

ORGANIC SYNTHESIS AND MODIFICATIONS

GENERAL OBSERVATIONS AND EXAMPLES

In order to synthesize organic compounds from inorganic raw material it is very useful to know that the following two organic compounds, acetylene $\text{CH}\equiv\text{CH}$ and methanol CH_3OH , can be easily prepared. These two compounds can be turned into more complex ones. Other compounds that can be easily synthesized from inorganic raw material like e.g. HCOONa , or $(\text{COONa})_2$ etc. have limited interest.

In many occasions we have to work reversibly in order to find the synthesis procedure, this means that we have to progressively 'simplify' the compound that we have to synthesize, up to the point that we get simple compounds with known synthesis procedure. Some examples follow in order to demonstrate the synthesis procedure.

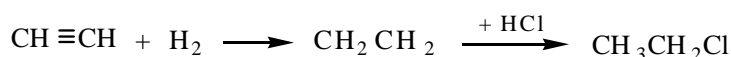
Example 1 :

From acetylene and inorganic materials we will prepare butane.

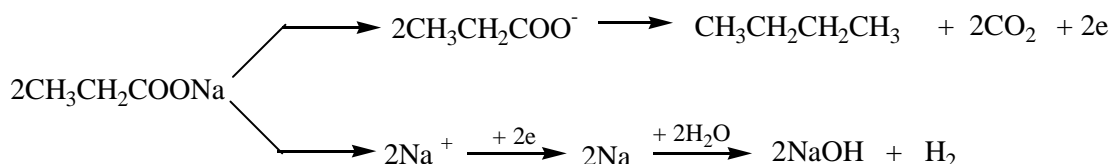
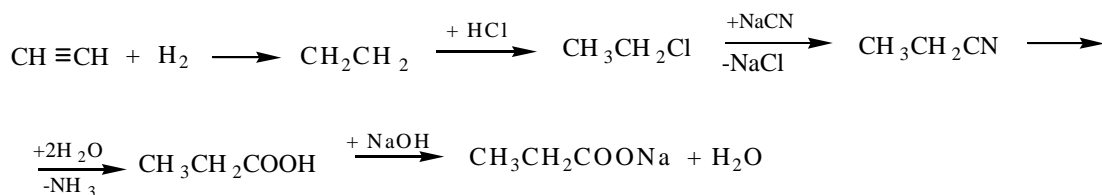
When the compound is relatively simple we work in the following way. We consider the general preparation methods of the corresponding series to which the compound belongs, we evaluate them one by one and we either apply them or reject them.

The general methods of alkane preparation are evaluated as follows, in order to be used for the preparation of butane:

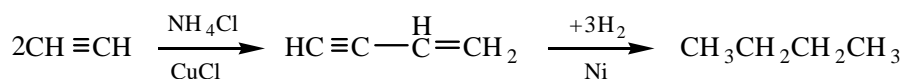
1. Two of the methods that we use in order to obtain alkane from alkyl halides, the addition of H_2 or the use of organo-magnesium compounds, should generally be rejected. The reason is that these methods require the synthesis of an alkyl halide with 4 carbon atoms, which is difficult to prepare.
2. In order to apply the Wurtz method, an alkyl halide with two carbon atoms should be prepared. This compound can be easily prepared from acetylene. The sequence of the reactions is the following:



3. The preparation method from salts of saturated monocarbonic acids with Na and with NaOH as an agent, in the presence of CaO, should be rejected, because it requires the preparation of a monocarbonic acid with 5 carbon atoms, which is difficult to prepare from acetylene.
4. The preparation method from electrolysis of saturated salts of monocarbonic acids with Na should also be rejected due to the fact that it is also complicated. Although, in case we choose to apply this method, the reaction sequence is the following:



5. The application of the alkaline preparation method, starting from the hydrogenation of unsaturated hydrocarbons, requires the easy preparation of an unsaturated hydrocarbon with 4 carbon atoms from CH-CH in a straight chain. Starting from acetylene after condensation we get vinyl acetylene. Thus, we have the following synthesis:

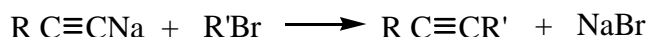


Example 2:

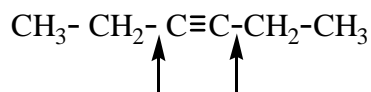
The compound 3 hexene (hexene 3) is going to be prepared from acetylene and inorganic materials.

In case we have to synthesize a compound which has a complex, or long, carbon chain, starting from simple compounds, the procedure that was mentioned in **example 1**, is not sufficient. Besides that method we have to choose additionally one of the synthesis methods of carbon chains.

In this case the appropriate method for carbon chain synthesis is the one based on the following reaction:

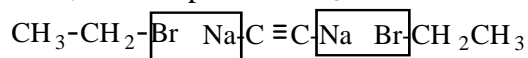


Thus, we need to prepare the following compound:

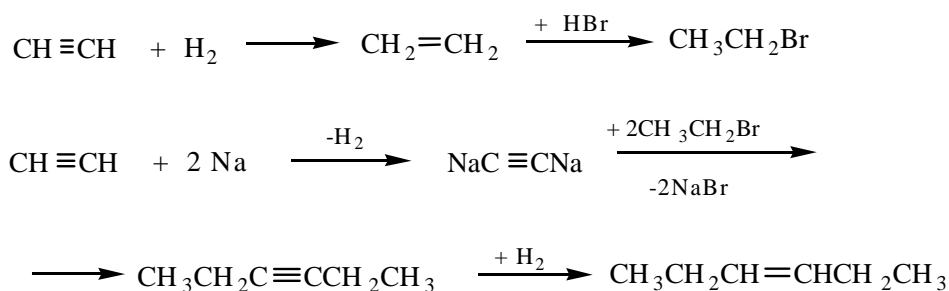


The attachment will take place at the points indicated by the arrows.

Thus, the compounds $\text{CH}_3\text{CH}_2\text{Br}$ and $\text{NaC} \equiv \text{CNa}$ should be prepared initially.



