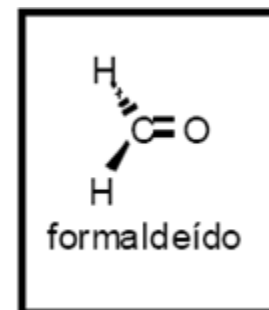
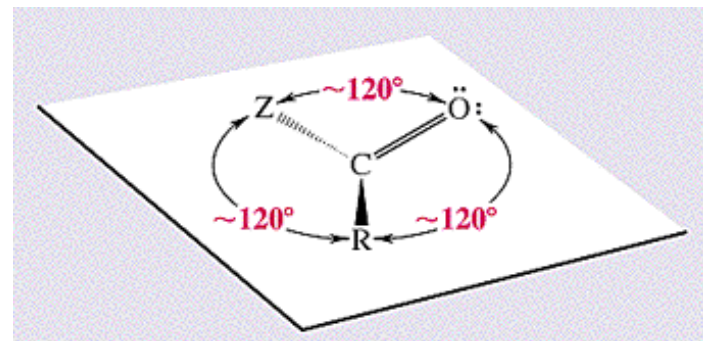
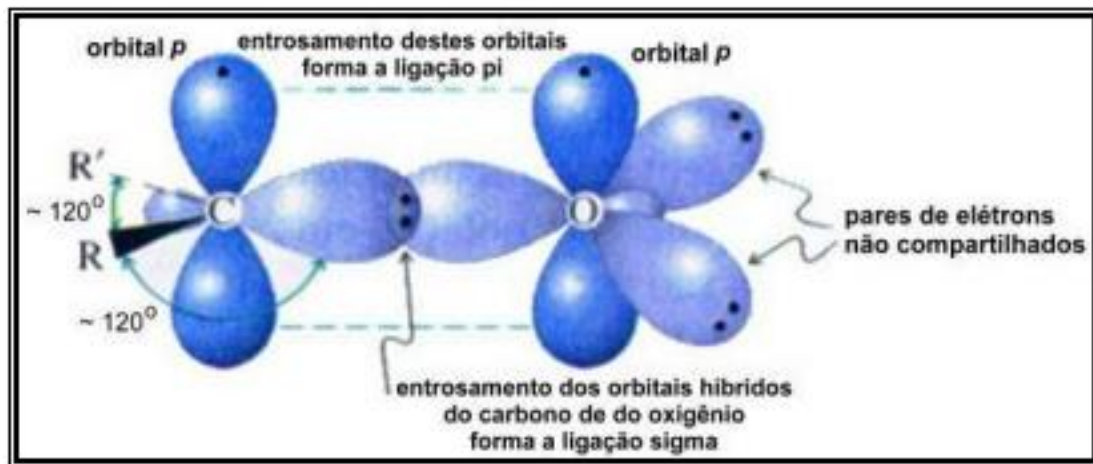
GRUPO 1 - Aldeídos, Cetonas, Iminas e Nitrilas



GRUPO 2 - Derivados de Ácidos Carboxílicos



2- Estrutura do grupo carbonila



aldeídos: $R^1 = H$

cetonas: $R^1 = \text{alquil ou aril}$

Ângulos de ligação
 α (graus)

H-C-O 121,8

H-C-H 116,5

Comprimentos de ligação
 λ (A, Angstrom)

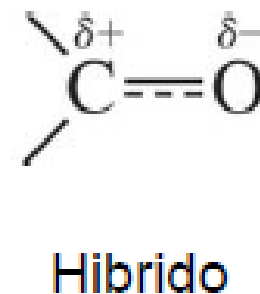
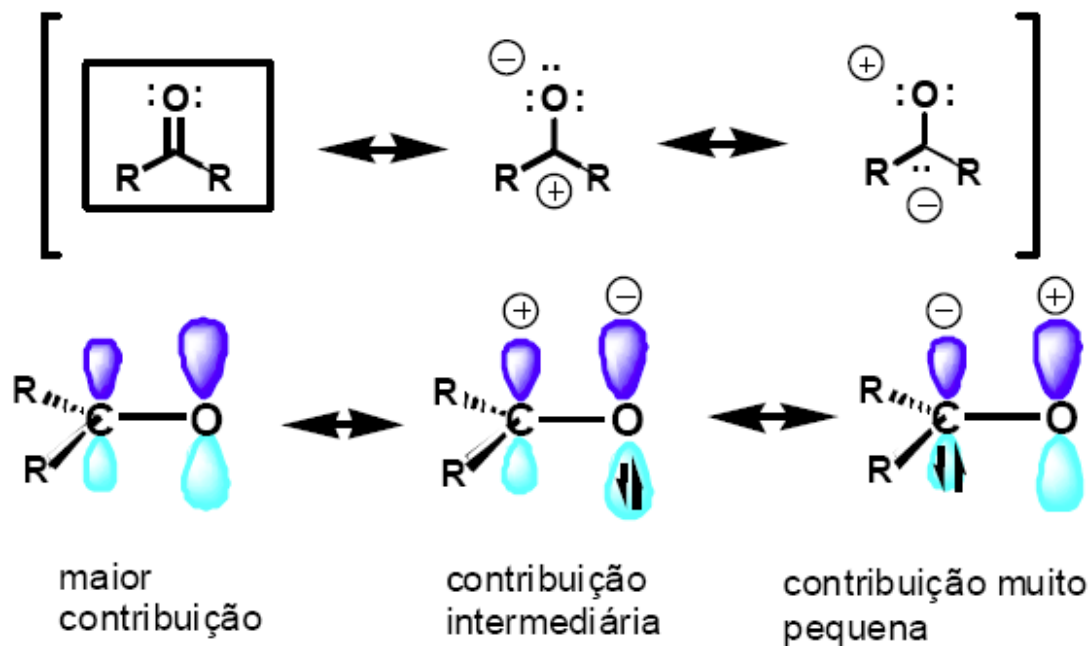
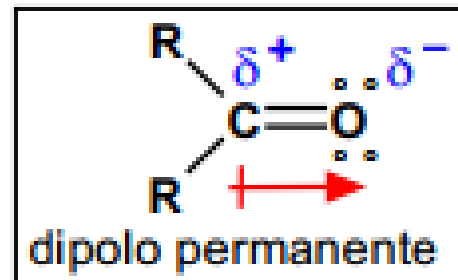
C=O 1,203

C-H 1,101₃

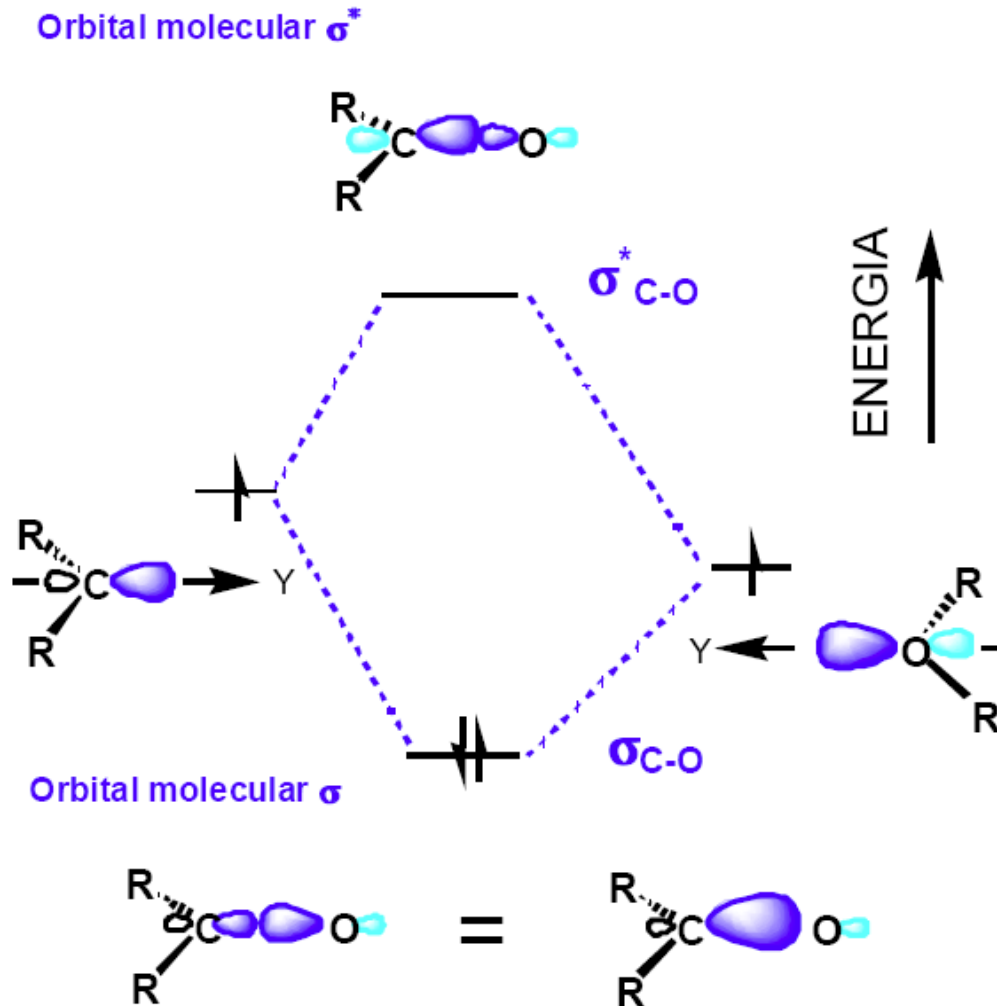
3-Formas de ressonância da carbonila

A carbonila é polar:

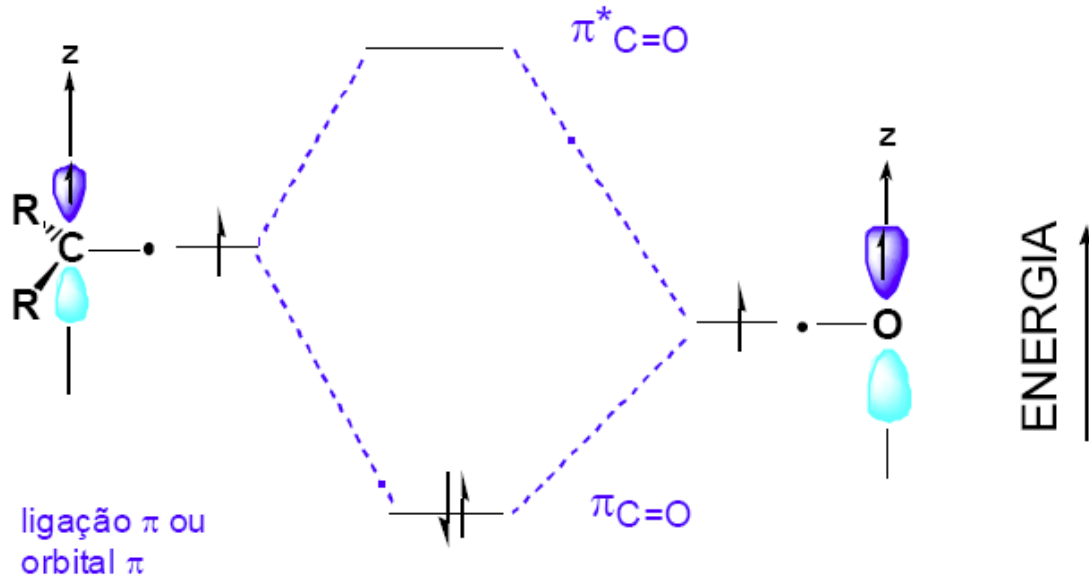
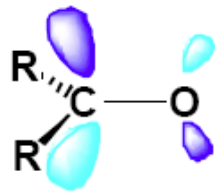
- átomo de oxigênio mais eletronegativo que o carbono
- efeitos indutivo e de ressonância



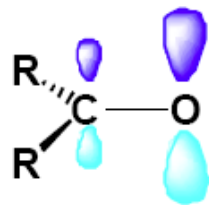
4-Orbitais Moleculares



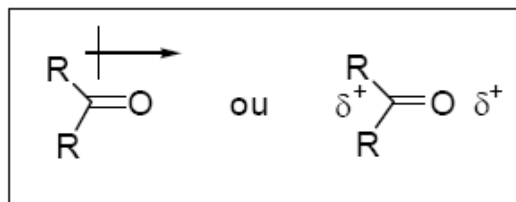
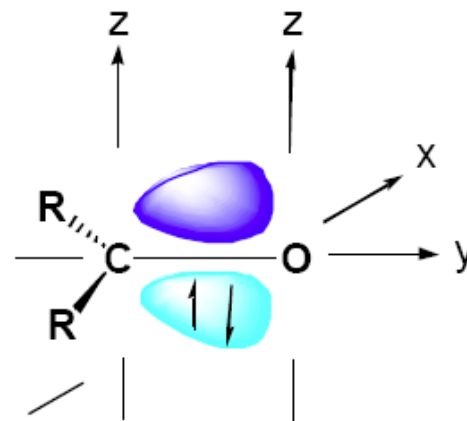
ligação π^* ou orbital π^*



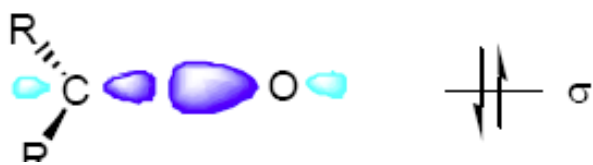
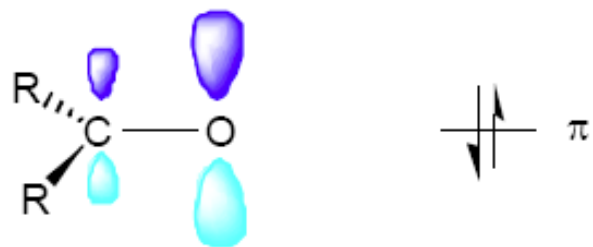
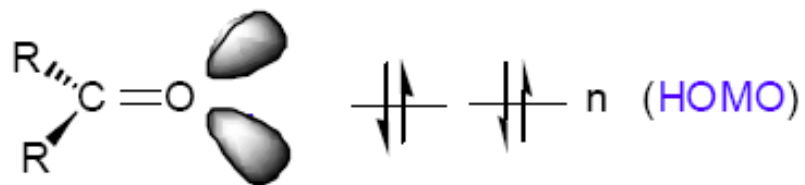
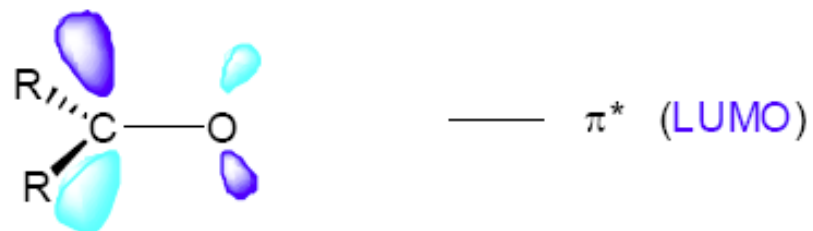
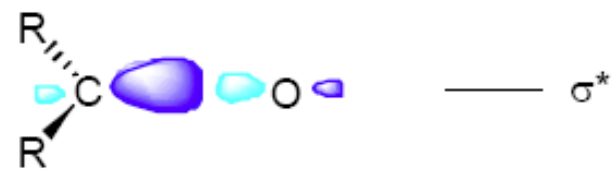
ligação π ou orbital π



=

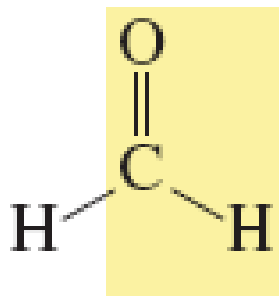


↑
ENERGIA

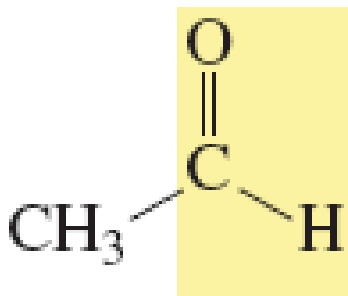


5) Nomenclatura de aldeídos

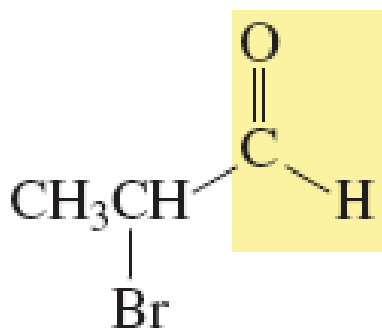
Dá-se o nome da cadeia carbônica com o sufixo “al”.



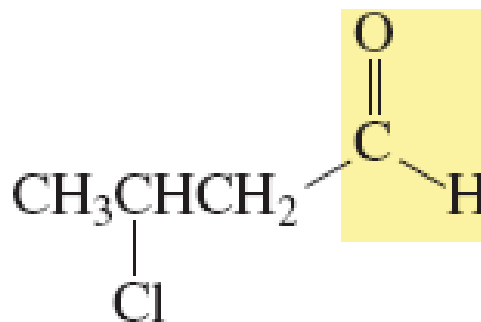
Metanal
(Formaldeído)



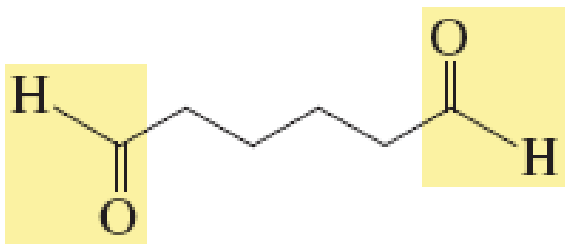
Etanal
(Acetaldeído)



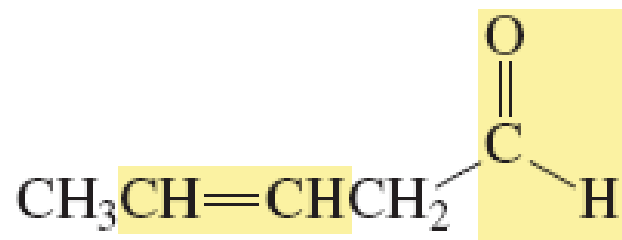
2-bromopropanal
(α -bromopropionaldeído)



3-clorobutanal
(β - clorobutiraldeído)

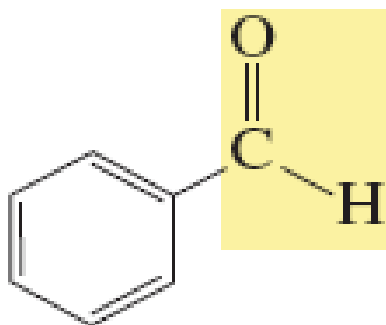


Hexanodial

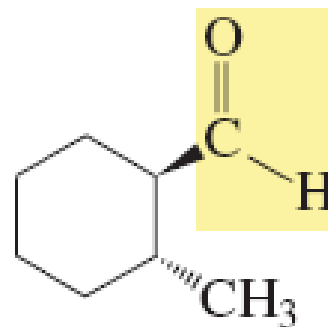


3-pentenal

Atenção:



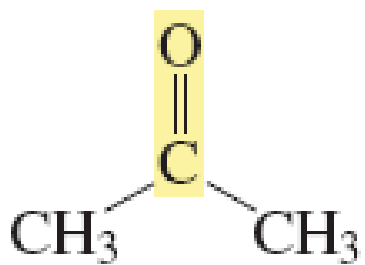
Benzenocarbaldeído
(Benzaldeído)



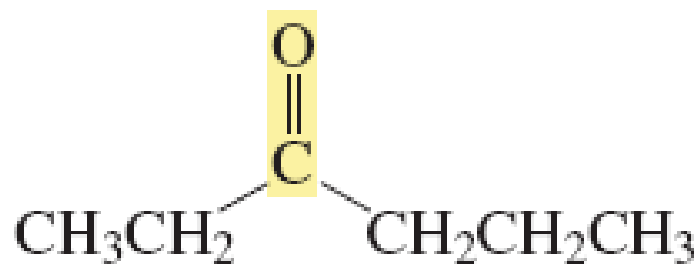
Trans-2-metilcicloexanocarbaldeído

6) Nomenclatura de cetonas

- Dá-se o nome da cadeia carbônica com o sufixo “ona”;
- Em cetonas com mais de quatro carbonos, deve-se indicar a posição do grupo carbonila.



