Ch10 Reactions Booklet

Name: \_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_

When alkanes and either of chlorine or bromine are combined in the absence of daylight/in the dark **no reaction occurs**. When exposed to **UV** light a reaction proceeds in which a hydrogen atom of the alkane is replaced by a chlorine or bromine atom according to the following net reaction equation:

R3C—H + X—X 🡪 R3C—X + H—X (X = Cl or Br)

In the reaction of methane with chlorine, if sufficient chlorine is present, multiple substitutions can occur to form substituted alkyl halide/halocarbon molecules, dichloromethane, trichloromethane, and tetrachloromethane. If a longer chain hydrocarbon reacts, e.g. ethane, a mixture of products is to be expected if more than one hydrogen is substituted a shown below:



The relative quantities of the 1,1 – dibromoethane and 1,2 – dibromoethane produced vary with the precise reaction conditions. It is more important to be aware that different substituted products are to be expected. In most situations an organic chemist would at this point set about separating the products by any of a variety of techniques available.

Halogen free radical substitutiondoes not happen with iodine. In the presence of even limiting quantities of fluorine the reaction proceeds violently towards multiple substitution products - a very messy reaction indeed.

For halogen substitution of benzene rings the reaction proceeds by a different route (electrophilic substitution) in the presence of the corresponding iron(III) halide catalyst. Multiple substitutions can occur in a variety of locations around the ring as shown:

 

1. Write structural equations and include the names the products for the following reactions in the presence of a UV light source (assume only one mole of halogen reacts unless otherwise indicated). *(…name the organic products)*

(i) methane + bromine 🡪

(ii) bromomethane + bromine 🡪

(iii) ethane + chlorine 🡪

(iv) cyclobutane + chlorine 🡪

(v) cyclohexane + bromine 🡪

(vi) bromoethane + bromine 🡪 (give 2-possible products)

(vii) 2-bromopropane + bromine 🡪 (give 3 possible products)

(viii) pentane + chlorine 🡪 (give 2 possible products)

(ix) cyclopropane + 2 chlorine 🡪 (give all possible products)

(x) benzene + 2 bromine 🡪 (give the 3 possible products)

A nucleophilic substitution reaction is one in which a **nucleophile** (a chemical species with a lone pair of electrons (a halide, hydroxide) is attracted to a slightly positive C-centre in a **substrate** molecule) replaces another atom/species, called a **leaving group**, that is ejected from the substrate molecule.

When alcohols are treated with a mixture of zinc chloride and hydrochloric acid in aqueous solution (Lucas reagent: actually – H2ZnCl4(aq)) the hydroxyl is readily replaced by chloride substituent. The less soluble chloroalkane product causes the reaction mixture to be cloudy. For example

CH3*—*C(CH3)2*—*OH+ H*—*Cl 🡪 CH3*—*C(CH3)2*—*Cl+ H*—*OH

in the presence of HCl(aq)/ZnCl2(aq).

If sufficient aqueous sodium hydroxide is added to a haloalkane and alcohol is formed.

CH3*—*C(CH3)2*—*I+ NaOH(aq) 🡪 CH3*—*C(CH3)2*—*OH+ NaI(aq)

1. Write a structural equation to represent the reactants and products of the following nucleophilic substitutions *(…name the organic products)*

(i) methanol + bromide ion 🡪

(ii) propan-2-ol + chloride ion 🡪

(iii) 2-bromo-2-methylpropane + hydroxide ion 🡪

(iv) 2-methylpropan-2-ol + chloride ion 🡪

(v) 2-iodopropane + hydroxide ion 🡪

**Addition Reactions**; the reaction of alkenes and small molecules

In an addition reaction a small molecule adds to a C=C double bond effectively converting it into a single bond. (The following discussion applies equally forcefully to alkenes). In all addition reactions there are two reactants but only one product. *At this point we should note that* ***benzene******does not undergo addition reactions*** *– it does not contain any double bonds!*

1. **Hydrogenation** : Alkene + H2 🡪 Alkane (Ni(s) or Pt(s) catalyst)



1. **Halogenation** : Alkene + X2 🡪 Dihaloalkane (X = Cl, Br, I)



1. **Hydrohalogenation** : Alkene + HX 🡪 Haloalkane (X = Cl, Br, I)



1. **Hydration**: Alkene + HOH 🡪 Alcohol (H2SO4(aq) catalyst)



The following diagram describes all the addition reactions of ethene. 