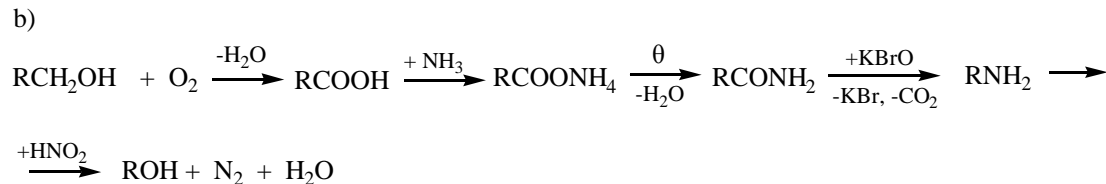
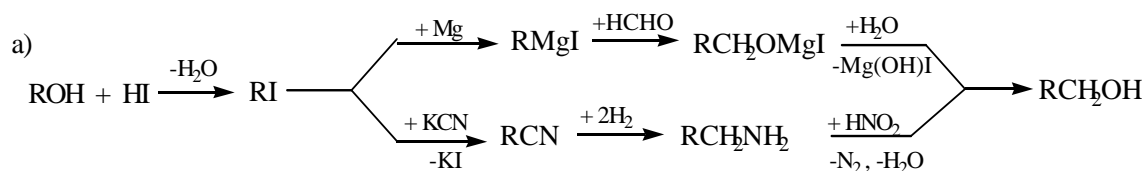
The sequence of the reactions is the following:



TWO SPECIFIC OCCASIONS

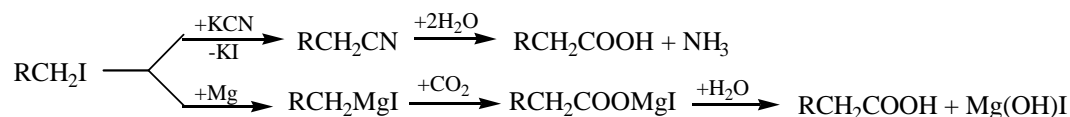
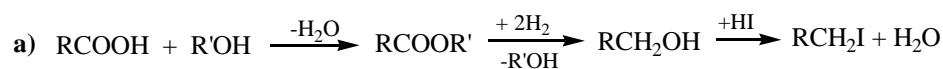
1. Write down the series of the reactions according to which a) the composition of the alcohols and b) the decomposition of the alcohols by one carbon atom is achieved.

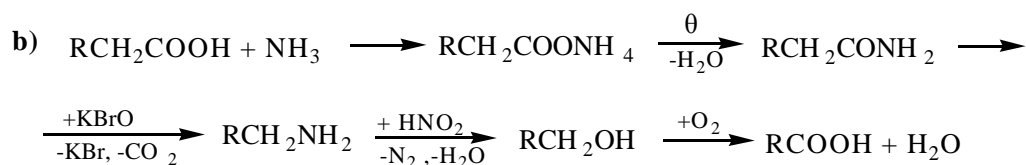
Solution



2. Write down the series of the reactions according to which a) the composition of the monocarboxylic acids and b) the decomposition of the monocarboxylic acids by one carbon atom is achieved.

Solution



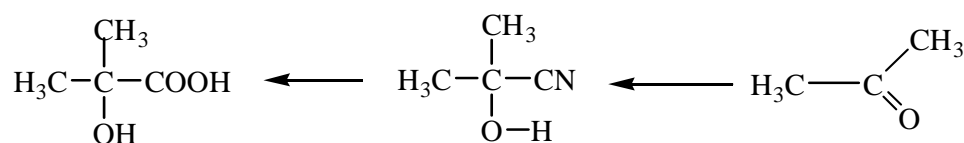


Synthesis of hydroxy-acids and unsaturated acids

3. Starting from the appropriate carbonylic compound prepare the following compounds: a) 2-methyl-2-hydroxy propanoic acid b) methacrylic acid.

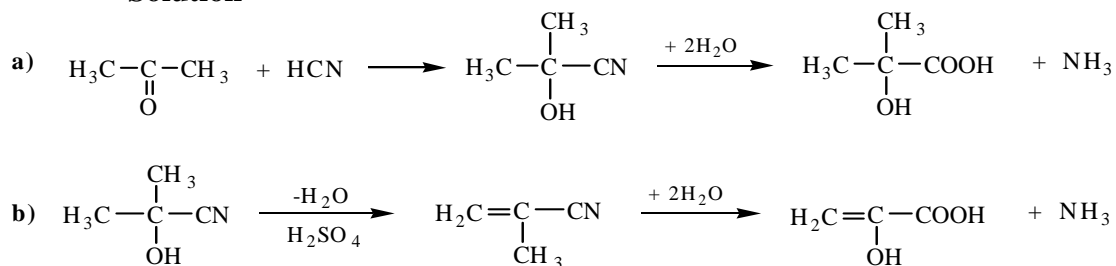
General instructions

When we want to prepare hydroxy acid in which the $-\text{OH}$ and the $-\text{COOH}$ groups are placed in the same carbon atom, we apply the synthesis method which is based in the addition of HCN in the appropriate carbonylic compound. The same initial procedure is also applied when we want to prepare unsaturated acid, in which the $-\text{COOH}$ group as well as the double bond are placed in the same carbon atom. In this case we start in a reverse way in order to find the sequence of the reactions:

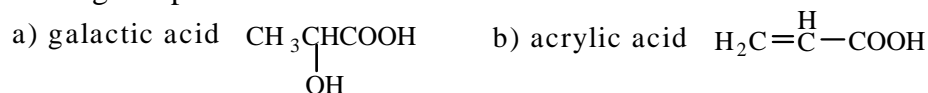


Thus for the solution of this problem we get the following reactions sequence.

