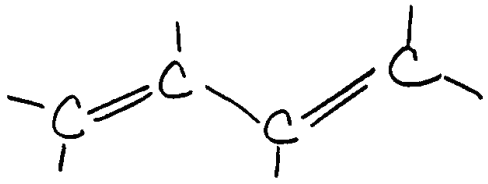
Figure 12.001



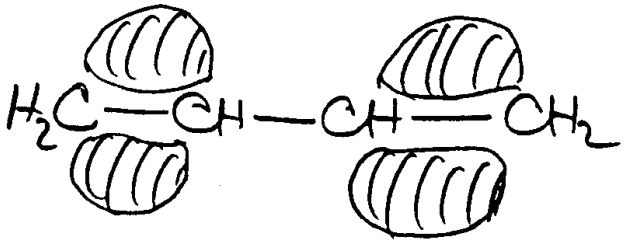
Two Conjugated Double Bonds

Figure 12.002

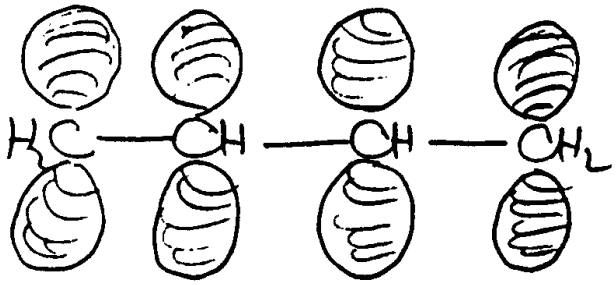
Orbital Overlap in 1,3-Butadiene

(1) $H_2C=CH-CH=CH_2$

(2)



(3)



(4)

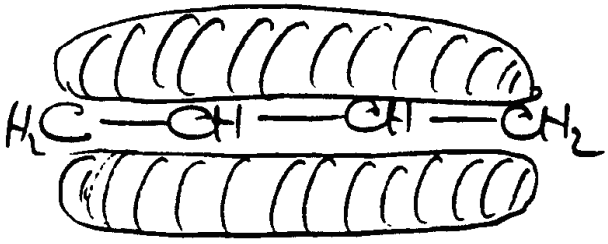


Figure 12.003

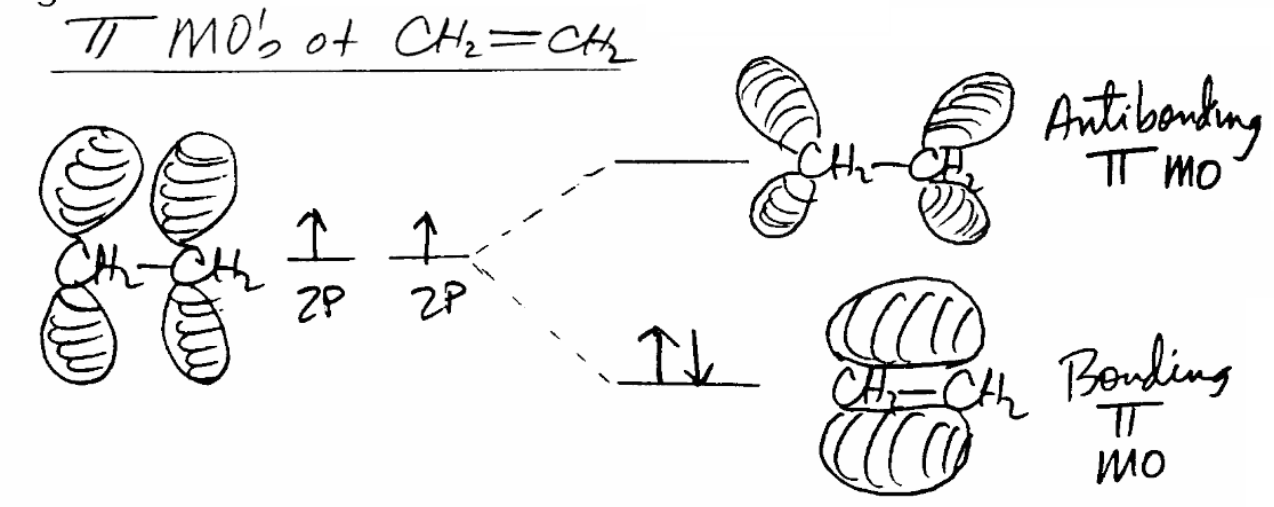


Figure 12.004

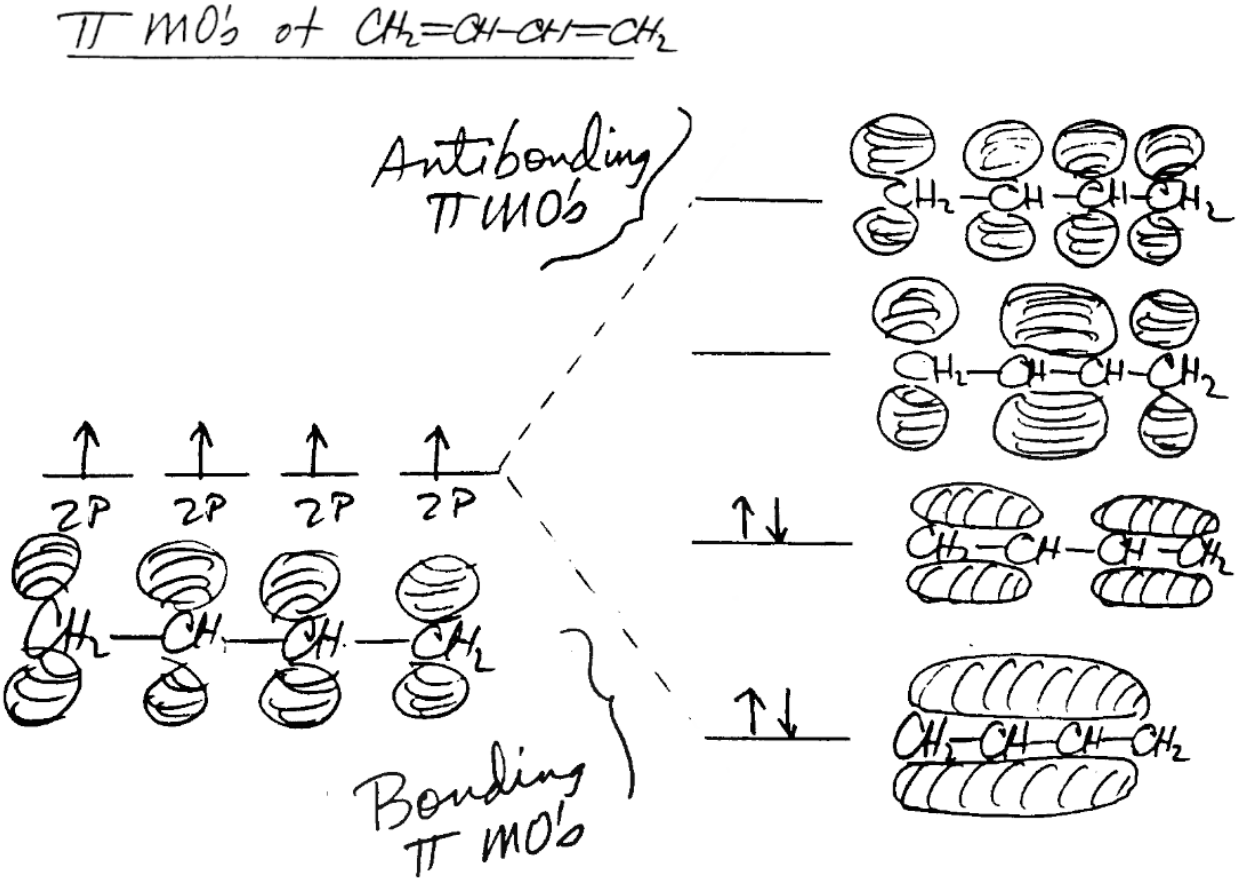
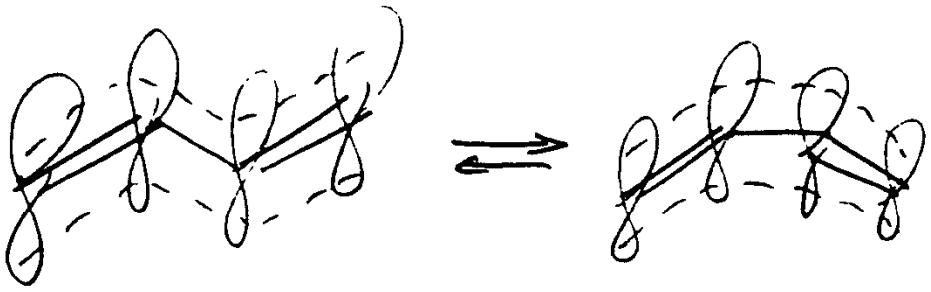


Figure 12.005 Conformations of 1,3-Butadiene



s-trans (s-E) ⇌ s-cis (s-Z)

Figure 12.006

Some Molecules with Conjugated Multiple Bonds

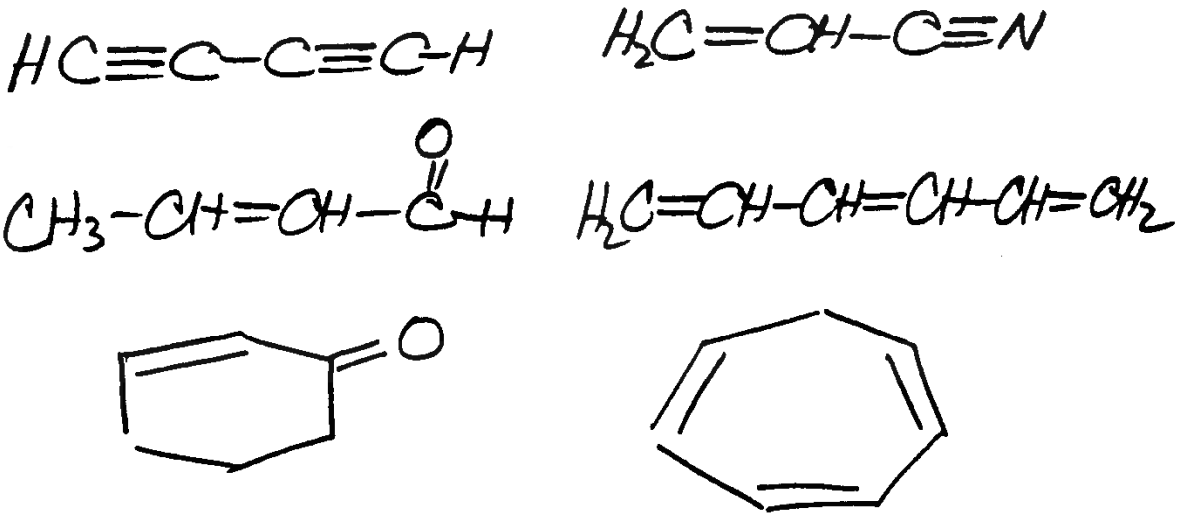
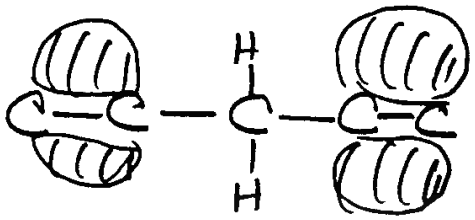


Figure 12.007

1,4-pentadiene

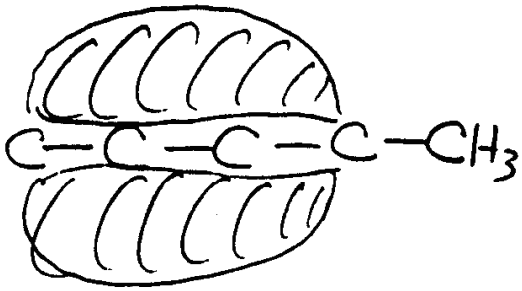
$H_2C=CH-CH_2-CH=CH_2$



Isolated C=C

1,3-Pentadiene

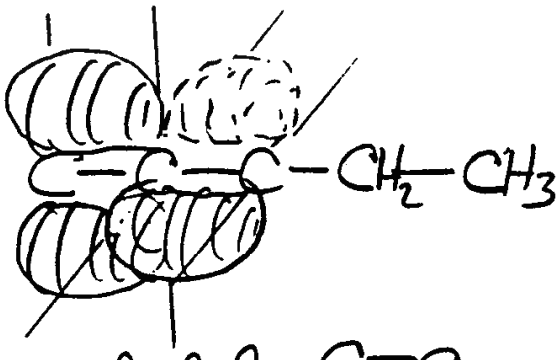
$H_2C=CH-CH=CH-CH_3$



Conjugated C=C

1,2-Pentadiene

$H_2C=C=CH-CH_2-CH_3$



Cumulated C=C

Figure 12.008

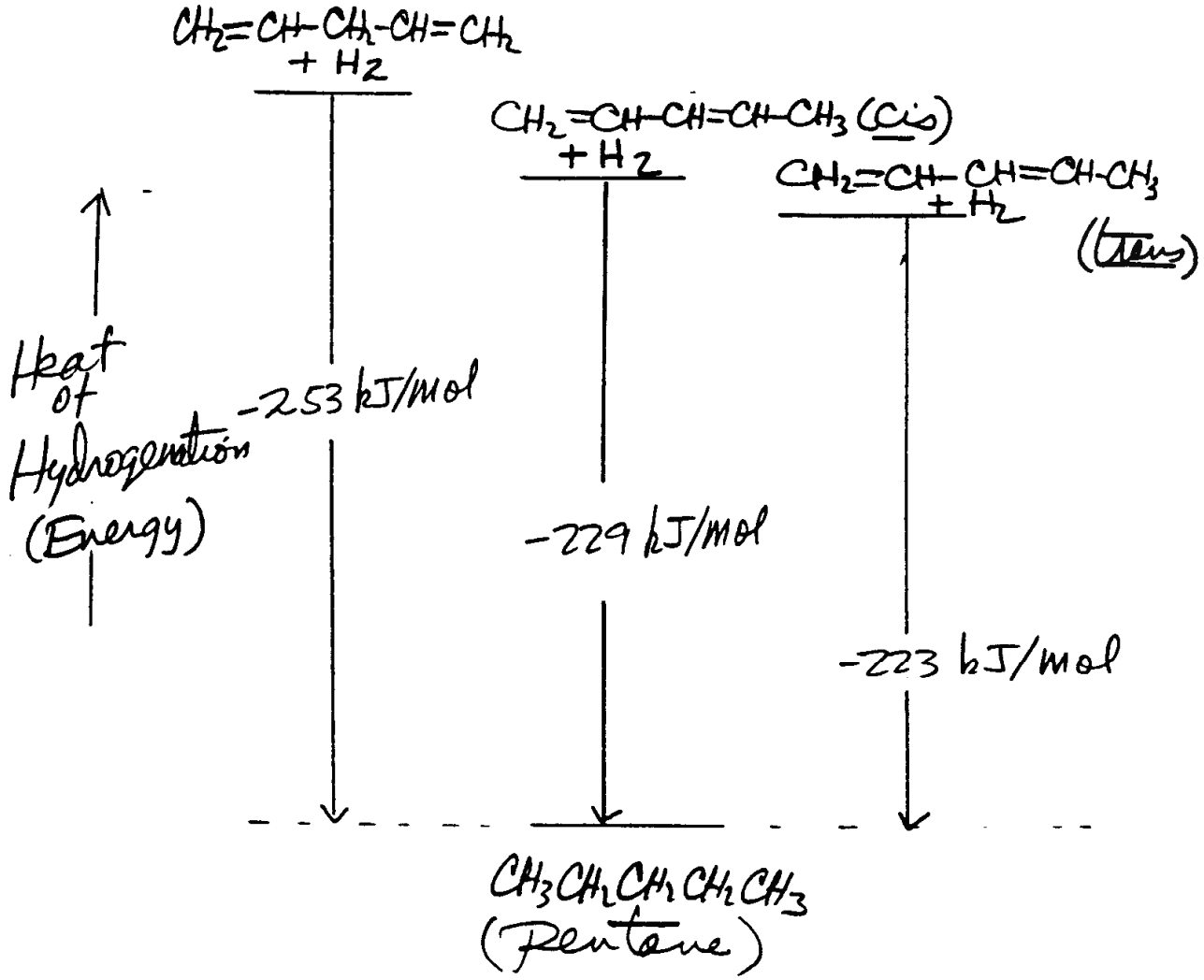
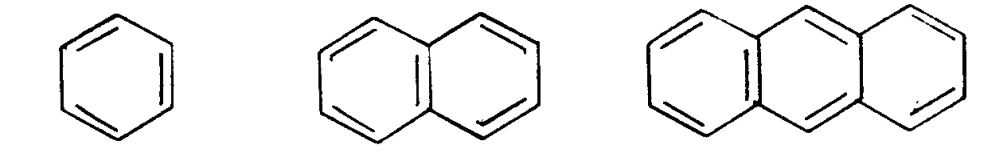


Figure 12.009 Some Aromatic Molecules



benzene naphthalene anthracene

Figure 12.010

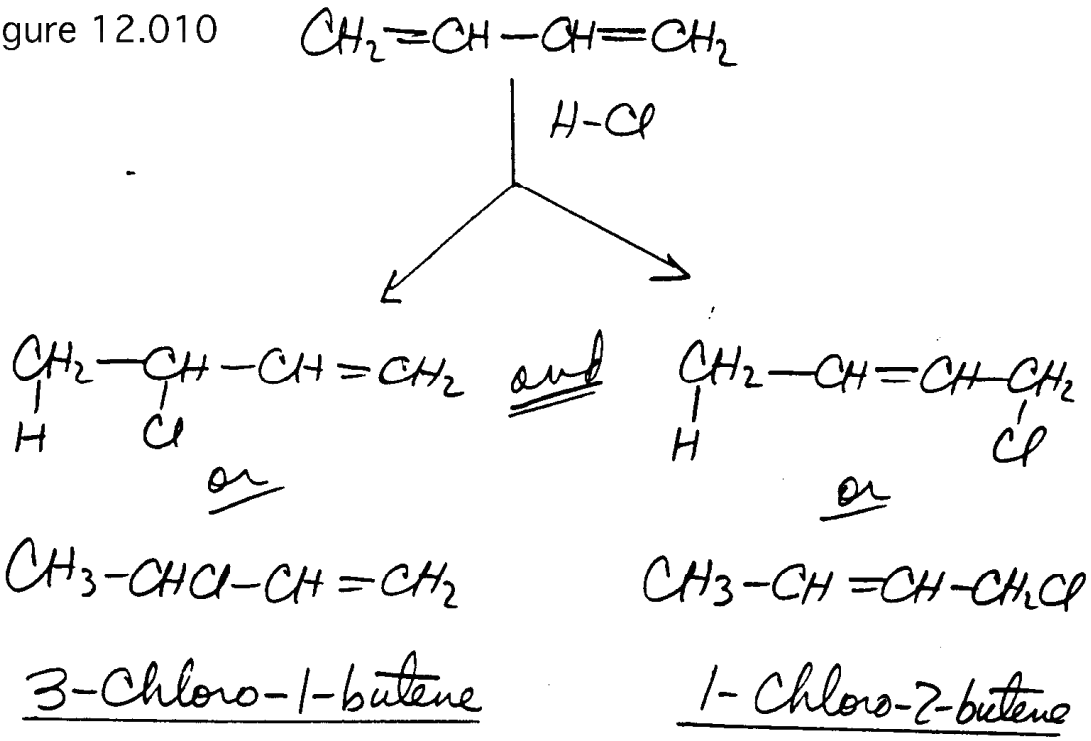


Figure12.011

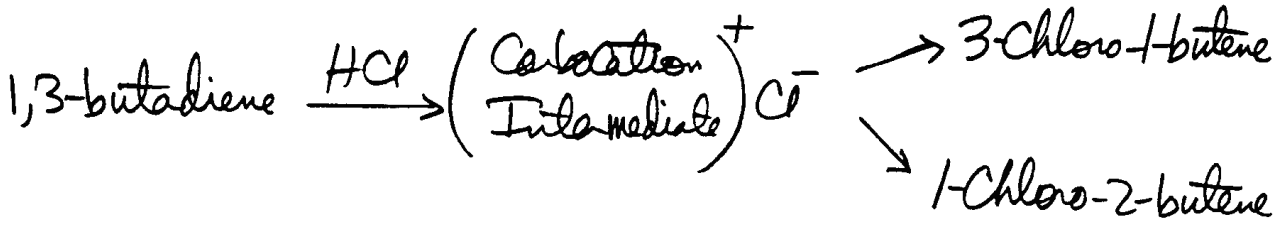


Figure 12.012 Hypothetical Localized C+ Formation

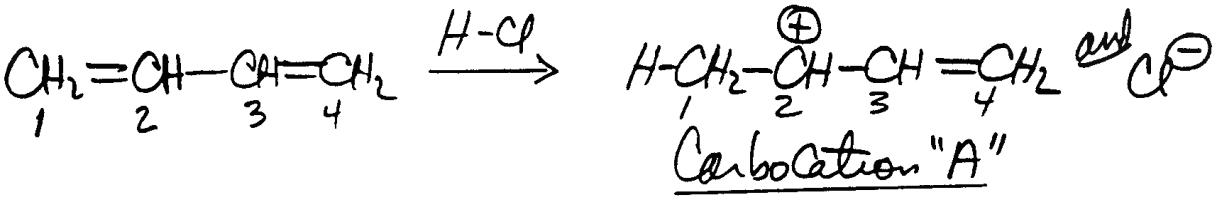


Figure 12.013

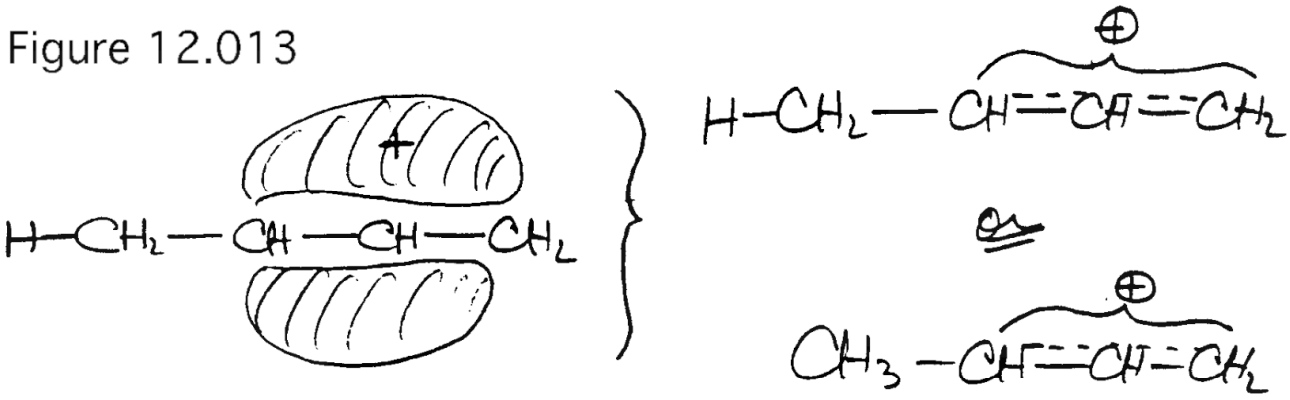


Figure 12.014

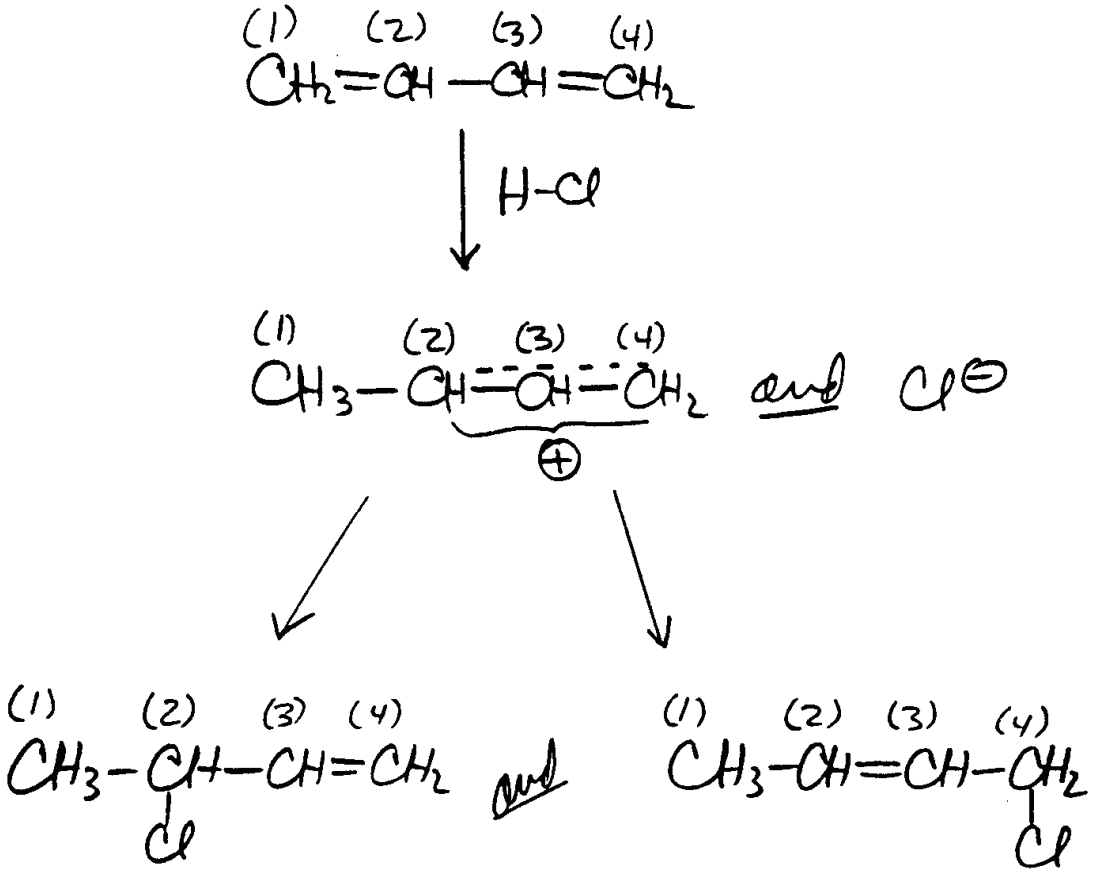
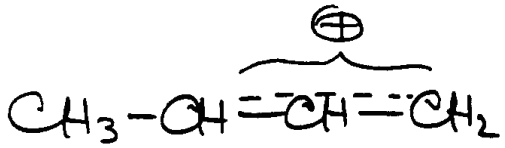
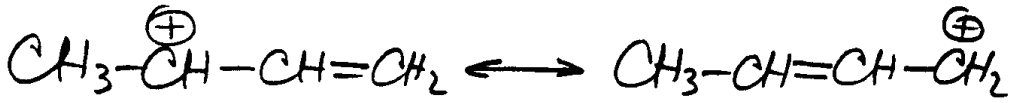


Figure 12.015 Delocalized Carbocation



represented by



Resonance Structures

Figure 12.016

Figure 12.017 $A \rightleftharpoons B$

A and B are real Chemical species in equilibrium

but in $A \longleftrightarrow B$

A and B are not real species - they are resonance structures of a single real species.

