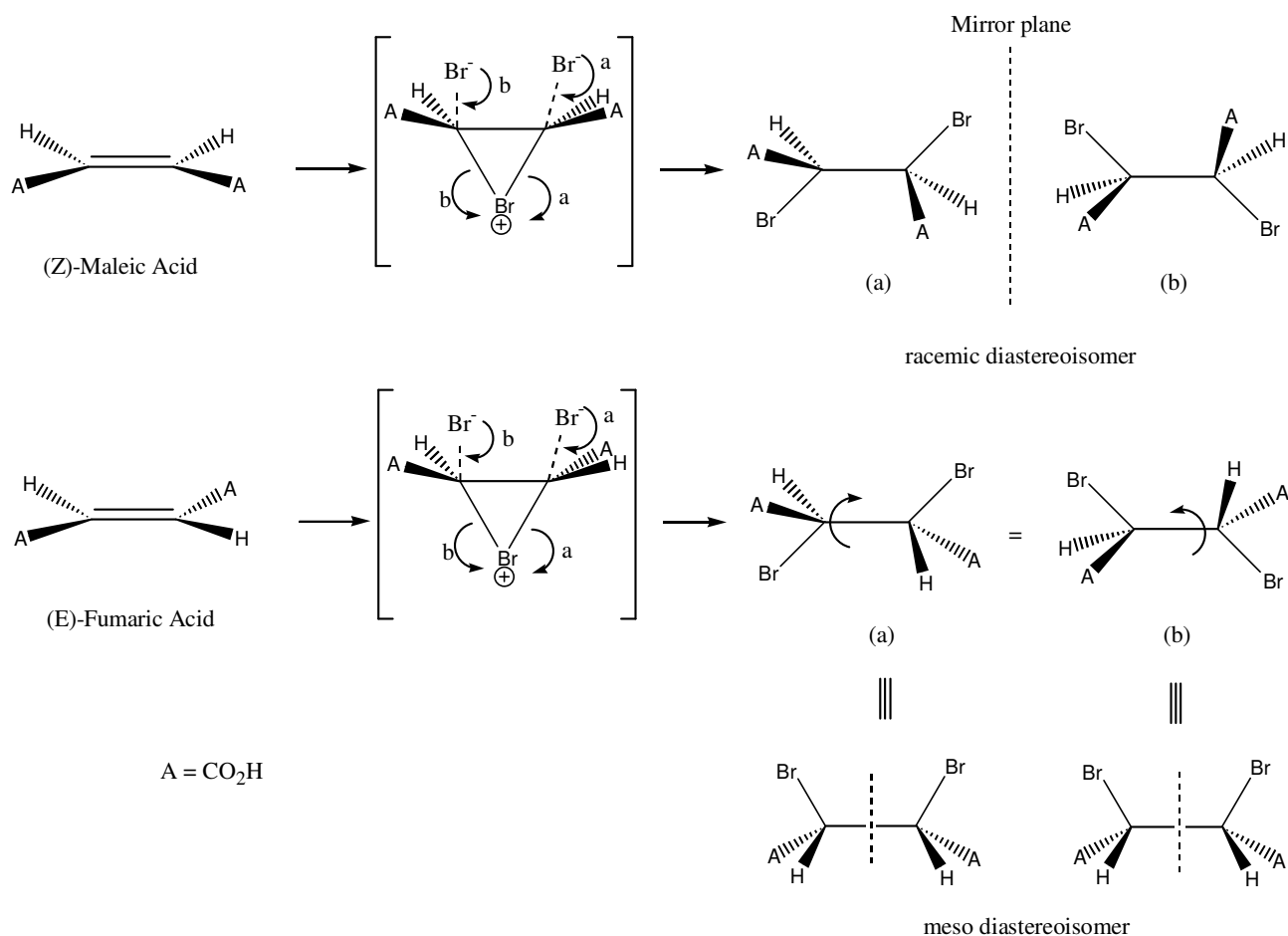


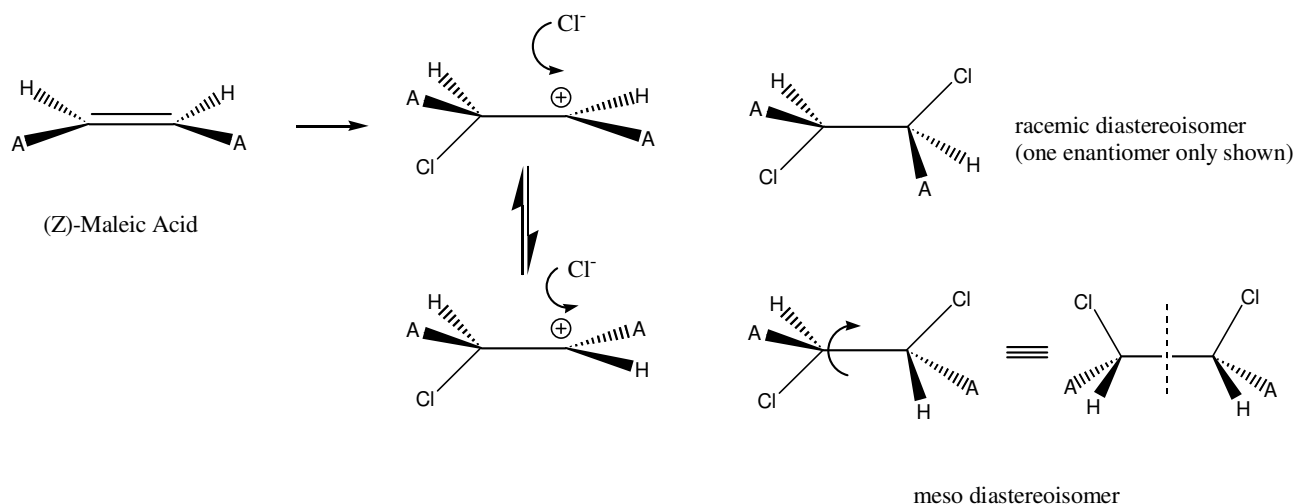
LECTURE 5

The stereoisomers of alkenes are simply the geometrical isomers. So let us now see how bromination is stereospecific:



The reaction of the Z-geometrical isomer of butane-1,4-dioic acid (maleic acid) gives equal amounts of the two enantiomers (by paths (a) and (b)) of only one diastereoisomer, the so-called racemic diastereoisomer, whereas the E-geometrical isomer (fumaric acid) only gives the meso diastereoisomer which has a plane of symmetry within it and is, therefore, optically inactive; there is no crossover between the two stereochemical series. Thus, the reaction is stereospecific. Note that the first-formed conformation of the product has the two bromine atoms ANTI to one another, hence the designation ANTI-addition.

Now let us look at non-stereospecific chlorination:



