

LECTURE 4

(d) Polyhalogenation

The products of the reactions of alkanes with halogens very often still contain C – H bonds and, therefore, may react further to give polyhalogenated products. The C – H bonds in the alkyl halides progressively get weaker as the number of halogens increases:

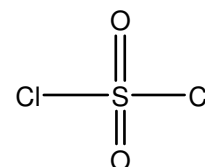
C – H Bond:	CH ₄	CH ₃ Cl	CH ₂ Cl ₂	CHCl ₃
Bond strength (kJ mol ⁻¹):	439	422	414	401

In order to avoid polyhalogenation the reactions are usually carried out under conditions of excess alkane. In those circumstances the halogen is much less likely to react with the more reactive mono-halogenated product because it will be formed in tiny amount compared to the amount of starting alkane. Alternatively, if we want the fully halogenated product then conditions of excess halogen may be used. For methane the first case leads to a mixture of a little methyl halide in an excess of methane whereas the second case leads to a little carbon tetrachloride (tetrachloromethane) in an excess of chlorine. In both cases the desired halogenated product can be isolated easily from the mixture because of the large differences in boiling points.

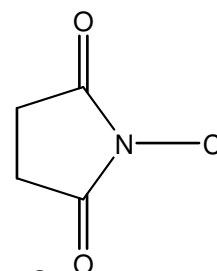
(e) Alternative Halogenating Agents

Where facilities are not so readily available for handling toxic, corrosive and gaseous chlorine or corrosive, liquid bromine there is a need for alternative halogenating agents. The three most important are:

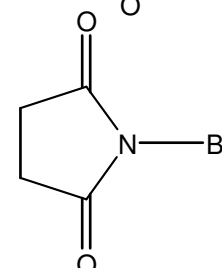
Sulphuryl chloride, liquid b.p. 69 °C



N-Chlorosuccinimide, solid m.p. 150 °C

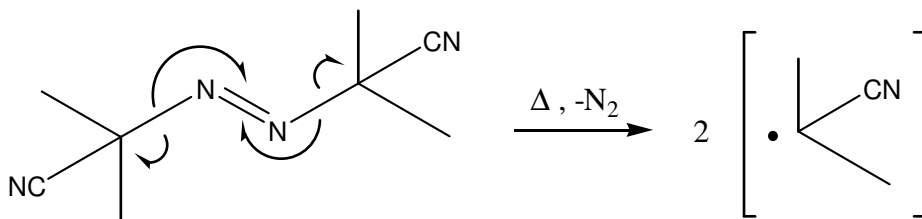


N-Bromosuccinimide, solid m.p. 173 °C

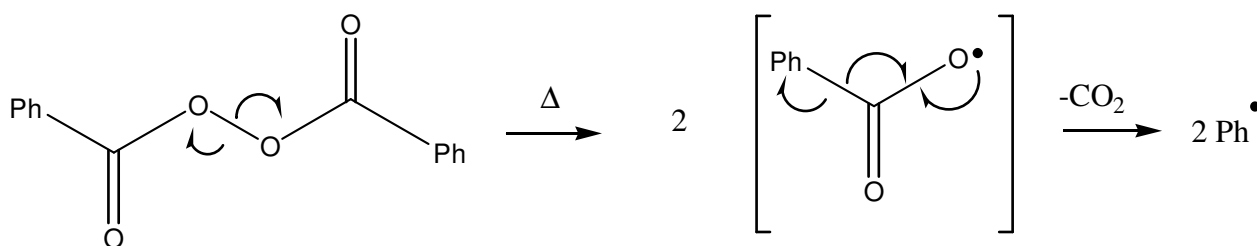


All three compounds have stronger X-Hal bonds than the parent halogens and therefore their use in free radical halogenation requires the presence of radical

initiator molecules to get the process started. The two most common of these radical initiators are:

