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 $CH \equiv CH$ and methanol CH₃OH, 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 (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:

 $CH \equiv CH + H_2 \longrightarrow CH_2 CH_2 \xrightarrow{+ HCl} CH_3 CH_2 Cl$ $2CH_3 CH_2 Cl + 2 Na \longrightarrow CH_3 CH_2 CH_2 H_3 + 2 NaCl$

- 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:

$$CH \equiv CH + H_{2} \longrightarrow CH_{2}CH_{2} \xrightarrow{+ HCl} CH_{3}CH_{2}Cl \xrightarrow{+NaCN} CH_{3}CH_{2}CN \longrightarrow$$

$$\xrightarrow{+2H_{2}O} CH_{3}CH_{2}COOH \xrightarrow{+ NaOH} CH_{3}CH_{2}COONa + H_{2}O$$

$$2CH_{3}CH_{2}COO^{-} \longrightarrow CH_{3}CH_{2}CH_{2}CH_{3} + 2CO_{2} + 2e$$

$$2CH_{3}CH_{2}COONa \xrightarrow{+ 2H_{2}O} 2Na^{+} \xrightarrow{+ 2e} 2Na \xrightarrow{+ 2H_{2}O} 2NaOH + H_{2}$$

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:

$$2CH \equiv CH \xrightarrow{\text{NH}_4\text{Cl}} HC \equiv C \xrightarrow{\text{H}} C \equiv CH_2 \xrightarrow{+3H_2} CH_3CH_2CH_2CH_3$$

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:

$$R C \equiv CNa + R'Br \longrightarrow R C \equiv CR' + NaBr$$

Thus, we need to prepare the following compound:

$$CH_3$$
- CH_2 - $C\equiv C$ - CH_2 - CH_3

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

Thus, the compounds CH_3CH_2Br and $NaC \equiv CNa$ should be prepared initially. CH_3-CH_2-Br Na $C \equiv C-Na$ Br CH_2CH_3 The sequence of the reactions is the following:

$$CH \equiv CH + H_{2} \longrightarrow CH_{2} = CH_{2} \xrightarrow{+ HBr} CH_{3}CH_{2}Br$$

$$CH \equiv CH + 2 Na \xrightarrow{-H_{2}} NaC \equiv CNa \xrightarrow{+ 2CH_{3}CH_{2}Br}$$

$$\longrightarrow CH_{3}CH_{2}C \equiv CCH_{2}CH_{3} \xrightarrow{+ H_{2}} CH_{3}CH_{2}CH = CHCH_{2}CH_{3}$$

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

a)
ROH + HI
$$\xrightarrow{-H_2O}$$
 RI $\xrightarrow{+Mg}$ RMgI $\xrightarrow{+HCHO}$ RCH₂OMgI $\xrightarrow{+H_2O}$
 $\xrightarrow{-KI}$ RCN $\xrightarrow{+2H_2}$ RCH₂NH₂ $\xrightarrow{+HNO_2}$
b)
RCH₂OH + O₂ $\xrightarrow{-H_2O}$ RCOOH $\xrightarrow{+NH_3}$ RCOONH₄ $\xrightarrow{\theta}$ RCONH₂ $\xrightarrow{+KBrO}$ RNH₂ $\xrightarrow{+KBrO}$ RNH₂ $\xrightarrow{+HNO_2}$
 $\xrightarrow{+HNO_2}$ ROH + N₂ + H₂O

