EXPERIMENT 6

AMYLENES

Preparation of 2-Methyl-2-Butene

Preparation of Alkenes by Dehydration of alcohols

- Amylene is a generic term applied to the alkenes of formula C_5H_{10}
- Alcohols undergoes dehydration by an E1 mechanism.
- The key intermediate in the mechanism is a alkyl cation, which can undergo substitution as well as elimination.
- To prepare an alkene in good yield, it is necessary to suppress the substitution reaction.
- A dehydration reaction is reversible and usually has a small equilibrium constant.

This means that the equilibrium favors the reactants and not the products. In fact, the reverse reaction is a method often used to synthesize alcohols.

Preparation of Alkenes by Dehydration of alcohols

- Alcohols undergoes dehydration by an E1 mechanism.

- In today`s experiment, ***2-Methyl-2-Butene*** is synthesized by dehydration of ***t-Amyl Alcohol*** .

➢ **In this experiment, the substitution reaction is suppressed by:**

1. the use of strong acids with anions that are relatively poor nucleophiles

Acids like HBr, HCl, HI, and similar acid, although of comparable acidity or even more acidic cannot be used for this purpose because they will yield substitution rather than elimination reaction yielding the corresponding halide as a result.

2. a high reaction temperature, which favors elimination.

3. distillation of alkene from the reaction mixture as it is formed.

Preparation of Alkenes by Dehydration of alcohols

- Concentrated sulfuric acid alone causes both oxidation and polymerization of the product alkene.
- Removal of the alkene by distillation as it is being formed in the reaction mixture is an excellent technique for preventing side reactions.

- Removal of the alkene reduces tar (polymer) formation by minimizing the contact time between the acid and the alkene.

- Water might also be removed from the acidic reaction mixture in this distillation, which prevents the reverse reaction from occurring.

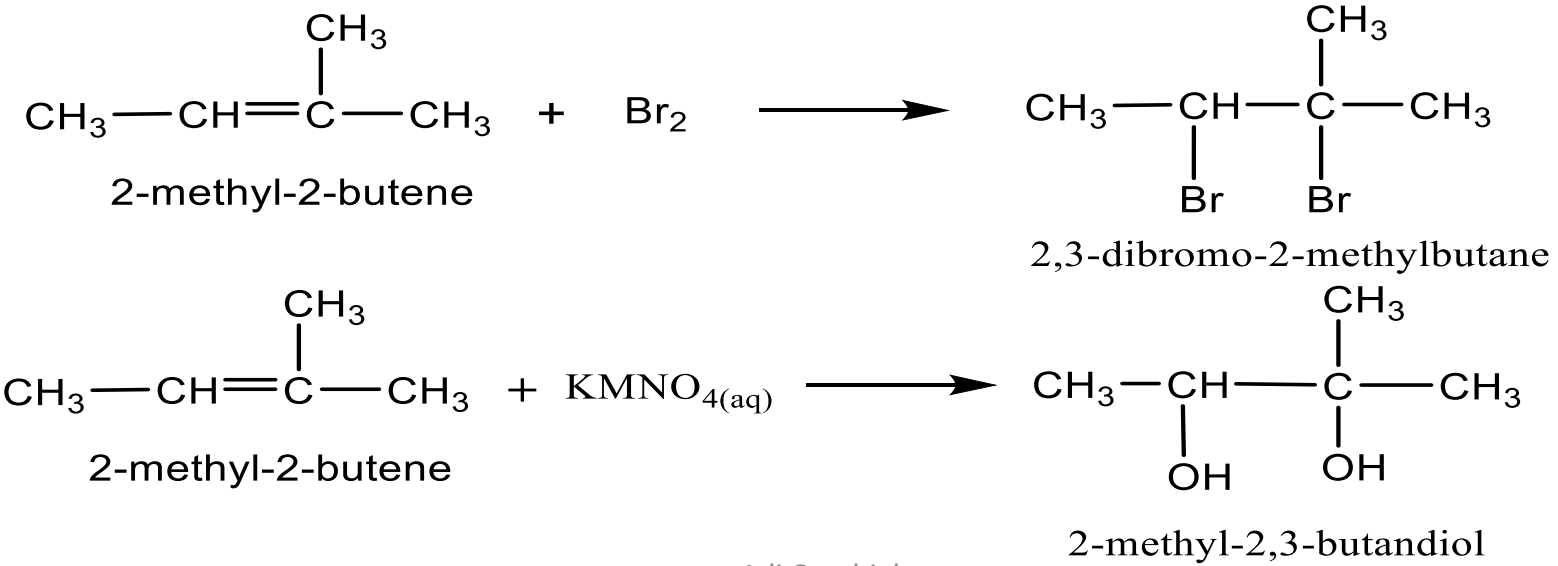
- The crude distillate is transferred to a separatory funnel and the aqueous layer is drawn off.

