uc3m | Universidad Carlos III de Madrid

OpenCourseWare (2023)

CHEMISTRY II

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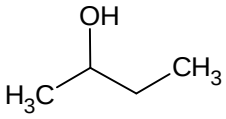
SOLUTIONS OF ORGANIC COMPOUNDS WITH OTHER FUNCTIONALITIES EXERCISES

Exercise 1. Propose the Grignard reagent and the carbonyl compound required to prepare the following alcohols:

a)



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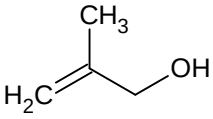
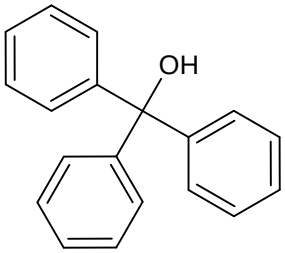
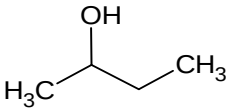
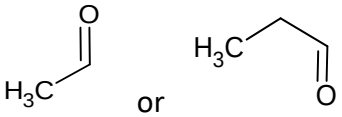
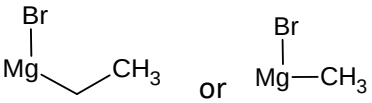
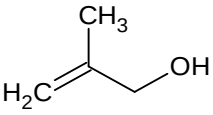
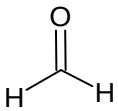
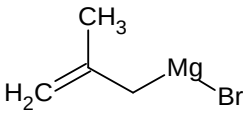
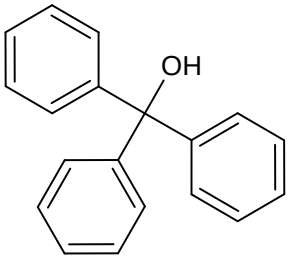
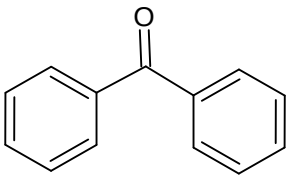
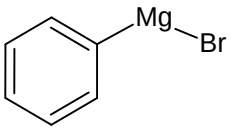


c)



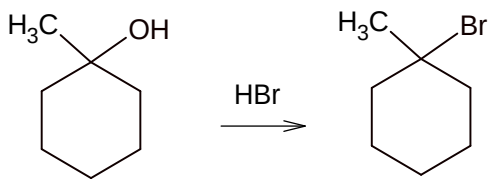
SOLUTION

	Compound	*Carbonyl compound*	*Grignard reagent*
a)			
b)			
c)			

Exercise 2. Indicate the products which result from reaction of 1-methylcyclohexanol with the following reagents: a) HBr, b) H_2SO_4, and c) $Na_2Cr_2O_7$.

SOLUTION

a)



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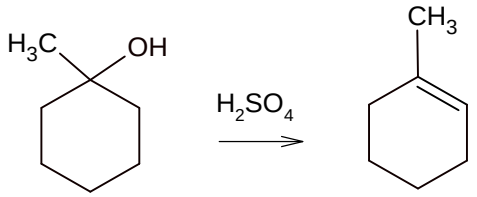

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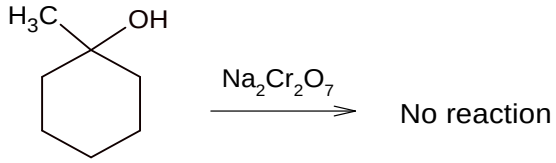


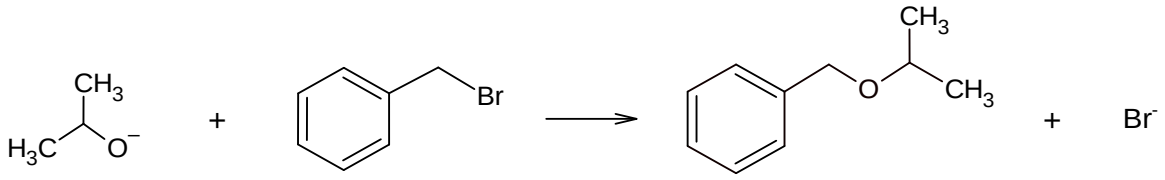
Exercise 3. Indicate how you would prepare the following ethers using a Williamson synthesis:

a) Benzyl isopropyl ether

b) Ethyl 2,2-dimethyl propyl ether

SOLUTION

a)



