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**CHEMICAL WEAPONS CONVENTION
VERIFICATION:
HANDBOOK ON
SCHEDULED CHEMICALS**



AUGUST 1993

CANADA

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VERIFICATION:
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SCHEDULED CHEMICALS**



Dept. of External Affairs
Min. des Affaires extérieures

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PREFACE

This Handbook was first compiled in 1992 to provide background information to Canadian officials with regard to the potential scope of verification of industry worldwide under a Chemical Weapons Convention (CWC). With the opening for signature in January 1993 of the CWC, elements of the Handbook were further examined and refined with a view to sharing the document with others now addressing questions related to the practical implementation of the Convention.

The Handbook includes chemical-specific information, such as physical properties, modes of synthesis, and toxicity, all categories of information that are reasonably 'stable' over time. Other data on uses and suppliers are also included, including numbers and locations of companies producing or making available scheduled chemicals for legitimate commercial purposes. Since this information comes from a variety of public sources, it suffers from the usual difficulties relating to timeliness, consistency and comprehensiveness. Taken together, however, they provide an interesting data bank, with both enduring and more current components, that can be used as a foundation for further detailed studies on the commercial availability of scheduled chemicals.

Written by a consultant from the University of Saskatchewan in conjunction with the Verification Research Unit of External Affairs and International Trade Canada, the document also reflects commentary received from contacts at Merck-Frosst Canada Inc. and the Department of Industry, Science and Technology Canada.

Introduction

The purpose of this Handbook is to bring together information on all chemicals listed in the schedules of the Chemical Weapons Convention (CWC) in a way which will be of use to developing National Authorities in countries which intend to become States Parties. It will also be of use to the Preparatory Commission and ultimately to the International Organization for the Prohibition of Chemical Weapons (OPCW) established under the CWC.

Each entry gives physical properties, synthesis, toxicology, uses and suppliers where such information is available for compounds listed by name. Further work will have to be done on the entries in the Schedules that list families of chemicals.

Annex 1 develops a literature base for materials that appear in Schedule 2 and these expand upon the information given in the specific entry. The twelve tables in this annex show the distribution of the citations among university, industry and government; the countries that are actively involved in research into these compounds; the distribution between research papers and patents; and finally an assessment of the distribution of research among science, technology and toxicology.

Table A is an indication of the level of worldwide industrial activity in Schedule 2 and 3 chemicals. This Directory shows that 5,265 companies in 60 countries are willing to provide chemicals commercially. Some of the companies listed may be suppliers rather than primary producers.

Table B shows that there are 11 countries with a total of 42 companies who can supply Schedule 2 chemicals commercially. Table C shows that 198 companies in 20 countries are able to supply Schedule 3 chemicals at this time. These numbers are indicative of the magnitude of the inspection problem that the OPCW will have in monitoring activities related to scheduled chemicals under the Chemical Weapons Convention.

Table D shows the actual number of literature citations that mention chemicals contained in the Schedules in the period from 1965 until the present day. There are over 43,000 literature citations in Chemical Abstracts.

Table E is an initial attempt to indicate the possible relationship with the pesticide industry in that it is a major consumer of raw materials of potential interest to the CWC and in that it has considerable expertise in organophosphorus chemistry.

Table F lists the sources of information used in compiling this Handbook.

**PART I:
INFORMATION
ON
SCHEDULE 1 CHEMICALS**

Schedule 1**A. Toxic chemicals:**

(1): O-alkyl ($\leq C_{10}$ incl. cycloalkyl) alkyl(methyl, ethyl, n- and isopropyl)-phosphonofluoridates

It has been estimated that there are 2001 saturated alcohols with up to 10 carbons i.e. if we look at the alkyl radicals that results and the fact that four possible alkyl-phosphorous bonds have been identified, then there would be 8004 possible phosphonofluoridates in this class; this would be a maximum number since there would be a limitation based upon commercial availability of the alcohols. (This calculation is due to CEFIC, Conseil European Des Federations De L'Industrie Chimique.)

There are two weaponized methylphosphonofluoridates. These are Sarin and Soman; GF has been reported to be part of Iraq's stockpile but no technical data is available.

SARIN, $C_4H_{10}FO_2P$
CAS No. 107-44-8
HS No. 29.31.00
Merck 8332

Synonyms: O-isopropyl methylphosphonofluoridate, GB.

Physical properties: MW: 140.11; mp: $-57^{\circ}C$; bp: $147^{\circ}C$; d. 1.10; colourless liquid that is miscible with water (also hydrolyzed by water) and very volatile.

Synthesis: The reaction of isopropyl alcohol (2-propanol) with methylphosphonyl difluoride.

Toxicology: rapidly absorbed through respiratory tract, the onset of symptoms observed from minutes to hours depending on concentration, LC_{50} 0.07 mg/liter, inhalation (humans), casualty dosage (unmasked) 35 mg-min/ m^3 , lethal dosage 100 mg-min/ m^3 . It is toxic by inhalation and absorption (skin and eyes) lethal dose also expressed as 0.01 mg/kg., TPQ 10 (pounds), RQ 1 (pound).

Key precursors: methylphosphonyl difluoride, (CAS. NO. 676-99-3) and methylphosphonyl dichloride, (CAS. NO. 676-97-1) or diisopropyl methylphosphonochloridate.

Precursors: Dimethyl methylphosphonate, $CH_3PO(OCH_3)_2$, (CAS. NO. 765-47-6) or isopropyl methylphosphonate (CAS No. 1445-76-7).

Other chemicals: Trimethylphosphite, (CAS. No. 121-45-9) and Phosphorus Trichloride, (CAS. No. 7719-12-2) or triisopropyl phosphite (CAS. No. 116-17-6).

SOMAN, C₇H₁₆FO₂P
CAS No. 96-64-01
HS No. 29.31.00
Merck 8668

Synonyms: Pinacolyl Methylphosphonofluoridate, GD.

Physical properties: MW: 182; bp: 198°C; colourless, odorless liquid that is sparingly soluble in water.

Synthesis: The reaction of pinacolyl alcohol with methylphosphonyl difluoride.

Toxicology: rapidly absorbed through respiratory tract, casualty dosage (unmasked) 35 mg-min/m³ and the lethal dosage 50 mg-min/m³. It is an oxime resistant nerve agent and acetylcholinesterase inhibited by Soman cannot be reactivated.

Key precursors: methylphosphonyl difluoride, (CAS No. 676-99-3), and methylphosphonyl dichloride, (CAS. No. 676-97-1).

Precursors: Dimethyl methylphosphonate, (CAS No. 765-79-6)

Other chemicals: Trimethyl phosphite, (CAS No. 121-450-9); and Phosphorus trichloride, (CAS NO. 7719-12-2).

Other phosphonofluoridates have been considered as nerve agents, these only differ in the alcohol reacted with methylphosphonyl difluoride, an example would be GF where the alcohol employed is cyclohexanol.

(2): O-alkyl ($\leq C_{10}$ incl. cycloalkyl) alkyl-N,N-dialkyl (methyl, ethyl, n and isopropyl) phosphoramidocyanidates.
The CEFIC have calculated that there are 20,010 possible agents of the phosphoramidocyanidate type.
There is apparently one weaponized phosphoramidocyanidate with the common name tabun.

Tabun, $C_5H_{11}N_2O_2P$
CAS NO. 77-81-6
HS NO. 29.31.00
Merck 9001

Synonyms: Ethyl dimethylaminophosphonocyanidate, GA

Physical properties: MW: 162.15; mp: $-50^{\circ}C$; bp: $240^{\circ}C$; d. 1.073; liquid moderately soluble in water.

Synthesis: The reaction of the cyanide ion with Diethyl-N,N-dimethyl phosphoramidate.

Toxicology: More toxic by ingestion than dermal absorption; casualty dosage (unmasked) 300 mg-min/ m^3 and the lethal dose 400 gm-min/ m^3 , lethal dose is 0.01 mg/kg, TPQ is 10 (pound), RQ 1 (pound).

Key precursors: Diethyl-N,N-dimethylphosphoramidate (CAS No. 2404-03-7) and N,N-dimethylamidophosphoryl dichloride (CAS No. 677-43-0).

Precursors: Phosphorous oxychloride (CAS No. 10025-87-3) and dimethylamine (CAS No. 124-40-3).

Other chemicals: Phosphorous Trichloride (CAS No. 7719-12-2) and Potassium Cyanide (CAS No. 151-50-8).

- (3) O-alkyl (H or $\leq C_{10}$ incl. cycloalkyl) S-2-dialkyl (methyl, ethyl, n- and isopropyl)-aminoethyl alkyl (methyl, ethyl, n- and isopropyl) phosphonothiolates and corresponding alkylated and protonated salts.
The CEFIC calculation suggests that these are 80,040 possible agents of the VX type.

VX, $C_{11}H_{24}NO_2PS$
CAS NO. 50782-69-9
HS NO. 29.31.00
Merck 9948

Synonyms: O-ethyl S-2-diisopropylaminoethyl methyl phosphonothiolate;
phosphonothioc acid, methyl-,
S-(2-(bis(1-methylethyl)amino)ethyl) O-ethyl ester.

Physical properties: MW: 267.37; bp: 298°C; d. 1.0083;
odourless liquid with an amber colour, 1-5% soluble in water,
resistant to hydrolysis and so persistent in the environment.

Synthesis: There are many described pathways to VX. The QL route involves the reaction of O-ethyl-2-diisopropyl aminoethyl methyl phosphonate with sulphur. The thionate route involves the reaction of the potassium salt of ethyl methyl phosphonothionate with diisopropylaminoethyl chloride. The dichloride route involves the reaction of diisopropylaminoethanethiol with ethyl methylphosphonyl chloride. (See S.R. Eckhaus, J.C. Davis, B.M. Zeffert and T.R. Moore, US Patent 3911119, 1960 and R.V. Ley and G.L. Sainsbury, B. Patent 1346409, 1962).

Toxicology: Extremely poisonous by dermal routes, casualty dose (unmasked) 5 mg-min/m³, lethal dose 10 mg-min/d³, LD dermal (human) 0.086 mg/kg, TDLO (oral) 4 mg/kg, it is a long term contact hazard, hydrolysis products (pH7) are almost as toxic.

Key precursors:

| | |
|------------------|--|
| QL Route | O-ethyl O-2 diisopropylaminoethyl methylphosphonite (CAS No. 57856-11-8) |
| Thionite Route | ethyl methylphosphonothionate (CAS No.18005-40-8) |
| Dichloride Route | ethyl methylphosphonyl chloride (CAS No.5284-09-3) |

Precursors:

| | |
|----------------|--|
| QL Route | ethyl methylphosphinyl chloride (CAS No.13213-38-2) diethyl methylphosphonite (CAS No.15715-41-0) methyl phosphinyl dichloride (CAS No.676-83-5) |
| Thionite Route | diethyl methylphosphonothionate (CAS No.6996-81-2) |

diethyl methylphosphonite (CAS No.15715-41-0)
Dichloride Route methyl phosphonyl dichloride (CAS No.676-97-1)

Other chemicals: Phosphorus trichloride (CAS No. 7719-12-1);
N,N-diisopropyl aminoethanol (CAS No.96-80-0),
diisopropylamino-ethyl chloride (CAS No.96-79-7), phosgene (CAS
No. 75-44-5), sulphur (CAS No. 7704-34-9).

(4) Sulphur Mustards:

| | |
|---|------------|
| 2-chloroethylchloromethylsulphide | 2625-76-5 |
| Mustard Gas (H): Bis(2-chloroethyl)sulphide | 505-60-2 |
| Bis(2-chloroethylthio)methane | 63869-13-6 |
| Sesqui Mustard (Q): | |
| 1,2-Bis(2-chloroethylthio)ethane | 3563-36-8 |
| 1,3-Bis(2-chloroethylthio)-n-propane | 63905-10-2 |
| 1,4-Bis(2-chloroethylthio)-n-butane | |
| 1,5-Bis(2-chloroethylthio)-n-pentane | |
| Bis(2-chloroethylthiomethyl)ether | 63918-90-1 |
| O-Mustard (T): | |
| Bis(2-chloroethylthioethyl)ether | 63918-89-8 |

Mustard Gas: $C_4H_8Cl_2S$
CAS NO. 505-60-2
HS NO. 29.30.90
Merck 6225

Synonyms: 1,1'-Thiobis[2-chloroethane]; bis-(2-chloroethyl) sulphide; b.b'-dichloroethyl sulphide; 2,2'-dichlorodiethyl sulphide, sulphur mustard, yellow cross liquid; kampfstoff "lost", yperite.

