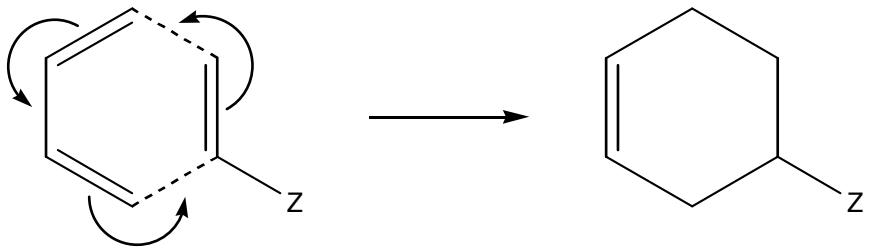
LECTURE 8

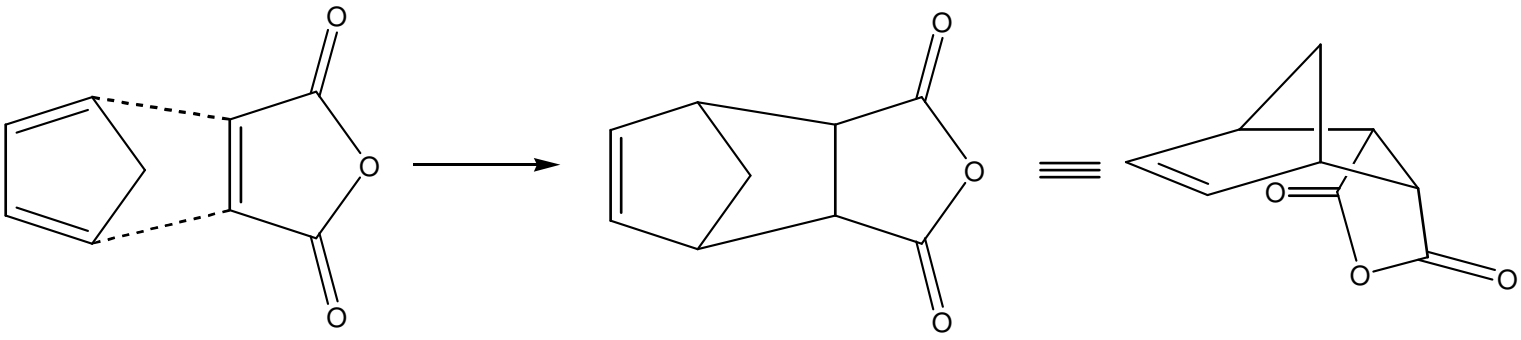
(f) 1,3-Dienes: The Diels-Alder Reaction

This is the archetypal pericyclic reaction and has become so useful for organic synthesis that Diels and Alder were awarded the Nobel prize in 1950 for its discovery. The most common variant involves the reaction of a 1,3-diene with an alkene bearing one or more electron-withdrawing groups and occurs simply on heating:



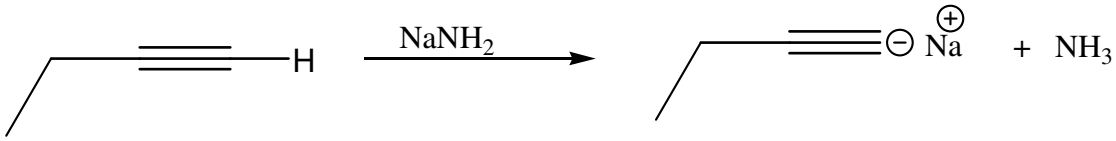
Z = CHO, COR, CO_2R, CN, NO_2 etc

For example:

