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IQSC USP

- Compostos Carbonílicos
  - Aldeídos e cetonas: estrutura, propriedades químicas e físico-químicas de compostos contendo o grupo carbonila.
  - Reações aldólicas
  - Ácidos carboxílicos e seus derivados
  - Adição e eliminação nucleofílica ao carbono acílico
  - Síntese e reações de compostos β-dicarbonilados
  - Aminas

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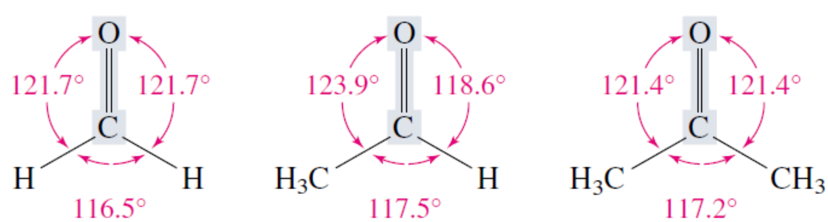
Estrutura & Ligação



Formaldehyde　　Acetaldehyde　　Acetone

$CH_3CH_2CH{=}CH_2$

1-Butene

Dipole moment: 0.3 D

$CH_3CH_2CH{=}O$

Propanal

Dipole moment: 2.5 D

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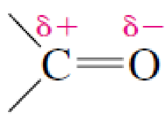
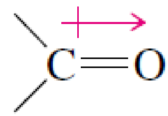
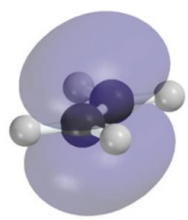
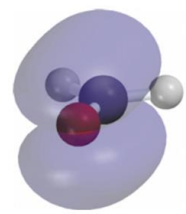


or





(*a*) Ethylene



(*b*) Formaldehyde

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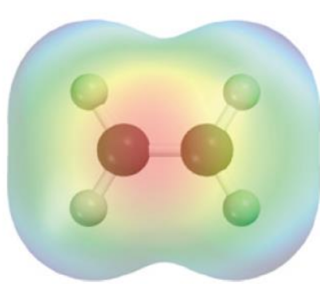
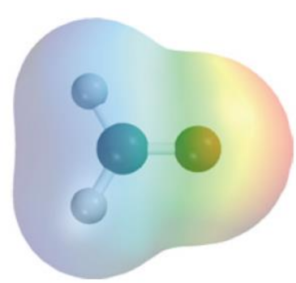
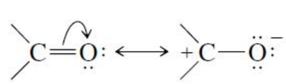


(*a*) Ethylene



(*b*) Formaldehyde



A B

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Estabilização da carbonila por grupos alquilas

	$CH_3CH_2CH_2CH(=O)$	$CH_3CH_2C(=O)CH_3$
	Butanal	2-Butanone
Heat of combustion:	2475 kJ/mol (592 kcal/mol)	2442 kJ/mol (584 kcal/mol)

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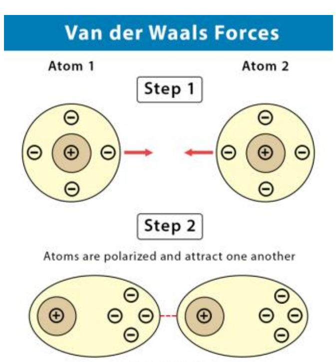
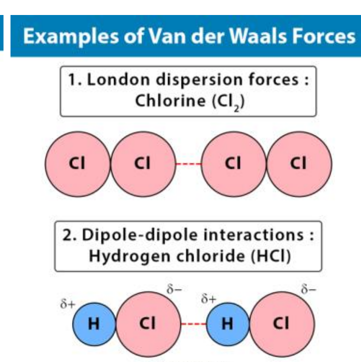
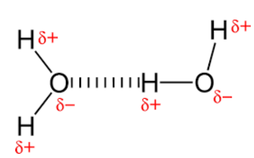
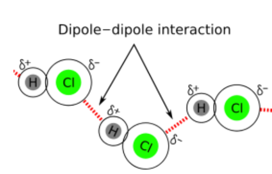
Propriedades Físicas

	$CH_3CH_2CH{=}CH_2$	$CH_3CH_2CH{=}O$	$CH_3CH_2CH_2OH$
	1-Butene	Propanal	1-Propanol
bp (1 atm)	−6°C	49°C	97°C
Solubility in water (g/100 mL)	Negligible	20	Miscible in all proportions









