Insect Control
by
Chemicals

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CHAPTER I

Insecticides of
the Mid-Twentieth Century
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The large-scale farming practices of the twentieth century have encountered a requirement for insect control which has resulted in the rapid evolution of chemical insecticides. In the early years of this period the available materials included the arsenicals, lime-sulphur, petroleum oils, and nicotine. During the interval between World Wars I and II, the fluorine compounds were added to the inorganics, pyrethrum and rotenone were added to the botanicals, and synthetic organic materials such as the dinitro compounds and thiocyanates made their appearance. The coming of World War II witnessed the rise of the chlorinated hydrocarbon insecticides, with DDT contributed by Switzerland and BHC by the United Kingdom and France; their subsequent development in the United States was followed by the appearance of toxaphene, chlordane, aldrin, and dieldrin. Meanwhile German work during the war intro-

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duced a powerful group of insecticides, the organic phosphates, among which TEPP and parathion were produced commercially in the United States, and the systemic insecticides were developed in the United Kingdom. As the century reaches the halfway mark, emphasis is returning to the eminently suitable pyrethrins, whose toxicity is being extended by admixture of the piperonyl compounds, and a synthetic analogue of which has appeared in the form of allethrin.

In this chapter, much information has been drawn from the recent publications by Frear,[44] DeOng,[34] and R. L. Metcalf.[91] Valuable background material may be obtained from the books of Martin,[84] Shepard,[107] and C. L. Metcalf and Flint,[90] published just before World War II. A number of books published in Germany during that war are listed in the bibliography of Martin and Shaw.[84a] Useful and up-to-date ancillary information is available in volumes by West and Campbell,[124] McClintock and Fisher,[87] and Isely,[70] and also recent editions of *Entoma*.[81] French developments have been covered by the contributions of Raucourt,[98, 99] and German prewar practices by the monographs of Trappmann[118] and of Peters.[95] Recently, Riemschneider has published a monograph on the new contact insecticides.[100a] Older contributions include those of Cunningham[31] in the 1930's and Bourcart,[20] Wardle and Buckle,[121] Anderson and Roth,[3] and Trappmann[117] in the 1920's. Two books are available on practical insect control, one American[81d] and the other French,[81b] primarily designed for the pest-control operator.

THE CHLORINATED HYDROCARBONS

DDT

p,p′-Dichlorodiphenyltrichloroethane, or, more correctly, 2,2-bis(*p*-chlorophenyl)-1,1,1-trichloroethane, is produced technically as a white amorphous powder, but the pure compound crystallizes in biaxial tabular crystals. The empirical formula is $C_{14}H_9Cl_5$, and chlorine constitutes 50.01% of the molecular weight. Its specific gravity is 1.556 at 25° C. The vapour pressure of DDT has been determined to be equivalent to 1.5×10^{-7} mm Hg at 20° C.[13] This exceptional lack of volatility (for an

organic compound) is responsible for its outstanding properties as a residual insecticide.

DDT is prepared by condensing 1 mole of chloral with 2 moles of chlorobenzene in 98% H_2SO_4 at a temperature of 15° C. The average commercial product contains 70% of the p,p' isomer, the remainder consisting mainly of o,p'-DDT along with a little DDD, o,p'-DDT sulphonate, PDB, and excess chlorobenzene. The purity of the p,p'-DDT is increased by using an excess of chloral.

The melting point of purified DDT is 109° C, and its setting point is between 103° and 105° C. Technical DDT shows a melting point of 89° C, and it is considered a satisfactory product if the setting point is not below 88° C. The more highly purified "aerosol grade" of DDT has a melting point of 103° C and is approximately 85% pure.

TABLE 1. SOLUBILITY OF CERTAIN CHLORINATED HYDROCARBONS
IN ORGANIC SOLVENTS

gm/100 cc at 25–30° C

	DDT	Lindane	Aldrin	Dieldrin	Toxa-phene
Acetone	58	44	159	54	450
Ethyl alcohol	2	6.4	9.0 *	4.9 *	12
Carbon tetrachloride	45	6.7	...	..	450
Cyclohexanone	116	37	...	..	...
Benzene	78	29	350	75	450
Xylene	53	25	...	..	450

* In methyl alcohol.

