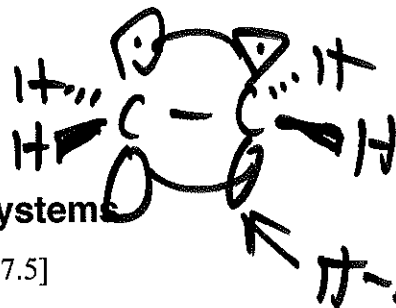
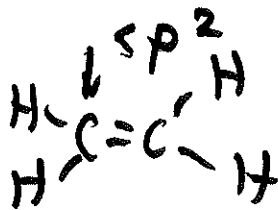


Chapter 17: Allylic and Conjugated Systems

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

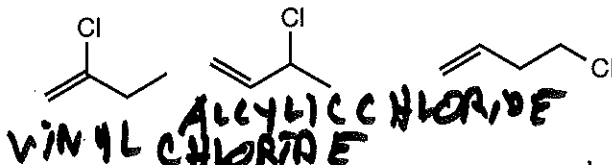
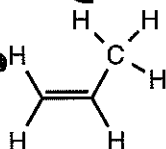
ALLYLIC H'S



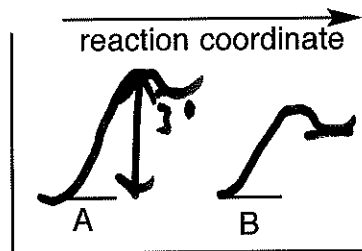
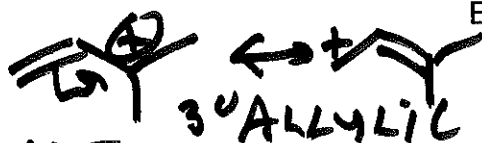
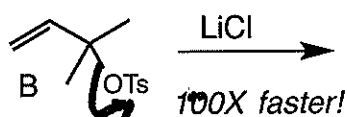
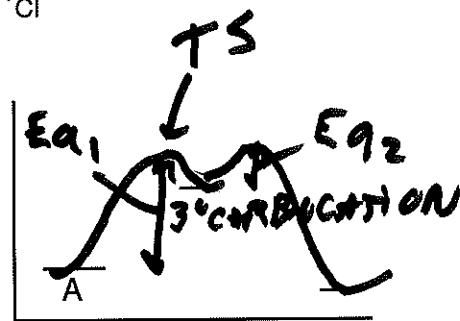
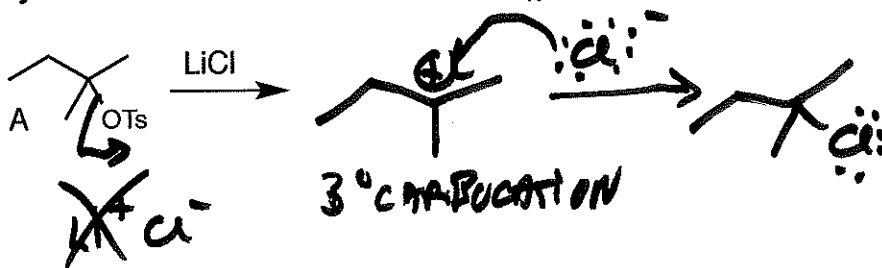
Defining Allylic and Vinylic

- 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

VINYL H'S

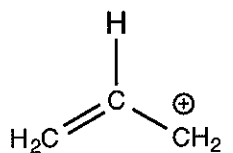


Allylic Carbocations: Formation via S_N1 and Reactivity

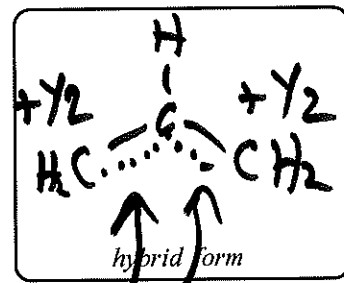
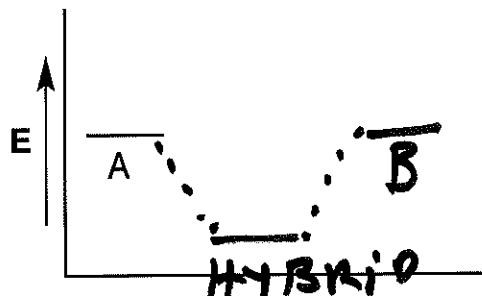
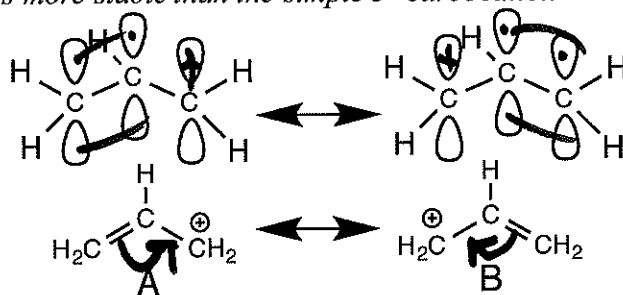


