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water, HNO_3 or H_2SO_4, as vapour. After 4h, the sulfur was cooled so that the reflux tube could be replaced by a bent air-cooled condenser. The sulfur was then distilled, rejecting the first and the final 100mL portions, and transferred in 200mL portions to 400mL glass cylinder ampoules (which were placed on their sides during solidification). After adding about 80mL of water, displacing the air with N_2, and sealing the ampoule was cooled, and the water was titrated with 0.02M NaOH, the process being repeated until the acid content was negligible. Finally, entrapped water was removed by alternate evacuation to 10mm Hg and refilling with N_2 while the sulfur was kept molten. Other purifications include crystn from CS_2 (which is less satisfactory because the sulfur retains appreciable amounts of organic material), *benzene or *benzene/acetone, followed by melting and degassing. Has also been boiled with 1% MgO, then decanted, and dried under vacuum at 40° for 2 days over P_2O_5. [For purification of S_6, "recryst. S_8" and "Bacon-Fanelli sulfur" see Bartlett, Cox and Davis *J Am Chem Soc* **83** 103, 109 *1961*.]

Sulfur dichloride *[10545-99-0]* **M 103.0, m -78°, b 59°/760mm(dec), d 1.621.** Twice distilled in the presence of a small amount of PCl_3 through a 12in Vigreux column, the fraction boiling between 55-61° being redistd (in the presence of PCl_3), and the fraction distilling between 58-61° retained. (The PCl_3 is added to inhibit the decomposition of SCl_2 into S_2Cl_2 and Cl_2). The SCl_2 must be used as quickly as possible after distn, within 1h at room temperature, The sample contains 4% S_2Cl_2. On long standing this reaches 16-18%. **HARMFUL VAPOURS.**

Sulfur dioxide *[7446-09-5]* **M 64.1, b -10°.** Dried by bubbling through concentrated H_2SO_4 and by passage over P_2O_5, then passed through a glass-wool plug. Frozen with liquid air and pumped to a high vacuum to remove dissolved gases. **HARMFUL VAPOURS.**

Sulfuric acid *[7664-93-9]* **M 98.1, d 1.83, pK_1^{25} ~ -8.3, pK_2^{25} 1.99.** Sulfuric acid, and also 30% fuming H_2SO_4, can be distilled in an all-Pyrex system, optionally from potassium persulfate. Also purified by fractional crystn of the monohydrate from the liquid. Dehydrates and attacks skin—wash immediately with H_2O.

Sulfur monochloride (sulfur monochloride) *[10025-67-9]* **M 135.0, m -77°; b 19.1°, 29-30°/12mm, 72°/100mm, 138°/760mm, d^{20} 1.677, n_D^{20} 1.67.** *Pungent, irritating golden yellow liquid.* When impure its colour is orange to red due to SCl_2 formed. It fumes in moist air and liberates HCl, SO_2 and H_2S in the presence of H_2O. Distil and collect the fraction boiling above 137° at atmospheric pressure. Fractionate this fraction over sulfur at *ca* 12mm using ground glass apparatus (**b** 29-30°). Alternatively purify by distn below 60° from a mixture containing sulfur (2%) and activated charcoal (1%), under reduced pressure (e.g. 50mm). It is soluble in EtOH, *C_6H_6, Et_2O, CS_2 and CCl_4. Store in a closed container in the dark in a refrigerator. [*Handbook of Preparative Inorganic Chemistry (Ed. Brauer)* Vol I 371 *1963*.] **HARMFUL VAPOURS.**

Sulfur trioxide pyridine complex *[26412-87-3]* **M 159.2, m 155-165°, 175°.** Wash the solid with a little CCl_4, then H_2O to remove traces of pyridine sulfate, and dry over P_2O_5 [*Chem Ber* **59** 1166 *1926*; *Synthesis* 59 *1979*].

Sulfuryl chloride *[7791-25-2]* **M 135.0, m -54.1°, b 69.3°/760mm, d_4^{20} 1.67, n_D^{30} 1.44.** *Pungent, irritating colourless liquid.* It becomes yellow with time due to decomposition to SO_2 and HCl. Distil and collect fraction boiling below 75°/atm which is mainly SO_2Cl_2. To remove HSO_3Cl and H_2SO_4 impurities, the distillate is poured into a separating funnel filled with crushed ice and *briefly* shaken. The lower cloudy layer is removed, dried for some time in a desiccator over P_2O_5 and finally fractionated at atmospheric pressure. The middle fraction boils at 69-70° and is pure SO_2Cl_2. It decomposes gradually in H_2O to H_2SO_4 and HCl. Reacts **violently** with EtOH and MeOH and is soluble in *C_6H_6, toluene Et_2O and acetic acid. [*Handbook of Preparative Inorganic Chemistry (Ed Brauer)* Vol I 383 *1963*; *Inorg Synth* **1** 114 *1939*]. **HARMFUL VAPOURS.**

Tantalium (V) chloride (tantalium pentachloride) *[7721-01-9]* **M 358.2, m 216.2°, 216.5-220°; b 239°/atm., d 3.68.** Purified by sublimation in a stream of Cl_2. Colourless needles when pure (yellow when contaminated with even less than 1% of $NbCl_5$). Sensitive to H_2O, even in conc HCl it decomposes to tantalic acid. Sol in EtOH. [*J Am Chem Soc* *80* 2952 *1958*; *Handbook of Preparative Inorganic Chemistry (Ed Brauer)* Vol II 1302 *1965*.]

Tantalium pentaethoxide *[6074-84-6]* **M 406.3, b 147°/0.2mm, 202°/10mm, pK_1^{25} 9.6, pK_2^{25} 13.0 (for tantalic acid).** Purified by distillation. It aggregates in $^*C_6H_6$, EtOH, MeCN, pyridine and diisopropyl ether. [*J Chem Soc* 726 *1955*, 5 *1956*.]

Telluric acid *[7803-68-1]* **M 229.6, pK_1^{25} 7.70, pK_2^{25} 11.04 (H_6TaO_6).** Crystd once from nitric acid, then repeatedly from hot water (0.4mL/g).

Tellurium *[13494-80-9]* **M 127.6, m 450°.** Purified by zone refining and repeated sublimation to an impurity of less than 1 part in 10^8 (except for surface contamination by TeO_2). [Machol and Westrum *J Am Chem Soc* **80** 2950 *1958*.] Tellurium is volatile at 500°/0.2mm. Also purified by electrode deposition [Mathers and Turner *Trans Amer Electrochem Soc* **54** 293 *1928*].

Tellurium dioxide *[7446-07-3]* **M 159.6, m 733°, d 6.04.** Dissolved in 5M NaOH, filtered and ppted by adding 10M HNO_3 to the filtrate until the soln was acid to phenolphthalein. After decanting the supernatant, the ppte was washed five times with distilled water, then dried for 24h at 110° [Horner and Leonhard *J Am Chem Soc* **74** 3694 *1952*].

Terbium oxide *[12037-01-3]* **M 747.7, pK^{25} 8.16 (for Tb^{3+} hydrolysis).** Dissolved in acid, ppted as its oxalate and ignited at 650°.

Tetraallyltin (tetraallylstannane) *[7393-43-3]* **M 283.0, b 52°/0.2mm, 69-70°/15mm, d 1.179, n 1.536.** Possible contaminants are allyl chloride and allyltin chloride. Check ^1H NMR and IR [Fishwick and Wallbridge *J Organometal Chem* **25** 69 *1970*], and if impure, dissolve in Et_2O and shake with a 5% aq soln of NaF which ppts allyltin fluoride. Separate the Et_2O layer, dry ($MgSO_4$) and dist at ~ 0.2mm. It decomposes slightly on repeated distn. [O'Brien et al. *Inorg Synth* **13** 75 *1972*; Fishwick et al. *J Chem Soc (A)* 57 *1971*.]

Tetrabutylammonium borohydride *[33725-74-5]* **M 257.3, m 128-129°.** Purified by recrystn from EtOAc followed by careful drying under vacuum at 50-60°. Samples purified in this way showed no signs of loss of *active* H after storage at room temperature for more than 1 year. Nevertheless samples should be stored at *ca* 6° in tightly stoppered bottles if kept for long periods. It is soluble in CH_2Cl_2. [*J Org Chem* **41** 690 *1976*; *Tetrahedron Lett* 3173 *1972*.]

Tetrabutylammonium chlorochromate *[54712-57-1]* **M 377.9, m 184-185°.** Recrystd from EtOAc-hexane. IR ν 920cm^{-1} in $CHCl_3$ [*Synthesis* 749 *1983*]. *Powerful oxidant.*

Tetrabutylammonium tetrafluoroborate *[429-42-5]* **M 329.3, m 161.8°, 161-163°, pK^{25} -4.9 (for HBF_4).** Recryst from H_2O, aq EtOH or from EtOAc by cooling in Dry ice. Also recrystd from ethyl acetate/pentane or dry acetonitrile. Dried at 80° under vacuum. [Detty and Jones *J Am Chem Soc* **109** 5666 *1987*; Hartley and Faulkner *J Am Chem Soc* **107** 3436 *1985*.] *Acetate* **m** 118±2° (from BuCl); *bromide* **m** 118° (from EtOAc) and *nitrate* **m** 120° (from $^*C_6H_6$). [*J Am Chem Soc* **69** 2472 *1947*, **77** 2024 *1955*.]

Tetrabutyl orthotitanate monomer (titanium tetrabutoxide) *[5593-70-4]* **M 340.4, b 142°/0.1mm, 134-136°/0.5mm, 160°/0.8mm, 174°/6mm, 189°/13mm, d_4^{35} 0.993, n_D^{25} 1.49.** Dissolve in $^*C_6H_6$, filter if solid is present, evaporate and vacuum fractionate through a Widmer 24inch column. The ester hydrolyses when exposed to air to give hydrated ortho-titanic acid. Titanium content can be determined thus: weigh a sample (*ca* 0.25g) into a weighed crucible and cover with 10mL of H_2O and a few drops of conc HNO_3. Heat (hot plate) carefully till most of the H_2O has evaporated. Cool and add more H_2O (10mL) and conc HNO_3 (2mL) and evaporate carefully (no spillage) to dryness and ignite residue at 600-650°/1h. Weigh the residual TiO_2. [*J Chem Soc* 2773 *1952*; *J Org Chem* **14** 655 *1949*.]

Tetrabutyl tin (tin tetrabutyl) *[1461-25-2]* **M 347.2, b 94.5-96°/0.28mm, 145°/11mm, 245-247°/atm, d_4^{20} 1.05, n_D^{24} 1.473.** Dissolve in Et_2O, dry over $MgSO_4$, filter, evaporate and distil under reduced pressure. Although it does not crystallise easily, once the melt has crystallised then it will recrystallise more easily. It is soluble in Et_2O, Me_2CO, EtOAc and EtOH but insoluble in MeOH and H_2O and shows no apparent reaction with H_2O. [*J Org Chem* *19* 74 *1954, J Chem Soc* 1992 *1954.*]

Tetraethoxysilane (tetraethyl orthosilicate) *[78-10-4]* **M 208.3, m -77°, b 165-166°/atm, d_4^{20} 0.933, n_D^{25} 1.382.** Fractionate through an 80cm Podbielniak type column (see p. 141) with heated jacket and partial take-off head. Slowly decomposed by H_2O, soluble in EtOH. ***It is flammable - irritates the eyes and mucous membranes.*** [*J Am Chem Soc* **78** 5573 *1956, cf J Chem Soc* 5020 *1952.*]

Tetraethylammonium hexafluorophosphate *[429-07-2]* **M 275.2, m >300°, 331°(dec), pK_1^{25}~ 0.5, pK_2^{25} 5.12 (for fluorophosphoric acid H_2PO_3F).** Dissolve salt (0.8g) in hot H_2O (3.3mL) and cool to crystallise. Yield of prisms is 0.5g. Solubility in H_2O is 8.1g/L at 19° [*Chem Ber* **63** 1067 *1930*].

Tetraethylammonium tetrafluoroborate *[429-06-1]* **M 217.1, m 235°, 356-367°, pK^{25} -4.9 (for HBF_4).** Dissolve in hot MeOH, filter and add Et_2O. It is soluble in ethylene chloride [*J Am Chem Soc* **69** 1016 *1947*, **77** 2025 *1955*]. See entry on p. 359 in Chapter 4.