Physical properties: MW: 159.1; mp: 14°C; bp: 217°C; d. 1.274; n_D^{20} 1.5313; slightly soluble in water (0.68 g/litre) soluble in most organic solvents; a colourless oily liquid with a garlic odour.

Synthesis: There are two major routes; the simplest involves the reaction of thiodiglycol with any chlorinating agent such as HCl or thionyl chloride while the original Levenstein process involved the reaction of ethylene with sulphur monochloride or sulphur dichloride. Vinyl chloride is also reported to react photochemically with hydrogen sulphide.

Toxicology: Causes conjunctivitis and blindness. Its effects are usually delayed (1-12 hr) and can cause edema, ulceration and necrosis of skin and respiratory tract; LD_{50} is 0.42 mg/liter/2m respiratory (rat) and median lethal dose (inhalation) is 1500 gm/min/m³.

Key precursors: Thiodiglycol (CAS No. 111-48-8), hydrogen sulphide (CAS No. 7783-06-4).

Precursors: Ethylene oxide (CAS No. 75-21-8), 2-chloroethanol (CAS No. 107-07-3), sodium sulphide (CAS No. 1313-82-2), sulphur monochloride (CAS No. 10025-67-9), sulphur dichloride (CAS No. 10545-99-0).

(5) Lewisites

| | | |
|-------------|--------------------------------|------------|
| Lewisite 1: | 2-chlorovinyl dichloroarsine | 541-25-3 |
| Lewisite 2: | Bis(2-chlorovinyl)chloroarsine | 40334-69-8 |
| Lewisite 3: | Tris(2-chlorovinyl) arsine | 40334-70-1 |

Lewisite 1, $C_2H_2AsCl_3$

CAS No. 541-25-3

HS No. 29.31.00

Merck 3051

Synonyms: Arsine, dichloro(2-chlorovinyl); Arsonous chloride, (2-chloroethenyl); chlorovinylarsine dichloride

Physical properties: MW: 207.3; mp: 0.1°C; bp: 190°C dec; d. 1.888; a light amber liquid with the smell of geraniums; insoluble in water and soluble in organic solvents.

Synthesis: The reaction of arsenic trichloride with acetylene in the presence of aluminum trichloride. Lewisite 2 and 3 also result from this reaction.

Toxicity: May cause blindness, immediate destruction of lung tissue and systemic blood poisoning; LD₅₀ dermal is 6 mg/kg (rabbit); TPQ 10 pounds; RQ 1 pound. Produces severe vesication, even through rubber.

Key precursors: arsenic trichloride (CAS No. 7784-34-1) and acetylene (CAS No. 74-86-2).

(6) Nitrogen Mustards

| | |
|------------------------------------|----------|
| HN1: Bis(2-chloroethyl)ethylamine | 528-07-8 |
| HN2: Bis(2-chloroethyl)methylamine | 51-75-2 |
| HN3: Tris(2-chloroethyl)amine | 555-77-1 |

HN1, $C_6H_{13}Cl_2N$
CAS No. 528-07-8
HS No. 29.21.19
Merck 4644

Synonyms: Bis(2-chloroethyl)ethylamine; 2,2'-dichlorotriethylamine

Physical properties: MW: 170.08; mp: $-34^{\circ}C$; bp: $194^{\circ}C$ dec; d. 1.09; very slightly soluble in water; miscible with most organic solvents; slow decomposition through quarternary ammonium salts.

Synthesis: The reaction of ethyldiethanolamine with thionyl chloride.

Toxicity: Toxic to subcutaneous tissue with formation of rashes and blisters over a 12 hr period; immediate effects on the eyes; median lethal dosage is 1,500 mg-min/ m^3 (inhalation) and 20,000 mg-min/ m^3 (skin). Deadly vesicant.

Key precursors: ethyldiethanolamine (CAS No. 139-87-7).

HN2, $C_5H_{11}Cl_2N$
CAS No. 51-75-2
HS No. 29.21.19
Merck 5655

Synonyms: 2,2-dichloro-N-methylethylamine; 2-chloro-N-(2-chloroethyl)-N-methylethanamine; 2,2'-dichloro-N-methyldiethylamine; N-methyl-2,2'-dichlorodiethylamine; chlormethine; mustine; mechlorethamine.

Physical properties: MW: 156.07; mp: $-60^{\circ}C$; bp: 87° ; d. 1.15 d_4^{20} 1.118; mobile liquid with odour of herring; very slightly soluble in water; miscible with most organic solvents; decomposes on standing to form polymeric salts.

Synthesis: Prepared by the reaction of thionyl chloride and 2,2'-(methylimino)diethanol in trichloroethylene [Prelog and Stephan, Coll. Czech. Chem. Commun., 7, 93 (1935)].

Toxicity: Immediate effect on eyes with rashes, blisters and pulmonary effects appearing over 12 hours; median lethal dose is 3000 mg-min/ m^3 (inhalation). It is a cumulative poison; high enough concentrations can cause blindness; death occurs through asphyxiation or heart failure.

Key precursors: methyldiethanolamine (CAS. No. 105-59-9).

Uses: The hydrochloride salt, $C_{15}H_{12}Cl_3N$, is used as an antineoplastic both in human and veterinary medicine. It is variously called Caryolysine, Chloramin, Dichloren, Embichin, Embikhine, Erasol, Mustargen hydrochloride, Mustine hydrochloride and Nitrogranulogen.

HN3, $C_6H_{12}Cl_3N$
CAS No. 55-77-1
HS No. 29.21.19
Merck 9560

Synonyms: Tris(2-chloroethyl)amine; 2,2,2-trichlorotriethylamine.

Physical properties: MW: 204.54; mp: $-3.7^{\circ}C$; bp: $256^{\circ}C$; n_D^{20} 1.4925; d. 1.24; mobile amber liquid with the smell of fish; slightly soluble in water and miscible with most organic solvents; polymerises on standing.

Synthesis: The reaction of thionyl chloride on triethanolamine [Ward, J.A.C.S., 57, 914 (1935); Contardi and Dymontel, Chim. Ind (Milan) 29, 169 (1947) and Wilson and Tishler, J.A.C.S., 73, 3635 (1951)].

Toxicity: Causes immediate eye irritation and respiratory tract damage; liquid splashes will cause rashes followed by blistering. Death is usually due to asphyxiation. Median lethal dose is 1500 mg-min/m³ (inhalation) and 10,000 mg-min/m³ (skin). Vesicant.

Key precursors: triethanolamine (CAS No. 102-71-6).

Uses: Its hydrochloride, $C_6H_{13}Cl_4N$, called trimustine, trichloromethine, Singlost or Trillekamin is used as an antineoplastic.

(7) Saxitoxin, $C_{10}H_{17}N_7O_4$
CAS No. 35523-8908
NIOSH:RTECS No. UY8708500
Merck 8344

Synonyms: 2,6-diamino-4-(((aminocarbonyl) oxy)methyl)-3a,4,8,9-tetrahydro-1H, 10H-pyrrolo (1,2-c) purine-10,10-diol (3aS-(3a-a-a-4-a,10aR*)).

Physical Properties: MW: 299, $[a]_D + 130^\circ$, it is a white amorphous solid (the hydrochloride salt is crystalline) and is a hydrate. Information on physical properties is found in J. Bordner et. al., J.A.C.S., 1975, 97, 6008

Synthesis: It is a natural neurotoxin sometimes found in Alaska butter clams, toxic mussels, and plankton. Its chemical synthesis has been reported by H. Tanino et al., J.A.C.S., 1977, 99, 2818.

Toxicity: It is one of the most potent neurotoxins known; its $LD_{50 \text{ ipr}}$ is 5 mg/kg (mouse). Data is also available on Saxitoxin hydrochloride ($C_{10}H_{17}N_7O_4 \cdot 2HCl$, MW372, CAS No. 35554-08-6, NIOSH/RTECS UY8708600. Both are deadly poisons by ingestion, intravenous and intraperitoneal routes.

Uses: It is used as a neuromuscular blocking agent, and in nerve fibre research.

Suppliers: Two suppliers are listed in the USA.

(8) Ricin

CAS No. 9009-86-3

NIOSH/RTECS No. VJ 26250000

Merck 8211

Synonyms: Ricin A, Ricin B, RCA (Ricin Communis Agglutin) RCA₆₀, RCA₁₂₀, Ricin D, RCL 111, RCA₁₁.

Physical Properties: It is a white powder obtained from castor beans. It is normally preformulated due to its great toxicity; RCA₆₀ and RCA₁₂₀ refer to molecular weights of 60000 and 120000 respectively.

Synthesis: Castor oil seeds are pressed to remove the commercially valuable castor oil. The oil cake residue is mainly protein and it is the source of the poisonous albumin called ricin which is a polymeric protein. The ricin is destroyed by steam treatment of the oil seed cake that is then used for animal feeds or fertilizer.

Toxicity: Amongst the most poisonous substances known. The lowest published lethal concentration (LDLo) is 300 mg/kg. It is a deadly poison by ingestion or inhalation. The effect of inhalation/ingestion is violent purging which leads to collapse and death; it causes destruction of red blood cells; as few as 5 castor beans have resulted in the death of children.

Uses: It is used in biochemical research and in medicine. Ricin conjugated with mono- or polyclonal antibodies is being investigated as a possible cancer treatment.

Suppliers: Two suppliers are listed for the USA. However 22 suppliers of castor oil are listed in 12 countries. These are: Canada (1), PRC (1), Mexico (1), India (3), Japan (5), Australia (2), Belgium (2), France (1), UK (1), Italy (1), Portugal (2) and Spain (2).

B. Precursors

(9) Alkyl (Me, Et, n-Pr and i-Pr) phosphonyldifluorides

example:

DF, $\text{CH}_3\text{P}(\text{O})\text{F}_2$

CAS No. 676-99-3

HS No. 29.31.00

NIOSH: RTECS No. TA 184077

Synonyms: Methylphosphonyl difluoride; methylphosphoric difluoride

Physical properties: MW:100.00; bp: 98°C; d_4^{20} 1.3320; n_D^{20} 1.3165; liquid.

Synthesis: The reaction of hydrogen fluoride with methylphosphonyl dichloride. The reaction of methyl tetrafluorophosphine with acetic anhydride gives the difluoride in 80% yield. [V.V. Lysenko et. al., Zh.obshch. Khim., 1966, 36, 1507 (1512 in English translation)].

Suppliers: Two suppliers are listed in the United States.

(10) O-alkyl (H or C \leq C₁₀ incl.cycloalkyl)O-2-dialkyl (Me, Et, n-Pr or i-Pr)-aminoethyl alkyl (Me, Et, n-Pr or i-Pr) phosphonites and corresponding alkylated and protonated salts.

example:

QL, C₁₁H₂₆NO₂P
CAS No. 57856-11-8
HS No. 29.31.00

Synonyms: O-ethyl O-2-diisopropylaminoethyl methylphosphonite.

Physical properties: M.W.: 235

Synthesis: The reaction of ethyl methylphosphinyl chloride with N,N-diisopropylaminoethanol or the transesterification of diethyl methylphosphonite. (See S.R. Eckhaus et. al., US Patent 3911119, 1962).

(11) Chlorosarin, $C_4H_{10}ClO_2P$
CAS 1445-76-7
HS 29.31.00

Synonyms: O-isopropyl methylphosphonochloridate.

Physical Properties: MW: 156.5; Bp: 40°C; d_4^{21} 1.15;
 n_D^{23} 1.4285; liquid for (\pm) form
Rform: liq.; $[a]_D^{27}$ -52.3°; n_D^{25} 1.4281

Sform: liq; $[a]_D^{31}$ +52.8°; n_D^{25} 1.4298

Synthesis: The reaction of dialkyl methyl phosphonates ($CH_3.P(O)(OR)_2$ with thionyl chloride, oxalyl chloride or phosgene leads to the formation of alkyl methylphosphonochloridates in high yield; yields for the isopropyl ester are in the 61-45% range (Z. Pelchowicz, J.C.S., 1961, 238; (Coe et. al., J.C.S., 1957, 3604) for resolution see H.S. Aaron et. al., J.A.C.S., 1962, 84, 617.