Solution

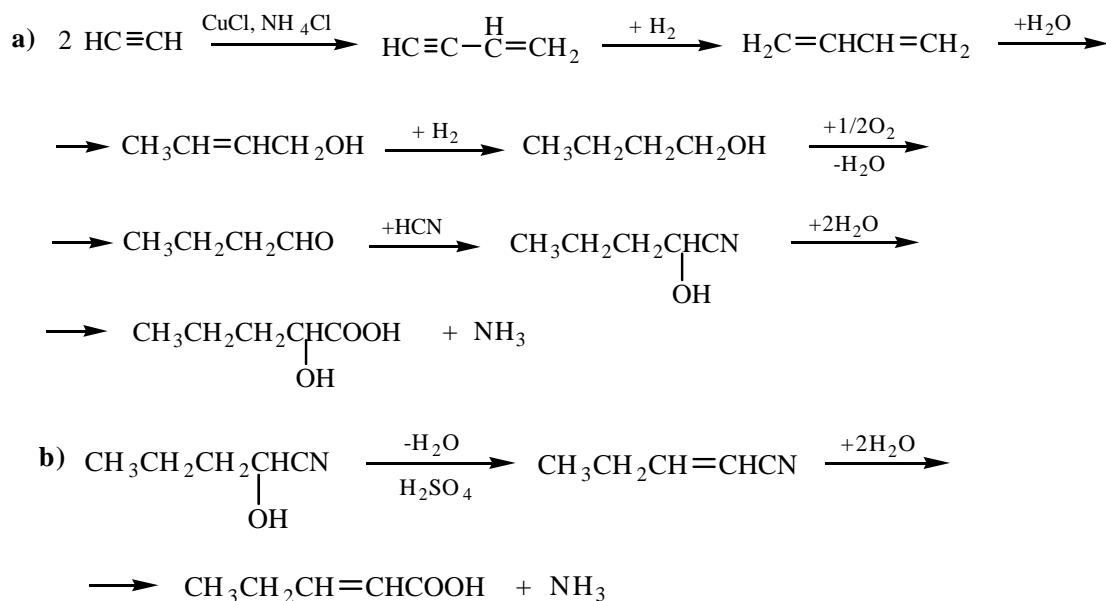


4. Starting from acetylene, hydrocyanic acid and inorganic material prepare the following compounds:



5. Starting from acetylene, hydrocyanic acid and inorganic material prepare the following compounds: a) 2-hydroxypentanoic acid b) 2-pentenoic acid.

Solution

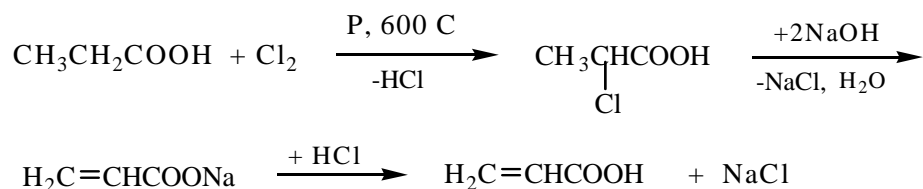


6. From propanoic acid prepare propenoic acid.

Instruction

When we want to modify a saturated monocarboxylic acid into an unsaturated acid with one double bond, in which the $-\text{COOH}$ group and the double bond are placed in the same carbon atom, we follow the modification procedure of the acid to an α -halide acid.

Solution

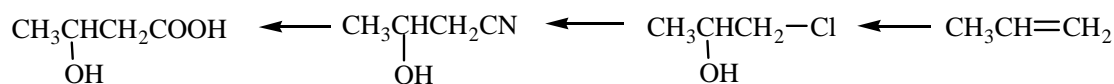


7. Starting from propene and inorganic material prepare the compound 3-hydroxybutanoic acid.

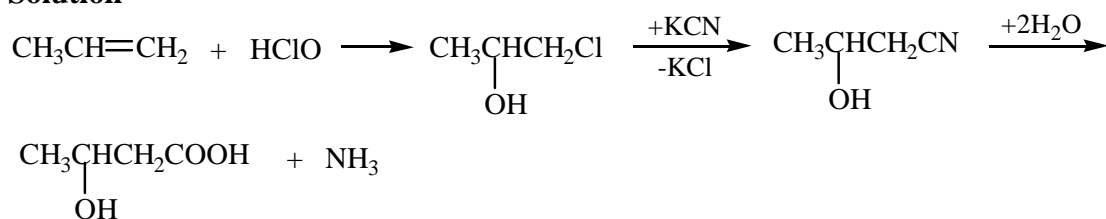
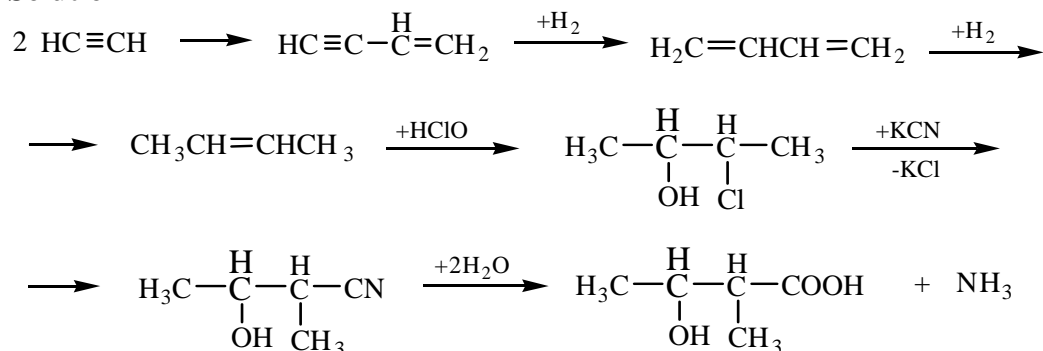
General instructions

When we want to prepare a hydroxy acid in which the $-\text{OH}$ and the $-\text{COOH}$ groups are placed in neighboring carbon atoms, then we apply the synthesis method which is based on the addition of the HClO in the double bond of an alkene.

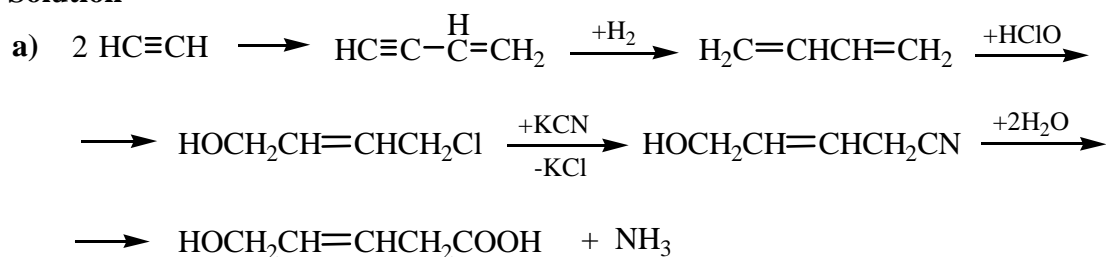
In this case in order to find the sequence of the reactions we start reversely as follows:



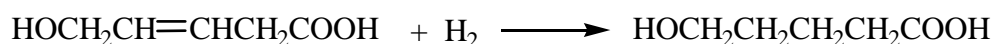
Thus, the solution of the problem is the following reactions sequence.

