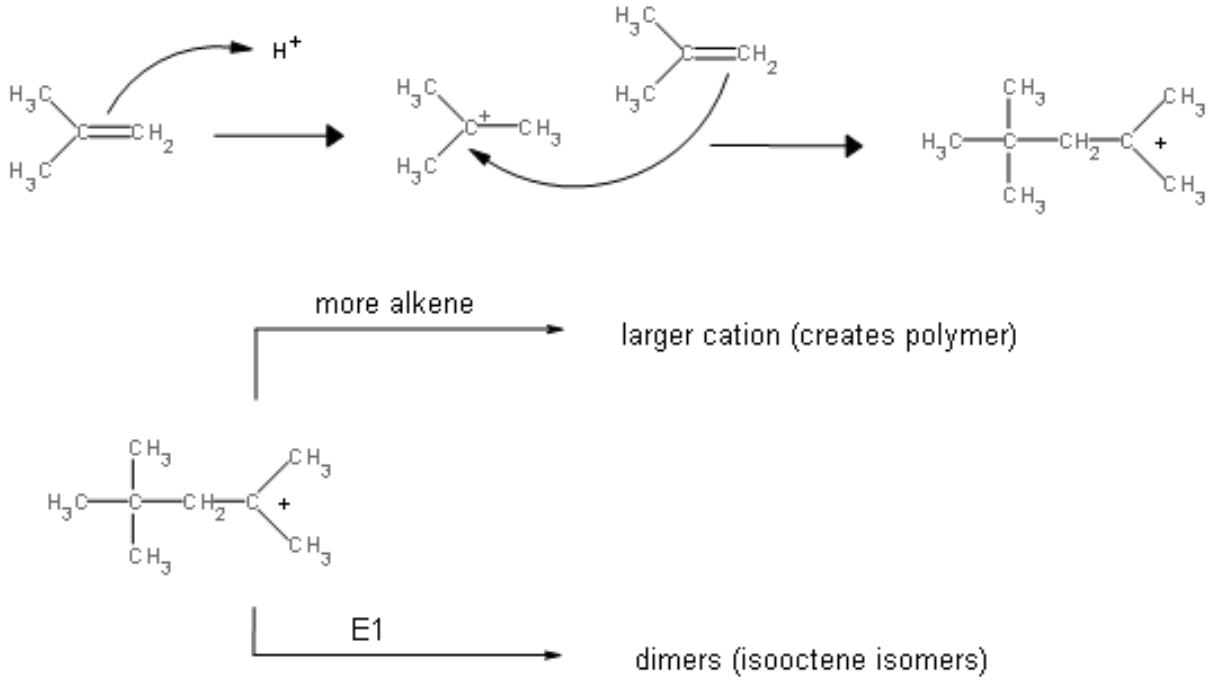
Experiment VIII-F: Dimerization (of Isobutylene)

Cationic Dimerization and Polymerization of Alkenes

Some alkenes, particularly those with a 3^o sp^2 C, can form dimers (two identical molecules condensed into one) and polymers (many molecules condensed into one) when treated with a cationic or radical initiator (catalyst). Cationic polymerization occurs by a chain reaction pathway (initiation, propagation, and termination) once some alkene molecules have been converted to carbocations by the cationic initiator. For this reason, the initiator is an acid, either Brønsted (proton donor) or Lewis (e- pair acceptor). The initiator will add H^+ (or E^+) to the less substituted sp^2 C by accepting the Π e- pair. This causes both C's to rehybridize to sp^3, and the more substituted C will bear the positive charge, creating a carbocation. This carbocation can add to another alkene molecule to create a larger carbocation. The new carbocation can either continue to add to more alkene molecules, or terminate by abstraction of H^+ from a neighboring C (that is, E1 elimination) to form a new, larger alkene. The most common commercial product prepared by cationic polymerization is polyisobutylene (a polymer, not the dimer) from isobutylene (2-methylpropene) with borane (BH_3) at − 80 ^{o}C. This polymer is typically used for tire inner tubes and flexible piping. Formation of the dimer will normally follow Zaitsev's rule, that is, the most substituted product will predominate. In this experiment, it does not, due to kinetic control from the two methyl groups, and the non-Zaitsev product is favored.



Recommended Reading

McMurry, J. Organic Chemistry, 9th Ed. Carbocation Mechanism in Figure 11.13 (pg 330), E1 Mechanism in Figure 11.21(pg 343), Step 1 in Figure 8.2 is the conversion of alkene to a carbocation, which can react with another alkene molecule (pg 228).

Ebbing D., and Gammon S. General Chemistry, 11th Ed. Separation of Mixtures by Chromatography (pp 13-14, between sections 1.4 and 1.5).

Zubrick, J.W. The Organic Chem Lab Survival Manual. Chapters 32 and 34 (GC and IR).

Keywords

Dimerization, Polymerization, Elimination Reaction, Zaitsev's Rule, Initiator, and Reflux

Compound, Reaction, and Yield Data

- Compound information should include masses, moles, BP's and densities.
- Include the intermediate alkene in the compound information.
- Provide overall balanced reaction, along with entire mechanism, from start to finish, including the appropriate curved arrows.
- Determine theoretic and actual yields of total alkenes, based on overall balanced reaction. Pay attention to stoichiometry.
- Report the temperature range at which you collected the product from the distillation in your Observations section.

Gas Chromatography Data

Include the product distribution (%'s) from your gas chromatogram in your Data section.

Infrared Spectral Data

Include the exact location of following infrared peaks in your Data section.