Tetraethyl lead *[78-00-2]* **M 323.5, b 200°, 227.7°(dec), d 1.653, n 1.5198.** Its more volatile contaminants can be removed by exposure to a low pressure (by continuous pumping) for 1h at 0°. Purified by stirring with an equal volume of H_2SO_4 (d 1.40), keeping the temperature below 30°, repeating this process until the acid layer is colourless. It is then washed with dilute Na_2CO_3 and distilled water, dried with $CaCl_2$ and fractionally distd at low pressure under H_2 or N_2 [Calingaert *Chem Rev* **2** 43 *1926*]. **VERY POISONOUS.**

Tetraethylsilane *[631-36-7]* **M 144.3, b 153.8°/760mm, d_4^{30} 0.77, n_D^{30} 1.427.** Fractionate through a 3ft vacuum jacketted column packed with 1/4" stainless steel saddles. The material is finally percolated through a 2ft column packed with alumina and maintained in an inert atmosphere. [*J Chem Soc* 1992 *1954*; *J Am Chem Soc* **77** 272 *1955.*]

1.1.3.3-Tetraisopropyldisiloxane *[18043-71-5]* **M 246.5, b 129-130°/6mm, d_4^{30} 0.89, n_D^{30} 1.47.** Fractionate under reduced pressure in a N_2 atm. [*J Am Chem Soc* **69** 1500 *1947.*]

Tetraisopropyl orthotitanate (titanium tetraisopropyl) *[546-68-9]* **M 284.3, m 18.5°; b 80°/2mm, 78°/12mm, 228-229°/755mm.** Dissolve in dry $^*C_6H_6$, filter if a solid separates, evap and fractionate. It is hydrolysed by H_2O to give solid $Ti_2O(iso\text{-}OPr)_2$ **m** *ca* 48°. [*J Chem Soc* 2027, *1952*, 469 *1957.*]

Tetrakis(diethylamino) titanium [(titanium tetrakis(diethylamide)] *[4419-47-0]* **M 336.4, b 85-90°/0.1mm, 112°/0.1mm, d_4^{30} 0.93, n_D^{30} 1.54.** Dissolve in $^*C_6H_6$, filter if a solid separates, evaporate under reduced pressure and distil. Orange liquid which reacts violently with alcohols. [*J Chem Soc* 3857 *1960.*]

Tetrakis(hydroxymethyl)phosphonium chloride *[124-64-1]* **M 190.6, m 151°.** Crystd from AcOH and dried at 100° in a vacuum. An 80% w/v aqueous solution has d_4^{20} 1.33 [*J Am Chem Soc* **77** 3923 *1955*].

Tetrakis(triphenylphosphine) palladium *[14221-01-3]* **M 1155.58, m 100-105°(dec).** Yellow crystals from EtOH. It is stable in air only for a short time, and prolonged exposure turns its colour to orange. Store in an inert atmosphere below room temp in the dark. [*J Chem Soc* 1186 *1957.*]

Tetrakis(triphenylphosphine) platinum *[14221-02-4]* **M 1244.3, m 118°.** Recrystd by adding hexane to a cold saturated solution in $^*C_6H_6$. It is soluble in $^*C_6H_6$ and $CHCl_3$ but insoluble in EtOH and hexane. A less pure product is obtained if crystd by adding hexane to a $CHCl_3$ soln. Stable in air for several hours and completely stable under N_2. [*J Am Chem Soc* 2323 *1958.*]

Tetramethoxysilane (tetramethyl orthosilicate) *[681-84-5]* **M 152.2, m 4.5°, b 122°/760mm.** Purification as for tetraethoxysilane. It has a vapour pressure of 2.5mm at 0°. [IR: *J Am Chem Soc* **81** 5109 *1959.*]

Tetramethylammonium borohydride *[16883-45-7]* **M 89.0.** Recrystn from H_2O three times yields *ca* 94% pure compound. Dry in high vacuum at 100° for 3h. The solubility in H_2O is 48% (20°), 61% (40°); and in EtOH 0.5% (25°) and MeCN 0.4% (25°). It decompose slowly in a vacuum at 150°, but rapidly at 250°. The rate of hydrolysis of $Me_4N.BH_4$ (5.8M) in H_2O at 40° is constant over a period of 100h at 0.04% of original wt/h. The rate decreases to 0.02%/h in the presence of Me_4NOH (5% of the wt of $Me_4N.BH_4$). [*J Am Chem Soc* **74** 2346 *1952.*]

Tetramethylammonium hexafluorophosphate *[558-32-7]* **M 219.1, m >300°, d_4^{25} 1.617, pK_1^{25}~ 0.5, pK_2^{25} 5.12 (for fluorophosphoric acid H_2PO_3F).** The salt (0.63g) is recrystd from boiling H_2O (76mL), yielding pure (0.45) $Me_4N.PF_6$ after drying at 100°. It is a good supporting electrolyte. [*Chem Ber* **63** 1067 *1930.*]

Tetramethylammonium perchlorate *[2537-36-2]* **M 123.6, m>300°, pK^{25} -2.4 to -3.1 (for $HClO_4$).** Crystallise twice from H_2O and dry at 100° in an oven. Insol in most organic solvents. [*J Chem Soc* 1210 *1933.*]

Tetramethylammonium triacetoxyborohydride *[109704-53-2]* **M 263.1, m 93-98°, 96.5-98°.** If impure, wash with freshly distd Et_2O and dry overnight in a vac to give a free flowing powder. Check ^1H NMR, and if still suspect prepare freshly from Me_4NBH_4 and AcOH in $*C_6H_6$ and store away from moisture [Banus et al. *J Am Chem Soc* **74** 2346 *1952*; Evans and Chipman *Tetrahedron Lett* **27** 5939 *1986*]. It is an **IRRITANT** and **MOISTURE SENSITIVE**.

Tetramethylammonium triphenylborofluoride *[437-11-6]* **M 392.2.** Crystd from acetone or acetone/ethanol.

2,4,6,8-Tetramethylcyclotetrasiloxane *[2370-88-9]* **M 240.5, m -69°, b 134°/750mm, 134.5-134.9°/755mm, d_4^{20} 0.99, n_D^{20} 1.3872.** It is purified by repeated redistillation, and fractions with the required ^1H NMR data are collected. [*J Gen Chem USSR (Engl Transl)* **29** 262 *1959*; *J Am Chem Soc* **68** 962 *1946*].

1,1,3,3-Tetramethyldisiloxane *[3277-26-7]* **M 134.3, b 70.5-71°/731mm, 71-72°/atm, d_4^{30} 0.75, n_D^{25} 11.367.** Possible impurity is 1,1,5,5-tetramethyl-3-trimethylsiloxytrisiloxane **b** 154-155°/733mm. Fractionate, collect fractions boiling below 80° and refractionate. Purity can be analysed by alkaline hydrolysis and measuring the volume of H_2 liberated followed by gravimetric estimation of silica in the hydrolysate. It is unchanged when stored in glass containers in the absence of moisture for 2-3 weeks. Small amounts of H_2 are liberated on long storage. *Care should be taken when opening a container due to pressure developed.* [*J Am Chem Soc* **79** 974 *1958*; *J Chem Soc* 609 *1958*; IR: *Z Anorg Chem* **299** 78 *1959.*]

***N,N,N'N'*-Tetramethylphosphonic diamide (methylphosphonic bis-dimethylamide)** *[2511-17-3]* **M 150.2, b 60.5°/0.6mm, 138°/32mm, 230-230°/atm, d_4^{30} 1.0157, n_D^{30} 1.4539.** Dissolve in heptane or ethylbenzene shake with 30% aqueous NaOH, stir for 1h, separate the organic layer and fractionate. [*J Org Chem* **21** 413 *1956*]. IR has ν 1480, 1460, 1300, 1184, 1065 and 988-970cm^{-1} [*Can J Chem* **33** 1552 *1955*].

Tetramethylsilane (TMS) *[75-76-3]* **M 88.2, b 26.3°, n 1.359, d 0.639.** Distilled from conc H_2SO_4 (after shaking with it) or $LiAlH_4$, through a 5ft vacuum-jacketted column packed with glass helices into an ice-cooled condenser, then percolated through silica gel to remove traces of halide.

2,4,6,8-Tetramethyl tetravinyl cyclotetrasiloxane *[2554-06-5]* **M 344.7, m -43.5°, b 111-112°/10mm, 145-146°/13mm, 224-224.5°/758mm, d_4^{30} 0.98, n_D^{30}1.434.** A 7mL sample was distilled in a small Vigreux column at atmospheric pressure without polymerisation or decomposition. It is soluble in cyclohexane. [*J Am Chem Soc* **77** 1685 *1955*.]

Tetraphenylarsonium chloride hydrate *[507-28-8]* **M 418.8, m 261-263°.** A neutralised aqueous soln was evaporated to dryness. The residue was extracted into absolute EtOH, evaporated to a small volume and ppted by addition of absolute Et_2O. It was again dissolved in a small volume of absolute EtOH or ethyl acetate and reppted with Et_2O. Alternatively purified by adding conc HCl to ppte the chloride dihydrate. Redissolved in water, neutralised with Na_2CO_3 and evaporated to dryness. The residue was extracted with $CHCl_3$ and finally crystallised from CH_2Cl_2 or EtOH by adding Et_2O. If the aqueous layer is somewhat turbid treat with Celite and filter through filter paper. **POISONOUS.**

Tetraphenylarsonium iodide *[7422-32-4]* **M 510.2.** Crystd from MeOH. **POISONOUS.**

Tetraphenylarsonium perchlorate *[3084-10-4]* **M 482.8, pK^{25} -2.4 to -3.1 (for $HClO_4$).** Crystd from MeOH. **POISONOUS.**

Tetraphenylboron potassium *[3244-41-5]* **M 358.2.** See potassium tetraphenylborate on p. 458.

Tetraphenylphosphonium chloride *[2001-45-8]* **M 374.9, m 273-275°.** Crystd from acetone. Dried at 70° under vacuum. Also recrystd from a mixture of 1:1 or 1:2 dichloromethane/pet ether, the solvents having been dried over anhydrous K_2CO_3. The purified salt was dried at room temperature under vasuum for 3 days, and at 170° for a further 3 days. *Extremely hygroscopic.*

Tetraphenylsilane *[1048-08-4]* **M 336.4, m 231-233°.** Crystd from *benzene.

Tetraphenyltin *[595-90-4]* **M 427.1, m 224-225°, 226°.** Yellow crystals from $CHCl_3$, pet ether (b 77-120°), xylene or *benzene/cyclohexane, and dried at 75°/20mm. [*J Am Chem Soc* **74** 531 *1952*.]

Tetrapropylammonium perchlorate *[15780-02-6]* **M 285.8, m 238-240°, pK^{25} -2.4 to -3.1 (for $HClO_4$).** Purified by recrystns from H_2O or $MeCN/H_2O$ (1:4.v/v), and dried in an oven at 60° for several days, or in vacuum over P_2O_5 at 100°. [*Z Phys Chem* **165A** 245 *1933*, **144** 281 *1929*, **140** 97 *1929*.]

Tetra-*n*-propylammonium perruthenate (TPAP, tetrapropyl tetraoxoruthenate) *[114615-82-6]* **M 351.4, m 160°(dec).** It is a strong oxidant and may explode on heating. It can be washed with aq *n*-propanol, then H_2O and dried over KOH in a vac. It is stable at room temp but best stored in a refrigerator. It is sol in CH_2Cl_2 and MeCN. [Dengel et al. *Transition Met Chem* **10** 98 *1985*; Griffith et al. *J Chem Soc, Chem Commun* 1625 *1987*.] § Polymer supported reagent is available commercially.

Tetrasodium pyrene-1,3,6,8-tetrasulfonate *[59572-10-0]* **M 610.5.** Recrystd from aqueous acetone [Okahata et al. *J Am Chem Soc* **108** 2863 *1986*].

Thallium (I) acetate *[563-68-8]* **M 263.4, m 126-128°, 127°, pK^{25} 13.2 (for Tl^+).** Likely impurity is H_2O because the white solid is deliquescent. Dry in a vacuum over P_2O_5 or for several days in a desiccator, and store in a well closed container. 7.5g dissolve in 100g of liquid SO_2 at 0°, and *ca* 2mol% in AcOH at 25°. **POISONOUS.** [*Trans Faraday Soc* **32** 1660 *1936*; *J Am Chem Soc* **52** 516.]