ALLYLIC TOSYLATE

- 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



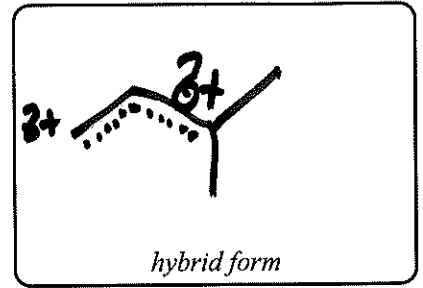
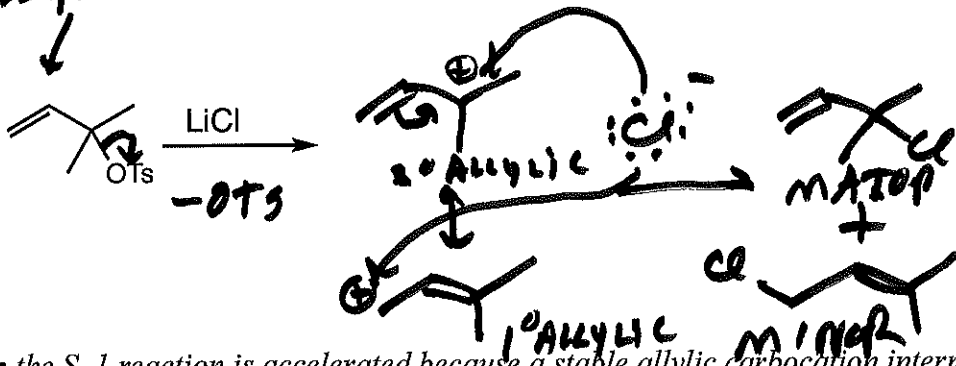
allylic carbocation