DDT is almost completely insoluble in water and is the least water-soluble organic compound known.[60] Its true solubility is 0.0002 part per million of water,[100] although it can form colloidal solutions up to 0.2 ppm in concentration. It is also possible to obtain gravity-stable suspensions of higher concentration, but they are precipitable. DDT is quite freely soluble in apolar organic solvents (see Table 1). Its solubility in aliphatic oils is limited: refined odourless kerosene 4%, crude kerosene 8–10%, no. 2 fuel oil 7–10%. In a natural oil, such as linseed, peanut, or cottonseed oil, the solubility is 10–12 gm/100 cc. Aromatic oils are superior solvents, an American petroleum product such as

APS-202 giving strengths of 45 gm/100 cc at 25° C. When they are refined, superior solvents for DDT are obtained in the form of methylnaphthalenes; an example is *Velsicol AR-50*, in which DDT is soluble to the extent of 55 gm/100 cc. The solubility of DDT in most solvents rises steeply with an increase in temperature.

DDT is very stable at normal temperatures. It decomposes at 195° C, but the decomposition may be inhibited by magnesium oxide, picolinic acid, or salicylalaminoguanidine.[56] It is labile in alkali, which dehydrochlorinates it to the dichloroethylene or the ethane analogue. It is catalytically decomposed in the same way by oxides or chlorides of iron or aluminum. This process may be delayed by solvents such as kerosene, fuel oil, or methylnaphthalenes; propylene oxide also inhibits decomposition of DDT in aerosol bombs. As a consequence of its lability to alkali, DDT is incompatible with kaolin, fuller's earth, and dolomite, and with the alkaloid nicotine. Bentonite, some talcs and pyrophyllites, sulphur, Bordeaux mixture, and the fungicide *Fermate* cause slight decomposition of DDT. Lead and calcium arsenate, Paris green, the fluosilicates, cryolite, hydrated lime, and lime-sulphur are safe as admixtures for this insecticide.

DDT is not normally decomposed by sunlight. It is almost completely stable to ultra-violet light when in solid form, but in oil solution it is slightly decomposed. DDT dusts have been found to lose their toxicity at a faster rate at higher relative humidities,[115] but this may be due to moisture rendering the diluent less compatible. Being water-insoluble, DDT is not leached away by rain. Deposits on citrus foliage in California were found to persist for 40 days before 50% loss, and 90 days before 90% loss, of material occurred.[56a] Tropical temperatures and humidities may decompose DDT comparatively rapidly; hot, dry weather also hastens its loss from orchard foliage, possibly by raising its volatility to an appreciable level.

DDT is formulated in 5% solutions for use as household space sprays, odourless kerosene being the solvent along with a small amount of xylene or methylnaphthalene as co-solvent. It is also put up as 25% emulsion concentrates, where the solvent is methylnaphthalene, cyclohexanone, isophorone, tetralin, or cumene;

the flash point should be above 110° F, which eliminates xylene from consideration.[74] The concentrate contains 15% of an oil-soluble emulsifier such as an alkyl aryl polyether alcohol (e.g. *Triton X-100*), which renders it self-emulsifiable on mixing with water. Emulsion concentrates have been made with a mixture of solvent naphtha or toluene with liquid rosin or turpentine as the solvent, and a soap or a sodium alkyl sulphate (e.g. *Teepol X*) as the emulsifier. The use of casein as an emulsion stabilizer for a concentrate in solvent naphtha allows the material to be shipped as a mayonnaise cream containing 27% water.[73] A fine suspension concentrate (colloidal DDT) may be made by stirring molten DDT into water with a solubilizer, whereupon the insecticide appears as fine crystals. One such concentrate (*Rucide*) contains 40% DDT in 35% water, with 20% petroleum oil and 5% emulsifier.[77]

Since DDT becomes waxy at temperatures approaching its melting point, it resists grinding because of its tendency to cake either during or after the process. It is therefore mixed with an equal amount of pyrophyllite or talc and is ground in a Raymond kiln mill or micronizer mill to a particle size of 0.5–5 microns (μ). When a little wetting agent is added, this product becomes a so-called "wettable powder"; it will go readily into suspension when added to water in the spray tank in concentrations of 1–4 lb/100 gal. If the ground material is further diluted with talc or pyrophyllite, it becomes a DDT dust. Concentrations of 1, 2, 3, or 5% are used for agricultural purposes, and 10% dusts for roach powders. A more effective dust is made by spraying a solution of DDT in a volatile solvent on to the inert diluent in a ribbon blender. These impregnated dusts are so much an improvement that a 3% impregnated dust is as effective as a 5% straight-mix dust,[66] and it kills the insects faster.[32a]

DDT may be effectively included in paints and washes for the treatment of walls to make them residually insecticidal. This stratagem is successful with casein paints, calcimines, and chalk whitewashes. In limewashes the DDT is decomposed by the alkali, but if enough insecticide is added it may retain its toxicity for at least 2 months.[57] A concentration of 3–5% DDT in flat oil paints is very effective.[47] With enamel paints the insecticide is sealed off by the glossy outer film, but these paints may

nevertheless be rendered effective if as much as 20% DDT is added.