- The alkene is extracted with 10% NaOH solution to remove excess sulfuric acid.
- Anhydrous $CaCl_2$ is the drying agent of choice because it forms molecular complexes with alcohols, as well as with water, and thus removes the last traces of alcohol.

Chemical testing

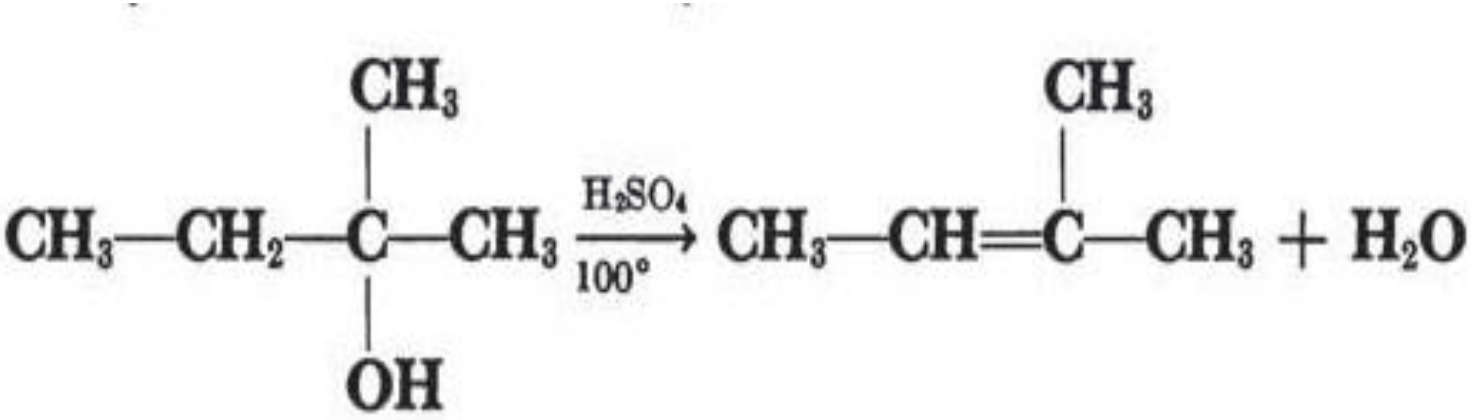
- Chemical Tests are chemical reactions accompanied with physical changes; like change in color, formation of a precipitate, evolution of gas, change of state,…etc,.

- The amylenes add bromine rapidly with the evolution of considerable heat.
- The oxidation of alkene is also possible .This reaction is known as the **Baeyer test.**
- The two equations below are two reaction to demonstrate this chemistry:



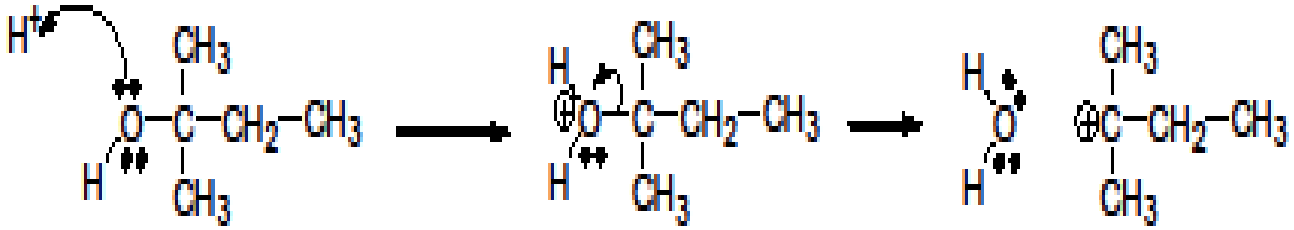
CHEMICAL REACTION

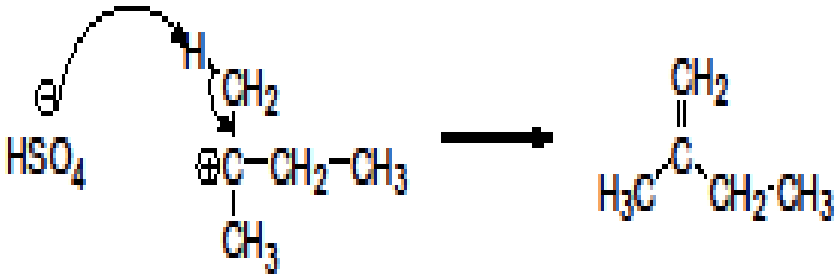
Dehydration of *t-Amyl Alcohol (2-Methyl-2-Butanol)*