Solution**8. From acetylene and inorganic material prepare the compound 2-methyl-3-hydroxybutanic acid.****Solution****9. From acetylene and inorganic material prepare the compounds a) 5-hydroxy-3-pentenic acid b) 5-hydroxypentanic acid.****Observation**

When the hydroxy acid does not belong to any of the categories mentioned in the exercises 5 and 9 then there is not a specific method that we have to follow.

Solution

b) Starting with the compound prepared in a,



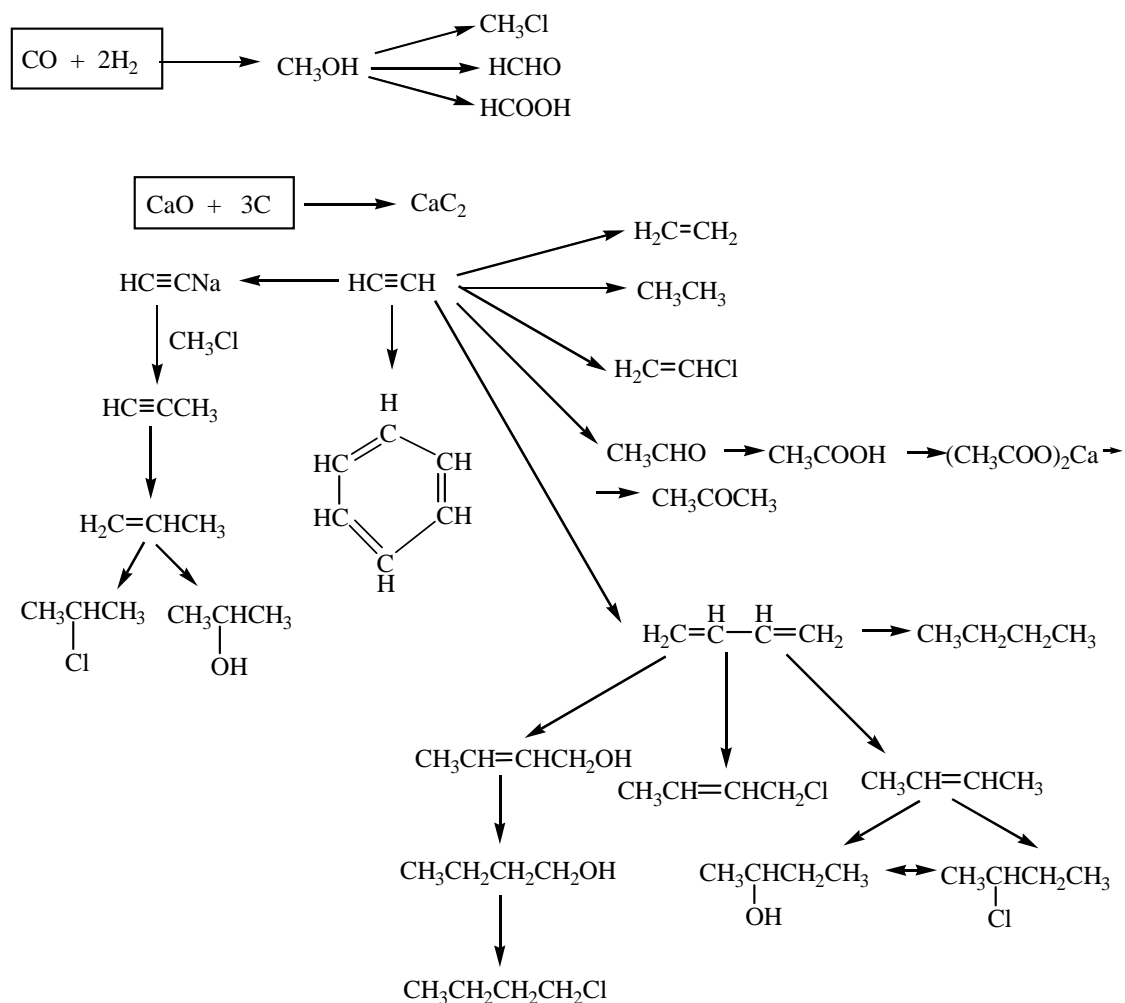
SYNTHESIS OF SIMPLE COMPOUNDS THAT ARE USEFUL FOR THE PREPARATION OF MORE COMPLEXED ONES

Starting from inorganic raw material it is easy to prepare the following 16 compounds, which in their turn could be used to prepare more complex compounds.

- | | | |
|---|--|---|
| 1) CH_3OH | 2) CH_3I | 3) $\text{HC}\equiv\text{CH}$ |
| 4) $\text{H}_2\text{C}=\text{CH}_2$ | 5) $\text{H}_2\text{C}=\text{CHCl}$ | 6) CH_3CHO |
| 7) $\text{CH}_3\text{CH}_2\text{Cl}$ | 8) $\text{CH}_3\text{CH}_2\text{OH}$ | 9) $\text{H}_2\text{C}=\text{CHCH}=\text{CH}_2$ |
| 10) $\text{CH}_3\text{CH}=\text{CHCH}_3$ | 11) $\text{CH}_3\text{CH}_2\underset{\text{Cl}}{\text{CH}}\text{CH}_3$ | 12) $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{OH}$ |
| 13) $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{Cl}$ | 14) $\text{CH}_3\text{C}\equiv\text{CH}$ | 15) $\text{H}_3\text{C}-\underset{\text{Cl}}{\overset{\text{H}}{\text{C}}}-\text{CH}_3$ |
| 16) CH_3COCH_3 | | |