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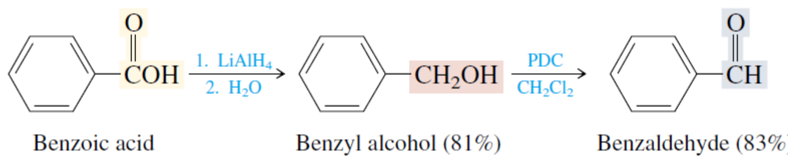
Fontes de aldeídos e cetonas

Síntese Química

$$\underset{\text{Carboxylic acid}}{RCO_2H} \xrightarrow{\text{reduce}} \underset{\text{Primary alcohol}}{RCH_2OH} \xrightarrow{\text{oxidize}} \underset{\text{Aldehyde}}{R\overset{O}{\overset{\|}{C}}H}$$



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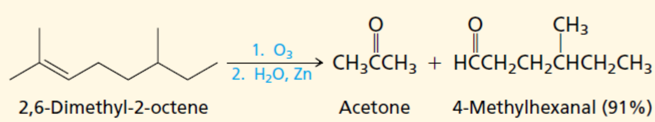
$$\underset{\text{Alkene}}{RR'C{=}CHR''} \xrightarrow[\text{2. } H_2O,\ Zn]{\text{1. } O_3} \underset{\text{Two carbonyl compounds}}{R\overset{O}{\overset{\|}{C}}R' + R''\overset{O}{\overset{\|}{C}}H}$$



$$\underset{\text{Alkyne}}{RC{\equiv}CR'} + H_2O \xrightarrow[HgSO_4]{H_2SO_4} \underset{\text{Ketone}}{R\overset{O}{\overset{\|}{C}}CH_2R'}$$

$$\underset{\text{1-Octyne}}{HC{\equiv}C(CH_2)_5CH_3} + H_2O \xrightarrow[HgSO_4]{H_2SO_4} \underset{\text{2-Octanone (91\%)}}{CH_3\overset{O}{\overset{\|}{C}}(CH_2)_5CH_3}$$

$$ArH + R\overset{O}{\overset{\|}{C}}Cl \xrightarrow{AlCl_3} Ar\overset{O}{\overset{\|}{C}}R + HCl \quad \text{or}$$

$$ArH + R\overset{O}{\overset{\|}{C}}O\overset{O}{\overset{\|}{C}}R \xrightarrow{AlCl_3} Ar\overset{O}{\overset{\|}{C}}R + RCO_2H$$

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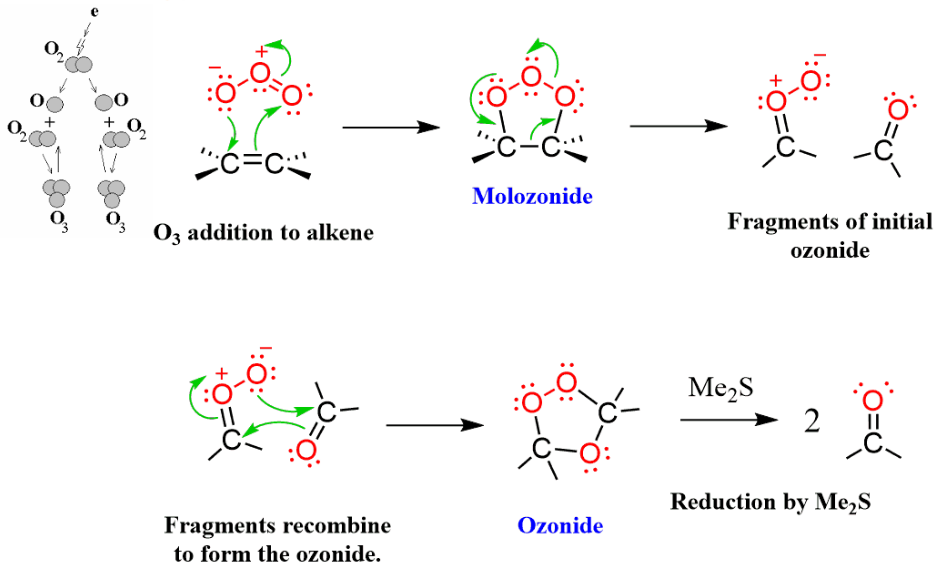
Ozonólise



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$$\mathrm{RCH_2OH} \xrightarrow[\mathrm{CH_2Cl_2}]{\text{PDC or PCC}} \mathrm{RCH{=}O}$$

Primary alcohol → Aldehyde

$$\mathrm{CH_3(CH_2)_8CH_2OH} \xrightarrow[\mathrm{CH_2Cl_2}]{\text{PDC}} \mathrm{CH_3(CH_2)_8CH{=}O}$$