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

a)
$$\operatorname{RCOOH} + \operatorname{R'OH} \xrightarrow{-H_2O} \operatorname{RCOOR'} \xrightarrow{+2H_2} \operatorname{RCH_2OH} \xrightarrow{+HI} \operatorname{RCH_2I} + H_2O$$

$$\xrightarrow{+KCN} \operatorname{RCH_2CN} \xrightarrow{+2H_2O} \operatorname{RCH_2COOH} + \operatorname{NH_3}$$
 $\operatorname{RCH_2I} \xrightarrow{+Mg} \operatorname{RCH_2MgI} \xrightarrow{+CO_2} \operatorname{RCH_2COOMgI} \xrightarrow{+H_2O} \operatorname{RCH_2COOH} + Mg(OH)I$

b)
$$\operatorname{RCH}_2\operatorname{COOH} + \operatorname{NH}_3 \longrightarrow \operatorname{RCH}_2\operatorname{COONH}_4 \xrightarrow{\theta} \operatorname{RCH}_2\operatorname{CONH}_2 \longrightarrow$$

$$\xrightarrow{+\operatorname{KBrO}} \operatorname{RCH}_2\operatorname{NH}_2 \xrightarrow{+\operatorname{HNO}_2} \operatorname{RCH}_2\operatorname{OH} \xrightarrow{+\operatorname{O}_2} \operatorname{RCOOH} + \operatorname{H}_2\operatorname{O}$$

Synthesis of hydroxy-acids and unsaturated acids

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

General instructions

When we want to prepare hydroxy acid in which the –OH and the -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 –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:

$$H_3C-C-COOH$$
 \leftarrow $H_3C-C-CN$ \leftarrow H_3C-CN \leftarrow H_3C-CN

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

Solution

CII

OII

b)
$$H_3C \xrightarrow{CH_3}_{l}CN \xrightarrow{-H_2O}_{H_2SO_4} H_2C \xrightarrow{-C}_{CH_3} H_2C \xrightarrow{+2H_2O}_{H_2SO_4} H_2C \xrightarrow{-COOH}_{OH} + NH_3$$

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

a) galactic acid $CH_3CHCOOH$ b) acrylic acid $H_2C = C - COOH$ OH

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

a)
$$2 \text{ HC} \equiv \text{CH} \xrightarrow{\text{CuCl, NH}_4\text{Cl}} \text{HC} \equiv \text{C} - \overset{\text{H}}{\text{C}} = \text{CH}_2 \xrightarrow{+\text{H}_2} \text{H}_2\text{C} = \text{CHCH} = \text{CH}_2 \xrightarrow{+\text{H}_2\text{C}}$$

 $\rightarrow \text{CH}_3\text{CH} = \text{CHCH}_2\text{OH} \xrightarrow{+\text{H}_2} \text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{OH} \xrightarrow{+1/2\text{O}_2}$
 $\rightarrow \text{CH}_3\text{CH}_2\text{CH}_2\text{CH} \xrightarrow{+\text{HCN}} \text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{OH} \xrightarrow{+2\text{H}_2\text{O}}$
 $\rightarrow \text{CH}_3\text{CH}_2\text{CH}_2\text{CH} \xrightarrow{-\text{H}_2\text{O}} \text{H}_3$
b) $\text{CH}_3\text{CH}_2\text{CH}_2\text{CHCN} \xrightarrow{-\text{H}_2\text{O}} \text{H}_2\text{SO}_4 \xrightarrow{-\text{H}_2\text{O}} \text{CH}_3\text{CH}_2\text{CH} = \text{CHCN} \xrightarrow{+2\text{H}_2\text{O}}$
 $\rightarrow \text{CH}_3\text{CH}_2\text{CH} = \text{CHCOOH} + \text{NH}_3$

6. From propanic acid prepare propenic acid.

Instruction

When we want to modify a saturated monocarbonic acid into an unsaturated acid with one double bond, in which the –COOH group and the double bond are placed in the same carbon atom, we follow the modification procedure of the acid to an a-halide acid.

