

Natubhai V. Patel College of Pure & Applied Sciences

T. Y. B.Sc. (Industrial chemistry)

IC – 302: Unit Process, Synthetic dyes and Pharmaceuticals

UNIT – 1C

Syllabus

Halogenations: Introduction, Mechanism and manufacturing of BHC and Chlorobenzene.

HALOGENATION

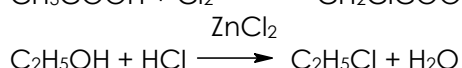
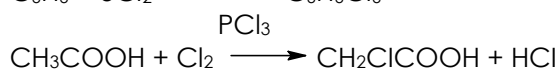
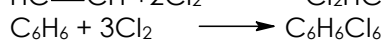
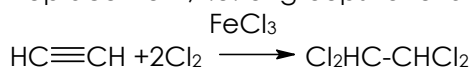
1.28 INTRODUCTION

Halogenation may be defined as the process whereby one or more halogen atoms are introduced into an organic compound.

The preparation of organic compounds containing fluorine, chlorine, bromine and iodine can be done by a variety of methods. The conditions and procedures differ, not only for each member of the halogen family but also with the type and structure of the compound undergoing treatment. The chlorine derivatives, because of the greater economy preparation, are the most important compound.

Halogenations may involve reactions of

- Addition
- Substitution i.e. of hydrogen,
- Replacement, i.e. of groups for example, the hydroxyl or sulfonic acid group

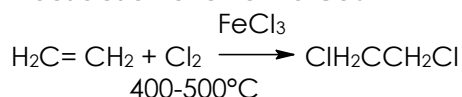


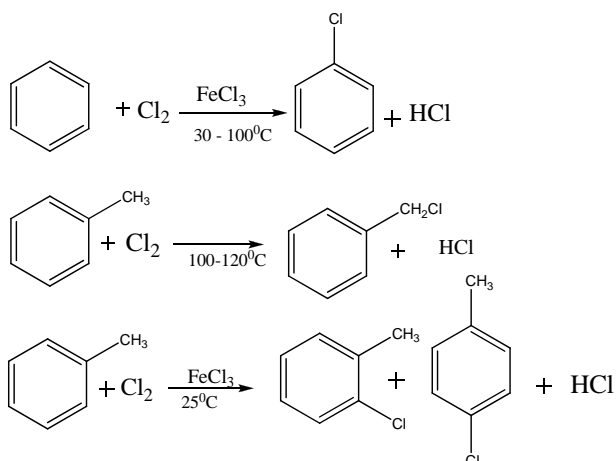
Many of the **catalysts** are halogen carriers. Iron, antimony, and phosphorous, which are able to exist in two valences as halogen compounds, are used as they are less stable at higher valence and give up part of their halogen during the process. In the presence of free halogen, such compounds alternatively add on and give up halogen to carry on the reaction. Iodine, bromine and chlorine, which are capable of forming mixed halogens, are also frequently used as catalysts in halogenation processes. Active carbon, clays, and other compounds are also catalyses halogenations processes.

