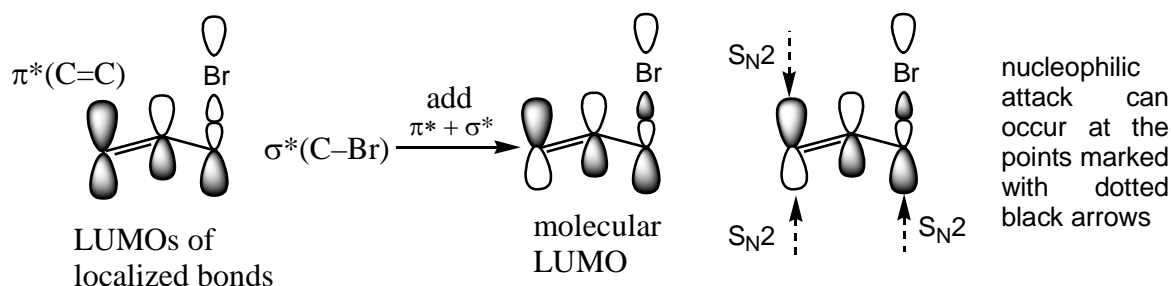
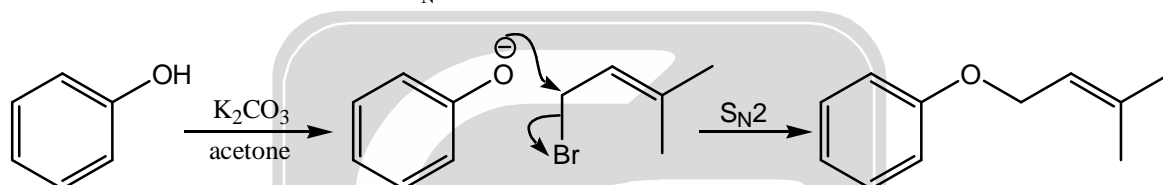


(C–Br) will as usual produce two new orbitals, one higher and one lower in energy. The lower-energy orbital, $\pi^* + \sigma^*$, will now be the LUMO. To construct this orbital we must put all the atomic orbitals parallel and make the contact between $\pi^* + \sigma^*$ a bonding interaction.

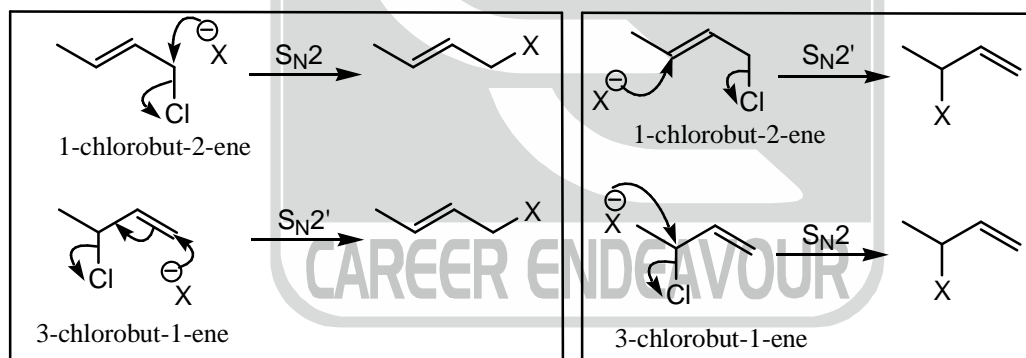
LUMO constructed from $\pi^* + \sigma^*$



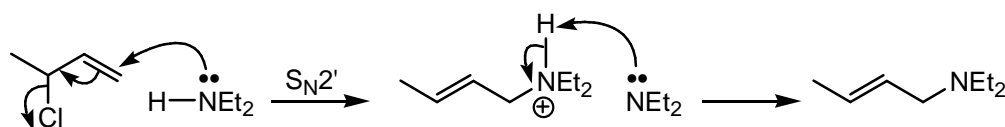
An important example is the reaction of prenyl bromide with phenols. This is simply carried out with K_2CO_3 in acetone as phenols are acidic enough ($pK_a \sim 10$) to be substantially deprotonated by carbonate. The product is almost entirely from the S_N2 route, and is used in the Claisen rearrangement.



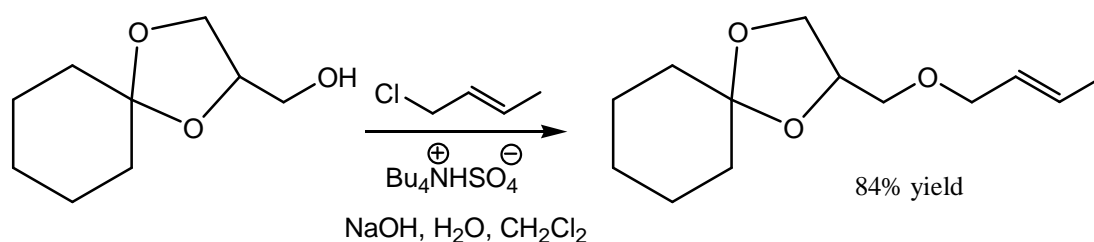
If we make the two ends of the allyl system more similar, say one end primary and one end secondary, things are more equal. We could consider the two isomeric butenyl chlorides.



