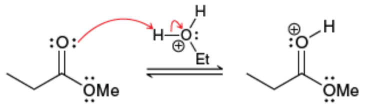
Gabarito da Lista de exercícios de fixação sobre Ácidos carboxílicos e derivados
1012020 - Química Orgânica II (2023) – Farmácia Noturno

1. Escreva o mecanismo das transformações abaixo:

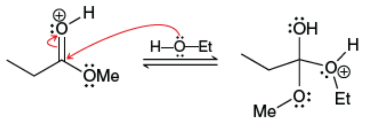
a)

Acidic conditions are employed in this case, so we must avoid formation of a strong base. This requirement dictates that we must draw proton transfer steps at all three possible points. The mechanism must begin with a proton transfer in order to protonate the carbonyl group, rendering it a better electrophile:

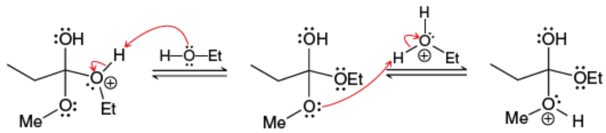


Notice the proton source that we show to protonate the carbonyl group. We cannot show EtOH as the proton source, because transfer of a proton from ethanol would involve creation of an ethoxide ion, which should be avoided in acidic conditions.

The next step is a nucleophilic attack, in which ethanol functions as a nucleophile and attacks the protonated carbonyl group, forming a tetrahedral intermediate that does not bear a negative charge.

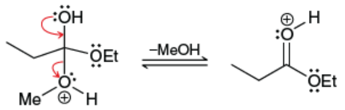


The tetrahedral intermediate formed in this step cannot immediately expel methoxide to re-form the carbonyl, because methoxide is a strong base, which should be avoided in acidic conditions. So, we must first protonate the methoxy group. However, protonating the methoxy group would involve the formation of two positive charges, which should also be avoided. As a result, two separate proton transfers are required.

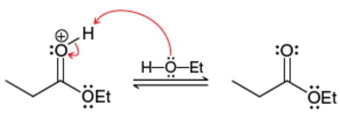


First, a proton is removed to form a new tetrahedral intermediate without a charge, followed by protonation of the methoxy group. Be careful not to show ethoxide as a base in the first step (remember—no strong bases in acidic conditions).

The next step is loss of the leaving group to re-form the carbonyl:

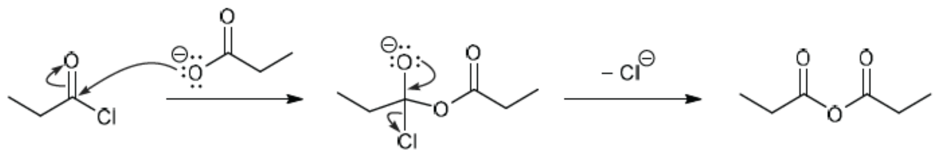


Finally, a proton transfer is drawn to remove the positive charge and form the product.

