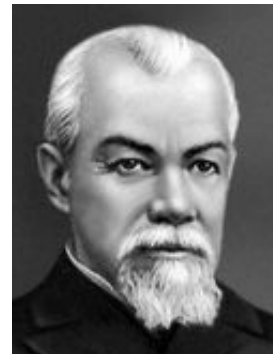


## Experiment 16

Fig. 16-1



# ELIMINATION REACTIONS

Aleksandr Zaitsev (1841 -1910)

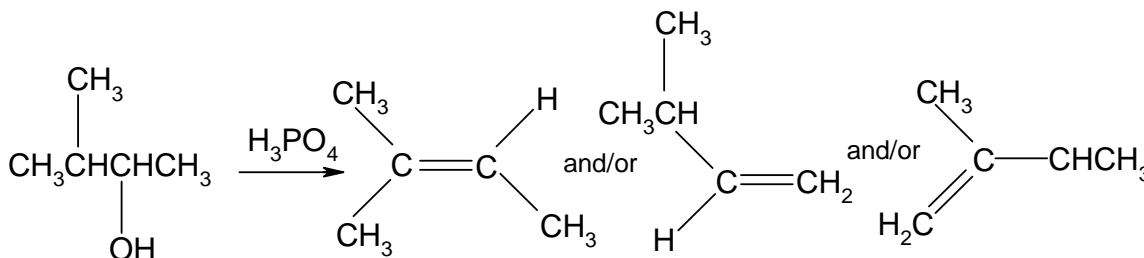
[http://en.wikipedia.org/wiki/Alexander\\_Mikhailovich\\_Zaytsev](http://en.wikipedia.org/wiki/Alexander_Mikhailovich_Zaytsev)

### Text Topics and Comments

$E_1$  and  $E_2$  mechanisms, Zaitsev and Hofmann eliminations. The products of the eliminations are very volatile (boiling points between 31 and 38°C) and must be carefully handled and tightly stoppered to prevent evaporation.

### Discussion

In earlier experiments, the stereochemistry of the addition of bromine to cinnamic acid and the regioselectivity of electrophilic addition to alkenes was investigated. Today's investigation involves the reverse reaction, the elimination of a small molecule such as HBr or HOH from a bromide or alcohol to give the alkene. When an elimination reaction is run with 3-methyl-2-butanol, three possible elimination products could be obtained.



In this experiment, you will collaborate in teams of four to investigate the elimination reactions of four related bromides and alcohols. The compounds your team will use and compare are:

<u>reaction</u>	<u>organic substrate</u>	<u>reagent</u>
A	2-bromo-2-methylbutane	potassium hydroxide in 2-ethoxyethanol
B	2-bromo-2-methylbutane	potassium <i>t</i> -butoxide in 2-methyl-2-butanol
C	2-methyl-2-butanol	phosphoric acid
D	2-methyl-1-butanol	phosphoric acid.

You should prepare for this experiment by writing the reactions to the expected products, 2-methyl-2-butene and 2-methyl-1-butene. Based on the concepts you are learning in the lecture portion of the course, predict which product should predominate for each reaction.

Because both products in this case are isomers and therefore contain the same carbon - hydrogen composition, the heats of formation for the two alkenes can be used to calculate the product ratio that should result if the product ratio is governed by the thermodynamic stabilities of the products. Evidence that the

reaction is thermodynamically controlled is provided if the experimental ratio agrees with the thermodynamic prediction. If the product ratio differs substantially from the prediction based on thermodynamics, then the product ratio is probably kinetically (rate) controlled. The thermodynamic product ratio is calculated from the equation:

$$(\Delta G_2 - \Delta G_1)/RT = -\ln(A_1/A_2)$$

where  $A_2$  represents 2-methyl-2-butene and  $A_1$  represents 2-methyl-1-butene. Values for the free energies of formation of the two alkenes can be found in the *Handbook of Chemistry and Physics* (under "Values of Thermodynamic Properties of Hydrocarbons") or possibly at one of the sites below:

<http://webbook.nist.gov/chemistry/>

[http://www.wiredchemist.com/chemistry/data/entropies\\_organic.html](http://www.wiredchemist.com/chemistry/data/entropies_organic.html)

[http://www.knovel.com/web/portal/browse/display?\\_EXT\\_KNOVEL\\_DISPLAY\\_bookid=761](http://www.knovel.com/web/portal/browse/display?_EXT_KNOVEL_DISPLAY_bookid=761)

## Procedure

**Reaction A - Elimination of HBr from 2-bromo-2-methylbutane using KOH.** Add 10 mL of 2-ethoxyethanol and 2.3 g of KOH to a 50 mL round bottom flask and stir for several minutes until some of the KOH dissolves. Add 2.6 mL of 2-bromo-2-methylbutane and a couple of boiling chips or a magnetic stirring bar to the flask. Set the flask up as a boiling flask for a small scale simple distillation with a steam bath or hot water bath for a heat source. **Place an ice bath around the receiver.** Heat and distill and collect the liquid with a boiling range of 30 to 45°C. Add a few pellets of calcium chloride to the distillate and swirl until the cloudiness disappears. Decant the liquid into a pre-weighed small flask with a ground glass joint. Tightly stopper the flask, weigh it and place it in a refrigerator until you are ready to analyze the ratio of alkenes using gc and/or