In this case the non-cyclic cation can rotate about the central C-C bond before it reacts with the chloride anion and this allows both diastereoisomers of the product to form from either geometrical isomer of the alkene (only one geometrical isomer is shown but the scheme is equally valid for the other). Thus, the chlorination is not stereospecific.

(c) Change of nucleophile in the second step

Because we proceed through an intermediate, either the bromonium (iodonium) ion or the free carbocation, we can replace the anion in the second step with another nucleophile and generate a wider range of products. The fact that we can do this, incidentally, is good evidence that these mechanisms are correct.

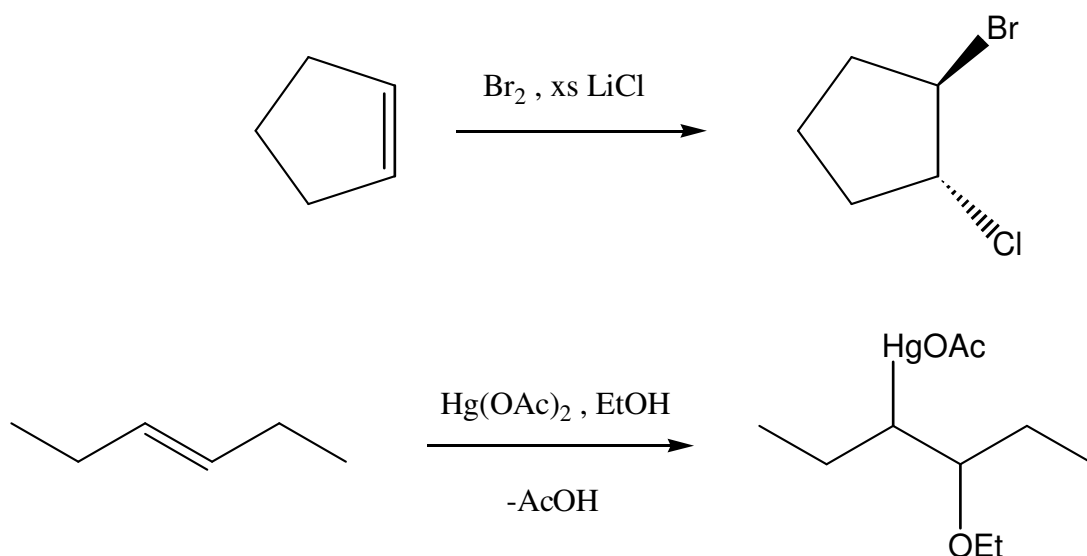


Fig. 1

This is synthetically very useful because the direct addition of these elements would involve reagents which are either difficult to obtain (BrCl) or possibly unreactive (EtOHgOAc).