Two colorimetric methods are available for the estimation of minute quantities (10 micrograms, i.e. μg) of DDT. One is the Stiff-Castillo method, where a red colour is obtained by heating DDT in pyridine with xanthydrol and KOH; however, the amount of water in the pyridine is critical.[28] The Schechter-Haller method has been generally found to be superior; in this method DDT is converted to its tetranitro derivative, which gives a blue colour with sodium methylate in the case of p,p'-DDT and a violet-red colour for o,p'-DDT.[104] No colour is given with any other chlorinated hydrocarbons, and the method is the most specific available; it is used for the examination of plant residues, foods, and animal tissues. The Alessandrini modification [*Bull. W.H.O.*, **2**:629 (1950)] is simpler but much less sensitive. DDT may be assessed directly by the spectrophotometer, showing maximum absorption at 236 millimicrons.

DDT may also be estimated by dehydrochlorinating it in alkali and titrating the chloride by Volhard's method. If it is refluxed with metallic sodium and isopropyl alcohol, all the chlorine atoms will be removed from the molecule and the amount of DDT is therefore twice the weight of the chlorine determined (total chlorine method).[41] If it is refluxed with KOH in ethyl alcohol [54] or treated at 45° C with 4.5 N ethanolic NH_4OH,[55] only one chlorine atom will be removed (hydrolysable chlorine method). It is possible to modify the conditions so that only the p,p'-DDT, and not o,p'-DDT or other impurities, is dehydrohalogenated.[61]

Methoxychlor

The methoxy analogue of DDT, namely 2,2-bis(p-methoxyphenyl)-1,1,1-trichloroethane, is a white solid which melts at 88° C. It is produced by the condensation of chloral with anisole.[114] The technical material is pale buff in colour and is 88% pure. Like DDT, it is insoluble in water but soluble in many of the common solvents. It may be determined quantitatively, after dehydrohalogenation, by nitration and treatment with sodium methylate according to the Schechter-Haller routine; a pink colour is obtained. The dehydrohalogenated methoxychlor may be

qualitatively detected by the pink colour it gives with 85% Na$_2$SO$_4$ solution.[8]

DDD

p,p'-Dichlorodiphenyldichloroethane, or tetrachlorodiphenylethane (TDE), is an analogue of DDT which has one less chlorine atom, being 2,2-bis(p-chlorophenyl)-1,1-dichloroethane. It is a white crystalline solid with a melting point of 109° C. It is produced by the condensation of dichloroacetal with chlorobenzene.[43] The commercial product has a minimum setting point of 86° C. It exhibits grinding and solubility characteristics similar to those of DDT, and is marketed as a 50% wettable powder (e.g. *Rhothane WP-50*) and a 25% solution in an aromatic oil (e.g. *Rhothane S-215*). It was also developed in Germany under the designation M-1700.[22a]

DFDT, Lucex, and Dilan

The difluoro analogue of DDT, namely 2,2-bis(p-fluorophenyl)-1,1,1-trichloroethane, is a solid with a melting point of 45° C. It is appreciably volatile, boiling at 177° C at 9 mm Hg, and thus has less residual persistence than DDT.[91] It was produced commercially in Germany under the name of *Gix*, which is a liquid contaminated by about 10% of the o,p' isomer.[22]

2-(p-Chlorophenyl)-1,1,2,2-tetrachloroethane has been used as an insecticide in Germany under the name of **Lucex**.[22a] The p,p'-dimethyl analogue of DDT, m.p. 90° C, has been used in the United States on a semicommercial scale.[91]

Dilan is the trade name applied to a mixture of 1 part of 2-nitro-1,1-bis(p-chlorophenyl)-propane (Compound CS-645A) with 2 parts of 2-nitro-1,1-bis(p-chlorophenyl)-butane (Compound CS-674A). These compounds are solids with melting points of 79° and 59° C, respectively, stable to acid and weak alkali, and the mixture has an odour of almonds. The materials are soluble in organic solvents, and an emulsion concentrate is made of 25% *Dilan* in pine oil. They offer about half as much toxic hazard as DDT, and are particularly insecticidal to the Mexican bean beetle.[30a] However, *Dilan* has caused russetting of susceptible varieties of apples.