Thallous bromide *[7789-40-4]* **M 284.3, m 460°.** Thallous bromide (20g) was refluxed for 2-3h with water (200mL) containing 3mL of 47% HBr. It was then washed until acid-free, heated to 300° for 2-3h and stored in brown bottles. **POISONOUS.**

Thallous carbonate *[6533-73-9]* **M 468.7, m 268-270°.** Crystd from hot water (4mL/g) by cooling. **POISONOUS.**

Thallous chlorate *[13453-30-0]* **M 287.8, d 5.05.** Crystd from hot water (2mL/g) by cooling. **POISONOUS.**

Thallous chloride *[7791-12-0]* **M 239.8, m 429.9°, d 7.0.** Crystd from 1% HCl and washed until acid-free, or crystd from hot water (50mL/g), then dried at 140° and stored in brown bottles. Also purified by subliming in vacuum, followed by treatment with dry HCl gas and filtering while molten. (Soluble in 260 parts of cold water and 70 parts of boiling water). **POISONOUS.**

Thallous hydroxide *[12026-06-1]* **M 221.4, m 139°(dec), pK^{25} 13.2 (for Tl^+).** Crystd from hot water (0.6mL/g) by cooling. **POISONOUS.**

Thallous iodide *[7790-30-9]* **M 331.3, m 441.8°, b 824°, d 7.1.** Refluxed for 2-3h with water containing HI, then washed until acid-free, and dried at 120°. Stored in brown bottles. **POISONOUS.**

Thallous nitrate *[10102-45-1]* **M 266.4, m 206°, b 450°(dec), d 5.55.** Crystd from warm water (1mL/g) by cooling to 0°. **POISONOUS.**

Thallous perchlorate *[13453-40-2]* **M 303.8, pK^{25} -2.4 to -3.1 (for $HClO_4$).** Crystd from hot water (0.6mL/g) by cooling. Dried under vacuum for 12h at 100° (protect from possible **EXPLOSION**).

Thallous sulfate *[7446-18-6]* **M 504.8, m 633°, d 6.77.** Crystd from hot water (7mL/g) by cooling, then dried under vacuum over P_2O_5. **POISONOUS.**

Thexyl dimethyl chlorosilane (dimethyl-[2,3-dimethyl-2-butyl] chlorosilane) *[67373-56-2]* **M 178.8, b 55-56°/10mm, 158-159°/720mm, d_4^{20} 0.970, n_D^{20} 1.428.** Purified by fractional distillation and stored in small aliquots in sealed ampoules. It is very sensitive to moisture and is estimated by dissolving an aliquot in excess of 0.1M NaOH and titrating with 0.1M HCl using methyl red as indicator. [*Helv Chim Acta* **67** 2128 *1984*].

***N*-(Thexyl dimethylsilyl)dimethylamine (*N*-[2,3-dimethyl-2-butyl]dimethylsilyl dimethylamine)** *[81484-86-8]* **M 187.4, b 156-160°/720mm.** Dissolve in hexane, filter, evaporate and distil. Colourless oil extremely sensitive to humidity. It is best to store small quatities in sealed ampoules after distillation. For estimation of purity crush an ampoule in excess 0.1N HCl and titrate the excess acid with 0.1M NaOH using methyl red as indicator. [*Helv Chim Acta* **67** 2128 *1984*.]

Thionyl chloride *[7719-09-7]* **M 119.0, b 77°, d 1.636.** Crude $SOCl_2$ can be freed from sulfuryl chloride, sulfur monochloride and sulfur dichloride by refluxing with sulfur and then fractionally distilling twice. [The $SOCl_2$ is converted to SO_2 and sulfur chlorides. The S_2Cl_2 (**b** 135.6°) is left in the residue, whereas SCl_2 (**b** 59°) passes over in the forerun]. The usual purification is to distil from quinoline (50g $SOCl_2$ to 10g quinoline) to remove acid impurities, followed by distillation from boiled linseed oil (50g $SOCl_2$ to 20g of oil). Precautions must be taken to exclude moisture.

Thionyl chloride for use in organic syntheses can be prepared by distillation of technical $SOCl_2$ in the presence of diterpene (12g/250mL $SOCl_2$), avoiding overheating. Further purification is achieved by redistillation from linseed oil (1-2%) [Rigby *Chem Ind (London)* 1508 *1969*]. Gas chromatographically pure material is obtained by distillation from 10% (w/w) triphenyl phosphite [Friedman and Wetter *J Chem Soc (A)* 36 *1967*; Larsen et al. *J Am Chem Soc* **108** 6950 *1986*]. **Harmful vapours.**

Thorium chloride *[10026-08-1]* **M 373.8, pK_1^{25} 10.45, pK_2^{25} 10.62, pK_3^{25} 10.80, pK_4^{25} 11.64 (for aquo Th^{4+}).** Freed from anionic impurities by passing a 2M soln of $ThCl_4$ in 3M HCl through a Dowex-1 anion-resin column. The eluate was partially evaporated to give crystals which were filtered off, washed with Et_2O and stored in a desiccator over H_2SO_4 to dry. Alternatively, a saturated solution of $ThCl_4$ in 6M HCl was filtered through quartz wool and extracted twice with ethyl, or isopropyl, ether (to remove iron), then evaporated to a small volume on a hot plate. (Excess silica ppted, and was filtered off. The filtrate was cooled to 0° and saturated with dry HCl gas.) It was shaken with an equal volume of Et_2O, agitating with HCl gas, until the mixture becomes homogeneous. On standing, $ThCl_4.8H_2O$ ppted and was filtered off, washed with Et_2O and dried [Kremer *J Am Chem Soc* **64** 1009 *1942*].

Thorium sulfate ($4H_2O$) *[10381-37-0]* **M 496.2, m 42°(loses H_2O), d 2.8.** Crystd from water.

Tin (powder) *[7440-31-5]* **M 118.7.** The powder was added to about twice its weight of 10% aqueous NaOH and shaken vigorously for 10min. (This removed oxide film and stearic acid or similar material sometimes added for pulverisation.) It was then filtered, washed with water until the washings were no longer alkaline to litmus, rinsed with MeOH and air dried. [Sisido, Takeda and Kinugama *J Am Chem Soc* **83** 538 *1961*.]

Tin tetramethyl *[594-27-4]* **M 178.8, m 16.5°, b 78.3°/740mm.** It is purified by fractionation using a Todd column of 35-40 plates at atmospheric pressure (p. 177). The purity of the fractions can be followed by IR [*J Am Chem Soc* **77** 6486 *1955*]. It readily dissolves stopcock silicone greases which give bands in the 8-10μ region. [*J Am Chem Soc* **76** 1169 *1954*.]

Titanium tetrabromide *[7789-68-6]* **M 367.5, m 28.3°, b 233.5°, d 3.3.** Purified by distn. Distillate forms light orange hygroscopic crystals. Store in the dark under N_2 preferably in sealed brown glass ampules. [Olsen and Ryan *J Am Chem Soc* **54** 2215 *1932*.]

Titanium tetrachloride *[7550-45-0]* **M 189.7, b 136.4°, 154°, d 1.730, pK_1^{25} 0.3, pK_2^{25} 1.8, pK_3^{25} 2.1, pK_4^{25} 2.4 (for aquo Ti^{4+} hydrolysis).** Refluxed with mercury or a small amount of pure copper turnings to remove the last traces of light colour [due to $FeCl_3$ and VCl_4], then distilled under N_2 in an all-glass system, taking precautions to exclude moisture. Clabaugh, Leslie and Gilchrist [*J Res Nat Bur Stand* **55** 261 *1955*] removed organic material by adding aluminium chloride hexahydrate as a slurry with an equal amount of water (the slurry being *ca* one-fiftieth the weight of $TiCl_4$), refluxing for 2-6h while bubbling in chlorine, which was subsequently removed by passing a stream of clean dry air. The $TiCl_4$ was then distilled, refluxed with copper and again distilled, taking precautions to exclude moisture. Volatile impurities were then removed using a technique of freezing, pumping and melting. [Baxter and Fertig *J Am Chem Soc 45* 1228 *1923*; Baxter and Butler *J Am Chem Soc 48* 3117 *1926*.] **HARMFUL VAPOURS.**

Titanium trichloride *[7705-07-9]* **M 154.3, m >500°, pK_1^{25} 2.55 (for hydrolysis of Ti^{3+} to $TiOH^{2+}$).** Brown purple powder that is very reactive with H_2O and pyrophoric when dry. It should be manipulated in a dry box. It is soluble in CH_2Cl_2 and tetrahydrofuran and is used as a M solution in these solvents in the ratio of 2:1, and stored under N_2. It is a powerful reducing agent. [*Inorg Synth* **6** 52 *1960*; *Synthesis* 833 *1989*.]

Titanocene dichloride *[1271-19-8]* **M 248.9, m 260-280°(dec), 289.2°, 298-291°, d 1.60.** Bright red crystals from toluene or xylene-$CHCl_3$ (1:1) and sublimes at 190°/2mm. It is moderately soluble in EtOH and insoluble in Et_2O, $^*C_6H_6$, CS_2, CCl_4, pet ether and H_2O. [IR: *J Am Chem Soc* **76** 4281 *1954*; NMR and X-ray: *Can J Chem* **51** 2609 *1973*, **53** 1622 *1975*.]

Titanyl sulfate ($TiOSO_4.2H_2O$) *[13825-74-6]* **M 160.0.** Dissolved in water, filtered and crystd three times from boiling 45% H_2SO_4, washing with EtOH to remove excess acid, then with Et_2O. Air dried for several hours, then oven dried at 105-110°. [Hixson and Fredrickson *Ind Eng Chem* **37** 678 *1945*.]

Tribenzyl chlorosilane *[18740-59-5]* **M 336.9, m 139-142°, 141-142°, b 300-360°/100mm.** It is recrystd three times from pet ether; slender colourless needles, **m** 141°, sparingly soluble in pet ether and soluble in Et_2O. Does not fume in air but is decomposed by H_2O to give *tribenzyl silanol* **m** 106° (from pet ether). [*J Chem Soc* **93** 439 *1908*; *J Org Chem* **15** 556 *1950*.]

Tribenzyl phosphine *[76650-89-7]* **M 304.4, m 96-101°, b 203-210°/0.5mm, pK_{Est}~8.8.** Dissolve in Et_2O, dry over Na_2SO_4, evap and distil in an inert atmosphere. Distillate solidifies on cooling and is sublimed at 140°/0.001mm. This has **m** 92-95°(evacuated capillary). When air is bubbled through an Et_2O solution, it is oxidised to *tribenzyl phosphine oxide* , **m** 209-212° (evacuated capillary) (from Me_2CO). [*J Chem Soc* 2835 *1959*.]

Tri-*n*-butyl borate *[688-74-4]* **M 230.2, b 232.4°, n 1.4092, d 0.857.** The chief impurities are *n*-butyl alcohol and boric acid (from hydrolysis). It must be handled in a dry-box, and can readily be purified by fractional distillation, under reduced pressure.

Tri-*n*-butyl chlorosilane *[995-45-9]* **M 234.9, b 93-94°/4.5mm, 134-139°/16mm, 250-252°/atm, 142-144°/29mm, d_4^{20} 0.88, n_D^{20} 1.447**. Fractionate and store in small aliquots in sealed ampoules. [*J Am Chem Soc* **74** 1361 *1952*; *J Org Chem* **24** 219 *1959*.]

