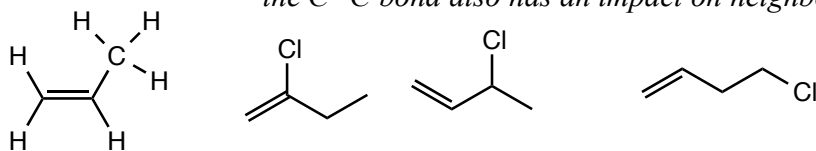


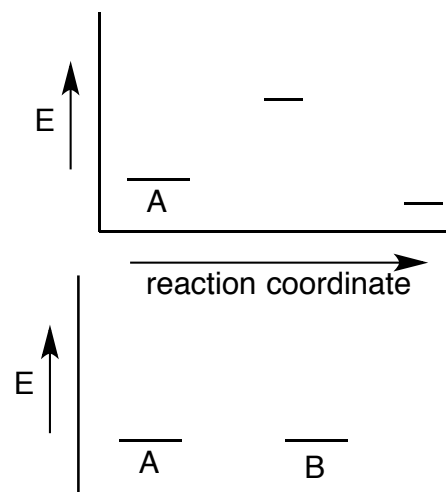
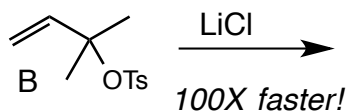
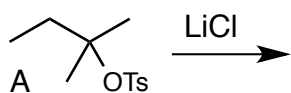
Chapter 17: Allylic and Conjugated Systems

[Sections: 2.10 (part 2, pg 77-78); 17.1-17.2, 17.4-17.5]

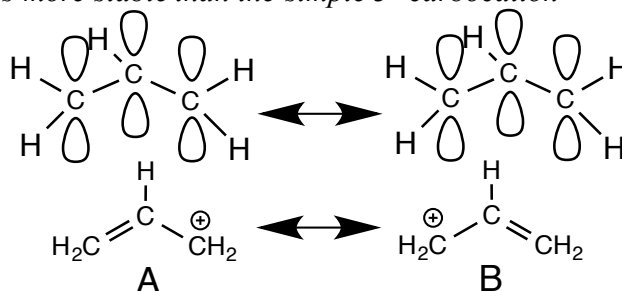
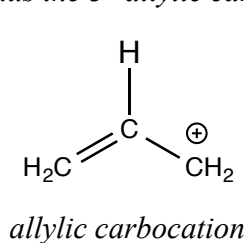
- Defining Allylic and Vinylic**
- $C=C$ double bond is reactive by virtue of the weak pi bond
 - the $C=C$ bond also has an impact on neighboring carbon atoms



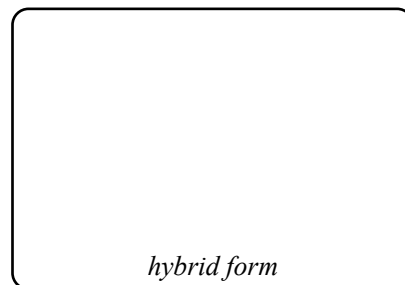
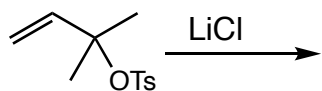
Allylic Carbocations: Formation via S_N1 and Reactivity



- the rate determining step (i.e., slow step; the step with the highest activation barrier) in an S_N1 reaction is formation of the unstable carbocation intermediate via loss of a good leaving group (X, or OTs)
- since the second reaction proceeds faster, this implies that the carbocation formed is of lower energy
- thus the 3° allylic carbocation is more stable than the simple 3° carbocation

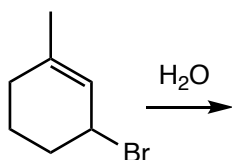


- allylic carbocations exist as two resonance forms
- the positive charge is delocalized over 2 carbon atoms
- delocalization of charge results in greater stability of the carbocation relative to a localized charge



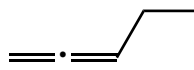
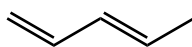
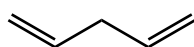
- the S_N1 reaction is accelerated because a stable allylic carbocation intermediate is formed
- allylic carbocations will always have two contributing resonance forms, both of which can lead to formation of product!
- in the hybrid structure, greater partial positive charge (δ^+) will be on the more stable cationic site(s)
- the major product generally derives from the more stable resonance form

