

Reference — Industrial Chemistry by B.K. Sharma

(I) Synthesis of DDT

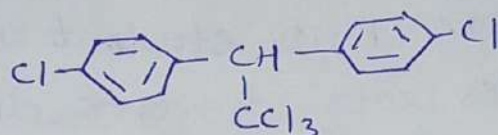
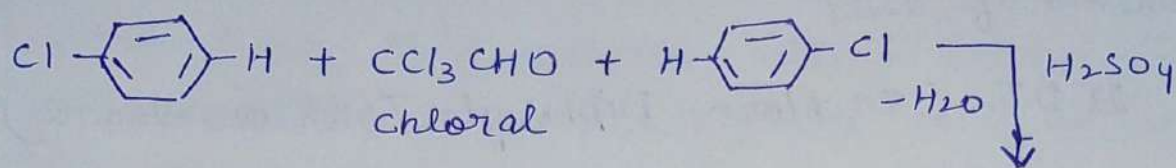
D.D.T. (Dichloro-Diphenyl-Trichloro ethane)

DDT was first prepared by O. Zidler, a German Ph.D. student in 1874. Its insecticidal properties were however discovered by a Swiss chemist, Paul Muller in 1939. DDT kills lice and mosquitoes which carry the germs of typhus and malaria fever respectively. DDT was the first chemical to have the property of killing insects only ~~insects~~ by means of contact. DDT is still the backbone of many insect control programmes, and is widely used as a household insecticide, against leaf hoppers and potatoes and in cotton insect control. Some insects possess an enzyme, which converts DDT into a harmless product by elimination of HCl from the chloral residue. Hence these enzymes are resistant to DDT. Fortunately, insects that are not controlled or killed by DDT, are killed by gammexane or Dieldrin, DDT is a remarkably powerful and persistent insecticide and soluble in kerosene oil, petrol and ethyl alcohol, but insoluble in water

⇒ Manufacture of DDT =

DDT is manufactured by exothermic condensation of chlorobenzene (2-4 parts), with chloral (1 part), at about 30°C in presence of oleum or 99% sulphuric acid (10 parts)



Chemical reaction  $\Rightarrow$ 

p-isomer of DDT

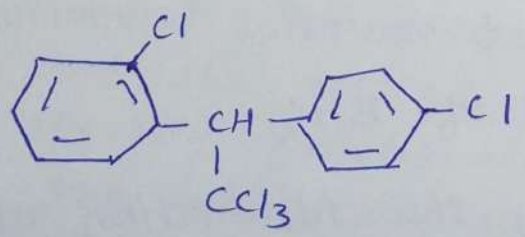
Chloral and chlorobenzene are condensed in a glass lined reactor in presence of 90-100% conc.  $\text{H}_2\text{SO}_4$ . The reaction takes 5-6 hours and temperature is maintained at 15-30°C, by external cooling. The external cooling is done by means of brine or steam coils. The spent acid is withdrawn and the crude mixture of DDT and unreacted chlorobenzene is then conveyed to a dryer, where steam melts the DDT and distils any unreacted chlorobenzene, overhead. The molten DDT is then passed to casting pans and practically pure product, thus obtained is pulverised for the market.

Chloral used for the purpose is obtained by the reaction of ethyl alcohol (0.75 parts) with chlorine (2.58 parts) in the presence of 98%  $\text{H}_2\text{SO}_4$  (1.73 parts) in a glass lined steel shell provided with a jacket for temperature control (45-50°C) through brine solution. In the beginning temperature is kept at about 30°C then raised to 45-50°C and maintained for about 1 hour, it is further increased to 75°C for another 1 hour and then raised slowly to 90°C at the rate of 1°C per hour.

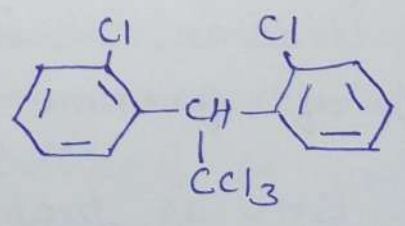


The overhead gases consist of excess alcohol vapours, some  $Cl_2$  and  $HCl$  along with some ethyl chloride. From this mixture, alcohol is recovered by condensation, and transferred back to the reactor to be used again. Water absorbs  $HCl$ . The heavy liquid consisting of chloral-alcoholate is decomposed by dilute  $H_2SO_4$  into chloral and alcohol. These are separated by fractional distillation.

Actually the commercial DDT is a mixture of various isomers in which the para isomer; 2,2-bis(p-chlorophenyl)-1,1-trichloroethane is present in 70%, the ortho-para 10-15% and the rest being related compounds and impurities.



O-p' prime isomer of DDT



O-o' prime isomer of DDT

The purified p-p' isomer is a white crystalline solid (m.p  $100^\circ C$ ). DDT is generally used as a dust containing 5-10% emulsions having 25% of the material and also as aerosols.



