7.13: CHARACTERISTICS OF THE E2 REACTION

Learning Objective

- determine the rate law & predict the mechanism based on its rate equation or reaction data for E2 reactions
- predict the products and specify the reagents for E2 reactions with stereochemistry
- propose mechanisms for E2 reactions
- draw and interpret Reaction Energy Diagrams for E2 reactions

In order of decreasing importance, the factors impacting E2 reaction pathways are

1) structure of the alkyl halide

2) strength of the base

3) stability of the leaving group

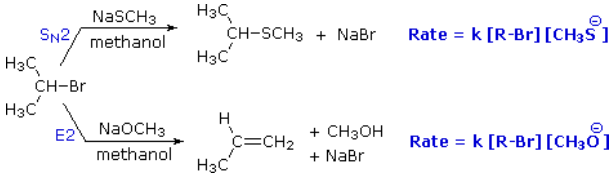
4) type of solvent.

The bimolecular transition state of the E2 pathway means that orientation of the base and leaving group are a primary consideration. Both the base and leaving group are electron rich and electrostatically repel each other forcing an anti-coplanar orientation between the base and leaving group. The structure of the alkyl halide must assume the orientation for an anti-coplar transition state. The strength of the base will also influence the reaction along with the stability of the leaving group. Solvents play a very minor role in E2 pathway.

INTRODUCTION

E2 reactions are typically seen with secondary and tertiary alkyl halides, but a hindered base is necessary with a primary halide. The mechanism by which it occurs is a single step **concerted** reaction with one transition state. The rate at which this mechanism occurs is second order kinetics, and depends on both the base and alkyl halide. A good leaving group is required because it is involved in the rate determining step. The leaving groups must be coplanar in order to form a pi bond; carbons go from sp^3 to sp^2 hybridization states.

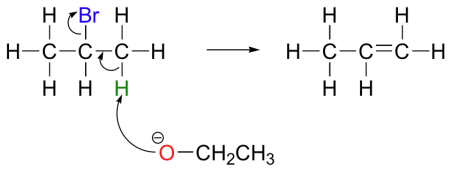
To get a clearer picture of the interplay of these factors involved in a a reaction between a nucleophile/base and an alkyl halide, consider the reaction of a 2º-alkyl halide, isopropyl bromide, with two different nucleophiles. In one pathway, a methanethiolate nucleophile substitutes for bromine in an S_N2 reaction. In the other (bottom) pathway, methoxide ion acts as a base (rather than as a nucleophile) in an elimination reaction. As we will soon see, the mechanism of this reaction is single-step, and is referred to as the E2 mechanism.



GENERAL REACTION

Below is a mechanistic diagram of an elimination reaction by the E2 pathway:

.



In this reaction, ethoxide ($CH_3CH_2O^-$) represents the base and Br representents a leaving group, typically a halogen. There is one transition state that shows the concerted reaction for the base attracting the hydrogen and the halogen taking the electrons from the bond. The product be both eclipse and staggered depending on the transition states. Eclipsed products have a synperiplanar transition states, while staggered products have anticoplanar (antiperiplanar) transition states. Staggered conformation is usually the major product because of its lower energy confirmation.

An E2 reaction has certain requirements to proceed:

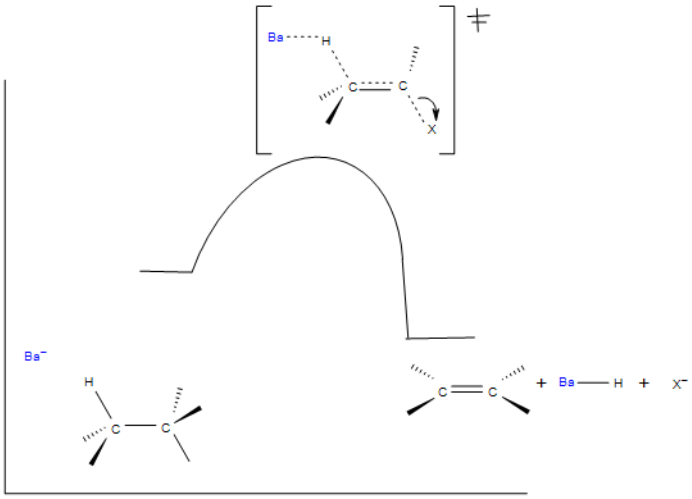
- A strong base is necessary especially necessary for primary alkyl halides. Secondary and tertirary primary halides will procede with E2 in the presence of a base (OH^-, RO^-, R_2N^-)
- Both leaving groups should be on the same plane, this allows the double bond to form in the reaction. In the reaction above you can see both leaving groups are in the plane of the carbons.
- Follows Zaitsev's rule, the most substituted alkene is usually the major product.