Tri-*n*-butyl phosphate (butyl phosphate) *[126-73-8]* **M 266.3, m -80°, b 47°/0.45mm, 98°/0.1mm, 121-124°/3mm, 136-137°/5.5mm, 166-167°/17mm, 177-178°/27mm, 289°/760atm (some dec), d_4^{20} 0.980, n_D^{20} 1.44249.** The main contaminants in commercial samples are organic pyrophosphates, mono- and di- butyl phosphates and butanol. It is purified by washing successively with 0.2M HNO_3 (three times), 0.2M NaOH (three times) and water (three times), then fractionally distilled under vacuum. [Yoshida *J Inorg Nucl Chem* **24** 1257 *1962*.] It has also been purified *via* its uranyl nitrate addition compound, obtained by saturating the crude phosphate with uranyl nitrate. This compound was crystd three times with *n*-hexane by cooling to -40°, and then decomposed by washing with Na_2CO_3 and water. Hexane was removed by steam distn and the water was then evaporated under reduced pressure and the residue was distilled under reduced pressure. [Siddall and Dukes *J Am Chem Soc* **81** 790 *1959*.]
Alternatively wash with water, then with 1% NaOH or 5% Na_2CO_3 for several hours, then finally with water. Dry under reduced pressure and fractionate carefully under vacuum. Stable colourless oil, sparingly soluble in H_2O (1mL dissolves in 165mL of H_2O), but freely miscible in organic solvents. [*J Am Chem Soc* **74** 4953 *1952*, **80** 5441 *1958*; ^{31}P NMR: *J Am Chem Soc* **78** 5715 *1956*; *J Chem Soc* 1488 *1957*.]

Tri-*n*-butyl phosphine *[998-40-3]* **M 202.3, b 109-110°/10mm, 115-116°/12mm, 149.5°/50mm, 240.4-242.2°/atm, d_4^{20} 0.822, n_D^{20} 1.4463, pK$_{Est}$~7.6.** Fractionally distilled under reduced pressure in an inert atm (N_2) through an 8" gauze packed column (**b** 110-111°/10mm) and redistilled in a vacuum and sealed in thin glass ampoules. It is easily oxidised by air to *tri-n-butylphosphine oxide,* **b** 293-296°/745mm. It has a characteristic odour, it is soluble in EtOH, Et_2O, and $^*C_6H_6$ but insoluble in H_2O and is less easily oxidised by air than the lower molecular weight phosphines. It forms complexes, e.g. with CS_2 (1:1) **m** 65.5° (from EtOH). [*J Chem Soc* 33 *1929*, 1401 *1956*.]

Tri-*n*-butyl phosphite *[102-85-2]* **M 250.3, b 114-115°/5mm, 122°/12mm, 130°/17mm, 137°/26mm, d_4^{20}0.926, n_D^{20} 1.4924**. Fractionate with an efficient column. Stable in air but is slowly hydrolysed by H_2O. [*J Chem Soc* 1464 *1940*, 1488 *1957*; *J Am Chem Soc* **80** 2358, 2999 *1958*.]

Tri-*n*-butyl tin chloride *[1461-22-9]* **M 325.5, b 98-100°/0.4mm, 140-152°/10mm, 172°/25mm, d_4^{20} 1.21, n_D^{20} 1.492.** Fractionate in an inert atmosphere, and seal in small aliquots in glass ampoules. Sensitive to moisture. [*J Chem Soc* 1446 *1947*; *J Appl Chem* **6** 93 *1956*.]

Tributyl tin hydride *[688-73-3]* **M 291.1, b 76°/0.7mm, 81°/0.9mm, d_4^{20} 1.098, n_D^{20} 1.473.** Dissolve in Et_2O, add quinol (500mg for 300mL), dry over Na_2SO_4, filter, evaporate and distil under dry N_2. It is a clear liquid if dry and decompose very slowly. In the presence of H_2O traces of tributyl tin hydroxide are formed in a few days. Store in sealed glass ampoules in small aliquots. It is estimated by reaction with aq NaOH when H_2 is liberated. **CARE**: stored samples may be under pressure due to liberated H_2. [*J Appl Chem* **7** 366 *1957*.]

B-Trichloroborazine *[933-18-6]* **M 183.1, m 87°, b 88-92°/21mm.** Purified by distillation from mineral oil.

Trichloromethyl trimethylsilane (trimethylsilyl trichloromethane) *[5936-98-1]* **M 191.6, m 130-132°, b 146-156°/749mm.** It distils at atmospheric pressure without decomposition and readily sublimes at 70°/10mm. It has one peak in the ^{1}H NMR spectrum (CH_2Cl_2) δ: 0.38. [*Synthesis* 626 *1980*.]

Tricyclohexylphosphine *[2622-14-2]* **M 280.4, m 82-83°, pK$_{Est}$~9.5.** Recrystd from EtOH [Boert et al. *J Am Chem Soc* **109** 7781 *1987*].

Triethoxysilane *[998-30-1]* **M 164.3, m -170°, b 131.2-131.8°/atm, 131.5°/760mm, d_4^{20} 0.98753, n_D^{20} 1.4377.** Fractionated using a column packed with glass helices of *ca* 15 theoretical plates in an inert atmosphere. Store in aliquots in sealed ampoules because it is sensitive to moisture. [*J Am Chem Soc* **72** 1377, 2032 *1950*; *J Org Chem* **13** 280 *1948*.]

Triethylborane *[97-94-9]* **M 146.0, b 118.6°, n 1.378, d 0.678.** Distilled at 56-57°/220mm.

Triethyl borate *[150-46-9]* **M 146.0, b 118°, n 1.378, d 0.864.** Dried with sodium, then distilled.

Triethyl phosphate *[78-40-0]* **M 182.2, b 40-42°/0.25-0.3mm, 98-98.5°/8-10mm, 90°/10mm, 130°/55mm, 204°/680mm, 215-216°/760mm, d_4^{25} 1.608, n_D^{20} 1.4053.** Dried by refluxing with solid BaO and fractionally distilled under reduced pressure. It is kept with Na and distilled. Stored in the receiver protected from light and moisture. Alternatively it is dried over Na_2SO_4 and distilled under reduced pressure. The middle fraction is stirred for several weeks over anhydrous Na_2SO_4 and again fractionated under reduced pressure until the specific conductance reached a constant low value of κ^{25} 1.19 x 10^8, κ^{40} 1.68 x 10^8, and κ^{55} 2.89 x 10^8 ohm^{-1} cm^{-1}. It has also been fractionated carefully under reduced pressure through a glass helices packed column. It is soluble in EtOH, Et_2O and H_2O (dec). [*J Am Chem Soc* **77** 4767 *1955*, **78** 6413, 3557 (P NMR) *1956*; *J Chem Soc* 3582 *1959*, IR: *J Chem Soc* 475 *1952* and *Can J Chem* **36** 820 *1958*; Kosolapoff *Organophosphorus Compounds*, Wiley p. 258 *1950*.]

Triethylphosphine *[554-70-1]* **M 118.2, b 100°/7mm, 127-128°/744mm, d_4^{15} 0.812, n_D^{18} 1.457, pK^{25} 8.69 (also available as a 1.0M soln in THF). All operations should be carried out in an efficient fume cupboard because it is flammable, toxic and has a foul odour.** Purified by fractional distn at atm pressure in a stream of dry N_2, as it is oxidised by air to the oxide. In 300% excess of CS_2 it forms Et_3PCS_2 (**m** 118-120° cryst from MeOH) which decomposes in CCl_4 to give Et_3PS as a white solid **m** 94° when recryst from EtOH. [Sorettas and Isbell *J Org Chem* **27** 273 *1962*; *J Am Chem Soc* **82** 5791 *1960*; pK: Henderson and Streuli *J Am Chem Soc* **82** 5791 *1960*; see also trimethylphosphine.] Store in a sealed vial under N_2.

Alternatively, dissolve in Et_2O and shake with a solution of AgI and KI to form the insoluble complex. Filter off the complex, dry over P_2O_5 and the Et_3P is regenerated by heating the complex in a tube attached to a vacuum system. [*J Chem Soc* 530 *1953*, 1828 *1937*; *J Org Chem* **27** 2573 *1962*; Kosolapoff *Organophosphorus Compounds*, Wiley p. 31 *1950*.]

Triethyl phosphite *[122-52-1]* **M 166.2, b 48-49°/11mm, b 52°/12mm, 57.5°/19mm, 157.9°/757mm, d_4^{20} 0.9687, n_D^{20} 1.4135.** Treat with Na (to remove water and any dialkyl phosphonate), then decant and distil under reduced pressure, with protection against moisture or distil in vacuum through an efficient Vigreux column or a column packed with Penn State 0.16 x 0.16 in protruded nickel packing and a variable volume take-off head. [*Org Synth* Coll Vol IV 955 *1963*; *J Am Chem Soc* **78** 5817 *1956*, **80** 2999 *1958*; Kosolapoff *Organophosphorus Compounds*, Wiley p. 203 *1950*.]

Triethyl phosphonoacetate (triethyl carboxymethyl phosphonate) *[867-13-0]* **M 224.2, b 83-84°/0.5mm, 103°/1.2mm, 143-144°/11mm, 260-262°/atm, d_4^{20} 1.1215, n_D^{20} 1,4310.** Purified by fractional distn, preferably *in vacuo*. ^{31}P NMR has P resonance at 19.5 relative to orthophosphate. [Kosolapoff and Powell *J Am Chem Soc* **68** 1103 *1946*; **72** 4198 *1950*; Speziale and Freeman *J Org Chem* **23** 1586 *1958*.]

Triethyl phosphonoformate *[1474-78-8]* **M 210.2, b 70-72°/0.1mm, 122.5-123°/8mm, 130-131°/10mm, 138.2°/12.5mm, d_4^{20} 1.22, n_D^{20} 1.423.** Dissolve in Et_2O, shake with H_2O (to remove any trace of NaCl impurity), dry (Na_2SO_4), evaporate and distil using an efficient fractionating column. [*Chem Ber* **57** 1035 *1924*.]

Triethyl 2-phosphonopropionate *[3699-66-9]* **M 238.2, b 76-77°/0.2mm, 137-138.5°/17mm, d_0^{20} 1.096, n_D^{20} 1.432.** Purified by fractional distillation with high reflux ratio, preferably using a spinning band column. [*J Am Chem Soc* 4198 *1950*.]

Triethylsilane *[617-86-7]* **M 116.3, b 105-107°, 107-108°, d 0.734. n 1.414.** Refluxed over molecular sieves, then distilled. It was passed through neutral alumina before use [Randolph and Wrighton *J Am Chem Soc* **108** 3366 *1986*].

Triethylsilyl-1,4-pentadiene (1,4-pentadien-3-yloxy-trimethylsilane) *[62418-65-9]* **M 198.4, b 72-74°/12mm, d_4^{20} 0.842, n_D^{20} 1.439.** Dissolve in pentane, wash with H_2O, dry (Na_2SO_4), evaporate, and distil under vacuum. R_F values on Kieselgel 60 are 0.15 (pentane) and 0.60 ($^*C_6H_6$). [IR, NMR, MS: *Helv Chim Acta* **64** 2002 *1981* .]

Triethyltin hydroxide *[994-32-1]* **M 222.9.** Treated with HCl, followed by KOH, and filtered to remove diethyltin oxide [Prince *J Chem Soc* 1783 *1959*].

Tri-*n*-hexylborane *[1188-92-7]* **M 265.3.** Treated with hex-1-ene and 10% anhydrous Et_2O for 6h at gentle reflux under N_2, then vacuum distilled through an 18in glass helices-packed column under N_2 taking the fraction **b** 130°/2.1mm to 137°/1.5mm. The distillate still contained some di-*n*-hexylborane [Mirviss *J Am Chem Soc* **83** 3051 *1961*].

Triiron dodecacarbonyl *[17685-52-8]* **M 503.7, m 140°(dec).** It usually contains 10% by weight of MeOH as stabiliser. This can be removed by keeping in a vacuum at 0.5mm for at least 5h. It can be sublimed slowly at high vacuum and is soluble in organic solvents. [*J Org Chem* **37** 930 *1972, J Chem Soc* 4632 *1960*; *Inorg Synth* **7** 193 *1963*.]

Triisoamyl phosphate *[919-62-0]* **M 308.4, b 143°/3mm.** Purified by repeated crystallisation, from hexane, of its addition compound with uranyl nitrate. (see *tributyl phosphate*.) [Siddall *J Am Chem Soc* **81** 4176 *1959*].

Triisobutyl phosphate *[126-71-6]* **M 266.3, b 119-129°/8-12mm, 192°/760mm, d 0.962, n 1.421.** Purified by repeated crystallisation, from hexane, of its addition compound with uranyl nitrate. (see *tributyl phosphate*.) [Siddall *J Am Chem Soc* **81** 4176 *1959*.]

Triisooctyl thiophosphate *[30108-39-5]* **M 450.6.** Purified by passage of its solution in CCl_4 through a column of activated alumina.