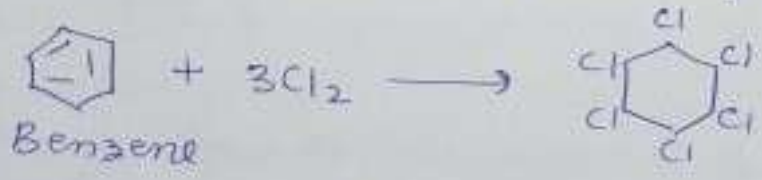
(II) B.H.C. or Benzene Hexachloride

BHC or Benzene hexachloride or more correctly 1, 2, 3, 4, 5, 6-hexachlorocyclohexane is another important potent insecticide, which exists in a number of stereoisomers, the gamma being the most toxic.

The commercial BHC possesses 5 main geometrical isomers. The percentage of each of the isomer in the commercial BHC is alpha (55-70%), beta (5-14%), gamma (10-13%), delta (6-8%), epsilon (3-4%). Later on various isomers were seperately prepared or seperated from the mixture and it was found that BHC has insectisidal property of gamma-isomer.

The gamma BHC is usually known as Gammexane or Lindane. It is refined material containing 99% of gamma isomer of BHC.

The BHC is prepared by the chlorination of benzene in presence of sunlight.



chlorine gas is passed into benzene liquid in the presence of sunlight. The product is a mixture of five out of eight possible isomers of which the physiologically active isomer does not exceed 18%. The amount and formation of  $\gamma$ -isomer has been found to increase in presence of some substances such as sulphur, selenium,



tellurium, nitrotoluenes, dialkyl peroxy dicarbo-  
nates etc. Excess of benzene is used in order  
to keep the products in solution and to continue  
the reaction under homogeneous conditions.

The reaction can also be carried out in presence  
of  $\gamma$ -radiation or Fluorine (elemental) instead  
of U. V. radiation.

The manufacture can be carried out by  
batch processor or by continuous process. In batch  
process technical grade benzene and chlorine  
are reacted in a lead lined vessel provided  
with cooling arrangements and mercury vapour  
lamp is used as a U. V. source. The temperature  
is kept between 15-20°C and pressure is main-  
tained slightly above atmospheric pressure in order  
to minimise the loss of benzene. The reaction  
is continued till the BHC concentration attain  
12-15%. The excess of chlorine is air blown  
and the mother liquor is concentrated and  
finally fractionally crystallised to isolate  
the biologically active  $\gamma$ -isomer.

In continuous process chlorination is  
carried in a glass lined pipe chlorinator in  
the continuous tube of which benzene is taken  
and U. V. source is two 40 watt fluorescent  
lamps. The temperature is 40-60°C and  
pressure is atmospheric. The chlorination is  
continued till the concentration of BHC  
reaches 13-14.5%. The chlorinated liquor  
is concentrated at 85-88°C till it becomes  
saturated in  $\gamma$ -isomer and almost all the  
 $\gamma$ - and  $\beta$ - isomers are crystallised out. The  
crystals are separated by filtration and



the filtrate or mother liquor is subjected to steam distillation.

The molten residue in the vessel is cooled to get lumps of crude BHC containing 25% of the  $\gamma$ -isomers. The isomer is then extracted by solvent extraction using hexane-nitromethane solvent mixture. The ground solid is then dedewised with treatment with oleum or agitation in air with  $CaCO_3$ ,  $MnO_2$ , kaolin and manganese linoleate.  $\gamma$ -isomer of BHC is more soluble than other in most organic solvents. It kills or controls insects, grass hoppers and common pests and used in the form of dust containing 5-10% of the ingredients in emulsion containing 25% of the  $\gamma$ -isomer and also as granules having 6-10% of the active principal

GAMMEXANE  $\rightarrow$  Crude BHC is generally not suitable for food crops, because of its strong musty order. Gammexane or lindane, a refined material containing 99% of the BHC, has largely overcome the odour  $\gamma$ -benzene hexachloride is a colourless, practically odourless solid, insoluble in water, but soluble in organic solvents.

Gammexane has exceptional insecticidal activity, comparable to that of DDT and may be used as a food crops. Insects that are not killed by DDT are killed by Gammexane. Gammexane has also been applied successfully against the common disease carrying insects, household stock horticulture, stored food and agriculture pests. It also used as an agricultural pesticide

(7) (A)

99% pure BHC, called lindane or Gammexane is prepared by its selective crystallisation followed by repeated solvent extraction. Lindane or Gammexane is sparingly soluble in water but soluble in acetone. It is stable to air, heat and light. It is also stable to strong acids but decomposes in contact with hot alkalies. It has no contact action on human system and so it is safe insecticides for domestic use. It is applied as dust, emulsion, granules and as water dispersion.