1-Decanol → Decanal (98%)

$$\mathrm{RCH(OH)R'} \xrightarrow{\mathrm{Cr(VI)}} \mathrm{RC({=}O)R'}$$

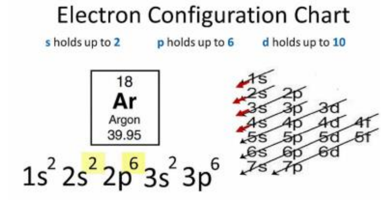
Secondary alcohol → Ketone

$$\mathrm{C_6H_5CH(OH)CH_2CH_2CH_2CH_3} \xrightarrow[\text{acetic acid/ water}]{\mathrm{CrO_3}} \mathrm{C_6H_5C({=}O)CH_2CH_2CH_2CH_3}$$

1-Phenyl-1-pentanol → 1-Phenyl-1-pentanone (93%)

Electron Configurations of Ions

Z	Element	e⁻ configuration		
19	K	$[Ar]4s^1$		
20	Ca	$[Ar]4s^2$		
22	Ti	$[Ar]3d^24s^2$		
24	Cr	$[Ar]3d^54s^1$	Cr^{3+}, Cr^{6+}	$[Ar]3d^3$, $[Ar]$
26	Fe	$[Ar]3d^64s^2$	Fe^{2+}, Fe^{3+}	$[Ar]3d^6$, $[Ar]3d^5$
29	Cu	$[Ar]3d^{10}4s^1$	Cu^+, Cu^{2+}	$[Ar]3d^{10}$, $[Ar]3d^9$
30	Zn	$[Ar]3d^{10}4s^2$	Zn^{2+}	$[Ar]3d^{10}$
31	Ga	$[Ar]3d^{10}4s^24p^1$	Ga^{3+}	$[Ar]3d^{10}$
35	Br	$[Ar]3d^{10}4s^24p^5$	Br^-	$[Kr]$



half-filled and filled subshells are energetically favored

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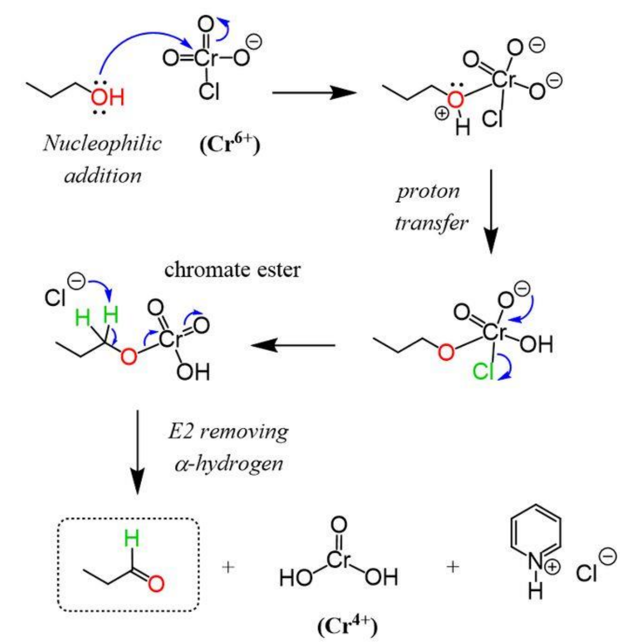
Pyridinium Chlorochromate (PCC) Oxidation Mechanism



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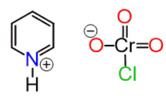
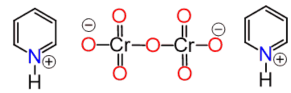
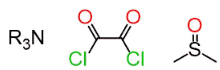
The Most Common Mild Oxidizing Agents



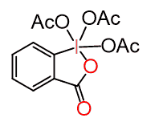
PCC



PDC



Swern



Dess-Martin

Dess-Martin periodinane (DMP)

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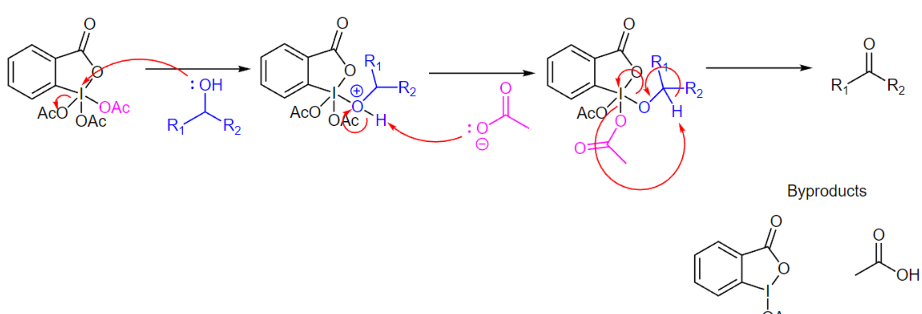
A primeira etapa do mecanismo envolve o álcool reagente atacando o átomo de iodo (V) e eliminando um grupo de saída acetato (AcO$^-$) para formar um intermediário de periodinato.