Solution

$$CH_{3}CH_{2}COOH + Cl_{2} \xrightarrow{P, 600 \text{ C}} CH_{3}CHCOOH \xrightarrow{+2NaOH} -NaCl, H_{2}O \xrightarrow{+HCl} H_{2}C = CHCOOH + NaCl$$

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

General instructions

When we want to prepare a hydroxy acid in which the –OH and the –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:

$$\begin{array}{cccc} CH_3CHCH_2COOH & \longleftarrow & CH_3CHCH_2CN & \longleftarrow & CH_3CHCH_2-Cl & \longleftarrow & CH_3CH=CH_2\\ OH & OH & OH & OH \end{array}$$

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

Solution

$$CH_{3}CH = CH_{2} + HCIO \longrightarrow CH_{3}CHCH_{2}CI \xrightarrow{+KCN} CH_{3}CHCH_{2}CN \xrightarrow{+2H_{2}O} OH CH_{3}CHCH_{2}COOH + NH_{3} OH$$

8. From acetylene and inorganic material prepare the compound 2-methyl-3-hydroxybutanic acid. Solution

$$2 \text{ HC} \equiv \text{CH} \longrightarrow \text{HC} \equiv \text{C} - \overset{\text{H}}{\text{C}} = \text{CH}_{2} \xrightarrow{+\text{H}_{2}} \text{H}_{2}\text{C} = \text{CHCH} = \text{CH}_{2} \xrightarrow{+\text{H}_{2}}$$

$$\longrightarrow \text{CH}_{3}\text{CH} = \text{CHCH}_{3} \xrightarrow{+\text{HCIO}} \text{H}_{3}\text{C} - \overset{\text{H}}{\overset{\text{C}}{\text{C}}} - \overset{\text{H}}{\overset{\text{C}}{\text{C}}} - \overset{\text{H}}{\overset{\text{C}}{\text{C}}} - \overset{\text{H}}{\overset{\text{C}}{\text{C}}} \xrightarrow{+\text{KCN}} \xrightarrow{-\text{KCI}}$$

$$\longrightarrow \text{H}_{3}\text{C} - \overset{\text{H}}{\overset{\text{C}}{\text{C}}} - \overset{\text{H}}{\overset{\text{C}}{\text{C}}} - \overset{\text{H}}{\underset{\text{OH}}{\overset{\text{C}}{\text{C}}} \xrightarrow{+\text{C}} \xrightarrow{-\text{KCI}} \xrightarrow{+\text{KCN}} \xrightarrow{-\text{KCI}} \xrightarrow{-\text{KCI}} \xrightarrow{+\text{H}_{2}} \xrightarrow{-\text{KCI}} \xrightarrow{-$$

9. From acetylene and inorganic material prepare the compounds a) 5hydroxy-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

a)
$$2 \text{ HC} \equiv \text{CH} \longrightarrow \text{HC} \equiv \text{C} - \text{C} = \text{CH}_2 \xrightarrow{+\text{H}_2} \text{H}_2\text{C} = \text{CHCH} = \text{CH}_2 \xrightarrow{+\text{HCIO}} \text{HOCH}_2\text{CH} = \text{CHCH}_2\text{CI} \xrightarrow{+\text{KCN}} \text{HOCH}_2\text{CH} = \text{CHCH}_2\text{CN} \xrightarrow{+2\text{H}_2\text{O}} \text{HOCH}_2\text{CH} = \text{CHCH}_2\text{COOH} + \text{NH}_3$$

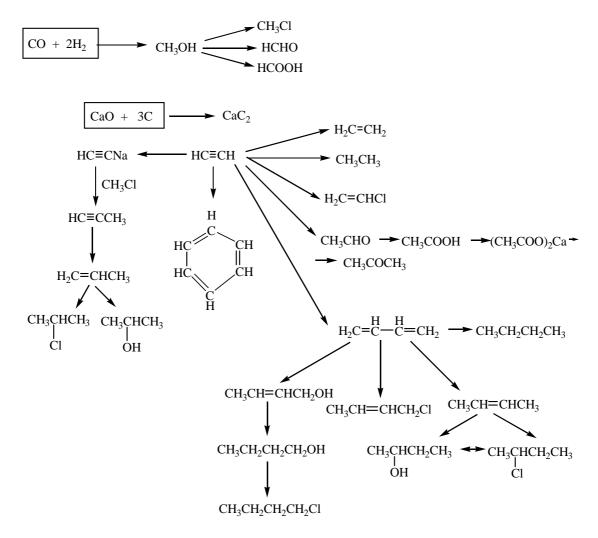
b) Starting with the compound prepared in a,