BHC

Benzene hexachloride, or, more correctly, 1,2,3,4,5,6-hexachlorocyclohexane, has the empirical formula $C_6H_6Cl_6$, from which is derived its original code name of 666; it contains 44.33% of chlorine. As commercially produced, it consists of buff-coloured crystals which have a pronounced musty odour, due to impurities and to breakdown products which subsequently develop. BHC is prepared by the chlorination of benzene in the presence of ultra-violet light; in its absence hexachlorobenzene (C_6Cl_6) is obtained.

Benzene hexachloride, as prepared by this method, consists of a mixture of optical isomers, of which the beta isomer constitutes some 55–70% of the material (Table 2). In addition, there may be some 4% of heptachlorocyclohexane and 0.6% of octachlorocyclohexane.[97] It is the gamma isomer of hexachlorocyclohexane that is the powerful insecticidal principle, so that the toxicity of BHC is proportional to its gamma content; the usual commercial preparations contain approximately 10–13% of this principle. The gamma isomer may be separated by dissolving BHC in methyl alcohol, which takes up the gamma and delta isomers only; upon evaporation of this methanolic solution the gamma isomer is the first to crystallize out, and it may be purified by solution in and recrystallization from chloroform.[109] Commercial preparations are now available which contain as much as 92% of the gamma isomer (e.g. *Hi-gam*). Purified preparations which contain not less than 99% of the gamma isomer are now given the name of **lindane**,* which replaces the trade name *Gammexane*.

The isomers of BHC are appreciably volatile (Table 2). Although the vapour-pressure values obtained by Slade appear entirely too high, there is a possibility that those obtained by Balson are low. The volatility of BHC in field deposits is sufficient not only to prevent it from showing adequate residual properties, but also to allow it to have a definite fumigant action on insects in crevices. The fumigant effect is an important factor

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* After van der Linden, who in 1912 discovered the existence of the isomer.

in laboratory testing of this material. The purified crystals of lindane are colourless, and comparatively odourless when first produced.

TABLE 2. PROPERTIES OF THE ISOMERS OF BENZENE HEXACHLORIDE

	Alpha	Beta	Gamma	Delta	Epsilon
Per cent in BHC	5	70	12	7	3
Melting point, °C	158	312	112.5	138	219
Vapour pressure, mm Hg at 40° C *	0.06	0.17	0.14	0.09	...
Vapour pressure, mm Hg at 20° C *	0.02	0.005	0.03	0.02	...
Vapour pressure, mm Hg at 20° C †	2.5×10^{-5}	2.8×10^{-7}	9.4×10^{-6}	1.7×10^{-5}	

* Values obtained by Slade.
† Values obtained by Balson.

The isomers of BHC are moderately soluble in organic solvents, in the order $\delta > \gamma > \alpha > \beta$. The gamma isomer is 18% soluble in heavy naphtha (b.p. 230–270° C) and 3.2% soluble in paraffin oil (b.p. 138–212° C), when measured as the grams/100 cc taken up at 20° C. It is readily soluble in the methylnaphthalenes and other aromatic oils. Lindane is relatively insoluble in water, the maximum solubility being approximately 10 ppm; of the other isomers, the beta has a solubility of 5 ppm, the remainder 10 ppm.

The isomers of BHC are stable to the effects of light under atmospheric conditions.[26] They are stated to be stable at high temperatures, although when thermally generated as smokes they show the same 30% destruction as DDT. They are stable to the action of hot water and concentrated nitric acid. BHC is not affected by natural chalky or limey waters. But the isomers are susceptible to alkali in the order $\alpha > \delta > \gamma > \epsilon > \beta$,[75] such that all except beta are destroyed by cold KOH, and all are destroyed by boiling KOH.[125] The process is one of dehydrochlorination to 1,2,4-trichlorobenzene, with smaller amounts of 1,2,3- and 1,2,5-trichlorobenzene.[30]