Toxicology: LD_{50} for the isopropyl ester is 4.5 mg/kg (rat) (Z. Pelchowicz).

(12) Chlorosoman, $C_7H_{16}ClO_2P$
CAS 7040-57-5
HS 29.31.00

Synonyms: O-pinacolyl methylphosphonochloridate.

Physical Properties: M.W.: 198.5

Synthesis: see chlorosarin on the reaction of methylphosphonyl dichloride with pinacolyl alcohol.

PART II
INFORMATION
ON
SCHEDULE 2 CHEMICALS

A. Toxic Chemicals

(1) Amiton, $C_{10}H_{24}NO_3PS$
CAS No. 78-53-5
HS No. 29.31.00.90
NIOSH/RTECS No. TF 0525000
Merck 502

Synonyms: S-[-2-(Diethylamino)ethyl] phosphorothioic acid
O,O-diethyl ester; O,O-diethyl
S-2-diethylaminoethylphosphorothiolate; tetram; chipman 6200,
Chipman R-6199, Citram, Metramak, Metramac.

Physical properties: MW: 269; bp_{0.2}: 110°C; n_D²⁷ 1.4655, liquid

Synthesis: Prepared by the thermal rearrangement of
O,O-diethyl-0-2-diethylaminoethyl phosphorothionate [T.R. Fukato
and E.M. Stafford, JACS, 79, 6083(1957); R. Ghosh and J.F.
Newman, Chem. and Ind., 118(1955)].

Toxicology: A deadly poison LD₅₀ 0.5 mg/kg (oral, human) and 5.4
mg/kg (oral/rat), cholinesterase inhibitor.

Uses: It was used as an insecticide but withdrawn commercially
because of its great toxicity. It was also sold as amiton
oxalate ($C_{10}H_{24}NO_3PS \cdot C_2H_2O_4$, MW: 359.42, mp:98-99°, CAS No.
3734-97-2, NIOSH: TF 1400000, LD₅₀ 3 mg/kg (rat)).

Suppliers: There are no commercial suppliers at this time.

Literature survey: Only 6 papers have appeared in the Chemical
Abstract literature since 1985 (32 in total since 1967). The
distribution is UK(2), PRC (2), Germany (1), and Russia (1).

- (2) **Perfluoroisobutylene**
1,1,3,3,3 - pentafluoro-2-trifluoromethyl-1-propene
CAS No. 382-21-8
HS No. 29.03.30.90

Synthesis: It is a by-product of the production of tetrafluoroethylene in the pyrolysis of chlorodifluoromethane. The reaction conditions chosen to prepare tetrafluoroethylene lead to the formation of perfluoroisobutylene (PFIB) to the extent of 0.1% of the pyrolysis product. Another product of the pyrolysis is hexafluoropropene which can also be pyrolyzed at 700-800°C when PFIB is obtained in yields of up to 30% (CD/CW/WP.239, 1989).

Toxicology: PFIB has approximately the same toxicity as hydrogen cyanide (See Schedule 3).

Uses: There are no known industrial applications of PFIB.

Literature Survey:

Examination of Chemical Abstracts from 1986 till May 1992 produced 55 references from five countries; Russia (34), USA (15), UK (3), Japan (21) and Germany (1). (Annex 1).

(3) BZ: 3-Quinuclidinyl benzilate $C_{21}H_{23}NO_3$
CAS No. 6581-06-2
HS No. 29.39.90
NIOSH/RTECS No. DD 4638000
see Merck 8110

Synonyms: 1-azabicyclo (2.2.2) octan-3-ol benzilate,
3-Chinuclidylbenzilate, R02-3308

Physical Characteristics: MW: 337.5; mp: 165°C

Synthesis: Prepared by the esterification of benzylic acid with 3-quinuclidinol; other esters would result when the latter alcohol is replaced by others; the commercial process involves diphenylchloroacetyl chloride.

Toxicology: Poisonous by intravenous routes; LD₅₀ is 25 mg/kg (mouse).

Uses: BZ is used in the preparation of clidinium bromide and also in combination with chlorodiazepoxid in several preparations used as anticholinergic e.g., Librax, Libraxin; clidinium bromide is the sole active agent in Dolibrax, it is sold as Quarzan in the USA. It is also considered to be an anxiolytic substance.

Suppliers: One supplier is listed for the United States.

B. Precursors

(4) Chemicals, except for these listed in Schedule 1, containing a phosphorous atom to which is bonded one methyl, ethyl or propyl (normal or iso) group but not further carbon atoms

i.e., $\text{CH}_3\text{P-}$; $\text{C}_2\text{H}_5\text{P-}$; $\text{nC}_3\text{H}_7\text{P-}$; $\text{ic}_3\text{H}_7\text{P-}$

Two examples of what would be a very large class of compounds are given; these are Methylphosphonyl dichloride (676-97-1) and Dimethyl Methylphosphonate (765-79-6).

(4a) Methylphosphonyl dichloride, $\text{CH}_3\text{Cl}_2\text{OP}$
 CAS No. 676-97-1
 HS No. 29.31.00.90
 NIOSH/RTECS No. TA 1840000

Synonyms: Phosphonic dichloride, methyl

Physical Characteristics: MW: 132.91; mp: 37°C; bp: 163°; a corrosive liquid.

Synthesis: Prepared by the reaction of dimethyl methyl phosphonate with thionyl chloride.

Toxicology: Poisonous if inhaled or swallowed, LC_{50} inhalation (rat) 0.141 mg/liter/4h, TPQ 100 (pounds), RQ 1 (pound).

Uses: A precursor in the production of G-nerve agents.

Suppliers: Nine suppliers listed; USA (8) and UK (1).

(4b) Dimethyl methylphosphonate, $\text{C}_3\text{H}_7\text{PO}$
 CAS No. 765-79-6
 HS No. 29.31.00.90
 NIOSH/RTECS No. SZ 9120000

Physical Characteristics: MW: 124.1; bp: 181°C; n_D^{20} 1.4130; d. 1.145; liquid

Synthesis: Prepared by the rearrangement of trimethyl phosphite catalyzed by sodium iodide.

Toxicology: No detailed information available.

Uses: A precursor in the production of G-nerve agents.

Suppliers: Eight suppliers listed; USA (5), UK (2) and Switzerland (1).

- (5) N,N-Dialkyl (CH_3 , C_2H_5 , nC_3H_7 , iC_3H_7)
phosphoramidic dihalides

No data collected.

- (6) Dialkyl (CH_3 , C_2H_5 , nC_3H_7 , iC_3H_7) N,N-dialkyl
(CH_3 , C_2H_5 , nC_3H_7 , iC_3H_7) phosphoramidates

No data collected.

(7) Arsenic Trichloride, AsCl₃

CAS No. 7784-34-1
HS No. 28.27.39.00
TDG 1560, Class 6.1, Packing Group I.
NIOSH/RTECS No. CG1750000
Merck 829

Synonyms: Arsenous trichloride, trichloroarsine, arsenic butter, caustic arsenic chloride

Physical Characteristics: MW: 181.28 colourless oily liquid. b.p:130°, mp: -13°, s.g. 2.205. Solubilities: miscible in chloroform, carbon tetrachloride and ether, sinks and reacts in water. Decomposed by ultraviolet light.

Synthesis: spontaneous combustion of arsenic in chlorine; the reaction of chlorine with arsenic trioxide, As₂O₃; the reaction of hydrochloric acid, HCl with arsenic trioxide; the reaction of sulphur chloride, S₂Cl₂ with As₂O₃.

Reactivity: reacts with water to produce hydrochloric acid, emits toxic fumes when heated to decomposition, explodes on contact with sodium, potassium or aluminium, corrodes metals.

Toxicology: All arsenic compounds are toxic with the trivalent inorganic compounds being the most toxic. The Threshold Limit Value for AsCl₃ is 0.2 mg/m³ as As; toxicity by ingestion is Grade 3; oral LD₅₀ 138 mg/kg (rat) with the fatal human dose in the range of 70-180 mg. AsCl₃ is poisonous by inhalation. It is reported in EPA TSCA inventory and on the EPA Extremely Hazardous Substance List.

Uses: Major use as an intermediate for the production of organic arsenicals for pharmaceuticals and insecticides. Arsenical compounds find uses as insecticides, herbicides, defoliants and rodent ocide.

Suppliers: A review of three directories of chemical suppliers produced two manufacturers, and at least six sources of its major precursor. There is one supplier in the United States and another in Germany.

Literature Survey:

Examination of Chemical Abstracts from 1986 till May 1992 produced 150 references from 23 countries. About a third of the publications are technology related e.g., semi-conductor related with 26% of the papers being published by industry and 26% being patents. (Annex 1).

(8) 2,2 - Diphenyl-2-hydroxyacetic acid, $C_{14}H_{12}O_3$
CAS No. 76-93-7
HS No. 29.18.19.90
NIOSH/RTECS No. DD 2064000
Merck 1089

Synonyms: Benzilic acid, α -phenyl- α -hydroxy benzeneacetic acid, diphenylglycollic acid, 2-hydroxy-2-2-diphenylethanoic acid

Physical Characteristics: MW: 228, mp: 151-2°, pk_a 3.04 (25°), soluble in hot water.

Synthesis: Prepared in high yield by the oxidation of benzoin, ($C_6H_5CHOHCOC_6H_5$) which is obtained by the self-condensation of benzaldehyde (C_6H_5CHO) catalyzed by the cyanide ion (Collected Organic Synthesis, Vol. 1, p. 94, 2nd Edition, John Wiley and Sons, N.Y., 1964), and also by the action of KOH on benzil, Organic Synthesis 1, 29 (1921).

Toxicology: No detailed information available.

Uses: Organic Synthesis, pharmaceutical industry and preparation of tranquilizers.

Suppliers: A review of the chemical supplier's literature produced seven manufacturers worldwide: USA (1), India (1), Japan (2), Italy (1) and Spain (2).

Literature Survey: Examination of Chemical Abstracts from 1986 till May 1992 produced 125 references, and these involve 20 countries.
(Annex 1).

(9) Quinuclidin-3-ol, C₇H₁₃NO
CAS No. 1619-34-7
HS No. 29.33.90.00
NIOSH/RTECS No. VD 6191700
Merck 8110

Synonyms: 3-quinuclidinol, 3-hydroxyquinuclidine

Physical Characteristics: MW: 127, R form m.p.: 223-4° [a]_D²⁰ + 45.3°, S form mp: 223-4° [a]_D²⁰ - 45.1°.

Synthesis: It is obtained in quantitative yield by the hydrogenation of 3-quinuclidone using either a platinum catalyst or raney nickel. A three step process from 3-vinylpyridine has also been described. (L.H. Sternbach et al., J.A.C.S., 74, 1331, 1952; and H.S. Aaron et al., J. Org. Chem., 30, 1331, 1965).

Toxicology: No detailed information available.

Uses: It has been described as a reagent to cleave α-keto esters, used in the synthesis of pharmaceuticals and has been used as a hypotensive agent.

Suppliers: Six producers have been identified worldwide in France (4), Switzerland (1) and Norway (1).

Literature Survey:

Examination of Chemical Abstracts from 1986 till May 1992 produced from 65 references from 14 countries; 43% of the references came from industry and 41.5% referred to the patent literature (Annex1).

(10) N,N-dialkyl (CH_3 , C_2H_5 , $n\text{C}_3\text{H}_7$, $i(\text{C}_3\text{H}_7)$) aminoethyl-2-chlorides and corresponding protonated salts.

No data collected.

(11) N,N-dialkyl (CH_3 , C_2H_5 , $n\text{C}_3\text{H}_7$, $i(\text{C}_3\text{H}_7)$) aminoethane-2-ols and corresponding protonated salts.

Exemptions: N,N-dimethylaminoethanol (108-01-0)

N,N-diethylaminoethanol (100-37-8)

and the corresponding protonated salts

No data collected.

(12) N,N-dialkyl (CH_3 , C_2H_5 , $n\text{C}_3\text{H}_7$, $i\text{C}_3\text{H}_7$) aminoethane-2-thiols and the corresponding protonated salts

No data collected.