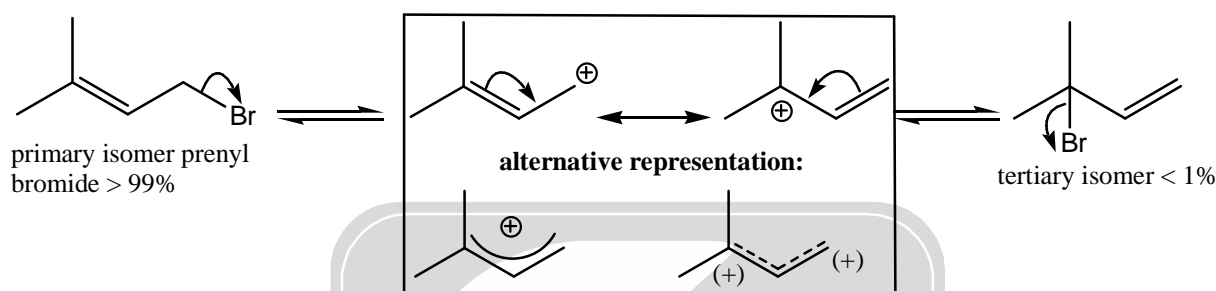
All routes look reasonable, although we might again expect faster attack at the primary carbon. The reactions in the left-hand box are preferred to those in the right hand box. But there is no special preference for the S_N2 over the S_N2' mechanism or vice versa – the individual case decides. If we react the secondary butenyl chloride with an amine we get the S_N2' mechanism entirely.



If the primary chloride is used, once again we get nucleophilic attack at the primary centre. The more stable product with the more highly substituted alkene is formed this time by the S_N2 reaction. Here is a slightly more advanced example:

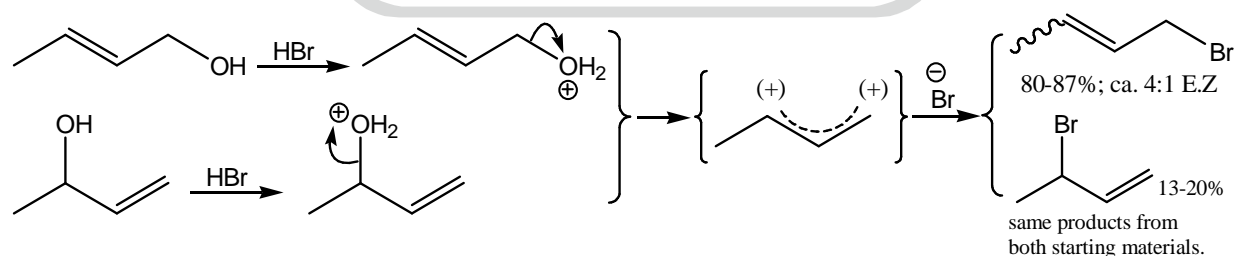


You might ask a very good question at this point. How do we know that these reaction really take place by S_N2 and S_N2' mechanism and not by an S_N1 mechanism via the stable allyl cation? Well in the case of prenyl bromide, we don't! In fact, we suspect that the cation probably is an intermediate because prenyl bromide and its allylic isomer are in rapid equilibrium in solution at room temperature.



The equilibrium is entirely in favour of prenyl bromide because of its more highly substituted double bond. Reactions on the tertiary allylic isomer are very likely to take place by the S_N1 mechanism: the cation is stable because it is tertiary and allylic and the equilibration tells us it is already there. Even if the reactions were bimolecular, no S_N2' mechanism would be necessary for the tertiary bromide because it can equilibrate to the primary isomer more rapidly than the S_N2 or S_N2' reaction takes place.

Even the secondary system we also considered is in rapid equilibrium when the leaving group is bromide. This time both allylic isomers are present, and the primary allylic isomer (known as crotyl bromide) is an E/Z mixture. The bromides can be made from either alcohol with HBr and the same ratio of products results, indicating a common intermediate in the two mechanisms. You saw at the beginning of this reaction is restricted to alcohols that can react by S_N1 .



Displacement of the bromide by cyanide ion, using the copper (I) salt as the reagent, gives mixture of nitriles in which the more stable primary nitrile predominates even more. These can be separated by a clever device. Hydrolysis in concentrated HCl is successful with the predominant primary nitrile but the more hindered secondary nitrile does not hydrolyse. Separation of compounds having two different functional groups is easy. In this case the acid can be extracted into aqueous base, leaving the neutral nitrile in the organic layer.