1. Write a structural equation to represent the reactants and products of the following addition reactions. (Apply Markownikow’s Rule where appropriate.) *(…name the organic products)*

(i) propene + chlorine 🡪

(ii) cis-but-2-ene + iodine 🡪

(iii) pent-1-ene + hydrogen bromide 🡪

(iv) propene + water 🡪

(v) cyclohexene + hydrogen chloride 🡪

(vi) cyclopentene + water 🡪

(vii) cyclopropene + chlorine 🡪

(viii) trans-hex-3-ene + hydrogen 🡪

(ix) but-2-ene + bromine 🡪

(x) cyclopentene + water 🡪

(xi) cyclohexene + iodine 🡪

**The Bromine Colour Test for Unsaturation**

An aqueous solution of bromine, Br2(aq) – sparingly soluble/orange solution, is rendered colourless when added in small amounts to hydrocarbons that contain carbon-carbon double and carbon-carbon triple bonds. Put another way, if a compound decolourizes bromine it is unsaturated. The reaction is complex and the product is a hydroxy-bromo-hydrocarbon, colourless, as follows



 

In a nonpolar solvent, i.e. no water present, the dibromide product forms.**Elimination Reactions**; a reaction that forms alkenes

In an elimination reaction a C=C double bond is formed, effectively converting an alkane, haloalkane, or an alcohol into an alkene.

1. **Dehydrogenation** : Alkane 🡪 Alkene At very high temperatures, small alkanes decompose to produce alkenes. This is not practical on the laboratory scale but it is a common industrial process. Ethene is manufactured in this way at the NOVA Chemicals ethane cracking plant near Red Deer. (With large alkanes a variety of small molecules are produced as the alkane breaks apart.)



1. **Dehydrohalogenation** of haloalkanes :

Haloalkane + NaOR\* 🡪 Alkene HOR+ NaX (X = Cl, Br, I) in ethanol. \*Hot concentrated sodium ethoxide, or sodium hydroxide, in ethanol



1. **Dehydration of Alcohols** : Alcohol 🡪 Alkene + HOH

(H2SO4(aq) or H3PO4) catalyst)



1. Write a structural equation to represent the reactants and products of the following elimination reactions. *(…some reactions can produce two organic products)*

(i) propane 

(ii) butane  (three C4 alkenes in varying amounts)

(iii) 1-chloropentane 

(iv) 2- bromopropane 

(v) cyclohexanol 

(vi) propan-2-ol 

(vii) ethanol 

(viii) 1-bromohexane 

Alkanes are dehydrogenated cleanly in the presence chromium (III) oxide catalyst, at high temperature and pressures, to produce an alkene. *(…name the organic products)*

(ix) cyclopentane 

(x) ethane 

(xi) butane 

(xii) pentane 

 **Esterification of Carboxylic Acids:**

Carboxylic Acid + Alcohol Ester + Water

…in the presence of either sulfuric acid or phosphoric acid as catalyst.

For example



ethanoic acid ethanol ethyl ethanoate

The water produced derives from the acid -OH and the alcohol -H.

1. Write a structural equation to represent the reactants and products in each the following esterifications. *Name all the organic products.*

(i) benzoic acid + ethanol 

(ii) benzoic acid + butan-1-ol 

(iii) ethanoic acid + propan-1-ol 

(iv) hexanoic acid + propan-2-ol 

(v) ethanoic acid + cyclohexanol 

(vi) benzoic acid + propan-2-ol 

 (vii) benzoic acid + methanol 

(viii) octadecanoic acid + ethanol 

**Ester Hydrolysis**

Esters may undergo **hydrolysis** – which is essentially the breakdown of an ester by water. This process is catalyzed both by acids and bases. The base-catalyzed process is called saponification. Hydrolysis yields an alcohol and a carboxylic acid (acid catalyzed) or its carboxylate salt (base catalyzed).

1. Write a structural equation to represent the reactants and products in each the following hydrolyses. *Name all the organic products.* (Polyester clothing exposed to strong acid or strong base decomposes in much the same as simple esters)

(i) ethyl benzoate 

(ii) butyl benzoate 

(iii) propyl ethanoate 

(iv) isopropyl hexanoate 

(v) cyclohexyl ethanoate 

(vi) pentyl propanoate 

(vii) methyl benzoate 

(viii) ethyl octadecanoate 

(ix) butyl propanoate 

 (x) propyl decanoate 