(13) **Thiodiglycol, C₄H₁₀O₂S**
CAS No. 111-48-8
HS No. 29.30.90.00
NIOSH/RTECS No. KM 2975000
Merck 9259

Synonyms: Bis (2-hydroxyethyl) sulphide; 2,2'-dithiobisethanol;
thiodiethylene glycol

Physical Characteristics: MW: 122.19, mp: -16°, n_D²⁰ 1.5215,
d_{1.221}, miscible with water and alcohol.

Synthesis: Ethylene can be oxidized either by air or oxygen over a silver catalyst to produce ethylene oxide, a chemical that is produced worldwide in large tonnages. This is a very reactive substance and on reaction with hydrogen sulphide, gives thiodiglycol in essentially quantitative yield. The process can be modified to form 2-mercaptoethanol which also can be converted to thiodiglycol. An alternative, but commercially obsolete process, involves the reaction of 2-chloroethanol (ethylene chlorohydrin) with sodium sulphide to give thiodiglycol in about 86% yield (Collected Organic Synthesis, Vol. 2 P. 576, John Wiley and Sons, New York, 1943).

Reactivity: Chlorination of thiodiglycol leads to mustard gas, chlorinating agents used are phosphorous trichloride, thionyl chloride or concentrated hydrochloric acid. Oxidation leads to the corresponding sulphone.

Toxicology: This has not been thoroughly investigated but it is not acutely harmful. The reported LD₅₀s are in the range of 3000-6000 mg/kg. Its vapour is irritating to the eyes, mucuous membranes and upper respiratory tract. It is harmful by inhalation, ingestion or skin absorption. Exposure leads to headaches, nausea and vomiting.

Uses: Thiodiglycol has industrial uses in elastomers, lubricants, stabilizers, antioxidants, inks, dyer, photographic and copying processes, antistatic agents, epoxides, coatings, metal plating and textiles. The textile industry would appear to be the major user.

Suppliers: There are seven listed suppliers currently: USA (1), Japan (3), France (1), Germany (1) and the Netherlands (1).

Literature Survey: A detailed literature survey was presented to the Conference on Disarmament in 1990 as CD/CW/WP.279. this was based on Chemical Abstracts from 1975 to 1988. It produced 346 references from 26 countries. An unusual feature was the fact that 56% of the references came from industry and 52% resulted from the patent literature. The USA, Japan, Germany, Russia and the UK accounted for 75% of the published work.

(14) 3,3-dimethyl-2-butanol, C₆H₁₄O
CAS No. 464-07-3
HS No. 29.05.19.00
NIOSH/RTECS No. EL2276000

Synonyms: Pinacolin alcohol, pinacolyl alcohol,
methyl t-butylcarbinol

Physical Characteristics: MW: 102, mp: 5.6°, b.p: 121°,
n²⁰_D1.4150, d._{0.812}, S Form (1517-67-5) [a]_D²⁰ + 7.71, sparingly
soluble in water.

Synthesis: Prepared by the reduction of pinacolone
(3,3-dimethyl-2-butanone; 75-97-8) that is readily available by
the dehydration of pinacol hydrate (Coll. Org. Syn. Vol. 1 pp.
459 and 462, John Wiley and Sons, N.Y., 1964). It can also be
prepared by the grignard reaction of acetaldehyde and t-butyl
magnesium bromide (R.H. Pickard et. al, J. Chem. Soc., 105, 1120,
1914).

Toxicology: No detailed information available.

Uses: No substantial industrial use at present.

Suppliers: Two suppliers are listed, one in the United States
(1) and the other in Germany (1).

Literature Survey: A literature review was presented to the
Conference on Disarmament in 1989 as CD/CW/WP.259. The survey of
Chemical Abstracts covered the period 1975-1988 and it produced
134 references from 24 countries. About 12% resulted from
industrial research and 5% of the references were patent
applications. The bulk of the research, 40%, originated in the
United States as did half of the patent applications. Major
potential interests involve the petrochemical and pharmaceutical
industries.

PART III
INFORMATION
ON
SCHEDULE 3 CHEMICALS

A. Toxic Chemicals:

- (1) Phosgene, COCl_2
CAS No. 75-44-5
HS No. 28.12.10.90
TDG 1076, Class 2, Secondary risks 6.1 and 8
NIOSH/RTECH No. SY5600000
Merck 7310

Synonyms: Carbonyl chloride, carbon oxychloride, chloroformyl chloride

Physical Characteristics: MW: 98.9; bp: $7.48^\circ \text{d}_{20} 1,387$; soluble in aromatic and aliphatic hydrocarbons, chlorinated hydrocarbons, organic acids and esters. It is a colourless gas or a yellow liquid with a sweet odour.

Synthesis: Manufactured on a large scale by the reaction of highly purified carbon monoxide and chlorine with the reagents being mixed in equimolar amounts over activated charcoal and the condensed phosgene removed. The vapours from the tubular-heat exchanges are scrubbed to remove the remaining phosgene before recirculation.

Reactivity: Decomposes slowly in water producing poisonous vapour, poisonous gases produced on heating, reacts with a wide variety of inorganic and organic substances.

Toxicology: It appears on the EPA extremely hazardous substance list and on the EPA TSCA inventory. It should be labelled as a poisonous gas. It is a severe irritant for eyes, skin and mucous membranes. It is poisonous by inhalation. There is a latent period of two to twenty four hours with death occurring 36 hours after exposure. Odour threshold is 0.5 to 1 ppm with a TLV of 0.1 ppm in air; concentrations in air should be below 0.1 ppm. Moisture leads to the formation of hydrochloric acid and carbon monoxide.

Uses: It is an important and widely used intermediate; mostly captive use within the plant boundary. About 85% of the production is used in the polyurethane industry. In 1977 U.S. demand was about 6.23×10^3 metric tons with a 10% growth per annum. Industrial use distribution was polymeric isocyanates 85%; polycarbonates 6%; pesticides, other isocyanates and speciality chemicals 9%. It has also been used to recover Pt, U, and Nb. Its use has been proposed for the manufacture of AlCl_3 , BeCl_2 and BCl_3 . It is used in the production of chloroformates and in the perfume, herbicide, insecticide and pharmaceutical industries.

Suppliers: The World Directory of Chemical Suppliers lists 22 manufacturers: Brazil (3), USA (4), PRC (1), India (1),

Japan(6), South Korea (1), France (1), Germany (3), United Kingdom (1) and Hungary (1). However the 1990 Directory of Chemical Producers United States list 14 producers with a total capacity of 2.342 million pounds, only one of which sells to the merchant market.

(2) **Cyanogen chloride, CNCl**
CAS No. 506-77-4
HS No. 28.12.10.90
TDG No. 1589
NIOSH/RTECS No. GT 2275000
Merck 2701

Synonyms: Chlorcyan, chlorine cyanide, chlorocyanide, mp: -65°,

Physical Properties: MW: 61.48, mp: -6.5°C, bp: 13.1°C, d 1.222 at 0°C, colourless as liquid and gas with a sharp, pungent-odour, soluble in water, alcohol and ether.

Synthesis: It is prepared by the reaction of chlorine with hydrogen cyanide on by the electrolysis of aqueous hydrogen cyanide in the presence of ammonium chloride.

Toxicology: Poisonous by ingestion, toxic by inhalation. It is a primary irritant and a very severe eye irritant, LD₅₀ 20 mg/kg (sc rabbit). Decomposition leads to toxic and corrosive fumes of chloride, cyanide and nitrogen oxides. It is reported on the EPA TSCA inventory.

Uses: Used in chemical synthesis.

Suppliers: There is only one listed supplier and that is in the United Kingdom. The corresponding cyanogen bromide is available in Brazil (1) and the USA (2).

(3) Hydrogen Cyanide, HCN
CAS No. 74-90-8
HS No. 28.11.19.90
TDG No. 1051 Class 6.1
Merck 4722

Synonyms: hydrocyanic acid, prussic acid, formonitrile

Physical Properties: MW: 27.03, mp: 13.24°C, bp: 25.70°C, d.0.7150. It is a colourless, low viscosity liquid with the odour of bitter almonds.

Synthesis: It has previously been prepared by the action of acid on sodium cyanide and the dehydration of formamide. There are two major commercial processes. The reaction of ammonia, methane (natural gas) and air using a platinum catalyst. This is the Andrussow process. The BMA process was developed by Degussa and involves the reaction of ammonia with methane. It can also be produced as a by-product in the manufacture of acrylonitrile by the ammoxidation of propylene (Sohio) where 15 kg HCN is produced for every 100 kg of acrylonitrile. The major commercial processes operate at a catalytic bed temperature of 1100°C and the major problem is the removal of excess heat since the products decompose above 400°C. Yields are of the order of 85%.

Reactivity: Hydrogen cyanide is a nitrile and so it hydrolyses to give formic acid and can be hydrogenated to methylamine. Aerial oxidation gives cyanic acid, HOCN and cyanogen [CN]₂. Chlorine reacts to form cyanogen chloride. It can add across CO and CC double bonds.

Toxicology: It is poisonous by inhalation, oral absorption and by skin absorption. The threshold limit value is 10 ppm, 100 ppm is dangerous for 30-60 minute exposure while 300 ppm is likely fatal. The LD₅₀ is less than 50 mg/kg. 2% HCN in air will cause poisoning in 3 minutes, oral absorption at 1 mg/kg can be fatal.

Uses: Estimates of the various uses of HCN in the USA are methyl methacrylate, 60%; cyanuric chloride, 15%; sodium cyanide, 10%; nitrilotriacetic acid and other chelates, 10%; others 5%. Herbicides based on cyanuric chloride showed the fastest growth.

Suppliers: The World Directory lists 24 manufacturers: USA (6), Japan (7), Belgium (1), France (1), Germany (4), UK (2), Italy(1), Netherlands (1) and Spain (1). The SRI International Directory lists 10 USA manufacturers with a total capacity of 1,534 million pounds most of which is processed further on-site.

(4) Trichloronitromethane CCl_3NO_2
CAS No. 76-06-2
HS No. 29.04.90.00
TDG 1580/1583
NIOSH/RTECS No. PB6300000

Synonyms: Chloropicrin, acquinite, chlor-o-pic, dolochlor, larvacide, microlysin, nitrochloroform, nitrotrichloromethane, picfume

Physical Properties: MW: 164.37, mp: -64° , bp: 112.3° , d.1.651, n_D^{20} 1.4608, soluble in water, alcohol and ether. It is an oily, colourless liquid.

Synthesis: Trichloroethylene can be converted to chloropicrin (R.B. Burrows & L. Hunter, J. Chem. soc., 1357 (1932)) by the chlorination of nitromethane and by the reaction of nitromethane with NaOCl.

Reactivity: Reacts violently with aniline, alcohol, sodium hydroxide or methoxide, it can be detonated by shock. Decomposition produces toxic fumes of halide ion and nitrogen oxides.

Toxicity: Poisonous by ingestion, moderately toxic by inhalation, and a powerful irritant. It causes lachrymation, vomiting and pulmonary edema. Oral LD_{50} 250 mg/kg (rat), TLV 0.1 ppm. It is on the EPA TSCA list.

Uses: Insect and rodent control in grain, soil fumigant and fungicide, a warning agent in commercial fumigants.

Suppliers: 8 producers are listed worldwide: USA (4), Japan (3), and PRC (1).

B. Precursors:

- (5) Phosphorus oxychloride POCl_3
CAS No. 10025-87-3
HS No. 28.12.10.10
TDG No. 1810
NIOSH/RTECS No. TH 4897000
Merck 7324

Synonyms: Phosphoryl chloride, phosphorous oxytrichloride

Physical Properties: MW: 153.3, mp: 1.2°C, bp: 105.1°, d.1.685.
It is a colourless to pale yellow fuming liquid.

Synthesis: Simple methods of preparation include the partial hydrolysis of a mixture of PCl_5 and P_2O_5 , oxidation of PCl_3 by oxygen or ozone or heating calcium phosphate with a mixture of carbon monoxide and chlorine. It is manufactured by bubbling oxygen through liquid phosphorous trichloride.