- 1) $\text{CO} + 2\text{H}_2 \xrightarrow{\text{ZnO}} \text{CH}_3\text{OH}$
- 2) $\text{CH}_3\text{OH} + \text{HI} \longrightarrow \text{CH}_3\text{I} + \text{H}_2\text{O}$
- 3) $\text{CaO} + 3\text{C} \xrightarrow{-\text{CO}} \text{CaC}_2 \xrightarrow{+2\text{H}_2\text{O}} \text{HC}\equiv\text{CH} + \text{Ca}(\text{OH})_2$
- 4) $\text{HC}\equiv\text{CH} + \text{H}_2 \longrightarrow \text{H}_2\text{C}=\text{CH}_2$
- 5) $\text{HC}\equiv\text{CH} + \text{HCl} \longrightarrow \text{H}_2\text{C}=\text{CHCl}$
- 6) $\text{HC}\equiv\text{CH} + \text{H}_2\text{O} \xrightarrow[\text{HgSO}_4]{\text{H}_2\text{SO}_4, \text{Hg}} \text{CH}_3\text{CHO}$
- 7) $\text{H}_2\text{C}=\text{CH}_2 + \text{HCl} \longrightarrow \text{CH}_3\text{CH}_2\text{Cl}$
- 8) $\text{H}_2\text{C}=\text{CH}_2 + \text{H}_2\text{O} \xrightarrow{\text{H}_2\text{SO}_4} \text{CH}_3\text{CH}_2\text{OH}$
- 9) $2\text{HC}\equiv\text{CH} \longrightarrow \text{HC}\equiv\text{C}-\overset{\text{H}}{\text{C}}=\text{CH}_2 \xrightarrow{+2\text{H}_2} \text{H}_2\text{C}=\overset{\text{H}}{\text{C}}-\overset{\text{H}}{\text{C}}=\text{CH}_2$
- 10) $\text{H}_2\text{C}=\overset{\text{H}}{\text{C}}-\overset{\text{H}}{\text{C}}=\text{CH}_2 + 2\text{H}_2 \longrightarrow \text{CH}_3\text{CH}=\text{CHCH}_3$
- 11) $\text{CH}_3\text{CH}=\text{CHCH}_3 + \text{HCl} \longrightarrow \text{CH}_3\text{CH}_2\underset{\text{Cl}}{\text{CH}}\text{CH}_3$
- 12) $\text{H}_2\text{C}=\overset{\text{H}}{\text{C}}-\overset{\text{H}}{\text{C}}=\text{CH}_2 + \text{H}_2\text{O} \xrightarrow{\text{H}_2\text{SO}_4} \text{CH}_3\text{CH}=\text{CHCH}_2\text{OH} \xrightarrow{+\text{H}_2} \text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{OH}$
- 13) $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{OH} + \text{SOCl}_2 \longrightarrow \text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{Cl} + \text{SO}_2 + \text{HCl}$
- 14) $\text{HC}\equiv\text{CH} + \text{Na} \xrightarrow{-1/2\text{H}_2} \text{HC}\equiv\text{CNa} \xrightarrow{\text{CH}_3\text{Cl}} \text{HC}\equiv\text{CCH}_3 + \text{NaCl}$
- 15) $\text{HC}\equiv\text{CCH}_3 + \text{H}_2 \longrightarrow \text{H}_2\text{C}=\text{CHCH}_3 \xrightarrow{+\text{HCl}} \text{H}_3\text{C}-\underset{\text{Cl}}{\overset{\text{H}}{\text{C}}}-\text{CH}_3$
- 16) $2\text{CH}_3\text{CHO} + \text{O}_2 \longrightarrow 2\text{CH}_3\text{COOH} \xrightarrow[-\text{H}_2\text{O}]{+\text{CaO}} (\text{CH}_3\text{COO})_2\text{Ca} \xrightarrow{\ominus} \text{CH}_3\text{COCH}_3 + \text{CaCO}_3$

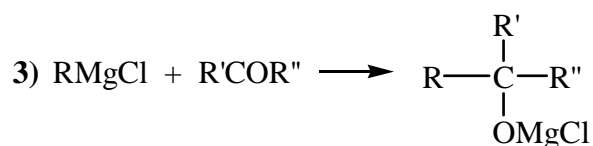
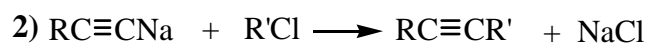
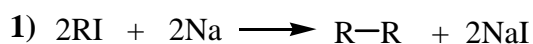
PREPARATION OF ORGANIC COMPOUNDS FROM INORGANIC RAW MATERIAL



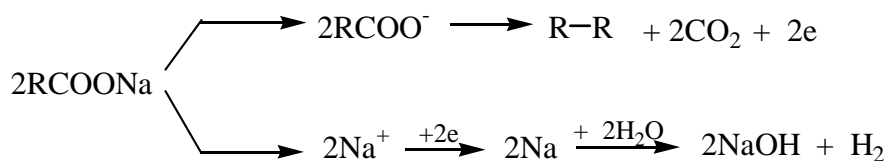
CONNECTION OF CARBON CHAINS

General

For the connection (joining) of two carbon chains that belong to two different compounds, three methods are mainly used. These methods are described in the following reactions.



Other methods for the connection of carbon chains like the Colb  method that is described in the following reaction, have limited interest.