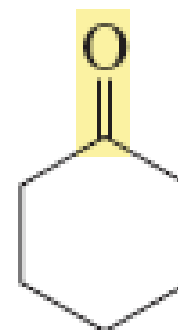
Propanona
Acetona
Dimetilcetona



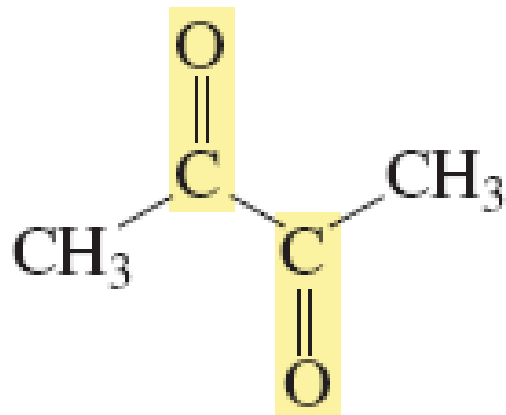
3-Hexanona
Etilpropilcetona



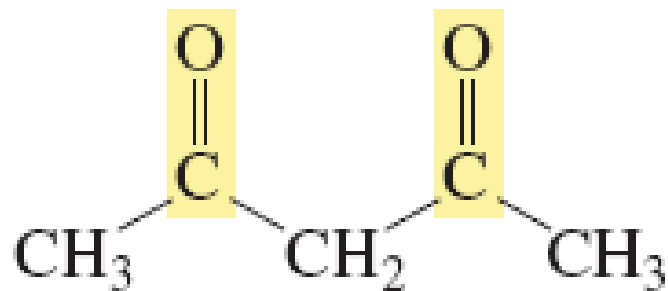
6-Metil-2-heptanona



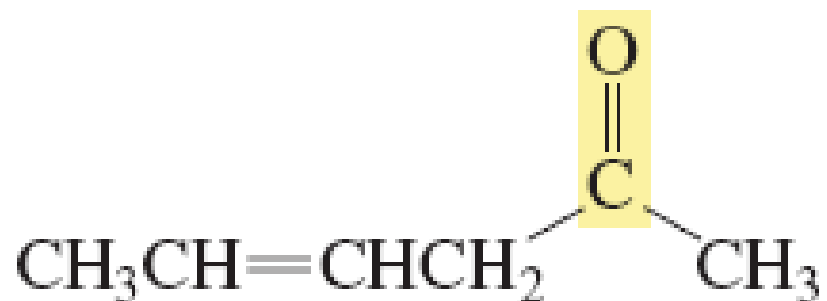
Cicloexanona



Butanodiona

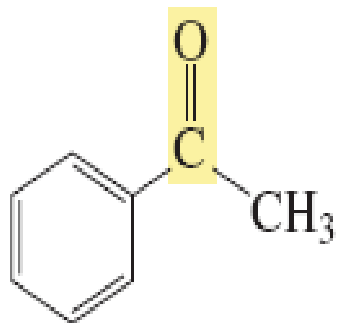


2,4-Butanodiona
acetilacetona

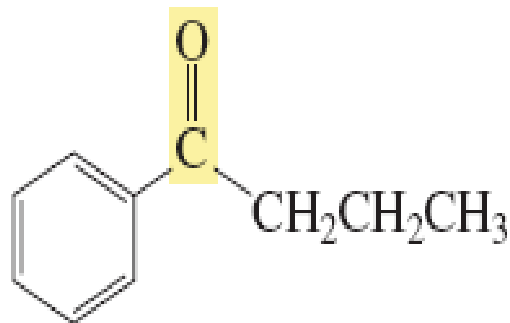


4-hexen-2-ona

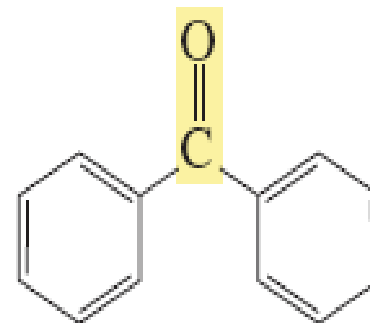
Nomes triviais



Acetofenona
Fenilmetilcetona

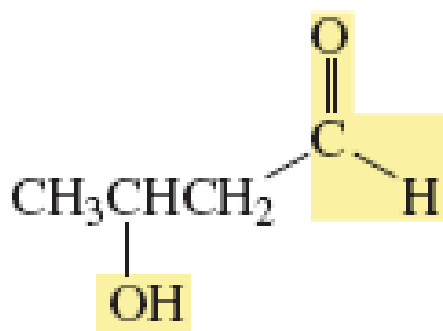


Butirofenona
Fenilpropilcetona

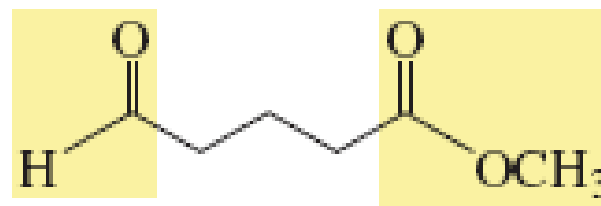


Benzofenona
difenilcetona

- **ORDEM DE PRIORIDADE QUANDO HOVER FUNÇÕES MISTAS NA MESMA MOLÉCULA**




3-Hidroxibutanal



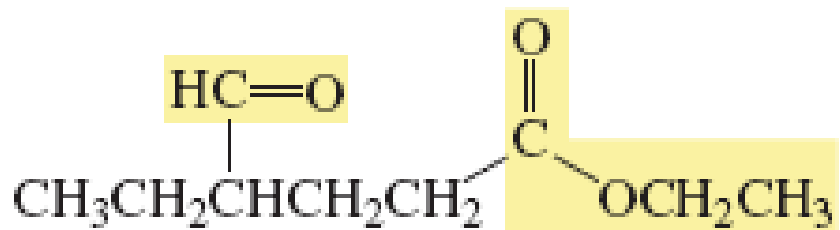
5-oxopentanoato de metila

ORDEM DE PRIORIDADE QUANDO HOUVER FUNÇÕES MISTAS NA MESMA MOLÉCULA

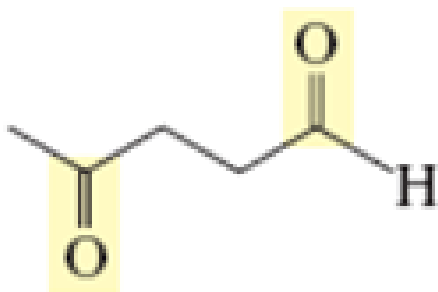


aumento de prioridade

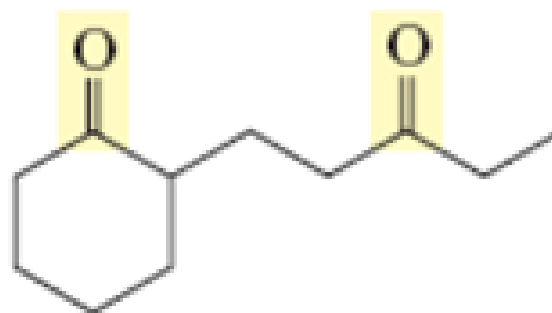
Classes	Sufixo do nome	Prefixo do nome
Ácido carboxílico	-óico (ácido no início)	Carboxi
Éster	-oato	Alcoxicarboxila
Amida	-amida	Amido
Nitrila	-nitrila	Ciano
Aldeído	-al	Oxo (=O)
Aldeído	-al	Formil ($-\text{CH}=\text{O}$)
Cetona	-ona	Oxo (=O)
Álcool	-ol	Hidroxi
Amina	-amina	Amino
Alceno	-eno	Alquenila
Alcino	-ino	Alquinila
Alcano	-ano	Alquila
Éter	—	Alcoxi
Haleto de alquila	—	Halo



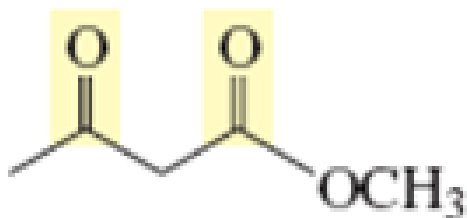
4-Formil-hexanoato de etila



4-oxopentanal

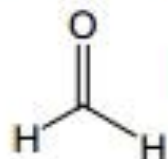


2-(3-oxopentil)-cicloexanona

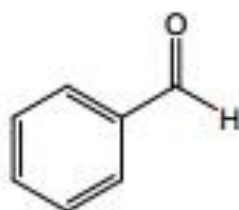


3-oxobutanoato de metila

Fontes e aplicações de aldeídos e cetonas



Formol: preservativo de espécimens biológicas e aplicado em indústria de plásticos e resinas (baquelite)