Reactivity: Similar to PCl_3 , the halogens can be replaced by R in RMgX , all three halogens can be replaced by RO from alcohols, hydrolysis yields phosphoric acid. It forms donor complexes with metal ions e.g., $\text{POCl}_3 \cdot \text{AlCl}_3$.

Toxicology: It volatilizes readily to give very irritating vapours. It is poisonous by inhalation and ingestion. It reacts explosively with water and many other liquids. Its LD_{50} is 380 mg/kg (rat). It is a corrosive liquid and is reported on the EPA TSCA inventory.

Uses: It is used to produce alkyl and aryl orthophosphate triesters that are used in the production of hydraulic fluids, plastic and elastomer additives, oil stabilizers, surfactants, sequestrants, pesticide and pharmaceutical intermediates. Trialkyl phosphates are used in uranium processing.

Suppliers: Twenty-five suppliers listed worldwide: These are Brazil (1), USA (6), PRC (2), India (3), Japan (4), France (2), Germany (3), UK (1), Italy (2) and Spain (1).

(6) Phosphorus trichloride, PCl_3
CAS No. 7719-12-2
HS No. 28.12.10.10
TDG 1809
NIOSH/RTECS No. TH 3675000
Merck 7333

Synonyms: Chloride of phosphorus, phosphorus chloride

Physical Properties: MW:137.3, mp: -111.8, bp: 76°, d 1.574. It is a clear colourless fuming liquid, it is soluble in benzene, chloroform and ether. It is decomposed by water and alcohol.

Synthesis: The trihalides of phosphorus are usually prepared by direct reaction with the halogen under controlled conditions. PCl_3 formation is moderated by combining the elements in the presence of a refluxing precharge of the trichloride with liquid chlorine and phosphorus being continuously introduced; the crude PCl_3 is treated with a further charge of phosphorous and then purified by fractional distillation. Yields of 95% are obtained.

Reactivity: It is extremely reactive. Reaction with alcohols results in $P(OR)_3$; carbanion sources give PR_3 , PR_2Cl and $PRCl_2$; aliphatic hydrocarbons give $RP(O)Cl_2$; oxygen yields Cl_3PO while water or ammonia give hydrolysis and ammonolysis products respectively.

Toxicology: It is poisonous by inhalation and highly toxic by ingestion. It is a corrosive irritant to skin, eyes and mucous membranes. The TLV is 0.5 ppm and the oral LD_{50} is 550 mg/kg (rat). It reacts violently with water and the resulting acids can form hydrogen or reaction with metals. On decomposition, fumes of PO_x which are highly toxic are formed. It appears on the EPA extremely hazardous substance list and reported in EPA TSCA.

Uses: It is an intermediate in the production of phosphorous oxychloride, phosphorous sulfochloride, phosphorous pentachloride and phosphorous acid. It is also the starting material for the production and dialkyl phosphonates, dialkyl alkyl phosphonates and trialkyl phosphites.

Suppliers: Twenty-six producers are listed: these are Brazil (1), USA (6), PCR (6), India (3), Japan (4), France (2), Germany (1), UK(1), Italy (1) and Switzerland (1).

(7) Phosphorus pentachloride PCl_5
CAS No. 10026-13-8
HS No. 28.12.10.10
TDG 1806
NIOSH/RTECS No. TB 6125000
Merck 7326

Synonyms: Phosphoric chloride, phosphorous perchloride

Physical Properties: MW: 208.22, mp: 179-181°, d 1.6. It is a yellowish-white crystalline mass with a pungent odour and it fumes in air.

Synthesis: It is made from PCl_3 and chlorine or by burning phosphorous in excess chlorine. It is made either by batch or continuous processing. In the batch process, PCl_3 is dissolved in carbon tetrachloride and the chlorine gas added above the liquid level when crystals of PCl_5 are formed. In the continuous process the trichloride is run countercurrent to the chlorine and the PCl_5 collected at the bottom of the tower.

Reactivity: It reacts violently with water and explosively with chlorine dioxide, urea, fluorine and many other substances. On decomposition, it emits highly toxic fumes containing PO_x and halide ions.

Toxicology: It is a severe irritant to eye, skin and mucous membranes. It is poisonous by inhalation and ingestion. The LD_{50} is 660 mg/kg (rat) and it is corrosive to body tissues. It is on the EPA extremely hazardous substance list and reported on the EPA TSCA inventory.

Uses: It is used as a catalyst, chlorinating and dehydrating agent and in the manufacture of chlorophosphazenes.

Suppliers: Four suppliers are listed in the World Directory: India(1), Japan (2) and Germany (1). The SRI directory lists one US manufacturer.

(8) Trimethyl Phosphite, $C_3H_9O_3P$
CA No. 121-45-9
HS No. 29.20.90.90
TDG No. 2329
NIOSH/RTECS No. TH 1400000

Synonyms: Methyl phosphite; phosphorous acid, trimethyl ester; trimethoxyphosphine

Physical Properties: MW 124.09, mp: -78° , bp: 112° , d 1.052, n_D^{20} 1.4080. Soluble in hexane, benzene, acetone, alcohol, ether and carbon tetrachloride; insoluble in water.

Synthesis: Phosphorous trichloride reacts with methanol in the presence of a base to form trimethyl phosphite.

Reactivity: Trialkyl phosphites react with carboxylic acids to form esters; at high temperatures these esters undergo an auto-Arbuzov rearrangement viz $(CH_3O)_3P-CH_3P(O)(OCH_3)_2$. Emits toxic fumes, PO_x , on decomposition and is a flammable liquid.

Toxicology: Moderately toxic by ingestion and dermal contact, it is a severe skin and eye irritant. Its LD_{50} is 1600 mg/kg (rat) with a TLV of 2 ppm. It is reported in EPA TSCA inventory.

Uses: An intermediate in the production of pesticides, fire retardants and organophosphorous additives. Also used in dyestuffs, optical brighteners, plasticizers and lubricants.

Suppliers: There are 8 suppliers listed worldwide. These are Mexico (1), USA (2), PRC (2), Japan (1), Germany (1) and Switzerland (1); SRI International lists 5 USA producers.

(9) Triethyl Phosphite, $C_6H_{15}O_3P$
CAS No. 122-52-1
HS No. 29.20.90.90
TDG No. 2323
NIOSH/RTECS No. TH 1130000

Synonyms: Ethyl phosphite; phosphorous acid, triethyl ester; triethoxy phosphine

Physical Properties: MW 166.18, bp: 156°, d.0.969, n_D^{20} 1.4130

Synthesis: The reaction of phosphorous trichloride with ethanol at low temperature in the presence of a t-amine base or with sodium ethoxide in alcohol.

Reactivity: See trimethyl phosphite.

Toxicology: A skin and eye irritant and moderately toxic by ingestion; LD_{50} is 3200 mg/kg (rat). It is reported in EPA TSCA inventory. It is a flammable liquid.

Uses: Organic synthesis, dyestuffs, plasticizers, optical brightners, and lubricant additives.

Suppliers: There are four listed producers: USA (2), Japan (1) and Germany (1); SRI International lists 3 suppliers in the USA.

(10) Dimethyl Phosphite, $C_2H_5O_3P$
CAS No. 868-85-9
HS No. 29.20.90.90
NIOSH/RTECS No. SZ771000

Synonyms: Dimethyl phosphonate; phosphonic acid dimethyl ester;
Dimethyl hydrogen phosphite

Physical properties: MW: 110.05, bp: 170-171°, n_D^{20} 1.4030,
d.1.200

Synthesis: Reaction of methanol in dry benzene with the dropwise
addition of phosphorus trichloride at temperatures below 10°.
Yield 87% (R.A. mcIvor et. al, Can. J. Chem., 34, 1819(1956)).

Toxicology: Moderately toxic by dermal contact or ingestion, LD₅₀
is 3050 mg/kg (rat). Reported in EPA TSCA inventory. Emits PO_x
toxic fumes on decomposition.

Uses: Used for fireproofing, flame retardants, lubricant
additive, pesticides and organic synthesis.

Suppliers: There are five suppliers listed: Mexico (1), USA
(1), PRC (1), Germany (1) and Hungary (1).

(11) Diethyl phosphite, $C_4H_{11}O_3P$
CAS No. 762-04-9
HS No. 29.20.90.90
NIOSH/RTECS No. TG 7875000

Synonyms: Diethyl hydrogen phosphite; Phosphorous acid, diethyl ester; phosphonic acid, diethyl ester.

Physical Properties: MW: 138.12, bp: 187-188°, d1.074, n_D^{20} 1.4076

Synthesis: Reaction of phosphorous trichloride with ethanol in dry benzene at temperatures below 10°. Yield 83% [R.A. McIvor et al., Can. J. Chem., 34, 1819 (1956)].

Toxicology: Moderately toxic by ingestion or dermal contact. LD₅₀ is 3900 mg/kg (rat). Decomposition produces toxic fumes of PO_x.

Uses: Organic synthesis, pesticides, lubricant additives and paint solvent.

Suppliers: There are four suppliers listed: USA (1), India (1), Germany (1) and the UK (1).

(12) Sulphur Monochloride, S_2Cl_2
CAS No. 10025-67-9
HS No. 28.12.10.90
TDG No. 1828
NIOSH/RTECS No. WS4300000
Merck 8949

Synonyms: Chloride of sulfur, Disulfur dichloride, sulfur chloride, Thiosulfurous dichloride, Sulfur subchloride.

Physical Properties: MW: 135.03, mp: -80° , bp: 138° , d_{1.688}, n_D²⁰ 1.6700; it is a yellow orange liquid with a pungent odour. Insoluble in water but soluble in many organic solvents such as benzene.

Synthesis: Sulphur monochloride is made commercially by the direct chlorination of sulphur usually using a heel of S_2Cl_2 from a previous batch; iron, iodine or ferric chloride may be added as a catalyst. Sulphur monochloride is also a byproduct of the chlorination of carbon disulphide in the preparation of carbon tetrachloride.

Reactivity: There are many useful reactions, it can be used to prepare thionyl chloride, it reacts with ethylene to form mustard gas, it gives resinous products with unsaturated oils, it vulcanizes (crosslinks) rubber, the chlorine atom can be displaced by nucleophiles, it gives disulphides with aromatic compounds and it can be used as a chlorinating agent.

Toxicology: It is poisonous by inhalation or ingestion. This fuming corrosive liquid is irritating to the eye, skin and mucous membranes. Hydrolysis produces HCl, thiosulphuric acid and sulphur. Exposure limit is 1 ppm. It is reported in the EDA TSCA inventory.

Uses: Principle uses are in the manufacture of lubricants and as a vulcanizing agent for rubber.

Suppliers: There are six listed suppliers: USA (1), India (1), Japan (2), France (1) and UK (1).

(13) Sulphur dichloride, SCl_2
CAS No. 10545-99-0
HS No. 28.12.10.90
TDG No. 1828
NIOSH/RTECS No. WS 4500000

Synonyms: Chloride of sulfur, chlorine sulfide, dichlorosulflane, monosulfur dichloride.

Physical properties: MW: 102.96, mp: -78° , bp: 59° , d.1355. It is a reddish brown liquid with a pungent odour; it is unstable and so sold as an 80% mixture of SCl_2 with S_2Cl_2 as 20%. It reacts rapidly with water and is soluble in benzene and carbon tetrachloride.

Synthesis: Preparation is similar to the monochloride except that the final state of chlorination proceeds slowly and should be carried out below 40°C . The crude product is 80% SCl_2 and it can be distilled with 0.1% PCl_3 to obtain pure SCl_2 which can be stored at room temperature.

Reactivity: It is oxidized by SO_3 or ClSO_3H to give thionyl chloride. Its reactions are similar to sulphur monochloride e.g., addition to alkenes.

Toxicology: It is a poisonous irritant and corrosive to the skin, eyes and mucous membranes. It reacts violently with Al, K, Na and solvents such as water, acetone, dimethyl sulphoxide. It emits SO_x and halide fumes which are toxic on decomposition.

Uses: Used as a chlorinating agent, vulcanization of rubber, insecticide intermediate production, as a chlorinating agent in parathion manufacture, on the production of antioxidants, lubricating oil additives and the production of the fungicide captafol.

Suppliers: Seven suppliers are listed: USA (1), India (1), Japan(2), France (1), Germany (1) and the UK (1).

