

5

Carbocations, electron-deficient N and O atoms and their reactions

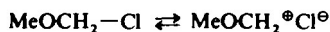
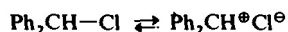
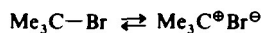
- 5.1 METHODS OF FORMING CARBOCATIONS, p. 101.
 - 5.1.1 Heterolytic fission of neutral species, p. 101; 5.1.2 Addition of cations to neutral species, p. 103; 5.1.3 From other cations, p. 104.
- 5.2 STABILITY AND STRUCTURE OF CARBOCATIONS, p. 104.
- 5.3 CARBOCATION REACTIONS, p. 107.
- 5.4 CARBOCATION REARRANGEMENTS, p. 109.
 - 5.4.1 Without change in carbon skeleton, p. 109: 5.4.1.1 Allylic rearrangements, p. 109; 5.4.2 With change in carbon skeleton, p. 110: 5.4.2.1 Neopentyl rearrangements, p. 110, 5.4.2.2 Rearrangement of hydrocarbons, p. 112, 5.4.2.3 Pinacol/pinacolone rearrangements, p. 113, 5.4.2.4 Stereochemistry of rearrangements, p. 116, 5.4.2.5 Wolff rearrangements, p. 119.
- 5.5 DIAZONIUM CATIONS, p. 119.
- 5.6 MIGRATION TO ELECTRON-DEFICIENT N, p. 122:
 - 5.6.1 Hofmann, Curtius, Lossen and Schmidt reactions, p. 122;
 - 5.6.2 Beckmann rearrangements, p. 123.
- 5.7 MIGRATION TO ELECTRON-DEFICIENT O, p. 127:
 - 5.7.1 Baeyer–Villiger oxidation of ketones, p. 127; 5.7.2 Hydroperoxide rearrangements, p. 128.

Reference has already been made in the last chapter to the generation of carbocations, in ion pairs, as intermediates in some displacement reactions at a saturated carbon atom, e.g. the solvolysis of an alkyl halide *via* the S_N1 mechanism. Carbocations are, however, fairly widespread in occurrence and, although their existence is often only transient, they are of considerable importance in a wide variety of chemical reactions.

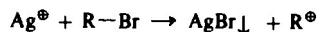
5.1 METHODS OF FORMING CARBOCATIONS

5.1.1 Heterolytic fission of neutral species

The obvious example is simple *ionisation*, the group attached to carbon departing with its bonding electrons to form an ion pair, R[⊕]Y[⊖]:

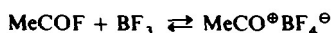


In each case a highly polar (high ϵ), powerful ion-solvating medium is generally necessary. In a similar context the effect of Ag^{\oplus} in catalysing reactions, often by a shift from $\text{S}_{\text{N}}2 \rightarrow \text{S}_{\text{N}}1$ mode,

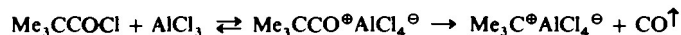


has already been referred to (p. 97). The catalytic effect of Ag^{\oplus} can be complicated, however, by the fact that the precipitated silver halide may itself act as a heterogeneous catalyst.

Ionisation may also be induced by Lewis acids, e.g. BF_3 ,

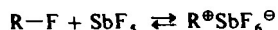


to yield in this case an *acyl cation*; the equilibrium here being considerably influenced by the very great stability of the anion, BF_4^{\ominus} . Also with AlCl_3 ,

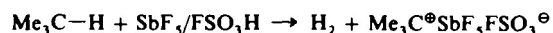


here the relatively unstable acyl cation decomposes to yield the very stable $\text{Me}_3\text{C}^{\oplus}$, the equilibrium being driven over to the right by the escape of CO.

Particularly striking examples are provided by the work of Olah with SbF_5 as a Lewis acid, with either liquid SO_2 or excess SbF_5 as solvent,



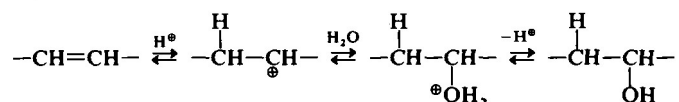
leading to the formation of simple alkyl cations in conditions that allow of their detailed study by n.m.r. spectroscopy and other means. The use of the same investigator's 'super acids', such as $\text{SbF}_5/\text{FSO}_3\text{H}$, allows of the formation of alkyl cations even from alkanes:



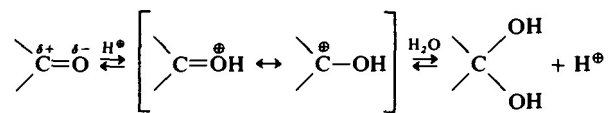
The relative stability of $\text{Me}_3\text{C}^{\oplus}$ is shown by the fact that under these conditions the isomeric carbocation, $\text{Me}\overset{\oplus}{\text{C}}\text{HCH}_2\text{Me}$, obtained from $\text{MeCH}_2\text{CH}_2\text{Me}$, was found to rearrange virtually instantaneously to $\text{Me}_3\text{C}^{\oplus}$. The structure/stability relationships, and rearrangements, of carbocations are discussed below (pp. 104 and 109, respectively).

5.1.2 Addition of cations to neutral species

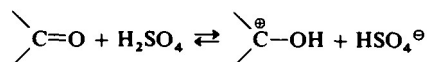
The most common cation is H^{\oplus} , adding to unsaturated linkages, i.e. *protonation*, in for example the acid-catalysed hydration of alkenes (p. 187):



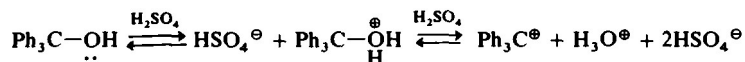
The reaction is reversible, the reverse being the perhaps better known acid-catalysed dehydration of alcohols (p. 247). Protonation can also occur on oxygen in a carbon-oxygen double bond,



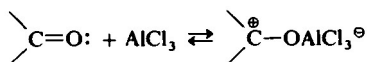
thus providing a more positive carbon atom for subsequent attack by a nucleophile, in this case H_2O : in acid-catalysed hydration of carbonyl compounds (*cf.* p. 207). That such protonation does indeed occur may be demonstrated, in the absence of water, by the two-fold depression of freezing point observed with ketones in concentrated sulphuric acid:



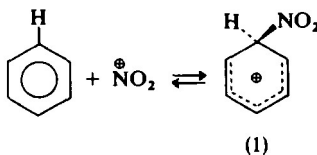
Carbocations may also be generated by protonation of lone pair electrons, if the protonated atom is converted into a better leaving group thereby and ionisation thus promoted:



cf. protonation of OH above; but here there is no H that can be lost (as H^{\oplus}) from an adjacent carbon. Lewis acids may also be used,



and other cations, e.g. $^{\oplus}\text{NO}_2$ in the nitration of benzene (p. 134),



where the intermediate (1) is a delocalised carbocation.