1.29 CHLORINATION

1.30 IMPORTANT METHODS FOR PREPARING CHLORINE COMPOUNDS

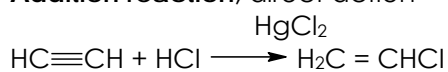
1.30.1 Direct action of chlorine Gas



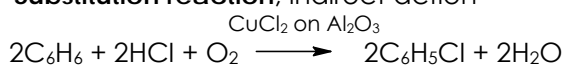


1.30.2 Hydrochloric acid as the chlorinating agent

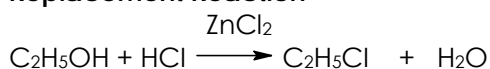
Addition reaction, direct action



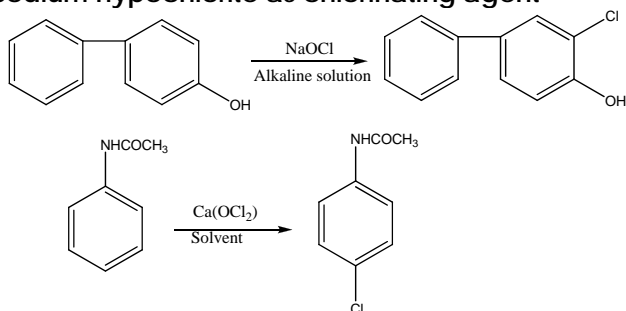
Substitution reaction, indirect action



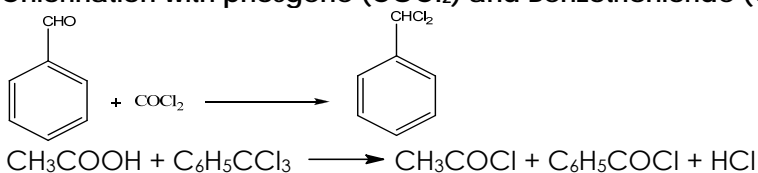
Replacement Reaction



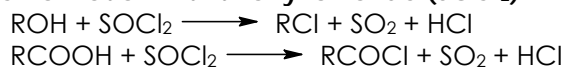
1.30.3 Sodium hypochlorite as chlorinating agent



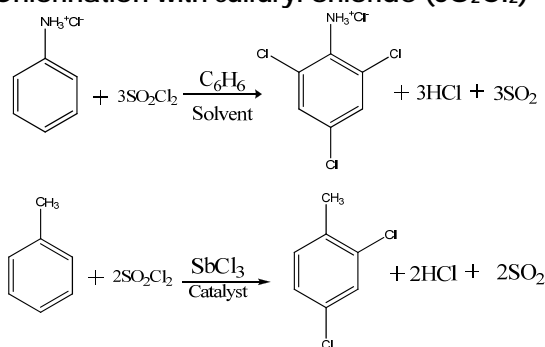
1.30.4 Chlorination with phosgene (COCl₂) and Benzotrichloride (C₆H₅CCl₃)

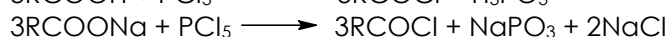
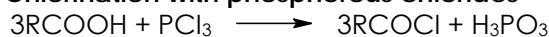


1.30.5 Chlorination with thionyl chloride (SOCl₂)



1.30.6 Chlorination with sulfuryl chloride (SO₂Cl₂)



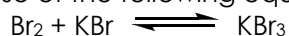
1.30.7 Chlorination with phosphorous chlorides**Preparation of chlorine derivatives by the Sandmeyer and Gattermann reactions****1.31 CONCLUSIONS FROM THE STUDY OF CHLORINATION OF HYDROCARBONS AND CHLORO-HYDROCARBONS**

- The rate of substitution chlorination of hydrogen on saturated carbon is greater than the rate of substitution of hydrogen on unsaturated carbons.
- The rate of substitution chlorination of hydrogen on saturated carbons is greater than the rate of addition chlorination to double bonds at high temperature; the reverse is true at lower temperature.
- The rate of addition chlorination on double bonds is greater than the rate of substitution of hydrogen on unsaturated carbons.
- The rate of substitution of hydrogen to chlorine is about the same as the normal rate of substitution of hydrogen on the type of carbon atom concerned.
- The rate of substitution of hydrogen to chlorine is markedly less than the normal rate of substitution of hydrogen on the type of carbon atom concerned.
- The rate of substitution of hydrogen to chlorine is only slightly less than the normal rate of substitution of hydrogen on the type of carbon atom concerned. For hydrogen and further removed from a chlorine, the rate of substitution is the normal one.

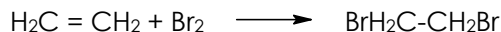
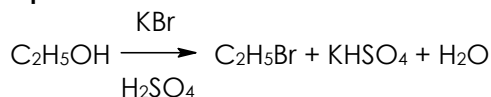
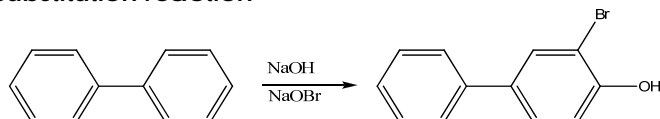
1.32 BROMINATION

In many instances, **bromination** may be carried out in a manner **similar to** that employed for the preparation of **chlorine derivatives**. Thus, bromine bromides, bromates and alkaline hypobromites may be used instead of the corresponding chlorine compounds.