BHC may be quantitatively assessed by the total chlorine method developed for DDT.[126] It may also be determined spectroscopically by means of the absorption band in the ultra-violet

range given by the 1,2,4-trichlorobenzene obtained by alkaline dehydrochlorination of BHC.[61] The gamma-isomer content may be assessed according to the hydrolysable chlorine method by treating the BHC with N alcoholic KOH at 0° C for 50 min (which dehydrochlorinates the alpha, delta, and gamma isomers) and subtracting the value obtained by treating a similar sample for 15 min (which dehydrochlorinates the alpha and delta isomers only).[79] It may also be determined by the separation and crystallization method described above, by cryoscopic methods based on the depression of the freezing point,[21] by chromatographic adsorption,[97] by infra-red spectroscopy,[32] and by bioassay of the insecticidal effectiveness of the sample.[67]

Chlordane

Technical chlordane (U. S. Dept. Agr.), or chlordan (Am. Chem. Soc.), is the name given to a product, formerly called *Compound 1068*, containing not less than 60% of 1,2,4,5,6,7,8,8-octachloro-4,7-methano-3a,4,7,7a-tetrahydroindane, with the remainder (25–40%) being related dicyclopentadiene derivatives. It is a highly viscous liquid, dark amber to brown in colour, with a terpene-like odour. The refined product is pale amber with a faintly aromatic odour. The specific gravity is 1.56 at 60° F, the viscosity 6900 cp at 25° C, and the refractive index 1.56 at 25° C. The empirical formula of the octachloromethanotetrahydroindane is $C_{10}H_6Cl_8$, its molecular weight is 409.8, and its calculated chlorine content is 69.22%. Technical chlordane boils at 175° C at reduced pressure (2 mm Hg). Its volatility is intermediate between that of DDT and BHC, the vapour pressure of the refined product being approximately 1×10^{-5} mm Hg at 25° C.

The octachloromethano-tetrahydroindane (alias -hexahydro-indene) occurs as two structural isomers, the *cis* and *trans* forms, which have been named alpha-chlordane and beta-chlordane, respectively. These isomers cannot be separated from each other or from the remaining constituents of technical chlordane by distillation, since the liquid superheats. However, by chromatographic adsorption on aluminum oxide, it has been possible to separate these two isomers and obtain two further derivatives of tetrahydroindene (namely hexachlor and heptachlor); and all

of them are white crystalline solids. In addition a white crystalline solid called trichlor-237 has also been isolated.

The known constituents of technical chlordane are therefore as follows:

    a. cis-2,3,4,5,6,7,8,8-octachloro-2,3,3a,4,7,7a-hexahydro-4,7-methanoindene (α-chlordane) ; melting point 102–104° C.

    b. trans-2,3,4,5,6,7,8,8-octachloro-2,3,3a,4,7,7a-hexahydro-4,7-methanoindene (β-chlordane) ; melting point 104–106° C.

    c. 1 or 3a,4,5,6,7,8,8-heptachloro-3a,4,7,7a-tetrahydro-4,7-methanoindene (heptachlor) ; melting point 92–94° C.

    d. 4,5,6,7,8,8-hexachloro-3a,4,7,7a-tetrahydro-4,7-methanoindene (hexachlor or compound 237) ; melting point 154° C, with decomposition.

    e. 1 or 3a,2,3,4,5,6,7,8,8-enneachloro-2,3,3a,4,7,7a-hexahydro-4,7-methanoindene (trichlor 237) ; melting point 122–123° C.

Of these materials, heptachlor is 4–5 times as insecticidal as technical chlordane, and the trans-chlordane is 10 times as toxic as the cis-chlordane but not quite as insecticidal as heptachlor.

Technical chlordane is completely miscible with all apolar solvents, including aromatic and aliphatic hydrocarbons, alcohols, ethers, and esters. It is insoluble in water. It should not be heated above 60° C if it is to maintain its toxicity. It is stable to acid and is compatible with dinitro compounds, arsenicals, fluosilicates, other chlorinated hydrocarbons, dithiocarbamates, and sulphur. It is readily detoxified by alkaline dehydrochlorination; thus it is not stored in galvanized iron or steel containers, but in glass, or else aluminum-clad or lacquered steel.