Triisopropyl phosphite *[116-17-6]* **M 208.2, b 58-59°/7mm, n^{25} 1.4082.** Distilled from sodium, under vacuum, through a column with glass helices. (This removes any dialkyl phosphonate).

Trimesitylphosphine *[23897-15-6]* **M 388.5, m 205-206°, pK_{Est}~8.0.** Recrystd from EtOH [Boert et al. *J Am Chem Soc* **109** 7781 *1987*].

Trimethallyl phosphate *[14019-81-9]* **M 260.3, b 134.5-140°/5mm, n^{25} 1.4454.** Purified as for triisoamyl phosphate.

Trimethoxysilane *[2487-90-3]* **M 122.2, m -114.8°, 81.1°/760mm, 84°/atm, d_4^{20} 0.957, n_D^{20} 1.359.** Likely impurities are $Si(OMe)_4$ and $H_2Si(OMe)_2$. Efficient fractionation is essential for removing these impurities [IR: *J Am Chem Soc* **81** 5109 *1959*].

Trimethyl borate (methylborate, trimethoxyboron) *[121-43-7]* **M 103.9, b 67-68°/742mm, d_4^{20} 0.928, n_D^{20} 1.3610.** Carefully fractionated through a gauze-packed column. Redistil and collect in weighed glass vials and seal. Keep away from moisture. It undergoes alkyl exchange with alcohols and forms azeotropes, e.g. with MeOH the azeotrope consists of 70% $(MeO)_3B$ and 30% MeOH with **b** 52-54°/atm, d 0.87. [*J Chem Soc* 2288 *1952*; *Chem Ind (London)* 53 *1952*; *J Am Chem Soc* **75** 213 *1953*.] Also dried with Na, then distilled.

Trimethyl boroxine *[823-96-1]* **M 125.5, b 80°/742mm, 79.3°/755mm, d_4^{20} 0.902.** Possible impurity is methylboronic acid. If present then add a few drops of conc H_2SO_4 and distil immediately, then fractionate through an efficient column. [*J Am Chem Soc* **79** 5179 *1957*; IR: *Z Anorg Chem* **272** 303 *1953*.]

Trimethyl chlorosilane (chlorotrimethylsilane) *[75-77-4]* **M 108.6, b 56-57°/atm, 58°/760mm, d 0.86, n 1.388.** Likely impurities are other chlorinated methylsilanes, and tetrachlorosilane (**b** 57.6°), some of which can form azeotropes. To avoid the latter very efficient fractional distillation is required. It has been fractionated through a 12 plate glass helices packed column with only the heart-cut material used. It has also been fractionated through a 90cm, 19mm diameter Stedman column (see p. 441). Also purified by redistilling from CaH_2 before use. [*J Am Chem Soc* **70**, 4254, 4258 *1948*; *J Org Chem* **23** 50 *1958*.] **FLAMMABLE and CORROSIVE.**

Trimethyloxonium tetrafluoroborate *[420-37-1]* **M 147.9, m 141-143°(sinters, open capillary), 179.6-180.0°(dec), 210-220°(dec).** The salt must be a white crystalline solid **m** ~ 179.6-180.0° (dec, sealed tube). Under a N_2 atmosphere (e.g. Dry Box), wash twice with CH_2Cl_2 then twice with Na-dried Et_2O, and dry by passing dry N_2 over the salt until free from Et_2O [Curphey *Org Synth* Coll Vol VI 1019 *1988*]. The oxonium salt purified in this way can be handled in air for short periods. The sample kept in a desiccator (Drierite) for 1 month at -20° had the same **m**, and samples stored in this way for >1 year are satisfactory for alkylations. ^1H NMR in liq SO_2 in a sealed tube had a single peak at δ 4.54 (impurities have δ at 3.39). [Meerwein *Org Synth* Coll Vol V 1096 *1973*.] If the sample looks good, dry in a vac desiccator for 2h (25°/1mm) and stored under N_2 at -20°. Melting point depends on heating rate.

Trimethylphenylsilane (phenyltrimethylsilane) *[768-32-1]* **M 150.3, b 67.3°/20mm, 170.6°/738mm, d_4^{25} 0.8646, n 1.491.** Fractionally distd at atm or reduced pressure (Podbielniak column, p.141) and estimated by GC with a column packed with Silicone Fluid No 710 on Chromosorb P support. [Gilman et al. *J Org Chem* **18** 1743 *1953*; Maienthal et al. *J Am Chem Soc* **76** 6392 *1954*; House and Respess *J Organomet Chem* **4** 95 *1965*; *J Am Chem Soc* **71** 2923 *1949*, **73** 4770 *1951*, **75** 2821 *1953*]

Trimethyl phosphate *[512-56-1]* **M 140.1, b 77°/12mm, 94°/22mm, 110°/60mm, 197.2°/atm, d_4^{20} 1.0213, n_D^{20} 1.3961.** Purified by fractionation through and efficient column at high reflux ratio. It is quite soluble in H_2O, solubility is 1:1 at 25°. [*J Am Chem Soc* **74** 2923 *1952*; IR: *J Chem Soc* 847 *1952*; *Can J Chem* *36* 820 *1958*; Kosolapoff *Organophosphorus Compounds*, Wiley p. 258 *1950*.]

Trimethylphosphine *[594-02-2]* **M 76.1, m -86°, b 38-39°/atm, pK^{25} 8.65, (also available as a 1.0M soln in THF or toluene). All operations should be carried out in an efficient fume cupboard because it is flammable, toxic and has a foul odor.** Distd at atm pressure in a stream of dry N_2 (apparatus should be held together with springs to avoid loss of gas from increased pressure in the system) and the distillate run into a soln of AgI in aq KI whereby the complex $[Me_3PAgI]_4$ separates steadily. Filter off the complex, wash with satd aq KI soln, then H_2O and dry in a vac desiccator over P_2O_5. The dry complex is heated in a flask (in a stream of dry N_2) in an oil bath at 140°, when pure Me_3P distils off (bath temp can be raised up to 260°). The vapour pressure of Me_3P at 20° is 466mm and the **b** is 37.8° [Thomas and Eriks *Inorg Synth* **9** 59 *1967*]. Alternatively, freshly distilled Me_3P (6g) is shaken with a solution of AgI (13.2g, 1.1mol) in saturated aqueous KI solution (50mL) for 2h. A white solid, not wetted with H_2O, separates rapidly. It is collected, washed with the KI solution, H_2O, and dried [*J Chem Soc* 1829 *1937*]. The silver complex is stable if kept dry in the dark in which state it can be kept indefinitely. Me_3P can be generated from the complex when required. Store under N_2 in a sealed container. It has been distd in a vacuum line at -78° *in vacuo* and condensed at -96° [IR and NMR: Crosbie and Sheldrick *J Inorg Nucl Chem* **31** 3684 *1969*]. The pK^{22} by NMR was 8.80 [Silver and Lutz *J Am Chem Soc* **83** 786 *1961*; pK 8.65: Henderson and Strueuli *J Am Chem Soc* **82** 5791 *1960*].

$[Me_2PAgI]_4$ *[12389-34-3]* complex is a flammable solid which has **m** 140-142°. It is decomposed by heating gently in one arm of an inverted U tube. The other arm is kept in a freezing mixture. The complex dissociates and pure Me_3P collects in the cold arm and is used at once. It should not be allowed to come in contact with air [*J Chem Soc* 708 *1938*]. The CS_2 complex has **m** 119° (cryst from 95% EtOH) and decomposes in CCl_4 to give Me_3PS **m** 154° (from EtOH) [Sorettas and Isbell *J Org Chem* **27** 273 *1962*].

Triphenylphosphine hydrochloride is unstable and volatilises at 75°/0.4mm (120°/14mm). [*J Am Chem Soc* **67** 503 *1945*; IR: *Trans Faraday Soc* **40** 41 *1944*; Kosolapoff *Organophosphorus Compounds,* Wiley p. 31 *1950*.]

Trimethyl phosphite *[121-45-9]* **M 124.1, b 22°/23mm, 86-86.5°/351mm, 111-112°/760mm, 111°/atm, d_4^{20} 1.0495, n_D^{20} 1.408.** Treated with Na (to remove water and any dialkyl phosphonate), then decanted and distilled with protection against moisture. It has also been treated with sodium wire for 24h, then distilled in an inert atmosphere onto activated molecular sieves [Connor et al. *J Chem Soc, Dalton Trans* 511 *1986*]. It has also been fractionally distilled using a spinning band column at high reflux ratio. It is a colourless liquid which is slowly hydrolysed by H_2O. [*J Am Chem Soc* **80** 2999 *1958*; IR: *J Chem Soc* 255 *1950*, P NMR: *J Am Chem Soc* **79** 2719 *1957*; Kosolapoff *Organophosphorus Compounds*, , Wiley p. 203 *1950*.]

Trimethylsilyl acetamide *[13435-12-6]* **M 131.3, m 38-43°, 52-54°, b 84°/13mm, 185-186°/atm.** Repeated distillation in an inert atmosphere, all operations to be performed under anhydrous atmosphere. In the presence of moisture trimethylsilanol (**b** 31-34°/26mm) is formed and is a likely impurity (check by NMR). [*Chem Ber* **96** 1473 *1963*.]

Trimethylsilyl acetonitrile (TMSAN) *[18293-53-3]* **M 113.2, b 49-51°/10mm, 65-70°/20mm, d_4^{20} 0.8729, n_D^{20} 1.4420.** Check if NMR and IR spectra are correct, if not dissolve in $^*C_6H_6$ (10vols), wash with buffer (AcOH-AcONa pH *ca* 7) several times, dry ($CaCl_2$), evaporate and distil. IR: ν (CCl_4) 2215 (CN) cm^{-1}; NMR δ (CCl_4): 0.23 (s, 9H, $SiMe_3$), and 1.53 (s, 2H, CH_2CN). [*J Chem Soc Perkin Trans 1* 26 *1979*.]

Trimethylsilyl azide *[4648-54-8]* **M 115.2, b 92-95°/atm, 95-99°/atm, d_4^{20} 0.878, n_D^{20} 1.441.** Distil through a Vigreux column in a N_2 atmosphere maintaining the oil bath temperature thermostated at 135-140°. Check the purity by ^1H NMR [$CHCl_3$, δ: single peak at 13cps from Me_4Si. Likely impurities are siloxane hydrolysis products. The azide is thermally stable even at 200° when it decomposes slowly without explosive violence. All the same it is advisable to carry out the distillation behind a thick safety screen in a fumehood because unforseen **EXPLOSIVE** azides may be formed on long standing. [Birkofer and Wagner *Org Synth* Coll Vol VI 1030 *1988*.]

Trimethylsilyl chloroacetate *[18293-71-5]* **M 166.7, m -20°, b 57-58°/14mm, 70-71°/30mm, 159°/760mm, d_4^{20} 1.057, n_D^{20} 11.4231 .** Purified by repeated fractionation and taking the fractions with clean NMR spectra. [*J Am Chem Soc* 2371 *1952*.]

Trimethylsilyl cyanide *[7677-24-9]* **M 99.2, m 8-11°, 10.5-11.5°, 11-12°, 12-12.5°; b 54-55°/87mm, 67-71°/168mm, 114-117°/760mm, 118-119°/760mm, d_4^{20} 0.79 n_D^{20} 1.43916.** Material should have only one sharp signal in the ^1H NMR (in CCl_4 with $CHCl_3$ as internal standard) δ: 0.4 and IR with ν at $2210cm^{-1}$ [*J Am Chem Soc* **74** 5247 *1952, 77* 3224 *1955*]; otherwise purify by fractionating through an 18 x 1/4 in column. [*J Am Chem Soc* **81** 4493 *1959*.] It has also been carefully distilled using a 60cm vac jacketed column. If volume of sample is small the cyanide can be chased (in the distillation) with xylene that had be previously distilled over P_2O_5. [*J Org Chem* **39** 914 *1974*.]

2-Trimethylsilyl-1,3-dithiane *[13411-42-2]* **M 192.2, b 54.5°/0.17mm, 100°/8mm, d_4^{20} 1.04, n_D^{20} 1.533 .** Fractionally distil through an efficient column and collect the fractions that have the correct NMR and IR spectra. ^1H NMR (CCl_4) τ 6.36 ($SiMe_3$), 9.87 (SCHS) and dithiane H at 7 and 8 (ratio 1:9:4:2) from Me_4Si; UV λ_{max} 244nm (ε 711); sh 227nm (ε 800). [*J Am Chem Soc* **89** 434 *1967*.]

