INDUSTRIAL CHEMISTRY

CHAPTER- CHEMISTRY OF PESTICIDES

ONLINE LECTURE

NO. 1

DATE:- 6, MAY 2021

TIME: (10.00A.M.)

1) Industrialization and urbanization
2) Population, Food shortage, Starvation
3) Biotic factors, Animal pests, Microorganisms, Weeds
4) 32-38% loss
5) Preservation of food a problem
6) Kill necessary enzymes, feeding of animals
7) Pesticides eliminate pests from agriculture and house
8) Quality and quantity of crops, protect humans from disease, livestocks
9) Without pesticide 50% loss
10) Cide means killer, troublesome harrasement
11) Fly killer, ant killer, repellants, rodenticides and fungicides, wood and carpet, wood preservation
12) Deliberate spreading of pesticide
13) But excess health hazards, pollution
14) Secondary metabolites are toxic

Introduction: - Due to the industrialization and urbanization, the agriculture area gets reduced day by day. There is always increase in food shortage due to increase in population. More than half the population present on the Earth is in the state of starvation. In accordance with the data present in the reliable estimates, biotic factors, such as animal pests (kitak in marathi), micro-organisms and weeds, reduces the yield from the agricultural sector by 32-38%. This loss is unacceptable, and attempts have been made to minimize it in the future. Similarly, the preservation of fresh agricultural products is also a major problem. Pesticides are many diverse groups of chemical compounds, which are used to eliminate pests in agriculture and households. They enable the quantities and the quality of crops and food to be controlled, and used to protect humans against the insect vectors of disease-causing pathogens, to protect crop plants from competition from abundant but unwanted plants (i.e., “weeds”), and to protect crop plants and livestock (Cattle) from diseases and depredations (destroy) by fungi, insects, mites, and rodents. Without the use of pesticides, up to 50% of the agricultural products would be lost.

A pesticide is a bug-killing poison. The Latin suffix cide means "killer," and in pesticide, it's combined with the English word pest, means a troublesome harassment.

There is a wide range of pesticides found used in non-agriculture situations such as industries, public health and for a number of purposes in the home. Domestic use of pesticides is mainly as fly killer, ant killer, repellants, rodenticides and fungicides etc. By and large industrial use of pesticide is of vital importance in the industries such as wood and carpet, wood preservation etc. Pesticides are therefore a major tool in public health, mainly for the control of vector borne diseases and harmful insects. At difference from any other chemical substance of human use, pesticides are deliberately spread into the environment with the aim of controlling undesired living species. However excessive use of these chemicals leads to the microbial imbalance, environmental pollution and health hazards.

The range of crop pests is exceptionally broad. The common pathogens (rogjanak in Marathi) responsible for the plant diseases are microorganisms-micro fungi (burashi), bacteria (jivanu) and viruses (vishanu) which are developed very rapidly within the host plant and having some bio-chemical interactions with the host. These guest attacks on the enzymes and proteins present in the host plant by producing toxic substances which are responsible for the inhibition of the activities of essential enzymes present in the host. Or the pathogens themselves create some other enzymes which degrade an important component of the host. As far animal pest is in the concern, insects of the highest economic significance, they can damage the host plant either directly by feeding on it, or indirectly by spreading numerous viral diseases. In general, the loss reduction is not the only aim of the protection of the plant. But, it has also been noted that certain rust (corrosion) and smut (kajali) fungi produces secondary metabolites which exhibits a toxic action not only over the crops, but also for human beings and domestic animals.

Today the probable number of pesticidally active substances present in the market is almost more than thousand. But nevertheless, the field of agriculture is far away from the goal of utilizing a separate pesticidally active substance for each individual crop, each individual disease, and, in general, for each individual risk/benefit situation. Pesticides will continue to be part of human life and the environment in order to increase crop production.

History of Pesticides: - Pesticides are chemical agents used since the beginning of human history to eradicate or to control undesired organisms (“pests”) in agriculture, animal breeding and public health. Pesticides are therefore a major tool in public health, mainly for the control of vector-borne diseases (infection caused due to bite of insects) and noxious (Harmful) insects.

Early contribution of China in the generalization of chemical pesticides in the period as early as 3000 B.C. towards the utilization of a mixture of lime, woods ash and chalk for killing insects. In the next, use of sulfur dioxide, burning sulfur, has also been tested for keeling insects. Notwithstanding, it has been evidenced that Leonardo-da Vinci also suggests the utility of arsenic against harmful insects, and in England, in the beginning of the 19th century, fruit trees were protected against powdery mildew (burashi in marathi) by coating them with lime-sulfur solution, which is to be made by boiling sulfur, lime and water.

However, the actual research work in the field has been started in the middle of the nineteenth century in synthetic organic chemical laboratories. In this regard, in the nineteen-thirties the insecticidal action of DDT, BHC and organophosphorus esters, and the herbicidal properties of phenoxyacetic acid derivatives, were discovered, and for the first time modem synthetic organic pesticides were introduced to the world. Furthermore, in the 20th century an outstanding development in the field of organic chemistry, it became an applied science, which very successfully coupled with bio-sciences, medical sciences and, last but not least, with agricultural science as well.

In 1939, Paul Muller discovered that DDT was a very effective insecticide. It quickly became the most widely used pesticide in the world. However, in the 1960s, it was discovered that DDT was preventing many fish eating birds from reproducing which was a huge threat to biodiversity.

The practices maintain the records of the attempts which have been made to combat (battle) pests with chemicals in several thousand years ago.

Definition of pesticide: -

"The substance or mixture of substances used to prevent, destroy, repel, attract, sterilize, mitigate (Reduce) any insects is called as pesticide".

Generally pesticides are used in three sectors viz. agriculture, public health and consumer use.

Importance of pesticides: -

1) They increase the yield and quality of agricultural products.

2) They control the numbers of pests which are responsible for destroying whole plants or their parts.

3) Increase the production of animal and plant biomass.

4) They fight against microorganisms causing farm produce to rot and to decay.

5) They fight against algae, bacteria, fungi and weeds.

6) They kill harmful organisms in farm buildings, the home, hospitals, stores and vehicles.

INDUSTRIAL CHEMISTRY

CHAPTER- CHEMISTRY OF PESTICIDES

ONLINE LECTURE

NO. 2

DATE:- 10, MAY 2021

TIME: (9.00A.M.)