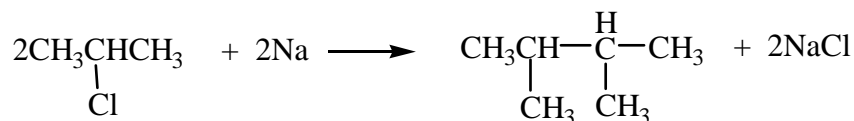
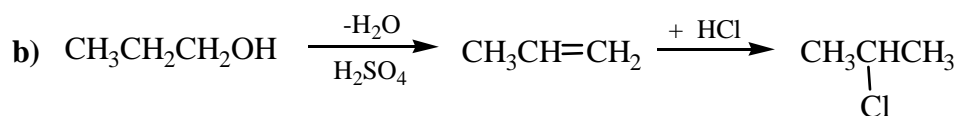
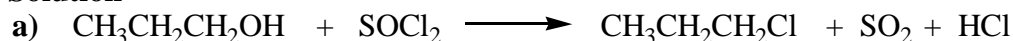


EXERCISES

A. Wurtz synthesis

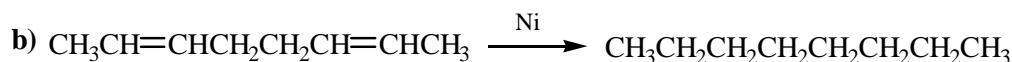
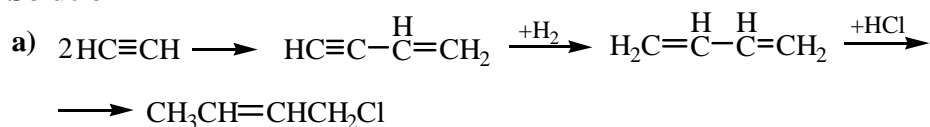
10. From 1-propanol (propanol-1) and inorganic raw material prepare the compounds: a) hexane b) 2,3-dimethylbutane

Solution

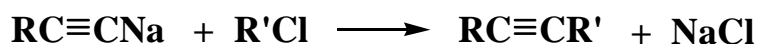


11. From acetylene and inorganic material prepare the compounds a) 2,6-oktadiene (oktadiene-2,6), b) octane.

Solution



B. Synthesis reactions that are based on the following reaction:

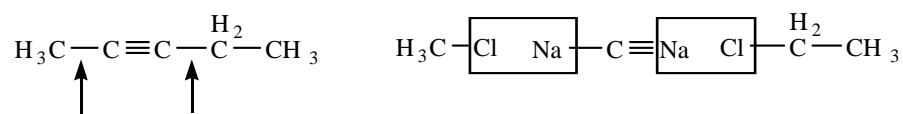
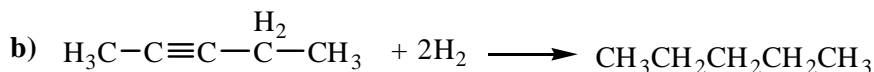
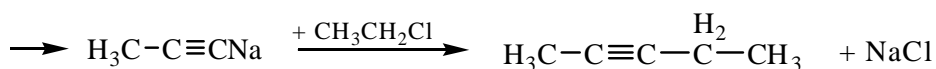
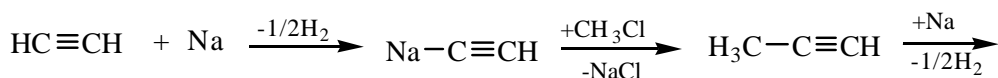
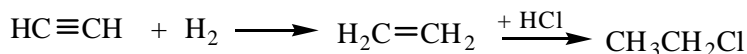
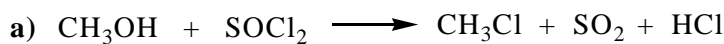


12. From CH_3OH , acetylene and inorganic material prepare the compounds:

a) 2-pentyne (pentyne-2) b) pentane.

Observation

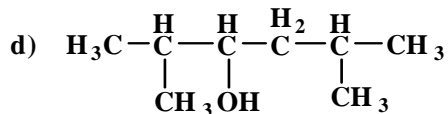
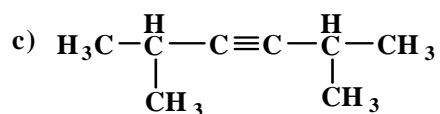
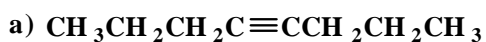
The procedure for the determination of the reactions sequence is showed in the next scheme.

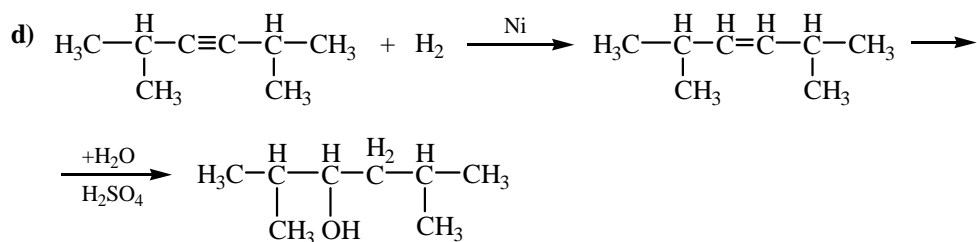
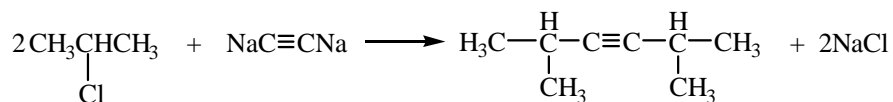
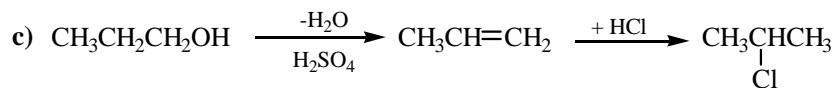
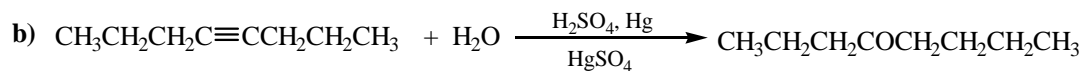
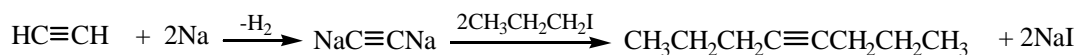
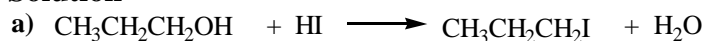
**Solution**

13. From CH_3OH , acetylene and inorganic material prepare the compounds: a) 4-methyl-2-hexyne (4-methylhexyne-2) b) 2-butyne (butyne-2).

