

# E2 ELIMINATION\*

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## 1 The E2 Elimination Reaction

### 1.1 Objective

This experiment illustrates the base-induced dehydrohalogenation of alkyl halides with strong base for the preparation of alkenes. The stereo and regiochemical effect of the size of the base is investigated, and the product mixture is analyzed by gas chromatography.

### 1.2 Background Information

Base-induced elimination (dehydrohalogenation) of alkyl halides is a general reaction for preparing alkenes. This process is often referred to as an E2 elimination, since a hydrogen atom is always removed in addition to a halide (leaving group): E2 indicates a bimolecular elimination reaction, where rate =  $k [B][R-LG]$ .

This pathway is a concerted process with the following characteristics:

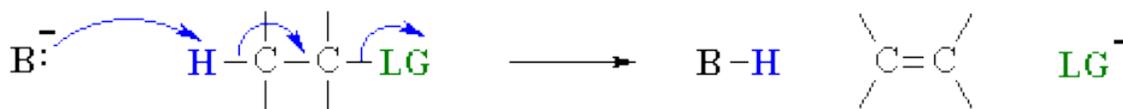


Figure 1

Simultaneous removal of the proton,  $H^+$ , by the base, loss of the leaving group, LG, and formation of the  $\pi$ -bond

Let's look at how the various components of the reaction influence the reaction pathway:

#### 1.2.1 Effects of R-

In an E2 reaction, the reaction transforms two  $sp^3$  C atoms into two  $sp^2$  C atoms. This moves the substituents further apart, decreasing any steric interactions. So, more highly substituted systems undergo E2 eliminations more rapidly. This is the same reactivity trend as seen in E1 reactions.

-LG The C-LG bond is broken during the rate-determining step, so the rate does depend on the nature of the leaving group. However, if a leaving group is too good, then an E1 reaction may result.

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B Since the base is involved in the rate-determining step, the nature of the base is very important in an E2 reaction. More reactive bases will favor an E2 reaction.

### 1.2.2 The E2 pathway is most common with:

a) high concentration of a strong base b) poor leaving groups c) R-LG that do not lead to stable carbocations (where the E1 mechanism will occur)

A high concentration of a strong base in a relatively nonpolar solvent is used to carry out the dehydrohalogenation reaction. Combinations include sodium methoxide in methanol, sodium ethoxide in ethanol, potassium isopropoxide in isopropanol, and potassium tert-butoxide in tert-butanol or dimethyl sulfoxide (DMSO).

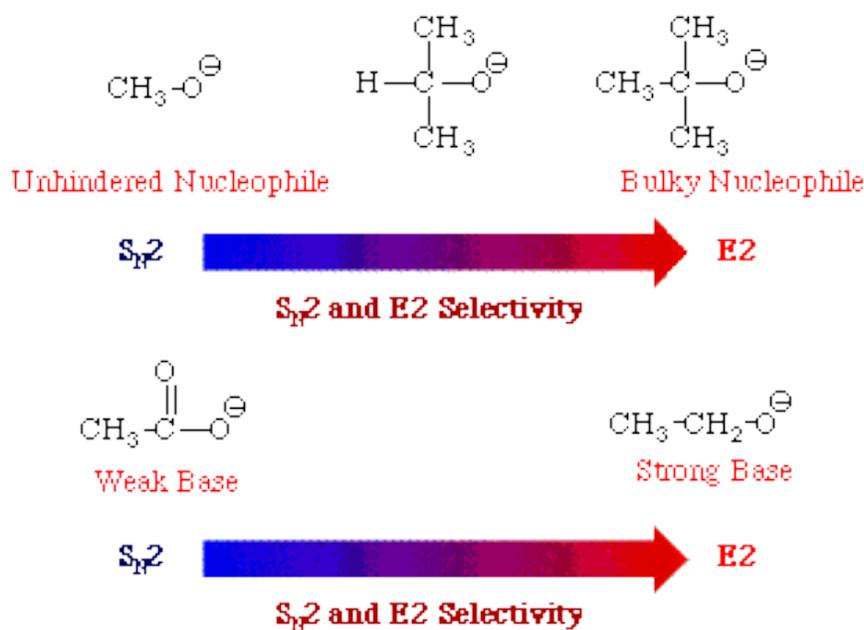


Figure 2

Elimination reactions nearly always yield an isomeric mixture of alkenes. Under the reaction conditions, the elimination is regioselective and follows the Zaitsev rule when more than one route is available for the elimination of HX from an unsymmetrical alkyl halide. Consequently, the reaction proceeds in the direction that yields the most highly substituted alkene. In cases where cis or trans alkenes can be formed, the reaction exhibits stereoselectivity, where the more stable trans isomer is the major product. For example,