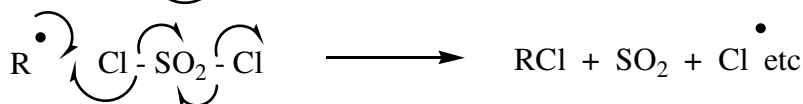
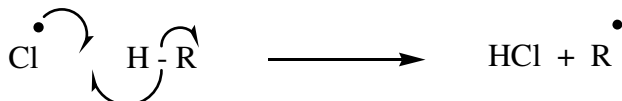
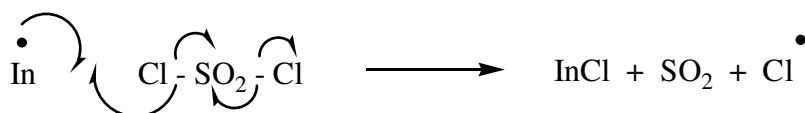
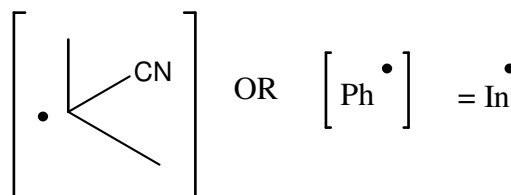


Azobisisobutyronitrile (AIBN)

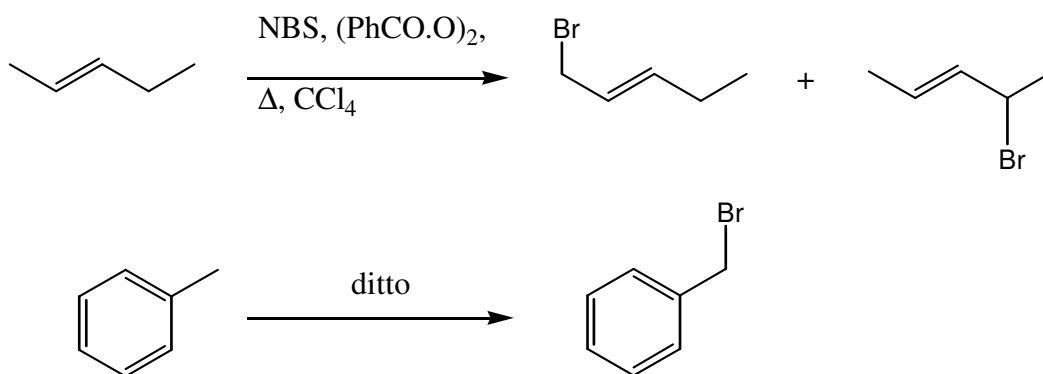


Dibenzoyl Peroxide

With these initiators the mechanism changes slightly:



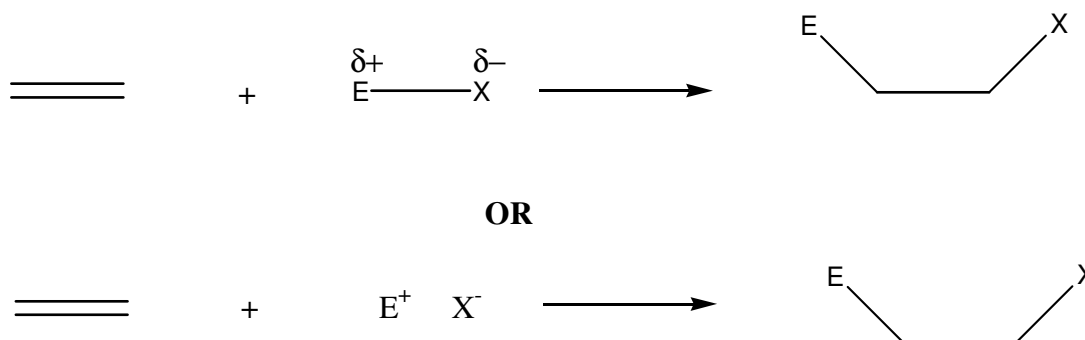
As we would expect from reagents which are somewhat less reactive than the halogens themselves, sulphuryl chloride, NCS and NBS are generally more selective. Indeed, NBS in particular is so selective that it only reacts with hydrogen atoms which are on the allylic carbon atoms (those next to double bonds) and benzylic carbon atoms (those next to benzene rings):



ELECTROPHILIC ADDITION TO ALKENES AND ALKYNES

A consequence of the existence of the π -bond in terms of reactivity derives from the fact that the electrons in this bond are not held so close to the two carbon nuclei as those in the σ -bond. Hence they are more readily available to form bonds with electron seeking species i.e. electrophiles. Thus, alkenes and alkynes can act as nucleophiles.