Reaction involving addition and substitution are common. Bromine dissolved in water is frequently employed, particularly in the bromination of phenols. Potassium bromide is generally added to aqueous bromine solution to increase the concentration of soluble molecular halogen. Concentrated bromide solutions are thus made available, presumable because of the following equilibrium.



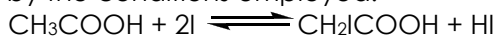
Bromine, hydrobromic acid and alkali hypobromites, like the corresponding chlorine compounds, find employment in technical brominations.

1.32.1 Addition reactions**1.32.2 Replacement reactions****1.32.3 Substitution reaction**

A number of organic compound carriers for bromide to produce specific types of bromine containing compounds have been explored through the use of N-bromo-succinimide, N-bromo-acetamide, 1,2,-dibromo, 5-5- dimethylhydantoin and associated compounds.

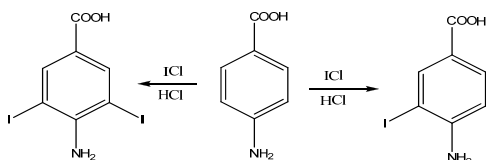
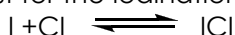
1.33 IODINATION

The relatively **weak C-I bond** makes permanent, direct union of carbon to iodine by the replacement of hydrogen possible only in exceptional cases. Such iodination are reversible in character as for instance, the iodination of acetic acid and are governed largely by the conditions employed.

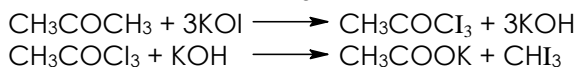
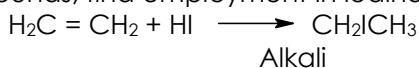


The hydrogen iodide tends to effect de-iodination of the halogenated compounds and indeed is sometimes thus employed. The removal of the hydrogen iodide by such means as oxidation or absorption in alkali is essential for successful iodination. Then nitric acid is employed as the oxidant; practically all the iodine enters the organic compound. In the ordinary direct halogenations in the absence of an oxidizing agent, half the reacting halogen is converted to the hydrogen halide.

Catalysts are only infrequently employed in iodination, phosphorus being the principal accelerator. Iodine monochloride because of its activity under mild operating is a useful catalyst for the iodination of amino compounds.



Hydroiodic acid and alkali hypoiodites; like the corresponding chlorine and bromine compounds, find employment in iodination.

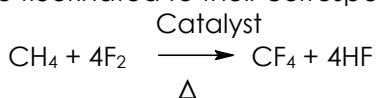


1.34 FLUORINATION

Fluorine acts directly on hydrocarbons to produce fluorides, but the reaction is violent and constitutes an explosion hazard. Some reactions can be carried out by careful control of temperature and fluorine concentration, but even then there may be a cleavage of carbon-carbon bonds.

1.32.1 Direct fluorination

Direct vapour phase fluorination using elemental fluorine is done by using large volumes of an **inert gaseous fluorine** and hydrocarbon carrier, such as nitrogen, a mixing system that rapidly and intimately brings the two reactants into contact and a reactor design that effectively removes the heat of reaction. Under these conditions, hydrocarbons can be fluorinated to their corresponding fluorides:



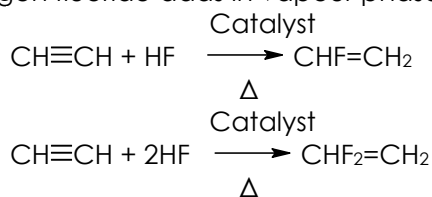
Dilute fluorine reacts with **metal carbides** such as UC_2 , ThC_2 , and CaC_2 producing **fluorocarbons** and **metal fluorides**. All these direct fluorination reaction are accompanied with high energy type of condensation reactions where fluorocarbons of higher carbon chain length are formed. Miller claims the use of elemental fluorine as a condensing agent in liquid phase reactions to form higher molecular weight compounds.

Liquid phase fluorination has been demonstrated on number of compounds, but the **hazards** of violent detonations and wide **diversity of products** so far have **limited** the use of these procedures.