(14) Thionyl chloride, SOCl_2
CAS No. 7719-09-7
HS No. 28.12.10.90
TDG No. 1836
NIOSH/RTECS No. XM5150000
Merck 9278

Synonyms: Sulfinyl chloride, sulfur chloride oxide, sulfurous dichloride, sulfurous oxychloride, thionyl dichloride.

Physical properties: MW: 118.96, mp: -105°C , bp: 79°C , d.1.631, n_D^{20} 1.5190, a colourless to yellow-red liquid with a suffocating odour. Soluble in benzene, carbon tetrachloride and chloroform.

Synthesis: It is prepared by the reaction of sulphur dichloride with (1) sulphur trioxide, (2) sulphur dioxide and chloride, or (3) sulphuryl chloride (SO_2Cl_2) obtained from sulphur dioxide and chlorine. It can be prepared by a batch process but the major commercial process appears to be the continuous reaction of SO_2 (or SO_3) with SCl_2 (or S_2Cl_2) mixed with excess Cl_2 in the gas phase over activated carbon. Purification requires the removal of unchanged sulphur chlorides by forming adducts with e.g. styrene as the thionyl chloride is redistilled; commercial thionyl chloride is 98-99.6% pure.

Reactivity: It has a very significant organic chemistry with organic compounds having hydroxyl groups. Carboxylic acids are converted to acyl halides, alcohols to alkyl halides (or alkyl sulphites or chlorosulphites) amongst others. It is a powerful chlorinating agent.

Toxicology: It is toxic by inhalation, it fumes in moist air to produce SO_2 and HCl which are severe toxic hazards. It is a corrosive irritant to skin, eyes and mucous membranes. It reacts violently with ammonia, dimethylformamide, and dimethyl sulphoxide. Decomposition produces toxic fumes, its TLV is 1 ppm.

Uses: Its main use is the conversion of acids to acid chlorides for use as intermediates in the manufacture of pesticides, herbicides, surfactants, drugs, vitamins, dyestuffs and engineering thermoplastics. There is also a lithium-thionyl chloride high density battery.

Suppliers: There are nine suppliers listed: USA (2), PRC (1), India (1), Japan (2), UK (1), Spain (1) and Switzerland (1). SRI international lists two suppliers in the USA.

(15) Ethyldiethanolamine, $C_6H_{15}NO_2$
CAS No. 139-87-7
HS No. 29.22.19.00
NIOSH/RTECS No. KK 9800000

Synonyms: 2,2'-(ethylamino)bisethanol; 2,2'-ethyliminodiethanol

Physical properties: MW: 133.2; mp: -50° ; bp: $246-52^\circ C$

Synthesis: See methyldiethanolamine except that ethylamine would be the amine employed.

Reactivity: See methyldiethanolamine

Toxicity: No detailed information available.

Uses: mainly used in the production of pharmaceuticals, flocculents, crop protection chemicals, paper and leather chemicals and in plastics.

Suppliers: Four suppliers are listed: USA (2), Japan (1) and the Netherlands (1).

(16) **Methyldiethanolamine, C₅H₁₃NO₂**
CAS 105-59-9
HS No. 29.22.19.00
NIOSH/RTECS No. KL 7525000

Synonyms: MDEA; 2,2'-methyliminodiethanol

Physical properties: MW: 119.2; mp: -21°C; bp: 247°C, d.1.028; n_d²⁰1.4694; liquid with an amine-like odour that discolours on storage unless additives present; readily soluble in water, alcohol and acetone.

Synthesis: N-alkylated ethanolamines are produced by the reaction of amines, RNH₂, with ethylene oxide with the latter being added to the amine. The reaction temperature is in the range of 50-170°C, under pressure (0.3 to 4 MPa) with water used to accelerate the reaction. Reaction with primary amines leads to two products, the N-alkylethanolamine and the N-alkyldiethanolamine; the former are best prepared by a continuous process. N-alkylethanolamines can also be prepared by the N-alkylation of ethanolamines. Methylamine is the amine used to prepare this ethanolamine.

Reactivity: Chemical properties correspond to those of the unsubstituted ethanolamines. They react with acid derivatives to form esters. They are converted to N-substituted morpholines by reaction with H₂SO₄ at high temperatures. Thermal decomposition leads to CO, CO₂ and NO_x.

Toxicity: Harmful if inhaled or swallowed, irritating to skin, eyes and mucous membranes. LD₅₀ (oral) is 4780 mg/kg (rat).

Uses: Mainly used in the production of pharmaceuticals, flocculents, crop protection chemicals, paper and leather chemicals and in plastics. It is the precursor of bis (2-chloroethyl) methylamine which is used in the treatment of Hodgkins disease and leukemias as chlormethine (caryolysine) as well as the chemical warfare agent HN2.

Suppliers: There are six producers listed in four countries; USA (2), Japan (1), Germany (2) and Netherlands (1).

(17) Triethanolamine, $C_6H_{15}NO_3$
CAS No. 102.71.6
HS No. 29.22.13.00
NIOSH/RTECS No. KL 9275000
Merck 9581

Synonyms: TEA; 2,2',2"-nitrilotriethanol; Tris (2-hydroxyethyl) amine

Physical properties: MW: 149.2; mp: 21.6°; bp: 336°, d. 1.1248; n_D^{20} 1.4835. A clear, colourless, viscous and hygroscopic liquid at room temperature and miscible with water, alcohol and acetone.

Synthesis: Reaction of ethylene chlorohydrin and aqueous ammonia. Ethanolamines are produced industrially by the reaction of ethylene oxide and excess ammonia. The product distribution between mono-, di- and tri ethanolamine is controlled by reactant ratios. The ethylene oxide has to be added to the aqueous ammonia. The reaction is carried out under pressure (16MPa) at temperatures up to 150°C and up to 40 mol excess of ammonia.

Reactivity: Exhibits the chemical properties of both amines and alcohols. Thionyl chloride or phosphorus pentachloride can be used to replace the hydroxyl group(s) by chlorine. The resulting chloroethylamines are hazardous because of skin toxicity. Triethanolamine can react further with ethylene oxide to give stable ethers as the end product. Thermal decomposition leads to CO, CO₂, and NO_x.

Toxicity: Skin irritant. Harmful by inhalation, ingestion and skin absorption. LD₅₀ (rat) is 7.2 g/kg.

Uses: Ethanolamines are used widely in the production of surfactants that are important as detergents, textile and leather chemicals, and emulsifiers. Other uses range from drilling and cutting oils to soaps and toiletries. Triethanolamine is a component of coolants for automobile engines where it acts as a corrosion inhibitor. It is also used in the cement industry as an additive to improve flow and setting behaviour. In 1985 world ethanolamine capacity was about 600,000 t/a with production at the 427 000 t level; about 15-20% of production would be triethanolamine.

Suppliers: There are 33 suppliers listed in 15 countries: Argentina (1), Brazil (2), Canada (2), Mexico (2), USA (5), PRC (1), Japan (3), Australia (1), Austria (1), France (4), Germany (4), UK (4), Italy (1), Spain (1) and Switzerland (1).

ANNEX 1

Tables based on a literature survey of Schedule 2 Chemicals

Perfluoroisobutylene (CAS 382-21-8)Table 1

| <u>Country</u> | <u>University</u> | <u>Industry</u> | <u>Govt</u> | <u>Total</u> | <u>(%)</u> |
|----------------|-------------------|-----------------|-----------------|--------------|------------|
| Russia | 34 | -- | -- | 34 | (61.8) |
| USA | 2 | 6 | 7 | 15 | (27.3) |
| UK | 1 | 1 | 1 | 3 | (5.5) |
| Japan | -- | 2 | -- | 2 | (3.6) |
| Germany | 1 | -- | -- | 1 | (1.8) |
| Total | 38 (69%) | 9 (16.4) | 8 (14.5) | 55 | |

Table 2

| <u>Country</u> | <u>Manuscript</u> | <u>Patent</u> |
|----------------|-------------------|---------------|
| Russia | 34 | -- |
| USA | 13 | 2 |
| UK | 2 | 1 |
| Japan | -- | 2 |
| Germany | 1 | -- |
| Total | 50 (91%) | 5 (9%) |

Table 3

| <u>Country</u> | <u>Science</u> | <u>Technology</u> | <u>Biology</u> | <u>Toxicology</u> |
|----------------|-------------------|-------------------|-----------------|-------------------|
| Russia | 33 | 1 | -- | -- |
| USA | 7 | 3 | 1 | 4 |
| UK | 1 | 2 | -- | -- |
| Japan | 1 | 1 | -- | -- |
| Germany | 1 | -- | -- | -- |
| Total | 43 (78.2%) | 7 (12.7%) | 1 (1.8%) | 4 (7.3%) |

Arsenic Trichloride (CAS 7784-34-1)Table 4

| <u>Country</u> | <u>University</u> | <u>Industry</u> | <u>Government</u> | <u>Total</u> | <u>%age</u> |
|----------------|-------------------|-----------------|-------------------|--------------|-------------|
| Japan | 10 | 23 | -- | 33 | 22% |
| Germany | 22 | 5 | -- | 27 | 18% |
| Russia | 26 | -- | 00 | 26 | 17% |
| USA | 11 | 7 | 5 | 23 | 15.3% |
| France | 4 | 2 | -- | 6 | 4% |
| Brazil | 4 | -- | -- | 4 | 2.7% |
| Canada | 2 | -- | 2 | 4 | 2.7% |
| India | 3 | -- | -- | 3 | 2% |
| Italy | 2 | -- | 1 | 3 | 2% |
| UK | 3 | -- | -- | 3 | 2% |
| Czechoslovakia | 1 | 1 | -- | 2 | 1.3% |
| Hungary | 2 | -- | -- | 2 | 1.3% |
| Netherlands | -- | 1 | 1 | 2 | 1.3% |
| Norway | 2 | -- | -- | 2 | 1.3% |
| Sweden | 2 | -- | -- | 2 | 1.3% |
| Belgium | 1 | -- | -- | 1 | 0.67% |
| Bulgaria | 1 | -- | -- | 1 | 0.67% |
| Chile | 1 | -- | -- | 1 | 0.67% |
| Greece | 1 | -- | -- | 1 | 0.67% |
| Jordan | 1 | -- | -- | 1 | 0.67% |
| PRC | 1 | -- | -- | 1 | 0.67% |
| Rumania | 1 | -- | -- | 1 | 0.67% |
| Turkey | 1 | -- | -- | 1 | 0.67% |
| Total | 102 (68%) | 39 (26%) | 9 (6%) | 150 | |

Table 5

| <u>Country</u> | <u>Manuscript</u> | <u>Patent</u> |
|----------------|-------------------|---------------|
| Japan | 11 | 22 |
| Germany | 20 | 7 |
| Russia | 26 | -- |
| USA | 18 | 5 |
| France | 4 | 2 |
| Brazil | 4 | -- |
| Canada | 3 | 1 |
| India | 3 | -- |
| Italy | 3 | -- |
| UK | 3 | -- |
| Czechoslovakia | 1 | 1 |
| Hungary | 2 | -- |
| Netherlands | 1 | 1 |
| Norway | 2 | -- |
| Sweden | 2 | -- |
| Belgium | 1 | -- |
| Bulgaria | 1 | -- |
| Chile | 1 | -- |
| Greece | 1 | -- |
| Jordan | 1 | -- |
| PRC | 1 | -- |
| Rumania | 1 | -- |
| Turkey | 1 | -- |
| | | |
| Total | 111 (74%) | 39 (26%) |

Table 6

| <u>Country</u> | <u>Science</u> | <u>Technology</u> | <u>Toxicology</u> |
|----------------|-----------------|-------------------|-------------------|
| Japan | 6 | 26 | 1 |
| Germany | 21 | 6 | -- |
| Russia | 21 | 5 | -- |
| USA | 15 | 6 | 2 |
| France | 4 | 2 | -- |
| Brazil | 4 | -- | -- |
| Canada | 2 | 2 | -- |
| India | 3 | -- | -- |
| Italy | 2 | -- | 1 |
| UK | 3 | -- | -- |
| Czechoslovakia | 2 | -- | -- |
| Hungary | 1 | 1 | -- |
| Netherlands | -- | 1 | 1 |
| Norway | 2 | -- | -- |
| Sweden | 2 | -- | -- |
| Belgium | 1 | -- | -- |
| Bulgaria | 1 | -- | -- |
| Chile | 1 | -- | -- |
| Greece | 1 | -- | -- |
| Jordan | 1 | -- | -- |
| PRC | 1 | -- | -- |
| Rumania | 1 | -- | -- |
| Turkey | 1 | -- | -- |
| Total | 96 (64%) | 49 (32.7%) | 5 (3.3%) |