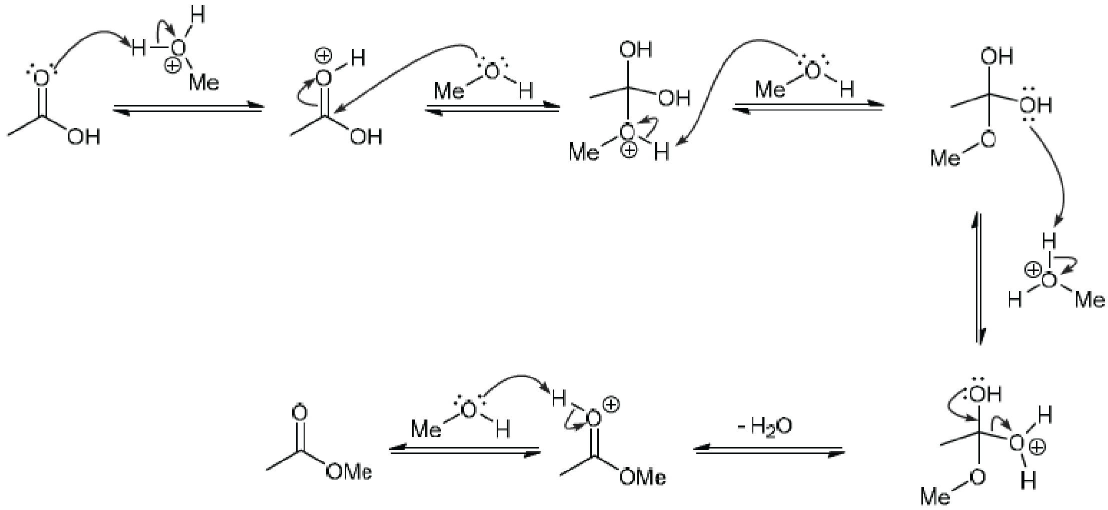


b)

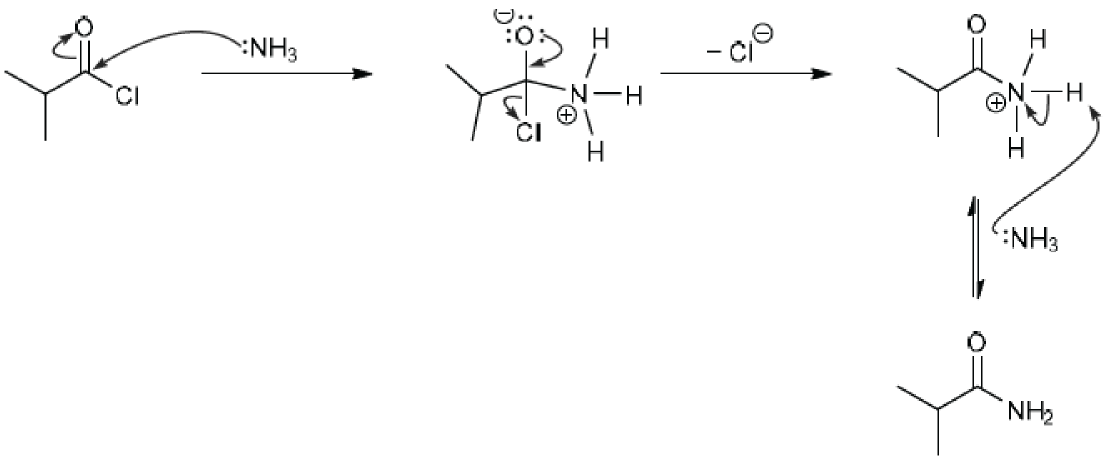
(a) This mechanism has two steps: 1) nucleophilic attack, and 2) loss of a leaving group. The first step (nucleophilic attack), requires two curved arrows, which show the carboxylate ion functioning as a nucleophile and attacking the electrophilic carbonyl group, resulting in a tetrahedral intermediate. In step two (loss of a leaving group), the carbonyl group is reformed and chloride leaves, as shown with two curved arrows, resulting in the formation of an anhydride, as shown.



c)



d)