Benzaldeído: Ingredientes do aroma de amêndoas

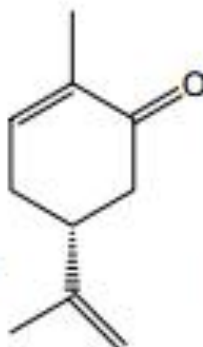


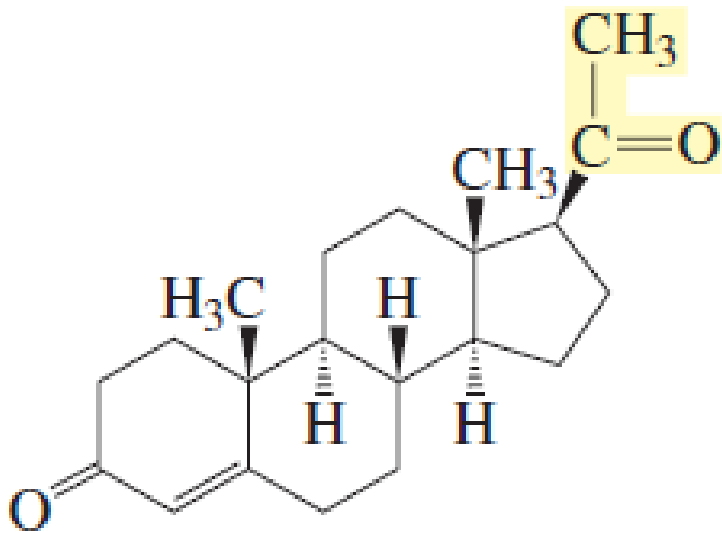
(+)-cânfora: *Cinnamomum camphora*
fins medicinais, inalantes

(R)-(-)-carvona

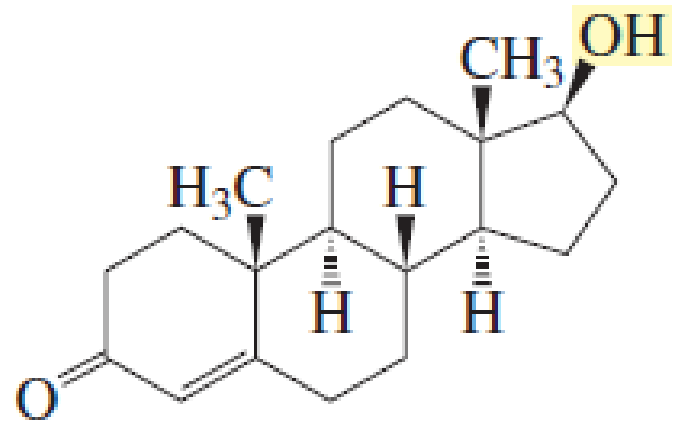
odor: hortelã

uso: pasta de dentes e confeitos

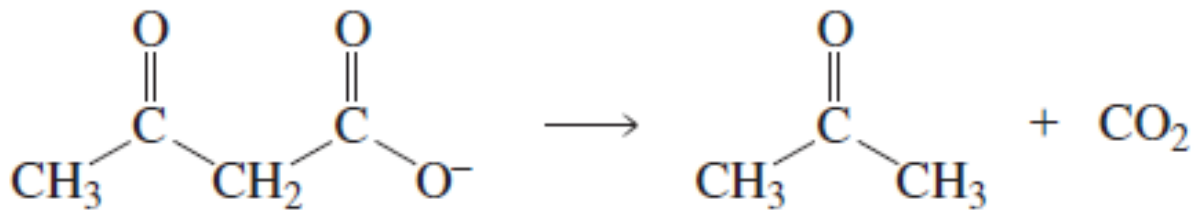




Progesterona
Hormônio sexual feminino



Testosterona
Hormônio sexual masculino



Conversão de acetoacetato em acetona (diabetes)

8-Propriedades Físicas de Aldeídos e Cetonas

Considerações sobre propriedades físicas de compostos carbonilados.

1- Ponto de ebulição:

a) polarização da carbonila → atração dipolo-dipolo

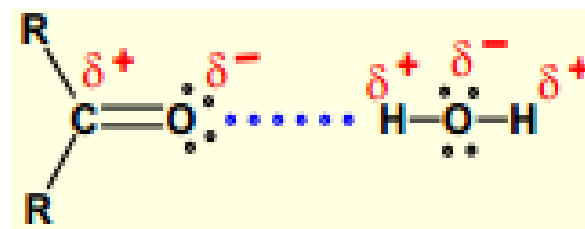
b) ausência de ligação O—H → impossibilidade para ligação hidrogênio

2- Solubilidade em água:

a) polarização da carbonila: favorável

a) ligação Hidrogênio com a água: favorável

c) cadeia carbônica: desfavorável (apolar e hidrofóbica)

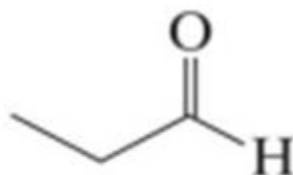


❖ PE mais elevados que hidrocarbonetos correspondentes;

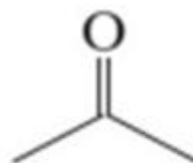
❖ PE mais baixos que álcoois de cadeias carbônicas correspondentes



Butano
PE = -0,5 °C
PM = 58



Propanal
PE = 49 °C
PM = 58



Acetona
PE = 56,1 °C
PM = 58



1-Propanol
PE = 97,2 °C
PM = 60

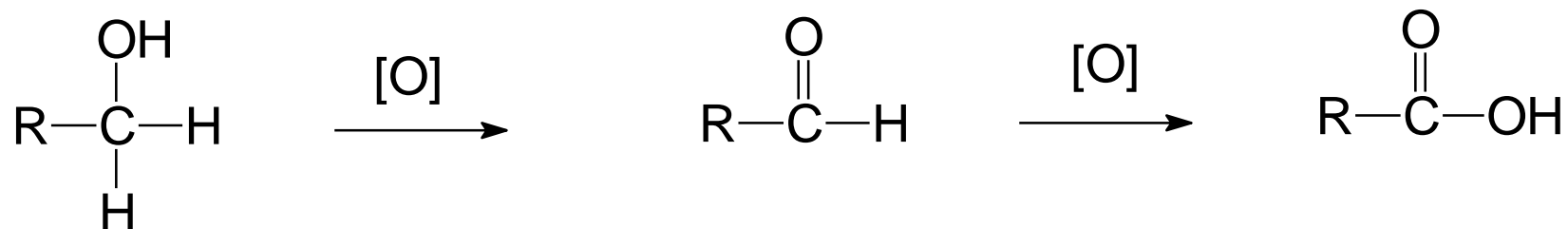
Propriedades Físicas de aldeídos e cetonas

Composto	Fórmula	Ponto de ebulição °C	Solubilidade em água g/100ml em H₂O
Formaldeído	HCHO	-21	Miscível
Acetaldeído	CH ₃ CHO	20	Miscível
Propionaldeído	CH ₃ CH ₂ CHO	49	16
Butiraldeído	CH ₃ CH ₂ CH ₂ CHO	76	7
Valeraldeído	CH ₃ CH ₂ CH ₂ CH ₂ CHO	103	Pouco solúvel
Benzaldeído	C ₆ H ₅ CHO	178	0,3
Acetona	CH ₃ COCH ₃	56	Miscível
Etil metil cetona	CH ₃ COCH ₂ CH ₃	80	26
Metil propil cetona	CH ₃ COCH ₂ CH ₂ CH ₃	102	6,3
Dietil cetona	CH ₃ CH ₂ COCH ₂ CH ₃	101	5

7)Preparação de aldeídos

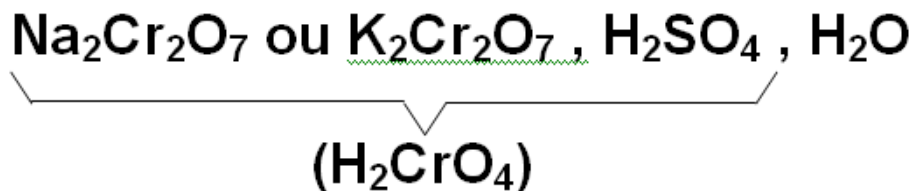
7.1) Processos oxidativos

Remoção de átomo de hidrogênio e formação de uma nova ligação entre átomos já presentes na molécula ou entre um átomo presente e um átomo de oxigênio.



Alguns agentes oxidantes: Cromo (+6) e Manganês (+7 e +4)

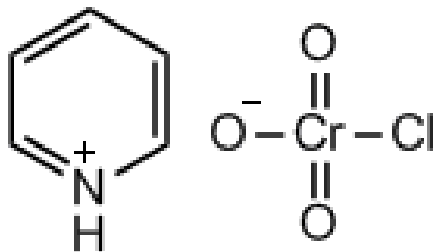
• **Compostos solúveis em água**



• **Compostos pouco solúveis em água**



C₆H₅N⁺CrO₃⁻Cl-PCC: clorocromato de piridínium, CH₂Cl₂



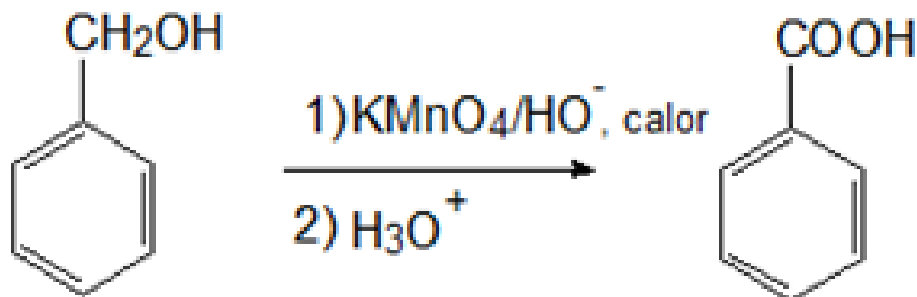
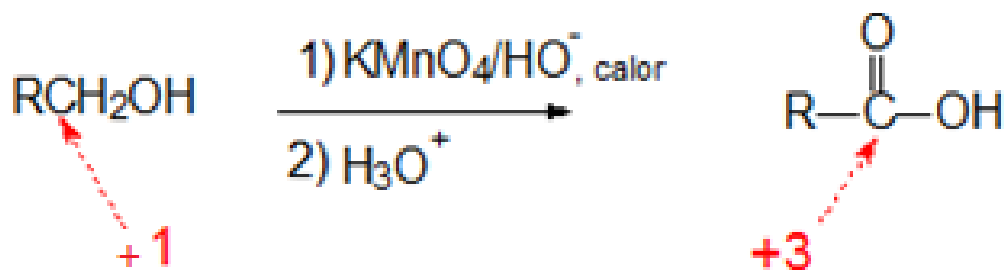
Vantagens da oxidação com CrO₃: Não reage com as ligações π C–C

Desvantagens da oxidação com o Manganês: oxida os álcoois primários diretamente a ácidos carboxílicos e reage com as ligações π C–C .