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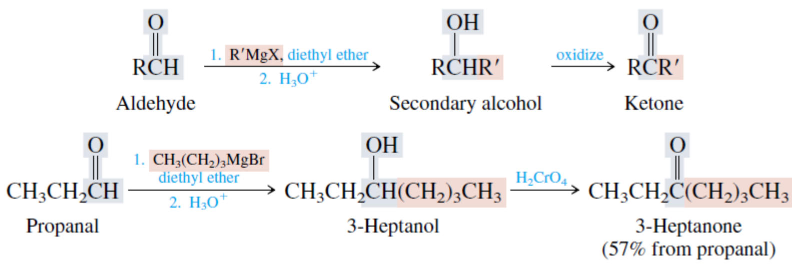
Para cetonas, formação C-C



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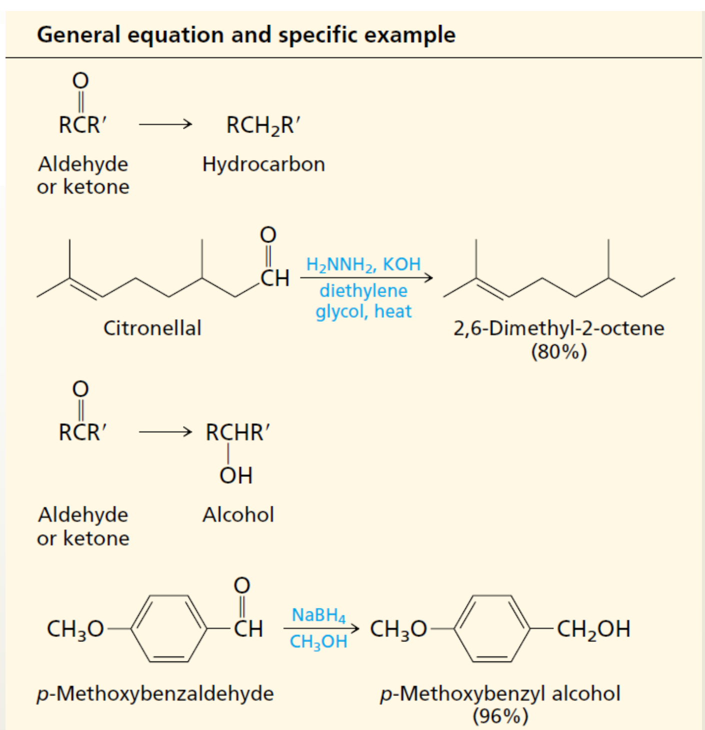
Reações de Aldeídos e Cetonas



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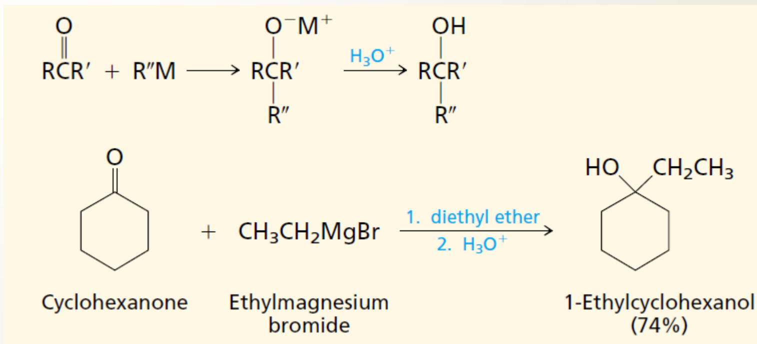

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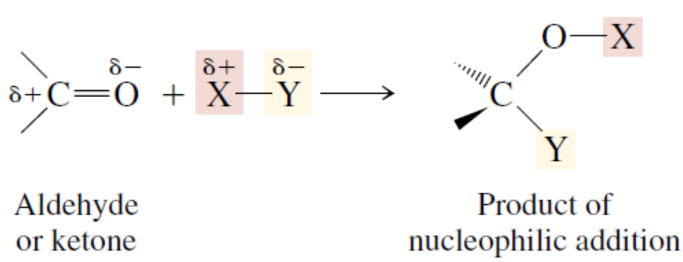
Propriedade química mais importante do grupo carbonila: reação de adição nucleofílica



