Quadrant II – Transcript and Related Materials

Programme: Bachelor of Science (First Year)

Subject: Chemistry

Paper Code: CHC 102

Paper Title: Physical and Organic Chemistry

Unit: Alkyl and Aryl Halides

Module Name: Reactivity and relative strength of C-Halogen bond in alkyl,

allyl, benzyl, vinyl and aryl halides.

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Notes:

Halides follow the following order when we study their reactivity:

Benzyl halide > Allyl halide > Alkyl halide > Vinyl halide > Aryl Halide

Benzyl Halides are most reactive because the intermediate (benzylic carbocation) obtained can stabilise itself to the maximum due to resonance.

Allyl Halides can give more stable allylic carbocation with the loss of halide ion.

$$H_2C$$
 H_2C
 H_2C

The two resonating structures are of equal energies thereby making it more stable intermediate carbocation. The stabilisation is by means of resonance.

Incase of Alkyl halides the Carbocation stabilisation is by a weaker phenomenon of inductive effect. The Reactivity of Alkyl Halides depends on two factors: 1) The nature of Alkyl Groups 2) The nature of Halogen Atom

1. **The Nature of Alkyl Groups:** Alkyl groups are electron releasing. More the number of alkyl groups greater will be the electron density at the carbon atom of C-X bond, hence there will be greater repulsion of electron pair shared between C and X.

$$CH_{3} \stackrel{\bullet}{-}Br \qquad \qquad \stackrel{\bullet}{-}CH_{3} + Br$$

$$\triangle H = 219 \text{ K Cal}$$

$$CH_{3} - CH_{2} - Br \qquad \qquad CH_{3} - CH_{2} + Br$$

$$\triangle H = 184 \text{ K Cal}$$

$$A H = 164 \text{ K Cal}$$

$$A H = 164 \text{ K Cal}$$

$$A H = 149 \text{ K Cal}$$

2. The Nature of Halogen Atom: Larger the size of the Halogen Atom, greater is the ease with which the Halogen Atoms can be substituted. The order of reactivity is as follows: Alkyl lodides > Alkyl Bromides > Alkyl Chlorides. Alkyl lodides are very reactive and are even decomposed by light.

Vinyl Halides are less reactive compared to Alkyl Halides due to the following resonance phenomenon:

Double bond character strengthens the C-X bond thereby making the removal of chloride ion difficult. Carbon is sp² hybridised thus C-X bond is shorter and stronger compared to alkyl halides.

Aryl Halides are less reactive than alkyl halides due to the resonance stabilisation of aryl halides as follows:

C-X bond is a double bond in the resonating structures and is not easily broken which makes the leaving of the X group difficult making it least reactive.