(d) Regiochemistry of Addition

If we have an unsymmetrical alkene and an unsymmetrical reagent then we can, in principle, produce two compounds:

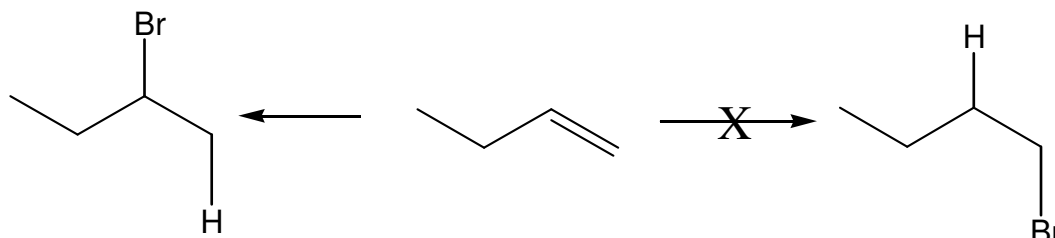


Fig.2

In fact only that compound predominates in which the nucleophilic part of the electrophile ends up on the most substituted carbon atom as above. This is known as Markovnikov's rule. The reason is that the reaction proceeds through a carbocation and the most stable carbocation is the most substituted one:

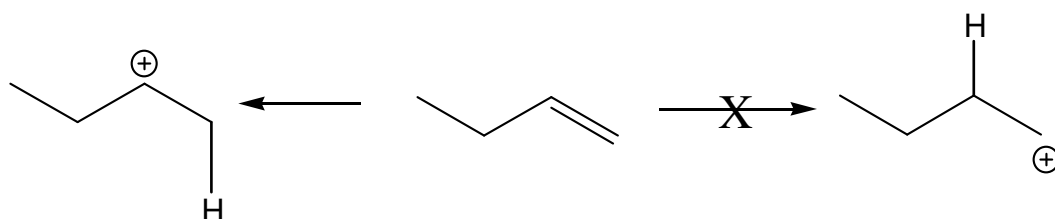
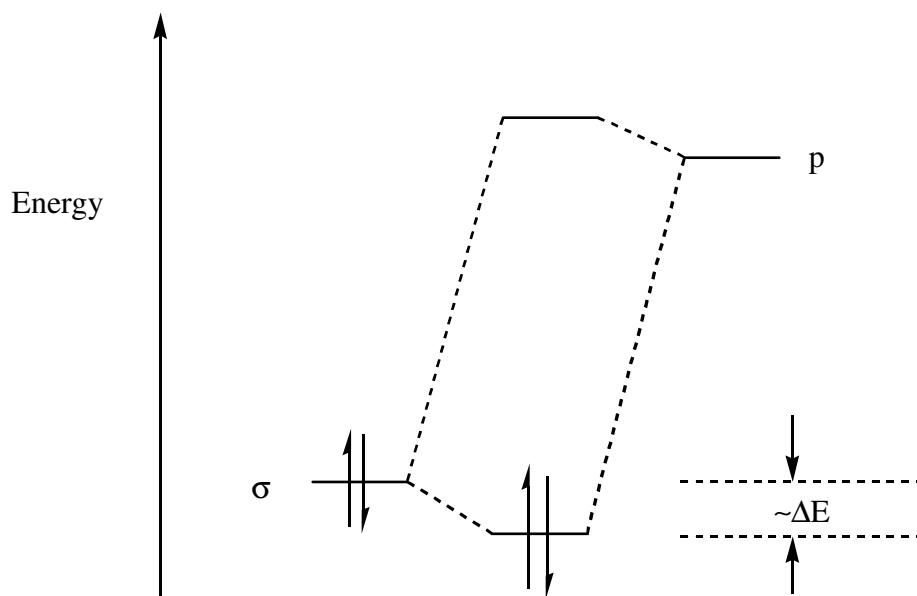


Fig.3

The order of stability of carbocations is the same as that for radicals i.e. $R_3C^+ > R_2CH^+ > RCH_2^+ > CH_3^+$ for the very same reason, hyperconjugation, except that only two electrons are involved instead of three (stabilisation = $2\Delta E$):



We have to be careful with the usual explanation of this stability by the inductive effects of alkyl groups since inductive effects tend to be important when the electronegativity difference between the two atoms is large; this is not the case with C-R when both atoms are carbon. However, a carbocation is electron-withdrawing by virtue of its charge and it will tend to attract the electrons in the σ -bond thereby giving the appearance of an inductively donating effect from the alkyl group.

