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Study Notes on Organic Reactive Intermediates

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Organic reactive intermediates

A reactive intermediate is short-lived, and highly reactive molecule. During a chemical reaction, it gets converted into a more stable molecule within a very short time. It exists only in one of the intermediate steps.

Common features of reactive intermediates:

1. It has a low concentration with respect to reaction substrate and final product of the reaction.
2. It is generally generated when a chemical compound undergoes decomposition.
3. It gets stabilized by resonance.
4. It is generally difficult to distinguish reactive intermediate from transition state.

Let us study reactive intermediates one by one:

1. **Carbocation:** It is an ion having positive charge on carbon and is an electron deficient species. It is a cation contains even number of electrons where major portion of positive charge resides on carbon atom. As it is electron deficient in nature, species that can electron density will stabilize it. Also, electron withdrawing groups will destabilize the carbocation.

   Alkyl group are electron donating due to which they can stabilize carbocation. In other words, more substituted the carbocation, more will be the stability. The stability order in terms of alkyl groups can be represented as:

   Tertiary> secondary>primary>methyl

2. **Carbanian:** It is an ion having negative charge on carbon and is an electron rich species. This is formed by the attack of nucleophile. In this, heterolytic cleavage of bond takes place where carbon has both the shared pair of electrons. The most basic form of carbanion is methide ion (CH_3^-). It stability and reactivity can be determined by several factors and these are:

   (a) Presence of electronegative atom adjacent to carbon tends to stabilize the charge.

   (b) Greater the s character of the atom having charge, more stable will be the ion.

   (c) Resonance

3. **Free radical:** A free radical is a species having unpaired valence electrons. They are generally
neutral and are highly reactive. The reactions of free radical proceed through homolytic cleavage, but it does not involve the donation or acceptance of electron lone pair. These are also electron deficient like carbocations. They become stable in the presence of electron donating groups. The stability order in terms of alkyl groups can be represented as: Tertiary> secondary>primary>methyl

4. Carbene: It contains a neutral carbon atom having two unshared valence electrons. Its general formula is H_2C:, known as methylene. They can be classified according to their electronic structures into singlet and triplet. Their life span is very short.

Singlet: These carbenes are spin paired and has sp^2 hybridization. Their total spin is zero and bond angle is around 102^0. These are stable in aqueous media.

Triplet: These carbenes contain two unpaired electrons and can be either linear or bent. These are paramagnetic and their total spin is 1. Bond angles for triplet carbene is $125\text{-}140^0$, and these are stable in gaseous state.

5. Nitrene: It is said to be an analogue of carbene. In this, N atom is uncharged and univalent and contains six valence electrons. It is an electron deficient species. The simplest nitrene is NH known as imidogen. Imidogen is a linera molecule having sp hybridization. Rearrangement of nitrenes can be initiated in the presence of heat or light. These are very reactive and cannot be isolated. There are following reactions from which these are produced as intermediates:

(a) Photolysis of azides

(b) From isocyanates

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