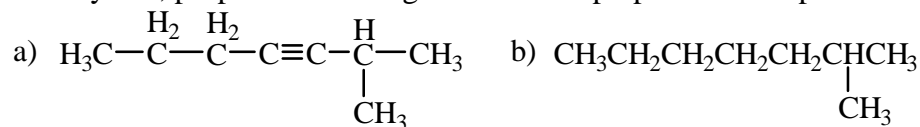
14. From inorganic raw material prepare the following compounds: a) 3-hexyne (hexyne-3) b) 3-hexanone (hexanone-3)
c) 3-hexanol (hexanol-3)

15. From acetylene, 1-propanol (propanol-1) and inorganic material prepare the compounds:

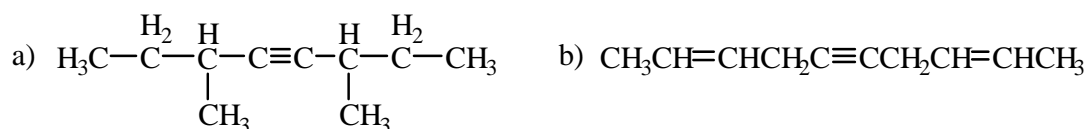


Solution

16. From acetylene, propanol and inorganic material prepare the compounds:

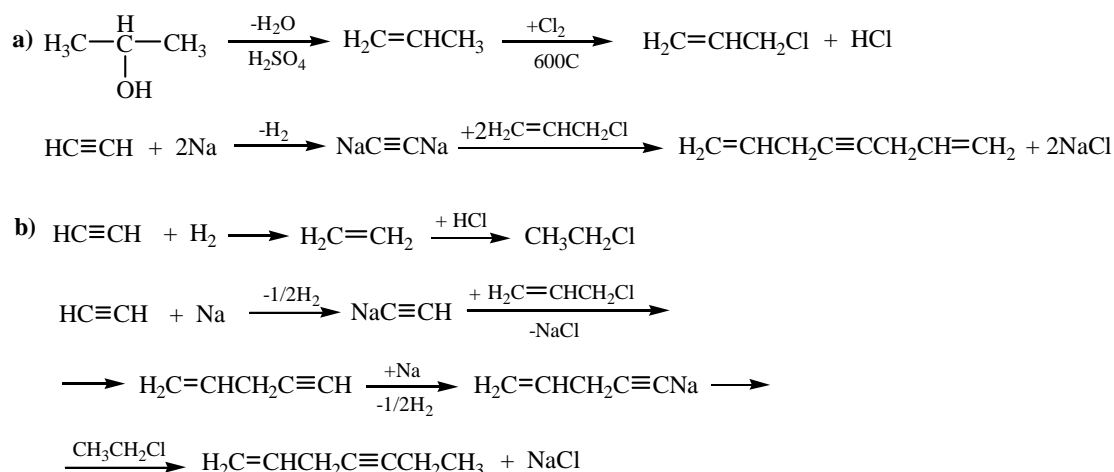


17. From acetylene and inorganic material prepare the compounds

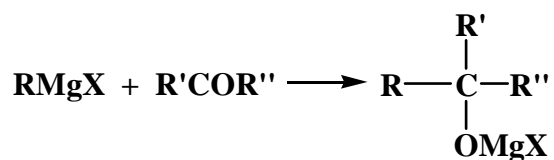


18. From acetylene, $\text{CH}_3\text{CH}(\text{OH})\text{CH}_3$ and inorganic material prepare the compounds:

**Solution**



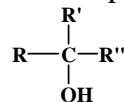
3. Synthesis reactions that are based on the following reaction:



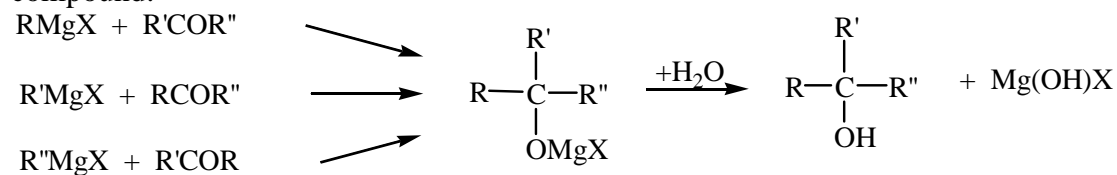
General instructions

The reaction above is mainly used to prepare complex alcohols and the compounds that may result from them. In order to apply this synthesis we have to choose the appropriate alkyl halide and the appropriate carbonylic compound, in such a way that these compounds can be easily prepared.

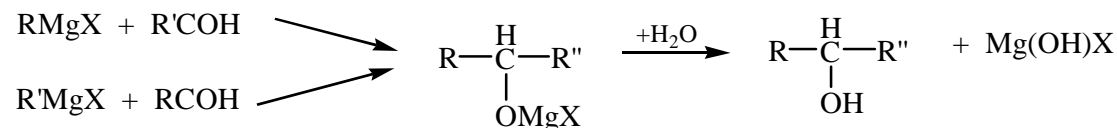
For the preparation of the tertiary alcohol of the type,



there are three possible combinations of organo-magnesium and carbonylic compound:



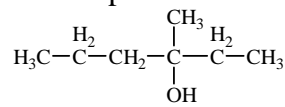
In a similar way for the preparation of a non symmetric secondary alcohol (using this method) there are two possible combinations:



For the preparation of a primary alcohol (using this method), there is only one possible combination. The only carbonylic compound that should be used is the HCHO compound.

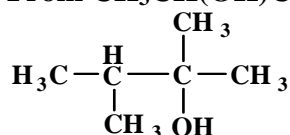
PROBLEMS

19. Prepare the following compound in three different ways



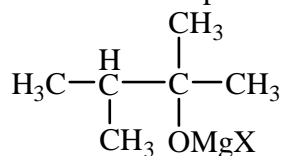
by choosing a different pair of alkyl halide and carbonylic compound each time.