Figure 12.018

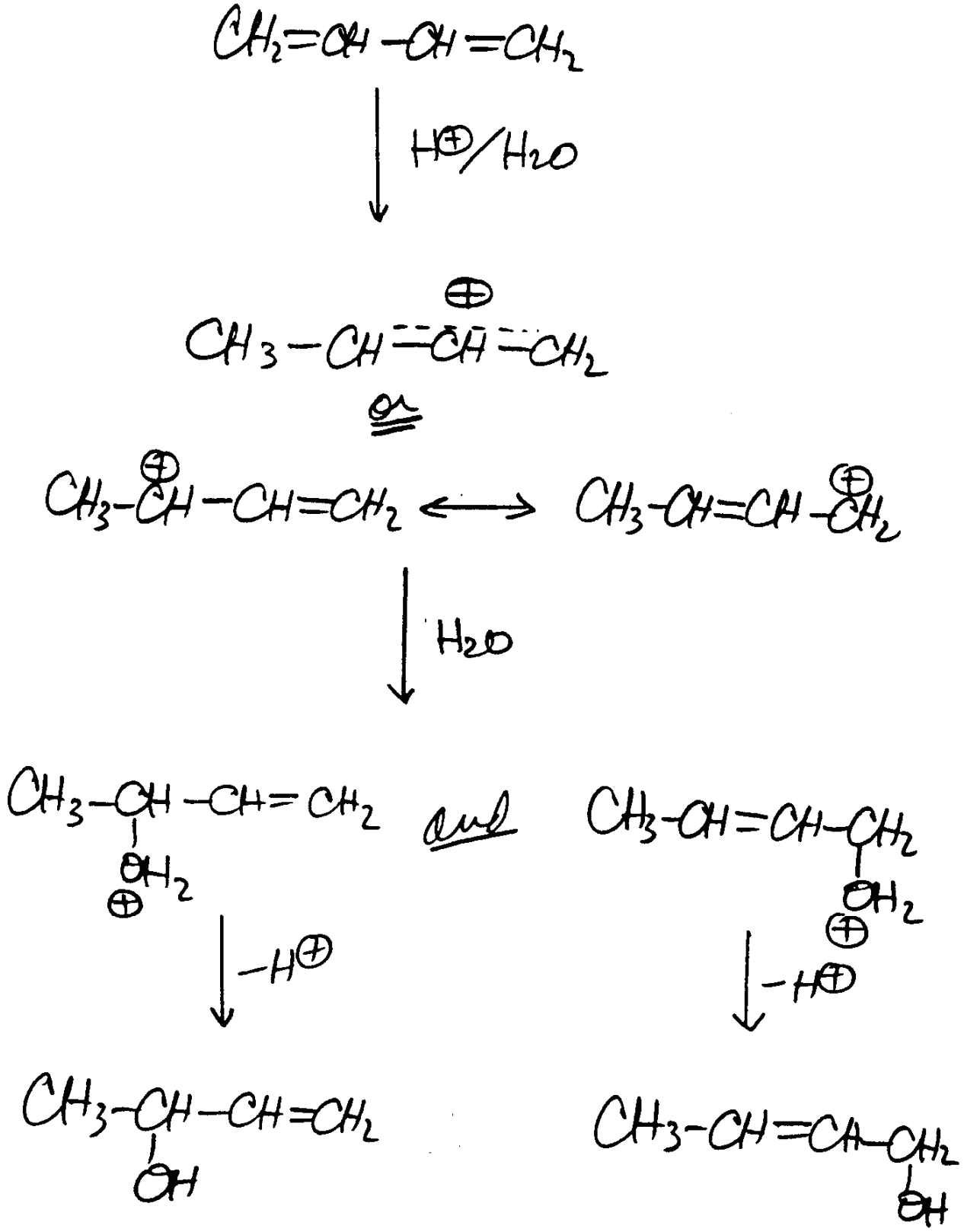


Figure 12.019

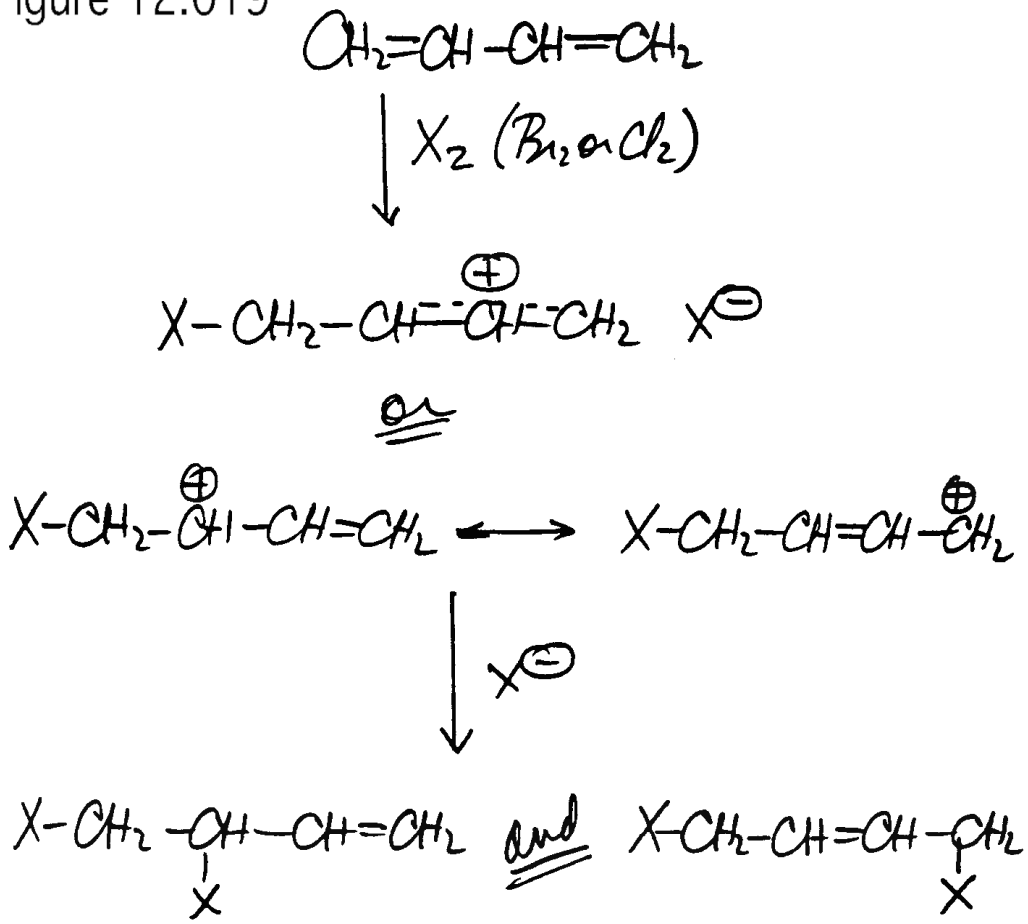


Figure 12.020

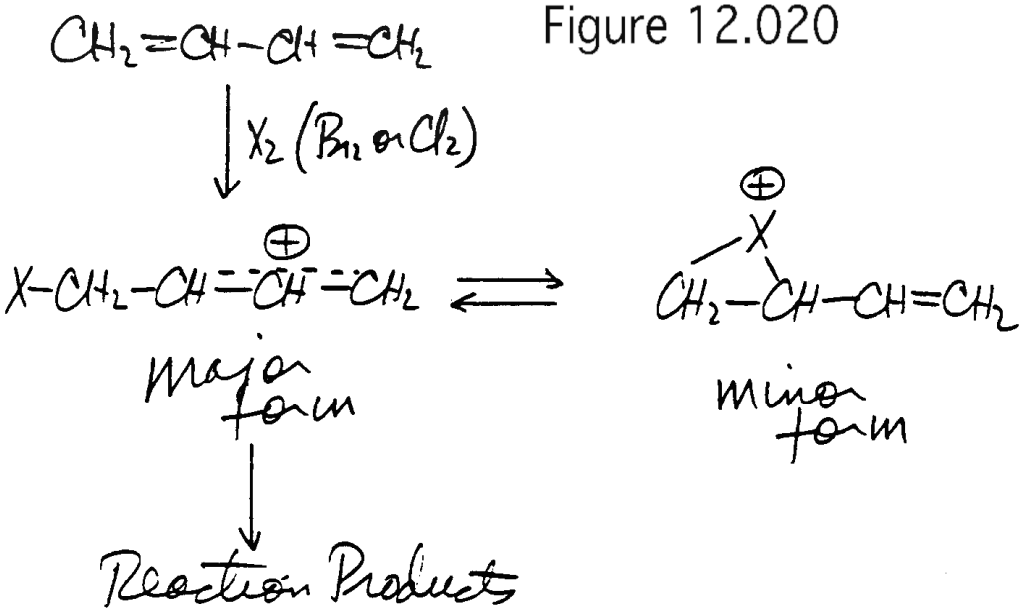


Figure 12.021

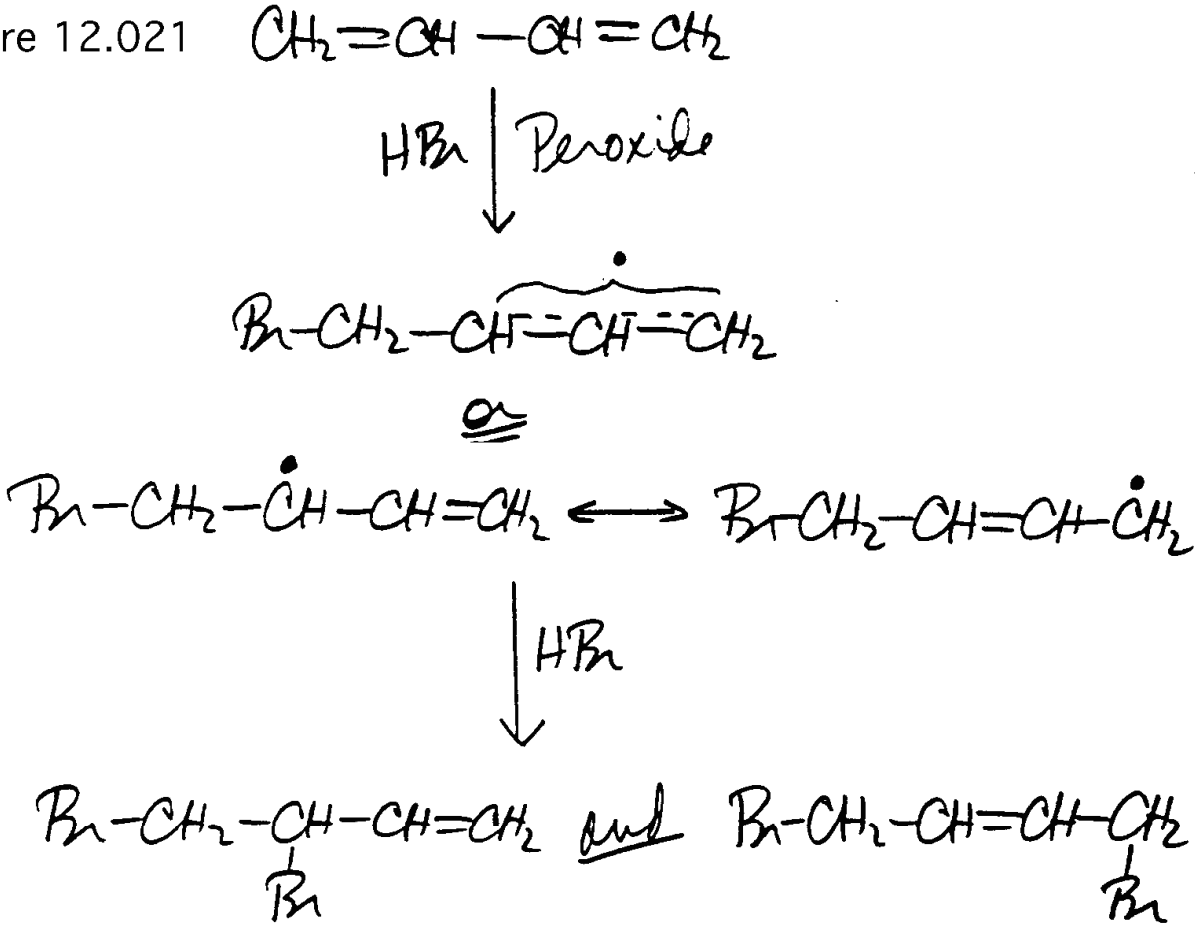
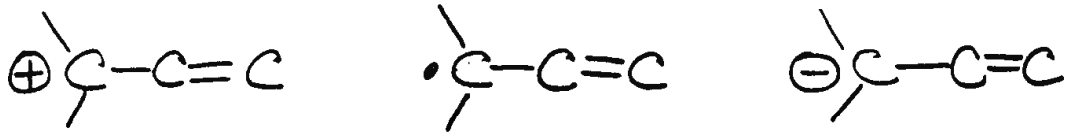


Figure 12.022



Each of these species has another resonance structure because the ⊕, ⊙ or ⊖ center is directly attached to C=C

Figure 12.023

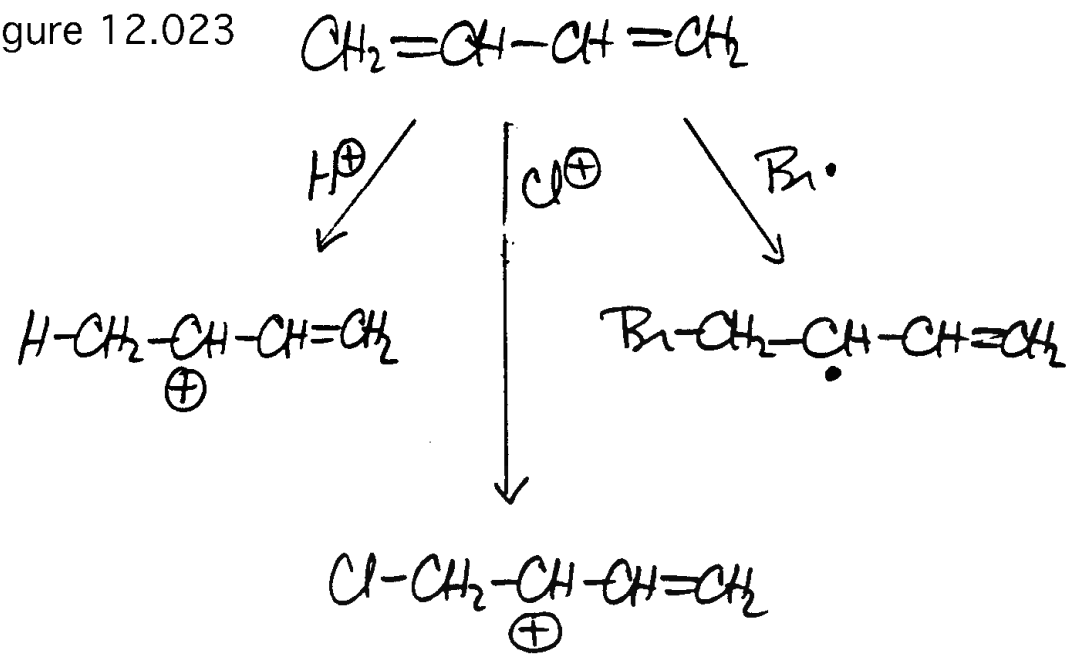
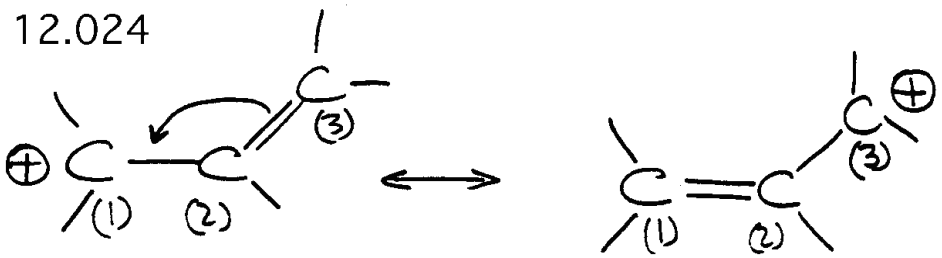


Figure 12.024



The electron pair moves like it is on a hinge!

For example

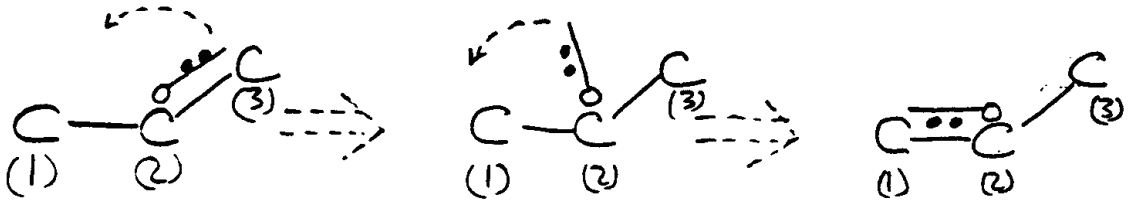
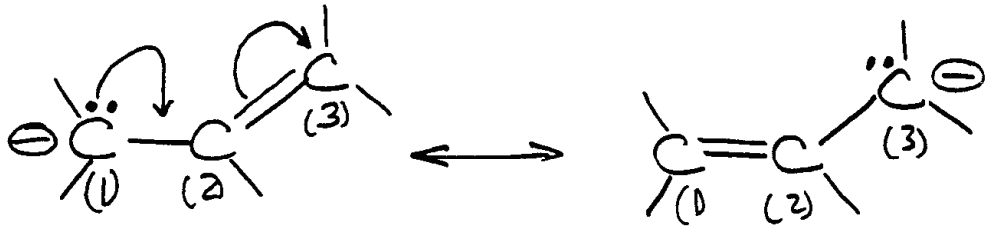


Figure 12.025



The electron pairs move like they are both on hinges

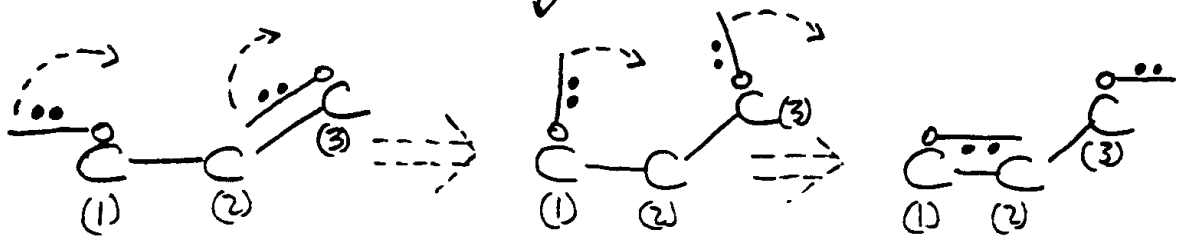
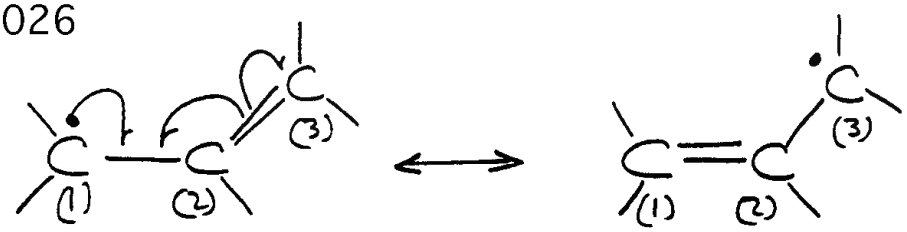


Figure 12.026



The electrons move as if they are on "half-hinges"

