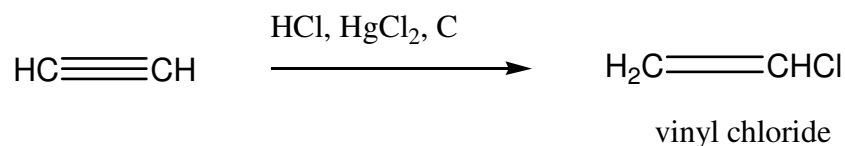


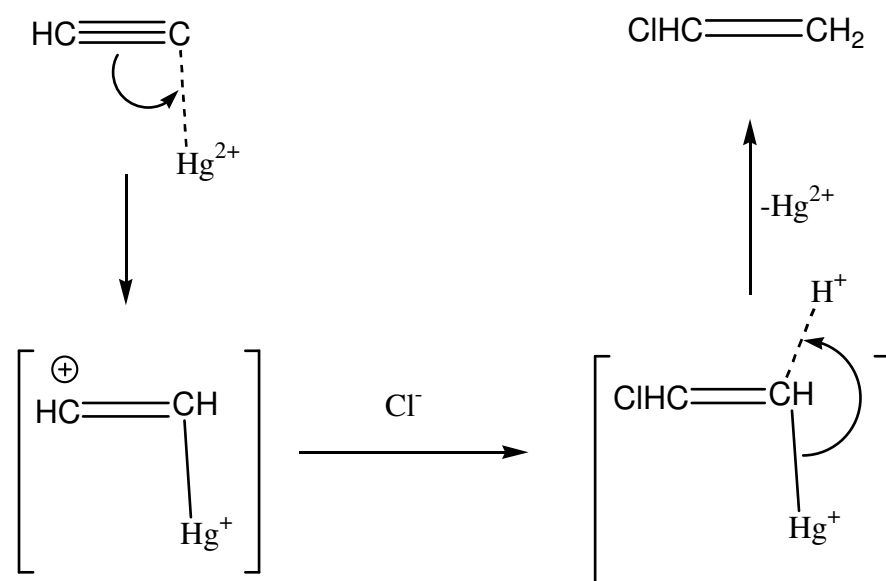
LECTURE 6

Electrophilic Addition to Alkynes

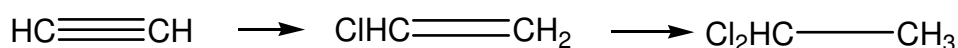
Alkynes are very similar to alkenes in their behaviour towards electrophiles except that they are slightly less reactive despite the lower steric hindrance and the greater number of π -electrons available. Thus addition of HCl or HBr is slow and usually requires catalysis by mercury salts and charcoal:



The mechanism involves the initial addition of mercuric ion which has a much higher affinity for π -bonds than H^+ . Subsequent trapping of the vinyl cation introduces the chloride and then the carbon-mercury bond is rapidly cleaved by the proton by an $\text{S}_{\text{E}}2$ mechanism:



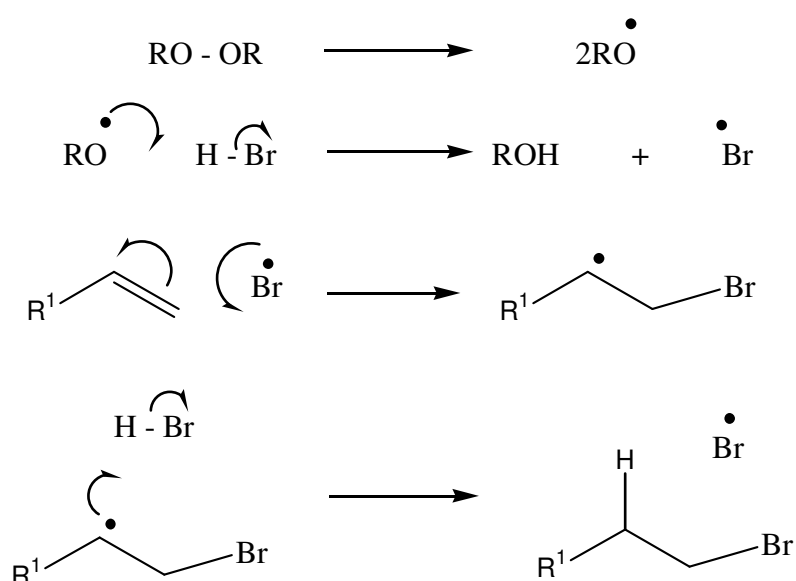
Unlike the addition to alkenes, the product still contains a double bond and hence a second addition occurs (generally rapidly since alkenes are more reactive than alkynes):



RADICAL ADDITION TO ALKENES AND ALKYNES

The most interesting examples of this reaction occur in the radical-initiated addition of HBr to alkenes, in the polymerisation of alkenes and in the related electron addition to alkynes.