A) Oxidação de Álcoois Primários

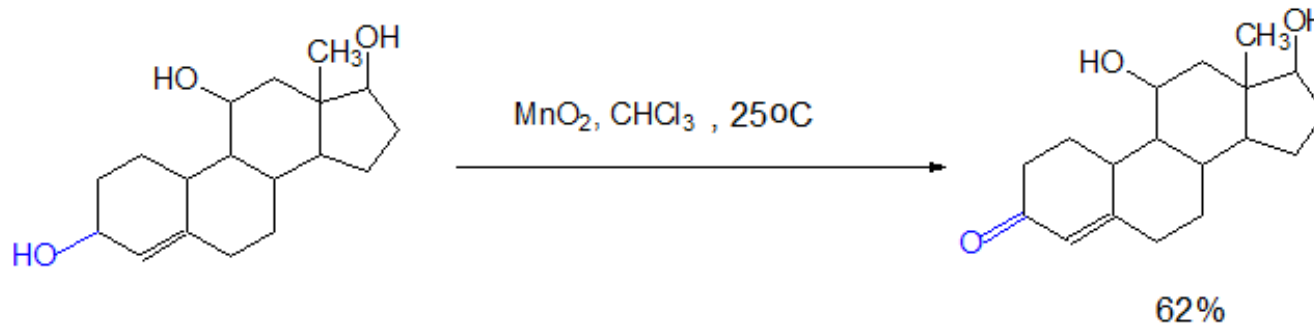
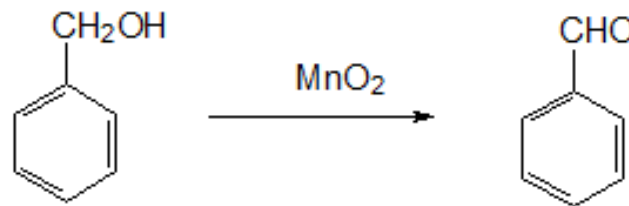
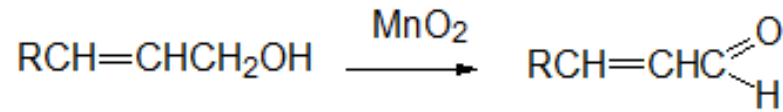
A.1- Processos oxidativos com manganês

- Processo com permanganato de potássio

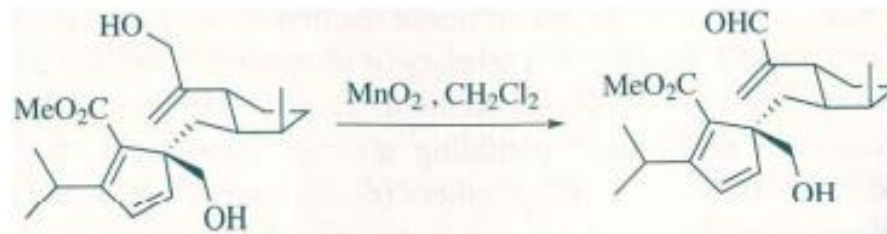


• Processo seletivo de oxidação de hidroxila alílica e benzílica

Oxidação com MnO_2 : oxida os álcoois alílicos e benzílicos, não afeta as ligações π .



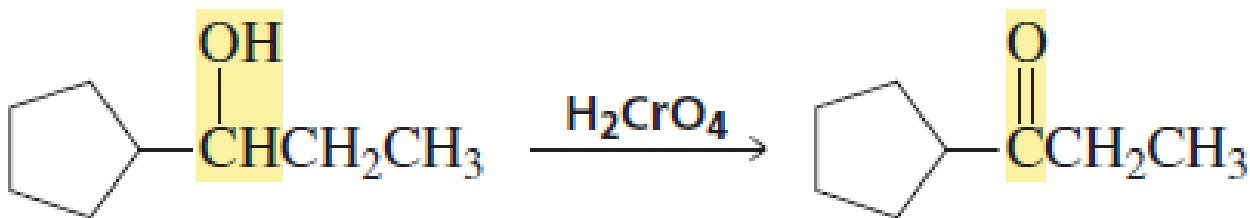
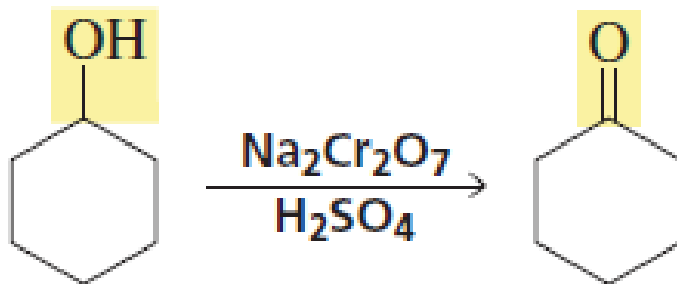
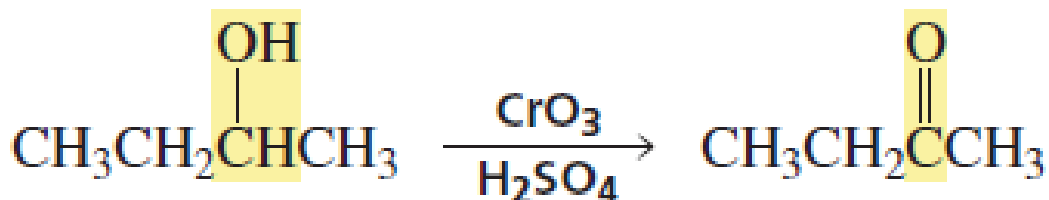
Reações quimiosseletivas



A reação ocorre via intermediários radiculares, o que explica maior reatividade de álcoois alílicos.

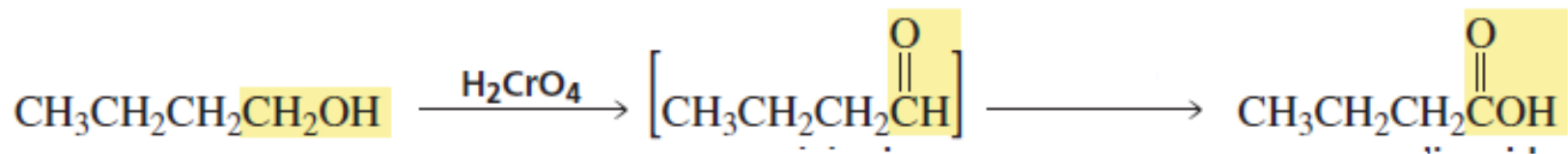
A.2- Processos oxidativos com cromo

O produto formado tem dependência com a espécie oxidante utilizada e com o substrato.



Álcoois secundários

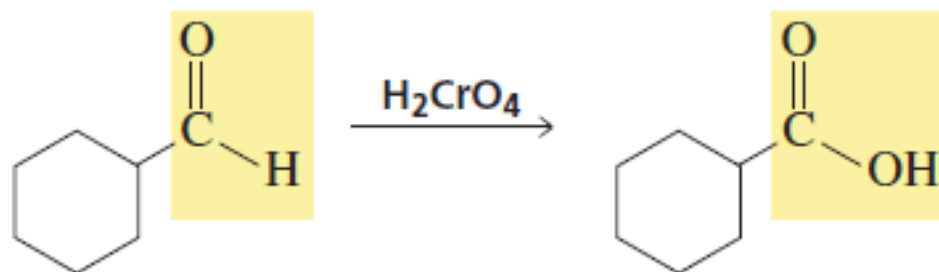
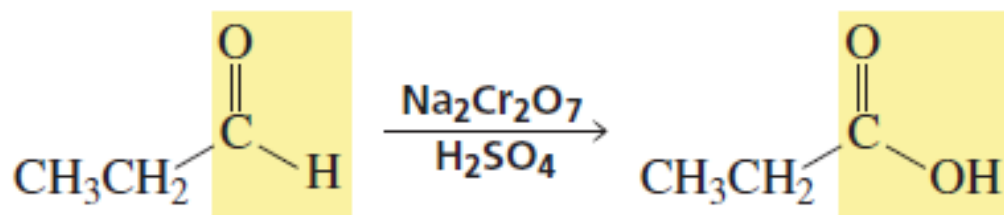
Cetonas