 $HOCH_2CH = CHCH_2COOH + H_2 \longrightarrow HOCH_2CH_2CH_2CH_2COOH$

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) CH₃OH 2) CH₃I 3) HC ≡CH 5) $H_2C = CHCl$ 6) CH₃CHO 4) $H_2C = CH_2$ 8) $CH_{3}CH_{2}OH$ 9) $H_{2}C = CHCH = CH_{2}$ 7) CH_3CH_2Cl **10)** CH $_3$ CH = CHCH $_3$ **11)** CH $_3$ CH $_2$ CHCH $_3$ **12)** CH $_3$ CH $_2$ CH $_2$ CH $_2$ CH $_2$ OH **13)** CH₃CH₂CH₂CH₂CH₂Cl **14)** CH₃C \equiv CH **15)** H₃C - CH₃ Cl 16) CH ₃COCH ₃ 1) CO + 2H₂ \xrightarrow{ZnO} CH₃OH 2) CH₃OH + HI \longrightarrow CH₃I + H₂O 3) CaO + 3C $\xrightarrow{-CO}$ CaC₂ $\xrightarrow{+2H_2O}$ HC=CH + Ca(OH)₂ 4) HC=CH + H₂ \longrightarrow H₂C=CH₂ 5) HC=CH + HCl \longrightarrow H₂C=CHCl 6) HC=CH + H₂O $\xrightarrow{H_2SO_4,Hg}$ CH₃CHO 7) $H_2C=CH_2 + HCl \longrightarrow CH_3CH_2Cl$ 8) $H_2C=CH_2 + H_2O \xrightarrow{H_2SO_4} CH_3CH_2OH$ 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) $H_2C = C - C = CH_2 + 2H_2 \longrightarrow CH_3CH = CHCH_3$ 11) CH₃CH=CHCH₃ + HCl \longrightarrow CH₃CH₂CHCH₃ \downarrow Cl 12) $H_2C = C - C = CH_2 + H_2O \xrightarrow{H_2SO_4} CH_3CH = CHCH_2OH \xrightarrow{+H_2} CH_3CH_2CH_2CH_2OH$ 13) $CH_3CH_2CH_2CH_2OH + SOCl_2 \longrightarrow CH_3CH_2CH_2CH_2Cl + SO_2 + HCl$ 14) $HC \equiv CH + Na \xrightarrow{-1/2H_2} HC \equiv CNa \xrightarrow{CH_3Cl} HC \equiv CCH_3 + NaCl$ 15) $HC \equiv CCH_3 + H_2 \longrightarrow H_2C = CHCH_3 \xrightarrow{+ HCl} H_3C \xrightarrow{- CH}_C - CH_3$ 16) $2CH_3CHO + O_2 \longrightarrow 2CH_3COOH \xrightarrow{+ CaO} (CH_3COO)_2Ca \xrightarrow{\theta} CH_3COCH_3 + CaCO_3$



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.

1)
$$2RI + 2Na \longrightarrow R-R + 2NaI$$

2) $RC\equiv CNa + R'Cl \longrightarrow RC\equiv CR' + NaCl$
3) $RMgCl + R'COR'' \longrightarrow R \xrightarrow{I}_{OMgCl} R''$

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

$$2RCOO^{-} \longrightarrow R-R + 2CO_{2} + 2e$$

$$2RCOONa \longrightarrow 2Na^{+} \xrightarrow{+2e} 2Na \xrightarrow{+ 2H_{2}Q} 2NaOH + H_{2}$$

EXERCISES

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

Solution
a)
$$CH_3CH_2CH_2OH + SOCl_2 \longrightarrow CH_3CH_2CH_2Cl + SO_2 + HCl$$