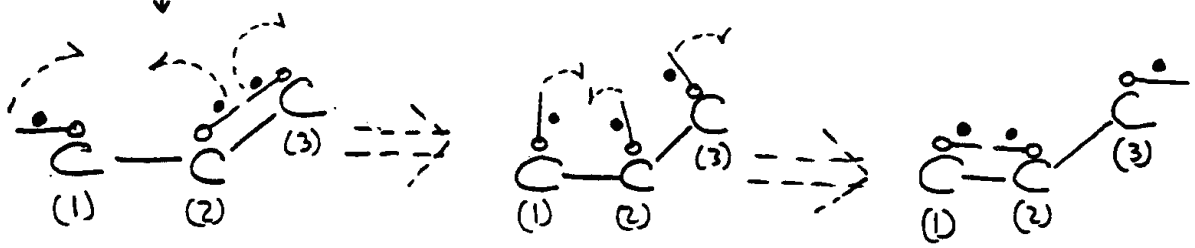


Figure 12.027

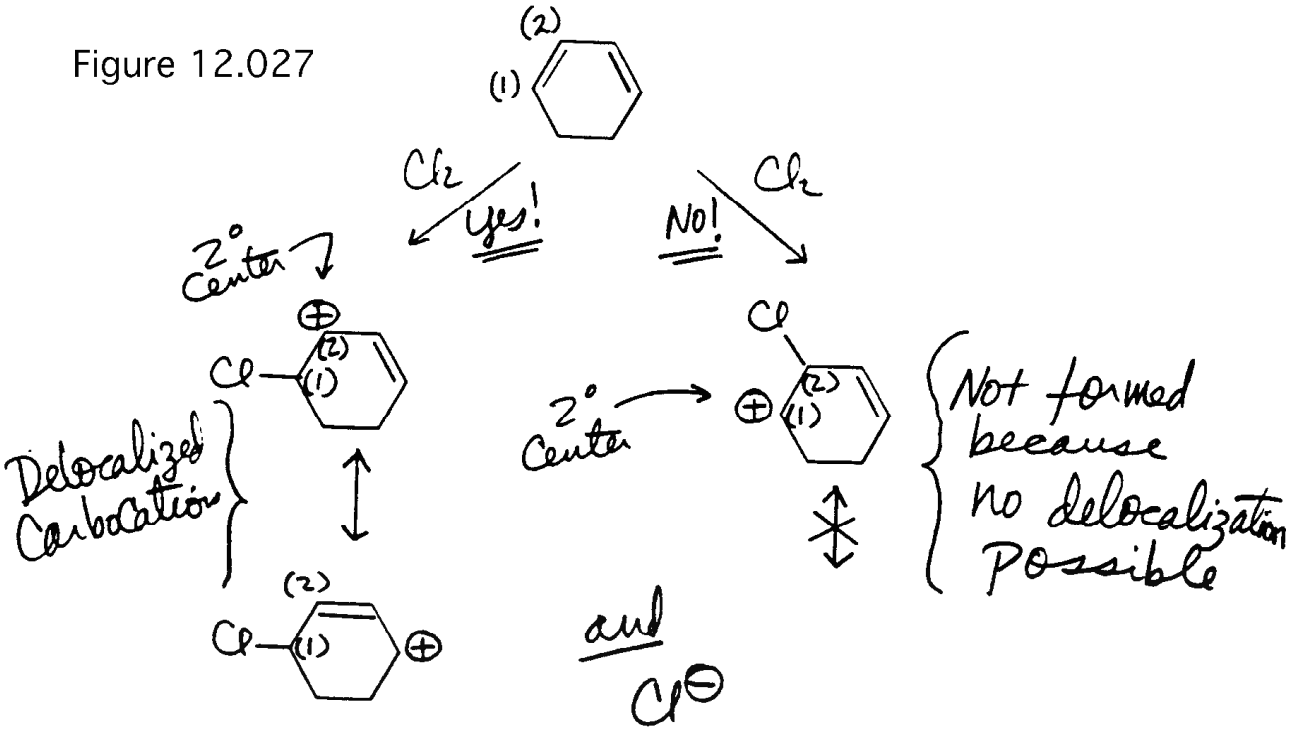


Figure 12.028

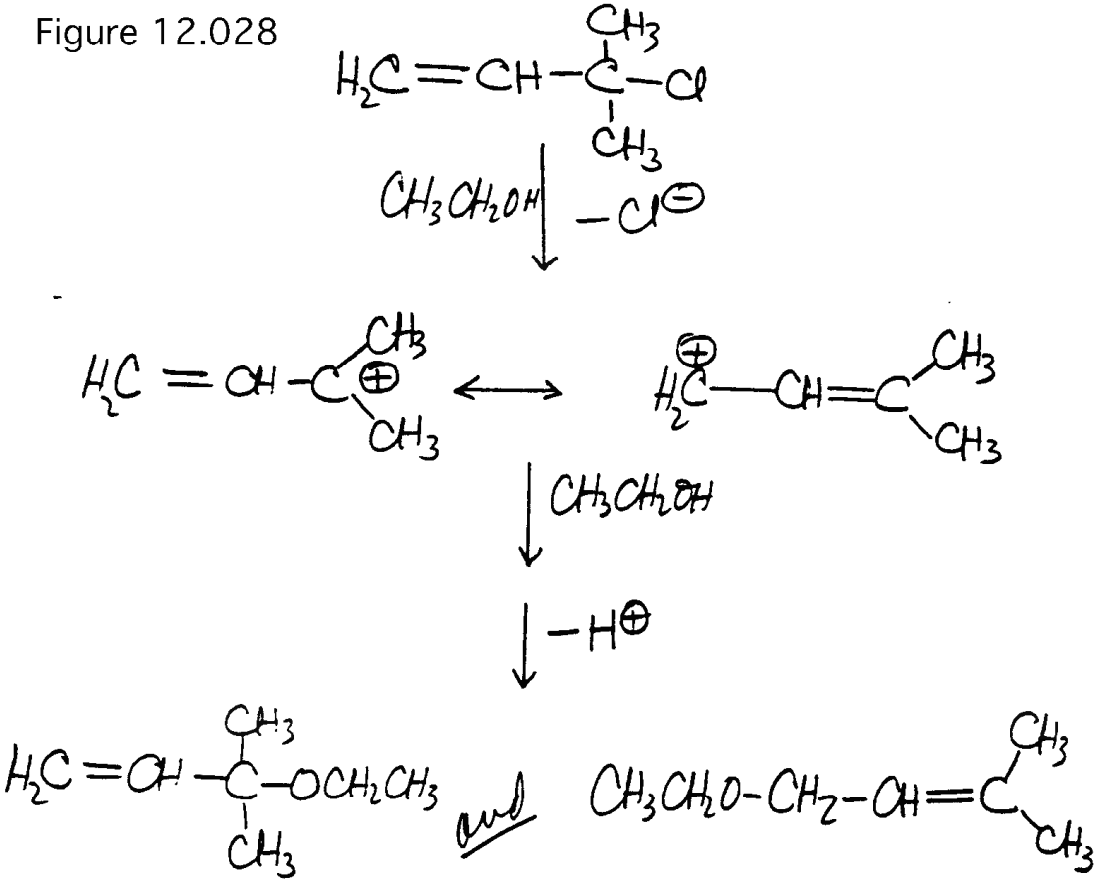


Figure 12.029

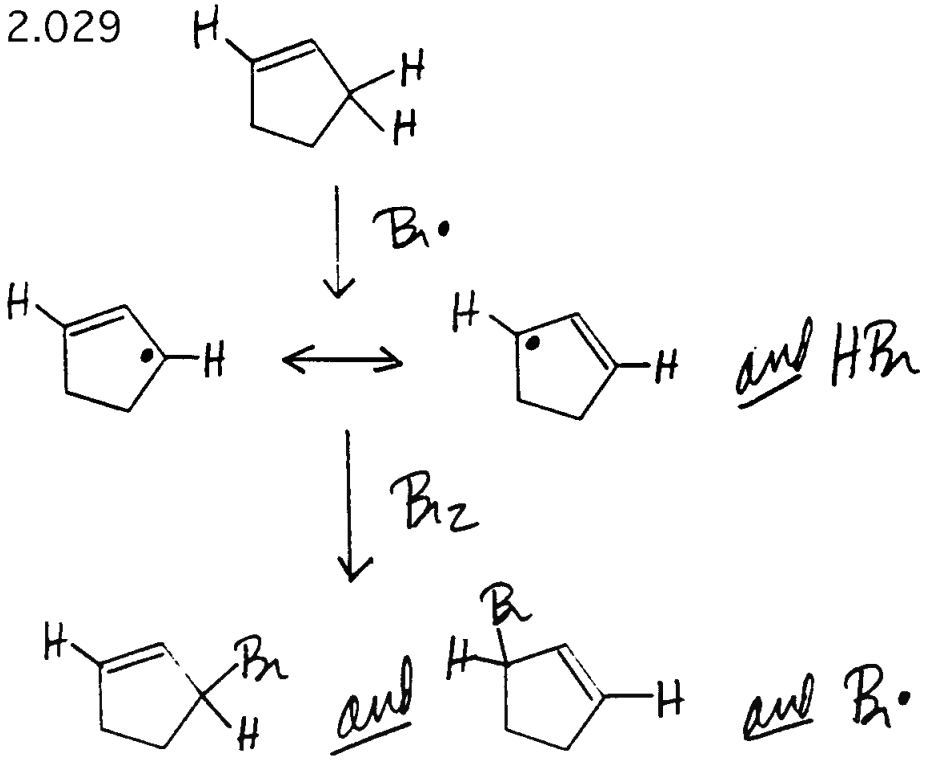


Figure 12.030

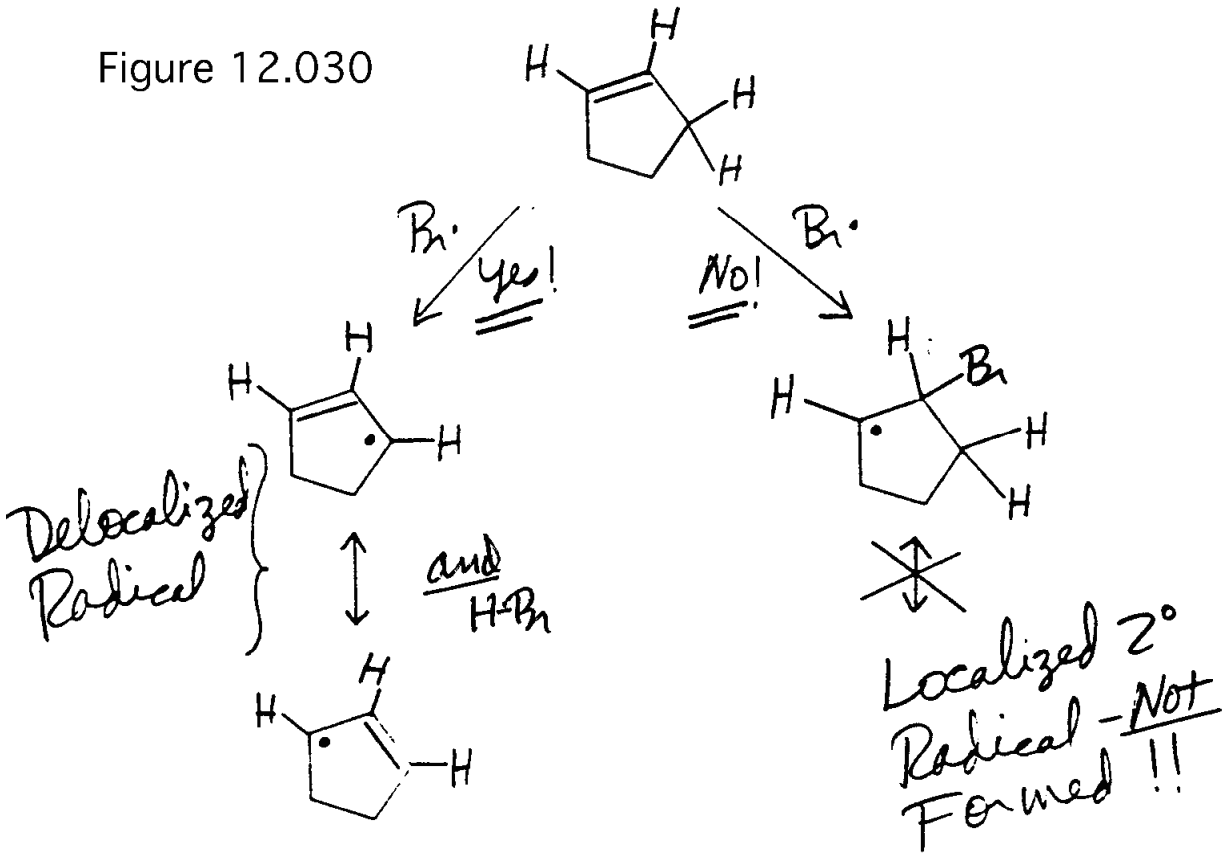


Figure 12.031

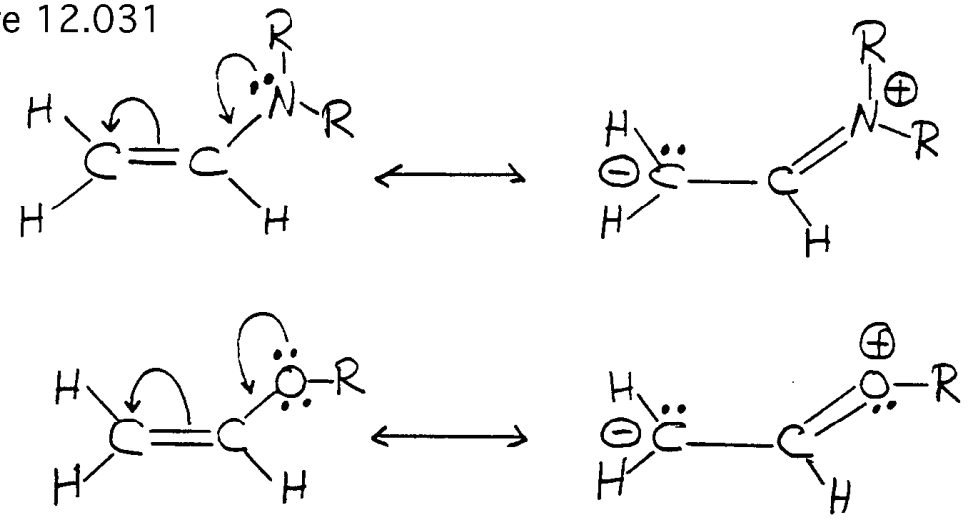


Figure 12.032

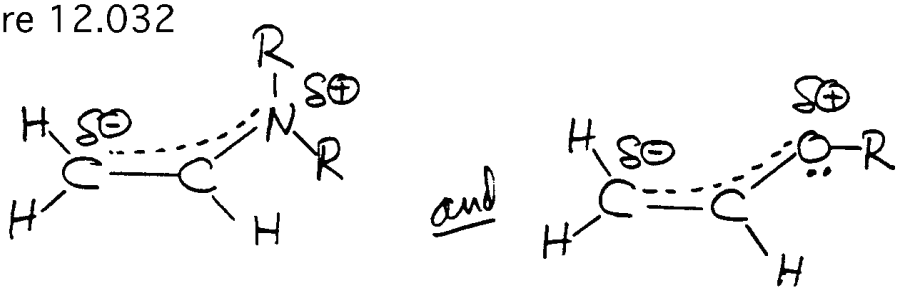


Figure 12.033

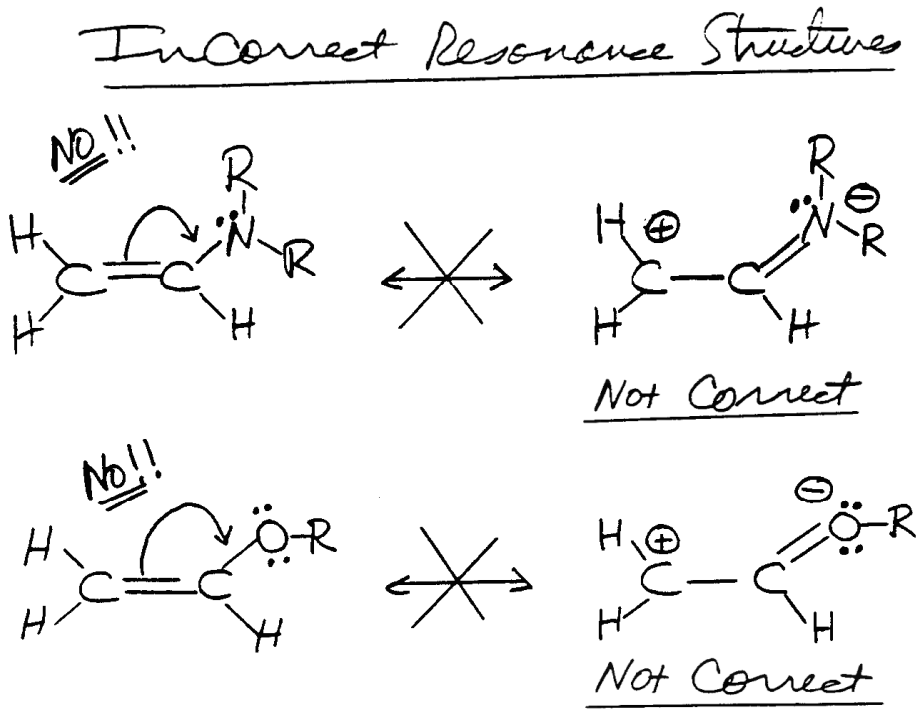


Figure 12.034

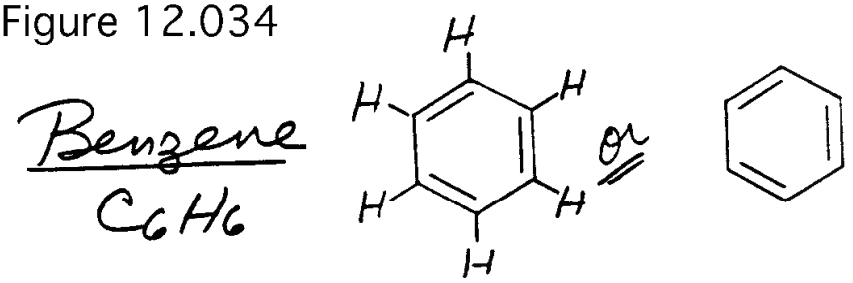


Figure 12.035

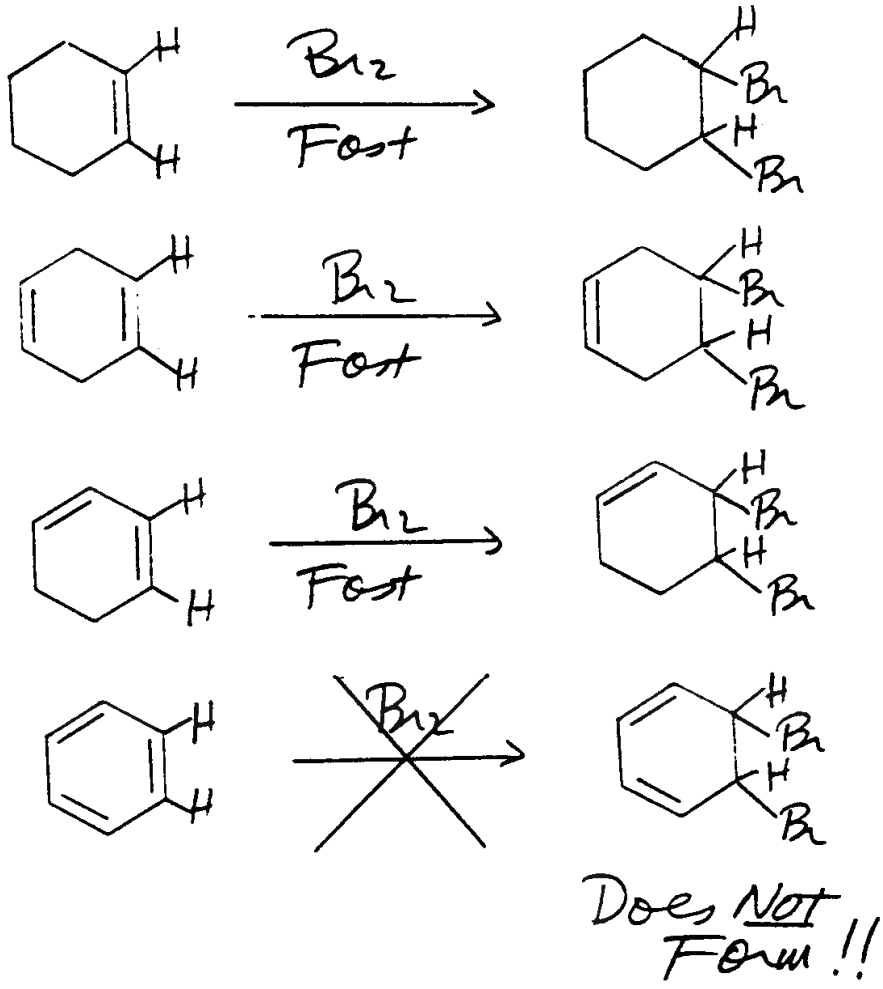


Figure 12.036

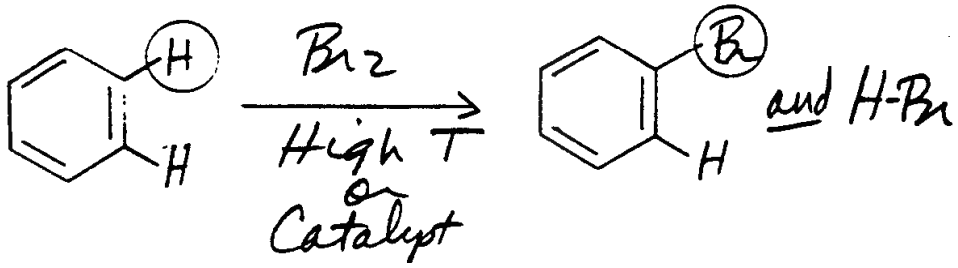


Figure 12.037

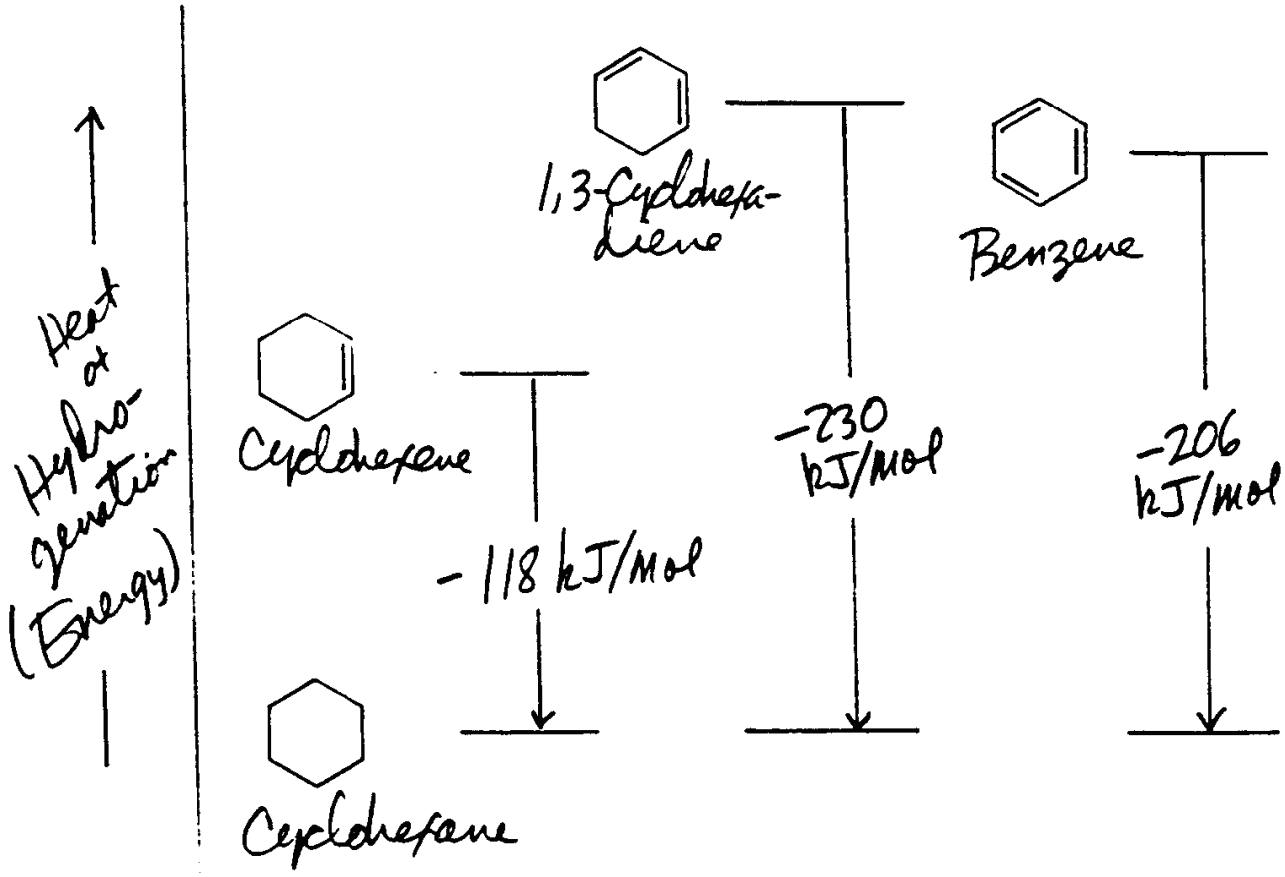


Figure 12.038 ^1H NMR Chemical Shifts for C=C-H Protons

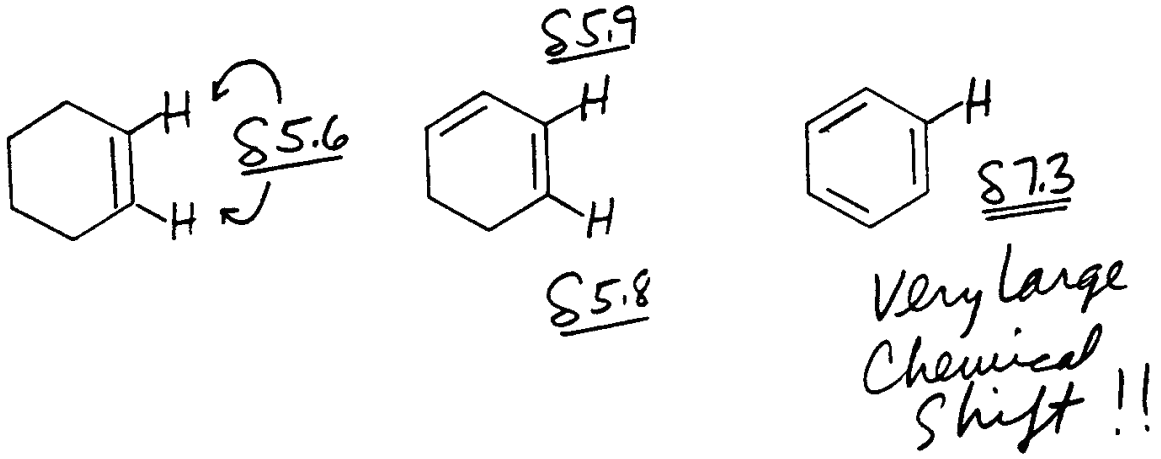
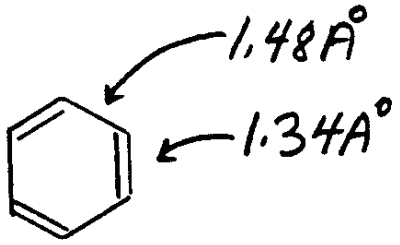
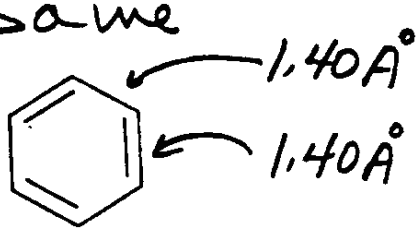


Figure 12.039

If Benzene Had Normal C-C and C=C It Would be an Asymmetric Molecule Which Would Look Like

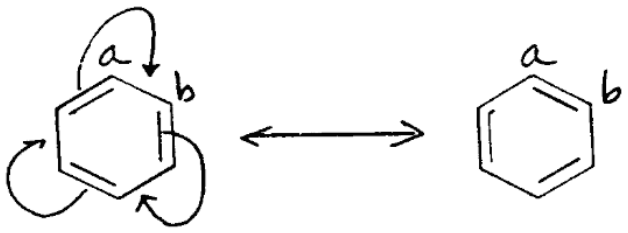


But Benzene is Symmetric with All C-C Distances the Same



Conclusion: C-C and C=C are Not Normal!!

