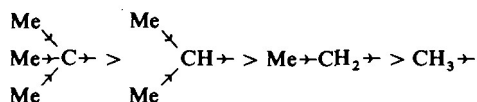


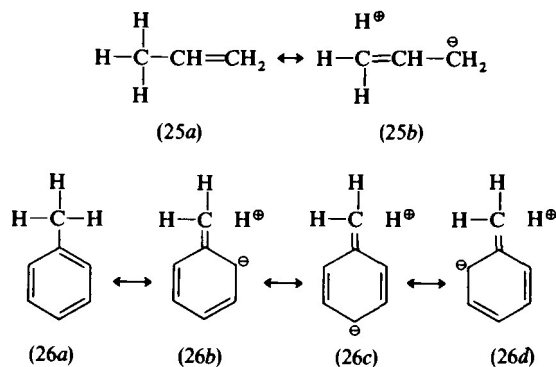
variable factors, the actual close approach of a reagent may have a profound effect in enhancing reactivity in a reactant molecule, and so in promoting reaction.

1.5.4 Hyperconjugation

The relative magnitude of the inductive effect of alkyl groups is normally found to follow the order,



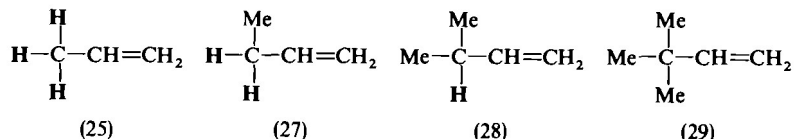
as would be expected. When, however, the alkyl groups are attached to an unsaturated system, e.g. a double bond or a benzene nucleus, this order is found to be disturbed, and in the case of some conjugated systems actually reversed. It thus appears that alkyl groups are capable, in these circumstances, of giving rise to electron release by a mechanism different from the inductive effect. This has been explained as proceeding by an extension of the conjugative or mesomeric effect, delocalisation taking place in the following way:



This effect has been called *hyperconjugation*, and has been used successfully to explain a number of otherwise unconnected phenomena. It should be emphasised that it is not suggested that a proton actually becomes free in (25) or (26), for if it moved from its original position one of the conditions necessary for delocalisation to occur would be controverted (p. 20).

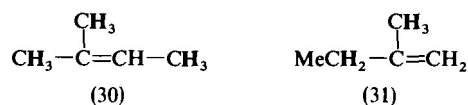
Reversal of the expected (inductive) order of electron-donation to $\text{CH}_3 > \text{MeCH}_2 > \text{Me}_2\text{CH} > \text{Me}_3\text{C}$ could be explained on the basis of

hyperconjugation being dependent on the presence of hydrogen on the carbon atoms α - to the unsaturated system. This is clearly at a maximum with CH_3 (25) and non-existent with Me_3C (29),



hence the increased electron-donating ability of CH_3 groups under these conditions. Hyperconjugation could, however, involve $\text{C}-\text{C}$ as well as $\text{C}-\text{H}$ bonds, and the differences in relative reactivity observed in a series of compounds may actually result from the operation of solvent, as well as hyperconjugative, effects.

Hyperconjugation has also been invoked to account for the greater thermodynamic stability of alkenes in which the double bond is not terminal, e.g. (30), compared with isomeric compounds in which it is, e.g. (31): in (30) there are nine 'hyperconjugable' α -hydrogen atoms, compared with only five in (31):



This results in the preferential formation of non-terminal alkenes, in reactions which could lead to either these or their terminal isomers on introduction of the double bond (p. 256), and to the fairly ready isomerisation of the less to the more stable compound, e.g. (31) \rightarrow (30).

1.6 STERIC EFFECTS

We have to date been discussing factors that may influence the relative availability of electrons in bonds, or at particular atoms, in a compound, and hence affect that compound's reactivity. The operation of these factors may, however, be modified or even nullified by the influence of steric factors; thus effective delocalisation *via* π orbitals can only take place if the p or π orbitals, on the atoms involved in the delocalisation, can become parallel or fairly nearly so. If this is prevented, significant overlapping cannot take place, and delocalisation may be inhibited. A good example of this is provided by a comparison between the behaviour of *N,N*-dimethylaniline (32) and its 2,6-dialkyl derivatives, e.g. (33). The NMe_2 group in (32), being electron-donating (due to the unshared electron pair on nitrogen interacting with the delocalised π orbitals of the nucleus), activates the nucleus towards attack by the diazonium cation PhN_2^{\oplus} , i.e. towards azo-coupling,