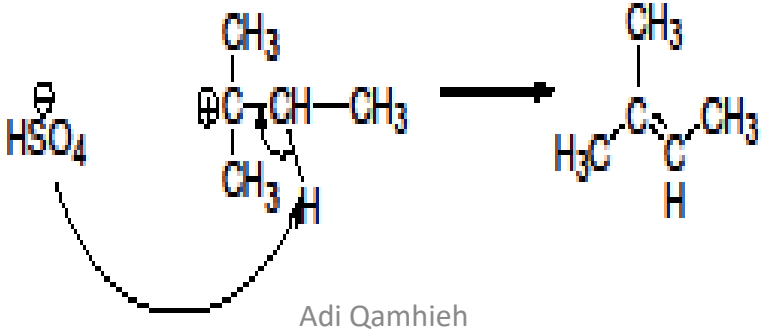


2-methyl -2-butanol (tert-amyl alcohol) **2-methyl-2-butene(major product)**

Reaction Mechanism







Experimental procedure

Preparation of 2-Methyl-2-butene :

1. In a 250-mL. round bottomed flask, add 81 mL of 2:1 sulfuric acid.

2. Add 54 ml. (44 g., 0.50 mole) of t-amyl alcohol with cooling and shaking.

3. Mount the flask over a steam bath (Note 1) on a ring stand

4. Attach the flask to an efficient condenser arranged for distillation (simple distillation).

5. Fit the condenser with a curved adapter which leads through a cotton plug into a 250-ml. Erlenmeyer receiving flask packed in ice (Note 2).

6. Heat the flask strongly with steam until alkene is no longer obtained in the distillate (Note 3).

Experimental procedure

7. Transfer the cooled product to a small separatory funnel .

8. Add 15 ml of cold 10% sodium hydroxide solution. Invert the funnel, open the stopcock to release the pressure, then close the stopcock and shake vigorously, stopping occasionally to release the pressure.

9. Tap off and discard the lower aqueous layer .

10. Pour the alkene through the mouth of the separatory funnel into a small, dry Erlenmeyer flask.

11. Add about 2 g of anhydrous calcium chloride and allow the flask to stand with cooling and occasional shaking.

12. Transfer the alkene into a clean, dry pre weighed 100 mL beaker.

13. Record the mass of the prepared alkene and calculate the percentage yield.

14. Do tests for unsaturation using a sample of the prepared alkene (See chemical tests for alkenes).

Notes

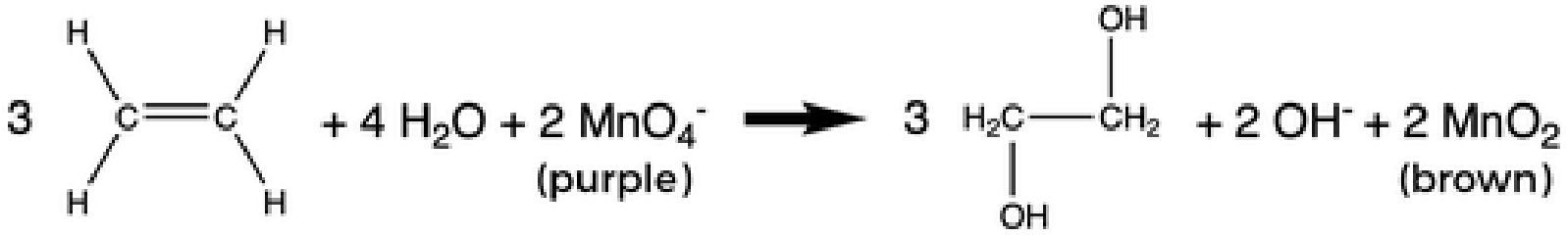
1. For efficient heating it is advisable to wrap a towel (or Aluminum foil) around the flask and extend the towel over the top of the steam bath. Escaping steam is then used effectively to heat the flask.
2. The amylenes are all low boiling and highly flammable, so efficient condensation is critical.
3. This requires about 25 minutes if heating is efficient.

	t-amyl alcohol	2-methyl 2-butene
Molar mass	88.15g/mol	70.14g/mol
Density	0.805g/mL	0.662g/mL
Boiling point	101-103 degree Celsius	39 degree Celsius
Solubility in water	Soluble	Insoluble

Chemical tests for alkenes

1. Baeyer test : Permanganate test:

- In a small test tube transfer 1 ml of cold aqueous 0.5% potassium permanganate, $KMNO_4$.
- Add 2-3 drops of **2-Methyl - 2-Butene** .
- Shake vigorously and notice the difference. The purple color of the permanganate solution will disappear.



- Write equation to show results with your alkene.

2. Bromine test : **Addition of Br_2/CCl_4** :

- In a second small test tube add 1ml of 5% of bromine/carbon tetrachloride
- and add 2-3 drops of **2-Methyl - 2-Butene** .
- Observe the change and write equations to show what happened.

3. Repeat the above tests using **t-amyl alcohol** instead of **2-Methyl - 2-Butene**