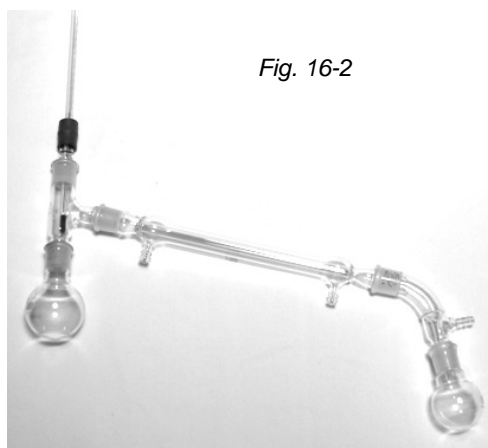


Fig. 16-2

by nmr integration. 2-Methyl-2-butene has a multiplet centered at 5.2  $\delta$  and 2-methyl-1-butene has an unresolved single peak at 4.7  $\delta$ . Be sure to take into account that a factor of two has to be introduced into the integration ratio to obtain the molar ratio. *Why the factor of two?* Dispose of the liquid remaining in the pot by slowly pouring it into a hood sink with the water running.

**Reaction B - Elimination of HBr from 2-bromo-2-methylbutane using potassium *t*-butoxide.** Repeat the procedure above except substitute 4.6 g of potassium *t*-butoxide and 10 mL of 2-methyl-2-butanol for the KOH and 2-ethoxyethanol.

**Reaction C - Elimination of HOH from 2-methyl-2-butanol using phosphoric acid.** Add 5 mL of phosphoric acid and 5 g of 2-methyl-2-butanol and a couple of boiling chips or a magnetic stirring bar to a 25 mL round bottom flask. Thoroughly mix and set the flask up as a boiling flask for a small scale simple distillation with a steam bath or hot water bath for a heat source. **Place an ice bath around the receiver.** Heat and distill and collect the liquid with a boiling range of 30 to 45°C. Add a few pellets of calcium chloride to the distillate and swirl until the cloudiness disappears. Decant the liquid into a pre-weighed small flask with a ground glass joint. Tightly stopper the flask, weigh it and place it in a refrigerator until you are ready to analyze the alkene ratio using gc and/or by nmr integration. 2-Methyl-2-butene has a multiplet centered at 5.2  $\delta$  and 2-methyl-1-butene has an unresolved single peak at 4.7  $\delta$ . Be sure to take into account that a factor of two has to be introduced into the integration ratio to obtain the molar ratio. *Why the factor of two?* Dispose of the liquid remaining in the pot by slowly pouring it into a hood sink with the water running.

**Reaction D - Elimination of HOH from 2-methyl-1-butanol using phosphoric acid.** Repeat the above procedure but substitute 2-methyl-1-butanol for 2-methyl-2-butanol. If nothing distills within 1 hour between 30 to 45°C, properly dispose of the reaction mixture down a hood sink with the water running.

## Reference

Zanger, M.; McKee, J. R. *Small Scale Syntheses: A Laboratory Textbook of Organic Chemistry*, W. C. Brown, 1995, pp. 135, 142.

## Prelaboratory Preparation - *Experiment 16*

First, be sure to list all the goals of the experiment. Write a mechanism for the reaction on the first page and show how the third product could be formed. Would you expect to obtain any of the third product? Write reactions for possible eliminations for each of the starting materials under each set of conditions. Which products do you expect in each case and why? Calculate theoretical yields for each reaction. **Look up the free energies of formation for the two alkenes and calculate the thermodynamic product ratio.** Locate these elimination reactions on the *Reaction-Map of Organic Chemistry* in **Appendix C** and include the reaction number in your report.

## Observations

Report all relevant observations including experimental yields, gas chromatograms and H-nmrs.

## Conclusions

This section should include the following:

1. Were the goals of the experiment achieved? Explain your answer.
2. Determine the ratio of alkenes for each of the four reactions. Compare the results to the thermodynamic calculations. What conclusions can you come to regarding the mechanism of each reaction?
3. If both were run, did the gc and nmr agree within experimental error? Which method do you have more confidence in? Could you have used another analysis method such as ir or refractive index to determine the product ratio?
4. How could the percent yield and recoveries have been improved?
5. Could any of these methods been used successfully as a synthesis of one of the alkenes? How would you modify the conditions if you were going to use the procedure as a preparation of one of the alkenes?
6. How good is Zaitsev's rule as a predictive tool? Explain your answer.