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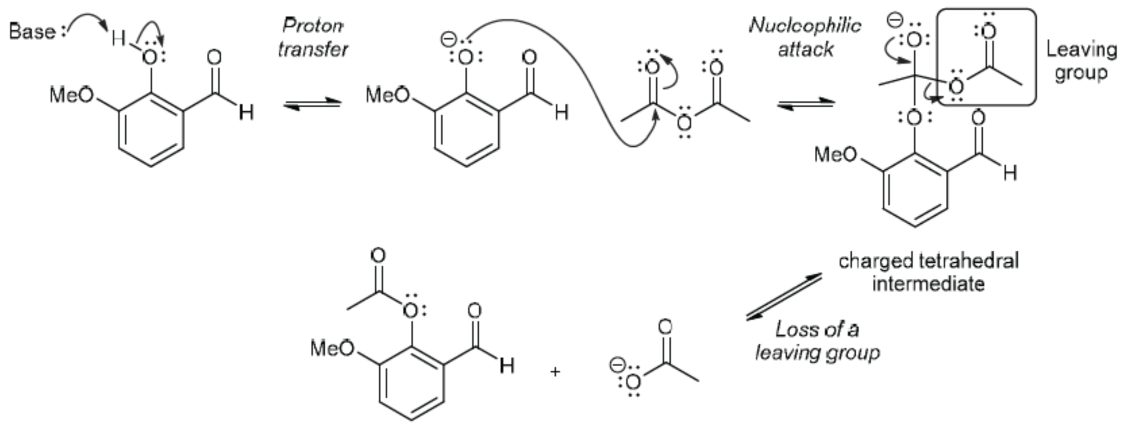
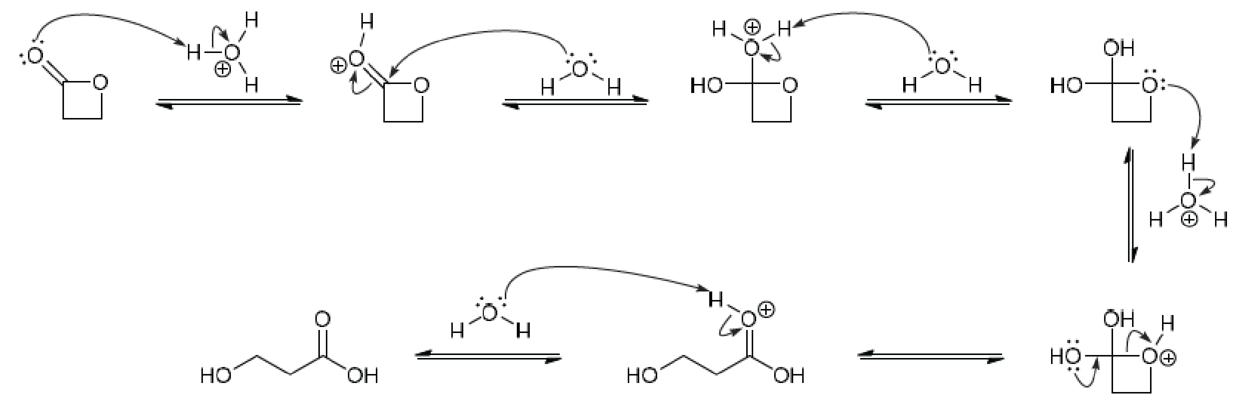
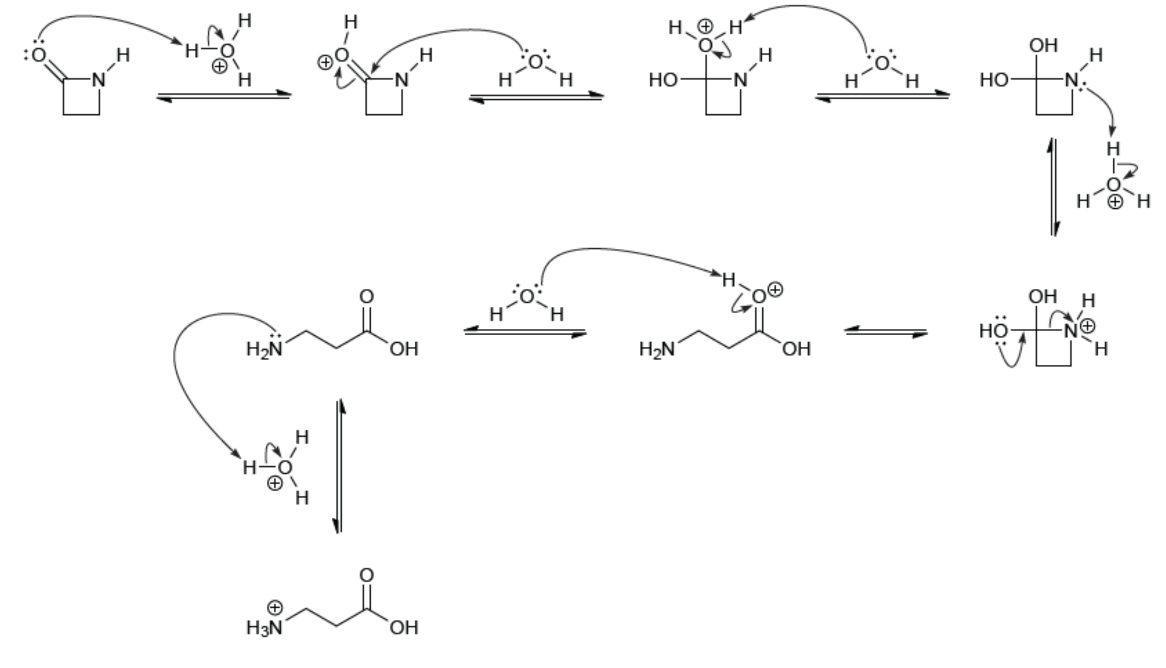