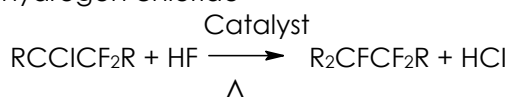
Fluorine reacts with graphite under a variety of conditions to form solids other than the usual C_nF_{2n+2} structures. Carbon tetrafluoride can also be produced if the temperature is high.

1.34.2 HF as a fluorinating agent

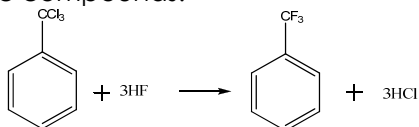
Hydrogen fluoride adds in vapour phase by means of catalysts to acetylene.



Hydrogen fluoride may also replace chlorine in aliphatic chlorofluorocarbons, liberating hydrogen chloride

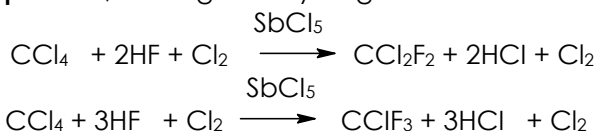


Hydrogen fluoride in a liquid-phase reaction readily replaced chlorine in many organic compounds.



1.34.3 Fluorination with metal fluorides

The majority of **organic fluorides** produced today are still made by the **antimony halide process**, starting with hydrogen fluoride and antimony pentachloride



The reaction proceeds through the antimony pentahalide salts, with the major reactants believed to be a mixture of SbCl_2F_3 and more highly fluorinated halide including SbF_5 .

A number of the polyvalent metal fluorides are excellent fluorinating agents and are used in commercial reactions.

1.34.4 Electrochemical process

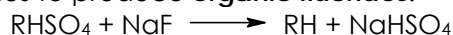
The preparation of a great number of **fully fluorinated compounds** by introducing **starting products such as** acids, amines, hydrocarbons, nitriles and alcohols is into cool anhydrous hydrogen fluoride in an **electrolytic cell** under about **5 volts** potential is a very ingenious economical means for many of these products. This process is limited to saturated perfluoro compounds. Non-electrolyte raw materials complicate this operation.

1.34.5 Inter-halogen Fluorination

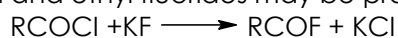
The use of **halogen fluorides** as a means of fluorination has been of **military importance** since their manufacture in World War II as potential of high-energy fuel for rockery. At low to moderate temperature, reaction results in the addition of fluorine to the double bond or the substitution of hydrogen or other halogen. At flame temperature the end products will be mainly CO , CO_2 , HF , F_2 or O_2 .

1.34.6 Fluorination with alkali metal fluorides

Sodium and potassium fluorides/ react with alkyl hydrogen sulfates and with acid chlorides to produce **organic fluorides**.

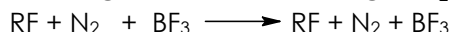
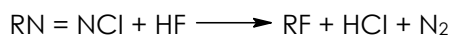


Methyl and ethyl fluorides may be produced in this manner.



1.34.7 Diazo reaction

Aromatic diazo compounds react with **hydrogen fluoride** and **boron trifluoride** to form aromatic fluorides with the liberation of nitrogen



These are still the best methods of obtaining fluorinated aromatic compounds.

1.35 CHLOROBENZENE /DICHLOROBENZENE

1.35.1 Raw materials

Basis - 1 ton chlorobenzene

Benzene - 1,900 lb

Chlorine- 1,750 lb

Iron turnings small (1 %)