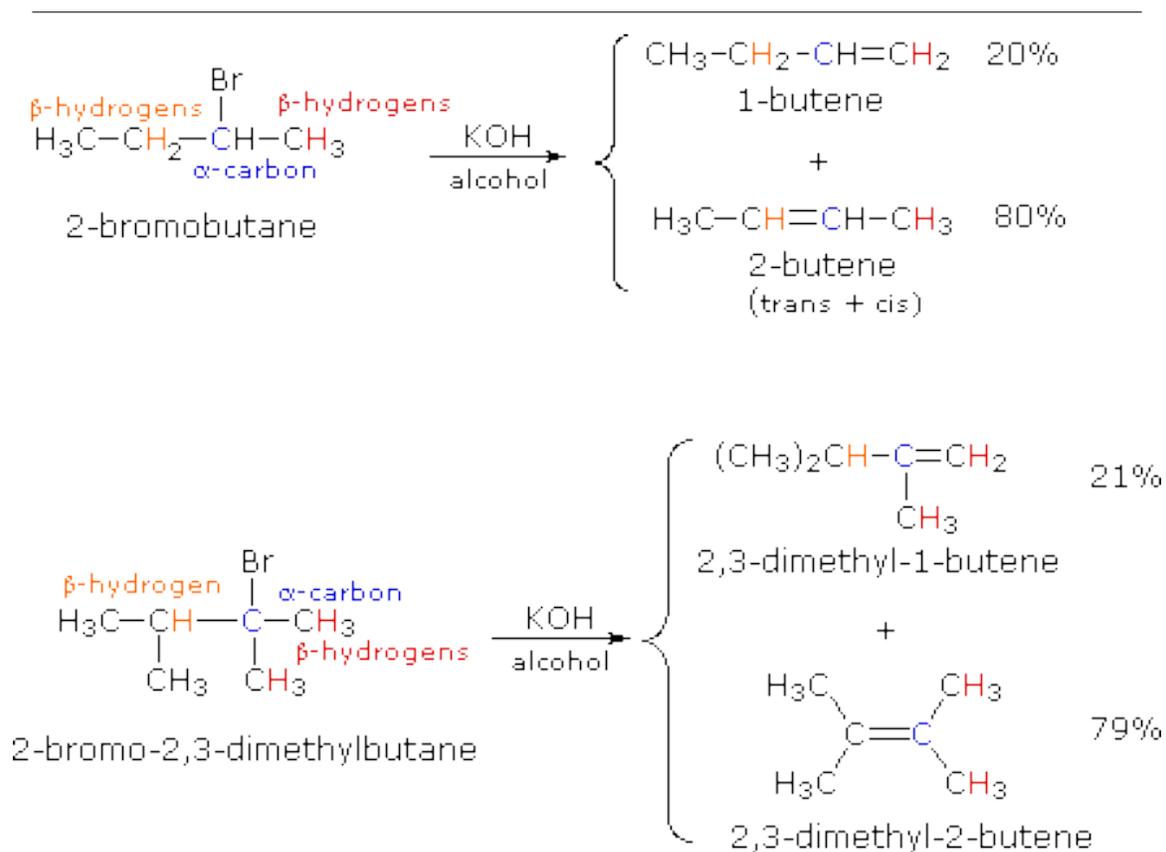


Figure 3

### 1.2.3 Mechanism of the E2 reaction:

Experimental evidence indicates that the five atoms involved in the E2 elimination reaction must lie in the same plane. The anti-periplanar conformation is preferred. This conformation is necessary so that orbital overlap can occur in order for the  $\pi$  bond to be generated in the alkene. The  $sp^3$ -hybridized atomic orbitals on carbon that comprise the C-H and C-X  $\sigma$  bonds broken in the reaction develop into the  $p$  orbitals comprising the  $\pi$  bond of the alkene formed:

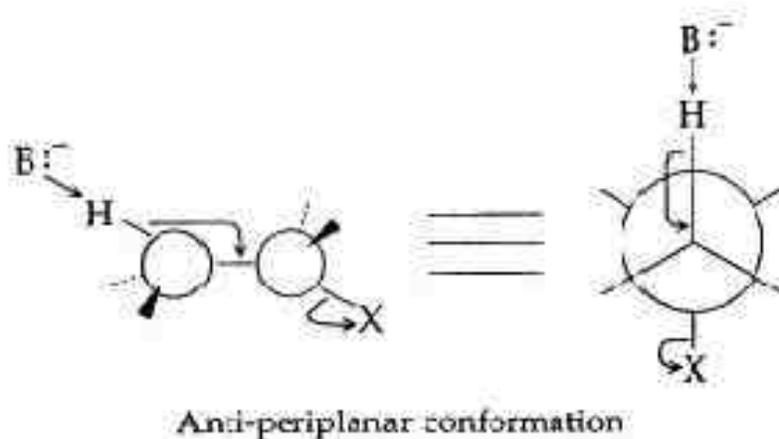


Figure 4

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There is a smooth transition between the reactants and products. Analogous to the  $S_N2$  reaction, no intermediate has been isolated or detected. Furthermore, no rearrangements occur under E2 conditions. This situation is in marked contrast to E1 elimination reactions, where carbocation intermediates are generated and rearrangements are frequently observed.

The alkyl halide adopts an anti-periplanar conformation in the transition state, and experimental evidence demonstrates that if the size of the base is increased, then it becomes more difficult for the large base to abstract an internal  $\beta$ -hydrogen atom. In such cases, the base removes a less hindered  $\beta$ -hydrogen, leading to the predominance of the thermodynamically less stable (terminal) alkene in the product mixture. This type of result is often referred to as anti-Zaitsev or Hofmann elimination. Thus, in the reaction of 2-bromo-2,3-dimethylbutane given above, 2,3-dimethyl-1-butene would be the major product (anti-Zaitsev) if the conditions involved use of a bulkier base. The anti-periplanar conformations are illustrated in the Newman projections below:

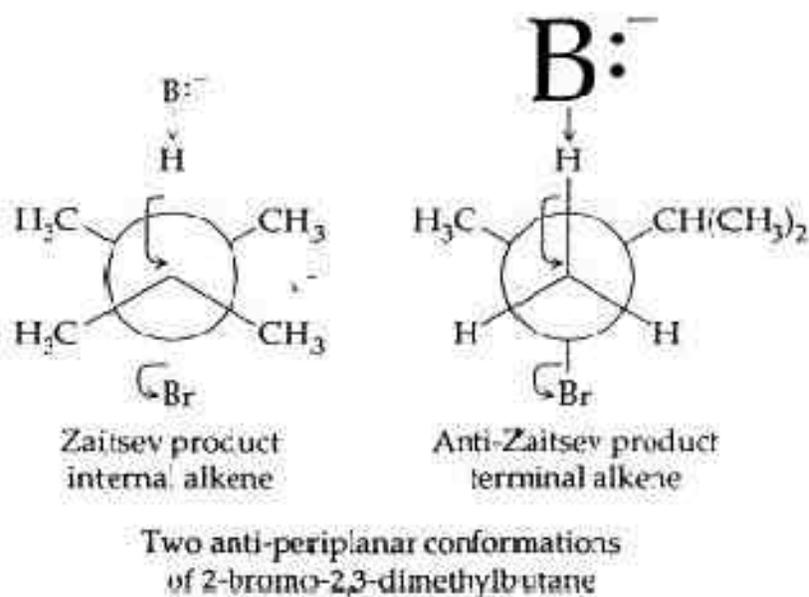
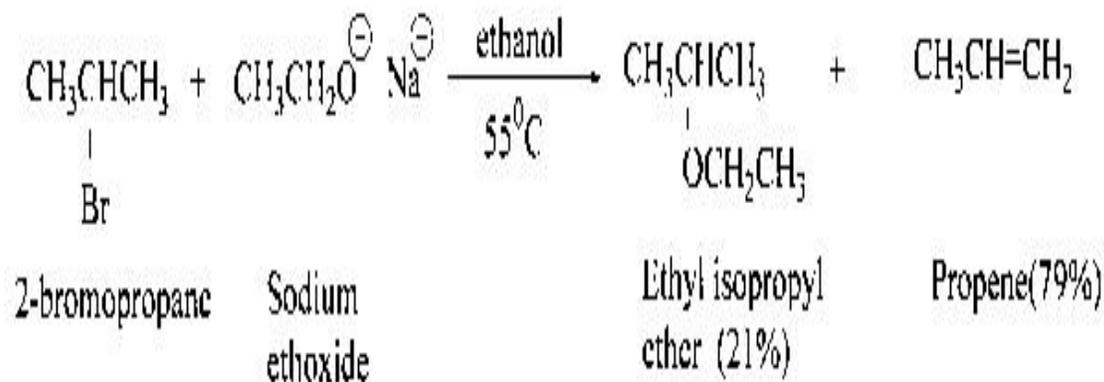
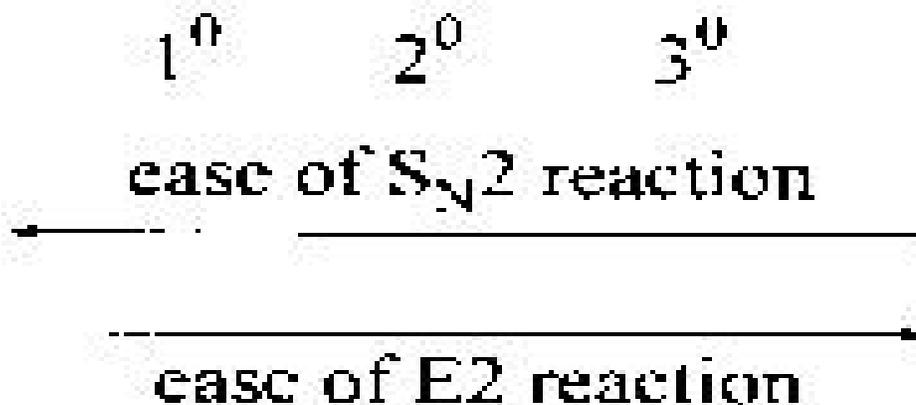