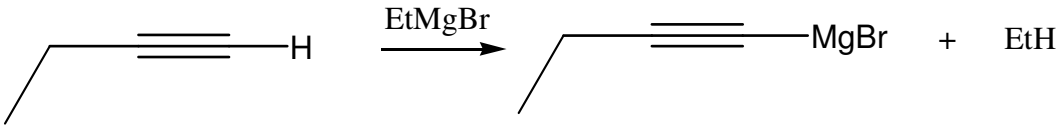


DEPROTONATION OF HYDROCARBONS: CARBANIONS

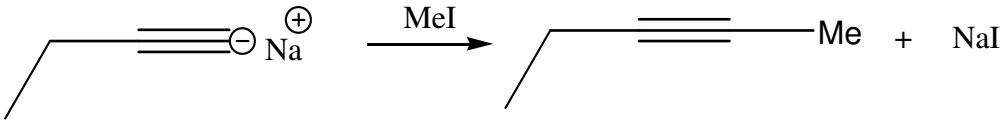
The removal of a proton from a hydrocarbon to generate an anionic species with the negative charge on carbon (a carbanion) is generally quite difficult because hydrocarbons are not acidic. With suitably strong bases, however, this can be done fairly readily with terminal alkynes:



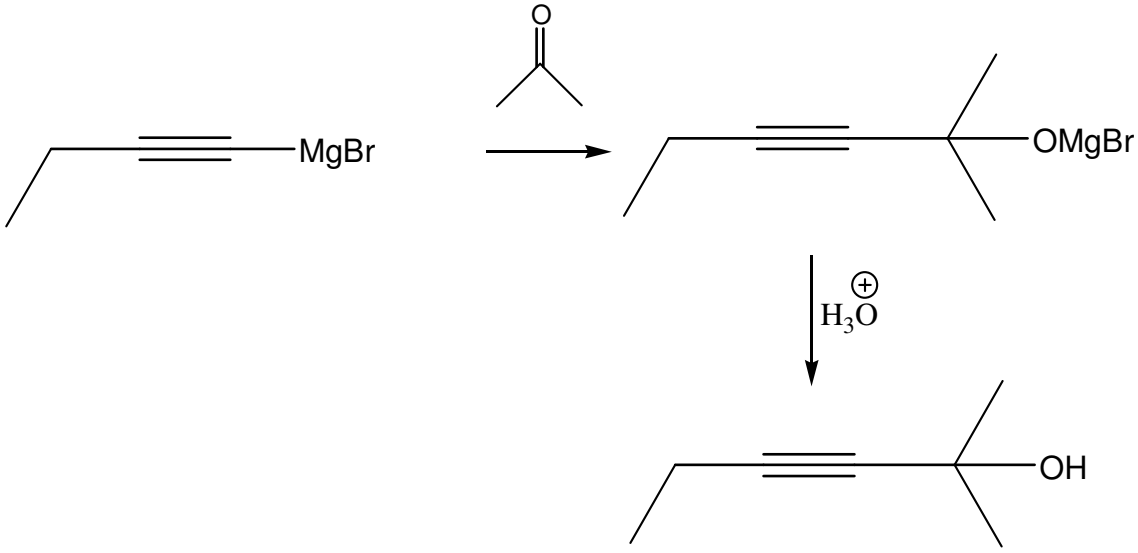
Because the C-H bond of a terminal alkyne is an sp(C)-s(H) bond it has electrons which are much closer to the nucleus than sp^2 – s or sp^3 – s bonds, simply because of the greater s-character of the σ-orbital. This closeness to the nucleus confers relative stability on the carbanion formed by deprotonation since the electron pair will be electrostatically closer to the positive nucleus. Thus, the pK_a (a measure of the acidity of the proton of that bond) of alkynic C-H bonds is approx. 25 compared to alkenic (pK_a approx. 44) and alkanic (pK_a approx. 50) C – H bonds (for comparison, water has a pKa of 15.7). Hence, sodamide can deprotonate alkynes but not alkenes or alkanes because ammonia has a pK_a of approx. 33. Likewise, Grignard reagents, also strong bases, can deprotonate terminal alkynes:



The sodium derivatives of alkynes are synthetically very useful as they can act as good nucleophiles towards alkyl halides:



This enables the synthesis of non-terminal alkynes from terminal ones. Similarly, the alkynyl magnesium halides will react with carbonyl compounds to give alkynic alcohols:



Again, the result is the production of a more complicated alkyne from a simpler one which is very useful synthetically.