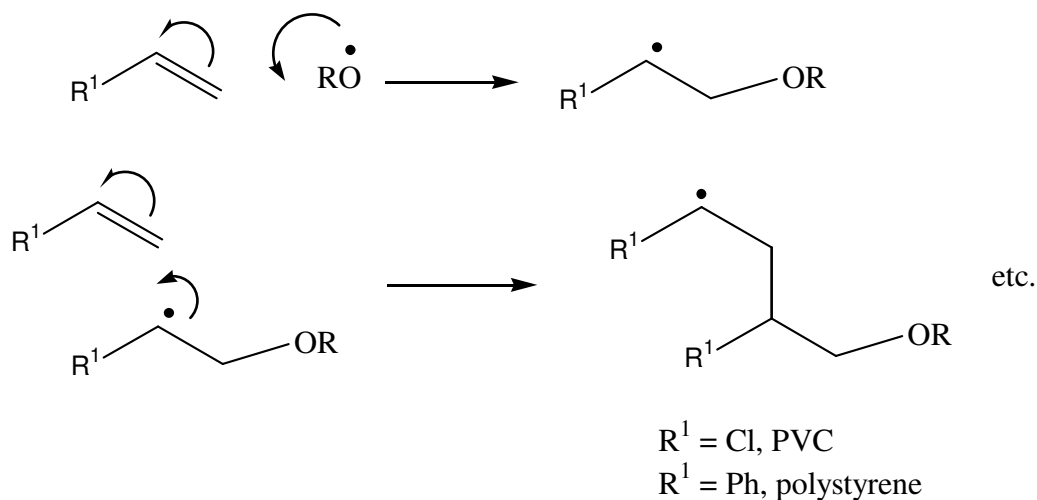
- (a) Addition of HBr to Alkenes in the Presence of Radical Initiators
Radicals derived from the decomposition of radical initiators, such as peroxides, will abstract hydrogen from HBr to give Br[•] which will add to the alkene to give the most stable radical; a chain is then set up:



The overall result is an anti-Markovnikov addition of HBr i.e. to give the opposite regioisomer from that formed in electrophilic addition of HBr. However, the reason for the regiochemistry is the same as that in the electrophilic addition, namely, that the most stable intermediate (radical in this case) is formed and the reversal of regiochemistry is purely because Br adds first instead of H.

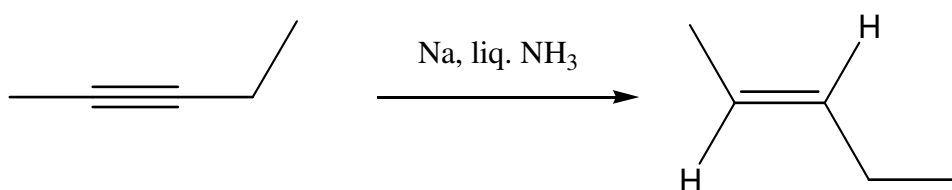
- (b) Polymerisation

If a radical initiator is decomposed in the presence of an alkene and in the absence of a hydrogen atom donor, polymerisation may result as follows:

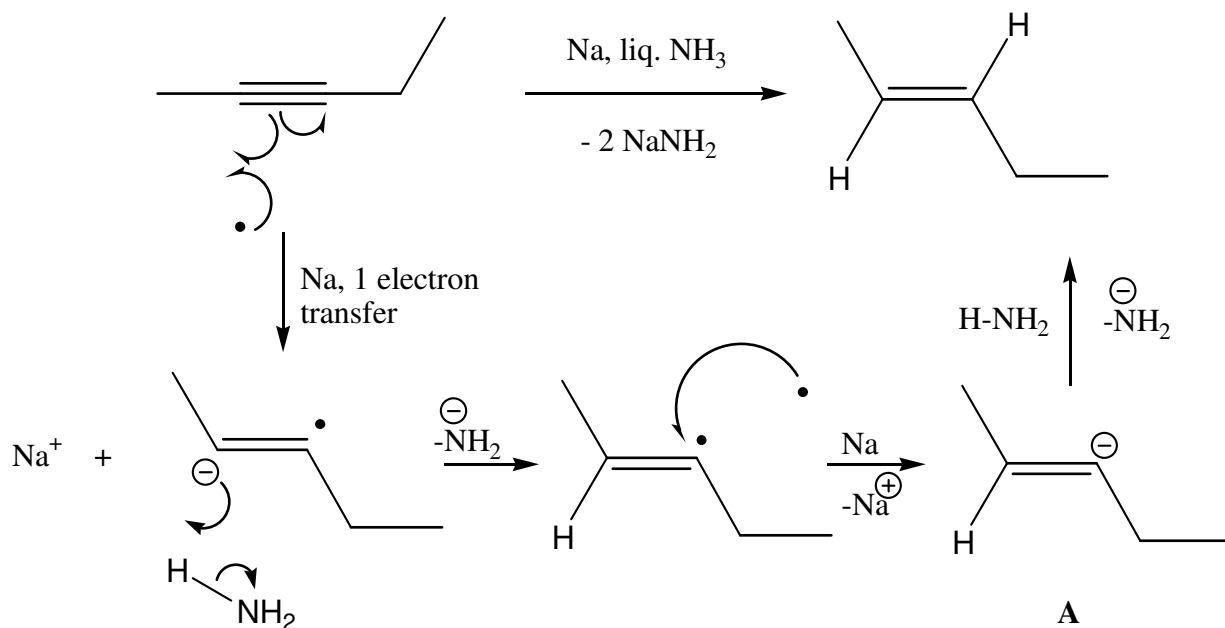


(c) Reduction of Alkynes to trans-Alkenes

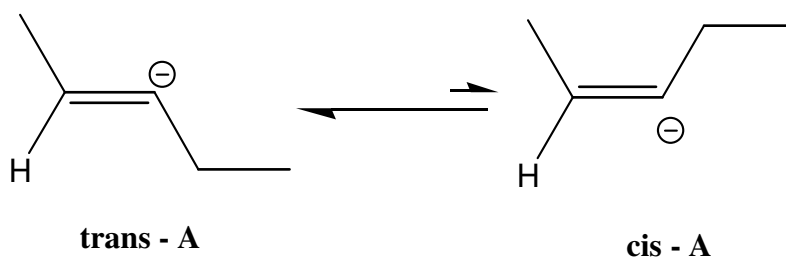
In a reaction which involves radical intermediates but which starts with the addition of electrons, rather than radicals, to the triple bond, alkynes may be reduced by sodium in liquid ammonia in a stereospecific anti-fashion to give trans-alkenes:



The reason for this stereospecificity follows, as usual, from the mechanism:



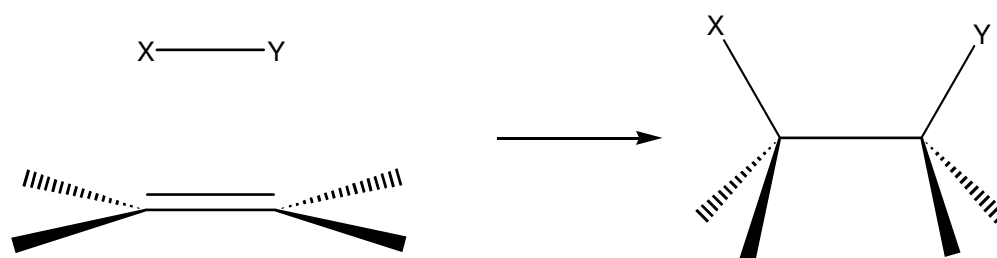
The carbanion **A** can adopt either the cis or trans configuration but prefers the latter because in that configuration there is less steric hindrance between the two alkyl groups on the double bond:



Hence on protonation with ammonia, the carbanion gives the trans-alkene. Note that two molecules of sodamide (NaNH_2), a strong base, are also formed in this reaction. It is because of the formation of this substance that this reduction does not work for terminal alkynes (those with the triple bond at the end of the chain), because of deprotonation (see later).

CONCERTED SYN ADDITION TO ALKENES AND ALKYNES

There are a large number of other reagents which add to alkenes and alkynes in a concerted manner, that is the two sides of the reagent add to the ends of the double or triple bond at the same time rather than in two steps (as in electrophilic or radical addition). The mechanisms of these reactions are varied. However, they all produce initially the syn-conformation of the product and are said to proceed by SYN-addition:



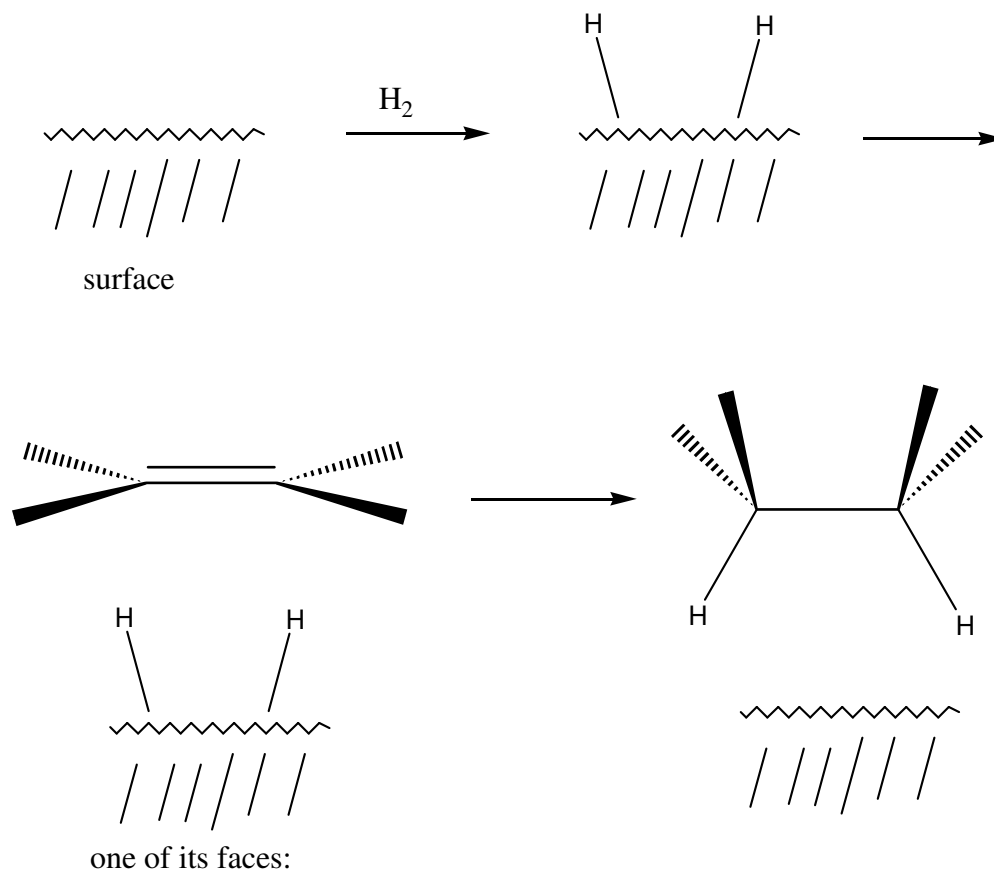
i.e. the opposite stereochemistry to that of the addition of bromine.

(a) Catalytic Hydrogenation ($X = Y = H$)

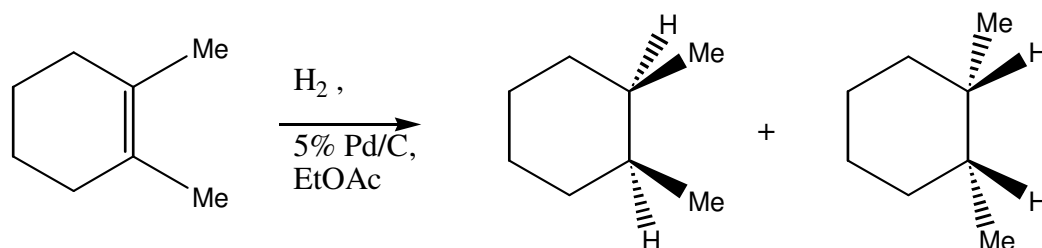
Hydrogen on its own will not add to alkenes; it requires a catalyst, usually PtO_2 (Adams catalyst), 5% Pd/C, 10% Rh/C or Raney Nickel. These catalysts are not soluble and hence the reaction is heterogeneous and occurs on the surface of the solid. The first three are commercially available but Raney nickel must be freshly prepared from a commercial nickel/aluminium alloy. This alloy is treated with concentrated sodium hydroxide solution which dissolves the

aluminium and leaves a finely divided suspension of nickel. This is highly pyrophoric when dry and must be kept wet with solvent.

In all cases it is believed that the alkene and the hydrogen become attached to the surface of the solid. The hydrogen is thought to be cleaved by the metal into two metal-hydrogen bonds which then react with the alkene. This would explain the syn-stereochemistry since the alkene can only approach the two M – H bonds simultaneously along

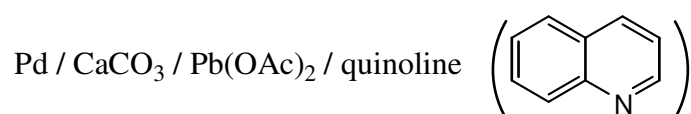


The reaction is very successful and has been used on innumerable occasions e.g.



(b) Reactions: Catalytic Hydrogenation of Alkynes to Alkanes and Z-Alkenes

Given the propensity to double add reagents to alkynes it would be expected that catalytic hydrogenation would reduce triple bonds completely to the saturated alkanes without stopping at the alkene stage. This is indeed true but in the presence of deactivated (poisoned) catalysts the reaction can be stopped half-way. The classic catalyst for this purpose is Lindlar's catalyst:



Palladium is the catalytic centre, the calcium carbonate is a support material and the lead diacetate and quinoline are the poisons. A related catalyst is Pd / BaSO₄ / quinoline where the barium sulphate acts as both support and second poison. With either catalyst stereospecific syn-addition takes place to give the Z-alkene (for the same reason that catalytic hydrogenation of alkenes goes by syn-addition, see earlier):