- 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

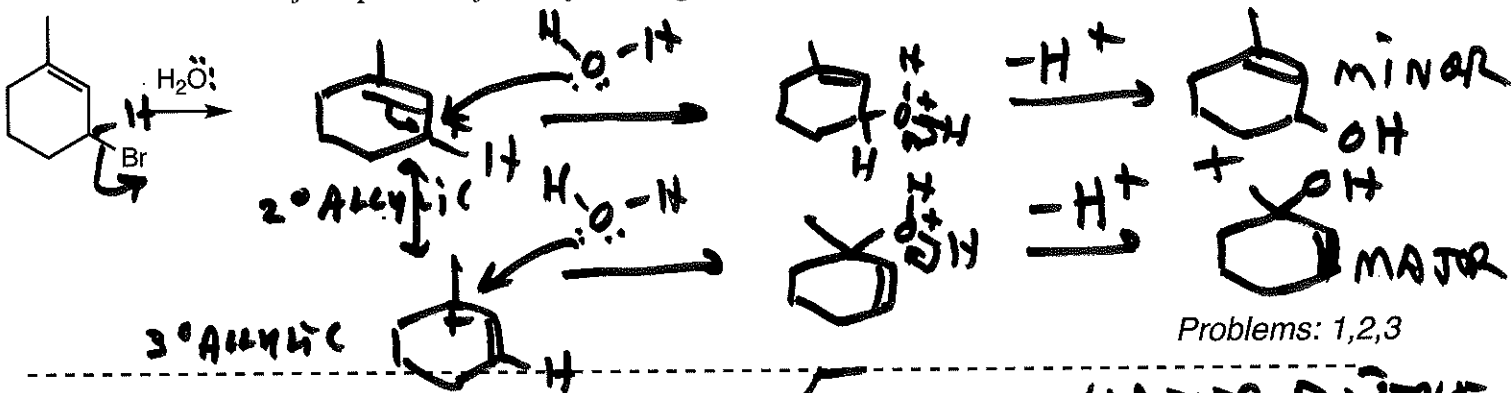
1/2 BOND

ALLYLIC SUBSTRATE



- 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

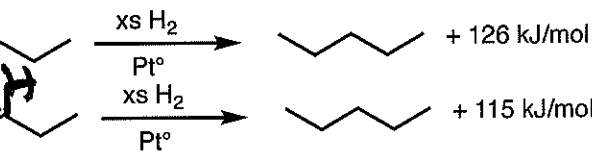
Dienes



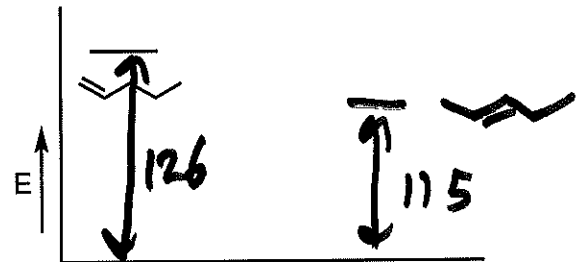
name:
type:

ISOLATED DIENE CONJUGATED DIENE

MONO SUB
DISUB



CUMULATED DIENE



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

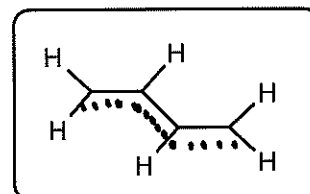
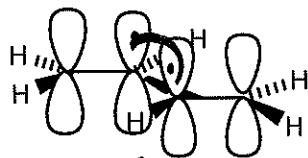
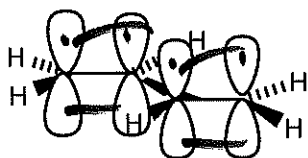
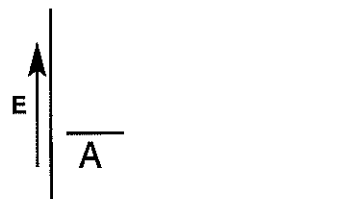
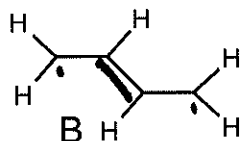
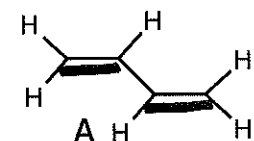
Diene	Reaction	Product	predicted	actual	Stability Difference
1,4-pentadiene	xs H_2 , Pt^0	alkane	126 + 126 = 252	253	15 kJ/mol MORE STABLE THAN EXPECTED
1,3-pentadiene	xs H_2 , Pt^0	alkane	126 + 115 = 241	226	15 kJ/mol MORE STABLE THAN EXPECTED
1,2-pentadiene	xs H_2 , Pt^0	alkane	126 + 115 = 241	298	57 kJ/mol LESS STABLE THAN PREDICTED

- conjugated double bonds are generally ~ 10-15 kJ/mol MORE stable than their isolated counterparts
- cumulated double bonds (allenes) are unstable species

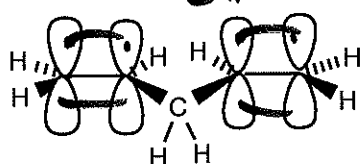
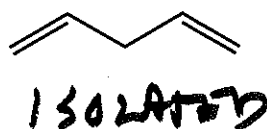
Conclusions from Heat of Hydrogenation Data:

- 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?



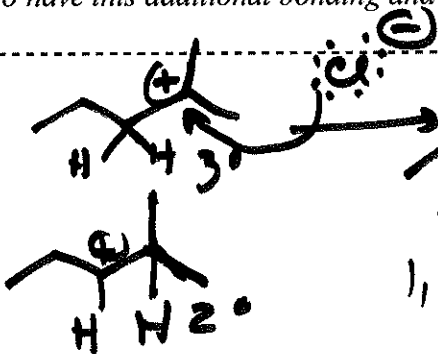
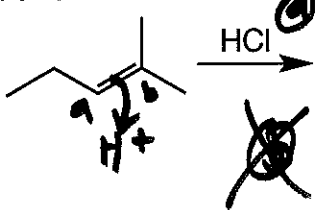
ADDED π -BOND CHARACTER BETWEEN CENTRAL CARBON ATOM 5



- 15 KJ/mol of ADDED STABILITY

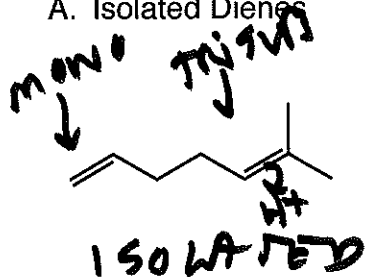
- conjugated dienes have greater-than-expected stability because of additional (albeit weak) pi-bonding between the two central carbon atoms
- isolated dienes are unable to have this additional bonding and are therefore less stable than their isomeric conjugated counterparts