Trimethylsilyl ethanol *[2916-68-9]* **M 118.3, b 53-55°/11mm, 75°/41mm, 95°/100mm, d_4^{25} 0.8254, n_D^{25} 1.4220.** If the NMR spectrum is not clean then dissolve in Et_2O, wash with aqueous NH_4Cl solution, dry (Na_2SO_4), evaporate and distil. The *3,4-dinitrobenzoyl* deriv has **m** 66° (from EtOH). [NMR: *J Am Chem Soc* **79** 974 *1957*; *Z Naturforsch* **14b** 137 *1959*.]

2-(Trimethylsilyl)ethoxymethyl chloride (SEMCl) *[76513-69-4]* **M 166.7, b 57-59°/8mm, d 0.942, n 1.4350.** Dissolve in pentane, dry ($MgSO_4$), evaporate and dist residual oil in a vac. Stabilise with 10ppm of diisopropylamine. Store under N_2 in a sealed container in a refrigerator. [Lipshutz and Pegram *Tetrahedron Lett* **21** 3343 *1980*.]

2-(Trimethylsilyl)ethoxymethyltrimethylphosphonium chloride *[82495-75-8]* **M 429.0, m 140-142°.** Wash the solid with AcOH and recryst from CH_2Cl_2-EtOAc. Dry in a vacuum desiccator. *Hygroscopic.* ^1H NMR ($CDCl_3$) δ: -0.2 (s, Me_3Si), 0.8 (t, 8Hz, CH_2Si), 3.83 (t, 8Hz, OCH_2), 5.77 (d, J_{PH} 4Hz, P^+-CH_2O) and 7.70 (m, aromatic H). [*Justus Liebigs Ann Chem* 1031 *1983*.]

Trimethylsilylethyl phenylsulfone (phenyl-2-trimethylsilylethylsulfone) *[73476-18-3]* **M 242.4, m 52°.** Dissolve in Et_2O, wash with saturated HCO_3^-, saturated NaCl, H_2O and dried ($MgSO_4$). Evaporation leaves residual crystals **m** 52°. [*Tetrahedron Lett* **23** 1963 *1982*, *J Org Chem* **53** 2688 *1985*.]

1-Trimethylsilyloxy-1,3-butadiene *[6651-43-0]* **M 142.3, b 131°/760mm (mixt of isomers), 49.5°/25mm (*E*-isomer), d 0.8237, n 1.447.** Purified by fractional distn and collecting the fractions with the required ^1H NMR. Store under N_2 — it is a flammable and moisture sensitive liquid. [Caseau et al. *Bull Soc Chim Fr* 16658 *1972*; Belge Patent 670,769, *Chem Abstr* **65** 5487d *1966*.]

1-(Trimethylsilyloxy)cyclopentene *[19980-43-9]* **M 156.3, b 45°/11mm, 75-80°/20-21mm, d_4^{20} 0.878, n_D^{20} 1.441.** If too impure as seen by the NMR spectrum then dissolve in 10 vols of pentane, shake with cold $NaHCO_3$(3 x 500mL), then 1.5M HCl (200mL) and aqueous $NaHCO_3$ (200mL) again, dry (Na_2SO_4), filter, evaporate and distil through a short Vigreux column. ^1H NMR: ($CDCl_3$) δ: 0.21 (s, 9H), 1.55 (m, 2H), 1.69 (m, 2H), 2.05 (br d, 4H) and 4.88 (br s, 1H). GLPC in a 6ft x 1/8in with 3% SP2100 on 100-120 mesh Supelcoport column should give one peak. [*Org Synth* Coll Vol VIII 460 *1993*.]

2-(Trimethylsilyloxy)furan *[61550-02-5]* **M 156.3, b 34-35°/9-10mm, 42-50°/17mm, 40-42°/25mm, d_4^{20} 0.950, n_D^{20} 1.436.** Fractionally distilled using a short path column. ^1H NMR in CCl_4 has δ: 4.90 (dd, *J* 1.3Hz, 3H), 6.00 (t, *J* 3Hz, 4H) and 6.60 (m, 5H). [*Heterocycles* **4** 1663 *1976*.]

4-Trimethylsilyloxy-3-penten-2-one (*cis*) (acetylacetone enol trimethylsilyl ether) *[13257-81-3]* **M 172.3, b 66-68°/4mm, 61-63°/5mm, d_4^{20} 0.917, n_D^{20} 1.452.** Fractionally distilled and stored in glass ampoules which are sealed under N_2. It hydrolyses readily in contact with moisture giving, as likely impurities, hexamethyldisiloxane and 2,4-pentanedione. [*J Am Chem Soc* **80** 3246 *1958*.]

Trimethylsilyl isocyanate *[1118-02-1]* **M 115.2, b 90-92°/atm, b 91.3-91.6°/atm, d_4^{20} 0.850 n $_D^{20}$ 1.43943.** Purified by repeated fractionation as for the isothiocyanate. [*J Chem Soc* 3077 *1950*.]

Trimethylsilyl isothiocyanate *[2290-65-5]* **M 131.3, m -33°, b 142.6-143.1°/759mm, 143.8°/760mm, n_D^{20} 1.4809.** The ^1H NMR spectrum should have only one peak, if not purify by repeated fractionation in an all glass system using a 50cm (4mm internal diameter) column without packing. [*J Am Chem Soc* **69** 3049 *1947*; *Chem Ber* **90** 1934 *1957*; *Synthesis* 51 *1975*.]

(Trimethylsilyl)methanol *[3219-63-4]* **M 104.2, b 120-122°/754mm, 122-123°/768mm, d_4^{20} 0.83 n_D^{20} 1.4176.** If the NMR indicates impurities (should have only two signals) then dissolve in Et_2O, shake with aqueous 5N NaOH, M H_2SO_4, saturated aqueous NaCl, dry ($MgSO_4$) and distil using an efficient column at atmospheric pressure. The *3,5-dinitrobenzoate* has **m** 70-70.5° (from 95% EtOH). [Huang and Wang *Acta Chem Sin* **23** 291 *1957*, *Chem Abs* **52** 19911 *1958*; Speier et al. *J Am Chem Soc* **81** 1844 *1959* and *J Am Chem Soc* **70** 1117 *1949*.]

(Trimethylsilyl)methylamine (aminomethyl trimethylsilane) *[18166-02-4]* **M 103.2, b 101.6°/735mm, d_4^{20} 0.77, n_D^{20} 1.416.** A possible contaminant is hexamethyldisiloxane. Should have two ^1H NMR signals in $CDCl_3$, if not, dissolve in $^*C_6H_6$, shake with 15% aq KOH, separate, dry (Na_2SO_4), filter, evaporate and distil using a still of *ca* 10 theoretical plates. The water azeotrope has **b** 83°/735mm, hence it is important to dry the extract well. The *hydrochloride* has **m** 198/199° (from MeOH or Me_2CO). [*J Am Chem Soc* **73** 3867 *1951*; NMR, IR: *J Organometal Chem* **44** 279 *1972*.]

Trimethylsilylmethyl phenylsulfone (phenyltrimethylsilylmethylsulfone) *[17872-92-3]* **M 228.4, m 28-32°, b 121°/0.01mm, 160°/6mm, n_D^{20} 1.5250.** Fractionate at high vacuum and recrystallise from pentane at -80°. If too impure (*cf* IR) dissolve in CH_2Cl_2 (*ca* 800mL for 100g), wash with 2M aqueous NaOH (2 x 200mL), brine, dry, evaporate and distil. [*J Chem Soc, Perkin Trans 1* 1949 *1985*; IR and NMR: *J Am Chem Soc* **76** 3713 *1954*.]

1-(Trimethylsilyl)-2-phenylacetylene (1-phenyl-2-trimethylsilylacetylene) *[78905-09-6]* **M 174.3, b 45-46°/0.1mm, 67°/5mm, 87.5°/9mm, d 0.8961 n 1.5284.** Dissolve in Et_2O, wash with H_2O, dry and fractionate through a Todd column (see p. 174). [*J Am Chem Soc* **80** 5298 *1958*.]

3-(Trimethylsilyl)propyne *[13361-64-3]* **M 112.3, b 99-100°/760mm, d 0.7581, n 1.4091.** Fractionally distilled and 0.5% of 2,6-di-*tert*-butyl-*p*-cresol added to stabilise it. [*Doklady Acad Nauk USSR* **93** 293 *1953*; *Chem Abs* **48** 13616 *1954*.]

1-Trimethylsilyl-1,2,4-triazole *[18293-54-4]* **M 141.3, b 74°/12mm, d_4^{20} 0.99, n_D^{20} 1.4604.** Fractionally distilled at atmospheric pressure in an inert atmosphere because it is moisture sensitive. [*Chem Ber* **93** 2804 *1960*.]

Trimethylsilyl trifluoromethane (trifluoromethyl trimethylsilane) *[81290-20-2]* **M 142.2, b 54-55°, 55-55.5°, d_4^{20} 0.962, n_D^{20} 1.332.** Purified by distilling from trap to trap in a vacuum of 20mm using a bath at 45° and Dry ice-Me_2CO bath for the trap. The liquid in the trap is then washed with ice cold H_2O (3x), the top layer is collected, dried (Na_2SO_4), the liquid was decanted and fractionated through a helices packed column at atmospheric pressure. ^{1}H, ^{13}C, ^{19}F, and ^{29}Si NMR can be used for assessing the purity of fractions. [*Tetrahedron Lett* **25** 2195 *1984*; *J Org Chem* **56** 984 1991.]

Trimethyl vinyl silane *[754-05-2]* **M 100.2, b 54.4°/744mm, 55.5°/767mm, d\S(25,4) 0.6865, n_D^{25} 1.3880.** If the ^{1}H NMR spectrum shows impurities then dissolve in Et_2O, wash with aq NH_4Cl soln, dry over $CaCl_2$, filter, evaporate and distil at atmospheric pressure in an inert atmosphere. It is used as a copolymer and may polymerise in the presence of free radicals. It is soluble in CH_2Cl_2. [*J Org Chem* **17** 1379 *1952*.]

Trineopentyl phosphate *[14540-59-1]* **M 320.4.** Crystd from hexane.

Tri-(4-nitrophenyl)phosphate *[3871-20-3]* **M 461.3, m 155-156°, 156°, 156-158°, 157-159°.** It has been recrystd from AcOH, dioxane, AcOEt and Me_2CO and dried in vacuum over P_2O_5. [*J Am Chem Soc* **72** 5777 *1950*, **79** 3741 *1957*.]

Tri-*n*-octylphosphine oxide *[78-50-2]* **M 386.7, m 59.5-60°, pK_{Est} <0.** Mason, McCarty and Peppard [*J Inorg Nuclear Chem* **24** 967 *1962*] stirred an 0.1M solution in *benzene with an equal volume of 6M HCl at 40° in a sealed flask for 48h, then washed the *benzene solution successively with water (twice), 5% aq Na_2CO_3 (three times) and water (six times). The *benzene and water were then evaporated under reduced pressure at room temperature. Zingaro and White [*J Inorg Nucl Chem* **12** 315 *1960*] treated a pet ether solution with aqueous $KMnO_4$ (to oxidise any phosphinous acids to phosphinic acids), then with sodium oxalate, H_2SO_4 and HCl (to remove any manganese compounds). The pet ether solution was slurried with activated alumina (to remove phosphinic acids) and recrystd from pet ether or cyclohexane at -20°. It can also be crystd from EtOH.

Triphenylantimony *[603-36-1]* **M 353.1, m 52-54°.** Recrystd from acetonitrile [Hayes et al. *J Am Chem Soc* **107** 1346 *1985*].

Triphenylarsine *[603-32-7]* **M 306.2, m 60-62°.** Recrystd from EtOH or aqueous EtOH [Dahlinger et al. *J Chem Soc, Dalton Trans* 2145 *1986*; Boert et al. *J Am Chem Soc* **109** 7781 *1987*].