 $2CH_3CH_2CH_2Cl + 2Na \longrightarrow CH_3CH_2CH_2CH_2CH_2CH_3 + 2NaCl$
b) $CH_3CH_2CH_2OH \xrightarrow{-H_2O}_{H_2SO_4} CH_3CH=CH_2 \xrightarrow{+HCl}_{Cl} CH_3CHCH_3$
 Cl
 $2CH_3CHCH_3 + 2Na \longrightarrow CH_3CH=CH_2 \xrightarrow{+HCl}_{C} CH_3 + 2NaCl$
 Cl

- 11. From acetylene and inorganic material prepare the compounds a) 2,6oktadiene (oktadiene-2,6), b) octane. Solution
- B. Synthesis reactions that are based on the following reaction:

$$RC \equiv CNa + R'Cl \longrightarrow RC \equiv CR' + NaCl$$

12. From CH₃OH, 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

a)
$$CH_{3}OH + SOCl_{2} \longrightarrow CH_{3}Cl + SO_{2} + HCl$$

 $HC \equiv CH + H_{2} \longrightarrow H_{2}C \equiv CH_{2} \xrightarrow{+HCl} CH_{3}CH_{2}Cl$
 $HC \equiv CH + Na \xrightarrow{-1/2H_{2}} Na - C \equiv CH \xrightarrow{+CH_{3}Cl} H_{3}C - C \equiv CH \xrightarrow{+Na} -1/2H_{2}$
 $\longrightarrow H_{3}C - C \equiv CNa \xrightarrow{+CH_{3}CH_{2}Cl} H_{3}C - C \equiv C - C - C - CH_{3} + NaCl$
b) $H_{3}C - C \equiv C - C - CH_{3} + 2H_{2} \longrightarrow CH_{3}CH_{2}CH_{2}CH_{2}CH_{3}$

- **13.** From CH₃OH, 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:

a)
$$CH_3CH_2CH_2C \equiv CCH_2CH_2CH_3$$

b) CH₃CH₂CH₂COCH₂CH₂CH₂CH₃

Solution
a)
$$CH_3CH_2CH_2OH + HI \longrightarrow CH_3CH_2CH_2I + H_2O$$

 $HC \equiv CH + 2Na \xrightarrow{-H_2} NaC \equiv CNa \xrightarrow{2CH_3CH_2CH_2I} CH_3CH_2CH_2C \equiv CCH_2CH_2CH_3 + 2NaI$
b) $CH_3CH_2CH_2C \equiv CCH_2CH_2CH_3 + H_2O \xrightarrow{H_2SO_4, Hg} CH_3CH_2CH_2COCH_2CH_2CH_2CH_2CH_3$
c) $CH_3CH_2CH_2OH \xrightarrow{-H_2O} CH_3CH \equiv CH_2 \xrightarrow{+HCI} CH_3CHCH_3$
 CI
 $2CH_3CH_2CH_2OH \xrightarrow{-H_2O} H_2SO_4 + NaC \equiv CNa \longrightarrow H_3C \xrightarrow{-H_2} C = C \xrightarrow{-H_2} C + CH_3 + 2NaCI$
 CI
 CI
 $CH_3CHCH_3 + NaC \equiv CNa \longrightarrow H_3C \xrightarrow{-H_2} C = C \xrightarrow{-H_2} C + CH_3 + 2NaCI$
 CI
 CI
 CI
 CI
 $CH_3CHCH_3 + NaC \equiv CNa \longrightarrow H_3C \xrightarrow{-H_2} C = C \xrightarrow{-H_2} C + CH_3 + 2NaCI$
 CI
 CI
 CI
 $CH_3CHCH_3 + NaC \equiv CNa \longrightarrow H_3C \xrightarrow{-H_2} C + CH_3 \xrightarrow{-CH_3} C + CH_3$
 $CH_3 \xrightarrow{-H_2O} H_3C \xrightarrow{-H_2} C + CH_3 + H_2 \xrightarrow{-Ni} H_3C \xrightarrow{-H_2} C + CH_3 \xrightarrow{-CH_3} C + CH_3$
 $\xrightarrow{-H_2O} H_3C \xrightarrow{-H_2} C \xrightarrow{-H_2} C + CH_3$
 $\xrightarrow{-H_2O_4} H_3C \xrightarrow{-H_2} C \xrightarrow{-H_2} C + CH_3$
 $\xrightarrow{-H_2O_4} H_3C \xrightarrow{-H_2} C \xrightarrow{-H_2} C + CH_3$