2,2-diphenyl-2-hydroxyacetic acid (CAS 76-93-7)Table 7

| <u>Country</u> | <u>University</u> | <u>Industry</u> | <u>Government</u> | <u>Total</u> | <u>(%)</u> |
|----------------|-------------------|-----------------|-------------------|--------------|------------|
| Japan | 13 | 10 | 1 | 24 | (19.2) |
| India | 16 | -- | -- | 16 | (12.8) |
| Germany | 10 | 5 | -- | 15 | (12) |
| Russia | 7 | -- | 6 | 13 | (10.4) |
| Italy | 8 | 3 | 1 | 12 | (9.6) |
| PRC | 3 | -- | 7 | 10 | (8) |
| USA | 3 | 3 | 3 | 9 | (7.2) |
| France | 4 | -- | 3 | 7 | (5.6) |
| Czechoslovakia | 2 | -- | 1 | 3 | (2.4) |
| Switzerland | 3 | -- | -- | 3 | (2.4) |
| Iran | 2 | -- | -- | 2 | (1.6) |
| Netherlands | -- | 1 | 1 | 2 | (1.6) |
| Sweden | 1 | 1 | -- | 2 | (1.6) |
| Austria | 1 | -- | -- | 1 | (0.8) |
| Australia | 1 | -- | -- | 1 | (0.8) |
| Belgium | 1 | -- | -- | 1 | (0.8) |
| Canada | 1 | -- | -- | 1 | (0.8) |
| Saudi Arabia | 1 | -- | -- | 1 | (0.8) |
| Thailand | 1 | -- | -- | 1 | (0.8) |
| UK | 1 | -- | -- | 1 | (0.8) |
| Total | 79(63.2) | 23(18.4) | 23(18.4) | 125 | |

Table 8

| <u>Country</u> | <u>Manuscript</u> | <u>Patent</u> | <u>Total</u> |
|----------------|-------------------|-----------------|--------------|
| Japan | 19 | 5 | 24 |
| India | 16 | -- | 16 |
| Germany | 13 | 2 | 15 |
| Russia | 12 | 1 | 13 |
| Italy | 9 | 3 | 12 |
| PRC | 10 | -- | 10 |
| USA | 6 | 3 | 9 |
| France | 7 | -- | 7 |
| Czechoslovakia | 3 | -- | 3 |
| Switzerland | 3 | -- | 3 |
| Iran | 2 | -- | 2 |
| Netherlands | 1 | 1 | 2 |
| Sweden | 1 | 1 | 2 |
| Austria | 1 | -- | 1 |
| Australia | 1 | -- | 1 |
| Belgium | 1 | -- | 1 |
| Canada | 1 | -- | 1 |
| Saudi Arabia | 1 | -- | 1 |
| Thailand | 1 | -- | 1 |
| UK | 1 | -- | 1 |
| Total | 109(87.2) | 16(12.8) | 125 |

Table 9

| <u>Country</u> | <u>Science</u> | <u>Technology</u> | <u>Biology</u> | <u>Toxicology</u> |
|----------------|-----------------|-------------------|-----------------|-------------------|
| Japan | 19 | 2 | 3 | -- |
| India | 16 | -- | -- | -- |
| Germany | 4 | 2 | 9 | -- |
| Russia | 10 | 1 | 2 | -- |
| Italy | 11 | 1 | -- | -- |
| PRC | 10 | -- | -- | -- |
| USA | 3 | 4 | -- | 2 |
| France | 6 | -- | 1 | -- |
| Czechoslovakia | 2 | -- | 1 | -- |
| Switzerland | 2 | 1 | -- | -- |
| Iran | 2 | -- | -- | -- |
| Netherlands | -- | 1 | -- | 1 |
| Sweden | -- | -- | 2 | -- |
| Austria | 1 | -- | -- | -- |
| Australia | 1 | -- | -- | -- |
| Belgium | -- | -- | 1 | -- |
| Canada | 1 | -- | -- | -- |
| Saudi Arabia | 1 | -- | -- | -- |
| Thailand | 1 | -- | -- | -- |
| UK | 1 | -- | -- | -- |
| Total | 91(72.8) | 12(9.6) | 19(15.2) | 3(2.4) |

Quinuclidin-3-ol (CAS 1619-34-7)Table 10

| <u>Country</u> | <u>University</u> | <u>Industry</u> | <u>Govt</u> | <u>Total (%)</u> |
|----------------|-------------------|-----------------|-------------|------------------|
| USA | 8 | 8 | 7 | 23 (35.38) |
| Japan | -- | 13 | -- | 13 (20) |
| UK | 2 | 4 | 2 | 8 (12.3) |
| South Africa | 5 | -- | -- | 5 (7.7) |
| Germany | 2 | 1 | -- | 3 (4.6) |
| PRC | -- | -- | 3 | 3 (4.6) |
| France | 1 | -- | 1 | 2 (3.1) |
| Russia | -- | -- | 2 | 2 (3.1) |
| Czechoslovakia | -- | 1 | -- | 1 (1.5) |
| Netherlands | -- | -- | -- | 1 (1.5) |
| Poland | 1 | -- | -- | 1 (1.5) |
| Qatar | 1 | -- | -- | 1 (1.5) |
| South Korea | 1 | -- | -- | 1 (1.5) |
| Switzerland | -- | 1 | -- | 1 (1.5) |
| Total | 21 (32.3) | 28 (43.1) | 16 (24.6) | 65 |

Table 11

| <u>Country</u> | <u>Manuscript</u> | <u>Patent</u> | <u>Total</u> |
|----------------|-------------------|---------------|--------------|
| USA | 16 | 7 | 23 |
| Japan | -- | 13 | 13 |
| UK | 4 | 4 | 8 |
| South Africa | 5 | -- | 5 |
| Germany | 2 | 1 | 3 |
| PRC | 3 | -- | 3 |
| France | 2 | -- | 2 |
| Russia | 2 | -- | 2 |
| Czechoslovakia | -- | 1 | 1 |
| Netherlands | 1 | -- | 1 |
| Poland | 1 | -- | 1 |
| Qatar | 1 | -- | 1 |
| South Korea | 1 | -- | 1 |
| Switzerland | -- | 1 | 1 |
| Total | 38 (58.5) | 27 (41.5) | 65 |

Table 12

| <u>Country</u> | <u>Science</u> | <u>Technology</u> | <u>Biology</u> | <u>Toxicology</u> | <u>Total</u> |
|----------------|----------------|-------------------|----------------|-------------------|--------------|
| USA | 8 | 1 | 10 | 4 | 23 |
| Japan | -- | 5 | 8 | -- | 13 |
| UK | 2 | 3 | 3 | -- | 8 |
| South Africa | 5 | -- | -- | -- | 5 |
| Germany | 2 | -- | 1 | -- | 3 |
| PRC | 1 | -- | 2 | 2 | 3 |
| France | 1 | -- | 1 | -- | 2 |
| Russia | -- | -- | 2 | -- | 2 |
| Czechoslovakia | -- | -- | 1 | -- | 1 |
| Netherlands | -- | -- | -- | 1 | 1 |
| Poland | -- | -- | 1 | -- | 1 |
| Qatar | -- | -- | 1 | -- | 1 |
| South Korea | 1 | -- | -- | -- | 1 |
| Switzerland | -- | -- | 1 | -- | 1 |
| Total | 20(30.8) | 9(13.8) | 31(47.7) | 5(7.7) | 65 |

Table A

Number of Chemical Producers Listed in World Directory *

| <u>Country</u> | <u>Producers</u> | <u>(% Total)</u> |
|-----------------|------------------|------------------|
| Egypt | 7 | (0.13) |
| South Africa | 25 | (0.47) |
| Libya | 1 | (0.02) |
| Morocco | 2 | (0.04) |
| Southern Africa | 1 | (0.02) |
| Argentina | 126 | (2.4) |
| Bolivia | 3 | (0.06) |
| Brazil | 233 | (4.43) |
| Canada | 160 | (3.04) |
| Chile | 13 | (0.25) |
| Colombia | 25 | (0.48) |
| Ecuador | 8 | (0.15) |
| Mexico | 200 | (3.8) |
| Peru | 27 | (0.51) |
| USA | 637 | (12.1) |
| Venezuela | 24 | (0.46) |
| Bangladesh | 2 | (0.04) |
| PRC | 169 | (3.2) |
| Hong Kong | 2 | (0.04) |
| India | 231 | (4.39) |
| Indonesia | 11 | (0.21) |
| Iran | 3 | (0.06) |
| Israel | 44 | (0.84) |
| Japan | 693 | (13.16) |
| Korea | 3 | (0.06) |
| Kuwait | 3 | (0.06) |
| Malaysia | 22 | (0.42) |
| Pakistan | 13 | (0.25) |
| Philippines | 12 | (0.23) |
| Saudia Arabia | 5 | (0.1) |
| Singapore | 14 | (0.27) |
| Taiwan | 274 | (5.20) |
| Thailand | 60 | (1.14) |
| Australia | 152 | (2.89) |
| New Zealand | 19 | (0.36) |
| Austria | 59 | (1.12) |
| Belgium | 82 | (1.56) |
| Bulgaria | 4 | (0.08) |
| Czechoslovakia | 2 | (0.04) |
| Denmark | 38 | (0.72) |
| Eire | 26 | (0.49) |
| Finland | 35 | (0.67) |
| France | 198 | (3.76) |

cont'd

Table A (cont'd)

| | | |
|---------------|------|--------|
| Germany | 226 | (4.29) |
| Great Britain | 280 | (5.32) |
| Greece | 16 | (0.30) |
| Hungary | 25 | (0.48) |
| Iceland | 2 | (0.04) |
| Italy | 304 | (5.77) |
| Netherlands | 79 | (1.5) |
| Norway | 46 | (0.87) |
| Poland | 1 | (0.02) |
| Portugal | 44 | (0.84) |
| Romania | 3 | (0.06) |
| Spain | 278 | (5.28) |
| Sweden | 59 | (1.12) |
| Switzerland | 57 | (1.08) |
| Turkey | 49 | (0.93) |
| Russia | 4 | (0.08) |
| Yugoslavia | 25 | (0.48) |
| Total 60 | 5265 | |

‡ Directory of World Chemical Producers 1992/93 Edition, Chemical Information Services Ltd., Dallas, USA.

Table BSchedule 2 Suppliers - Discrete Substances

| Total(%) | <u>Chemical Entry Number*</u> | | | | | | | | | | |
|-----------------------|-------------------------------|---|---|----|----|---|---|---|----|----|----|
| | 1 | 2 | 3 | 4a | 4b | 7 | 8 | 9 | 13 | 14 | |
| <u>Country</u> | | | | | | | | | | | |
| France 5(11.9) | - | - | - | - | - | - | - | 4 | 1 | - | |
| Germany 3(7.1) | - | - | - | - | - | 1 | - | - | 1 | 1 | |
| India 1(2.4) | - | - | - | - | - | - | 1 | - | - | - | |
| Italy 1(2.4) | - | - | - | - | - | - | 1 | - | - | - | |
| Japan 5(11.9) | - | - | - | - | - | - | 2 | - | 3 | - | |
| Netherlands 1(2.4) | - | - | - | - | - | - | - | - | - | 1 | |
| Norway 1(2.4) | - | - | - | - | - | - | - | 1 | - | - | |
| Spain 2(4.8) | - | - | - | - | - | - | 2 | - | - | - | |
| Switzerland 2(4.8) | - | - | - | - | 1 | - | - | 1 | - | - | |
| U.K. 3(7.1) | - | - | - | 1 | 2 | - | - | - | - | - | |
| U.S.A. 18(42.9) | - | - | 1 | 8 | 5 | 1 | 1 | - | 1 | 1 | |
| Total | - | - | 1 | 9 | 8 | 2 | 7 | 6 | 7 | 2 | 42 |

*Entries 5, 6, 10, 11 and 12 are families and, as such, are not amenable to a simple listing of suppliers. Two exceptions are given in entry 11; n,n-dimethylaminoethanol and n,n-diethylaminoethanol. The former is commercially available with 11 listed producers in 6 countries: USA (1), Japan (4), France (1), Germany (3), UK (1) and Sweden (1). Some 14 producers in 7 countries list the latter compound: USA (2), Japan (3), France (1), Germany (3), Netherlands (1), UK (3) and Sweden (1). Fonofos is listed as an exception in entry 4; there is one listed supplier in the USA.