Triphenylbismuth (bismuth triphenyl) *[603-33-8]* **M 440.3, m 75-76°, 77-78°, 78.5°, $d_4^{98.5}$ 1.6427(melt).** Dissolve in EtOH, ppte with H_2O, extract with Et_2O, dry and evaporate when the residue crystallises. It has been recrystd from EtOH and Et_2O-EtOH and is a stable compound. [*J Chem Soc* suppl p121 *1949*; *Chem Ber 37* 4620 *1904*; *J Am Chem Soc* **62** 665 *1940*; UV: *J Chem Phys* **22** 1430 *1954*.]

Triphenyl borane (borane triphenyl) *[960-71-4]* **M 242.1, m 134-140°, 137°, 139-141°, 142-142.5°, 147.5-148°, 151°, b 203°/15mm.** Recryst three times from Et_2O or $^*C_6H_6$ under N_2 and dry at 130°. It can be distilled in a high vacuum at 300-350°, and has been distilled (**b** 195-215°) in vacuum using a bath temp of 240-330°. N_2 was introduced into the apparatus before dismantling. It forms complexes with amines. [*Chem Ind (London)* 1069 *1957*; *Justus Liebigs Ann Chem* **563** 110 *1949*; *J Am Chem Soc* **57** 1259 *1935*.]

Triphenylchlorostannane (triphenyltin chloride) *[639-58-7]* **M 385.5, m 103-106°(dec).** See triphenyltin chloride on p. 494.

Triphenyl phosphate *[115-86-6]* **M 326.3, m 49.5-50°, b 245°/0.1mm.** Crystd from EtOH.

Triphenylphosphine *[603-35-0]* **M 262.3, m 77-78°, 79°, 79-81°, 80.5°, 80-81°, b >360°(in inert gas), d_4^{25} 1.194, d_4^{80} 1.075 (liq), pK 2.73.** Crystd from hexane, MeOH, diethyl ether, CH_2Cl_2/hexane or 95% EtOH. Dried at 65°/<1mm over $CaSO_4$ or P_2O_5. Chromatographed through alumina using (4:1) *benzene/$CHCl_3$ as eluent. [Blau and Espenson et al. *J Am Chem Soc* **108** 1962 *1986*; Buchanan et al. *J Am Chem Soc* **108** 1537 *1986*; Randolph and Wrighton *J Am Chem Soc* **108** 3366 *1986*; Asali et al. *J Am Chem Soc* **109** 5386 *1987*.] It has also been crystd twice from pet ether and 5 times from Et_2O-EtOH to give **m** 80.5°. Alternatively, dissolve in conc HCl, and upon dilution with H_2O it separates because it is weakly basic; it is then crystallised from EtOH-Et_2O. It recrystallises unchanged from AcOH. [*J Chem Soc* Suppl. p121 *1949*; *J Am Chem Soc* **78** 3557 *1956*.] *$3Ph_3P$ .4HCl* crystallises when HCl gas is bubbled through an Et_2O solution; it has **m** 70-73°, but recrystallises very slowly and is deliquescent. The *HI*, made by adding Ph_3P to hydriodic acid is not hygroscopic and decomps at ~100°. The *chlorate* (1:1) *salt* has **m** 165-167°, but decomposes slowly at 100°. All salts hydrolyse in H_2O to give Ph_3P [IR, UV: *J Am Chem Soc* **80** 2117 *1958;* pK: *J Am Chem Soc* **82** 5791 *1960*; Kosolapoff, *Organophosphorus Compounds*, Wiley *1950*].
§ Available commercially on a polystyrene or polyethyleneglycol support.

Triphenyl phosphine dibromide *[1034-39-5]* **M 422.1, m 235°, 245-255°(dec).** Recrystd from MeCN-Et_2O. Although it has been recrystd from EtOH, this is not recommended as it converts alcohols to alkyl bromides. It deteriorates on keeping and it is best to prepare it afresh. [Anderson and Freenor *J Am Chem Soc* **86** 5037 *1964*; Horner et al. *Justus Liebigs Ann Chem* **626** 26 *1959*.]

Triphenylphosphine oxide *[791-28-6]* **M 278.3, m 152.0°, pK_{Est} ~ -2.10 (aq H_2SO_4).** Crystd from absolute EtOH. Dried *in vacuo.*

Triphenyl phosphite *[101-02-0]* **M 310.3, b 181-189°/1mm, d 1.183.** Its ethereal soln was washed succesively with aqueous 5% NaOH, distilled water and saturated aqueous NaCl, then dried with Na_2SO_4 and distilled under vacuum after evaporating the diethyl ether.

Triphenylphosphorylidene acetaldehyde (formylmethylenetriphenylphosphorane) *[2136-75-6]* **M 304.3, m 185-187°, 186-187°(dec).** Recryst from Me_2CO, or dissolve in $^*C_6H_6$, wash with N NaOH, dry ($MgSO_4$), evap, and cryst residue from Me_2CO. It can be prepd from its precursor, formylmethyltriphenylphosphonium chloride (crystd from $CHCl_3$/EtOAc), by tratment with Et_3N and extraction with $^*C_6H_6$. [Tripett and Walker *Chem Soc* 1266 *1961*.]

Triphenyl silane *[789-25-3]* **M 260.4, m 45°, b 148-151°/1mm.** Purified by recrystn from MeOH. [*J Am Chem Soc* **81** 5925 *1959*; *Acta Chem Scand* **9** 947 *1955*; IR: *J Am Chem Soc* **76** 5880 *1954*.]

Triphenylsilanol (hydroxytriphenylsilane) *[791-31-1]* **M 276.4, m 150-153°, 151-153°, 154-155°, 156°.** It can be purified by dissolving in pet ether, passing through an Al_2O_3 column, eluting thoroughly with CCl_4 to remove impurities and then eluting the silanol with MeOH. Evaporation gives crystals **m** 153-155°. It can be recrystallised from pet ether, CCl_4 or from *benzene or Et_2O-pet ether (1:1). It has also been recrystallised by partial freezing from the melt to constant melting point. [*J Am Chem Soc* **81** 3288 *1959*; IR: *J Org Chem* **17** 1555 *1952* and *J Chem Soc* 124 *1949*.]

Triphenyltin chloride (chlorotriphenylstannane) *[639-58-7]* **M 385.5, m 103-106°(dec), 108°(dec), b 240°/13.5mm.** Purify by distillation, followed by recrystn from MeOH by adding pet ether (b 30-60°), **m** 105-106° [*Chem Ber* **67** 1348 *1934*], or by crystn from Et_2O [Krause *Chem Ber* **51** 914 *1918*]. It sublimes in a vacuum. **HIGHLY TOXIC.**

Triphenyltin hydroxide *[76-87-9]* **M 367.0, m 122-123.5°, 124-126°.** West, Baney and Powell [*J Am Chem Soc* **82** 6269 *1960*] purified a sample which was grossly contaminated with tetraphenyltin and diphenyltin oxide by dissolving it in EtOH, most of the impurities remaining behind as an insoluble residue. Evaporation of the EtOH gave the crude hydroxide which was converted to triphenyltin chloride by grinding in a mortar under 12M HCl, then evaporating the acid soln. The chloride, after crystallisation from EtOH, had **m** 104-105°. It was dissolved in Et_2O and converted to the hydroxide by stirring with excess aqueous ammonia. The ether layer was separated, dried, and evaporated to give triphenyltin hydroxide which, after crystn from EtOH and drying under vacuum, was in the form of white crystals (**m** 119-120°), which retained some cloudiness in the melt above 120°. The hydroxide retains water (0.1-0.5 moles of water per mole) tenaciously.

Triphenyl vinyl silane *[18666-68-7]* **M 286.5, m 58-59°, 57-59.5°, 67-68°, b 190-210°/3mm.** It has been recrystallised from EtOH, 95% EtOH, EtOH-$^*C_6H_6$, pet ether (b 30-60°) and Et_2O, and has been distilled under reduced pressure. [*J Am Chem Soc* **74** 4582 *1952*; *J Org Chem* **17** 1379 *1952*.]

Tri-*n*-propyl borate *[688-71-1]* **M 188.1, b 175-177°, d 0.857, n 1.395.** Dried with sodium and then distilled.

Triquinol-8-yl phosphate *[52429-99-9]* **M 479.4, m 193-197°, 202-203°.** Purified by recrystn from dimethylformamide. Purity was checked by paper chromatography, R_F 0.90 [*i*-PrOH, saturated $(NH_4)_2SO_4$, H_2O; 2:79:19 as eluent]; IR (KBr) ν 1620–1570 (C=C, C=N) and 1253 (P=O). [*Bull Chem Soc Jpn* **47** 779 *1974*.]

Tri-ruthenium dodecacarbonyl *[15243-33-1]* **M 639.1, m 154-155°.** Recryst from $^*C_6H_6$ or cyclohexane as orange-red crystals, and sublime at 80-100°/0.1mm. It has ν_{CO} 2062 and 2032. [*J Chem Soc, Chem Commun* 684 *1966*; *J Chem Soc (A)* 1238 *1967*; IR,UV: *Angew Chem Int Ed Engl* **7** 427 *1968*.]

Tris-(2-biphenylyl) phosphate *[132-28-5]* **M 554.6, m 115.5-117.5°.** Crystd from MeOH containing a little acetone.

Tris(2,2'-bipyridine)ruthenium(II) dichloride ($6H_2O$) *[50525-27-4]* **M 748.6.** Recrystd from water then from MeOH [Ikezawa et al. *J Am Chem Soc* **108** 1589 *1986*].

Tris-(1,2-dioxyphenyl)cyclotriphosphazine {trispiro[1,3,5,2,4,6-triazatriphosphorine]-2,2':-2,4":2,6"'-tris(1,3,2)benzodioxaphosphole} *[311-03-5]* **M 459.0, m 244-245°, 245°, 245-246°.** Recrystd from $^*C_6H_6$ or chlorobenzene, then triple sublimed (175°/0.1mm, 200°/0.1mm, 230°/0.05mm). UV has λ_{max}nm (log ε): 276 (3.72), 271 (3.79) 266sh (3.68) and 209 (4.38) in MeCN. IR (ν): 1270 (O-Ph), 1220 (P=N), 835 (P-O-Ph) and 745 (Ph) cm^{-1}. [Alcock *J Am Chem Soc* **86** 2591 *1964*; Alcock et al. *J Am Chem Soc* **98** 5120 *1976*; Meirovitch *J Phys Chem* **88** *1522 1984*.]

(±)-Tris-(2-ethylhexyl)phosphate (TEHP, tri-isooctylphosphate, "trioctyl" phosphate, *[78-42-2; 25103-23-5]* **M 434.6, b 186°/1mm, 219°/5mm, d^{25} 0.92042, n 1.44464.** TEHP, in an equal volume of diethyl ether, was shaken with aqueous 5% HCl and the organic phase was filtered to remove traces of pyridine (used as a solvent during manufacture) as its hydrochloride. This layer was shaken with aqueous Na_2CO_3, then water, and the ether was distilled off at room temperature. The ester was filtered, dried for 12h at 100°/15mm, and again filtered, then shaken intermittently for 2 days with activated alumina (100g/L). It was decanted through a fine sintered-glass disc (with exclusion of moisture), and distd under vacuum. [French and Muggleton *J Chem Soc* 5064 *1957*.] *Benzene can be used as a solvent (to give 0.4M soln) instead of ether. IR: 1702, 1701, 481 and 478cm^{-1} [Bellamy and Becker *J Chem Soc* 475 *1952*]. The *uranyl nitrate* salt was purified by partial crystallisation from hexane [Siddall *J Am Chem Soc* **81** 4176 *1959*].

Trisodium citrate (2H_2O) *[68-04-2]* **M 294.1, m 150°(loses H_2O).** Crystd from warm water by cooling to 0°.

Trisodium 8-hydroxy-1,3,6-pyrenetrisulfonate *[6358-69-6]* **M 488.8, m >300(dec).** Purified by chromatography with an alumina column, and eluted with *n*-propanol-water (3:1, v/v). Recrystd from aqueous acetone (5:95, v/v) using decolorising charcoal.

Trisodium 1,3,6-naphthalenetrisulfonate *[5182-30-9]* **M 434.2.** The free acid was obtained by passage through an ion-exchange column and converted to the lanthanum salt by treatment with La_2O_3. This salt was crystallised twice from hot water. [The much lower solubility of $La_2(SO_4)_3$ and its retrograde temperature dependence allows a good separation from sulfate impurity]. The lanthanum salt was then passed through an appropriate ion-exchange column to obtain the free acid, the sodium or potassium salt. (The sodium salt is *hygroscopic*). [Atkinson, Yokoi and Hallada *J Am Chem Soc* **83** 1570 *1961*.] Also recrystd from aqueous acetone [Okahata et al. *J Am Chem Soc* **108** 2863 *1986*].