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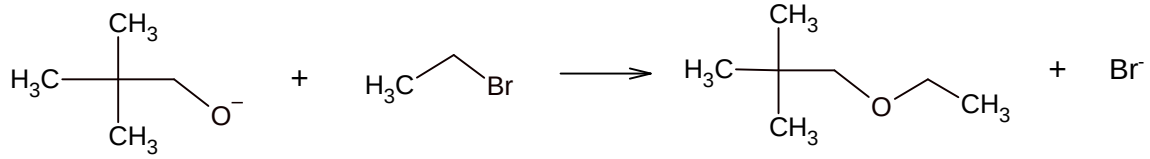
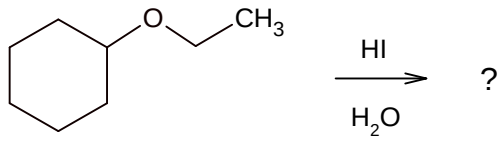


Exercise 4. Which products would be obtained from the following ether cleavage reactions?

a)



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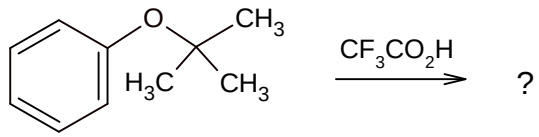

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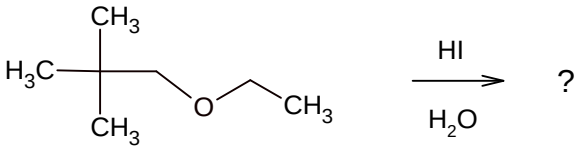
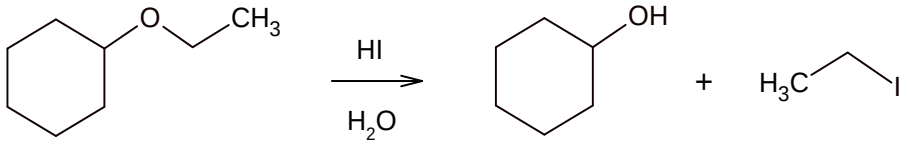


SOLUTION

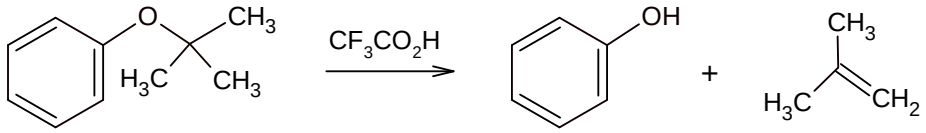
a)

S_N2



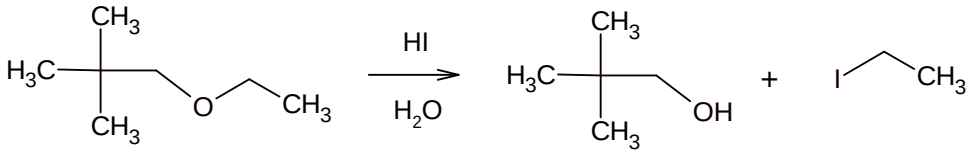
b)

E1



c)

S_N2



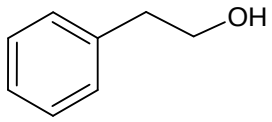
Exercise 5. Predict the products of the reaction of phenylacetaldehyde with the following reagents:

a) $NaBH_4$ followed by H_3O^+

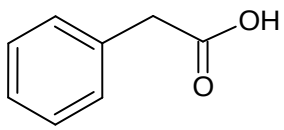
b) Dess–Martin reagent

SOLUTION

a) Reduction



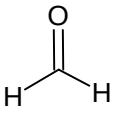
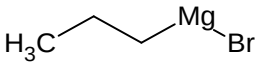
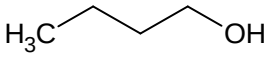
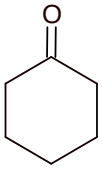
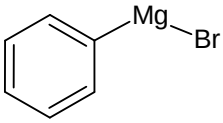
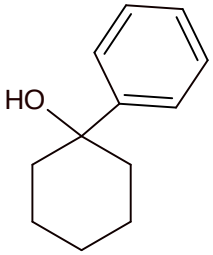
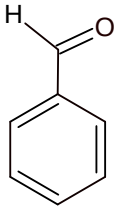
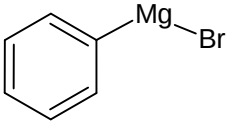
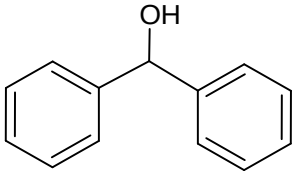
b) Oxidation