Base
Proton transfer
Nucleophilic attack
Leaving group
charged tetrahedral intermediate
Loss of a leaving group

f)



g)



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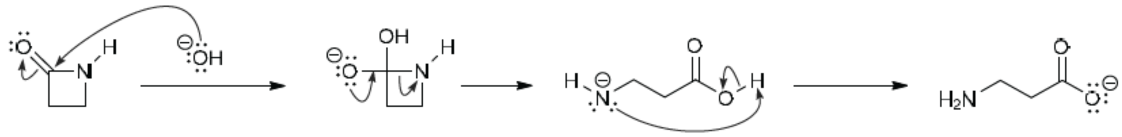
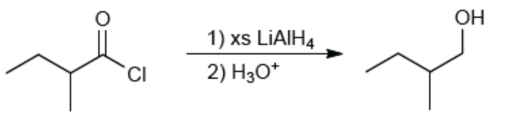


2. Escreva os produtos das reações abaixo.

a)



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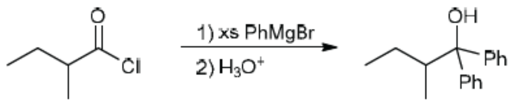

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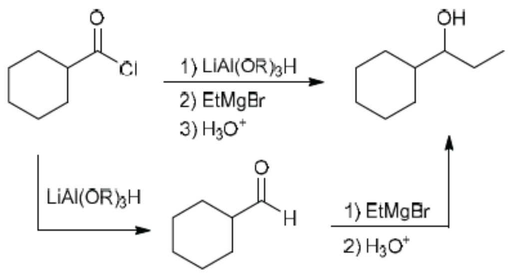

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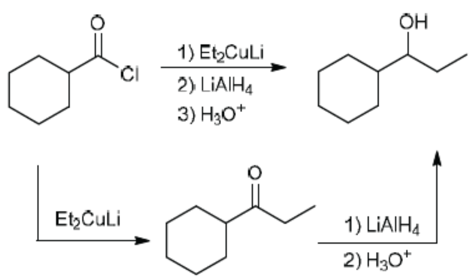

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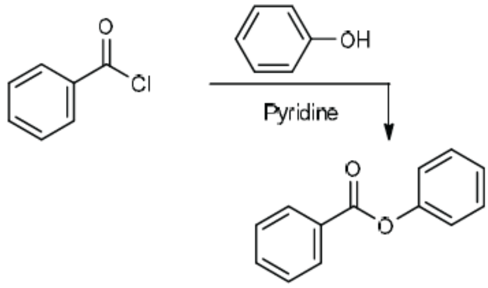

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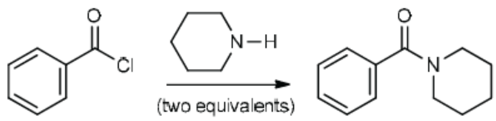

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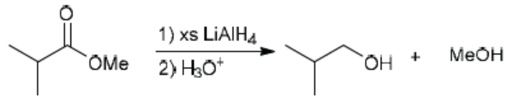

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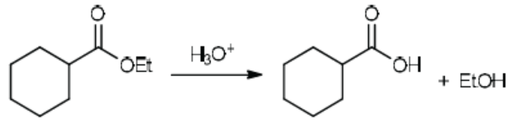