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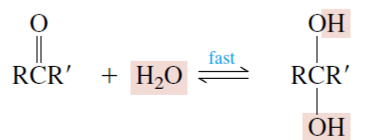
Hidratação de Aldeídos e Cetonas



Aldehyde or ketone   Water   Geminal diol (hydrate)

$$K_{hydr} = \frac{[\text{hydrate}]}{[\text{carbonyl compound}][\text{water}]}$$

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Constantes de equilíbrio (K_{hydr}) para hidratação de alguns aldeídos e cetonas

Carbonyl compound	Hydrate	K_{hydr}*	Percent conversion to hydrate†
$H\overset{\overset{O}{\|}}{C}H$	$CH_2(OH)_2$	41	99.96
$CH_3\overset{\overset{O}{\|}}{C}H$	$CH_3CH(OH)_2$	1.8×10^{-2}	50
$(CH_3)_3C\overset{\overset{O}{\|}}{C}H$	$(CH_3)_3CCH(OH)_2$	4.1×10^{-3}	19
$CH_3\overset{\overset{O}{\|}}{C}CH_3$	$(CH_3)_2C(OH)_2$	2.5×10^{-5}	0.14

$^*K_{hydr} = \dfrac{[\text{hydrate}]}{[\text{carbonyl compound}][\text{water}]}$. Units of K_{hydr} are M^{-1}.

†Total concentration (hydrate plus carbonyl compound) assumed to be 1 M. Water concentration is 55.5 M.

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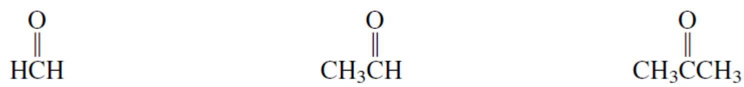
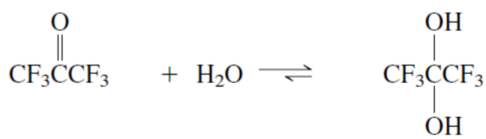
Considere primeiramente os efeitos eletrônicos

Increasing stabilization of carbonyl group; decreasing K for hydration



Formaldehyde (almost completely hydrated in water) | Acetaldehyde (comparable amounts of aldehyde and hydrate present in water) | Acetone (hardly any hydrate present in water)



$K_{hydr} = 22{,}000$

Hexafluoroacetone | Water | 1,1,1,3,3,3-Hexafluoro-2,2-propanediol

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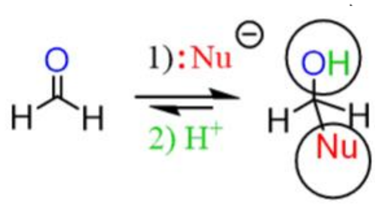
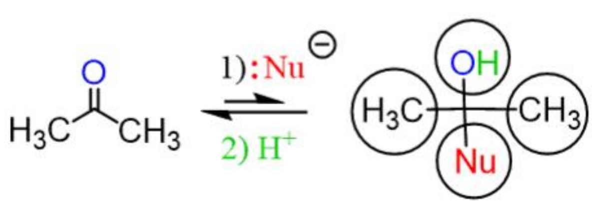
Efeitos estéricos



unhindered

Hy(ne



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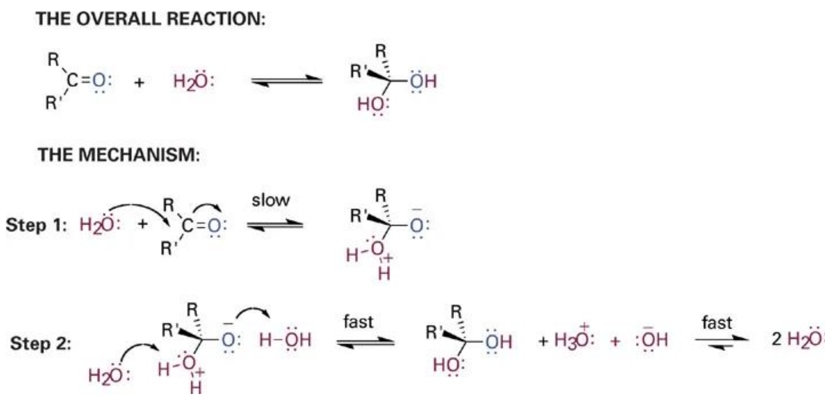
Mecanismo de hidratação