Table C
Schedule 3 Suppliers

| Country | Chemical Entry Number | | | | | | | | | | | | | | | | | Total (%) |
|--------------|-----------------------|----------|-----------|----------|-----------|-----------|----------|----------|----------|----------|----------|----------|----------|----------|----------|----------|-----------|------------|
| | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 | 11 | 12 | 13 | 14 | 15 | 16 | 17 | |
| Argentina | - | - | - | - | - | - | - | - | - | - | - | - | - | - | - | - | 1 | 1 (0.5) |
| Australia | - | - | - | - | - | - | - | - | - | - | - | - | - | - | - | - | 1 | 1 (0.5) |
| Austria | - | - | - | - | - | - | - | - | - | - | - | - | - | - | - | - | 1 | 1 (0.5) |
| Brazil | 3 | - | - | - | 1 | 1 | - | - | - | - | - | - | - | - | - | - | 2 | 7(3.5) |
| Belgium | - | - | 1 | - | - | - | - | - | - | - | - | - | - | - | - | - | - | 1(0.5) |
| Canada | - | - | - | - | - | - | - | - | - | - | - | - | - | - | - | - | 2 | 2(1.0) |
| France | 1 | - | 1 | - | 2 | 2 | - | - | - | 1 | 1 | 1 | - | - | - | - | 4 | 13(6.6) |
| Germany | 3 | - | 4 | - | 3 | 1 | 1 | 1 | 1 | 1 | - | - | 1 | - | - | 2 | 4 | 22(11.1) |
| Hungary | 1 | - | - | - | - | - | - | - | - | 1 | - | - | - | - | - | - | - | 2(1.0) |
| India | 1 | - | - | - | 3 | 3 | 1 | - | - | - | 1 | 1 | 1 | 1 | - | - | - | 12(6.1) |
| Italy | - | - | 1 | - | 2 | 1 | - | - | - | - | - | - | - | - | - | - | 1 | 5(2.5) |
| Japan | 6 | - | 7 | 3 | 4 | 4 | 2 | 1 | 1 | - | 2 | 2 | 2 | 2 | 1 | 1 | 3 | 41(20.7) |
| Mexico | - | - | - | - | - | - | - | 1 | - | 1 | - | - | - | - | - | - | 2 | 4(2.0) |
| Netherlands | - | - | 1 | - | - | - | - | - | - | - | - | - | - | - | 1 | 1 | - | 3(1.5) |
| PRC | 1 | - | - | 1 | 2 | 6 | - | 2 | - | 1 | - | - | - | 1 | - | 1 | - | 15(7.6) |
| S. Korea | 1 | - | - | - | - | - | - | - | - | - | - | - | - | - | - | - | - | 1(0.5) |
| Spain | - | - | 1 | - | 1 | - | - | - | - | - | - | - | - | 1 | - | - | 1 | 4(2.0) |
| Switzerland | - | - | - | - | - | 1 | - | 1 | - | - | - | - | - | 1 | - | - | 1 | 4(2.0) |
| UK | 1 | 1 | 2 | - | 1 | 1 | - | - | - | - | 1 | 1 | 1 | 1 | - | - | 4 | 14(7.1) |
| USA | 4(14)* | - | 6(10)* | 4 | 6 | 6 | - | 2 | 2 | 1 | 1 | 1 | 1 | 2 | 2(4)* | 5 | 2(4)* | 45(22.7) |
| Total | 22 | 1 | 24 | 8 | 25 | 26 | 4 | 8 | 4 | 5 | 6 | 6 | 7 | 9 | 4 | 6 | 33 | 198 |

* These brackets indicate the number of suppliers contained in a national directory; of course all of these numbers are indicative only since there will be more producer/suppliers than shown by one specific directory.

TABLE D

SCHEDULES OF CHEMICALS - NUMBER OF LITERATURE
CITATIONS IN CHEMICAL ABSTRACTS 1965 - AUGUST 1992

Schedule 1

| A. | Toxic chemicals: | <u>No. of References</u> | <u>CAS number</u> |
|-----|---|--------------------------|-------------------|
| (1) | Sarin | 508 | (107-44-8) |
| | Soman | 962 | (96-64-0) |
| (2) | Tabun | 187 | (77-81-6) |
| (3) | VX | 235 | (50782-69-9) |
| (4) | Sulphur mustards: | | |
| | 2-Chloroethylchloromethylsulphide | 1 | (2625-76-5) |
| | Mustard gas (H): Bis(2-chloroethyl) sulphide | 398 | (505-60-2) |
| | Bis(2-chloroethylthio)methane | 1 | (63869-13-6) |
| | Sesquimustard (Q): | | |
| | 1,2-Bis(2-chloroethylthio)ethane | 16 | (3563-36-8) |
| | 1,3-Bis(2-chloroethylthio)-n-propane | 1 | (63905-10-2) |
| | 1,4-Bis(2-chloroethylthio)-n-butane | - | (not assigned) |
| | 1,5-Bis(2-chloroethylthio)-n-pentane | - | (not assigned) |
| | Bis(2-chloroethylthiomethyl)ether | 0 | (63918-90-1) |
| | O-Mustard (T): | | |
| | Bis(2-chloroethylthioethyl)ether | 11 | (63918-89-8) |
| (5) | Lewisites: | | |
| | Lewisite 1: | 37 | (541-25-3) |
| | Lewisite 2: | 3 | (40334-69-8) |
| | Lewisite 3: | 3 | (40334-70-1) |
| (6) | Nitrogen mustards: | | |
| | HN1: | 20 | (538-07-8) |
| | HN2: | 407 | (51-75-2) |
| | HN3: | 98 | (555-77-1) |
| (7) | Saxitoxin | 413 | (35523-89-8) |
| (8) | Ricin | | (9009-86-3) |

B. Precursors:

| | | | |
|------|--------------|----|--------------|
| (9) | DF | 73 | (676-99-3) |
| (10) | QL | 3 | (57856-11-8) |
| (11) | Chlorosarin: | 23 | (1445-76-7) |
| (12) | chlorosoman: | 11 | (7040-57-5) |

Schedule 2

A. Toxic chemicals:

| | | | |
|-----|--------|-----|-------------|
| (1) | Amiton | 32 | (78-53-5) |
| (2) | PFIB | 237 | (382-21-8) |
| (3) | BZ | 337 | (6581-06-2) |

B. Precursors:

- (4) Chemicals, except for those listed in Schedule 1, containing a phosphorus atom to which is bonded one methyl, ethyl or propyl (normal or iso) group but not further carbon atoms,

| | | |
|-------------------------------------|-----|------------|
| e.g. Methylphosphonyl dichloride | 303 | (676-97-1) |
| Dimethyl methylphosphonate | 0 | (765-79-6) |
| Exemption: Fonofos: | 619 | (944-22-9) |

- | | | | |
|-----|---|-----|-------------|
| (5) | N,N-Dialkyl (Me, Et, n-Pr or i-pr) phosphoramidic dihalides | | |
| (6) | Dialkyl (Me, Et, n-Pr or i-Pr) N,N-dialkyl(Me, Et, n-Pr or i-Pr)-phosphoramidates | | |
| (7) | Arsenic trichloride | 815 | (7784-34-1) |
| (8) | 2,2-Diphenyl-2-hydroxyacetic acid | 367 | (76-93-7) |
| (9) | Quinuclidine-3-ol | 142 | (1619-34-7) |

- (10) N,N-dialkyl (Me, Et, n-Pr or i-Pr) aminoethyl-2-ols and corresponding protonated salts
- (11) N,N-Dialkyl (Me, Et, n-Pr or i-Pr) aminoethane-2-ols and corresponding protonated salts

Exemptions:

- | | | |
|---|------|------------|
| N,N-Dimethylaminoethanol and corresponding protonated salts | 2196 | (108-01-0) |
| N,N-diethylaminoethanol and corresponding protonated salts | 1106 | (100-37-8) |
| (12) N,N-Dialkyl (Me, Et, n-Pr or i-pr) aminoethane-2-thiols and corresponding protonated salts | | |
| (13) Thiodiglycol: | 453 | (111-48-8) |
| (14) Pinacolyl alcohol: | 168 | (464-07-3) |

Schedule 3

A. Toxic chemicals:

- | | | |
|-----------------------|------|------------|
| (1) Phosgene | 3645 | (75-44-5) |
| (2) Cyanogen chloride | 682 | (506-77-4) |
| (3) Hydrogen cyanide | 6224 | (74-90-8) |
| (4) chloropicrin | 498 | (76-06-2) |

B. Precursors:

- | | | |
|------------------------------|------|--------------|
| (5) Phosphorusoxychloride | 2791 | (10025-87-3) |
| (6) Phosphorus trichloride | 3048 | (7719-12-2) |
| (7) Phosphorus pentachloride | 1429 | (10026-13-8) |
| (8) Trimethyl phosphite | 2125 | (121-45-9) |
| (9) Triethyl phosphite | 2686 | (122-52-1) |

| | | | |
|------|----------------------|------|--------------|
| (10) | Dimethyl phosphite | 1164 | (868-85-9) |
| (11) | Diethyl phosphite | 1521 | (762-04-9) |
| (12) | Sulphur monochloride | 961 | (10025-67-9) |
| (13) | Sulphur dichloride | 774 | (10545-99-0) |
| (14) | Thionyl chloride | 2534 | (7719-09-7) |
| (15) | Ethyldiethanolamine | 145 | (139-87-7) |
| (16) | Methyldiethanolamine | 789 | (105-59-9) |
| (17) | Triethanolamine | 7013 | (102-71-6) |

Table E

**Pesticide Raw Materials of Concern
to the Chemical Weapons Convention**

Source: Pesticide Manufacturing and Toxic Materials Control Encyclopedia, Editor M. Sittig, Noyes Data Corp., U.S.A., 1980

A. Basic Chemicals

- | | |
|---------------------------|-------------------------------|
| 1. Ammonia | 17. Hydrogen cyanide |
| 2. Arsenic acid | 18. Hydrogen fluoride |
| 3. Arsenic pentoxide | 19. Hydrogen sulphide |
| 4. Arsenic trioxide | 20. Phosgene |
| 5. Calcium carbide | 21. Phosphorous |
| 6. Chlorine | 22. Phosphorous oxychloride |
| 7. Cyanogen chloride | 23. Phosphorous pentasulphide |
| 8. Diethylamine | 24. Phosphorous pentoxide |
| 9. Diisobutylamine | 25. Phosphorous trichloride |
| 10. Diisopropylamine | 26. Pinacolone |
| 11. Dimethylamine | 27. Potassium cyanide |
| 12. Dimethyl phosphite | 28. Sodium cyanide |
| 13. Di n-propylamine | 29. Sulphur |
| 14. Ethylene chlorohydrin | 30. Sulphonyl chloride |
| 15. Ethylene oxide | 31. Thionyl chloride |
| 16. Hydrogen chloride | |

B. Organophosphorous Compounds

1. Chloromethyl phosphonic acid
2. Diethyl phosphite
3. Diethyl phosphorochloridate
4. 0,0-diethyl thiophosphoric acid chloride
5. 0,0-diethyl dithiophosphoric acid
6. 0,0-diisopropyl hydrogen phosphorodithioate
7. Dimethyl hydrogen phosphonodithioate
8. 0,0-dimethyl thiophosphoric acid chloride
9. 0,0-dimethyl phosphorothioic acid
10. 0-ethyl ethylphosphorochloridothionate
11. Ethyl phosphorodichloridate
12. 0-ethyl-s-n-propyl chlorothiophosphate
13. 0-methyl phosphorothionodichloridate
14. Thiophosphoryl chloride
15. Triethyl phosphite
16. Trimethyl phosphite

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