For 2-methyl-2-propanol, the O-H stretch is ~3400 cm^{-1} and very broad.
The sp^3 C-H stretch at ~2900 cm^{-1} is also very broad.
Report the entire range for both absorptions.
Also, note the location of the C-O stretch at ~1200 cm^{-1}.

For the product, note the location of the sp^2 =C-H stretch just above 3000 cm^{-1}.
Does the product have an sp^3 C-H stretch as well? Indicate its range.
Then, note the location of the C=C absorption between 1640 and 1680 cm^{-1}.
Also, the major product has a strong absorption for $R_2C{=}CH_2$ at ~890 cm^{-1}, while the minor product has a medium absorption for $R_2C{=}CRH$ at 800 - 850 cm^{-1}.
Indicate their exact positions, and use this information in your conclusion to describe which alkene predominated.

Apparatus

Items in kit
100-mL round-bottom flask, 25-mL round-bottom flask, condenser
125-ml separatory funnel, glass stopper, distillation head (three-way adapter)
thermometer adapter (glass with rubber), vacuum adapter (leave side nozzle open)

Items not in kit
thermometer, two water hoses, two stands with clamps
ice-water bath (400-ml beaker), hot water bath (400-ml beaker), heating mantle
three 50-ml Erlenmeyer flasks, rubber stopper
gas chromatograph (GC) and/or infrared (IR) spectrophotometer

Substances

20 ml 2-methyl-2-propanol (t-butyl alcohol)
20 ml concentrated sulfuric acid (H_2SO_4)
20 ml DI water
3 g drying agent (anhydrous $CaCl_{2(s)}$)
boiling stone

Procedure

1. Put 20 ml of DI water in a 100-ml round-bottom flask. Clamp flask to stand and place in an ice-water bath. Then, slowly and carefully, add 20 ml of concentrated sulfuric acid.

   Caution – Concentrated H_2SO_4 solutions are corrosive and cause acid burns.
   Use gloves and avoid all contact with skin and eyes.

2. Cool solution to 5.0 ^oC.

3. Slowly add 20 ml of 2-methyl-2-propanol while swirling with a stir bar.
   Mix thoroughly. Place alcohol bottle in warm water bath if frozen.
   Do not dispense the liquid from the bottle until you are ready to use it as it will solidify if allowed to stand in the graduated cylinder.

4. Add a boiling chip, and then dry the outside of the flask with a paper towel.
   Set up the flask in a reflux assembly with a heating mantle.
   Ensure sufficient water is flowing through reflux condenser.
   Boil very *gently* (that is *mildly* bubbling) for 30 minutes.
   The product will form as a clear upper layer.
   The bottom layer may become colored, generally yellow or orange.
   Ignore those color variations.

5. Remove the flask from the heating mantle, and allow the flask to cool sufficiently, so that you can handle it safely.
   Then, transfer the mixture to a 125-ml separatory funnel and allow the layers to separate.
   Do not allow the boiling chip to fall into the separatory funnel.

6. Drain the lower layer. Test removed layer with drops of water to ensure that it is aqueous. Then, discard it in the appropriately labeled waste jar.

7. Wash the remaining organic phase (product) with 20 ml of DI water.
   Use the glass stopper from your kit along with the separatory funnel.
   Shake and vent the funnel to mix the layers. Allow the layers to separate, and then drain the lower aqueous layer. Discard it in the appropriately labeled waste jar.

   Caution - Pressure typically builds inside separatory funnel when shaken!
   Be sure to ***vent*** stopcock frequently while shaking!
   Do not vent towards yourself or any other individual!

8. Remove the glass stopper from the separatory funnel.
   Drain the organic layer into a 50-ml Erlenmeyer flask.
   Add 2 g of anhydrous $CaCl_2$, and then stopper the flask.
   Note that stopper size is printed on the flask.

9. Let flask stand for 10 minutes with occasional swirling.
   If drying agent clumps or appears slimy, add another 1 g of $CaCl_2$.
   If time is limited, skip steps 10, 11, and 12.
   Decant liquid into a weighed 50-ml Erlenmeyer flask instead.

10. Decant liquid into a 25-ml round-bottom flask.
    Use centrifuge to remove the remaining $CaCl_2$ if product is cloudy.
    Dispose of used drying agent in the appropriately-labeled waste jar.

11. Add a boiling chip to the flask.
    Set up a simple distillation assembly with a heating mantle.
    Use a weighed 50-ml Erlenmeyer flask as a receiver.

12. Collect fraction that boils between 85 ^{o}C and 95 ^{o}C.
    Bulb temperature will typically remain much less than the actual solution BP.
    Do not discard any foreruns until they have been analyzed.

13. Determine mass of product.

14. With the instructor's assistance, analyze the product by IR and/or GC.
    The major product has a strong IR absorption at 890 cm^{-1}, while the minor product has a medium IR absorption at 800 - 850 cm^{-1}.
    The major product should elute from the GC column first, as it has a slightly lower BP than the minor product.

Post-Lab Questions

1. Why is acid added to water and not the reverse?

2. Why does the water and acid get hot when mixed?
   Write a balanced reaction that includes H_3O^{+1}.

3. What two substances does the water wash remove in step 7?

4. Consider what dimerization means. Identify the molecule that dimerizes in this experiment, and explain how it dimerizes.

5. Describe how a gas chromatograph separates the components of a mixture.
   In addition to the recommended reading section and the hyperlink listed previously, you may also use this Gas Chromatography link.