Exercise 6. Indicate the reagents required to synthesize the following compounds by using a Grignard reaction:

a) 1-Butanol
b) 1-Phenylcyclohexanol
c) Diphenylmethanol

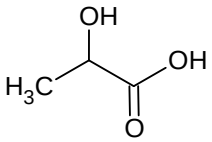
SOLUTION

	Carbonyl compound	*Grignard reagent*	*Product*
a)			
b)			
c)			

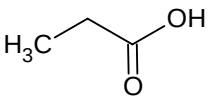
Exercise 7. Justify which of these two acids, lactic acid and acetic acid, will be stronger.

SOLUTION

Lactic acid (I) is expected to be stronger than acetic acid (II). The hydroxyl group of lactic acid is an electron-withdrawing group by inductive effect which could stabilize the negative charge of lactate anion.



I



II

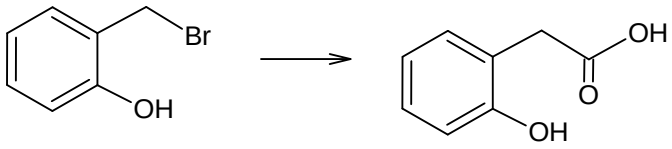
Exercise 8. Rank the following compounds in order of increasing acidity: *p*-Nitrobenzoic acid, acetic acid, and benzoic acid.

SOLUTION

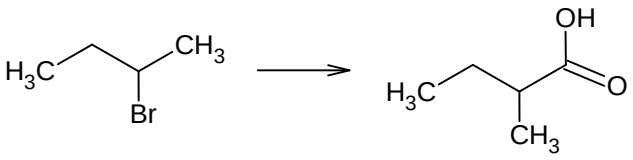
acetic acid < benzoic acid < *p*-Nitrobenzoic acid

Exercise 9. Indicate which method, Grignard carboxylation or nitrile hydrolysis, is more appropriated to carry out the following reactions:

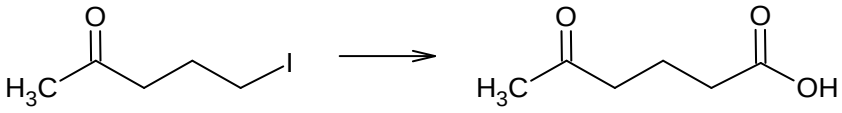
a)



b)



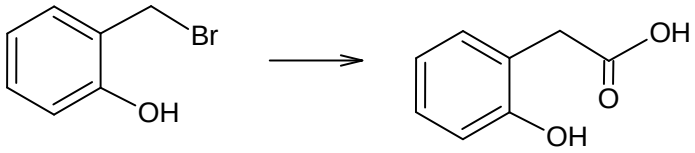
c)



SOLUTION

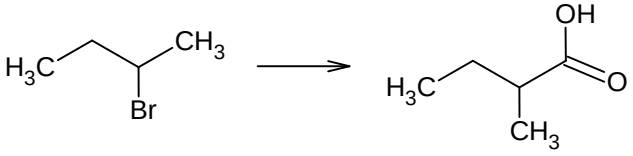
a)

Nitrile hydrolysis. Grignard carboxylation can not be used.