We deal with the electrophilic addition to alkenes first, the general equation for which is:



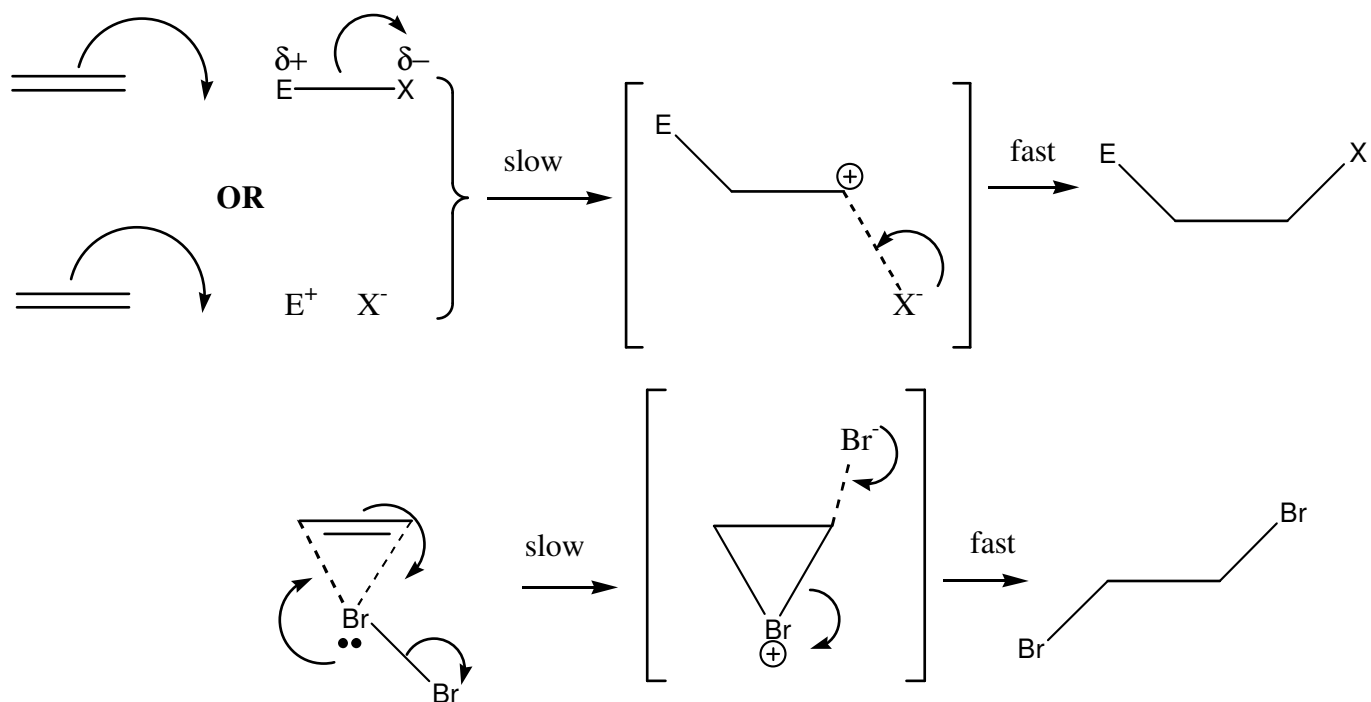
where E represents the electrophilic part of the reagent.

Scope

If we look at the Table we see that EX can be a wide variety of electrophilic species. In the main the reactions are NOT stereospecific, a term to be defined shortly, but those involving bromine and iodine reagents are. This suggests that the mechanism of addition of bromine and iodine reagents is different to that for the other species.

Mechanisms

The equations for the two types of mechanism are:



In both cases the slow step is the first one because it involves the breaking of bonds. The second step is fast because it is the collapse of ions i.e. it is favoured electrostatically. The first step thus controls the overall rate of reaction and hence is called the rate determining step (rds) i.e. the overall reaction cannot proceed faster than this step.

Since in both mechanisms the reagent and the alkene are both involved in the rds, they are said to be bimolecular; the mechanisms both describe electrophilic additions and hence the designation of both mechanisms is Ad_E2 (addition, electrophilic, bimolecular).

Stereospecific ANTI-Bromination

The term stereospecific is defined as follows:

IF one stereoisomer (i.e. geometrical isomer or optical isomer) of the starting material gives one stereoisomer of the product and the other stereoisomer of the starting material gives the other stereoisomer of the product in a reaction, that reaction is said to be stereospecific.

BUT IF both stereoisomers of the starting material give one stereoisomer of the product

OR one stereoisomer of the starting material gives both stereoisomers of the product in a reaction, then that reaction is **NOT** stereospecific.