Figure 5

Dehydrohalogenation of alkyl halides in the presence of strong base (E2) is often accompanied by the formation of substitution ( $S_N2$ ) products. The extent of competitive substitution depends on the structure of the alkyl halide. Primary alkyl halides give predominantly substitution products (the corresponding ether), secondary alkyl halides give predominantly elimination products, and tertiary alkyl halides give exclusively elimination products. For example, the reaction of 2-bromopropane with sodium ethoxide proceeds as follows:



In general, for the reaction of alkyl halides with strong base:



#### 1.2.4 Physical Properties of Reactants: (Table 1.1)

Compound	MW	Amount	mmol	bp (°C)	D	n <sub>p</sub>
2-Bromobutane	137.03	100 mL	0.92	91.2	1.26	1.4366
Methanol	32.04	3.5 mL	64.9	0.791	1.3288	
2-Propanol	60.09	3.5 mL	82.4	0.785	1.3776	
2-Methyl-2-propanol (tertbutanol)	74.12	3.5mL	82-83	0.786	1.3838	
3- Ethyl-3-pentanol	116.20	3.5 mL	140-142	0.839	1.4266	
Sodium	22.98	60 mg	2.6	883	0.97	
Potassium	39.10	60 mg	1.5	760	0.86	

#### 1.2.5 Reagent Combinations: (Table 1.2)

Alcohol	Solvent	Metal	Alkoxide	Base	Produced
Methanol	Sodium	Sodium	methoxide		
2-Propanol	Potassium	Potassium	2-propoxide		
2-Methyl-2-propanol (tertbutanol)	Potassium	Potassium	2-methyl-1-2- propoxide (potassium tert- butoxide)		
3-Ethyl-3-pentanol	Potassium	Potassium	3-ethyl-3- pentoxide		

#### 1.2.6 Reagents and Equipment:

The combinations of reagents in Table 1.2 may be used to prepare the alkoxide base. Students should compare results to observe a total picture of the effect.

#### 1.2.7 Reaction Conditions: (Table 1.3)

Temperature	Conditions	Base	Temperature (°C)
NaOCH <sub>3</sub>	100-110		
KOCH (CH <sub>3</sub> ) <sub>2</sub>	130-140		
KOC (CH <sub>3</sub> ) <sub>3</sub>	140-150		