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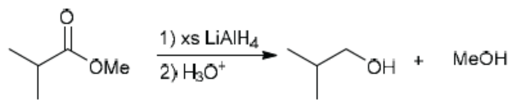

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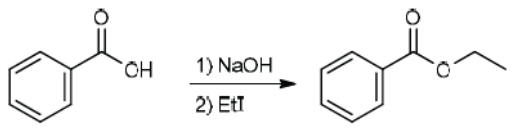

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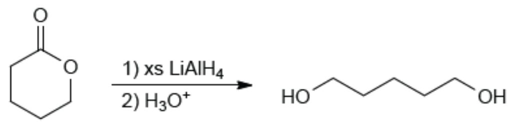

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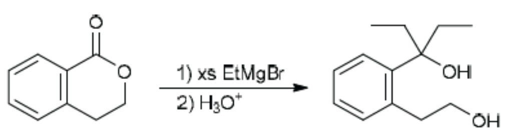

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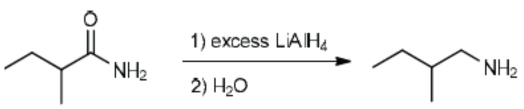

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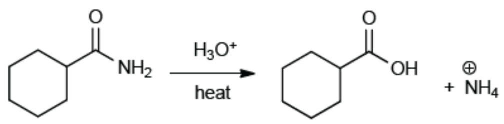

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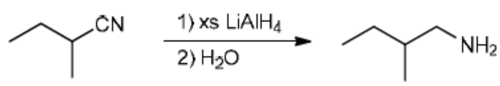

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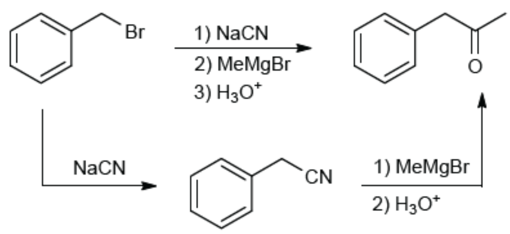

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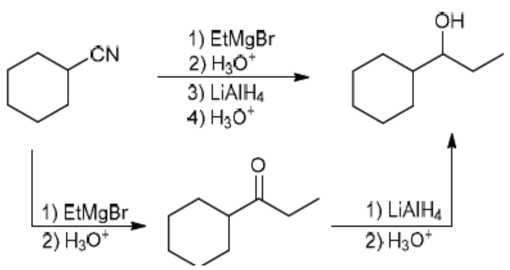

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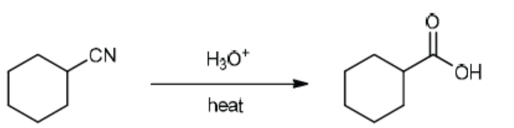

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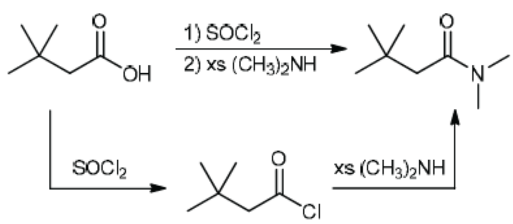

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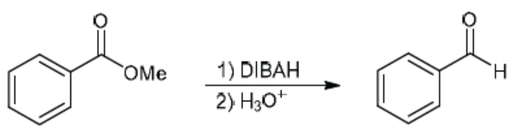

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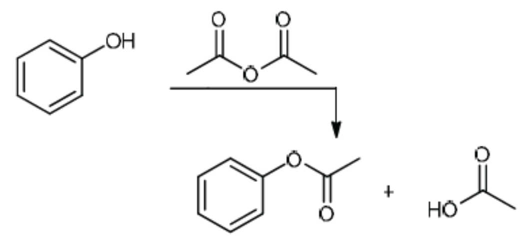

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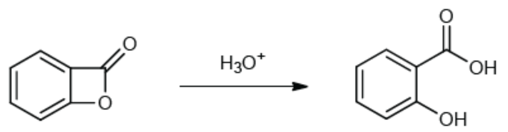

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