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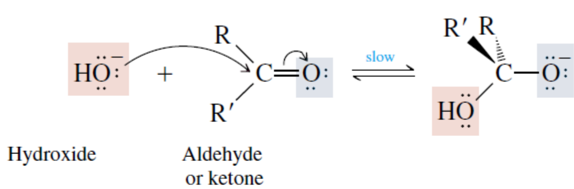
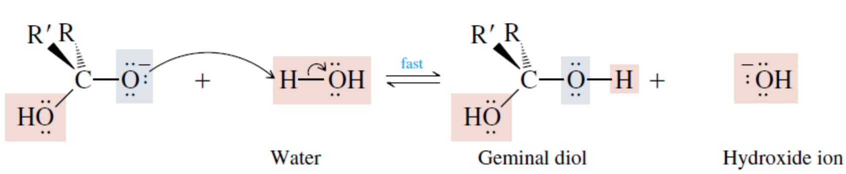
Mecanismo de hidratação em solução básica

Step 1: Nucleophilic addition of hydroxide ion to the carbonyl group



Step 2: Proton transfer from water to the intermediate formed in the first step



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Trajetória de Bürgi-Dunitz

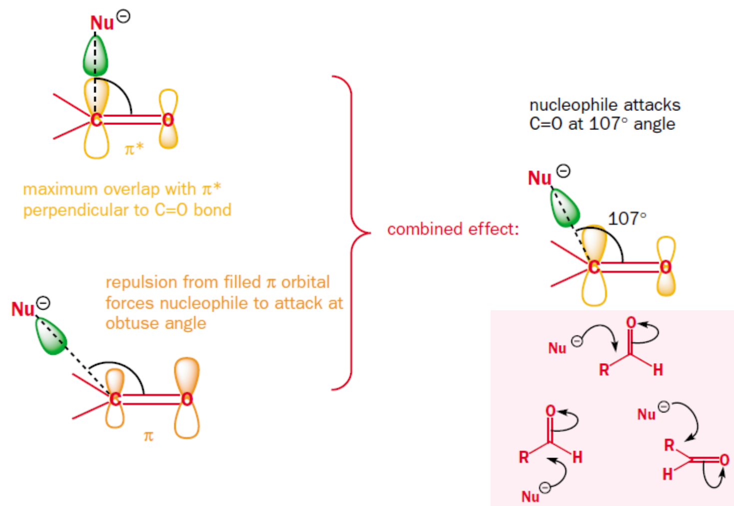

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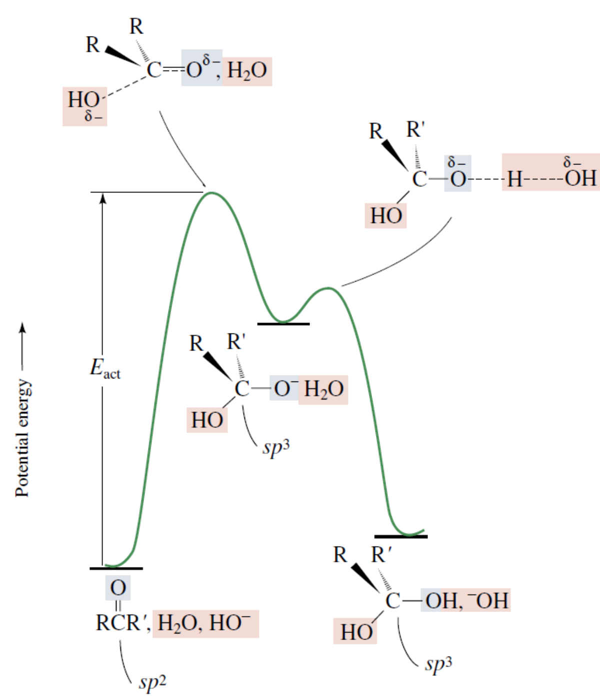
Diagrama de Energia Potencial para a reação de hidratação base-catalisada



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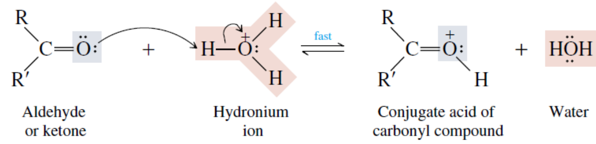
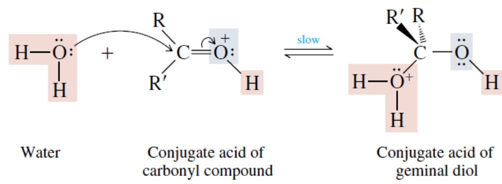
Mecanismo em solução ácida: íon hidrônio catalítico