Figure 12.040



Benzene Resonance Structures

Figure 12.041 π MO Energy Levels for Benzene

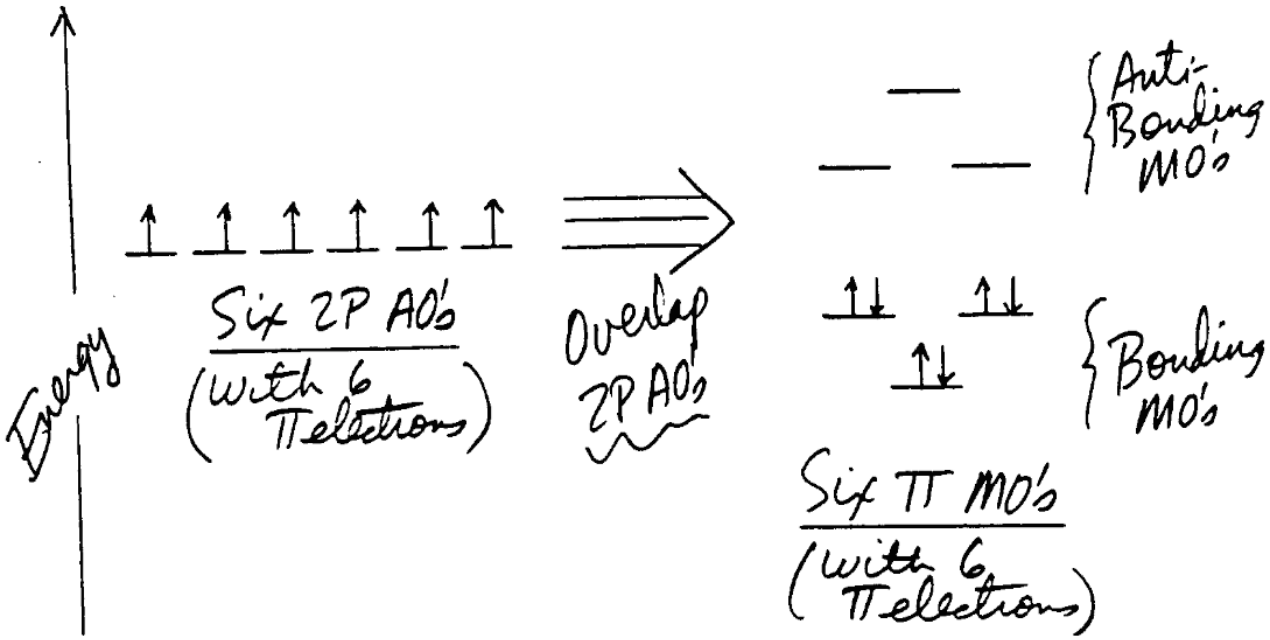


Figure 12.042

Bonding π MO's in Benzene

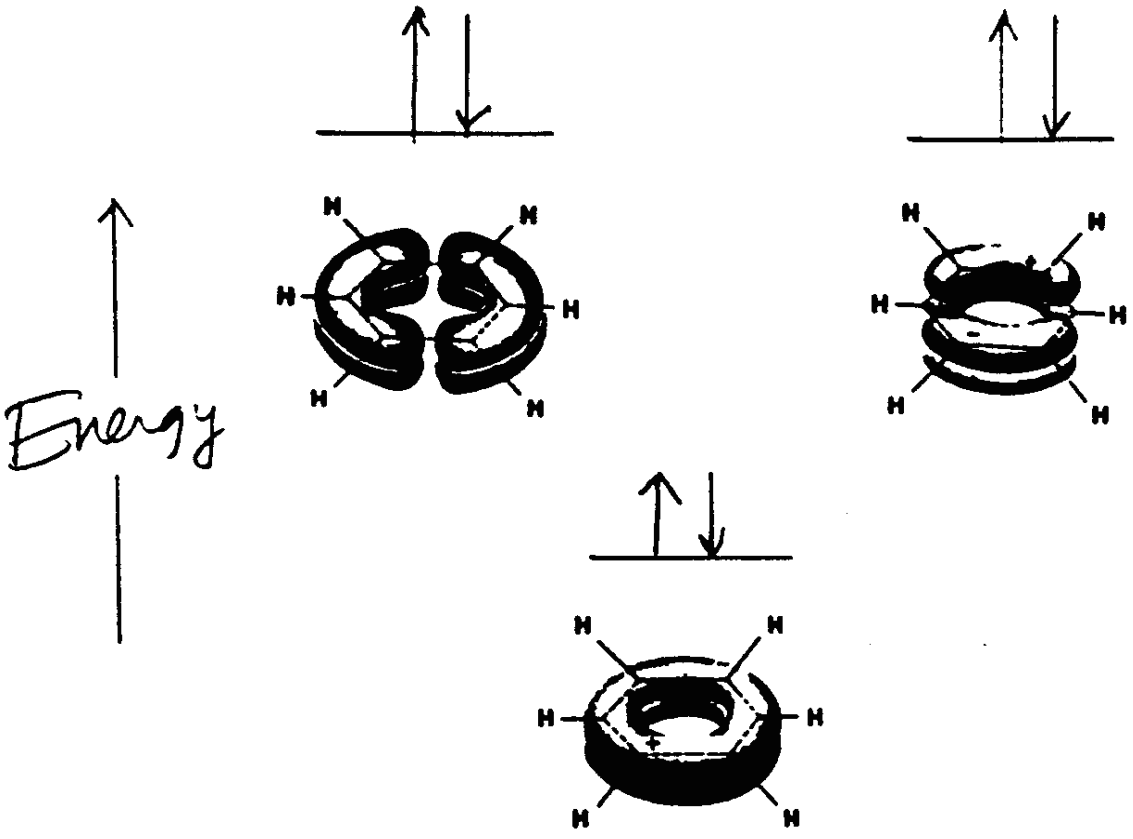


Figure 2.1 Taken from "Advanced Org Chem," March, 4th Ed, Wls, 1992

Figure 12.043 Representation of Benzene Showing Electron Delocalization

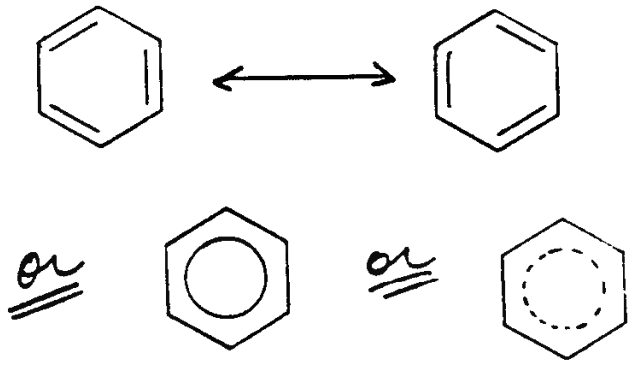


Figure 12.044 Stepwise Hydrogenation of Benzene

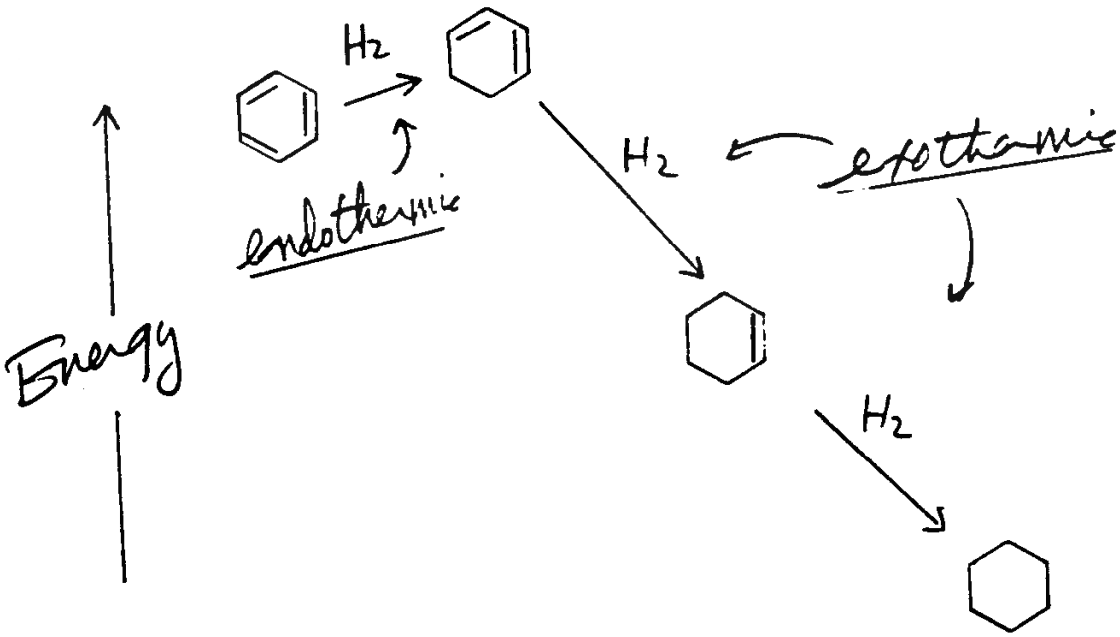


Figure 12.045

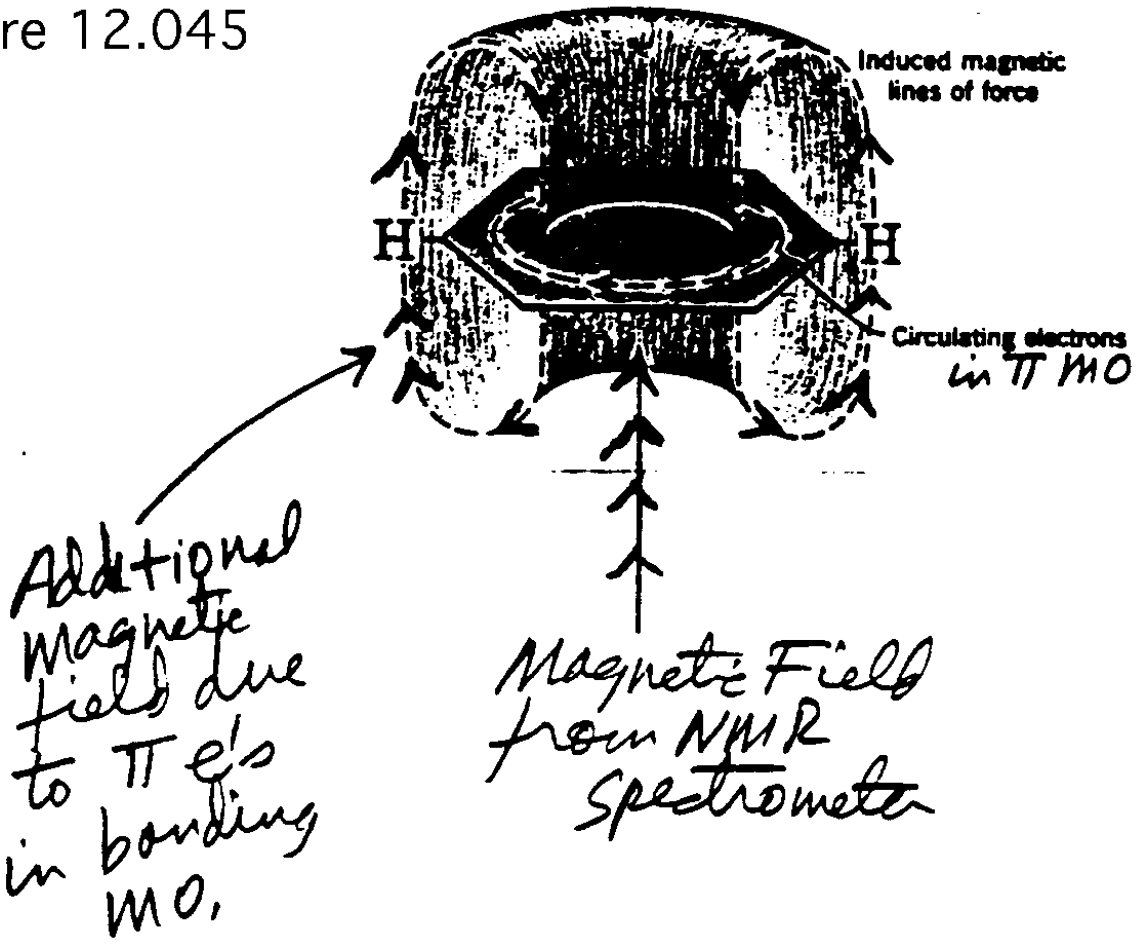


Figure 4.17. From "Spectrometric Identification of Organic Compounds" by Silverstein, Bassler, and Morrill, 5th Ed., Wiley, 1991

Figure 12.046 Substituted Benzenes are Also Aromatic

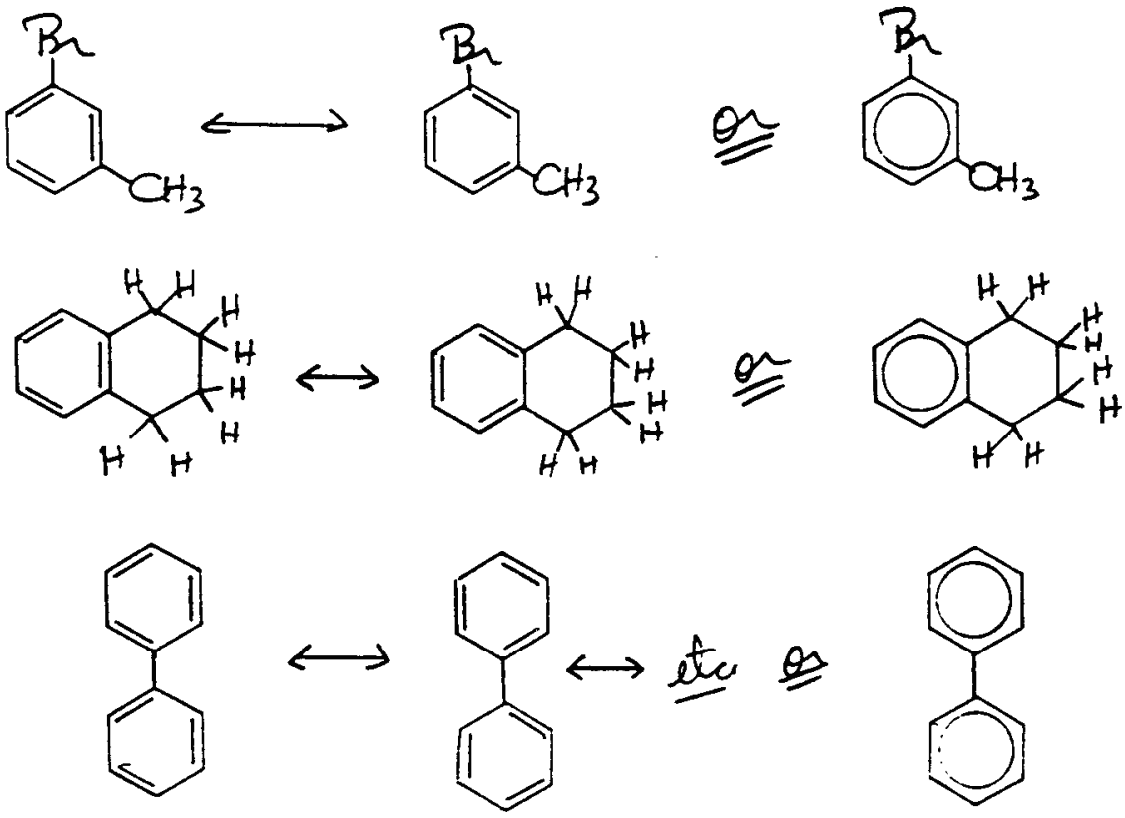
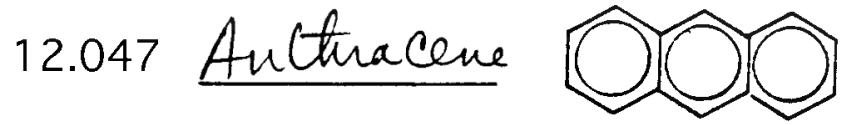


Figure 12.047 Anthracene



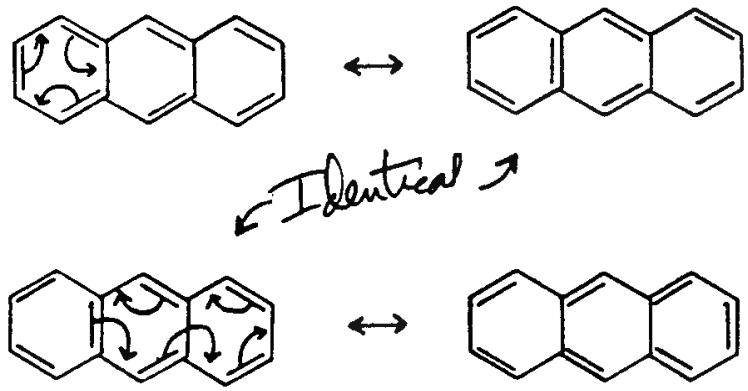
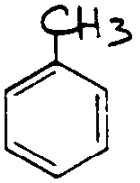
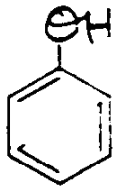


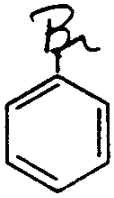
Figure 12.048 Systematic Names for Selected Monocyclic Arenes



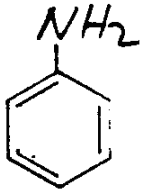
Methylbenzene



benzenol

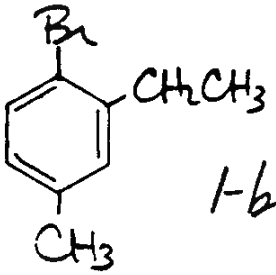


bromobenzene

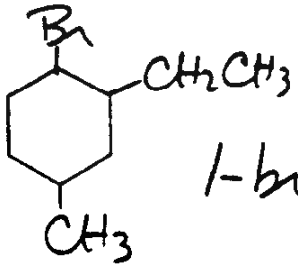


benzenamine

Figure 12.049

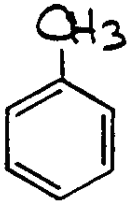


1-bromo-2-ethyl-4-methyl-benzene

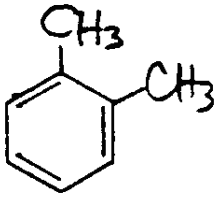


1-bromo-2-ethyl-4-methyl Cyclohexane

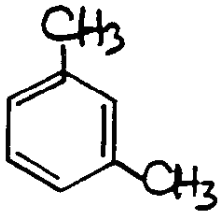
Figure 12.050



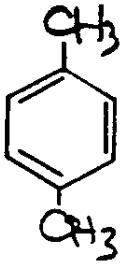
Methylbenzene
or
toluene



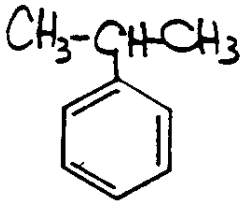
1,2-dimethylbenzene
or
ortho-xylene



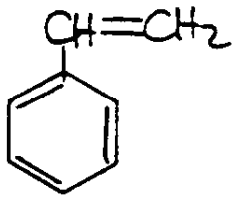
1,3-dimethylbenzene
or
meta-xylene



1,4-dimethylbenzene
or
Para-xylene

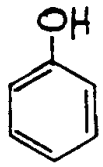


isopropylbenzene
or
Cumene



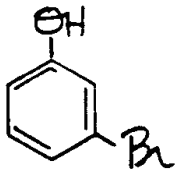
Vinylbenzene
or
styrene

Figure 12.051

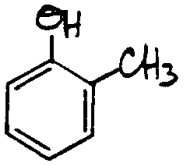


benzenol
or
Phenol

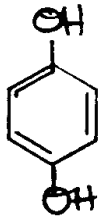
and substituted phenols such as



meta-bromophenol

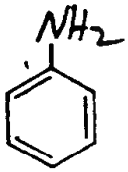


Ortho-toluol



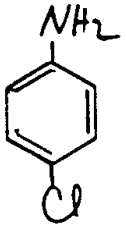
hydroquinone

(Note: Include anisole here)

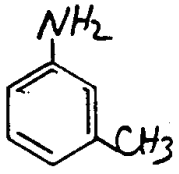


benzenamine
or
aniline

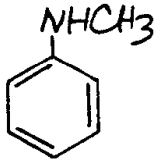
and substituted anilines such as



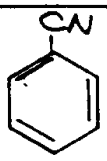
Para-Chloroaniline



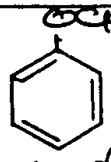
meta-Methylaniline



N-methylaniline



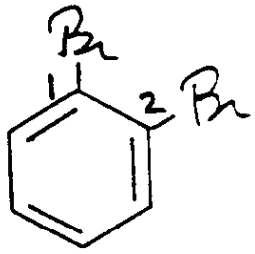
benzenitrile
or
benzonitrile



(see above)

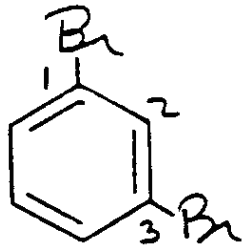
Methoxybenzene
or
anisole

Figure 12.052



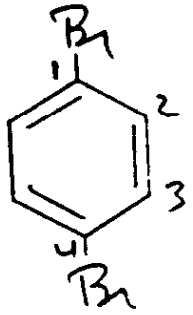
1,2-dibromobenzene
ortho-dibromobenzene
o-dibromobenzene

C2 is ortho to C1 and vice-versa



1,3-dibromobenzene
meta-dibromobenzene
m-dibromobenzene

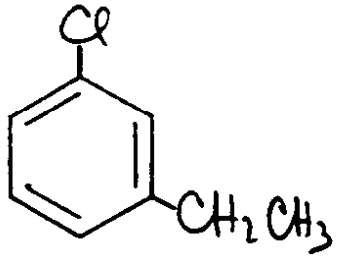
C3 is meta to C1 and vice-versa



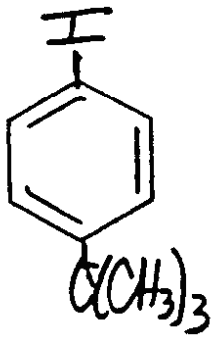
1,4-dibromobenzene
para-dibromobenzene
p-dibromobenzene

C4 is para to C1 and vice-versa

Figure 12.053

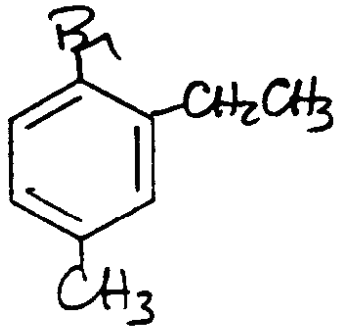


1-Chloro-3-ethylbenzene
or
Meta-Chloroethylbenzene



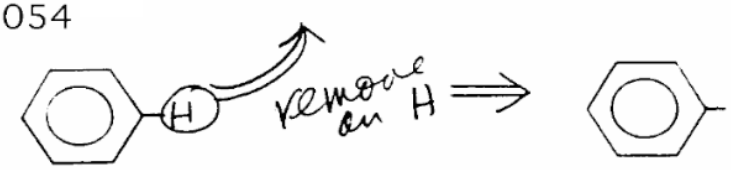
1-t-butyl-4-iodobenzene
or
Para-t-butyliodobenzene

but



The terms O, M, and/or P
Cannot be used to
Name this molecule,
but they can be used to
describe relationships
between groups.