KOC (CH<sub>2</sub>CH<sub>3</sub>)<sub>3</sub> 175-180

### 1.2.8 Important Table to Memorize:

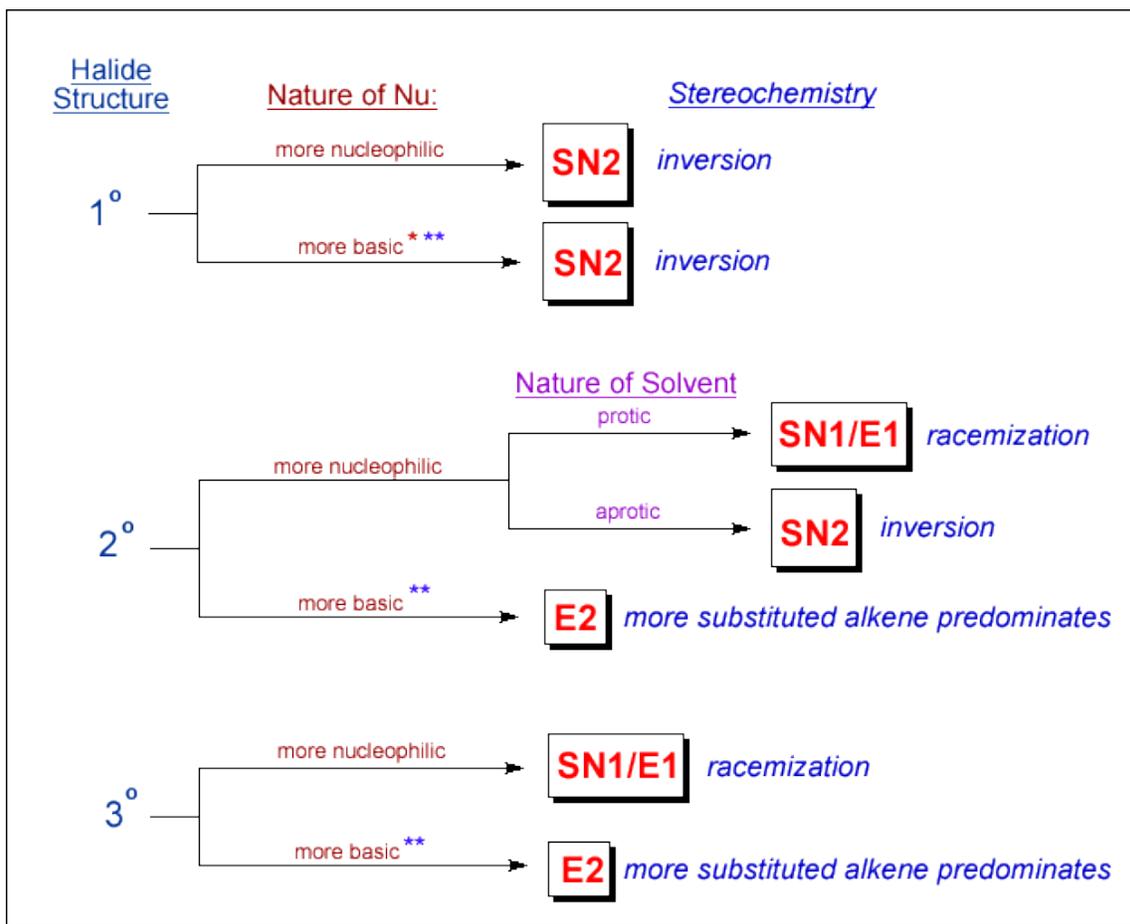


Figure 6

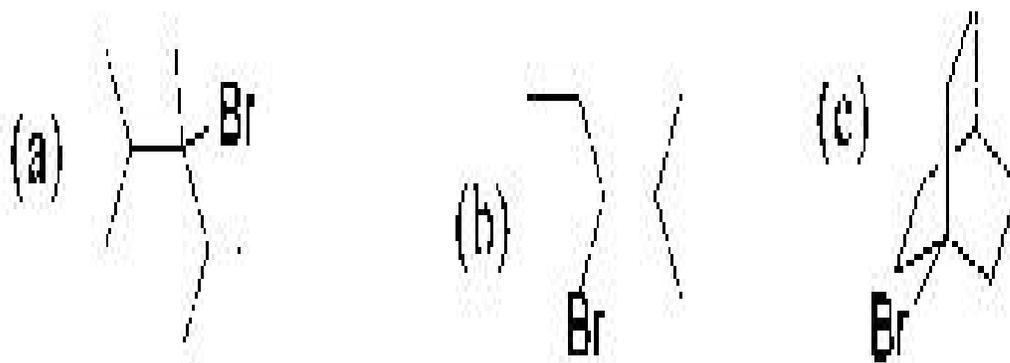
## 2 PreLab: The E2 Elimination (Total 10 Points)

On my honor, in preparing this report, I know that I am free to use references and consult with others. However, I cannot copy from other students' work or misrepresent my own data.