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

a)
$$H_3C - C - C = C - C = C - CH_3$$
 b) $CH_3CH_2CH_2CH_2CH_2CH_2CH_3$
 CH_3 CH_3 CH_3

17. From acetylene and inorganic material prepare the compounds

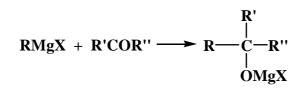
- 18. From acetylene, CH₃CH(OH)CH₃ and inorganic material prepare the compounds:
 - a) $\hat{H}_2C=CHCH_2C\equiv CCH_2CH=CH_2$ b) $H_2C=CHCH_2C\equiv CCH_2CH_3$

Solution

a)
$$H_{3}C \xrightarrow{-H_{2}}{C} H_{2}C=CH_{3} \xrightarrow{-H_{2}O}{H_{2}SO_{4}} H_{2}C=CHCH_{3} \xrightarrow{+Cl_{2}}{600C} H_{2}C=CHCH_{2}Cl + HCl$$

 $HC\equiv CH + 2Na \xrightarrow{-H_{2}}{Na}C\equiv CNa \xrightarrow{+2H_{2}C=CHCH_{2}Cl} H_{2}C=CHCH_{2}C\equiv CCH_{2}CH=CH_{2} + 2NaCl$
b) $HC\equiv CH + H_{2} \longrightarrow H_{2}C=CH_{2} \xrightarrow{+HCl}{CH_{3}CH_{2}Cl}$
 $HC\equiv CH + Na \xrightarrow{-1/2H_{2}}{Na}C\equiv CH \xrightarrow{+H_{2}C=CHCH_{2}Cl}{-NaCl}$
 $\longrightarrow H_{2}C=CHCH_{2}C\equiv CH \xrightarrow{+Na}{-1/2H_{2}} H_{2}C=CHCH_{2}C\equiv CNa \longrightarrow$
 $\xrightarrow{CH_{3}CH_{2}Cl}{H_{2}C=CHCH_{2}C\equiv CCH_{2}CH_{3} + NaCl}$

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

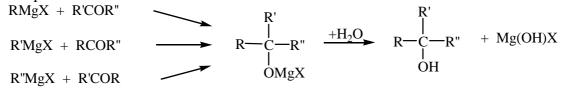


General instructions

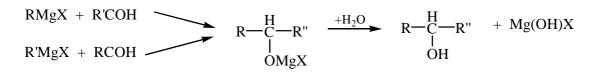
The reaction above is mainly used to prepare complex alcohols and the compounds that may result from them. In order to apply this synthesis we have to choose the appropriate alkyl halide and the appropriate carbonylic compound, in such a way that these compounds can be easily prepared.

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

Prepare the following compound in three different ways 19.

 $\begin{array}{c} H_2 \\ H_2 \\ H_3 C - C - C H_2 - C - C - C \\ O H \end{array} \qquad by choosing a different pair of alkyl halide and carbonylic \\ \end{array}$ compound each time.