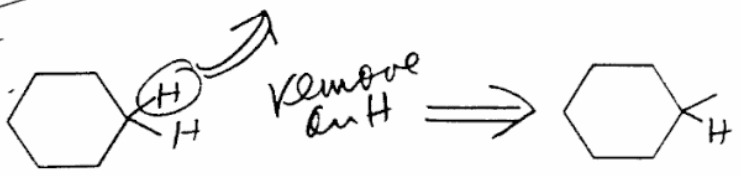
Figure 12.054



benzene

Phenyl (group)

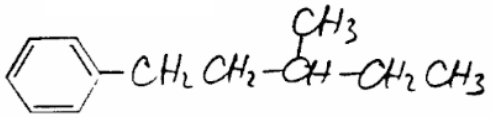
Compare to



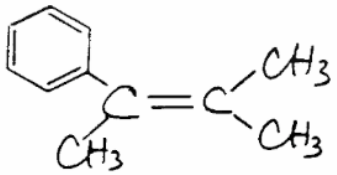
Cyclohexane

Cyclohexyl (group)

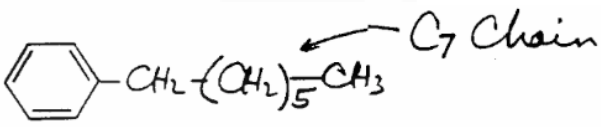
Figure 12.055



3-methyl-1-phenylpentane

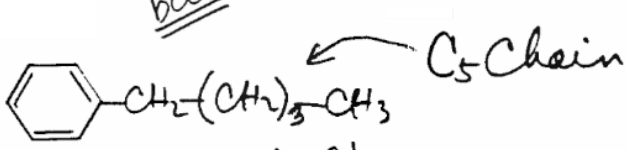


2-phenyl-3-methyl-2-butene



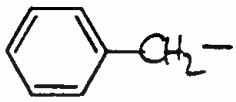
1-phenylheptane

but



pentylbenzene

Figure 12.056



phenylmethyl or benzyl

Figure 12.057

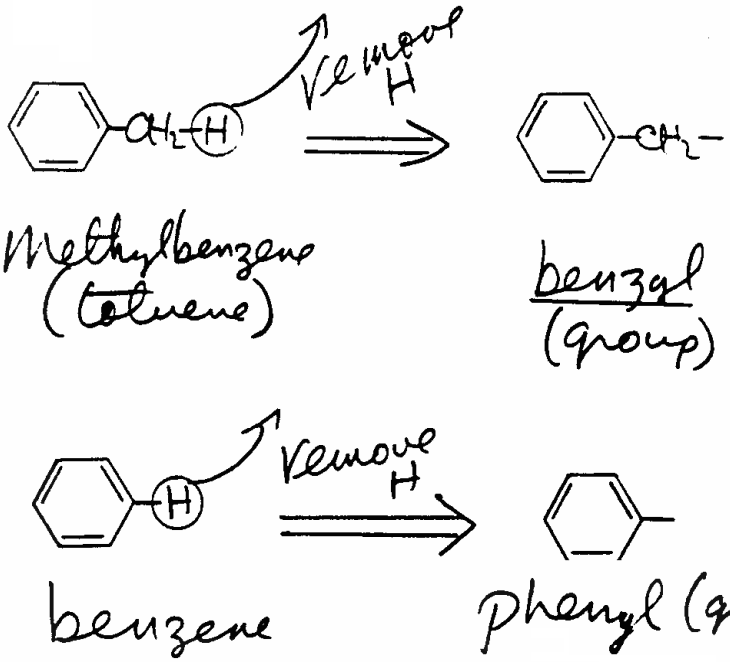
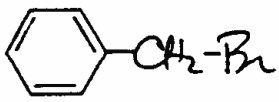
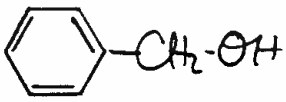


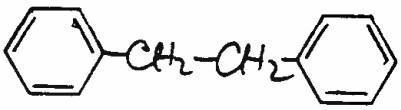
Figure 12.058



benzyl bromide
(bromophenylmethane)

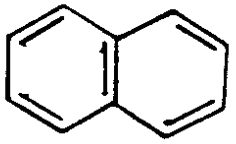


benzyl alcohol
(Phenylmethanol)

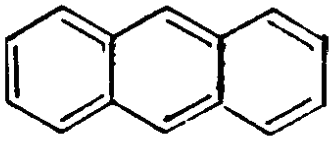


bibenzyl
(1,2-diphenylethane)

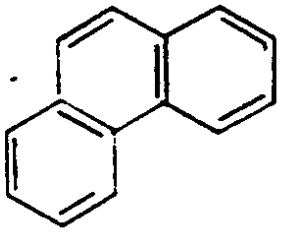
Figure 12.059



Naphthalene

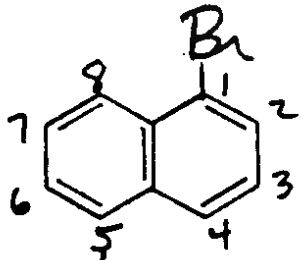


Anthracene

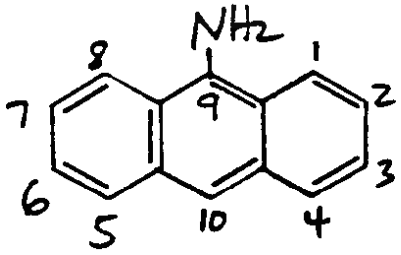


Phenanthrene

Figure 12.060



1-bromonaphthalene



9-anthracenamine

Figure 12.061 Some Annulenes

C_4H_4  1,3-Cyclobutadiene

C_6H_6  benzene

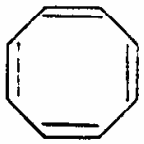
C_8H_8  1,3,5,7-Cyclooctatetraene

Figure 12.062 Cyclooctatetraene

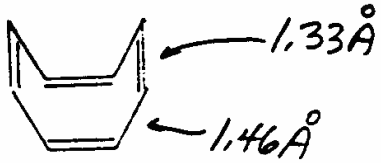
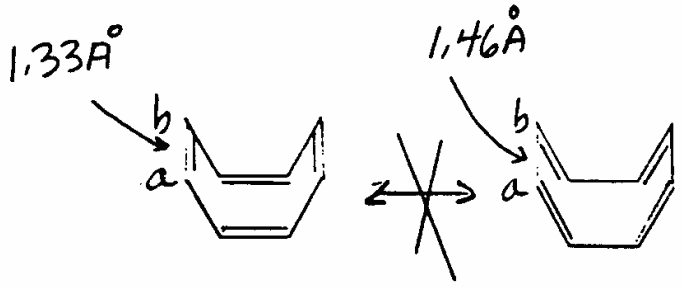
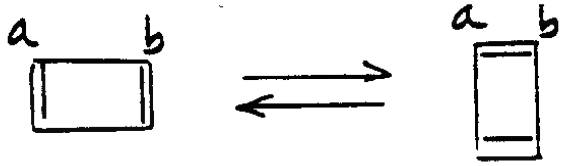


Figure 12.063



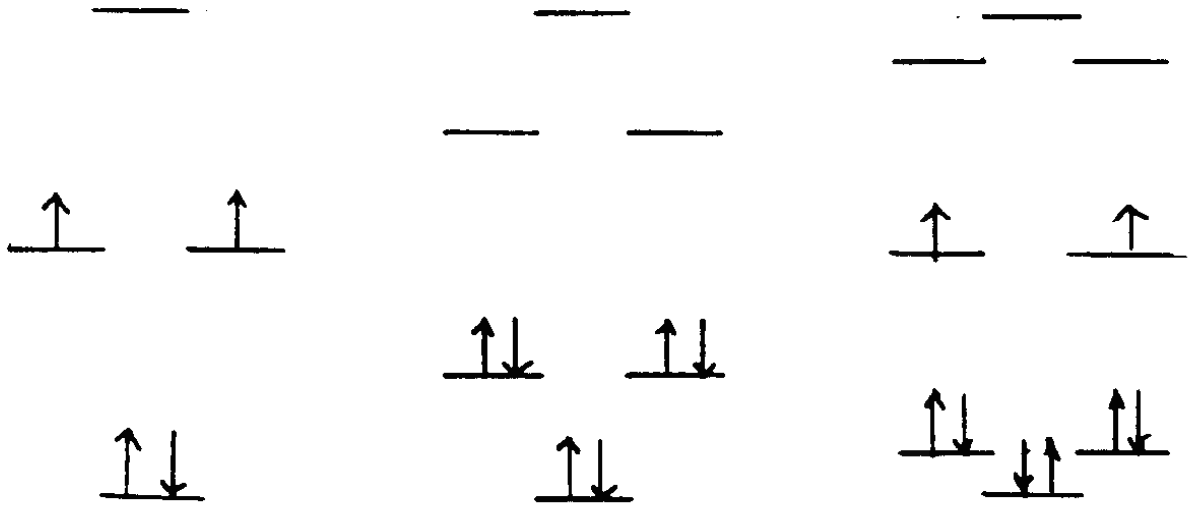
These Cannot be Resonance Structures Because the Bond Lengths Change

Figure 12.064 Cyclobutadiene



Equilibrium – Not Resonance

Figure 12.065 π MO's for Planar Annulenes

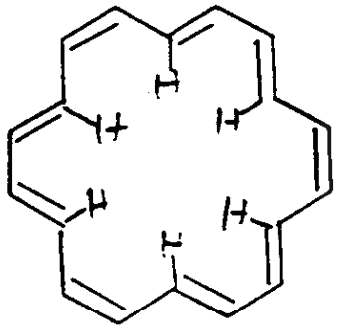


C_4H_4 with 4 π e's

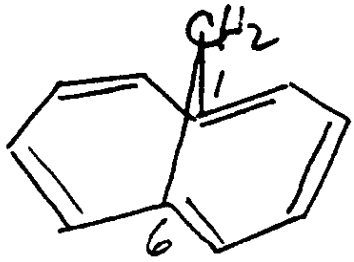
C_6H_6 with 6 π e's

C_8H_8 with 8 π e's

Figure 12.066

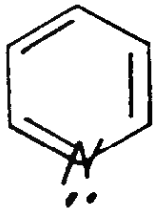


[18] annulene
(18 π e)



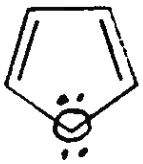
1,6-methano[10]annulene
(10 π e)

Figure 12.067



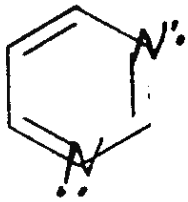
Pyridine

Pyrrole

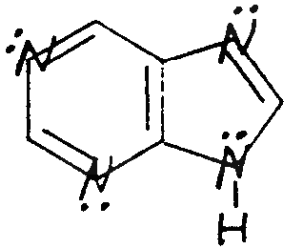


furan

thiophene



Pyrimidine



Purine

Figure 12.068

Overlapping 2P AO's in Pyridine

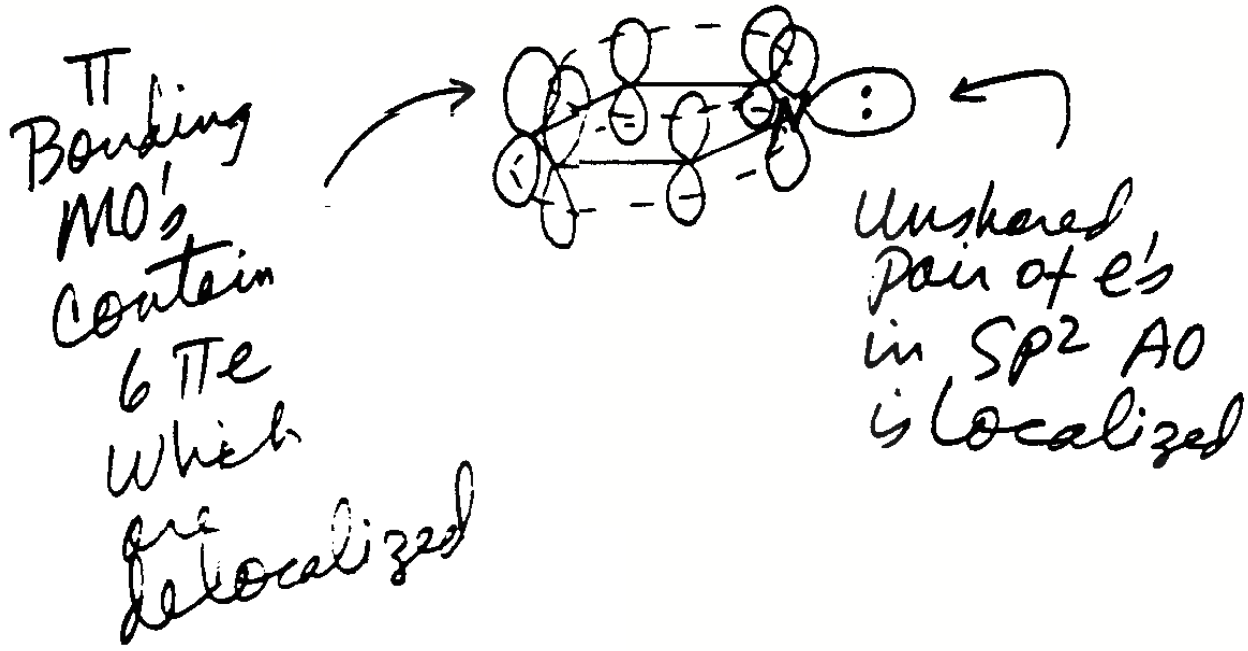
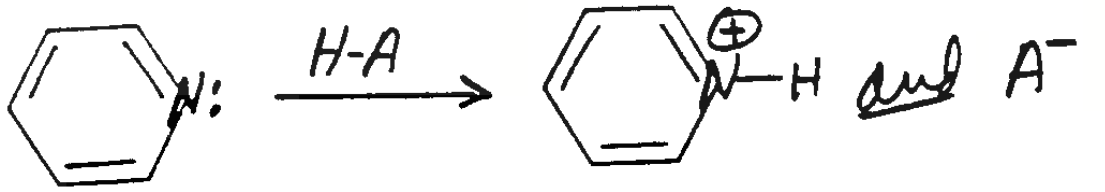


Figure 12.069



Pyridine is weakly basic!

Pyridinium ion ($pK_a \simeq 5$)

Figure 12.070

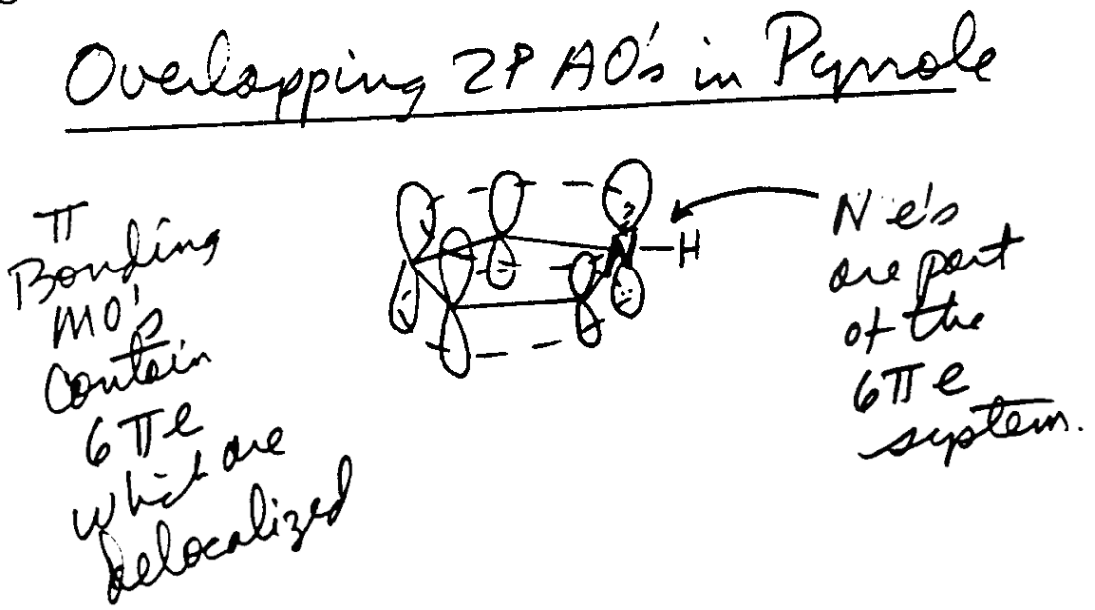


Figure 12.071

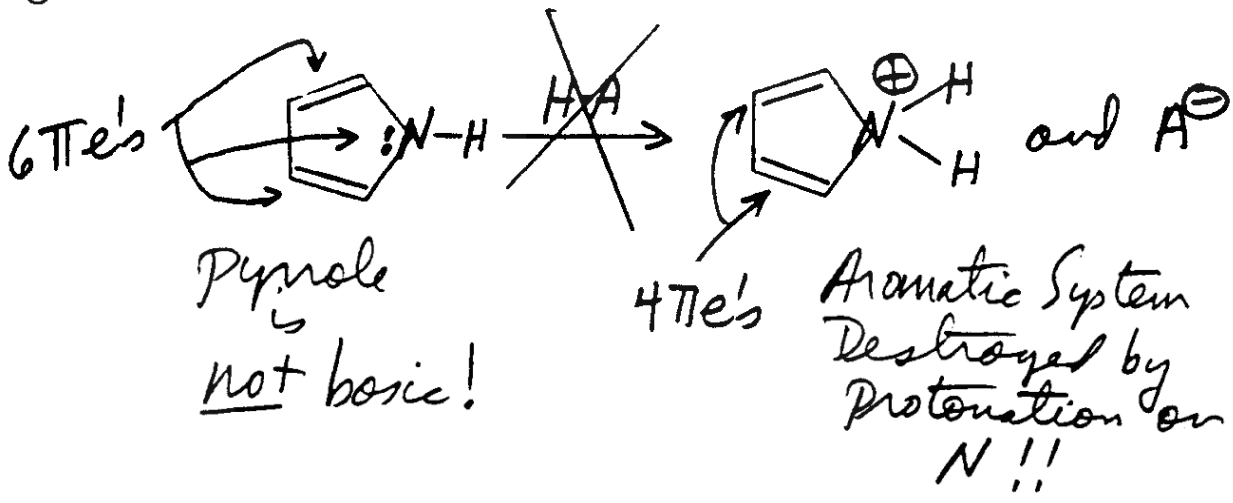


Figure 12.072

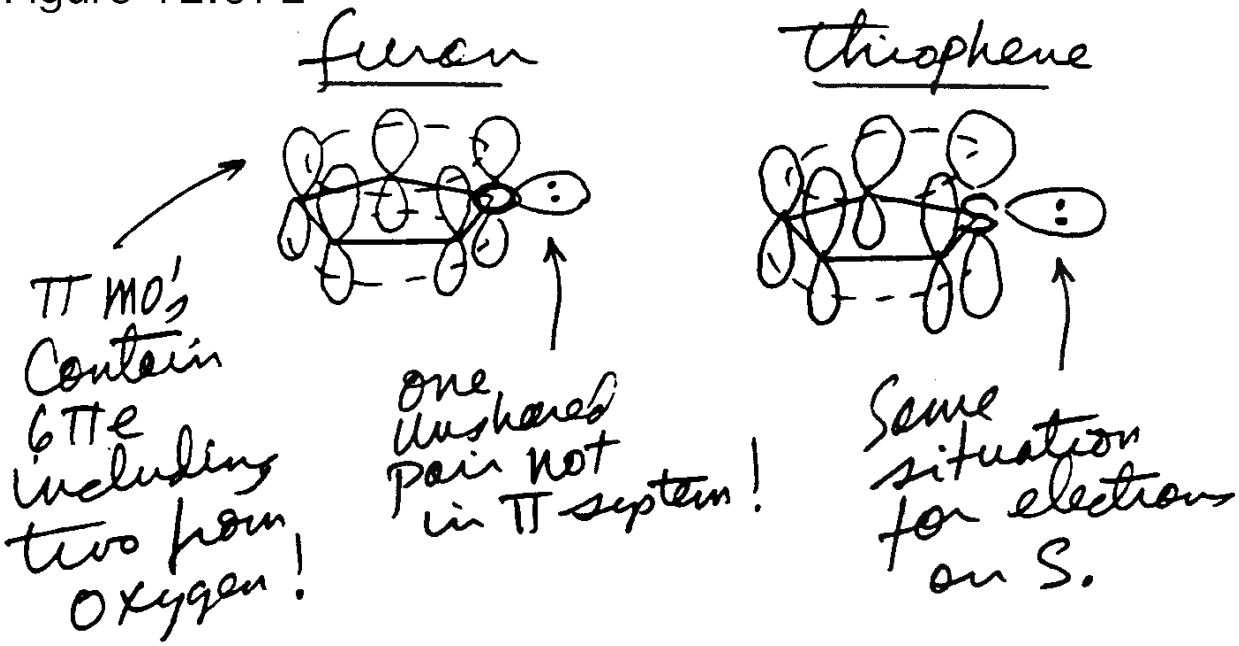
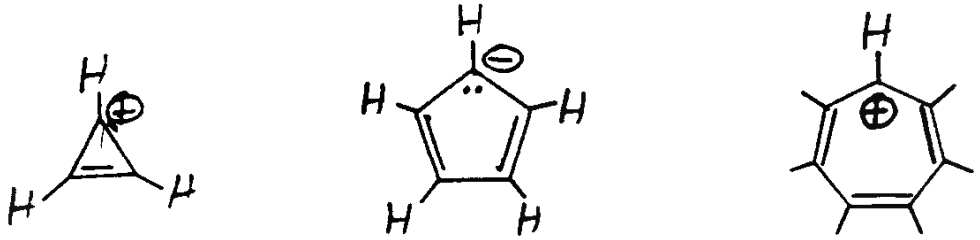


Figure 12.073



$C_3H_3^{\oplus}$ (2π e) Cyclopropenyl Cation

$C_5H_5^{\ominus}$ (6π e) Cyclopentadienyl anion

$C_7H_7^{\oplus}$ (6π e) Cycloheptatrienyl Cation (tropylium ion)