Emulsion concentrates containing 45% or 75% chlordane are made by mixing the technical product with kerosene and adding 10% of a wetting agent. A 90% concentrate may be made by omitting the kerosene. The concentrates are stabilized by the addition of starch or dextrin to retard creaming. Wettable powders are made by spraying chlordane heated to 130° F onto diatomaceous earth in a ribbon blender to give a 50% (wt./wt.) mixture; the wetting agent is then added. Alternatively the 50% mixture may be diluted with pyrophyllite to give 5% or 10% dusts.[23]

Chlordane may be quantitatively determined by the total chlorine methods employed for DDT. It may also be assessed by the hydrolysable chlorine method,[55] two atoms of chlorine being removed per molecule. Liquid technical chlordane gives a purple colour on being heated with diethanolamine and methanolic KOH; and a red colour on being heated with pyridine, ethylene glycol monoethyl ether, and alcoholic KOH. The crystalline constituents of technical chlordane themselves fail to give these colour reactions.[61]

Aldrin and dieldrin

Aldrin (formerly called *Compound 118* or *Octalene*) is 1,2,3,-4,10,10-hexachloro-1 : 4,5 : 8-diendomethano-1,4,4a,5,8,8a-hexahydronaphthalene; dieldrin (*Compound 497* or *Octalox*) is the 6,7-epoxy derivative of aldrin. Thus the empirical formulae are $C_{12}H_8Cl_6$ for aldrin, and $C_{12}H_8Cl_6O$ for dieldrin.

Aldrin is a white crystalline solid, with a melting point at 100–103° C. It emits a mild piney odour when warmed. It is much less volatile than lindane and is intermediate between chlordane and DDT in residual effectiveness. It is insoluble in water, but as much as 89 gm/100 cc dissolve in refined kerosene (*Deobase*) at 26–30° C. It is stable to alkali and metallic chlorides. Residues on plants may be determined by the Danish-Lidov colorimetric method. Aldrin is equivalent to lindane in its toxicity to insects.

Dieldrin is an odourless white crystalline solid, with a melting point at 173° C. It is scarcely volatile, showing a residual toxicity whose persistence is comparable to that of DDT. It is less soluble in organic solvents than aldrin (see Table 1), and 4.3 gm/100 cc are taken up by base oil (standard no. 10) at 26–30° C. Although decomposed by strong acid, it is completely stable to weak acids and to alkalis. It is the most toxic and residually effective of the present insecticides.

Toxaphene

Toxaphene (formerly called *Compound 3956*) is a chlorinated camphene whose empirical formula is $C_{10}H_{10}Cl_8$ and which contains 67–69% of chlorine.[129] It is a cream-coloured waxy solid with a mild terpene odour. Toxaphene melts in the range from

65 to 95° C, and its specific gravity is 1.66 at 27° C.[93] It is scarcely volatile, showing only 0.1% loss in weight in being heated to 100° C for 20 hr. It is insoluble in water but highly soluble in organic solvents and oils (Table 1). Lubricating oil will take up 75 gm/100 cc, fuel oil 260 gm/100 cc, and kerosene more than 280 gm/100 cc at 27° C.

Toxaphene is stable either alone or in solution. When heated or exposed to ultra-violet light it is very slowly dehydrochlorinated; at a temperature of 300° C it yields only 10 ppm of HCl per hour. Oil solutions may be stored in clear glass bottles without appreciable deterioration. The dehydrochlorination is hastened by alkali and Fe, but iron containers are safe for storage of toxaphene at room temperatures. There is one labile chlorine atom per molecule, which suggests the use of the hydrolysable chlorine method of assessment. However, toxaphene residues are determined by the total chlorine method, using the nitrobenzene modification of the Volhard titration.[9]

Chlorinated acaricides

Three compounds have been developed for the control of tetranychid mites infesting orchard trees. They resemble DDT in containing two p-chlorophenyl groups, but differ in the lack of chlorine in the nucleus of the molecule.

DMC is the name given to di(p-chlorophenyl)methylcarbinol (occasionally called DCPC), or, more correctly, 1,1-bis(p-chlorophenyl)-ethanol. It is a crystalline solid, of empirical formula $C_{14}H_{12}OCl_2$, with a melting point of 70–71° C. Although susceptible to decomposition by acid, it is stable to alkali and thus compatible with most agricultural chemicals. It is readily soluble in organic solvents (Table 3) and is taken up by D.C. naphtha and Skellysolve B to the extent of 7.2 and 4.3 gm/100 cc, respectively. It is formulated as a 25% miscible concentrate (e.g. *Dimite*). DMC is not easily manufactured and is an expensive material.