20. From CH₃CH(OH)CH₃ and inorganic material prepare the compound $H_{3}C - C - C - C H_{3}$

Determining the synthesis procedure

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

$$H_{3}C - C - C - C H_{3}$$

$$H_{3}C - C - C - C H_{3}$$

$$H_{3}C - C - C H_{3}$$

$$H_{3}C - C - C H_{3}$$

which is best to be prepared from the following compound,

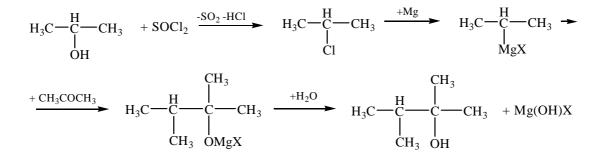
$$H_3C - C - CH_3$$

 M_gX

Solution

$$H_3C - CH_3 + 1/2O_2 \longrightarrow H_3C - CH_3 + H_2O$$

OH



- 21. From CH₃CH₂OH and inorganic material prepare the compound CH₃CH₂CH(OH)CH₃
- 22. From CH₃CH₂OH, CH₃CH(OH)CH₃ and inorganic material prepare the compounds:

23. From acetylene, CH₃CH(OH)CH₃ and inorganic material prepare the compound,

$$\begin{array}{c} H_2 \quad H_2 \quad H_2 \quad H_2 \quad | \\ H_3C - C - C - C - C - C - C H_3 \\ & 0 \\ & 0 \\ H \end{array}$$

Solution $CH_{3}CHCH_{3} + 1/2O_{2} \longrightarrow CH_{3}COCH_{3} + H_{2}O$ OH $2 HC \equiv CH \longrightarrow HC \equiv C - C \equiv CH_{2} \xrightarrow{+H_{2}} H_{2}C = C - C \equiv CH_{2} \xrightarrow{+HCI}$ $\longrightarrow CH_{3}CH \equiv CHCH_{2}CI \xrightarrow{+Mg} CH_{3}CH \equiv CHCH_{2}MgCI \longrightarrow$ $\xrightarrow{+CH_{3}COCH_{3}} CH_{3}CH \equiv CHCH_{2}CCH_{3} \xrightarrow{+H_{2}O} CH_{3}CH \equiv CHCH_{2}CCH_{3} \xrightarrow{-Mg(OH)CI} CH_{3}CH \equiv CHCH_{2}CCH_{3} \xrightarrow{-Mg(OH)CI} OH$ $\xrightarrow{+H_{2}} CH_{3}CH_{2}CH_{2}CH_{2}CH_{2}CH_{3} \xrightarrow{-Mg(OH)CI} OH$

24. From CH₃CH₂CH₂OH and inorganic material prepare the compounds:

a)
$$H_3C \stackrel{H}{-} \stackrel{H}{-} \stackrel{H_2}{-} \stackrel{H_2}{-} \stackrel{H_2}{-} \stackrel{H_2}{-} \stackrel{H_2}{-} \stackrel{H_2}{-} \stackrel{H_2}{-} \stackrel{H_3}{-} \stackrel{H_3}{-}$$

Solution

a)
$$CH_3CH_2CH_2OH + 1/2O_2 \longrightarrow CH_3CH_2CHO + H_2O$$

 $CH_3CH_2CHO \xrightarrow{-H_2O}_{H_2SO_4} H_3C \xrightarrow{-C}_{C} = CH_2 \xrightarrow{+HCl}_{H_3} H_3C \xrightarrow{-C}_{Cl} C \xrightarrow{-C}_{Cl} CH_3 \xrightarrow{+Mg}_{Cl}$
 $\longrightarrow H_3C \xrightarrow{-C}_{H_2C} - CH_3 \xrightarrow{+CH_3CH_2CHO}_{H_3C} H_3C \xrightarrow{-C}_{C} \xrightarrow{-C}_{C} \xrightarrow{-C}_{C} CH_3 \xrightarrow{+H_2O}_{CH_3} \xrightarrow{-H_2O}_{CH_3} H_3C \xrightarrow{-C}_{CH_3} \xrightarrow{-H_2O}_{CH_3} \xrightarrow{-H_2O}_{CH_3} \xrightarrow{-H_2O}_{CH_3} H_3C \xrightarrow{-C}_{C} \xrightarrow{-H_2O}_{C} \xrightarrow{-C}_{C} \xrightarrow$

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