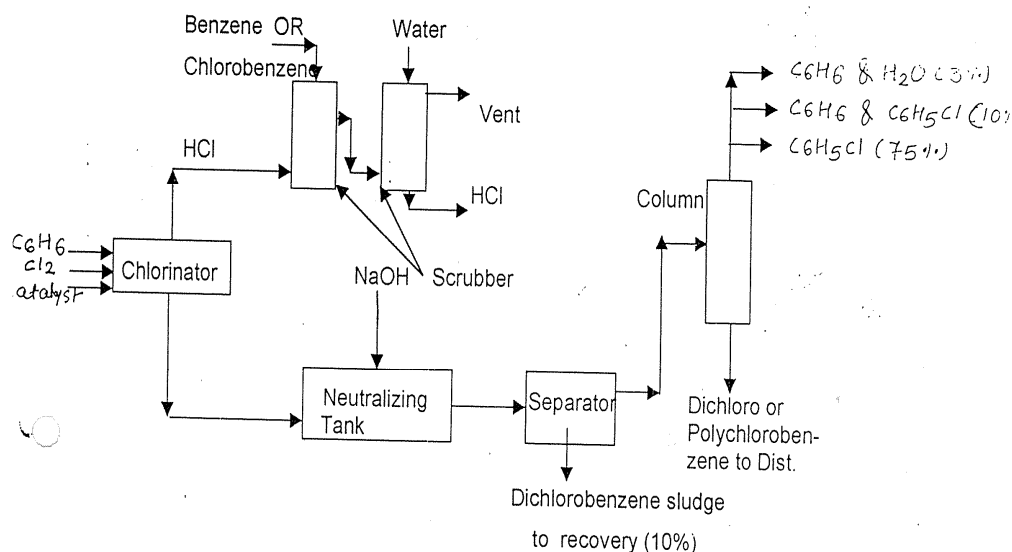
1.35.2 Reaction



1.35.3 Manufacture

Batch process

Dry **benzene** is charged into a tall **cast iron or steel tank** (chlorinator) lined with lead or glass. About **1%** by weight (of the benzene charge) or **iron turnings** is used by weight of the benzene charge or iron turnings are used as the catalyst and remains in the chlorinator after each batch. **Chlorine** is bubbled into the charge at a rate of keep the temperature at **40°C to 60°C**. The chlorination is continued until the proper density is reached. When only mono-chlorobenzene is desired, the chlorination temperature is **maintained** at about **40°C** and about 60% of the theoretical chlorine is used. When all the benzene is chlorinated, the reaction is run at the temperature **55-60°C** and a **density of 1.280 gm/cm³** (15°C) is reached in about **6hr**.



HCl given off during the reaction is **scrubbed with** benzene or chlorobenzene to remove organic spray and is absorbed in water in a suitable absorption system to give hydrochloric acid. In most modern continuous plants, a low vapour pressure oil is used as the scrubbing medium and high grade acid is recovered.

The **chlorinated benzene** is delivered to the **neutralizer** a jacketed steel tank equipped with a **reflux condenser** and vent containing an aqueous solution (10%) of **caustic soda**. The charge is thoroughly **agitated** to ensure neutrality and is kept warm by jacketed steam. The faintly alkaline chlorinated benzene is allowed to settle in the **separator**. **Sludge** collected from the bottom for **distillation**. The bulk of the material is distilled and separated into several fractions. If the chlorination is carried out so that the theoretical quantity of chlorine is consumed (100% chlorination), the following fractions are obtained in approximately the indicated percentage.

Material	Percent
Benzene and water	3
Benzene and chlorobenzene	10
Chlorobenzene	75
Chlorobenzene & dichlorobenzene	10
Resinous materials and loss	2

The **first two fractions** are returned to the system for further processing and the **third** (chlorobenzene) is run to storage. The **fourth fraction** is allowed to accumulate and is then distilled. The **para isomer** is collected in the distillate; the **residue** contains the ortho isomer contaminated with some para isomer and polychlorobenzenes, principally 1,2,4-trichlorobenzene. Of the two isomeric dichlorobenzene (practically no meta isomer formed.), the para to ortho formed in the larger quantity; the **ratio of para to ortho** is approximately **3:1**. The composition of the chlorinated products varies according to the chlorination temperature, rate, degree and catalyst. However, 100 percent chlorination will yield approximately the following composition:

Material	Percent
Chlorobenzene	80
p-dichlorobenzene	15
o-dichlorobenzene including polychlorobenzene	05

When **monochlorobenzene** is **desired** with the formation of a minimum amount of higher chlorinated products, the combination chlorination and fractionation apparatus may be used. In this manner, the **monochlorobenzene** is **isolated as quickly** as it is formed and only fresh benzene is exposed to the chlorine. Dry benzene and catalyst (iron turnings of anhydrous ferric chloride) are charged simultaneously into a chlorinator and fractionating chamber. The **benzene** in the chlorinator is **heated** to its **boiling point** and chlorine is introduced. The **partially chlorinated** material is **distilled**, condensed and return to the chlorinator. The **monochlorobenzene** is **withdrawn** from the fractionating column and is **neutralized** and **distilled** in the manner described in the batch process.