Figure 12.075

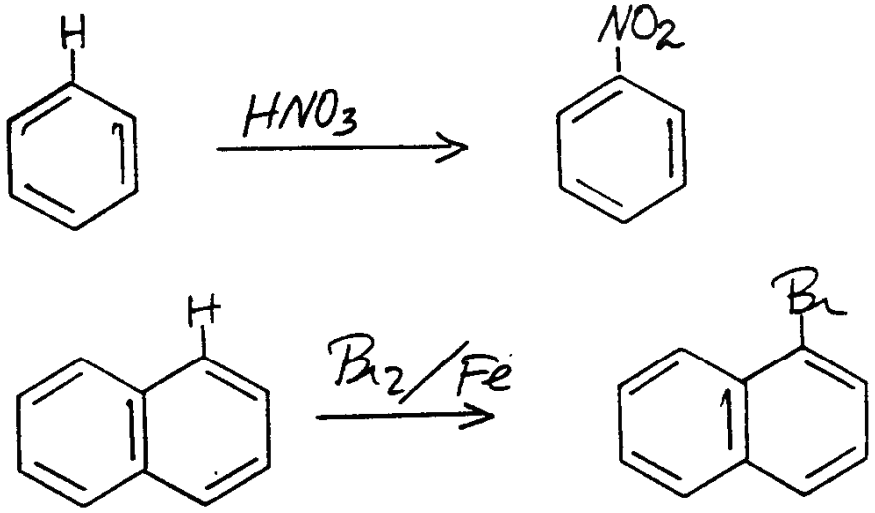


Figure 12.077

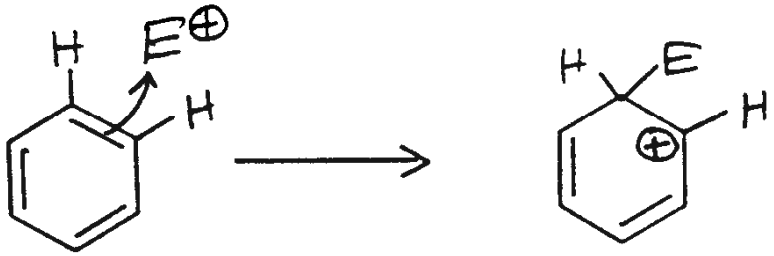


Figure 12.078

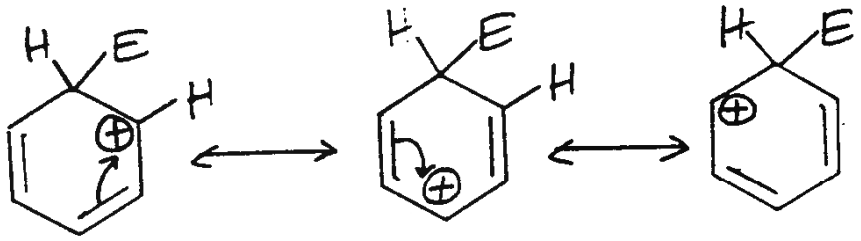


Figure 12.079

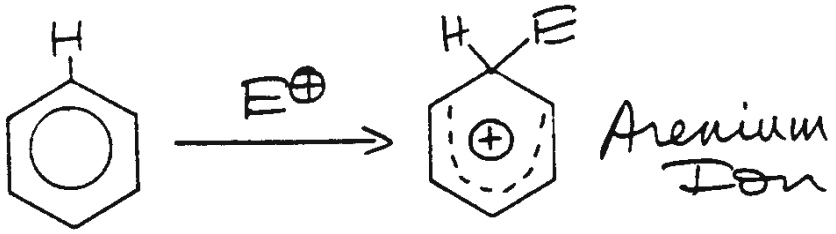


Figure 12.079a

Substitution Occurs in Electrophilic Reaction of Aromatic Systems

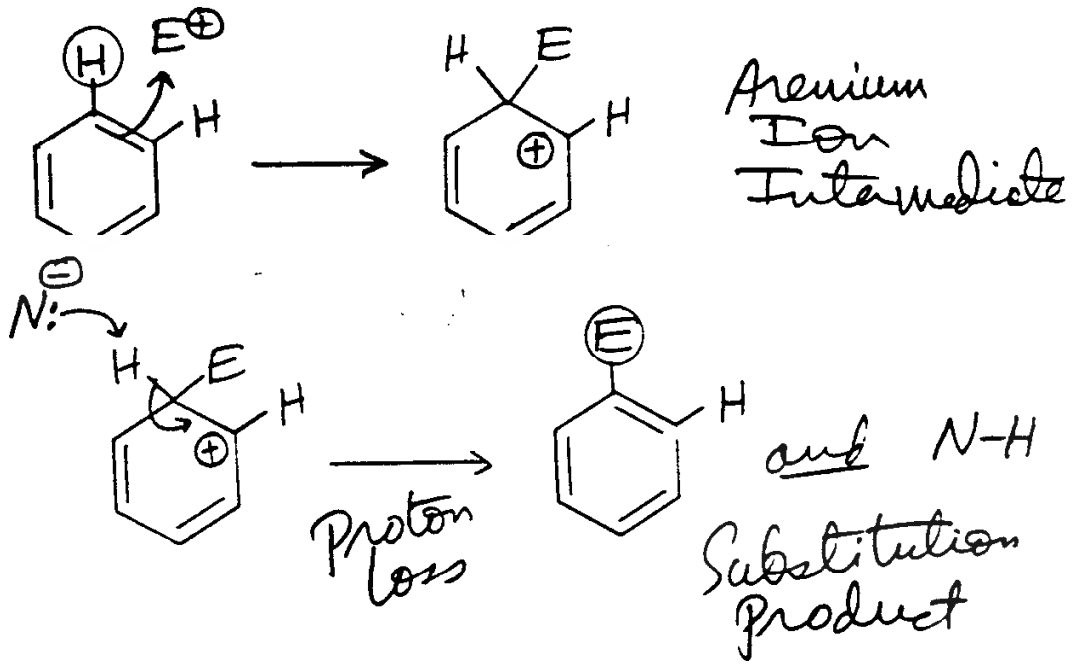


Figure 12.080 Addition Occurs in Electrophilic Reaction of Nonaromatic Cyclic Polyenes

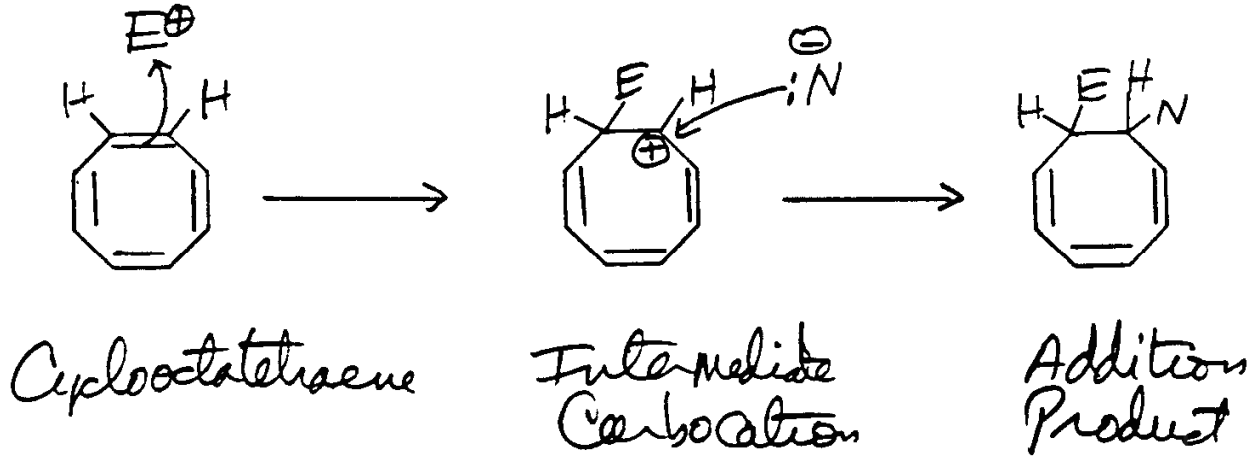


Figure 12.081

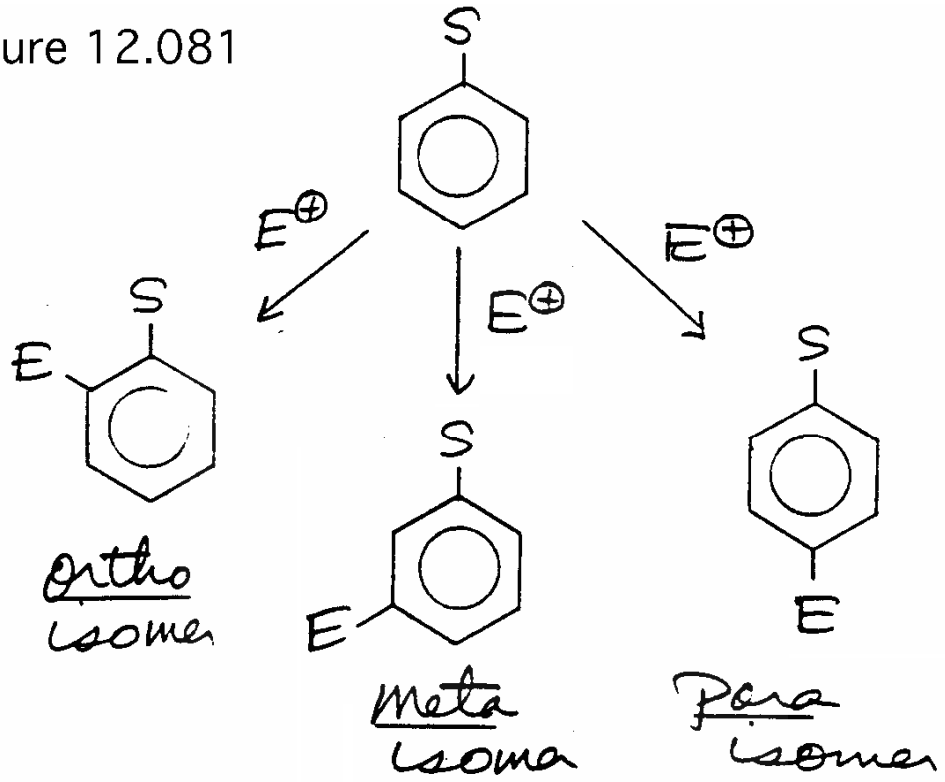


Figure 12.082

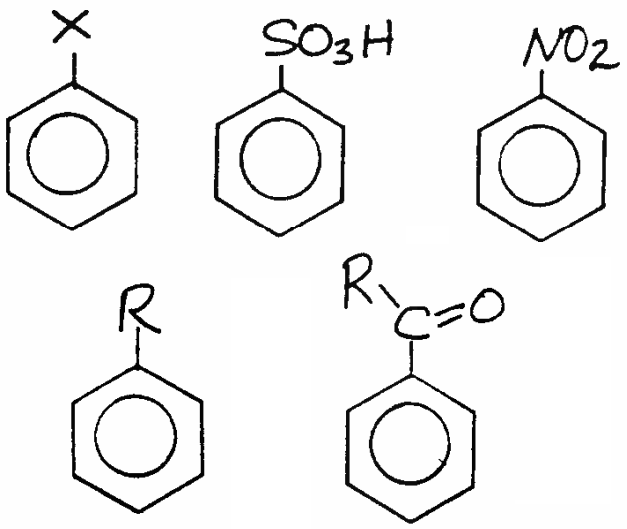


Figure 12.083

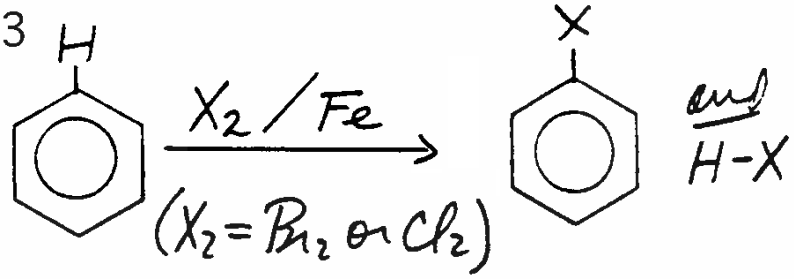


Figure 12.084

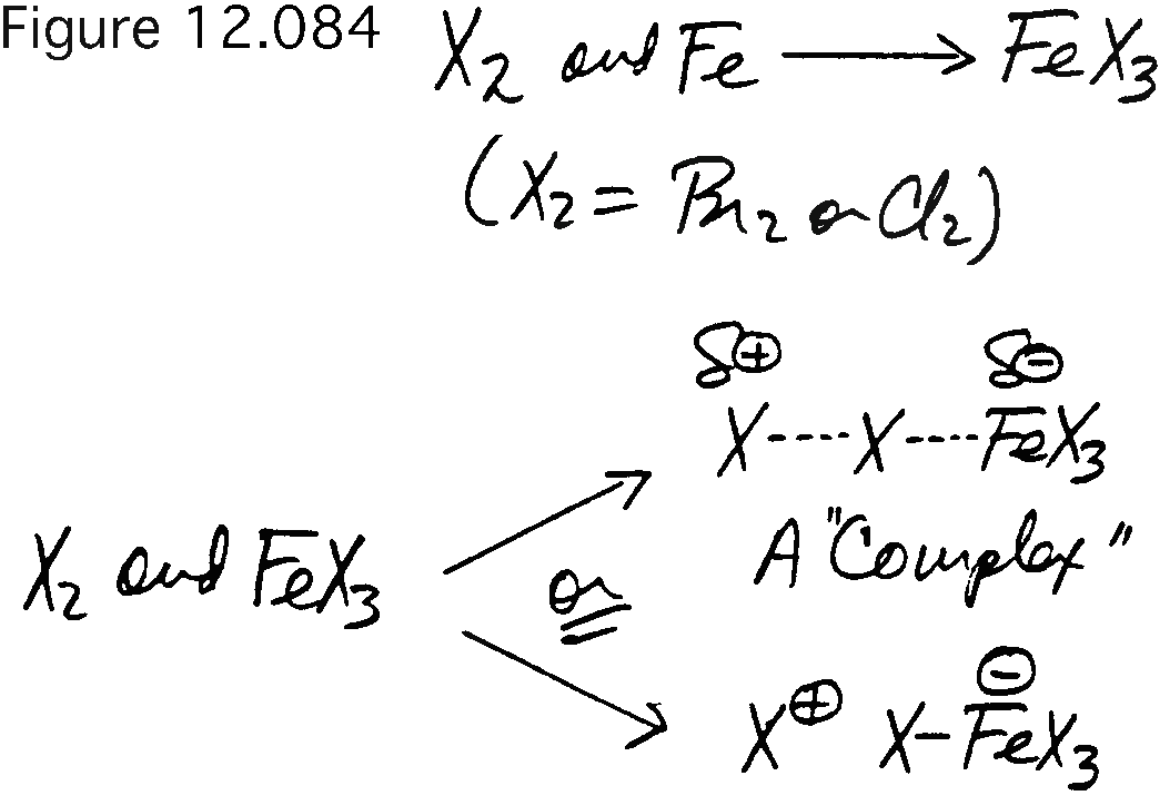


Figure 12.085

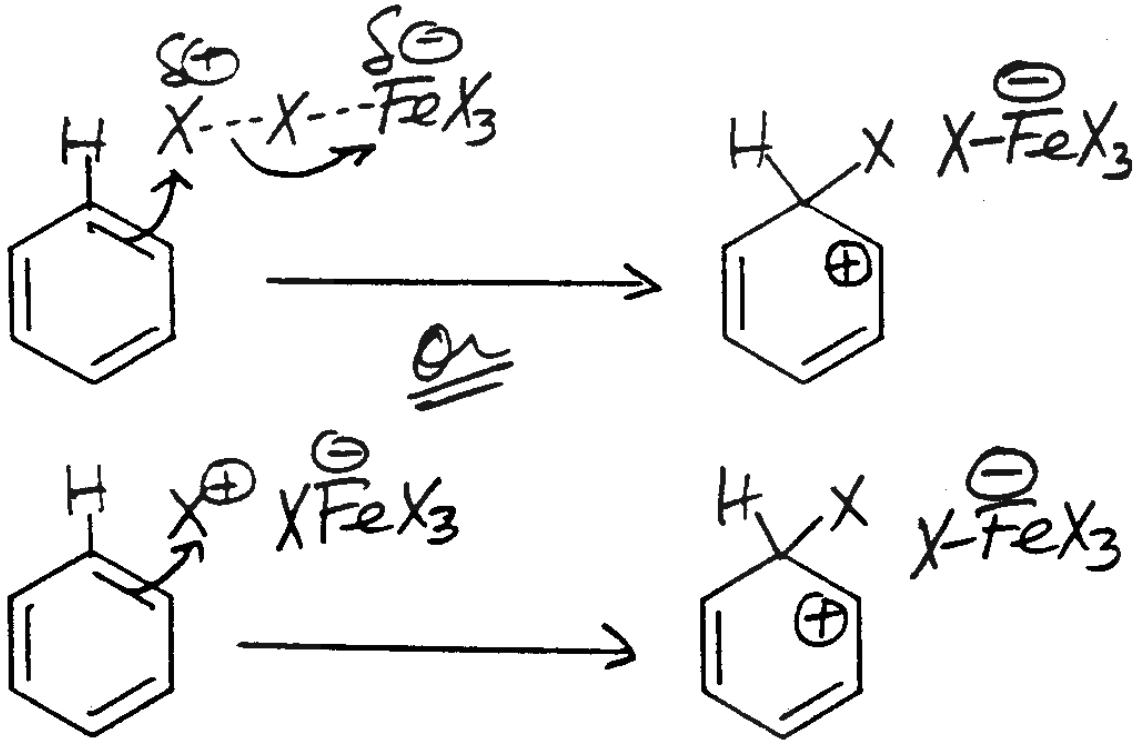


Figure 12.086

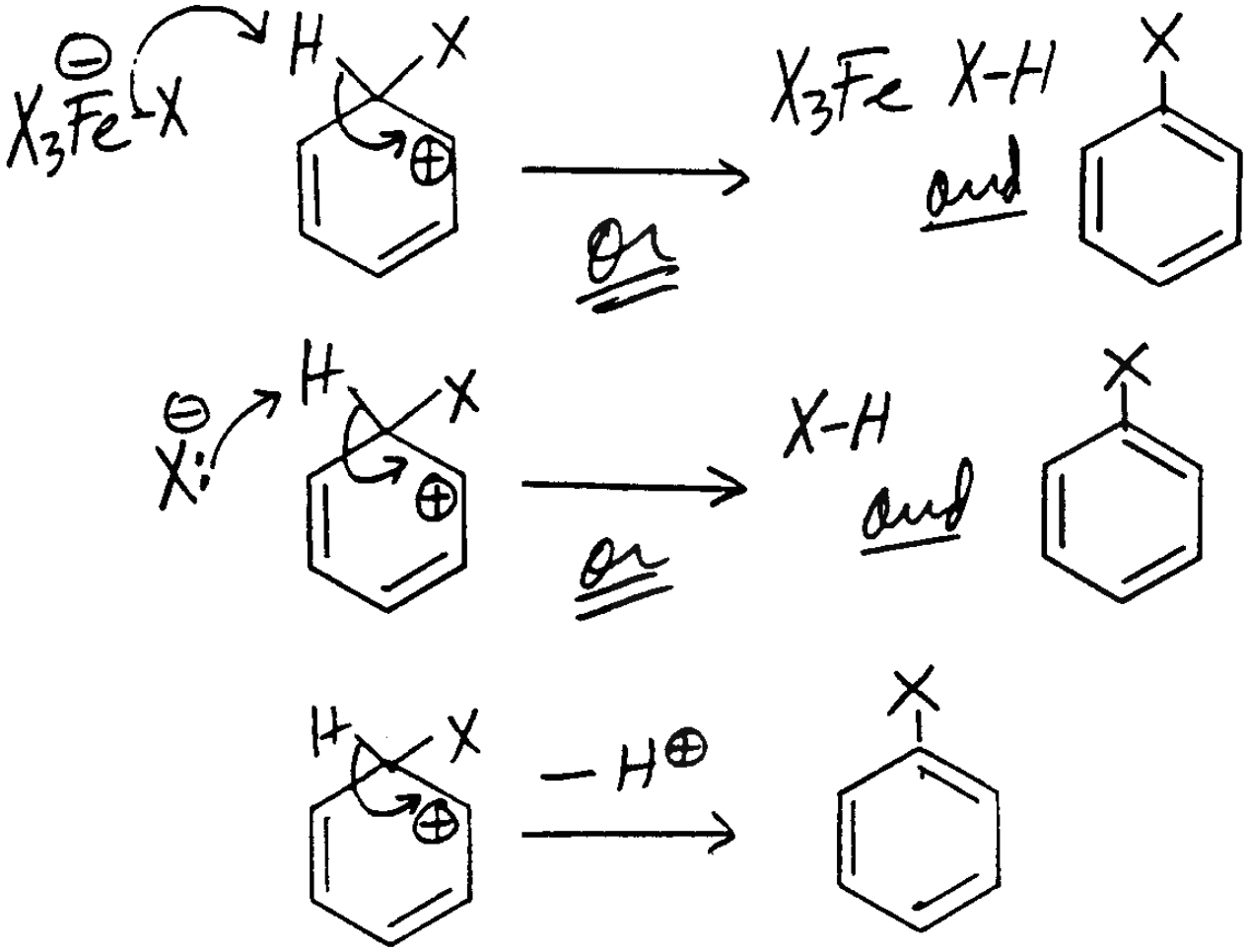


Figure 12.087

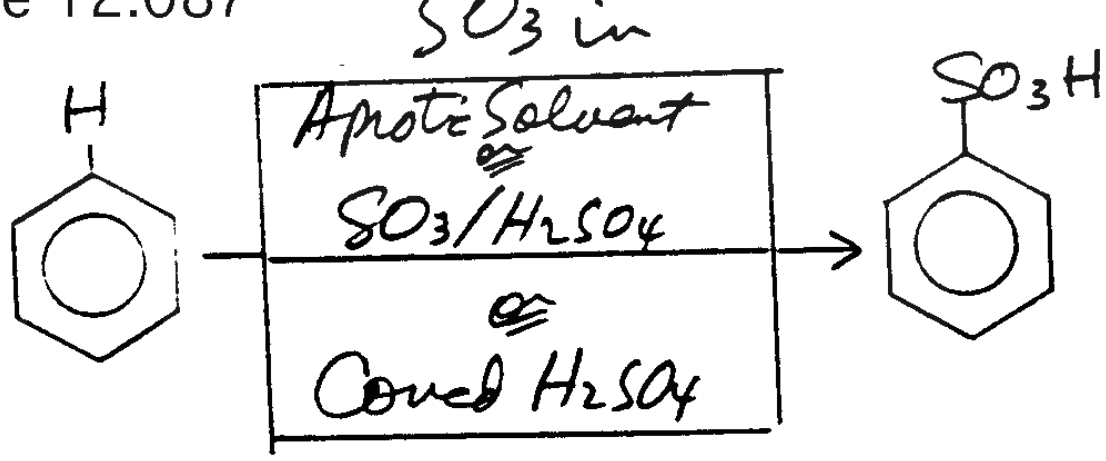


Figure 12.088

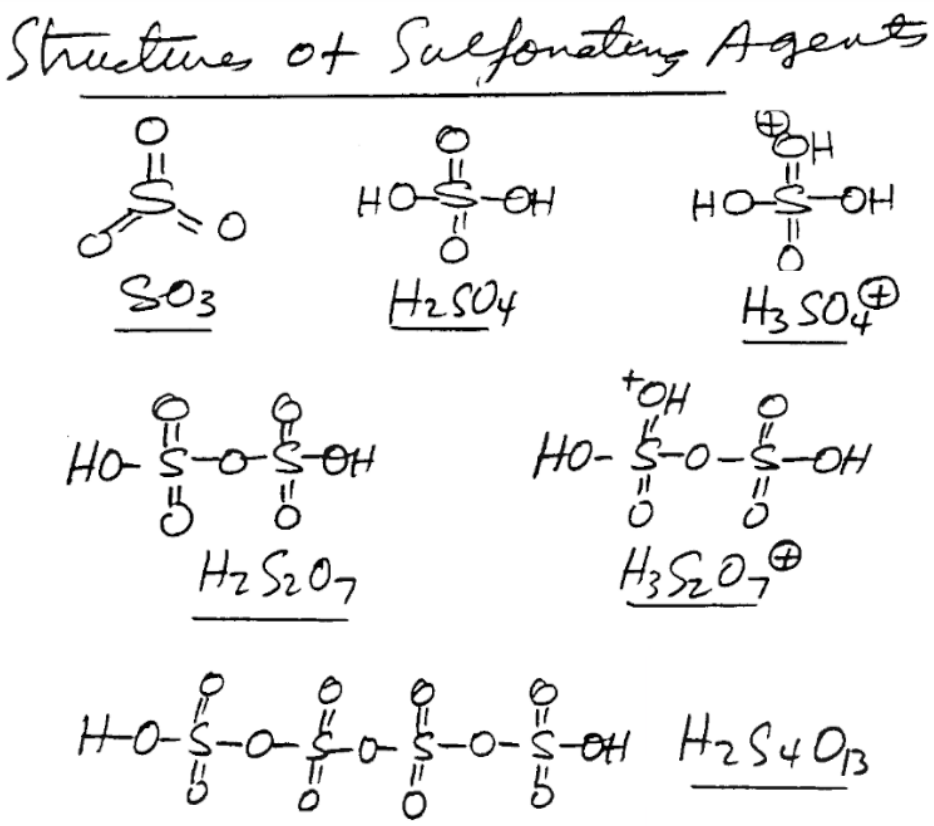
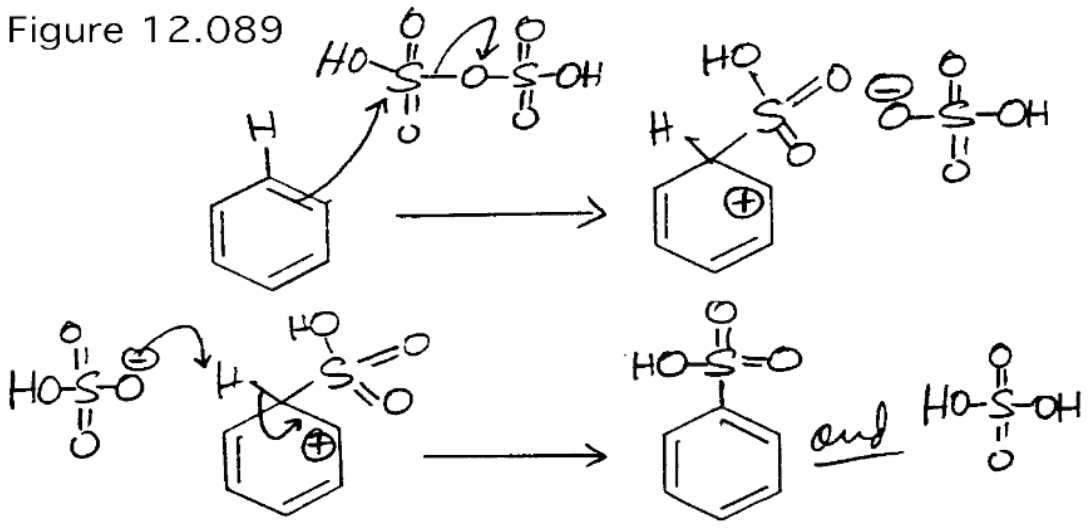