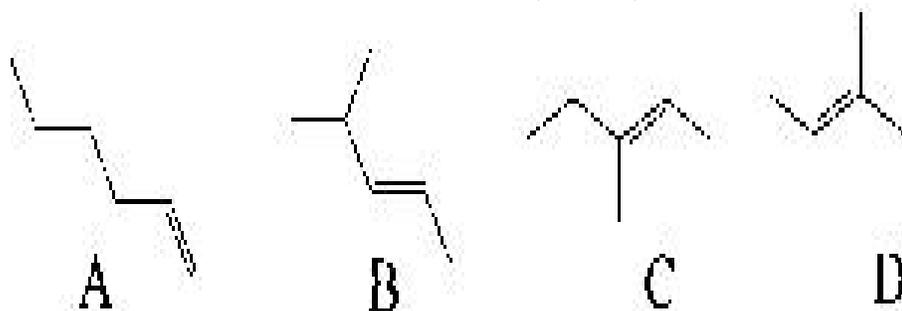
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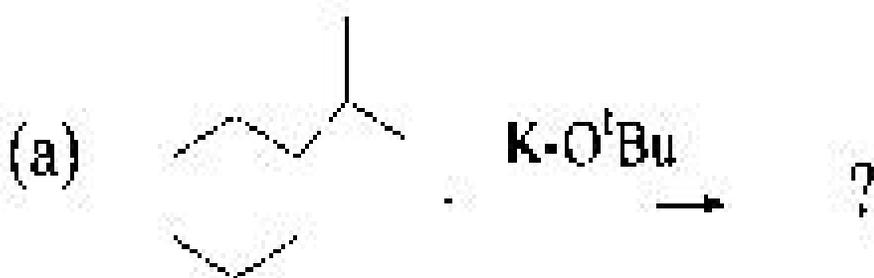
1. Predict the products when the following compounds are treated with sodium hydroxide (base). (3 points)

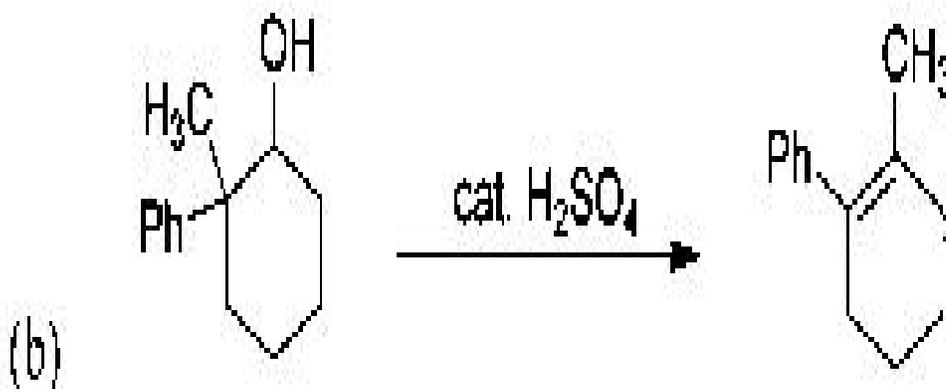


2. Which is the more stable structure and why? (2 points)



3. Write the major product from the following reactions. (1+ 4= 5 points)





(b)  
Write the mechanism for this reaction. (Hint: carbocationic rearrangement takes place)

## 2.1 Grading

- Completion of Pre Lab Questions.
- Write-up in your Lab Notebook.
- Completion of Report Questions.
- TA Points.

## 2.2 Materials Required

Equipment	Chemicals
Water bath with a beaker	Anhydrous alcohol (Ethanol)
Reflux condenser	Sodium metal
5 mL conical vial	Needle
Stirring vane	2-bromobutane