Because of the increasing uses for p-dichlorobenzene, it's by product production has been supplemented by its manufacture as a primary product. This is accomplished by chlorinating benzene in the presence of **aluminium chloride** to give a **high yield of p-dichlorobenzene**. Monochlorobenzene may also be made by the vapour phase oxy-chlorination of benzene with hydrogen chloride and air in the presence of a catalyst. At present, this process is carried out only in conjunction with a phenol process.

1.36 BHC : Benzene hexachloride or Hexachlorocyclohexane

1.36.1 Raw material

Benzene

Chlorine

1.36.2 Manufacture

Benzene is chlorinated in the **liquid phase** in the presence of **an activation agent** such as activating light, gamma rays, or elemental chlorine. A mixture of five isomers of 1,2,3,4,5,6-hexachlorocyclohexane is produced. Only the **gamma isomer** is **insecticially active**

The continuous co-current gas pipe chlorinator modified to include external cooling is the most interesting from an engineering standpoint

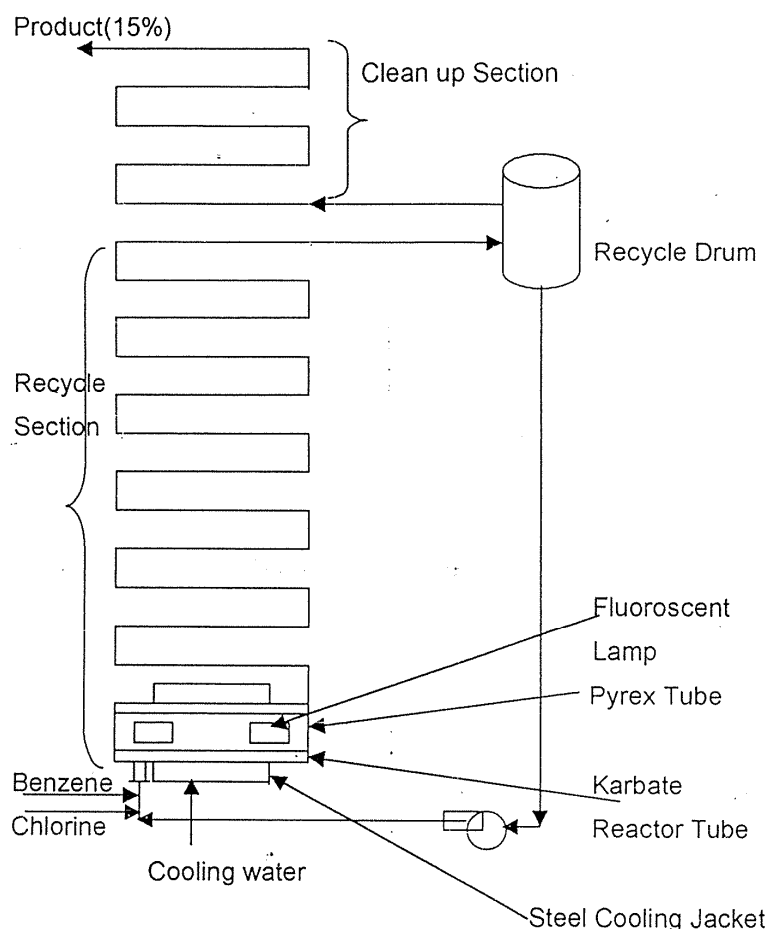


Figure: Two stage BHC petrochemical reactor

The **commercial reactor** consists of **13 reactor tube** in the **recycle section** and **5 reactor tubes** in the **clean up section**. Each **reactor tube** consists of a concentric arrangement of a **2-in Pyrex tube** into which, two **40 - watt fluorescent lamps** are inserted a **4 inch Karbate tube** enclosing the reactor section and an **8-inch steel pipe** enclosing the **cooling section**. **Chilled water** at **60°F** circulates in the annular section enclosed by the steel pipe and removes the heat of reaction, which is estimated and checked calorimetrically to be around **190,000 Btu per lb mole BHC**. A reaction **velocity constant** of **1.5 min⁻¹** is used throughout, although a lower constant should probably apply for the cleanup selection. This reactor has a **chlorine conversion** capacity of around **600 lb per hr** and produces **14 -15% gamma BHC** operating at temperature in the range **90 -100°**. The actual design feed concentration is around **11 weight percent, Cl₂** in order to keep the resulting BHC level below **15 weight percent** of the contents.

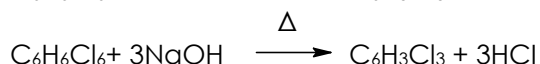
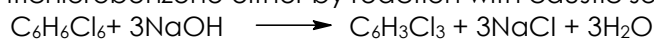
The use of a polar solvent can materially alter the course of a liquid phase photochlorination.

The **product** leaving the chlorinator is a mixture of **15 % benzenehexachloride** in a **solvent**, which may be completely removed by evaporation leaving a musty smelling crystalline product.

Most commercial producers, however, **evaporate** the **solvent** until a solution just saturate in gamma isomer exists. Under these conditions much of the alpha and beta isomers may be filtered from the mother liquor, which can then be dried to fortify BHC of **35-50% gamma** content.