1) Industrialization and urbanization
2) Population, Food shortage, Starvation
3) Biotic factors, Animal pests, Microorganisms, Weeds
4) 32-38% loss
5) Preservation of food a problem
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11) Fly killer, ant killer, repellants, rodenticides
12) and fungicides, wood and carpet,

wood preservation

12) Deliberate spreading of pesticide
13) But excess health hazards, pollution

3.3. Classification of the Pesticides: - Pesticides can be classified in several ways. The clearest and most widely used classification is based on the practical purpose of application.

1)Microbicides: - These have their action against microbial pests. Amongst the microbes, fungi are responsible for the heaviest agricultural loss and consequently, fungicides are associated with the most important group of microbicides. Moreover, the plant diseases originated from bacteria are of considerably less significant, and therefore, the research in the field of bactericides has not been well-developed or remains unattained.

2) Zoocides: - Pesticides are classified as zoocides for their action against animal pests. Any substance intended to kill or controlling animals is called as Zoocide. It is evident that almost all animal pests, insects cause the greatest losses in agricultural sector. Hence, the anti-insect agents are considered as the most important zoocides. These agents can further be divided into two groups on the basis of their mode of action.

3.3.2 a] Conventional insecticides as anti-insect agents: -

The conventional insecticides on the basis of their action on the nervous system of an insect has been further classified as a chemical compound or a group of chemical compounds obtained from natural origin, arsenic based compounds, chlorinated hydrocarbons, organophosphorus compounds, carbamates, and other compounds.

3.3.2 b] Novel insecticides as anti-insect agents with specific action: -

Although, novel anti-insect agents are again classified on the basis of their mode of action, however this biological subdivision at the same time comprises with the group of chemicals. The most significant categories of novel anti-insect agents are insect growth regulators, chemo-sterilants, pheromones and anti-feeding agents, which are used numerously in the farm lands. In addition to that, zoocides are also classified as, acaricides (mite killers), nematocides (nematode killers) and rodenticides (rodent killers), which are used rarely.

3.3.3. Herbicides: - Pesticides have been classified as herbicides for their significant action against the weeds. In this regard, weed-killers (herbicides) are the chemical tools or the chemical compositions which are developed especially for controlling weeds those are harmful to the crops. Herbicides are also commonly known as weedkillers, which are the substances used to control unwanted plants. Due to their tenacity, rapid methods of growth and reproduction, they deprive of the nutrients from the farm, which otherwise would have been available to the crop plants. In short, they compete with the crop plants and many a times hamper the growth and development of the crop. The cultivator suffers to getting proper output from his crop.

Herbicides include an unlimited variety by means of their chemical composition and with respect to their mode of action as well. The later classification i.e. their mode of application, have also been distinguished as foliar herbicides and soil herbicides, and with respect to the time of application, pre- and post-emergent herbicides.

It is surprising that, almost forty thousand compounds are prepared successfully and screened for biological applications, out of which only one fulfils the requirements for practical application. Furthermore, pesticide residue creates significant hurdles in the official registration of a new pesticide. In this regard, several ways has been very aptly developed for the safe application of the pesticide. The maximal permissible residue; is the highest tolerable quantity of the pesticide residue in mg/kg, which is properly set down by the proper Government regulatory authorities on the basis of daily intake and the actual residue quantities found in the trials. Moreover, the waiting time which is the minimal period, generally expressed in days, which must pass between the last treatment and harvest. Furthermore, the waiting time has been established on the basis of the toxicity exerted by the active substance and its rate of degradation.

3.4 Benefits and adverse effects of pesticides: -

Currently, the term pesticide is considered as a group of different chemicals proposed for preventing, destroying, repelling or mitigating any sort of the pest. For example, algicides, antifouling agents, antimicrobials, biopesticides, biocides, disinfectants, fungicides, fumigants, herbicides, insecticides and the list has been grown day by day. Pesticides have been used throughout the world to decrease the damage by insects and other pests to plants, to regulate the growth of undesirable plant species and to provide an effective shield to public health against disease-causing organisms, as well as disease carriers like mosquitoes, ticks, cockroaches, and rats.

In short, the benefits of pesticides can be summarized as-

Advantages of pesticides are: -

1) Improved crop and livestock quality and yields.
2) Food security, pesticides help to keep food affordable.
3) Reduced international spread of disease.
4) Pesticides reduce waste of crops, land, water, time, and other valuable resources.
5) Pesticides can save farmers' money by preventing crop losses due to insects and other pests.
6) Pesticides help to reduce waterborne and insect transmitted diseases.
7) Pesticides help to conserve the environment.
8) Herbicides have removed the hardship of hand weeding.
9) Pesticides have transformed developing countries into food producers.
10) Securing what is in storage.

On the other hand, tremendous use of pesticides in agricultural and domestic sector leads so oftenly the exposure of non-target organisms, including humans to these biocides.

Therefore, toxicological details of the pesticides and their toxic potential have to be sensibly assessed before their marketing and distribution. Every time it is taking into an account that each and every organic compound might be harmful to humans, as well as to other animal species, and the environment. In this regard, risk assessment procedures have been designed with the aim, to evaluate the impact of pesticides on the environment and from the perspectives of sustainable developments risk assessment procedures are enormously demanding in terms of health, money and time as well.

In short, the adverse effects of pesticides can be summarized as-

The disadvantages of pesticides are: -

1) Domestic animal contaminations and deaths.

2) Loss of natural oppose to pests. 3) Pesticide resistance.

4) Honeybee and pollination decline. 5) Contamination of groundwater.

6) Losses to adjacent crops, fishery and bird losses.

7) The fertility of soil is affected by the death or damage to microorganisms caused by pesticides.

8) Some pesticides induce immunotoxicity in humans which may lead to immunosuppression, hypersensitivity (allergies), autoimmune diseases, and inflammation. People who work regularly with pesticides, suffers from adverse effects that can occur months or years after exposure. Examples of acute health effects include stinging eyes, rashes, blisters, blindness, nausea, dizziness, diarrhea and death such as farmers, are at greater risk of cancer.