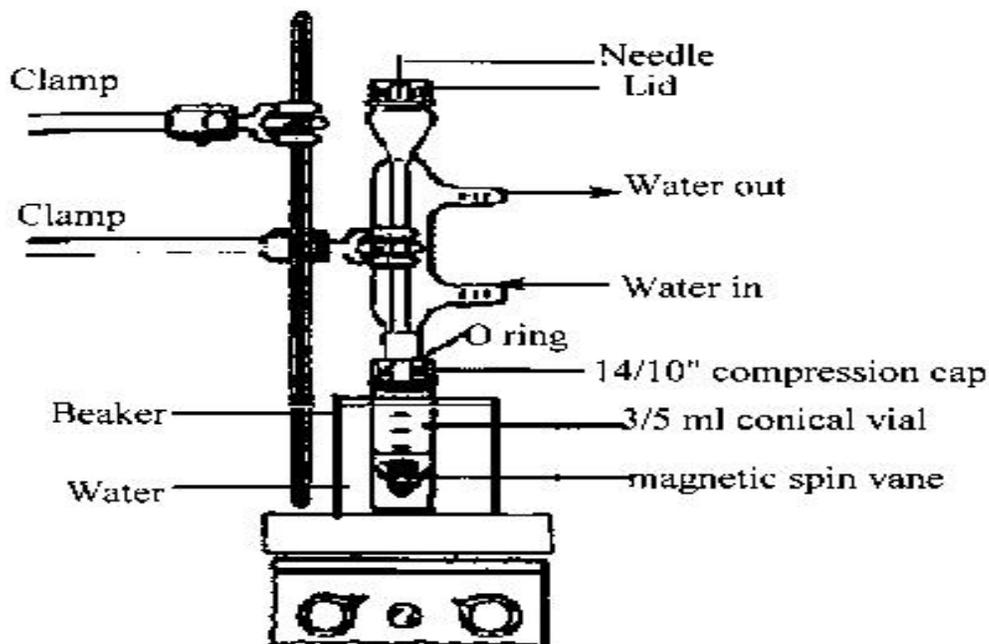
Table 1

### Safety

Wear gloves all the time, especially when you use the metals. Keep safety glasses on all the time.

## 2.3 Experimental Procedure

Preparation of the Alkoxide Base: Add to a 5.0 mL conical vial containing a magnetic spin vane 3-3.5 mL of the anhydrous alcohol (see Table 4.2). Add a 60-mg piece of potassium (or sodium) metal (or ~2 pellets) and immediately attach the vial to a reflux condenser closed by a lid. Place a needle above the reflux condenser to remove extra pressure generated during reflux. Place the whole arrangement in a water bath and, heat the mixture gently (~50 °C) with stirring. (DO NOT HEAT THE CLOSED SYSTEM) When all the metal has reacted, remove the assembly from the water bath and cool to near room temperature (remove the needle).



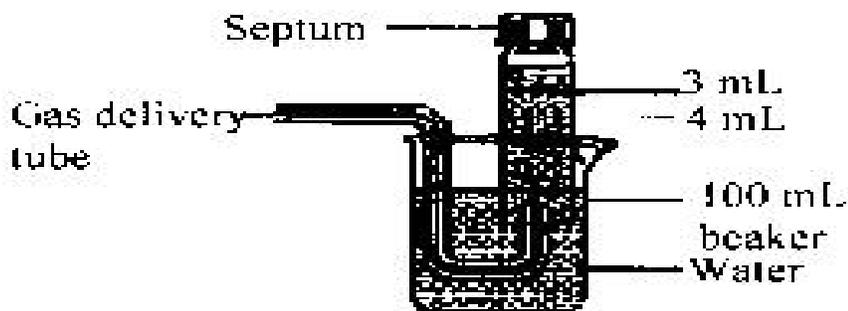
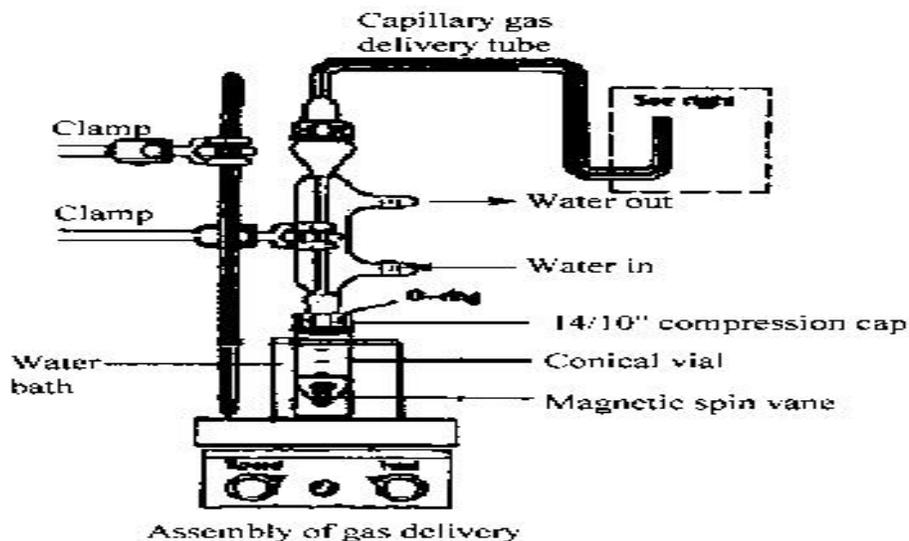
### Assemble for preparation of alkoxide base