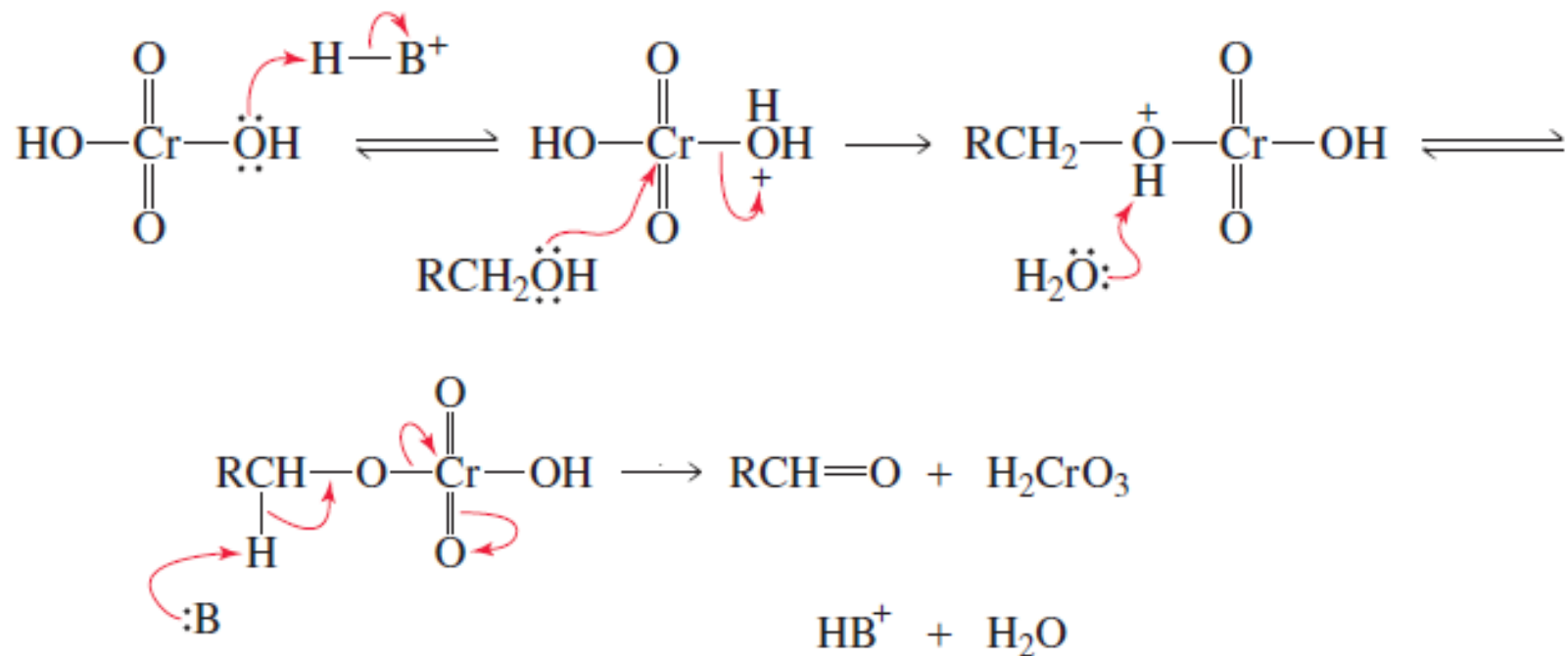
Álcool primário

Aldeído

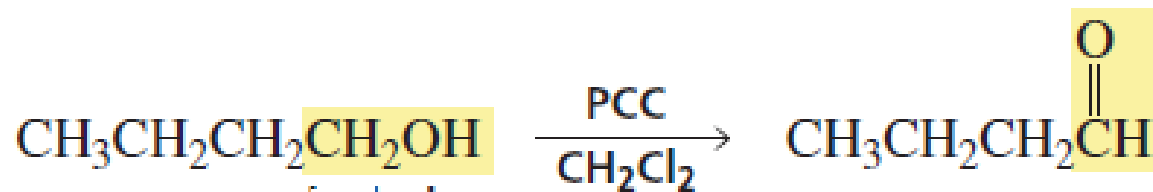
Ácido carboxílico



Mecanismo



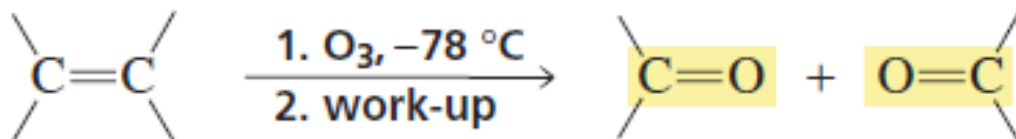
Oxidação seletiva



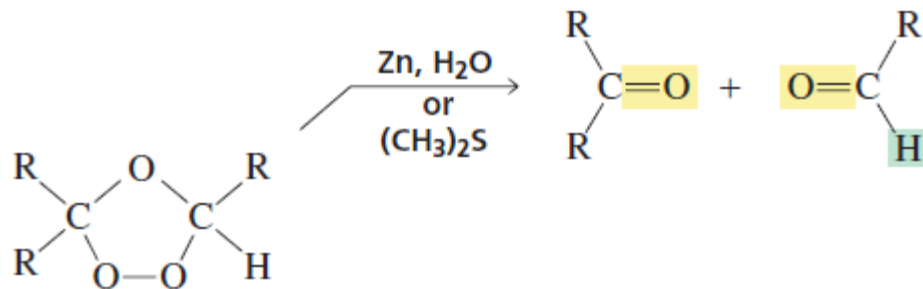
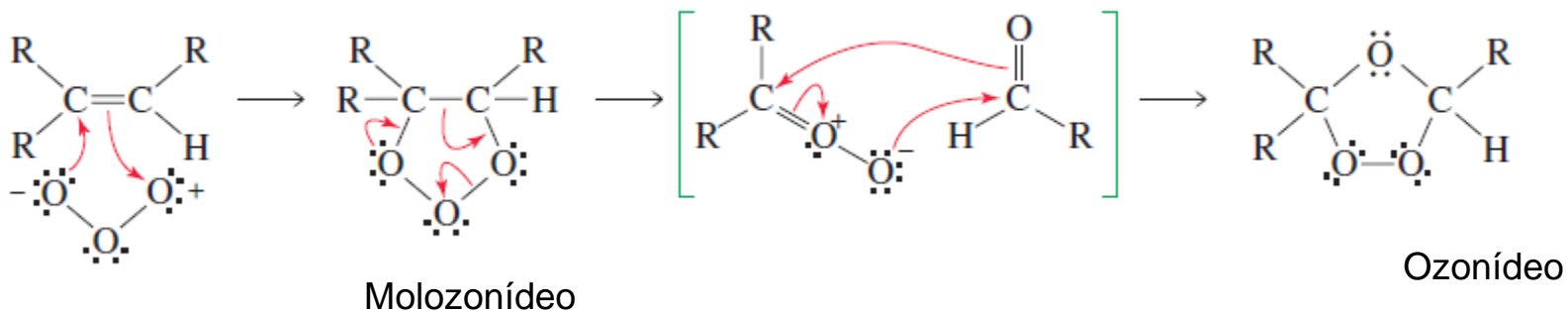
B) A PARTIR DE ALQUENOS

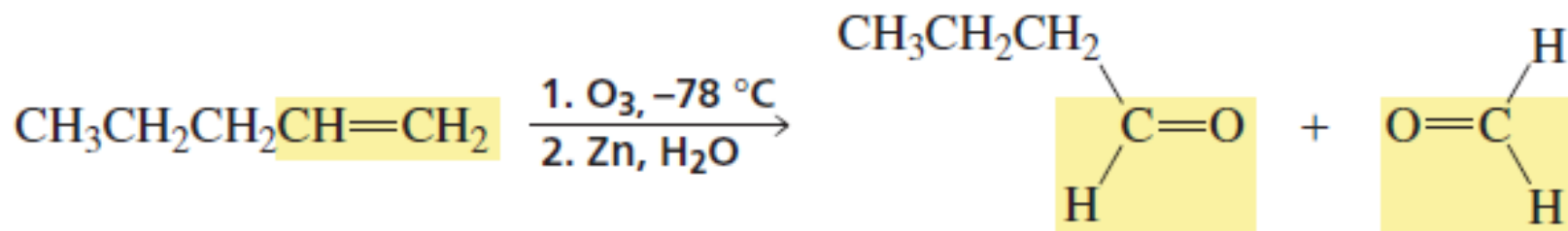
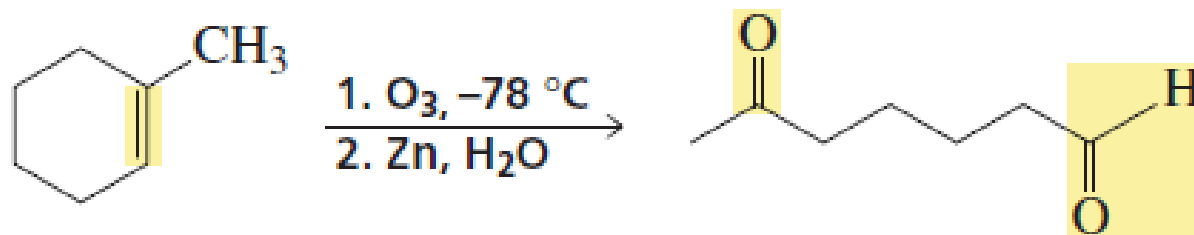
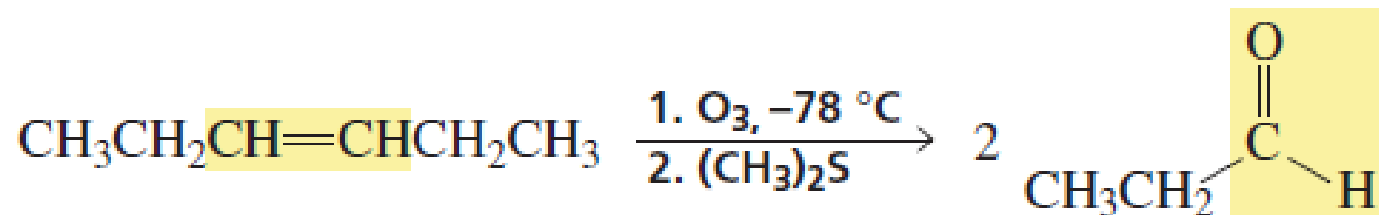
B.1- Processos oxidativos com ozônio

Nestes processos ocorre a clivagem da dupla ligação, e a função do produto depende da natureza do substrato.