Despite the fact that bromonium and iodonium ions are not free carbocations, Markovnikov's rule still holds true for these intermediates:

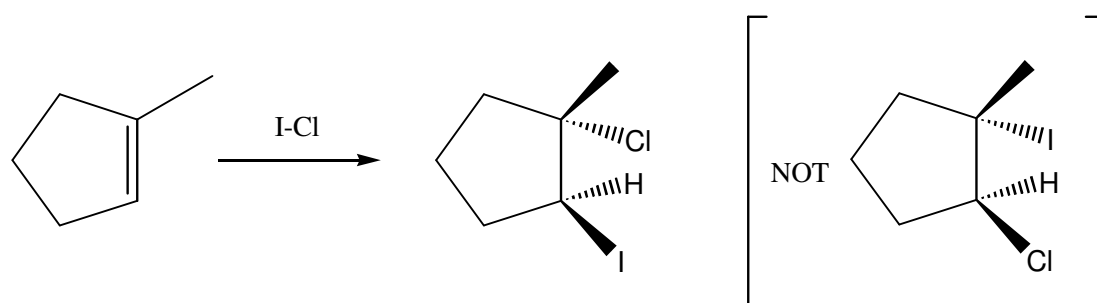


Fig. 4

This is because in the iodonium (bromonium) ion some of the charge is inductively spread onto the adjacent carbon atoms and this small charge is stabilised by hyperconjugation in the same way as a full carbocation:

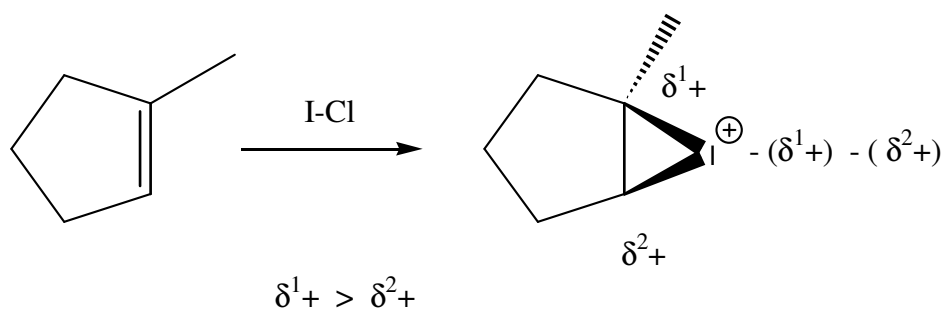


Fig.5

(e) Rearrangement of carbocations

A consequence of the stability order of carbocations noted above (tert > sec > prim > methyl) is that sometimes in addition the initially formed carbocation may rearrange to a more stable one before the nucleophilic part of the electrophile attacks:

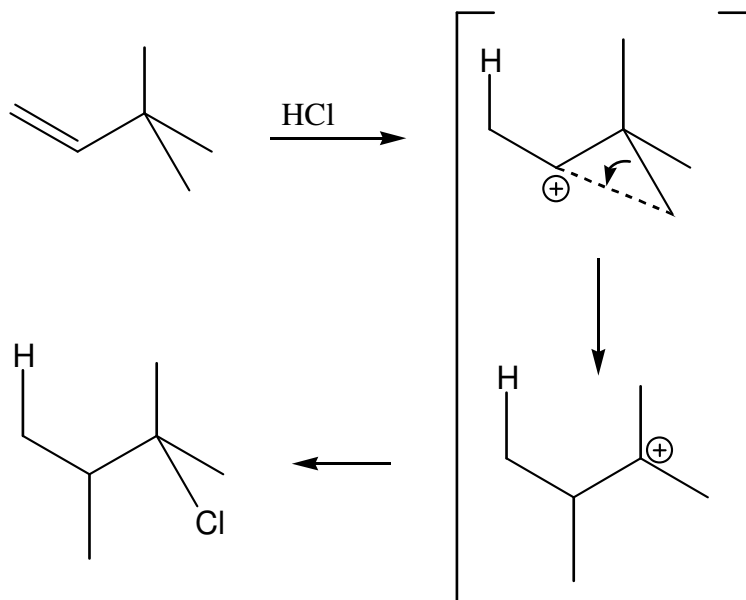


Fig. 6

Such rearrangements are called Wagner-Meerwein shifts.