3.5 Structure Activity Relationships: -

The study on the relationships between molecular structure and physicochemical and biological response is collectively known as Structure-Activity Relationships (SAR). When performing a SAR analysis, it is assumed that the chemical or biological response produced by a substance (usually an organic compound) is a direct function of its chemical structure. The basic assumption for all molecule based hypotheses is that the same substance will always produce the same response, under a given set of experimental conditions. This principle is also called Structure–Activity Relationship (SAR). However, "chemical structure" cannot be dealt with directly.

During synthesis of different compounds, non-targeted organisms such as pets, birds, fishes and mammalians, and adverse effects on eye and skin irritation, neurotoxicity, cancer and birth defects, has to be tested before marketing pesticides. Such study necessitates enormous efforts in terms of testing animals and no-doubt huge money as well. In the modern science variety of tools are available to reduce direct costs of the formulation, quite a large number of probable alternatives have been proposed and evaluated by the Government regulatory authorities. Amongst them, the utilization of (Quantitative) Structure-Activity Relationships [(Q) SAR] has strongly been encouraged by both EU and USA regulators as a sophisticated tool for supporting and optimizing risk assessment strategies. Quantitative Structure-Activity Relationships (QSAR) is a method to derive certain effects or properties of chemical substances in the absence of experimental data. For pesticides, the data requirements demanded for their authorization.

Quantitative structure-activity relationship (QSAR) methods are important for prediction of biological effect of chemical compounds based on mathematical and statistical relations. (Q)SARs are the structure-oriented methods of estimation, which are developed and used to visualize certain set of properties of the chemicals or the formulations. An effective utilization of (Q) SAR practices will allow likely the savings of millions of test animals and billions of euros, enhancing cost- and time-effectiveness of the risk assessment procedure. Generally, the use of (Q)SARs is proposed for the following purposes:

1. Providing an assistance for data evaluation,
2. Contributing very significantly in the decision-making process,
3. Establishing very clearly the input parameters which are necessary to conduct exposure assessment, and
4. Identifying effects which may be of potential concern on which test data are not available.

All the above listed purposes state and explain the importance of (Q)SAR in supporting the risk assessment procedures.

Presently, the REACH (Registration, Evaluation and Authorization of Chemicals) legislation very clearly mentioned that the QSAR is one of the most significant tools, which minimizes the use of animals and resources up to certain extents for the purpose of evaluating industrial chemicals. This also advocates that (Q)SARs are the ideal tools for addressing regulatory tasks, and undeniably, they are very widely used by USEPA (U.S. Environmental Protection Agency). At present, the lack of standardized, reproducible, and reliable (Q)SAR protocols has raised serious concerns about the reliability of current methodology.

INDUSTRIAL CHEMISTRY

CHAPTER- CHEMISTRY OF PESTICIDES

ONLINE LECTURE

NO. 3

DATE:- 11, MAY 2021

TIME: (9.00A.M.)

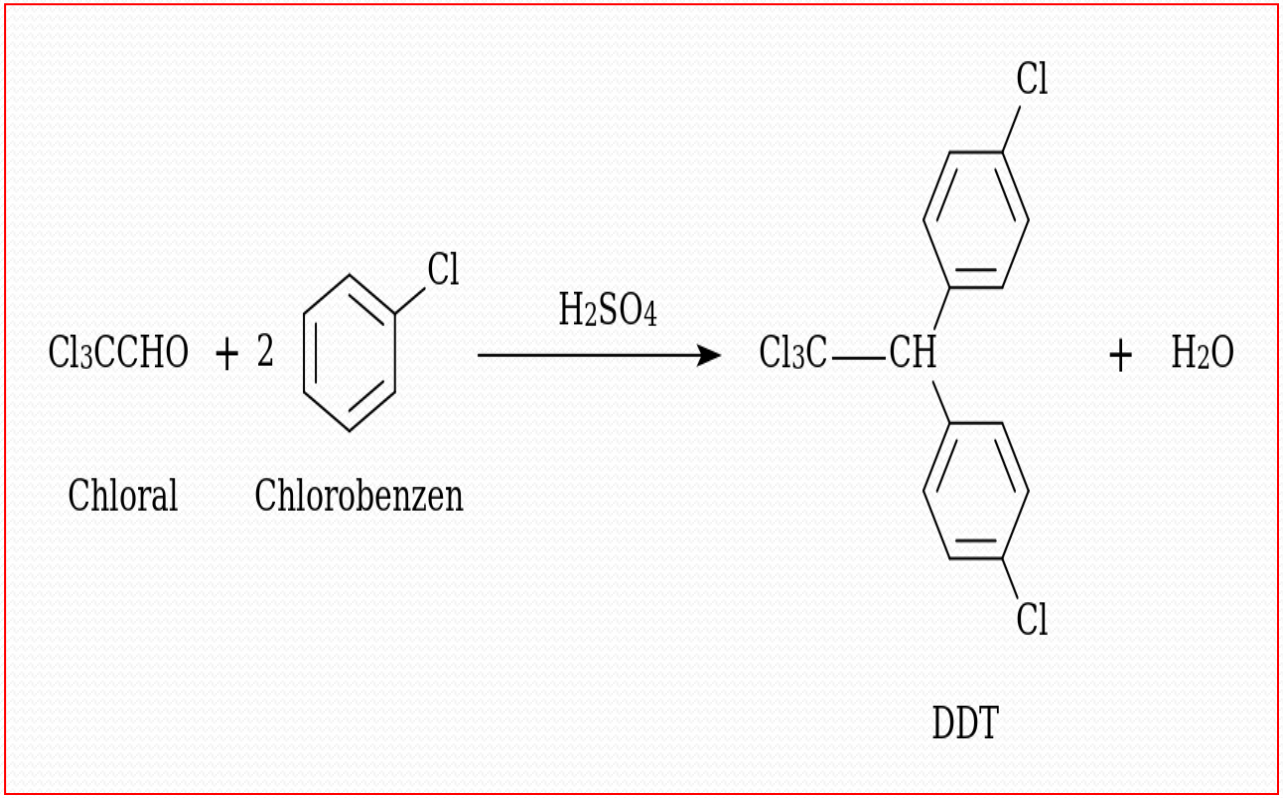
3.4. Synthesis and uses of representative pesticides in the following classes: -

3.4.1] Organochlorines: - The development of chlorinated hydrocarbons has been initiated in the 1940s after the discovery (1939) of the insecticidal properties of DDT. Additionally, BHC, Chlorobenzilate, methoxychlor, and the cyclodienes (which include aldrin, dieldrin, chlordane, heptachlor, and endrin) are also turned in the family. Toxic action of these compounds still not fully understood, but it is to be considered that they are having a potential to disrupt the central nervous system. As these compounds found toxic to human beings therefore these insecticides have been banned.

