## Electrophilic Addition to C=C and C≡C

This includes both polar and radical reactions, but do the polar ones first. It excludes nucleophilic addition to C=C-C=O (Michael additions) for the moment

**Reading**: Sykes will cover all of the topics listed below, some Primers are also suggested. Read and learn the general chemistry (preparation and properties, bonding, shape etc,) of alkenes and alkynes. See **Meakins, OUP Primer no. 35, Chapters 5 and 6**. [There will be much more on alkenes than on alkynes – why?]

Read and learn some simple aromatic chemistry; mechanisms of halogenation. nitration, sulfonation, Friedel- Crafts reactions; orientation of electrophilic substitution on PhX. See **Sainsbury, Aromatic Chemistry, OUP Primer no. 4**.

**Notes and Questions:**
a) Summary on not more than 6 sides. In your summary, consider the mechanisms (with evidence to support them, especially for the trans addition of bromine to C=C), stereochemistry, effects of substituents on the rate of reaction and on mechanism, etc; any selectivity shown, with reasons; uses of these reactions in synthesis.

The following reagents **must** be included:

| | |
|---|---|
| $Halogen_2$ | $KMnO_4$ |
| H-Hal | $OsO_4$ |
| $H_2$/catalyst (various) | $O_3$ |

also hydration; hydroxylation, the Wittig reaction; epoxidation; hydroboration (followed by oxidation with alkaline $H_2O_2$); radical addition of $Hal_2$, H-Hal.

This should outline the possible mechanisms and the evidence on which they are based, in particular the evidence for inversion during $S_N2$ reactions. Consider the effects of changes in solvent, nucleophile, leaving group as well as in substrate structure – include a range of nearby functional groups, such as α-haloketones and α-haloethers. Discuss stereochemical effects and rate differences etc. Include $S_Ni$ and neighbouring group effects with examples of both.

b) Check that you can do the easy problems on this subject in Hornby and Peach 'Foundations of Organic Chemistry: worked examples', OUP Primer no. 87, chapter 4, Q 1-7.

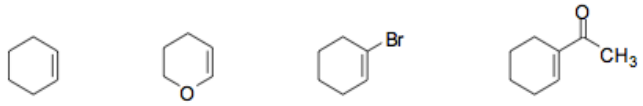
c) Learn the general chemistry of alcohols, alkyl halides, vinyl halides etc. See Meakins, Functional Groups: characteristics and interconversions.

d) Do the problems attached. These are particularly important. For additional problems with answers and explanations, see Chapter 2 of Stereochemistry at a glance.

1. Draw the mechanisms and the structures of the products of each of the following reactions?
a) 2-methyl pent-1-ene + HBr, dark

b) 1-methylcyclohex-1-ene + $H_2O/H+$
c) Pent-1-ene + $IN_3$
d) methylenecyclopentane + $B_2H_6$ followed by $H_2O_2/NaOH$
e) 2,3,3-trimethylcyclohexene + $Pd/D_2$ [no mechanism needed for (e)]

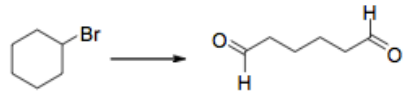
2. Rank the following according to their rates of reaction with HBr (polar). *Justify your order.*




3. Suggest reagents for the following, and draw mechanisms for the reactions. [More than one stage may be needed.]

a)



b)
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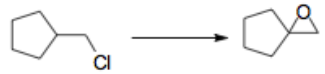


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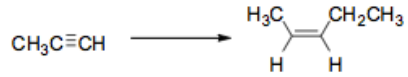
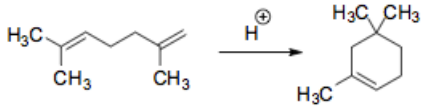



4. Give mechanisms for the following:

a)
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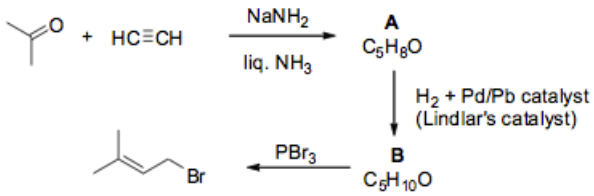


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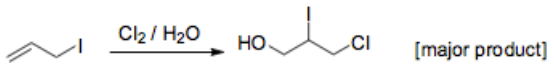
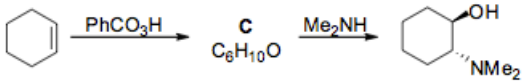
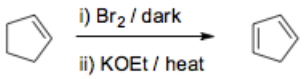
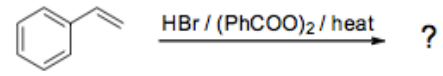


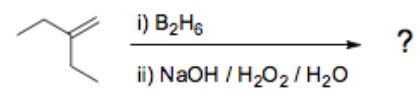

d)



e)


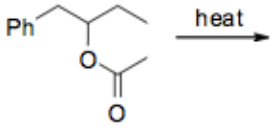

f)



g)



h)


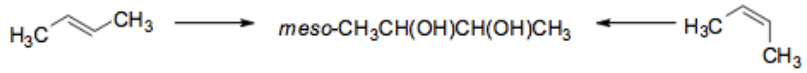
5. By drawing the mechanisms explain what products you would expect from the following reactions:

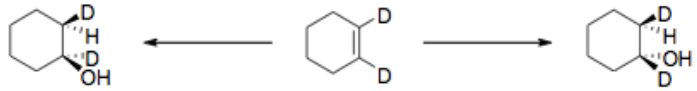
a) $CH_3CH_2CH_2C(CH_3)_2Br$ $\xrightarrow{KOH\ /\ EtOH}$

g) 


h) $Ph_3\overset{\oplus}{P}CH_3\overset{\ominus}{Br}$ $\xrightarrow[ii)\ Cyclohexanone]{i)\ NaH,\ Me_2SO}$

6. a) How would you carry out the following?

i) 


ii) 


b) Explain clearly the meaning of the terms stereoselective and regioselective using reactions of 1- methylcyclopentene as examples.

7. Answer **both** parts **A** and **B** of this question.

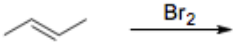
A. For the alkenes $CH_2$=CHX where X=H, Me, Ph, $NO_2$, OMe, COMe, Br and CN predict

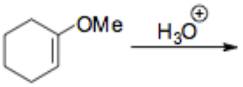
i) the orientation of addition of HBr and hence the structure of the major product that is formed;

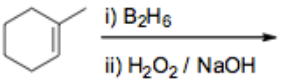
ii) the relative rate of addition of HBr to the first FIVE alkenes (i.e. X = H, Me, Ph, $NO_2$, OMe).

**[10]**

B. Indicate the major product for each of the following reactions and give the mechanism of each reaction

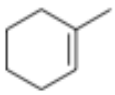
i) 


ii) 


iii) 


**[3 x 5]**

8. Draw the products obtained from reaction of **A** with each of the following reagents. Include any relevant stereochemistry in your diagrams.

**A** 

a) $Br_2$ in the dark.
b) HBr in the presence or absence of $(PhCO_2)_2$ and heat.
c) HOBr than aqueous hydroxide.
d) $OsO_4$ then water.
e) ICl in the dark.
f) aqueous KOH and $CHCl_3$
g) $B_2H_6$ then aqueous hydroxide/$H_2O$

*Now check your work:*
http://paton.chem.ox.ac.uk/teaching/files/Y1_Additions_Alkenes_Alkynes.pdf