Reactions of Dienes

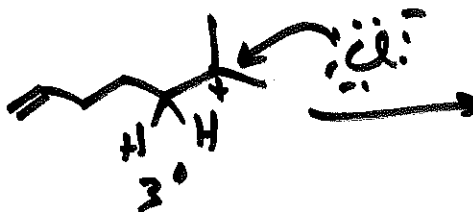


hydrohalogenation
 addition of HX across pi bond
 Markovnikov addition ✓
 potential for rearrangement
 1,2-ADDITION

A. Isolated Dienes

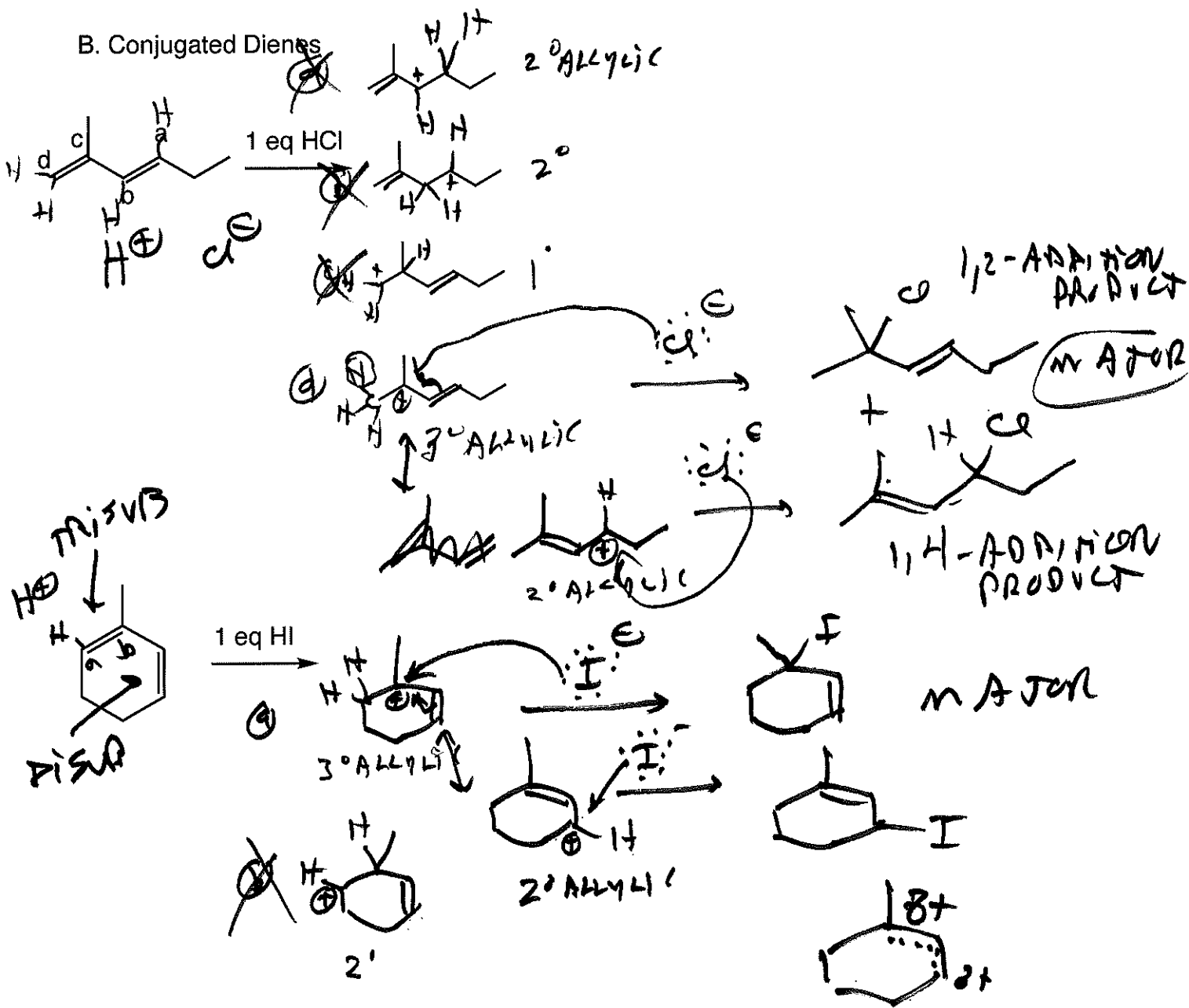


1 eq HCl



- 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 > 3° > 2° >> 1° > CH_3 >> vinyl ~ phenyl