3.4.1. a] DDT: - DDT, or dichlorodiphenyltrichloroethane, also known as 1,1,1-trichloro-2,2-bis(p-chlorophenyl) ethane, a synthetic insecticide belonging to the family of organic halogen compounds, having strong ability to attack on central nervous system and recognized as highly toxic material towards a wide variety of insects as a contact poison.

Synthesis of DDT: -

The compound DDT was already described by Zeidler in 1873 and Baeyer *et al*. in1974. They industrially synthesize DDT by the reaction between chloral and chlorobenzene in the presence of sulfuric acid as a condensing agent (Rueggeberg and Torrance, 1946) (Scheme 1).



DDT have broad window of insecticidal efficiency. In 1942, DDT as a crop protection agent was marketed for the first time as Guesarol, while in the field of human hygiene DDT was named as Neocid.

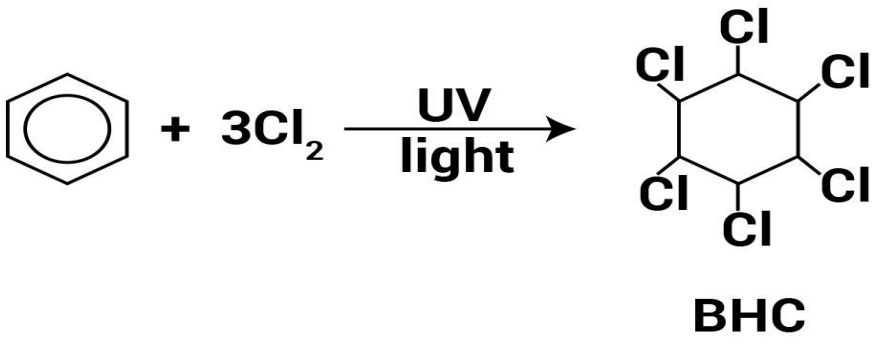
3.4.1. b] Gammaxene or BHC: -

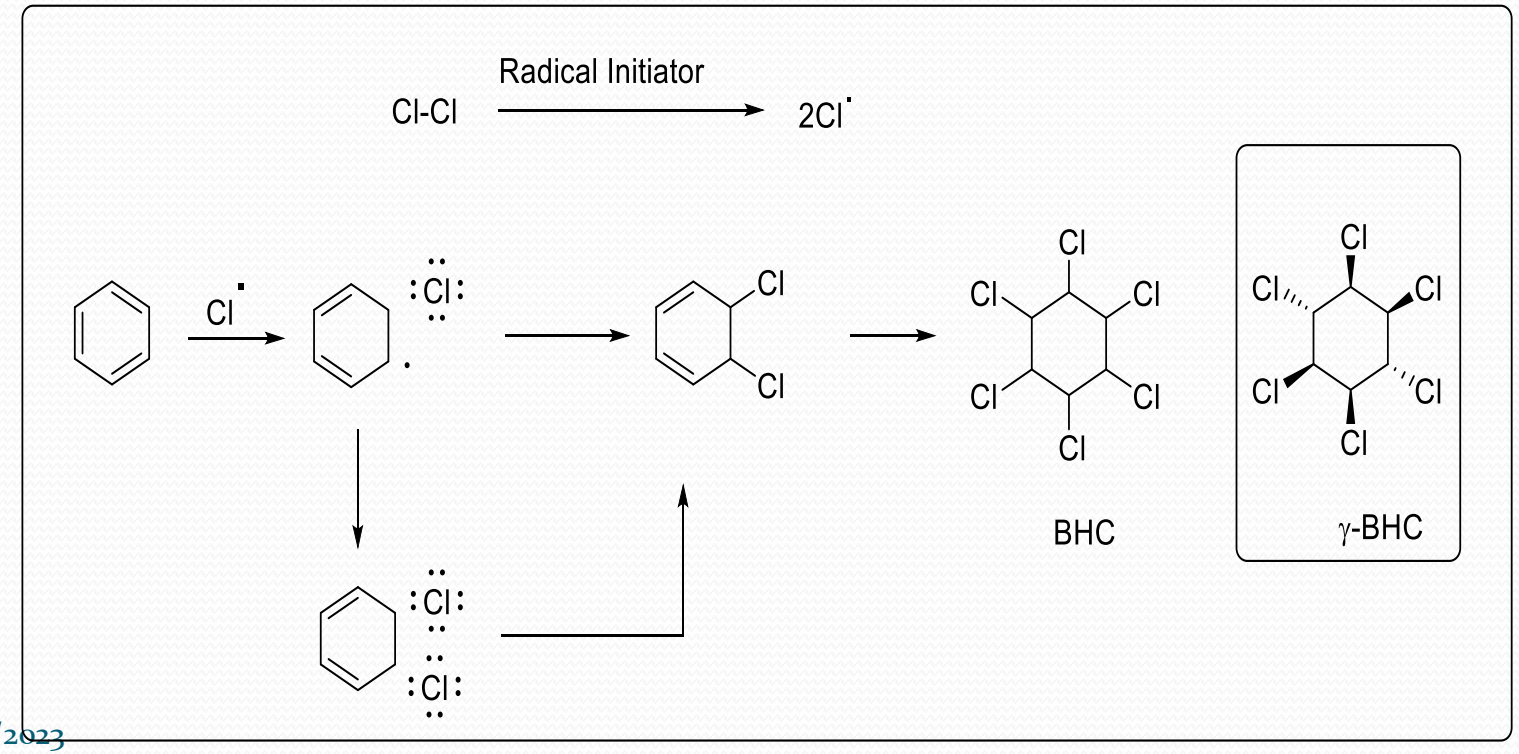
Benzene hexachloride (BHC) or Lindane or Gammaxene.