- Hoffman Rule, a strically hindered base will result in the least substituted product.

E2 REACTION COORDINATE

In the reaction energy diagram below, the base is represented as Ba^-. The bimolecular transition state determines the overall reaction rate. It is important to note the anti-coplanar orientation of the base and the leaving group. Both the base and leaving group are electron rich and electrostatically repel each other forcing an anti-coplanar orientation between the base and leaving group.

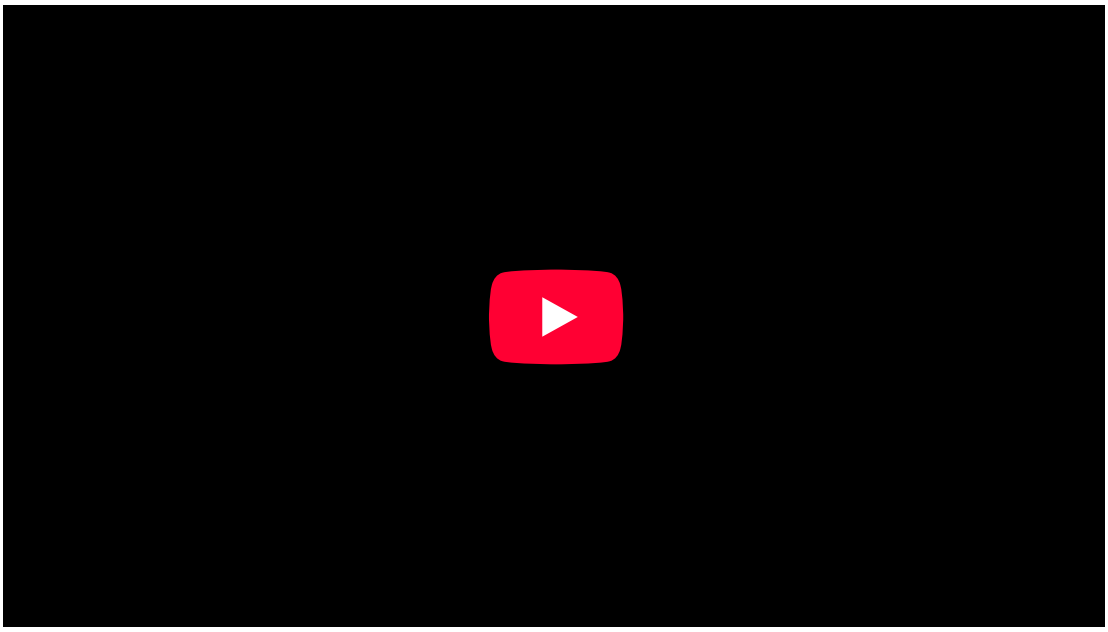
anti-coplanar transition state



THE LEAVING GROUP EFFECT IN E_2 REACTIONS

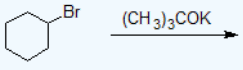
As Size Increases, The Electron Density Decrease, The Ability of the Leaving Group to Leave Increases: Here we revisit the effect size has on basicity. If we move down the periodic table, size increases. With an increase in size, basicity decreases, and the ability of the leaving group to leave increases. The relationship among the following halogens, unlike the previous example, is true to what we will see in upcoming reaction mechanisms.

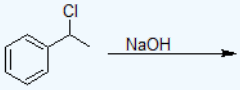
F	<	Cl	<	Br	<	I
Worst		Fair		Good		Excellent

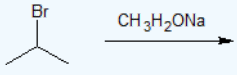


Exercise

1. Ignoring the alkene stereochemistry show the elimination product(s) of the following compounds.

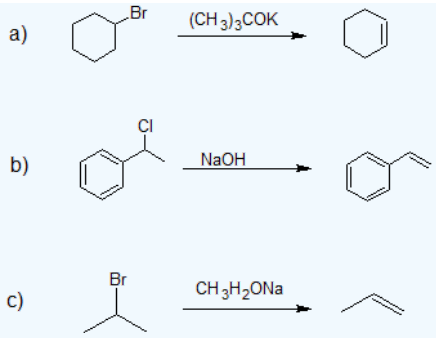
a) 

b) 

c) 

Answer

1.



Organic Chemistry With a Biological Emphasis by Tim Soderberg (University of Minnesota, Morris)

- Layne A. Morsch (University of Illinois Springfield)