# **Quadrant II – Transcript and Related Materials**

**Programme:** Bachelor of Science (Third Year)

**Subject:** Chemistry

Paper Code: CHC-109

Paper Title: Inorganic Chemistry (Section A)

Unit: 1

Module Name: Preparation and Properties of Alkyls and Aryls of Hg and Ti.

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#### **Notes**

### ORGANOMERCURY COMPOUNDS

Organomercury compounds are of two types

- R-Hg-X
- R<sub>2</sub>-Hg

Where R is an alkyl group and X is an Halide group

## **Method of Preparation**

1. By the reaction of Grignard reagent

2. By the reaction of diazomethane with HgCl<sub>2</sub>

$$\begin{array}{cccc} CH_2N_2 & + HgCl_2 & \longrightarrow & Cl(CH_2)HgCl + N_2 \\ & & Chloro \ Methyl \ Mercuric \ Chloride \\ \\ CH_2N_2 & + Cl(CH_2)HgCl & \longrightarrow & (CH_2Cl)Hg + N_2 \\ & & Bis \ (Chloro \ Methyl) \\ & & Mercury \end{array}$$

3. By the decorboxylation of mercuric trifluoro acetate

$$(CF_3COO)_2 Hg \xrightarrow{-CO_2} (CF_3COO)HgCF_3 \xrightarrow{-CO_2} F_3C-Hg-CF_3$$
Mercury Trifluoro Acetate
$$Bis (Trifluoro Methyl)$$
Mercury

4. By the treatment of alkyl halides or aryl sulfates with sodium amalgam

$$2 RX + 2Na + Hg \longrightarrow (R)_{2} Hg + 2NaX$$

5. Mercuration of Aryl halides

$$ArX + HgX_{2} \longrightarrow Ar-HgX + HX$$
Aryl Halides

Aryl mercuric halide

6. By the reaction of alkyl halides with Hg in the presence of light

$$RX + Hg \xrightarrow{hv} R-Hg-X$$
Alkyl Halides Alkyl mercuric halide

7. By the reaction of organolithium compounds with mercuric halides

R-Li + HgX<sub>2</sub> 
$$\longrightarrow$$
 R-HgX + LiX

Alkyl Lithium Aryl mercuric halide

R-HgX + R-Li  $\longrightarrow$  R<sub>2</sub>-Hg + LiX<sub>2</sub>

#### **Physical Properties**

- 1. Organometallic compounds of Mercury are colourless, volatile liquids.
- 2. They are covalent compounds that are soluble in organic solvents (non-polar solvents) like benzene.
- 3. They are very poisonous

### **Chemical Properties**

1. They are slowly hydrolysed by water but rapidly by acid to give alkanes

$$(CH_3)_2Hg + H_2O \longrightarrow HgO + 2CH_4$$

$$(CH_3)_2Hg + HCl \longrightarrow CH_3HgCl + 2CH_4$$

Dimethyl Mercury

Methyl Mercuric Chloride

2. They are decomposed by halogens to give alkyl halides

$$(CH_3)_2Hg + 2Br_2 \longrightarrow HgBr + 2CH_3Br$$
  
Dimethyl Mercury Methyl Bromide

3. They react with more electropositive metals to form organometallic compounds

$$(CH_3)_{2}Hg + 2Li \longrightarrow 2CH_3Li + Hg$$
Dimethyl Mercury Methyl Lithium

$$3(CH_3)_{2}Hg + 2AI \longrightarrow AI_{2}(CH_3)_{6} + Hg$$
Trimethyl Aluminium

$$2(CH_3)_{12}Hg + Sn \longrightarrow (CH_3)_{14}Sn + 2Hg$$
Tetramethyl Tin

#### Uses

- 1. Mercurochrome (2,7-dibromo-4-hydoxy mercurifluoroscein) is used as an antiseptic.
- 2. Ethyl mercuric chloride is used as a fungiside to protect young plants and seeds from fungal infection.
- 3. Organo mercury compounds are used in the synthesis of different types of compounds.

## **ORGANOTITANIUM COMPOUNDS**

- Compound containing a C-Ti bond are called organotitanium compounds
- Ti can be in the tetravalent, trivalent or divalent state in these compounds

### **Method of Preparation**

1. From organolithium and organoaluminium compounds

$$CH_{3}AlCl_{2} + TiCl_{4} \xrightarrow{Hexane} CH_{3}TiCl_{2} + AlCl_{3}$$

CH<sub>3</sub>Li + TiCl<sub>4</sub> 
$$\xrightarrow{\text{Ether}}$$
 (CH<sub>3</sub>) Ti + 4LiCl<sub>4</sub>  $\xrightarrow{\text{-50 C to -80 C}}$ 

2. From Grignard reagent

3. From organozinc compounds

$$CH_3TiCl_3 + (CH_3)_2Zn \xrightarrow{Hexane} (CH_3)_2TiCl_2 + CH_3ZnCl$$

4. From cyclopentadienyl compounds

$$2NaC_{5}H_{5} + TiCl_{4} \longrightarrow (C_{5}H_{5})_{2}TiCl_{2} + 2 NaCl$$

$$Bis (Cyclopentadienyl)$$

$$Titanium (IV) Dichloride$$

5. From organomercury compounds

$$(C_{6}H_{5})_{2}Hg + TiCl_{4} \longrightarrow (C_{6}H_{5})_{2}TiCl_{2} + HgCl_{2}$$
  
Bis (Phenyl) Titanium (IV) Dichloride

#### **Physical Properties**

- (C<sub>2</sub>H<sub>5</sub>)<sub>2</sub>Ti is a green crystalline solid. It is thermally unstable and decomposes at about 140°C before melting.
- Alkyls and aryls of Titanium are unstable and decompose at room temperature
- They are readily oxidized by air and are rapidly hydrolysed by water.

#### **Chemical Properties**

1. Synthesis of organomercury compounds

$$CH_3TiCl + HgCl_2 \longrightarrow CH_3HgCl + TiCl_4$$

2. Synthesis of neopentyl derivatives

$$\begin{array}{c} \mathsf{CH_3} \\ \mathsf{CH_3}\mathsf{TiCl_3} \\ \mathsf{CH_3}\mathsf{TiCl_3} \\ \mathsf{CH_3} \\ \mathsf{CH_3} \\ \mathsf{CH_3} \\ \mathsf{CH_3} \\ \mathsf{Neopentyl Titanium (IV)} \\ \mathsf{Trichloride} \\ \end{array}$$

3. Synthesis of organomercury compounds

$$(C_5H_5)_2\text{TiCl}_2 \xrightarrow{\text{CO + Mg}} (C_5H_5)_2\text{Ti(CO)}_2$$

$$Dicarbonyl \ Bis \ (Cyclopentadienyl) \ Titanium$$

$$Na/Zn \longrightarrow (C_5H_5)_2\text{Ti-Cl}_2\text{-Ti}(C_5H_5)_2$$

$$Bis \ (Cyclopentadienyl) \ Titanium \ (III) \ Chloride$$

$$LiNR_2 \longrightarrow (C_5H_5)_2\text{Ti}(NR_2)_2$$