DCPM (*Compound K-1875*) is the name given to bis(p-chlorophenoxy)methane. It is a crystalline solid of empirical formula $C_{13}H_{10}O_2Cl_2$, with a melting point of 70–72° C.[91] Although hydrolysed by boiling dilute acid, it is stable to alkali.[4] It is

readily soluble in organic solvents (Table 3) but is insoluble in water and (curiously enough) VMP naphtha. DCPM is formulated as a 40% wettable powder (e.g. *Neotran*).

TABLE 3. SOLUBILITY OF CHLORINATED ACARICIDES IN ORGANIC SOLVENTS

	DCPM	DMC	K-6451
Acetone	189	...	130
Carbon tetrachloride	28	...	41
Diethyl ether	87	152	...
Ethyl alcohol	0.5	125	1.4
Benzene	40	110 *	78 †

* Toluene.
† Xylene.

Chlorinated sulphonyl compounds

These materials contain both sulfonyl and *p*-chlorophenyl radicals, and have recently proved valuable as acaricides.

K-6451, or *p*-chlorophenyl *p*-chlorobenzenesulphonate, is a highly persistent mite ovicide, although a poor insecticide. The technical product is a flaky tan-brown material, with a melting point at 80° C. It is insoluble in water but readily soluble in organic solvents (Table 3). The solubilities in cyclohexanone, methylnaphthalene (*Velsicol AR-60*), and kerosene (*Deobase*) are 110, 52, and 2 gm/100 cc respectively. K-6451 is compatible with most of the insecticides. It is formulated as a 50% wettable powder (e.g. the product *C-854*).

Genitol 923 is the 2,4-dichlorophenyl ester of benzenesulphonic acid. It is an effective residual acaricide, but has injured the foliage of orchard trees.

R-242, or *p*-chlorophenyl phenyl sulphone, has proved to be of value as a residual acaricide.

THE ORGANIC PHOSPHATES

HETP

The name of hexaethyl tetraphosphate was given to a commercial product whose composition tallied with the empirical formula $C_{12}H_{30}O_{13}P_4$ and which showed an apparent molecular weight of 506.3. In reality, however, this product is a mixture of linear polyphosphates, linear hexaethyl tetraphosphate, penta-

ethyl triphosphate, tetraethyl pyrophosphate, and triethyl phosphate.[29] The main insecticidal principle is tetraethyl pyrophosphate or TEPP, which is present in proportions between 10 and 20% in commercial HETP.

HETP is a light amber, oily liquid whose freezing point is approximately $-40°$ C, and which on heating decomposes at 145–150° C. Its specific gravity is 1.28–1.29, and its refractive index 1.426 at 27° C. It is produced by reacting 9 moles of ethyl alcohol with 4 moles of phosphorus oxychloride, or more usually by reacting 2–3 moles of triethyl phosphate with 1 mole of phosphorus pentoxide.[85] It was originally marketed in Germany as a 60% emulsion in 20% toluene and 20% emulsifier, under the trade name of *Bladan*.[84a] It is available in North America as the undiluted liquid.

TEPP

If as much as 5 moles of triethyl phosphate are reacted with 1 mole of phosphorus pentoxide, a product is obtained which contains 40% of tetraethyl pyrophosphate and is thus called TEPP.[29] This material is a dark amber to colourless mobile liquid whose freezing point is below $-60°$ C and which decomposes above 165° C. It boils at 150° C at 10 mm Hg, and its specific gravity is 1.19–1.20.

The pure tetraethyl pyrophosphate may be made by treating silver pyrophosphate with ethyl iodide, or may be isolated from commercial TEPP. It is a water-white mobile liquid which boils at 104–110° C at 0.08 mm Hg, and whose refractive index is 1.4200 at 20° C. Its empirical formula is $C_8H_{20}O_7P_2$, its molecular weight 290.2, and its specific gravity 1.1845 at 25° C[58]

Both TEPP and HETP are readily miscible with water, to the extent that they are hygroscopic. They are miscible with the organic solvents and with aromatic oils; but they are not miscible with kerosene or other paraffin oils, or with petroleum ether. TEPP, like HETP, is marketed as the undiluted liquid (e.g. *Nifos-T*).

Tetraethyl pyrophosphate rapidly hydrolyses in water to produce 2 moles of diethyl phosphoric acid. At a temperature of 25° C, 50% hydrolysis occurs in 7 hr, and at 30° C in 5 hr. Hexaethyl tetraphosphate is hydrolysed in the same way at a