Faraday, in 1825 for a first time prepared BHC via addition reaction between benzene and three molecules of chlorine in presence of sunlight with various isomers of hexachloro cyclohexane (benzene hexachloride, BHC). From these isomers, Lindane was the first single isomer isolated in 1912. But, among the various isomers which are formed during the reaction, only the γ-isomer of BHC exhibits insecticidal properties. Thereafter, Bender in 1936, granted a patent for his discovery to find out the insecticidal properties of BHC.

Synthesis of BHC: -

The preparation of BHC involves an additive chlorination of benzene in the presence of ultraviolet light or in the presence of a chemical activator or radical initiator such as sodium hypochlorite, boron trichloride and organic peroxides. Schwabe and Rammelt, in 1955 proposed the detailed mechanism for the formation of BHC. In accordance with Schwabe and Rammelt, the formation of free radical in the presence of ultraviolet radiation and a radical initiator shifts the mechanism from substitution to addition reaction. After homolysis the resulting chlorine radical disrupts the π-electron sextet of the benzene ring to form a chlorophenyl radical. Thereafter, a free chlorophenyl radical either collides with chlorine radical to form dichloro cyclohexadiene or initiates a chain reaction by homolysis of another chlorine molecule. Once dichlorocyclohexadiene is formed the process of additive chlorination continues towards the formation of BHC (Scheme 2).


+ 3Cl2
UV
light
Cl
Cl
Cl
Cl
Cl
Cl
BHC


Radical Initiator
Cl-Cl
2Cl·
Cl·
Cl
Cl
Cl
Cl
Cl
Cl
Cl
Cl
Cl
Cl
Cl
Cl
Cl
Cl
BHC
γ-BHC

BHC has very wide spectrum of insecticidal action as it includes almost all insects, whether sucking or chewing. BHC exhibits both a contact and a stomach poisoning, and due to its volatile nature it also act as a fumigant.

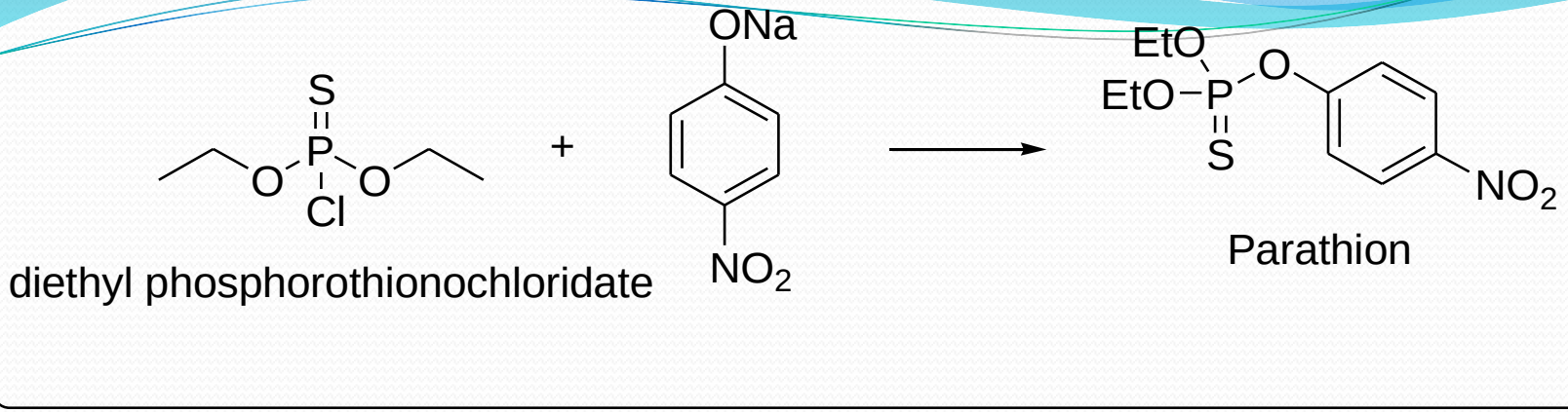
3.4.2] Organophosphates: -

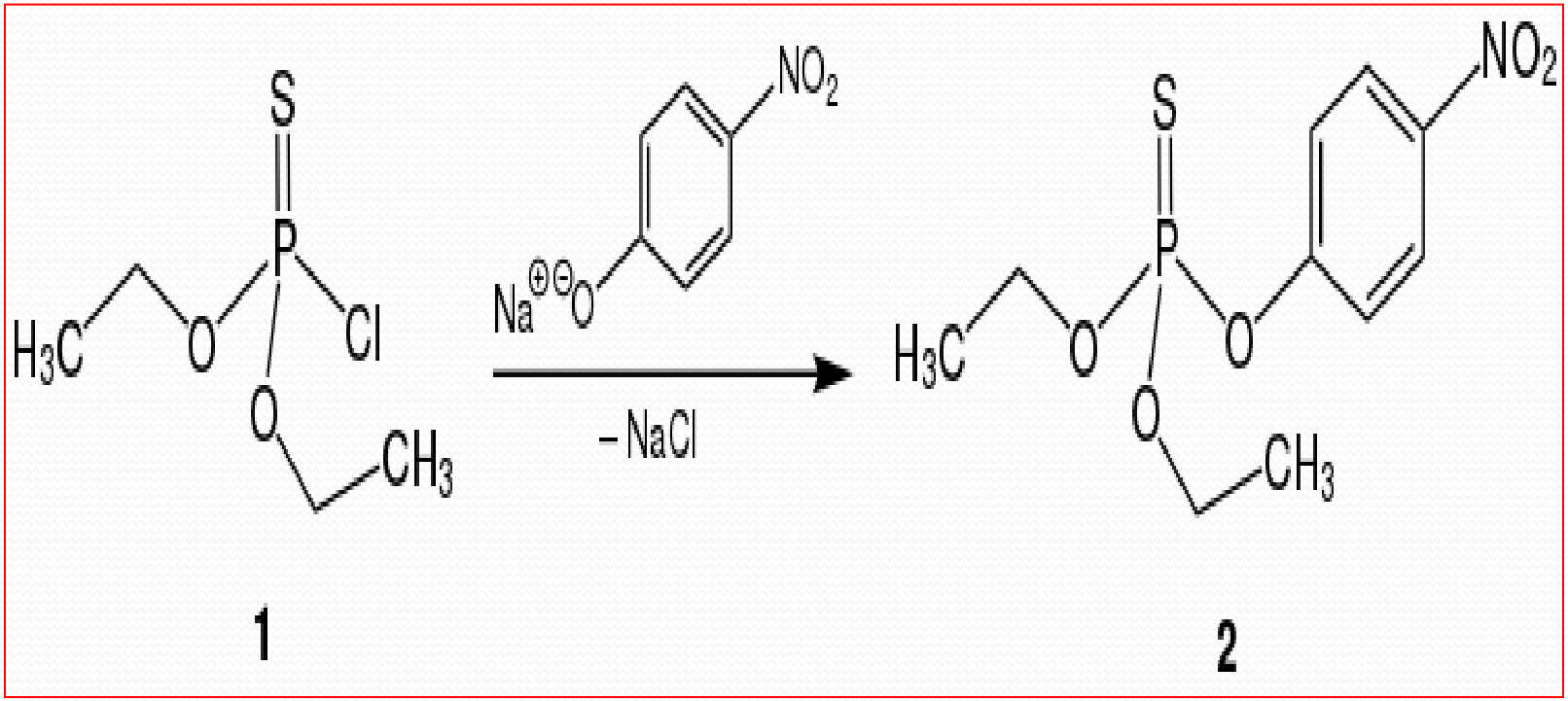
In addition to their toxic behavior to warm-blooded animals, some of the organophosphorus compounds are also very strongly toxic to insects. Therefore, the research on phosphorus compounds was persistently directed towards the development of pesticides for better agricultural production. In this regard, Schrader initiates the development of the phosphorus ester based insecticides which have been used in agriculture was commonly known as bladan, parathion, potasan, systox and many more.