Draw the structures of the products for the following S_N1 reaction and predict the major product:

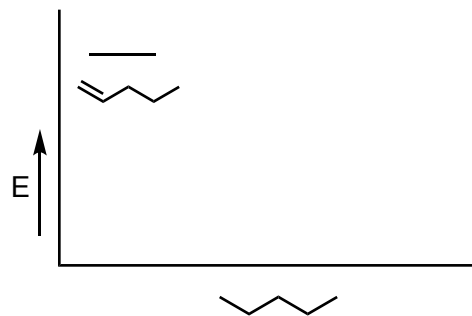
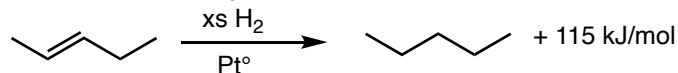


Problems: 1,2,3

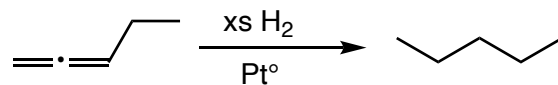
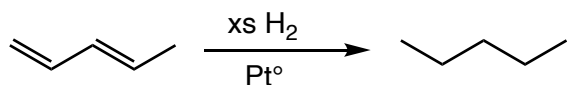
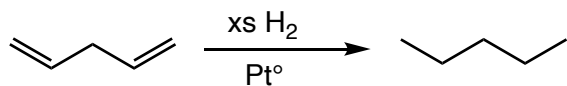
Dienes



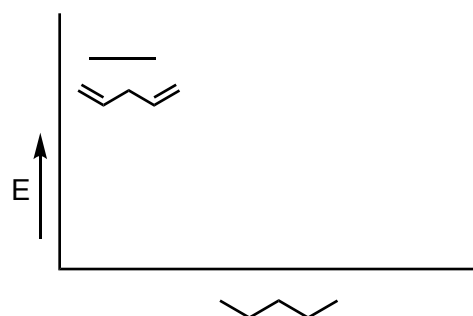
name:
type:



- heat of hydrogenation, like heat of combustion, can be used to determine relative stabilities of isomeric compounds



predicted, actual

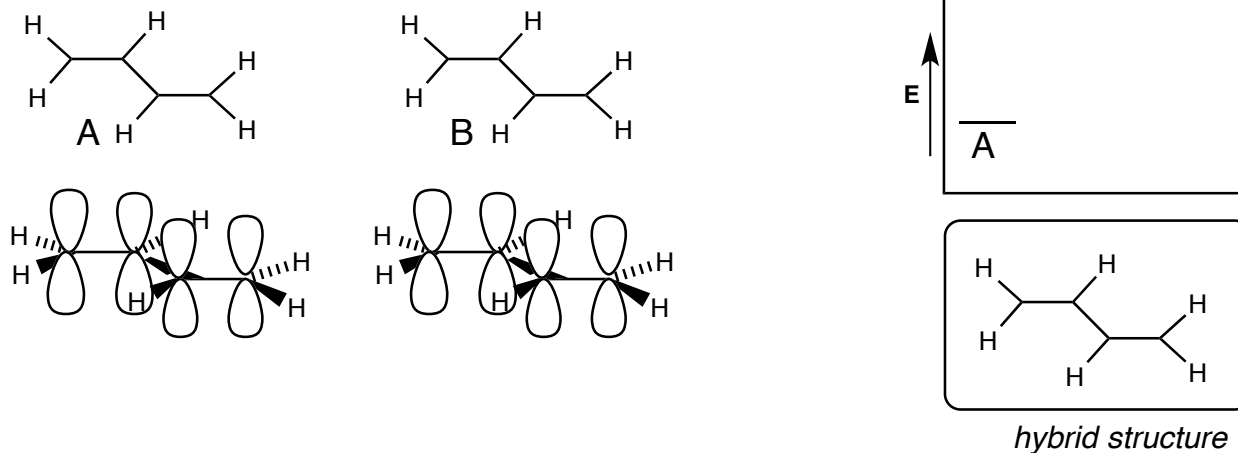


- conjugated double bonds are generally $\sim 10\text{-}15 \text{ kJ/mol}$ MORE stable than their isolated counterparts
- cumulated double bonds (allenes) are unstable species

Conclusions from Heat of Hydrogenation Data:

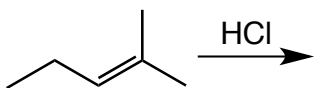
- *isolated dienes act as two individual C=C bonds*
- *conjugated dienes have greater stability than expected*
- *cumulated dienes are much less stable than expected*

What Accounts for the Greater-Than-Expected Stability of Conjugated Dienes?