A **number of processes** have been developed for the **purification of the gamma isomer to 99 %** purity which is commercially marketed as Lindane.

The **waste isomers** from either the fortification process or the Lindane process can be converted to trichlorobenzene either by reaction with caustic soda or other alkalis.



Or they can be thermally decomposed; with or without catalyst to trichlorobenzene. The isomers formed in either case are predominantly 1, 2, 4-trichlorobenzene and about 10-20 % of the 1, 2, 4 – isomers. In the thermal dehydrochlorination, some disproportionation occurs with the formation of dichlorides and tetrachlorides and shift to the stable 1,3,5 – trichlorobenzene isomer can be produced in the presence of catalyst.

1.36.3 Uses

Gamma BHC has great utility for the control of vegetable, field crop, animal and household insects. The gamma isomer is produced in concentration ranging from 9-30% of the mixture of crude isomers. The other isomers have no insecticidal value, the delta isomer being toxic to many leafy plants.

1.37 EXERCISE

1. Differentiate between unit process and unit operation 02
2. Discuss the advantages of continuous process and batch process over each other 05
3. Describe the continuous nitration of benzene with fortified spent acid
4. Define nitration. Enlist various nitrating agents and discuss the function of sulphuric acid in the mixed acid used for nitration 05
5. Describe the batch nitration of benzene with mixed acid 05
6. Give an account on methods of reduction for the preparation of amines. Illustrate various products of reduction of nitrobenzene 06
7. With the help of flow diagram describe the manufacture of aniline from nitrobenzene 05
 1. By Bechamp reduction or
 2. By catalytic vapour phase halogenation
8. Describe various methods of chlorination of organic compounds 03
9. Explain kinetics and mechanism of aromatic nitration. What is the effect of nitrous acid on nitration 04
10. Give various reagents used for aromatic chlorination 05
11. Describe gas phase and liquid phase nitration 05
12. Define nitric ratio, D.V.S. with example 04
13. Describe the manufacture of BHC 05
14. What is amination by reduction? State various methods of preparation of amines. Write a note on Bechamp reduction 07
15. Describe the manufacture of p – nitroacetanilide 05
16. Define unit process. Why is it so called? How do unit processes differ from unit operation? 02
17. Give an account of oxy-nitration of benzene 03
18. Describe the manufacture of m-dinitrobenzene from benzene 05
19. Describe construction, working and uses of 06
 1. Schmidt nitrator
 2. Biazzi nitrator for continuous nitration process
20. Give a brief account of nitration of paraffinic hydrocarbon 05
21. Give evidence to establish the formation of nityl ions in a nitration process conducted using mixed acids 03

1.38 FURTHER READING

1. Unit Processes in Organic Synthesis by P. H. Grogins