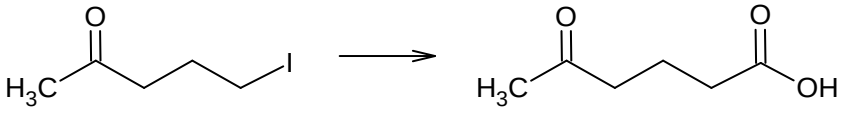
b)

Grignard carboxylation and nitrile hydrolysis

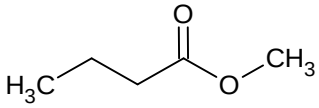


c)

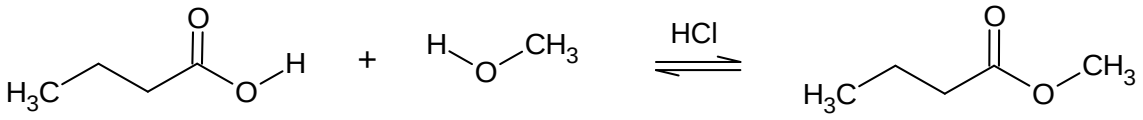
Neither method



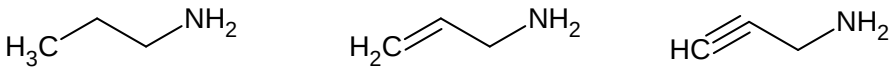
Exercise 10. How might you prepare the following ester from the corresponding carboxylic acid?



SOLUTION

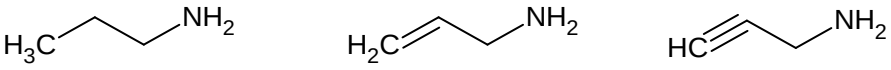


Exercise 11. Explain the decreasing pK_a values of the following (protonated) amines:



pK_a	10.7	9.5	8.2

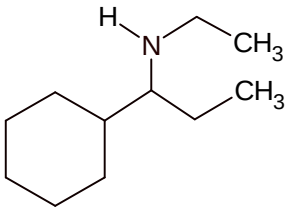
SOLUTION



pK_a	10.7	9.5	8.2

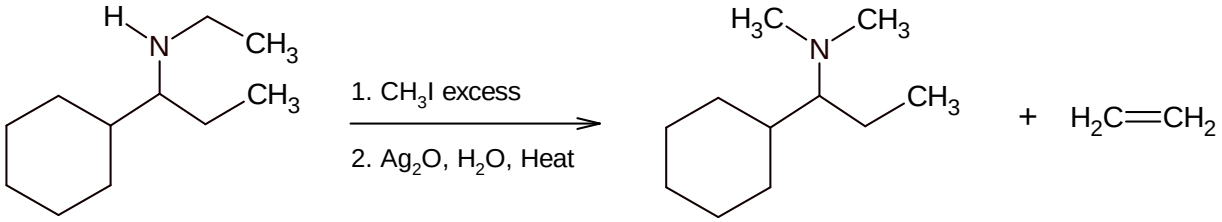
The hybridization at C2 of these compounds changes from sp^3 to sp^2 to sp. In this sequence, the inductive electron-withdrawing character of carbon increases, the electron density at nitrogen decreases, the basicity decreases and the pK_a value of the conjugate acid decreases.

Exercise 12. What product would you expect from Hofmann elimination of the following amine?



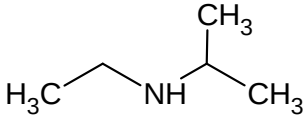
SOLUTION

The primary position is the most accessible and leads to the least highly substituted alkene, ethylene.

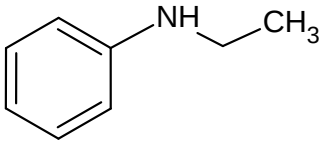


Exercise 13. Indicate the precursors used to prepare the following amines by means of reductive amination reaction.

a)



b)



SOLUTION

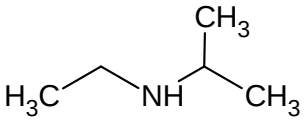
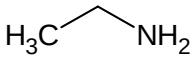
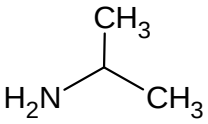
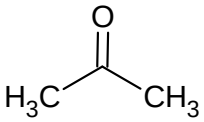
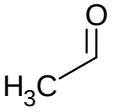
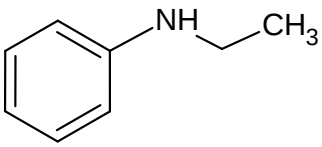
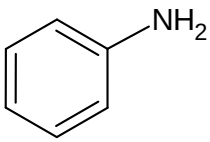
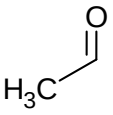
	Amine (product)	*Carbonyl precursor*		*Amine precursor*
a)		 	or	 
b)				

IMAGE CREDITS

- Images of all exercises were made by authors.