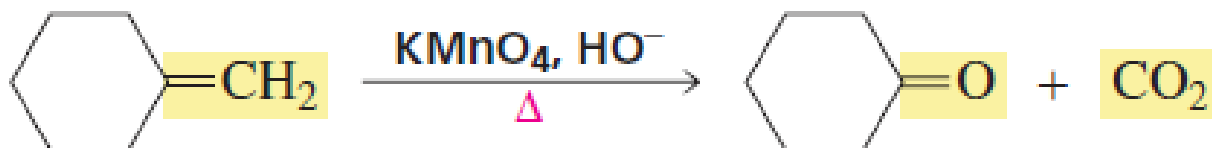
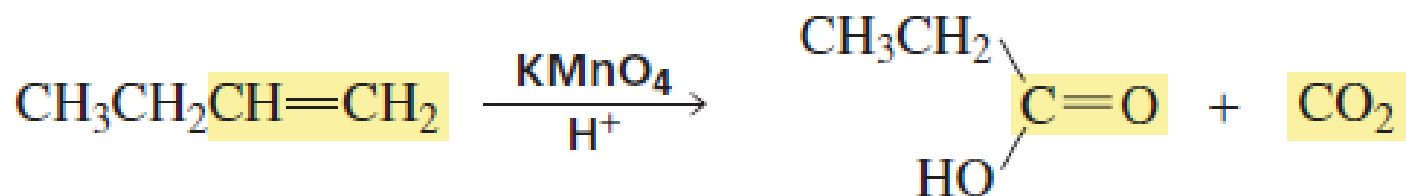
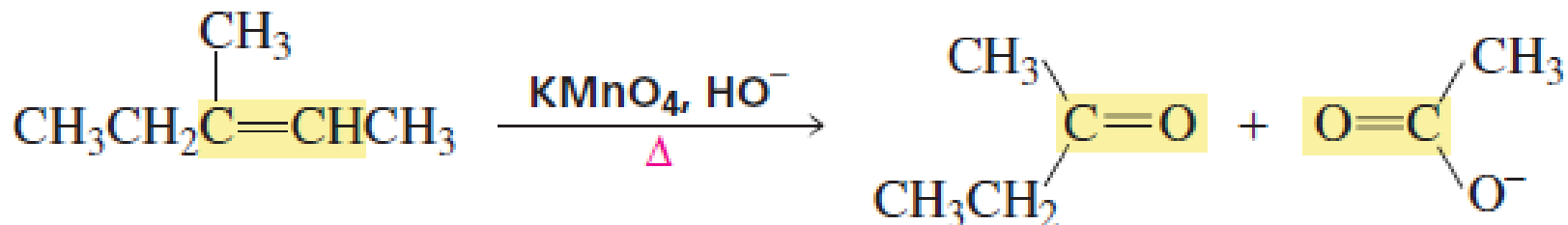


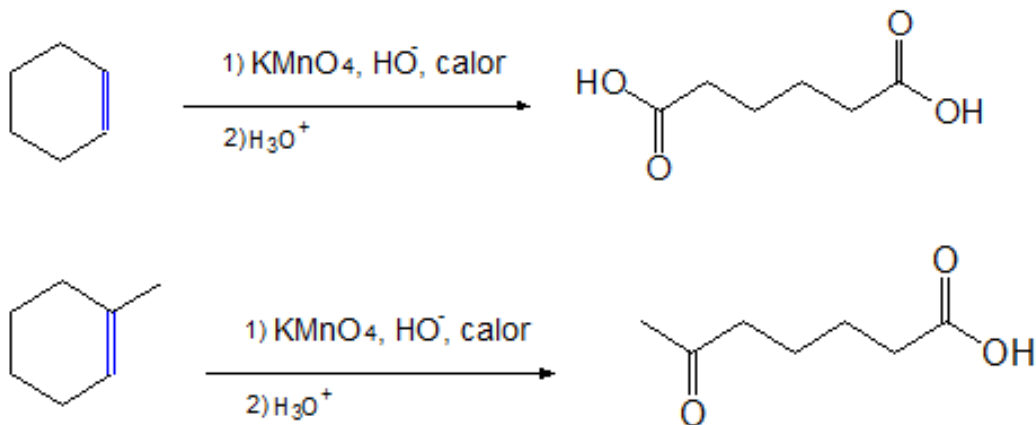
Mecanismo





B.2) Processos oxidativos com permanganato de potássio, em meio básico, a quente.

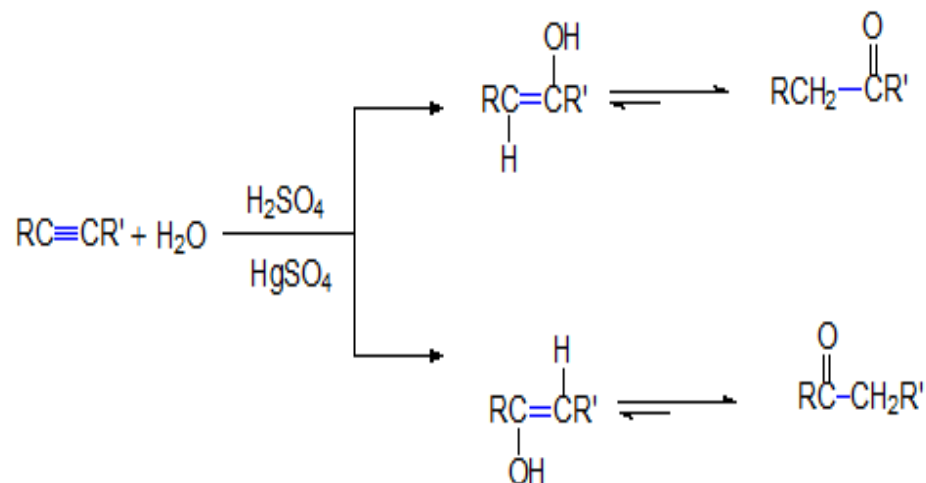




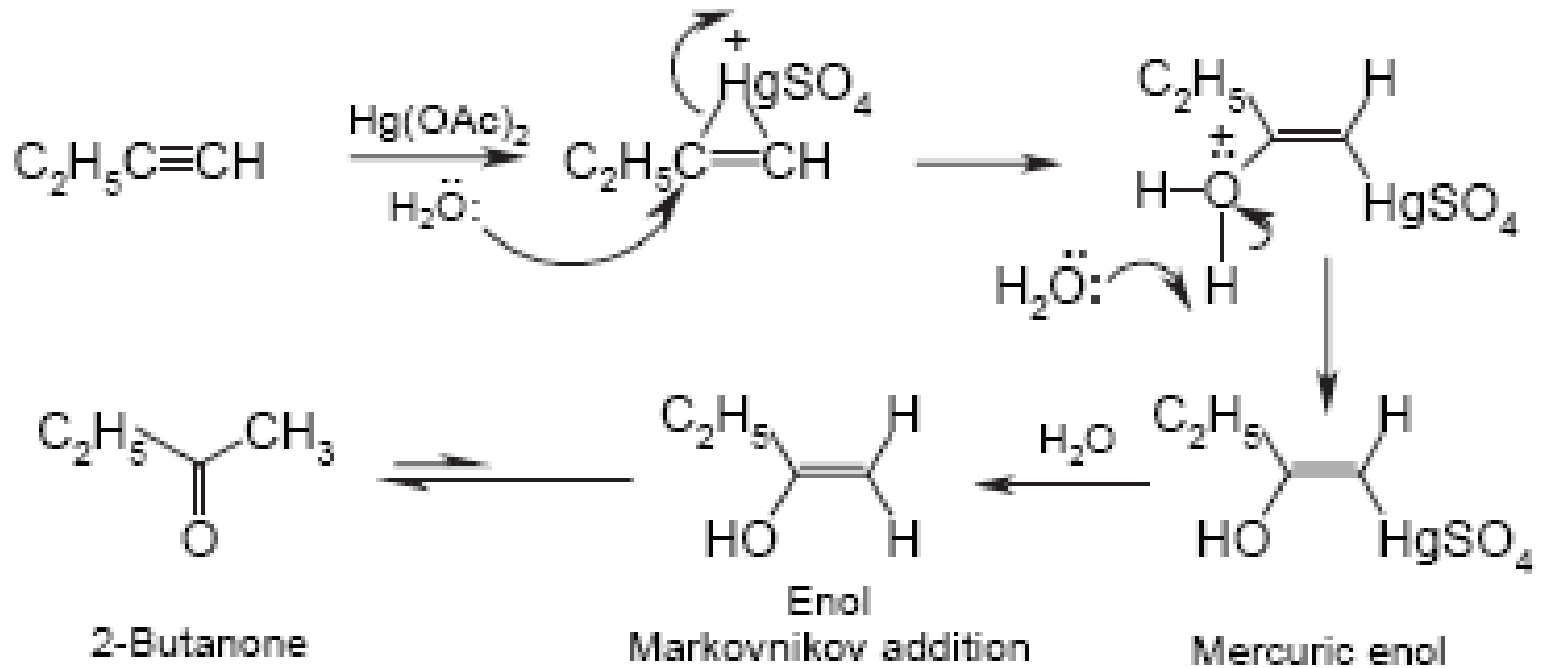
Preparação de cetonas

C) A PARTIR DE ALQUINOS

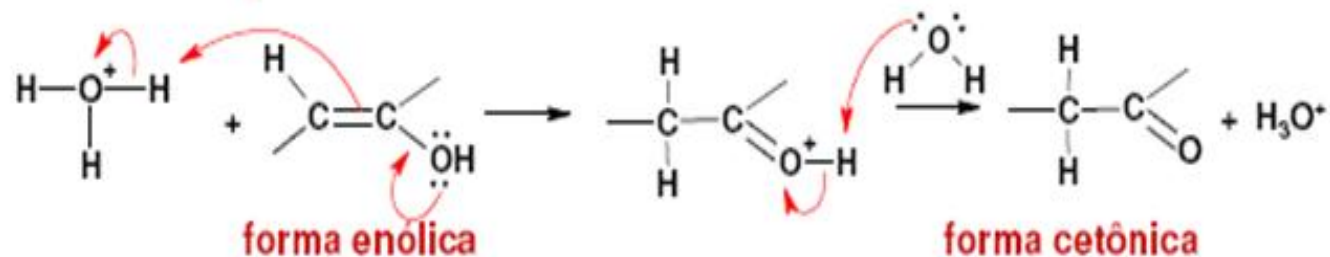
C.1- Processos oxidativos com água em meio ácido (Markovnikov)