3.4.2 a] Parathion: - Parathion, is an organic phosphorus based compound, which is well known for its insecticide activity and it is extremely toxic to humans. Parathion having activities in mammals, as in insects, as a cholinesterase inhibitor (Enzyme that controls the normal functioning of the central nervous system), and causing death by attacking respiratory system. Therefore, a great care has been taken before handling parathion and similar insecticides, because these substances posing toxicity even if they swallowed, inhaled, or absorbed through the skin.

Synthesis of Parathion: - The thio- analogue of paraoxon, *O*, *O*-Diethyl *O*-(4-nitrophenyl) phosphorothioate is also known as parathion, is practically more suitable than paraoxon because of its low toxicity to warm-blooded animals and high order of stability against hydrolysis. Parathion has been prepared by Schrader in 1944, and the elucidation of its biological properties has been performed by Schrader and Kiikenthal, in 1948, Unterstenhofer 1948 and Schrader, 1952.

Parathion is prepared by allowing diethyl phosphorothionochloridate to react with sodium p-nitrophenolate (Scheme 3)


S
O
P
O
Cl
diethyl phosphorothionochloridate
+
ONa
NO2
EtO
EtO
P
O
S
NO2
Parathion


S
P
H3C
O
Cl
O
CH3
1
NO2
Na⊕⊖O
– NaCl
NO2
S
P
H3C
O
O
O
CH3
2

Industrial manufacturing of parathion began in 1947 in the USA. Mostly it is used as insecticide. It is used against aphids, nites, caterpillar, etc. It is pale yellow coloured oily liquid and about 5-20 times more toxic than DDT.

3.4.2 b] Malathion: - Malathion is also known as carbophos, mercaptothion, and maldison having a broad-spectrum of applications, this organophosphate insecticide and acaricide is used widely to kill ticks and mites. Malathion due to its less toxic nature to humans as compare to parathion, have also been utilized to control the household and garden insects. Additionally malathion is used to control mosquitoes, boll weevils, fruit flies, and lice.

Synthesis of Malathion: - Cassaday in 1950, prepared Diethyl 2-[(dimethoxyphosphorothioyl)sulfanyl]butanedioate (or malathion) by the addition reaction between dimethyl phosphoro-dithioic acid and maleic acid diethyl ester. There after malathion became one of the most significant phosphorus ester insecticides because of its slow toxicity to warm-blooded animals.

INDUSTRIAL CHEMISTRY

CHAPTER- CHEMISTRY OF PESTICIDES

ONLINE LECTURE

NO. 4

DATE:- 13, MAY 2021

TIME: (9.00A.M.)

Industrial manufacturing of parathion began in 1947 in the USA. Mostly it is used as insecticide. It is used against aphids, nites, caterpillar, etc. It is pale yellow coloured oily liquid and about 5-20 times more toxic than DDT.

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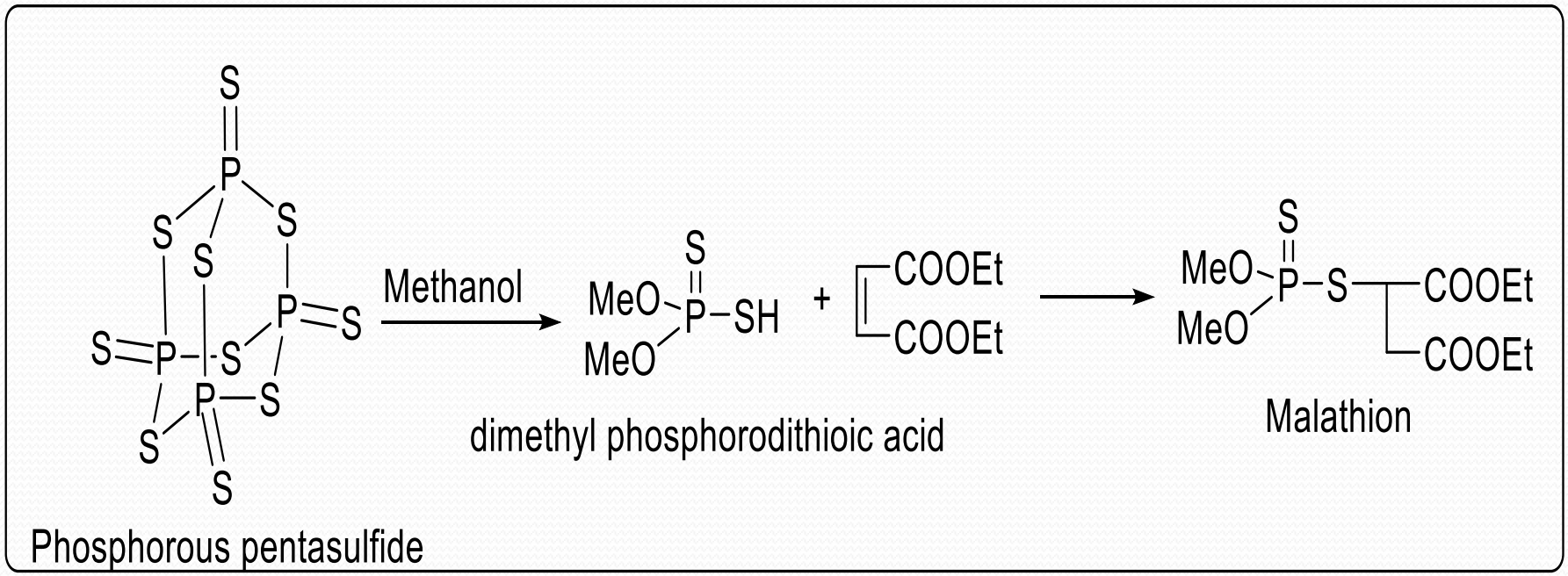
Matolcsyand Oswald has reported the technical industrial scale production of malathion, in which the reaction between dimethyl phosphorodithioic acid (synthesizes in-situ from phosphorus pentasulfide and methanol) and maleic acid diethyl ester (or Diethyl malenate) yielded malathion.