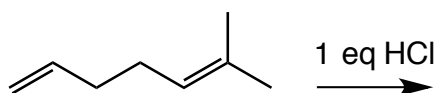
- *conjugated dienes have greater-than-expected stability because of additional (albeit weak) pi-bonding between the two central carbon atoms*
- *isolated dienes are unable to have this additional bonding and are therefore less stable than their isomeric conjugated counterparts*

Reactions of Dienes



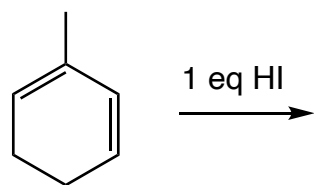
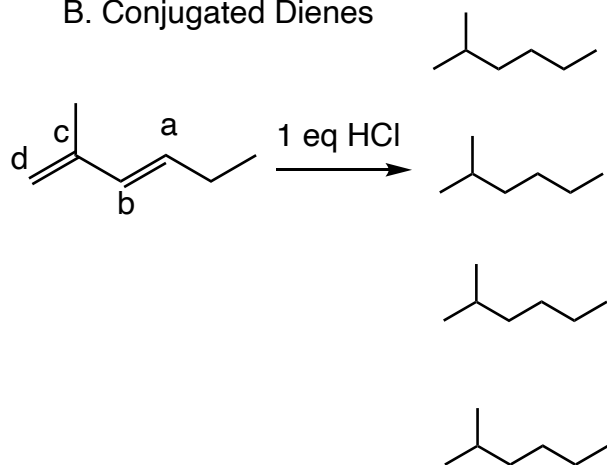
- *hydrohalogenation*
- *addition of HX across pi bond*
- *Markovnikov addition*
- *potential for rearrangement*

A. Isolated Dienes



- *isolated dienes behave as two separately-reacting alkenes*
- *greater substitution on the double bond increases reactivity with electrophiles*

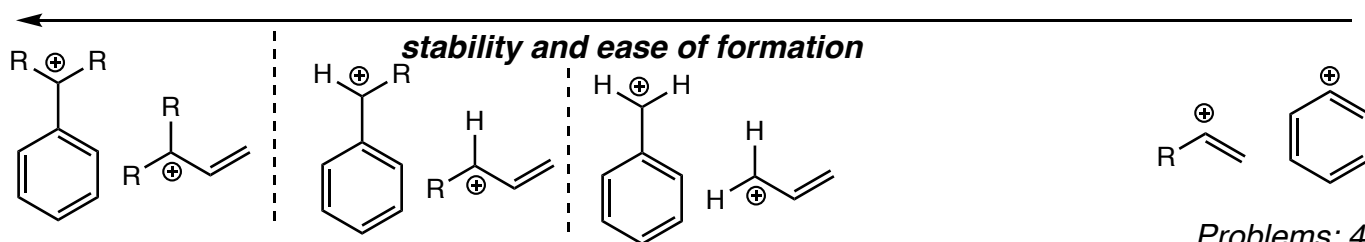
B. Conjugated Dienes



- *conjugated dienes react with HX to form resonance-stabilized allylic carbocations*
- *two products result, one from 1,2-addition and one from 1,4-addition*

General Stabilities of Carbocations

3° allylic/benzylic > 2° allylic/benzylic > 1° allylic/benzylic \sim 3° > 2° >> 1° > CH_3 >> vinyl \sim phenyl



Chapter 17 *Essential Concepts*

1. Understand the terms allylic and vinylic and how to identify groups at these positions.
2. Understand the source of stabilization afforded to allylic carbocations and be able to draw resonance forms using appropriate conventions (curved arrows, proper resonance double-headed arrow).
3. Be able to draw products resulting from S_N1 reactions of allylic substrates.
4. Understand the difference between isolated, conjugated, and cumulated dienes, and their energies relative to one another.
5. Understand how heat of hydrogenation data can be used to determine the relative energies of dienes.
6. Understand the orbital basis for stabilization of conjugated dienes.
7. Be able to predict products from the reactions of HX with isolated and conjugated dienes. Be able to identify 1,2- and 1,4-addition products.
8. Know the general relative stabilities of carbocations.