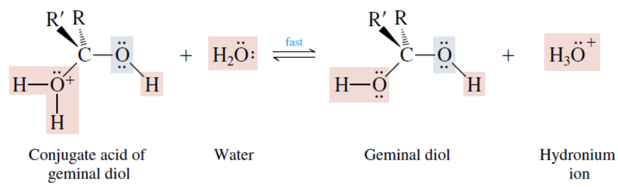
Step 1: Protonation of the carbonyl oxygen



Step 2: Nucleophilic addition to the protonated aldehyde or ketone



Step 3: Proton transfer from the conjugate acid of the geminal diol to a water molecule



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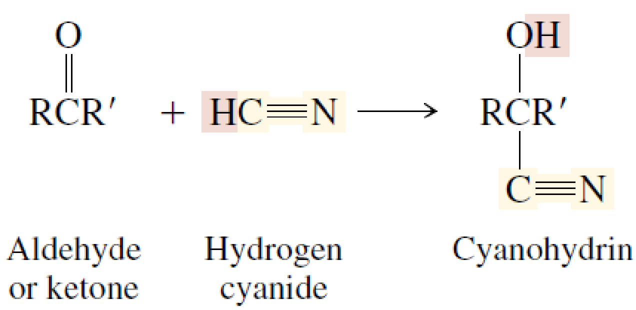
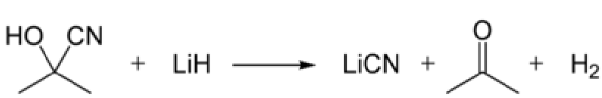
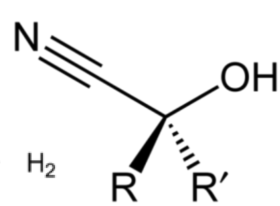
Formação da cianidrina







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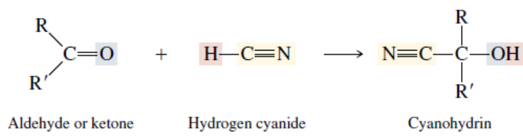
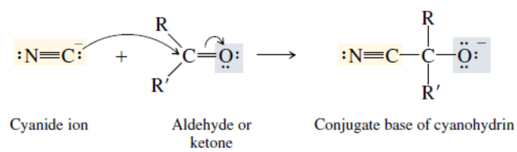
Mecanismo que usa HCN catalítico

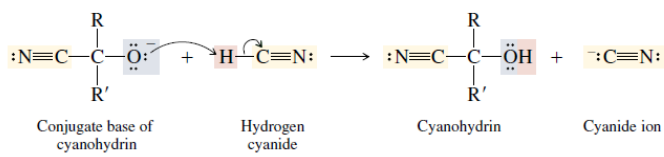
The overall reaction:

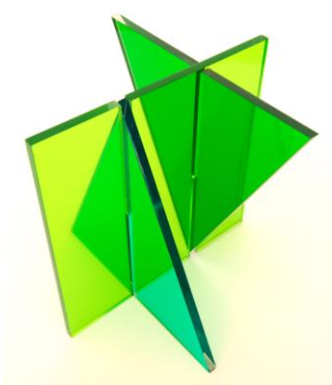


Step 1: Nucleophilic attack by the negatively charged carbon of cyanide ion at the carbonyl carbon of the aldehyde or ketone. Hydrogen cyanide itself is not very nucleophilic and does not ionize to form cyanide ion to a significant extent. Thus, a source of cyanide ion such as NaCN or KCN is used.

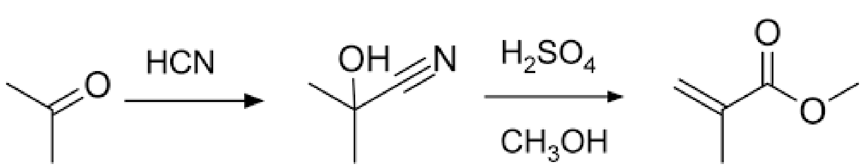


Step 2: The alkoxide ion formed in the first step abstracts a proton from hydrogen cyanide. This step yields the cyanohydrin product and regenerates cyanide ion.





Importante para a produção em larga escala do acrílico, o poli(metil metacrilato) (PMMA).