Figure 12.089



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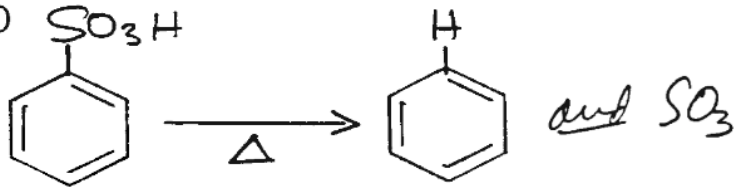
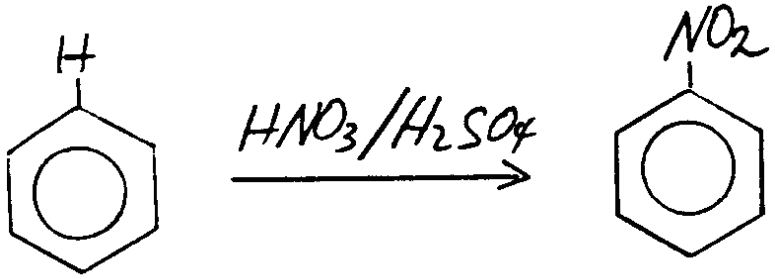


Figure 12.091



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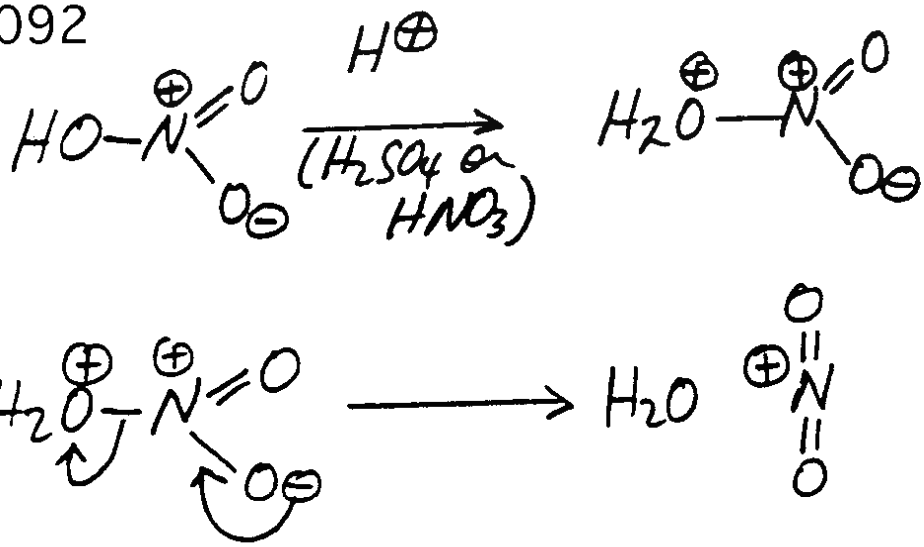


Figure 12.093

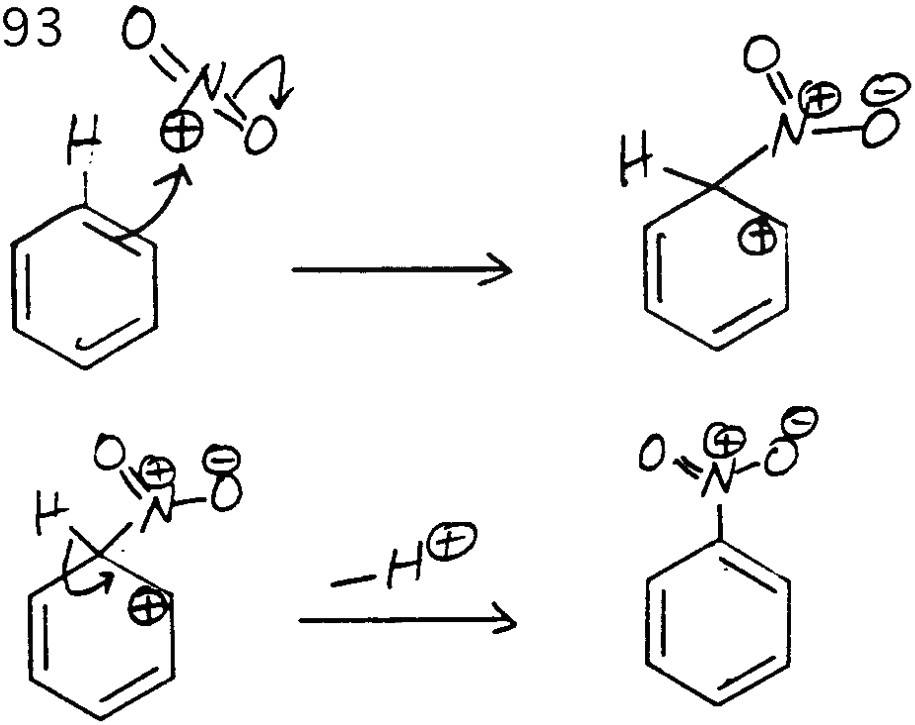
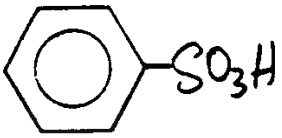


Figure 12.094



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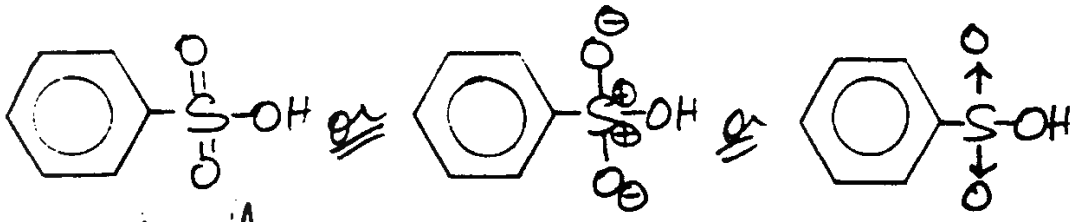
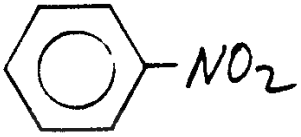


Preferred

Figure 12.095



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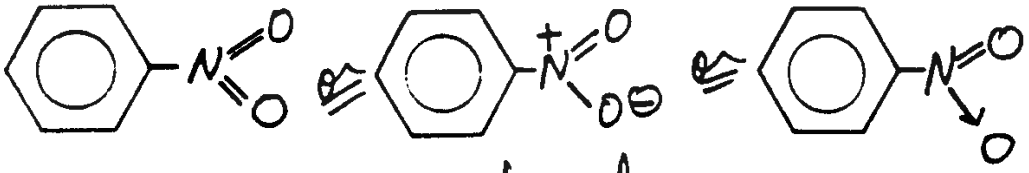

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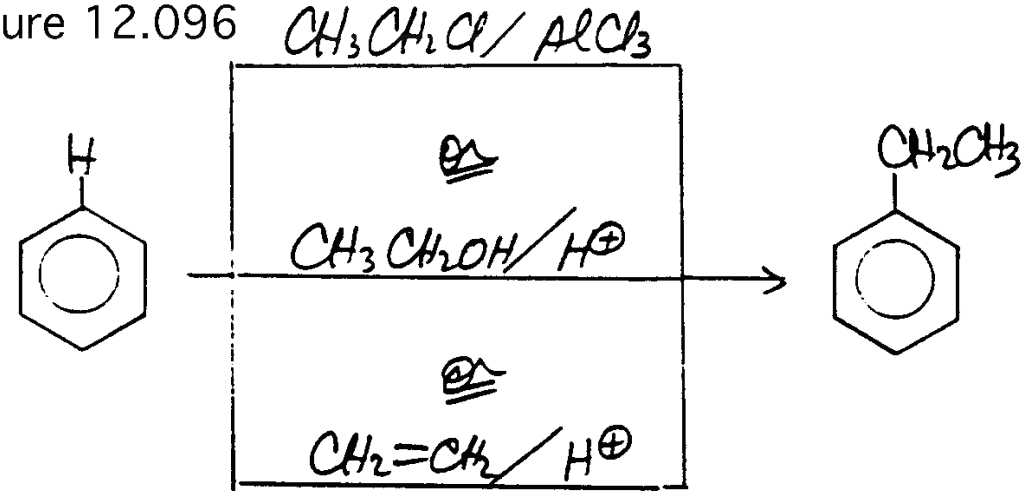
Figure 12.096



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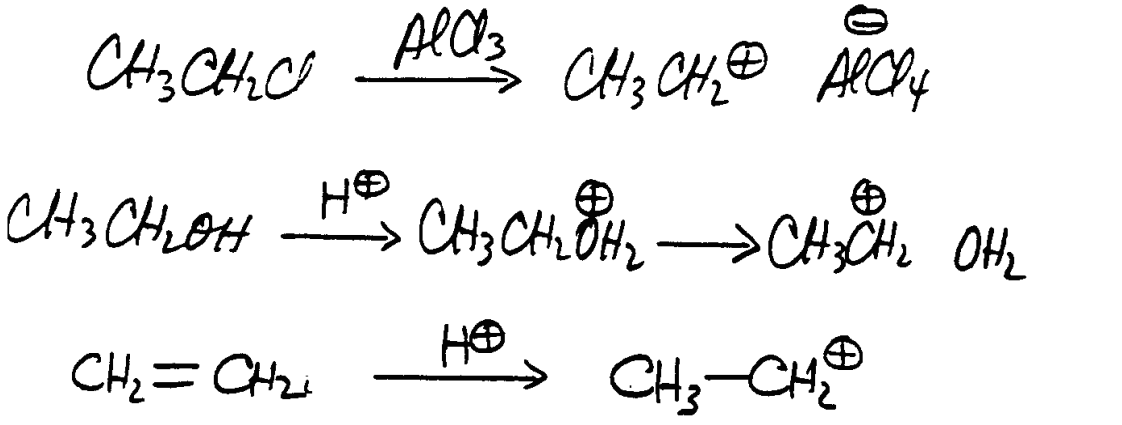

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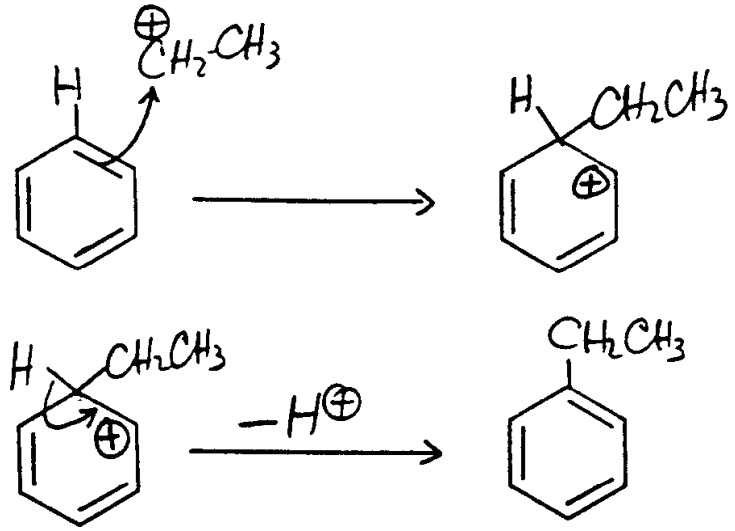

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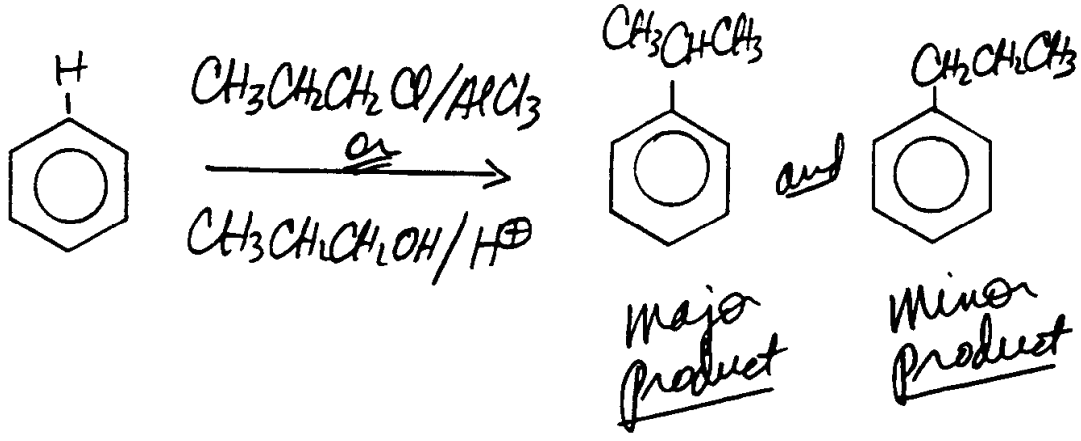

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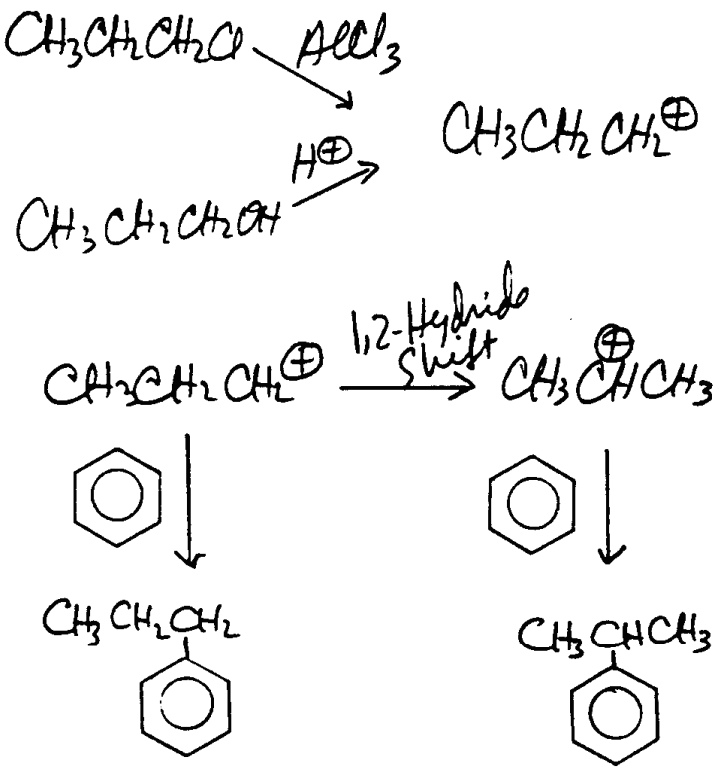

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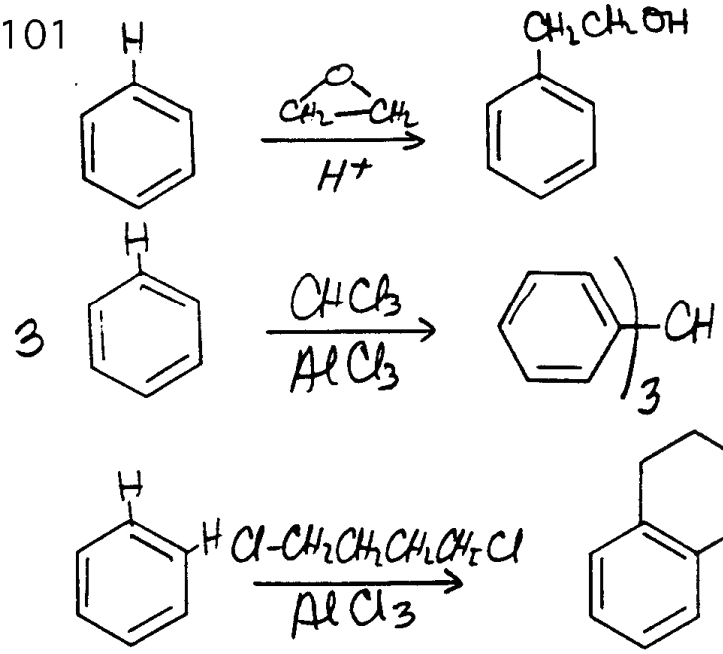
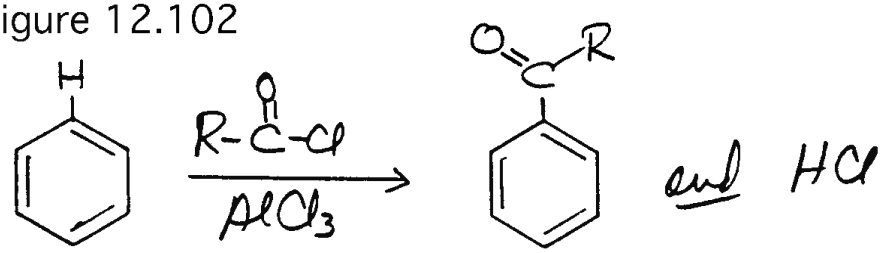


Figure 12.102



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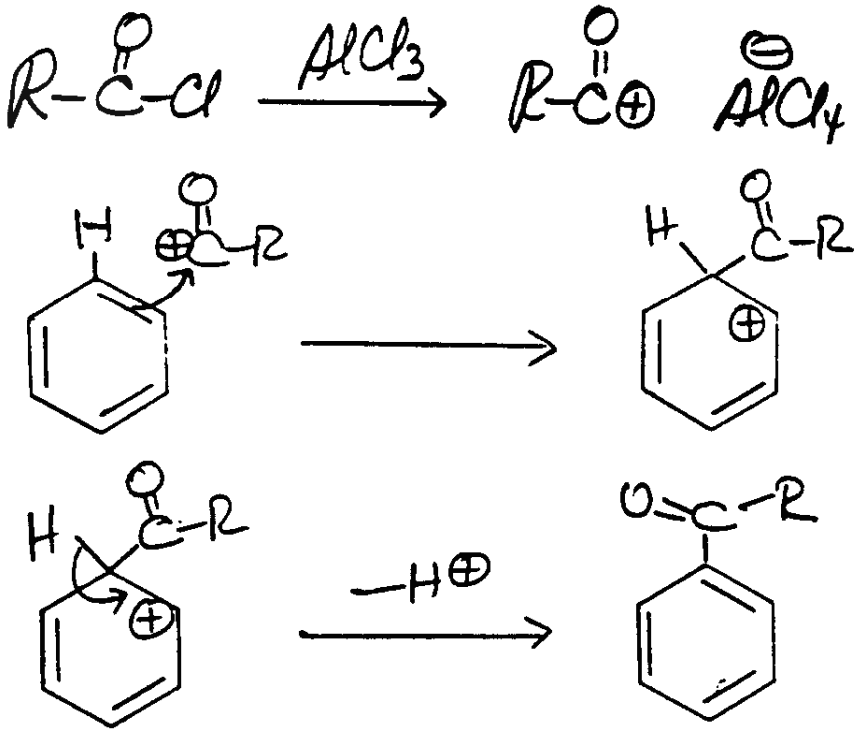
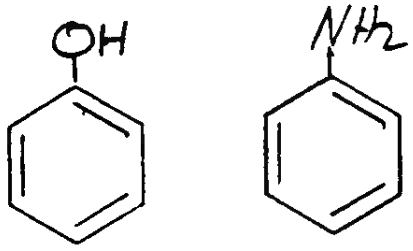


Figure 12.104



phenol aniline

Figure 12.105

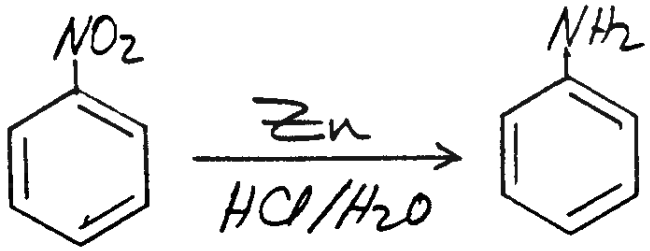


Figure 12.106

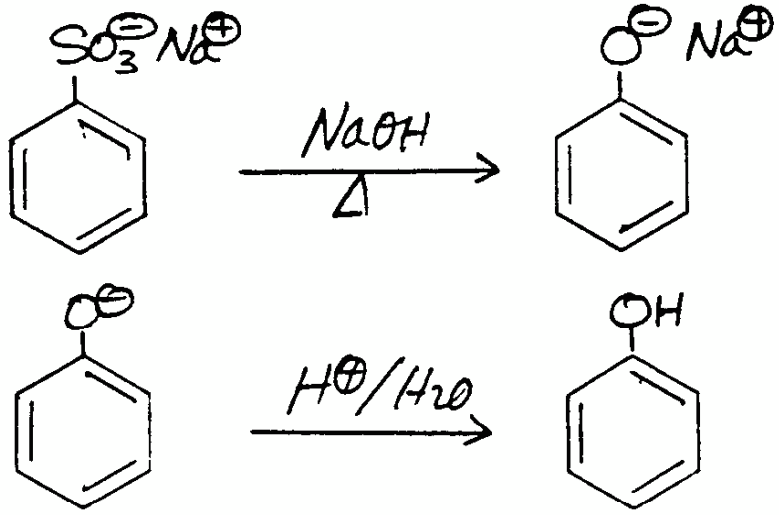
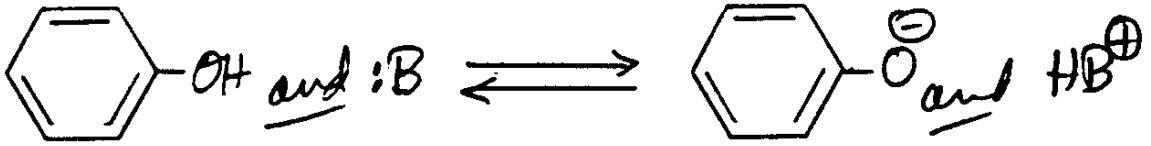