Remove the lid from the condenser and use a calibrated Pasteur pipette to introduce  $100\ \mu\text{L}$  of 2-bromobutane down through the condenser into the vial. Place the assembly in the preheated water bath (see Table 1.3). Attach the gas delivery tube to the top of the condenser so that the open end of the tube is beneath the water level of the reservoir. If the connection to the top of the condenser is not made with an O-ring cap seal connection, lightly grease the ground-glass joint to insure a gas-tight seal. After about 10-15 minutes, air bubbles emerge. Place the water-filled gas collection tube over the open end of the gas delivery tube.

**Isolation of Product:** Collect about 6-7 mL of gas in the collection reservoir and then use a hypodermic syringe to withdraw a 0.7 to 0.8 mL sample through the rubber septum for GC analysis.

**NOTE.** Remove the gas delivery tube from the collecting reservoir and then from the water before discontinuing the heat on the reaction vial. This order of events prevents water from being drawn back into the reaction flask.

**Purification and Characterization:** The collected gas is analyzed by gas chromatography without further purification.



### CAUTION

Handle sodium and potassium with care. These metals react vigorously with moisture and are kept under paraffin oil or xylene. Remove a small piece of metal from the oil using a pair of forceps or tongs-never use your fingers! Dry the metal quickly by pressing it with filter paper (to soak up the oil), and immediately add it to the alcohol in the reaction vial. Any residual pieces of sodium/potassium should be stored in a bottle marked "sodium/potassium residues." Never throw small pieces of these metals in the sink or in water.

### 2.3.1 Waste Disposal

There will be a large beaker of isopropanol for you to dispense your unused metal. To destroy the metal, add small amounts to methanol.

### 2.3.2 Approximate Lab Time: 2.5-3 hours

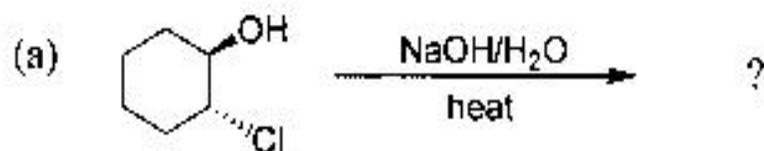
Report: E2 Elimination (Total 30 Points)

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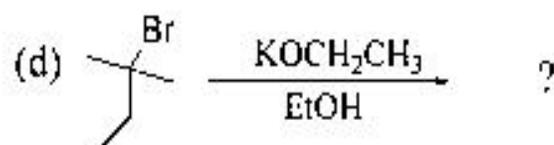
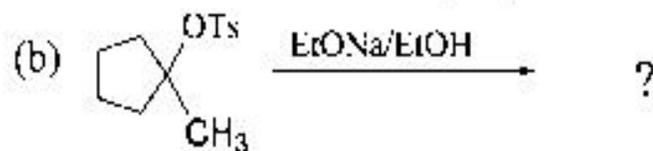
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1. Predict the more stable alkene and supply with reasons for your choice: (6 points)
  - (a) 1-hexene or trans-3-hexene
  - (b) trans-3-hexene or cis-3-hexene
  - (c) 2-methyl-2-hexene or 2,3-dimethyl-2-pentene
2. Starting with the appropriate alkyl halide and base-solvent combination, outline a synthesis that would yield each of the following alkenes as the major or only product and include your reasoning: (8 points)
  - (a) 1-Butene
  - (b) 3-Methyl-1-butene
  - (c) 2,3-Dimethyl-1-butene
  - (d) 4-Methylcyclohexene
3. When cis-1-bromo-4-tert-butylcyclohexane reacts with sodium ethoxide in ethanol, it reacts rapidly to yield 4-tert-butylcyclohexene. Under similar conditions, trans-1-bromo-4-tert-butylcyclohexane reacts very slowly. Using conformational chair structures, explain the difference in reactivity between these stereo isomers. (4 points)
4. Write the major product of the following reactions with proper stereochemistry.  
(4+ 2+ 2+ 4= 12 points)



Hint: Both functional groups are in *trans* stereochemistry



Which mechanism E1/E2 ?