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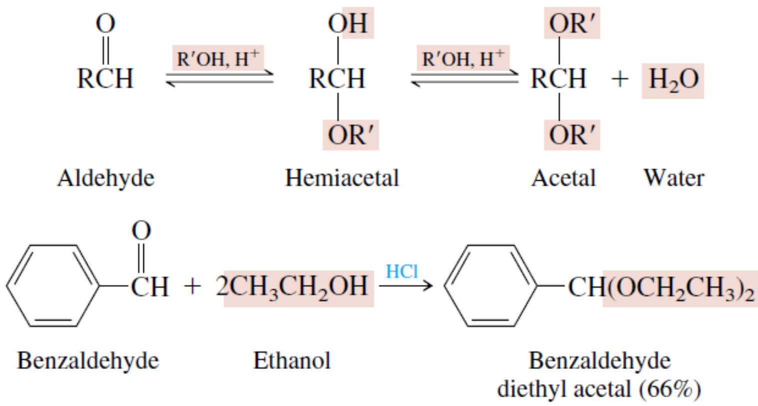
Formação de Acetal



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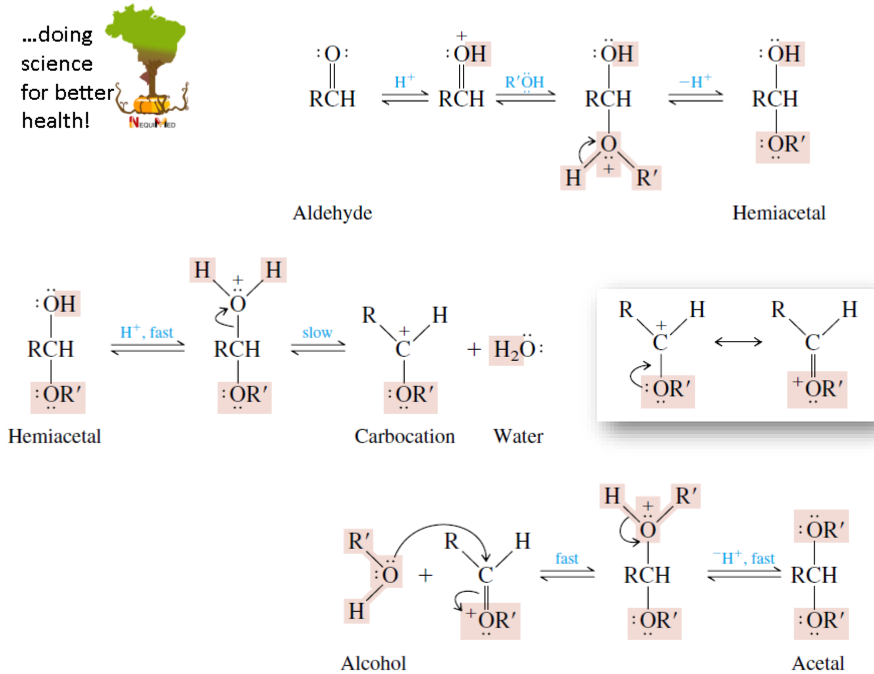

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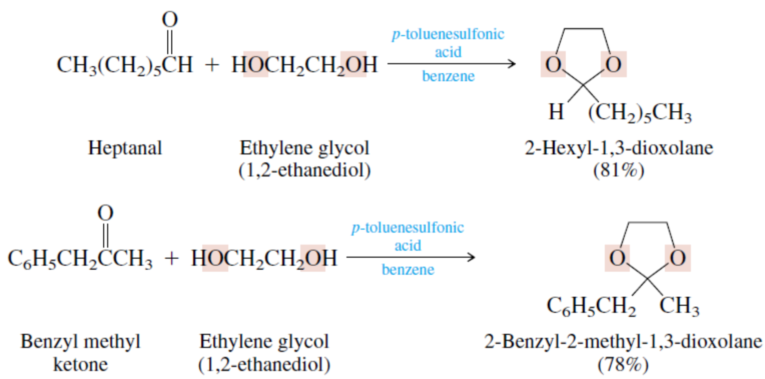
Acetais cíclicos



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Hidrólise de acetais

$$\underset{\text{Acetal}}{\mathrm{R}\overset{\displaystyle \mathrm{OR''}}{\underset{\displaystyle \mathrm{OR''}}{\mathrm{C}}}\mathrm{R'}} + H_2O \xrightleftharpoons{H^+} \underset{\text{Aldehyde or ketone}}{\mathrm{R}\overset{\displaystyle \mathrm{O}}{\overset{\|}{\mathrm{C}}}\mathrm{R'}} + \underset{\text{Alcohol}}{2\mathrm{R''OH}}$$