20. From $\text{CH}_3\text{CH}(\text{OH})\text{CH}_3$ and inorganic material prepare the compound

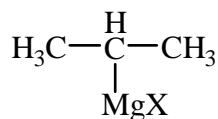


Determining the synthesis procedure

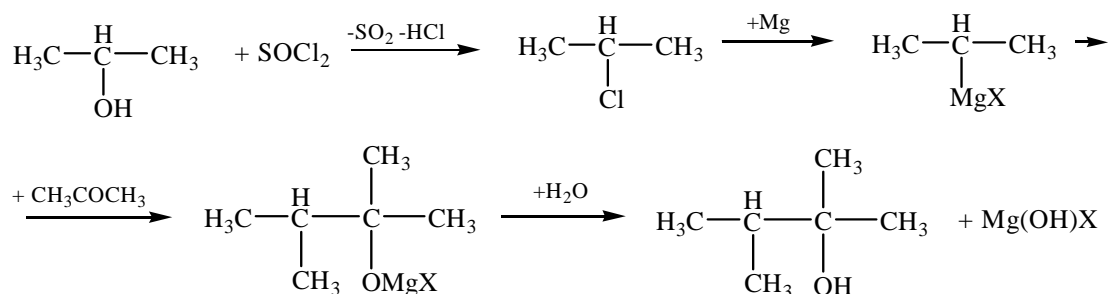
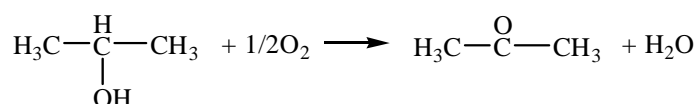
The above compound will result from the hydrolysis of the following compound



which is best to be prepared from the following compound,

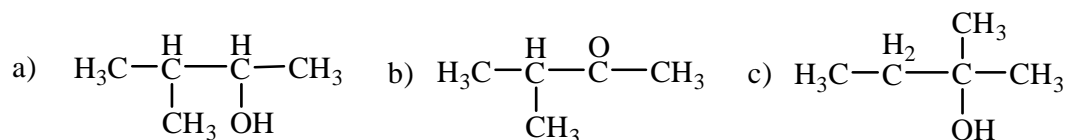


Solution

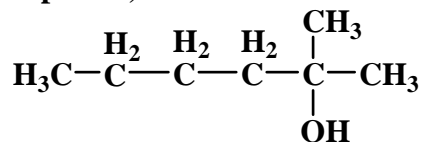


21. From $\text{CH}_3\text{CH}_2\text{OH}$ and inorganic material prepare the compound $\text{CH}_3\text{CH}_2\text{CH}(\text{OH})\text{CH}_3$

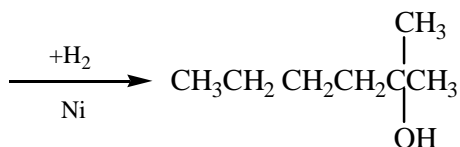
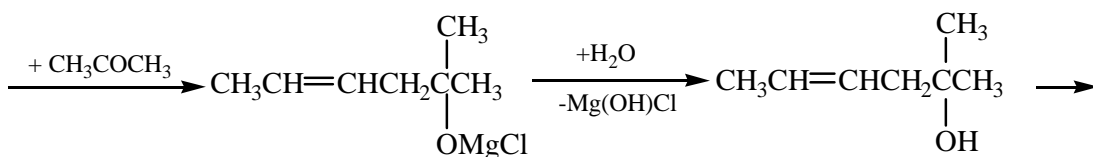
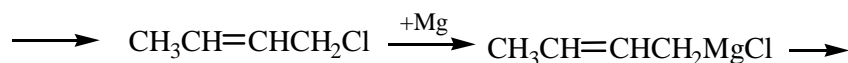
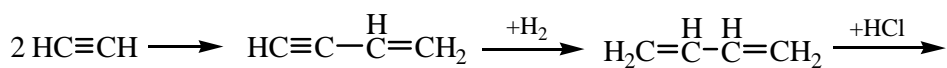
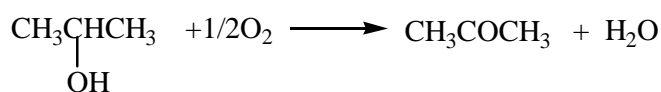
22. From $\text{CH}_3\text{CH}_2\text{OH}$, $\text{CH}_3\text{CH}(\text{OH})\text{CH}_3$ and inorganic material prepare the compounds:



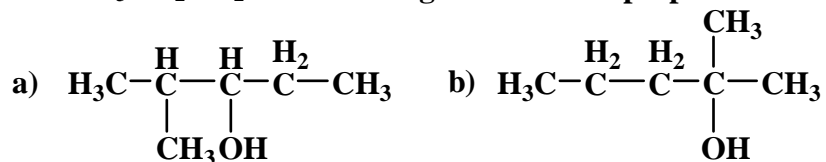
23. From acetylene, $\text{CH}_3\text{CH}(\text{OH})\text{CH}_3$ and inorganic material prepare the compound,



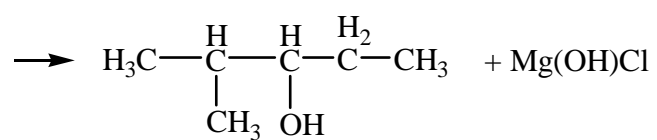
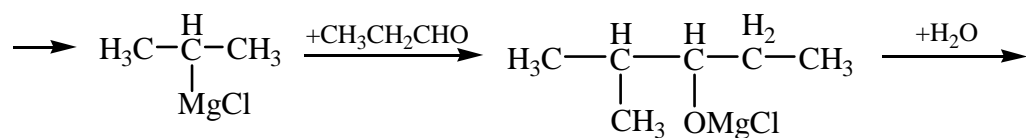
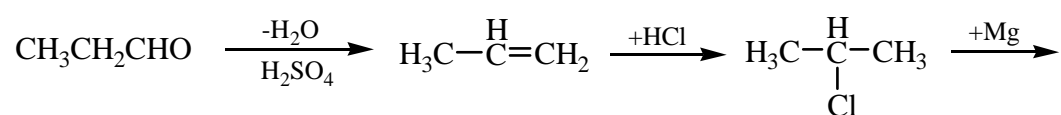
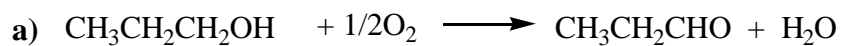
Solution



24. From $\text{CH}_3\text{CH}_2\text{CH}_2\text{OH}$ and inorganic material prepare the compounds:



Solution



Polychronis Karagkiozidis

www.polkarag.gr