Malathion exhibits a broad range of insecticidal action, and it is effective against both sucking and chewing insects. As malathion is belonging to the family of phosphorus ester insecticides is found least toxic to the warm-blooded animals.

3.4.3] Anilides: -

Anilide based herbicides are very promising agents of weed control in turf and in a variety of economically important crops, including rice, cotton, soybeans, corn, and tomatoes. Additionally, these herbicides are well-known for their effectiveness, selectivity, low mammalian toxicity, and biodegradability.

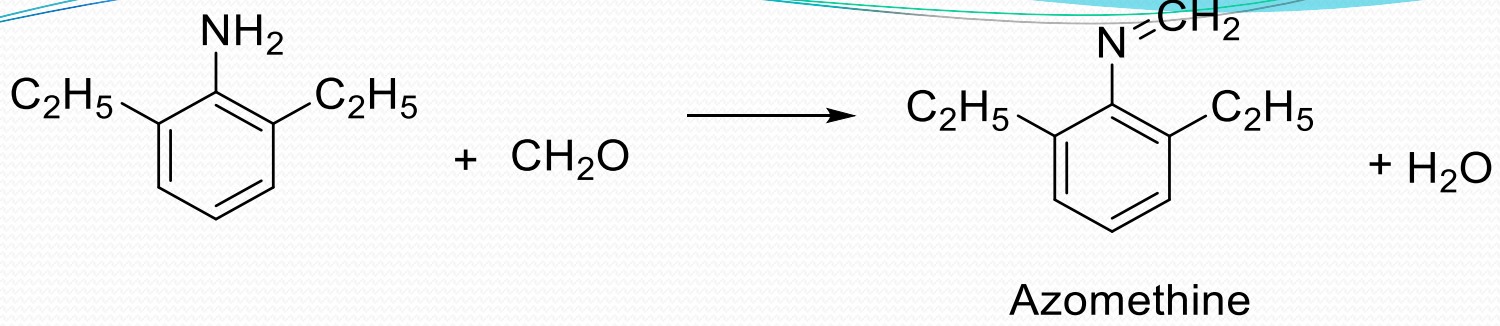
3.4.3a] Alachlor: -

Alachlor is considered as a selective pre-emergence soil herbicide With its poorer solubility in water alachlor wants more soil moisture to exert its satisfactory herbicidal action. The thorough study on the mode of action of alachlor suggests that, the alachlor is absorbed mainly by the shoots (stem) of the plant and, to a lesser degree, by the roots of the plant.

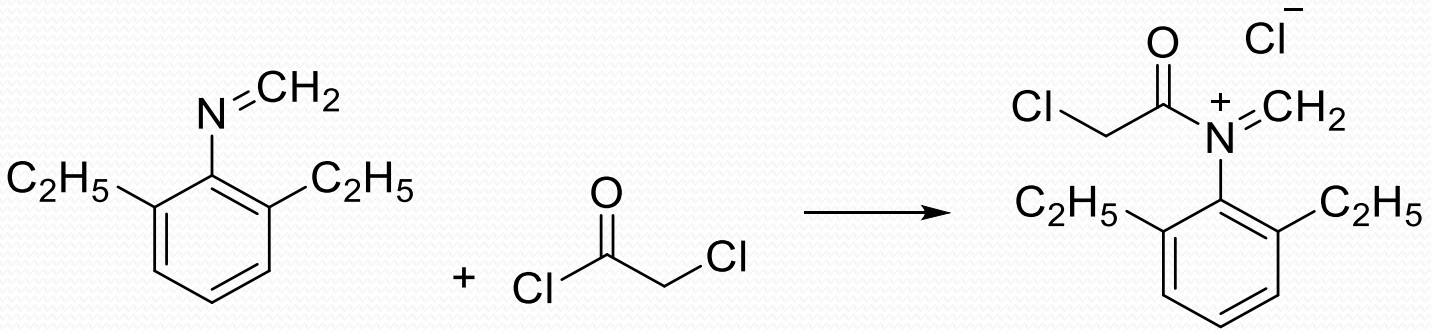
Synthesis of Alachlor: -

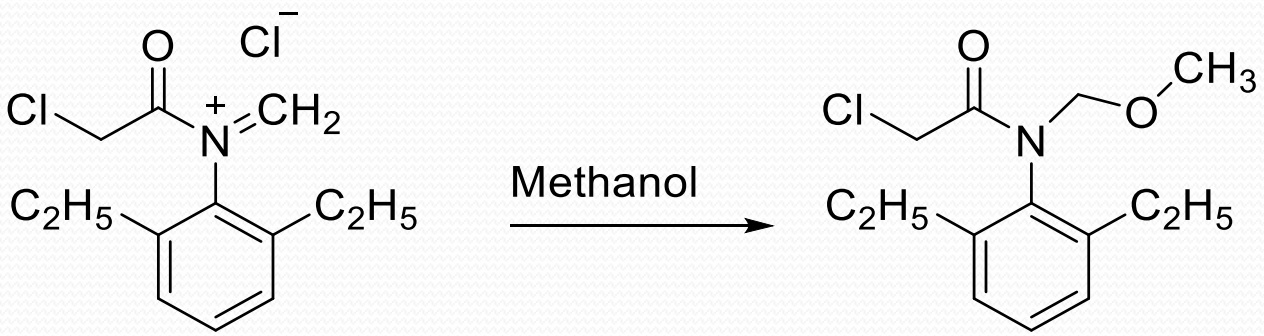
The first active product i.e. 2-Chloro-*N*-(2,6-diethylphenyl)-*N*-(methoxymethyl) acetamide or alachlor has been described by Husted *et al*. (1966), Allott (1966) and Roberts and Wilson (1966).