Figure 12.107



Stabilized by Resonance

Compare to

No Resonance Stabilization

Figure 12.108

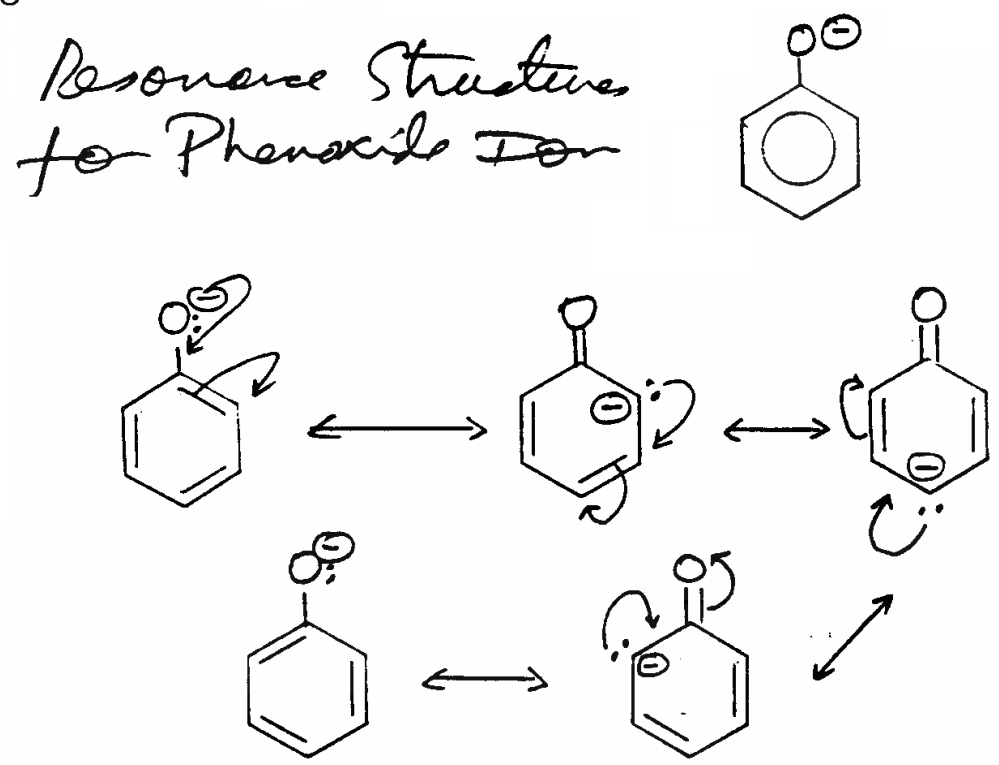


Figure 12.109

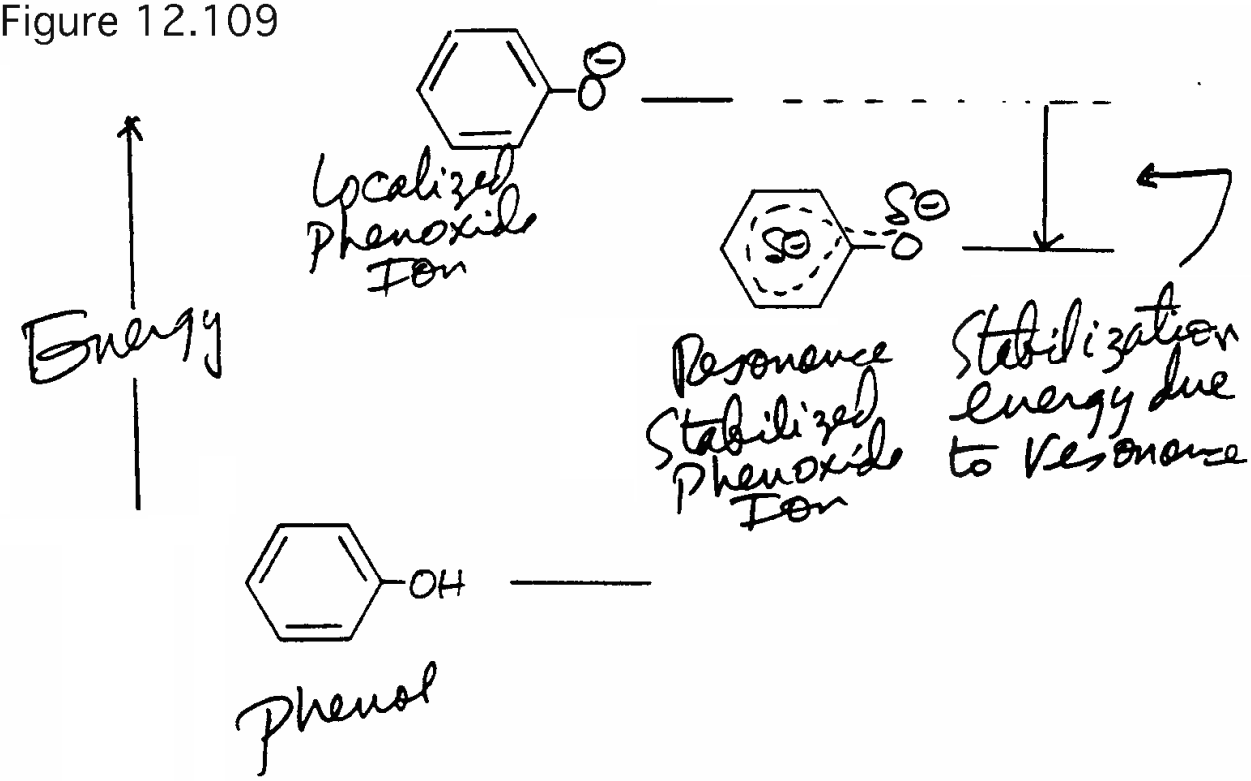


Figure 12.110

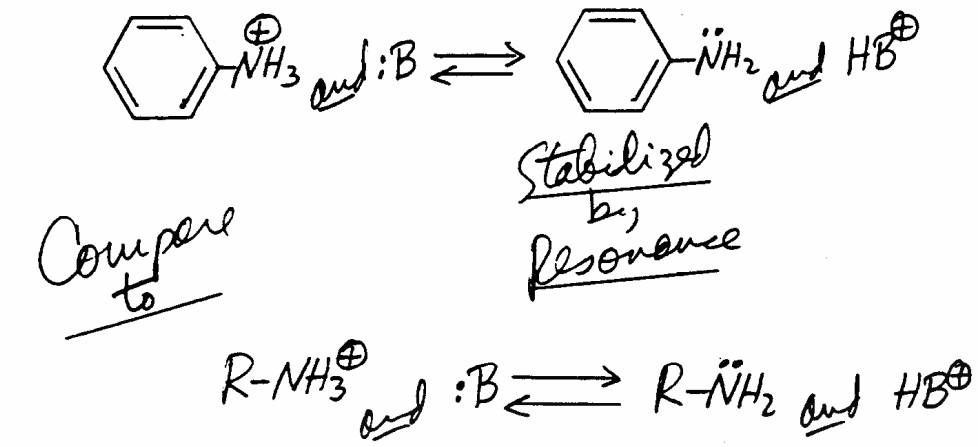


Figure 12.111

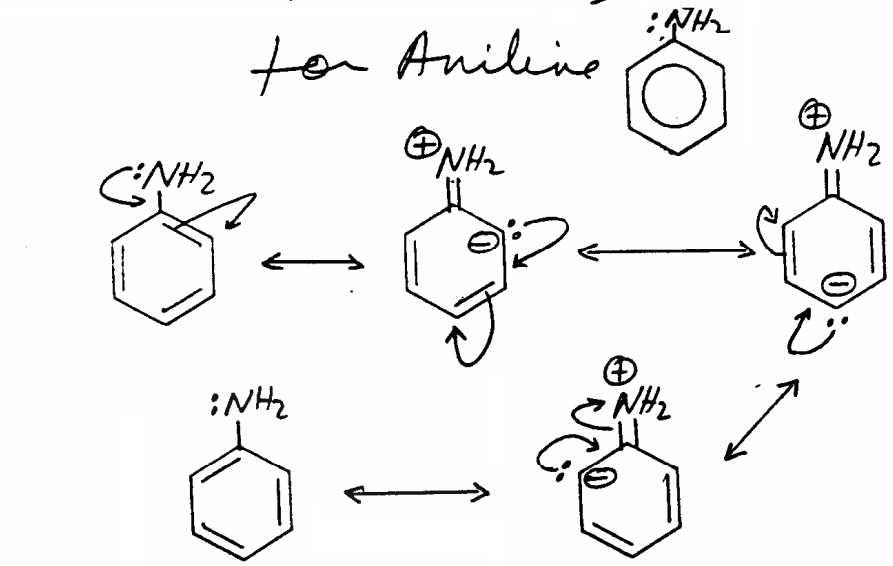


Figure 12.112

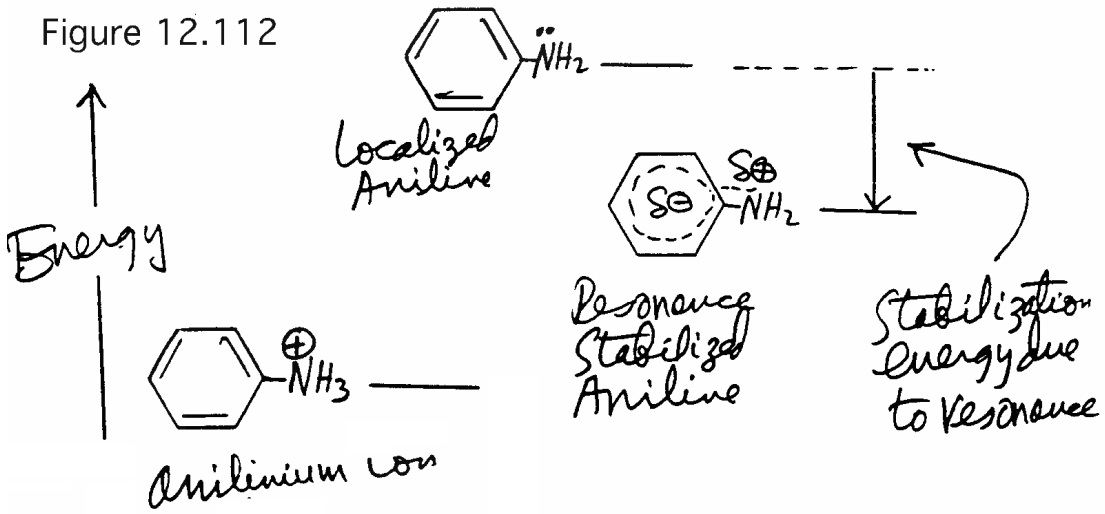


Figure 12.113

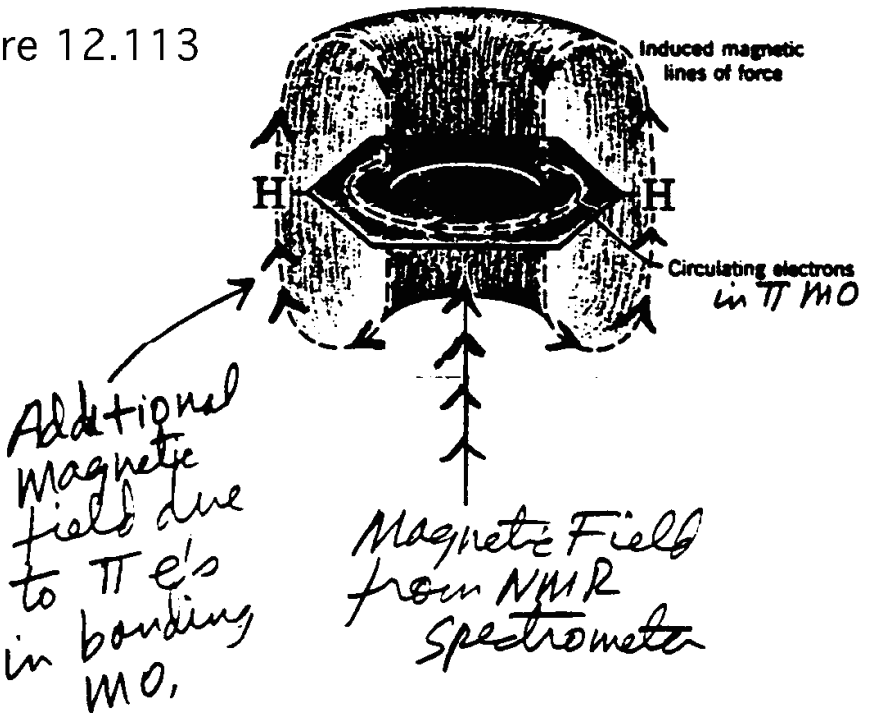


Figure 4.17. From "Spectrometric Identification of Organic Compounds." by Silverstein, Bassler, and Morrill, 5th Ed., Wiley, 1991

Figure 12.114

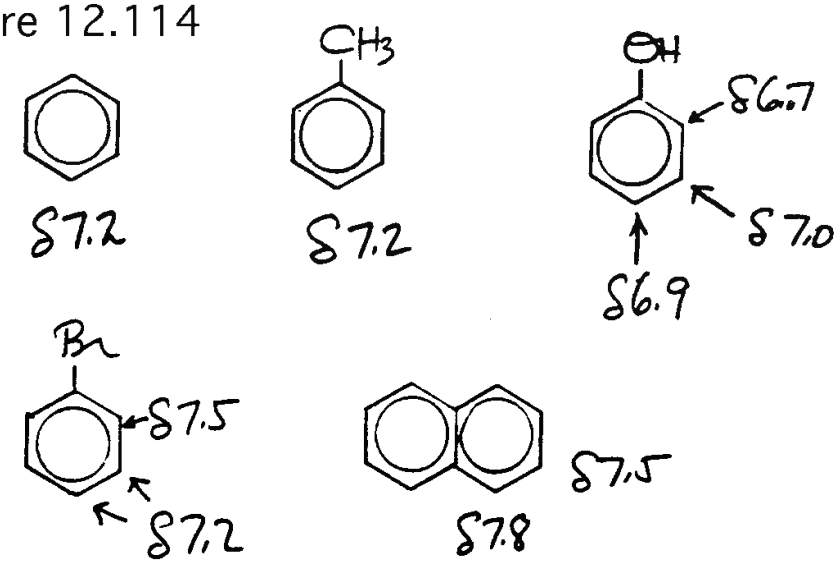
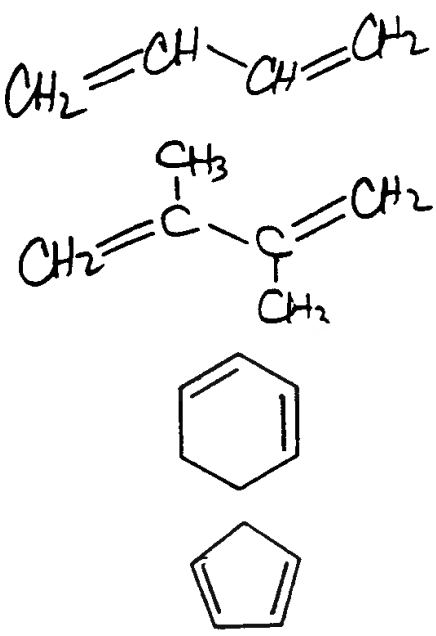


Figure 12.115



	λ_{max} (nm)	ϵ
	217	21,000
	226	21,400
	256	8,000
	239	3,400

Figure 12.116

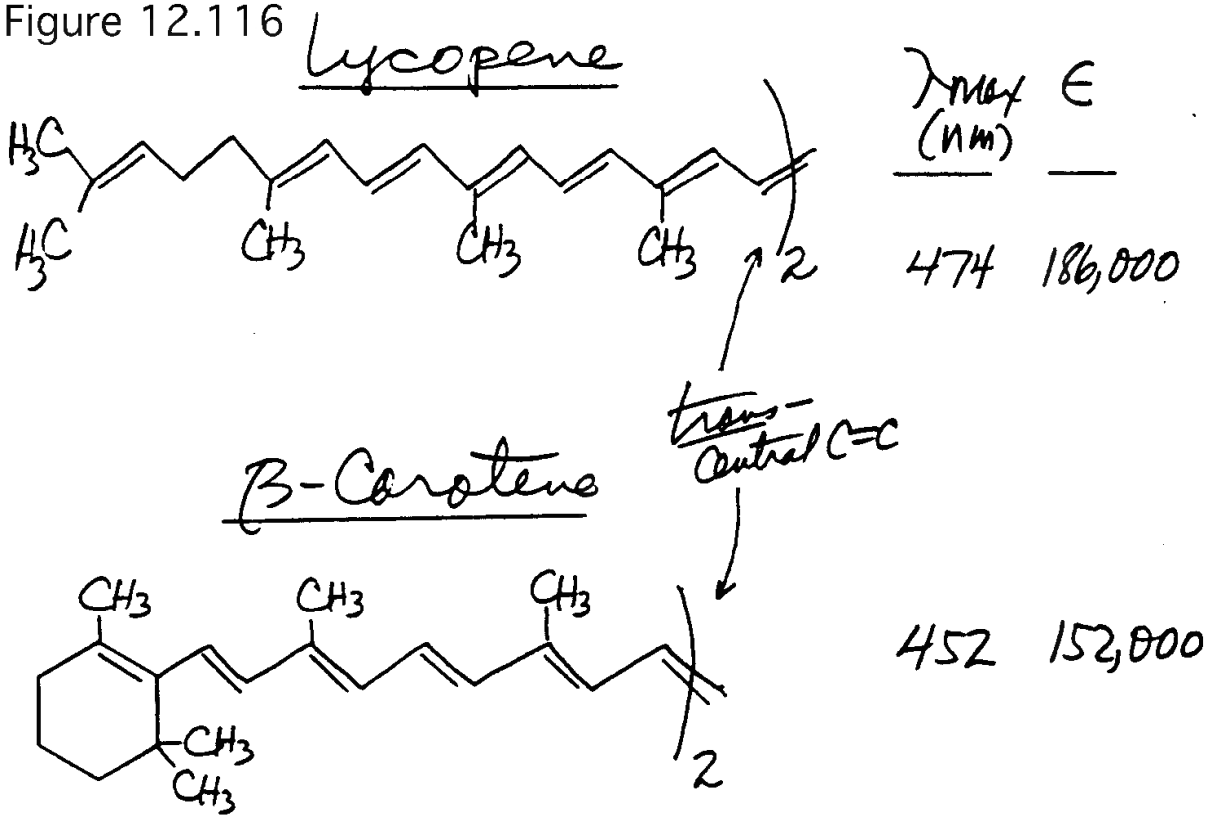


Figure 12.117 Origin of UV Spectrum of 1,3-Butadiene

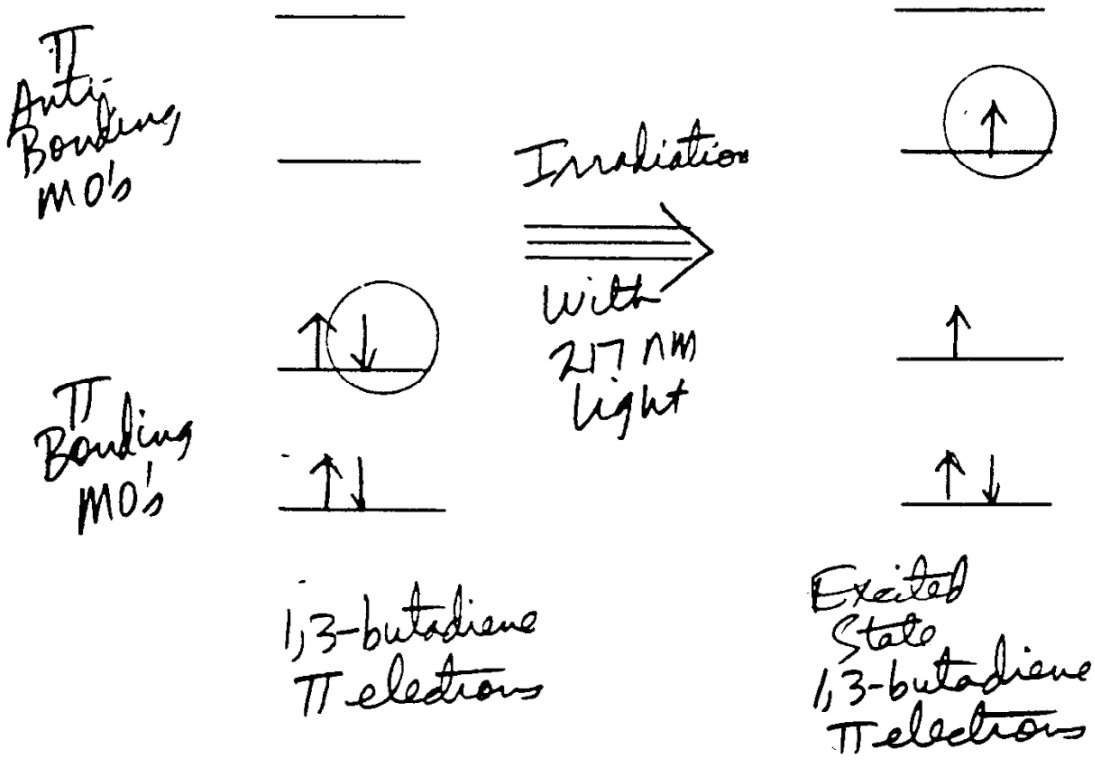


Figure 12.118

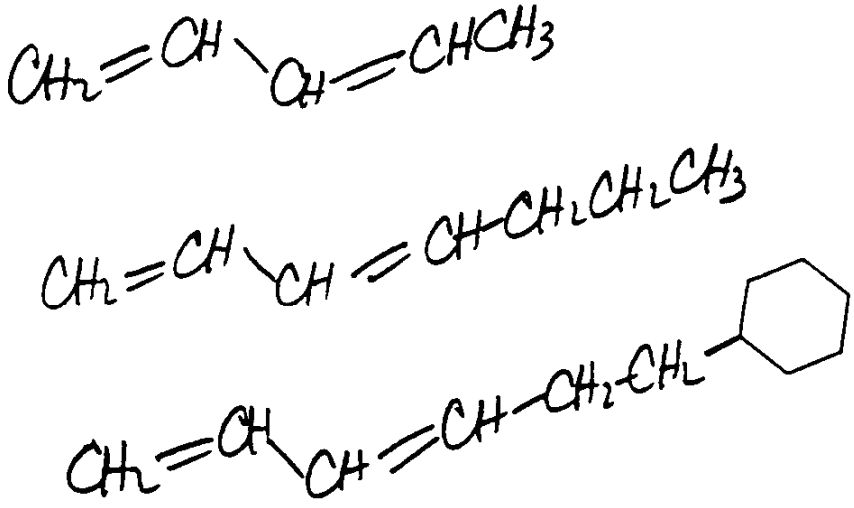
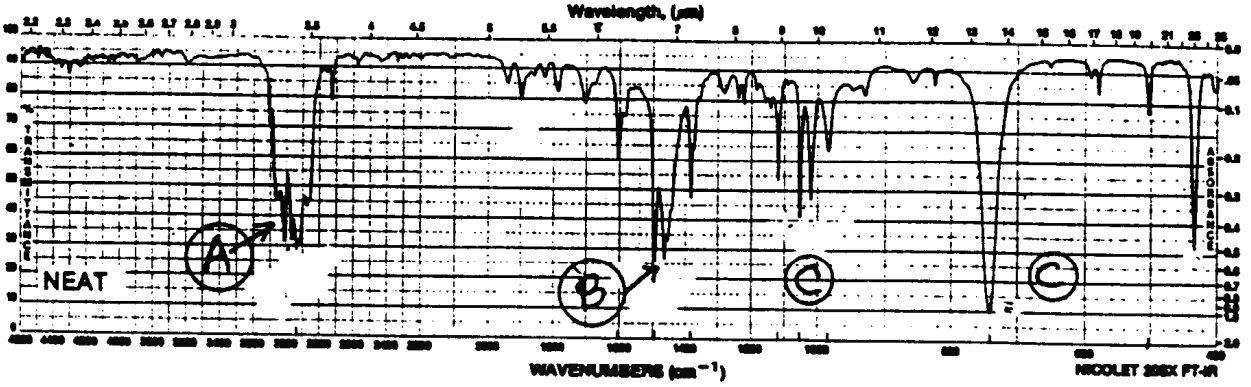
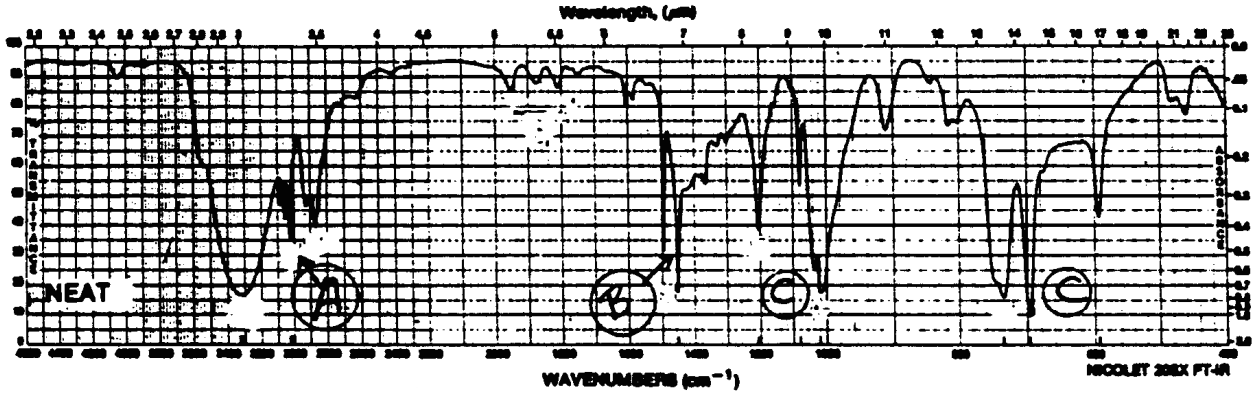


Figure 12.119

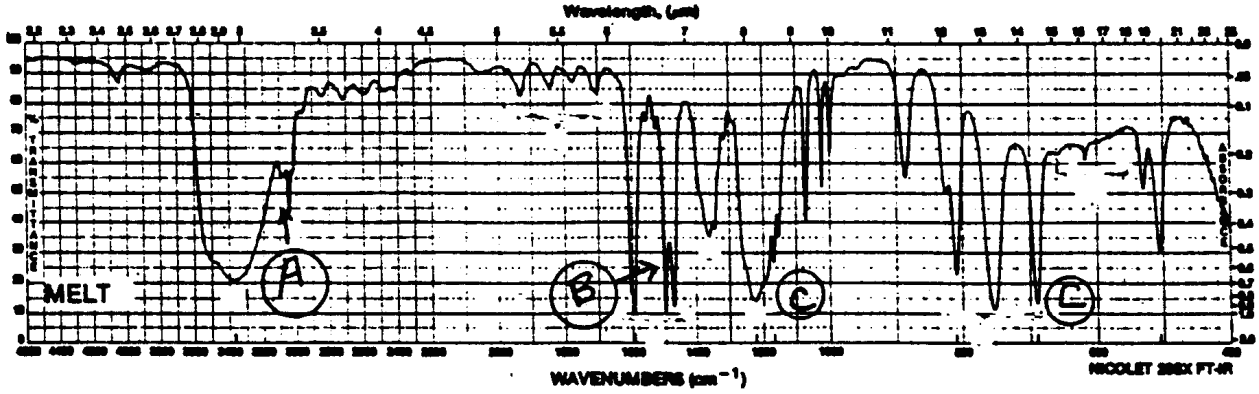
o-Xylene, 97%



Benzyl alcohol, 99 + %



Phenol, 99 + %



These are Figs 3.13, 3.14 and 3.16 in Silverstein + Bassler