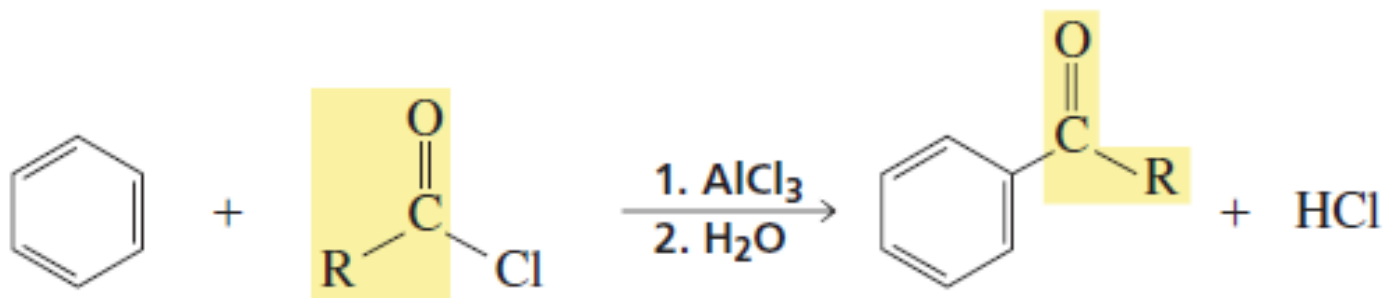
Mecanismo



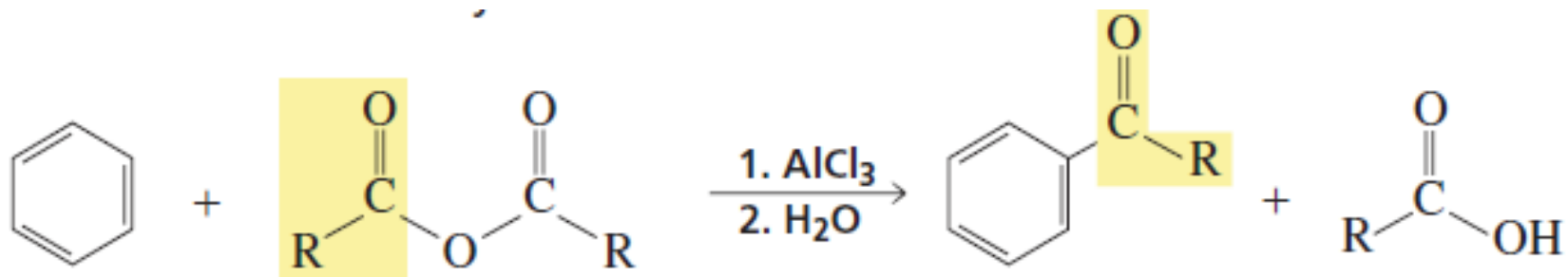
Tautomerização ceto-enólica



D) Alquilação de Friedel Crafts



Haleto de acila

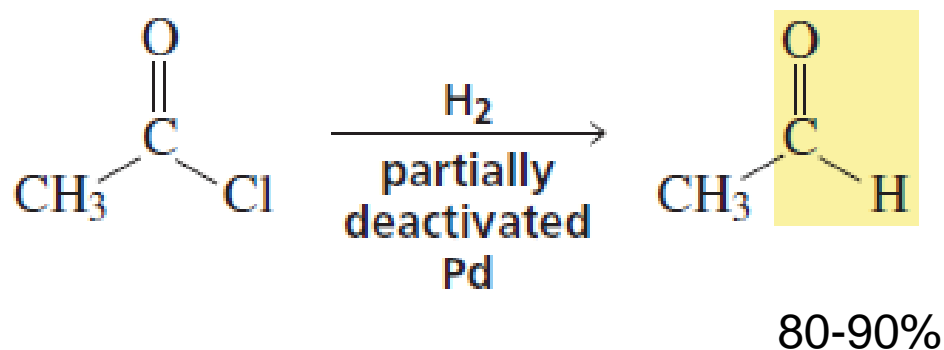


Anidrido de ácido

7.2-Processos redutivos

A- Redução Catalítica

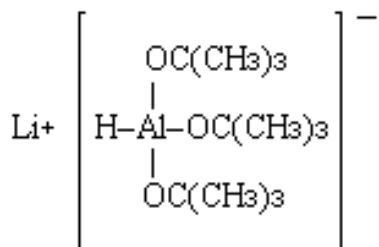
A.1) Redução de Rosemund



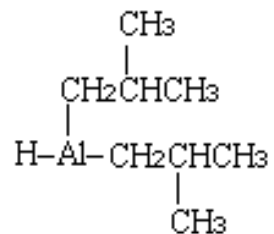
A.2) Redução com hidretos

Os melhores resultados são obtidos quando se utiliza um cloreto de ácido na presença de um agente redutor estericamente impedido:

AGENTES REDUTORES



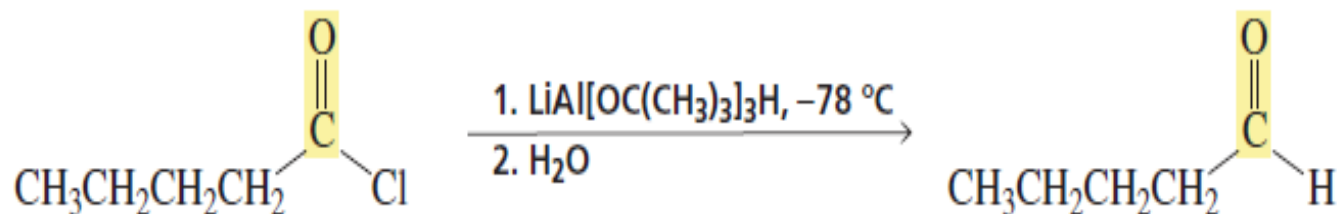
Hidreto de tri-terc
butoxialumínio e lítio



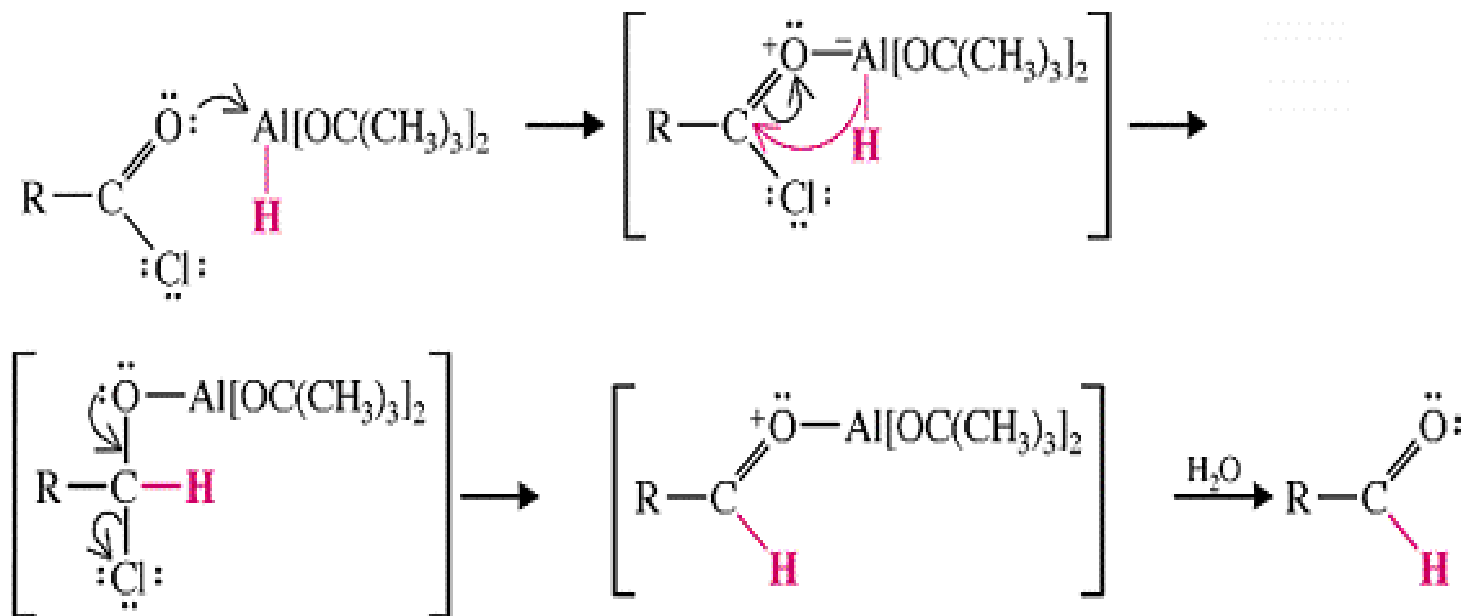
Hidreto de diisobutilalumínio
(DIBAL-H)



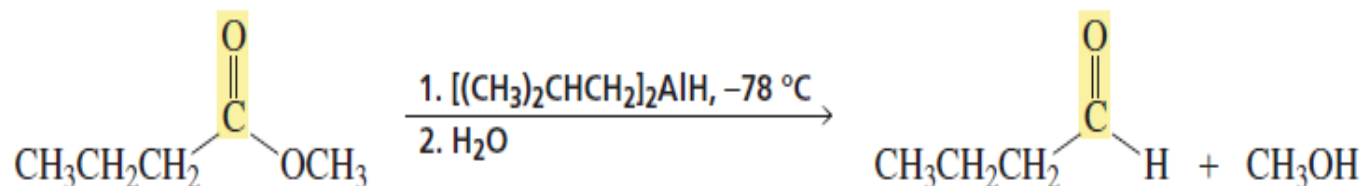
A.2.1) Redução de cloreto de ácido carboxílico



Proposta mecanística:



A.2.2) Redução de ésteres



A.2.3) Redução de nitrilas



Resumindo