Olin, in 1965 have been proposed an efficient strategy for the manufacture of alachlor and its related compounds by following the sequence of reactions. Olin's synthesis involves the reaction between azomethines (which is prepared by the reaction between alkylaniline with formaldehyde) with chloroacetyl chloride, gives product (salt), thereafter with methanol to give alachlor (Scheme 5).



Azomethine





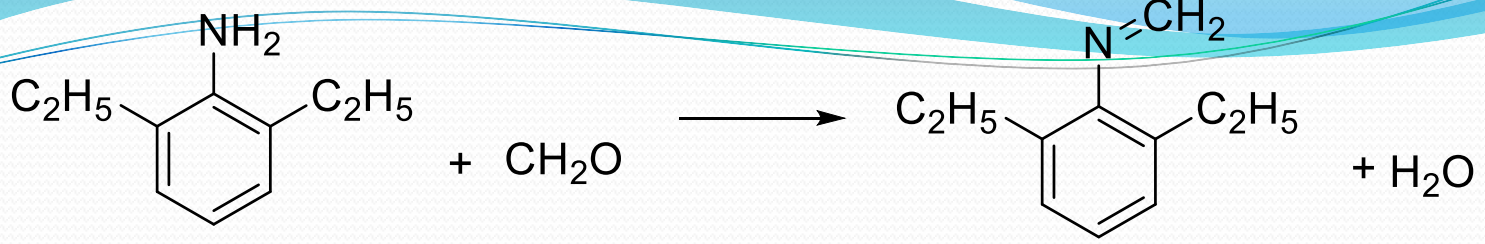
Alachlor

3.4.3b] Butachlor: -

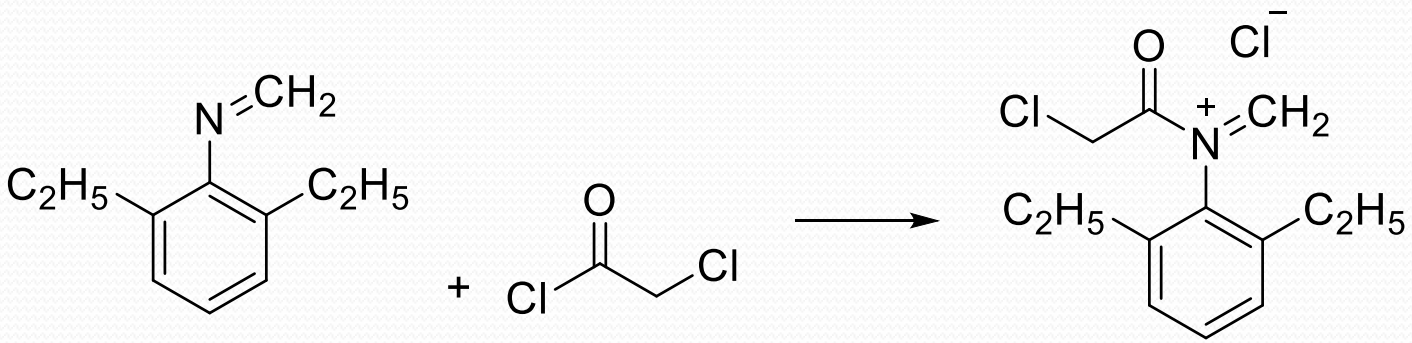
Butachlor having low solubility in water than alachlor and therefore requires higher soil moisture to exert a suitable herbicidal action. In order to control grass weeds and a few broad-leaved weeds, butachlor is an excellent pre- and early post-emergence selective herbicide.

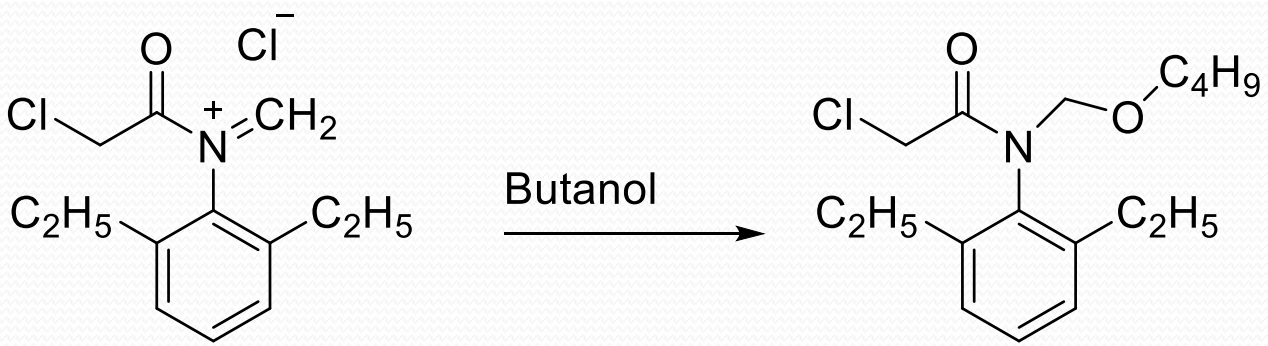
Synthesis of Butachlor: -

N-(Butoxymethyl)-2-chloro-*N*-(2, 6-diethylphenyl) acetamide is Butachlor, the butyl homologue of alachlor and therefore it is prepared according to the same reaction scheme utilised for the preparation of alachlor (Scheme 6).



Azomethine





Butachlor

Thank You.

STAY HOME,
STAY SAFE