Trisodium orthophosphate **(12H_2O)** *[10101-89-0]* **M 380.1, pK_1^{25} 2.15, pK_2^{25} 7.21, pK_3^{25} 12.33 (for H_3PO_4).** Crystd from warm dilute aqueous NaOH (1mL/g) by cooling to 0°.

Tris(2,4-pentandionate)aluminium *[13963-57-0]* **M 324.3.** See aluminum acetylacetonate on p. 390.

Tris-(trimethylsilyl)silane **(TTMSS)** *[1873-77-4]* **M 248.7, b 73°/5mm, d 0.808, n 1.49.** Purified by fractional distn and taking the middle cut. Store under N_2 or Ar as it is an **IRRITANT** and **PYROPHORIC**. [Chatgilialoglu *Acc Chem Res* **25** 188 *1992*; NMR: Gilman et al. *J Organomet Chem* **4** 163 *1965*.]

Tritium *[10028-17-8]* **M 6.0.** Purified from hydrocarbons and ^{3}He by diffusion through the wall of a hot nickel tube [Landecker and Gray *Rev Sci Instrum* **25** 1151 *1954*]. **RADIOACTIVE.**

Tri-*p*-tolyl phosphate *[20756-92-7; 1330-78-5 (isomeric tritolyl phosphate mixture)]* **M 368.4, b 232-234°, d^{25} 1.16484, n 1.56703.** Dried with $CaCl_2$, then distd under vacuum and percolated through a column of alumina. Passage through a packed column at 150°, with a counter-current stream of nitrogen, under reduced pressure, removed residual traces of volatile impurities.

Tri-*o*-tolylphosphine *[6163-58-2]* **M 304.4, m 129-130°, pK_{Est} <0.** Crystd from EtOH [Boert et al. *J Am Chem Soc* **109** 7781 *1987*].

Tungsten (rod) *[7440-33-7]* **M 183.6. m 3410°, b 5900°, d 19.0.** Cleaned with conc NaOH solution, rubbed with very fine emery paper until its surface was bright, washed with previously boiled and cooled conductivity water and dried with filter paper.

Tungsten hexacarbonyl *[14040-11-0]* **M 351.9, d 2.650.** Sublimed *in vacuo* before use [Connoe et al. *J Chem Soc, Dalton Trans* 511 *1986*].

Tungsten (VI) trichloride *[13283-01-7]* **M 396.6, m 265°(dec), 275°, b 346°, d$_4^{25}$ 3.520, pK_1^{25} 2.20, pK_2^{25} 3.70 (for tungstic acid, H_2WO_4).** Sublimed in a stream of Cl_2 in a high temperature furnace and collected in a receiver cooled in a Dry Ice-acetone bath in an inert atmosphere because it is sensitive to moisture. It is soluble in CS_2, CCl_4, $CHCl_3$, $POCl_3$, *C_6H_6, pet ether and Me_2CO. Solns decompose on standing. Good crystals can be obtained by heating WCl_6 in CCl_4 to 100° in a sealed tube, followed by slow cooling (tablets of four-sided prisms). Store in a desiccator over H_2SO_4 in the dark. [*Inorg Synth* **3** 163 *1950*, **9** 133*1967*; *Handbook of Preparative Inorganic Chemistry (Ed. Brauer)* Vol II 1417 *1965*.]

Uranium hexafluoride *[7783-81-5]* **M 352.0, b 0°/17.4mm, 56.2°/765mm, m 64.8°, pK^{25} 1.68 (for hydrolysis of U^{4+} to UOH^{3+}).** Purified by fractional distillation to remove HF. Also purified by low temperature trap-to-trap distillation over pre-dried NaF [Anderson and Winfield *J Chem Soc, Dalton Trans* 337 *1986*].

Uranium trioxide *[1344-58-7]* **M 286.0, d 7.29.** The oxide was dissolved in $HClO_4$ (to give a uranium content of 5%), and the solution was adjusted to pH 2 by addition of dilute ammonia. Dropwise addition of 30% H_2O_2, with rapid stirring, ppted U(VI) peroxide, the pH being held constant during the pptn, by addition of small amounts of the ammonia soln. (The H_2O_2 was added until further quantities caused no change in pH.) After stirring for 1h, the slurry was filtered through coarse filter paper in a Büchner funnel, washed with 1% H_2O_2 acidified to pH 2 with $HClO_4$, then heated at 350° for three days in a large platinum dish [Baes *J Phys Chem* **60** 878 *1956*].

Uranyl nitrate ($6H_2O$) *[13520-83-7]* **M 502.1, m 60.2°, b 118°, pK^{25} 5.82 (for aquo UO_2^{2+}).** Crystd from water by cooling to -5°, taking only the middle fraction of the solid which separated. Dried as the hexahydrate over 35-40% H_2SO_4 in a vacuum desiccator.

Vanadium (metal) *[7440-62-2]* **M 50.9, m 1910°, d 6.0.** Cleaned by rapid exposure consecutively to HNO_3, HCl, HF, de-ionised water and reagent grade acetone, then dried in a vacuum desiccator.

Vanadium (III) acetonylacetonate *[13476-99-8]* **M 348.3, m 181-184°, 185-190°, pK_1^{25} 2.92, pK_2^{25} 3.5(for aquo V^{3+} hydrolysis).** Crystd from acetylacetone as brown plates. It can be distilled in small quantities without decomposition. It is soluble in $CHCl_3$ and $^*C_6H_6$ and evaporation of a $CHCl_3$ solution yields brown crystals which are washed with cold EtOH and dried in vacuum or at 100° in a CO_2 atmosphere. Under moist conditions it readily oxidises [$V(AcAc)_3$ to $V(AcAc)_2O$]. [*J Chem Soc* **103** 78 *1913, Inorg Synth* **5** 105 *1957*; *Anal Chem* **30** 526 *1958*; UV: *J Am Chem Soc* **80** 5686 *1958*.]

Vanadyl acetylacetonate *[3153-26-2]* **M 265.2, m 256-259°.** Crystd from acetone.

Vanadyl trichloride ($VOCl_3$) *[7727-18-6]* **M 173.3, m-79.5°, b 124.5-125.5°/744mm, 127.16°/760mm, d^0 1.854, d^{32} 1.811.** Should be lemon yellow in colour. If red it may contain VCl_4 and Cl_2. Fractionally distil and then redistil over metallic Na but be careful to leave some residue because the residue can become **EXPLOSIVE** in the presence of the metal **USE A SAFETY SHIELD** *and avoid contact with moisture.* It readily hydrolyses to vanadic acid and HCl. Store in a tightly closed container or in sealed ampoules under N_2. [*Inorg Synth* **1** 106 *1939*, **4** 80 *1953*.]

Vinyl chlorosilane *[75-94-5]* **M 161.5, b 17.7°/46.3mm, 82.9°/599.4mm, 92°/742mm, 91-91.5°/atm, d_4^{20} 0.1.2717, n_D^{20} 1.435.** Fractionally distil at atmospheric pressure. It is H_2O sensitive and is stored in the dark and is likely to polymerise. [*Chem Ber* **91** 1805 *1958*, **92** 1012 *1959*; *Anal Chem* **24** 1827 *1952*]

Vinylferrocene (ferroceneylethene) *[1271-51-8]* **M 212.1, m 51-52.5°, b 80-85°/0.2mm.** Dissolve in Et_2O, wash with H_2O and brine, dry (Na_2SO_4), evap to a small vol. Purify through an Al_2O_3 (Spence grade H) column by eluting the yellow band with pet ether (b 40-60°). The low melting orange crystals which can be sublimed. The *tetracyanoethylene adduct* [49716-63-4] crysts from $^*C_6H_6$-pentane and has **m** 137-

139°(dec). [Horspool and Sutherland *Can J Chem* **46** 3453 *1968*; Berger et al. *J Org Chem* **39** 377 *1974*; Rauch and Siegel *J Organomet Chem* **11** 317 *1968*.]

Vinyltributylstannane (vinyltributyltin) *[7486-35-3]* **M 317.1, b 104-106°/3.5mm, d 1.081, n 1.4751.** Fractionate under reduced pressure and taking the middle fraction to remove impurities such as (n-Bu)$_3$SnCl. [Seyferth and Stone *J Am Chem Soc* **79** 515 *1957*.]

Water

[7732-18-5] **M 18.0, m 0°, b 100°, pK^{25} 14.00.** Conductivity water (specific conductance *ca* 10^{-7} mho) can be obtained by distilling water in a steam-heated tin-lined still, then, after adding 0.25% of solid NaOH and 0.05% of $KMnO_4$, distilling once more from an electrically heated Barnstead-type still, taking the middle fraction into a Jena glass bottle. During these operations suitable traps must be used to protect against entry of CO_2 and NH_3. Water only a little less satisfactory for conductivity measurements (but containing traces of organic material) can be obtained by passing ordinary distilled water through a mixed bed ion-exchange column containing, for example, Amberlite resins IR 120 (cation exchange) and IRA 400 (anion exchange), or Amberlite MB-1. This treatment is also a convenient one for removing traces of heavy metals. (The metals Cu, Zn, Pb, Cd and Hg can be tested for by adding pure concentrated ammonia to 10mL of sample and shaking vigorously with 1.2mL 0.001% dithizone in CCl_4. Less than 0.1µg of metal ion will impart a faint colour to the CCl_4 layer.) For almost all laboratory purposes, simple distillation yields water of adequate purity, and most of the volatile contaminants such as ammonia and CO_2 are removed if the first fraction of distillate is discarded.

Xylenol Orange (sodium salt)

[3618-43-7]. See entry on p. 387 in Chapter 4.

Zinc (dust)

[7440-66-6] **M 65.4.** Commercial zinc dust (1.2Kg) was stirred with 2% HCl (3L) for 1min, (then the acid was removed by filtration), and washed in a 4L beaker with a 3L portion of 2% HCl, three 1L portions of distilled water, two 2L portions of 95% EtOH, and finally with 2L of absolute Et_2O. (The wash solutions were removed each time by filtration.) The material was then dried thoroughly and if necessary, any lumps were broken up in a mortar.

Zinc (metal) *[7440-66-6]* **M 65.4, m 420°, d 7.141.** Fused under vacuum, cooled, then washed with acid to remove the oxide.

Zinc acetate ($2H_2O$) *[5970-45-6]* **M 219.5, m 100°(loses $2H_2O$), 237°, d 1.74, pK^{25} 8.96 (for hydrolysis of Zn^{2+} to $ZnOH^+$).** Crystd (in poor yield) from hot water or, better, from EtOH.

Zinc acetonylacetate *[14024-63-6]* **M 263.6, m 138°.** Crystd from hot 95% EtOH.

Zinc bromide *[7699-45-8]* **M 225.2, m 384, b 697.** Heated to 300° under vacuum (2×10^{-2}mm) for 1h, then sublimed.

Zinc caprylate *[557-09-5]* **M 351.8.** Crystd from EtOH.

Zinc chloride *[7646-85-7]* **M 136.3, m 283°, 290°.** The anhydrous material can be sublimed under a stream of dry HCl, followed by heating to 400° in a stream of dry N_2. Also purified by refluxing (50g) in dioxane (400mL) with 5g zinc dust, filtering hot and cooling to ppte $ZnCl_2$. Crystd from dioxane and stored in a desiccator over P_2O_5. It has also been dried by refluxing in thionyl chloride. [Weberg et al. *J Am Chem Soc* **108** 6242 *1986*.] *Hygroscopic: minimal exposure to the atmosphere is necessary.*

Zinc cyanide *[557-21-1]* **M 117.4, m 800°(dec), d 1.852.** It is a **POISONOUS** white powder which becomes black on standing if $Mg(OH)_2$ and carbonate are not removed in the preparation. Thus wash well with H_2O, then well with EtOH, Et_2O and dry in air at 50°. Analyse by titrating the cyanide with standard $AgNO_3$. Other likely impurities are $ZnCl_2$, $MgCl_2$ and traces of basic zinc cyanide; the first two salts can be washed out. It is soluble in aq KCN solns. However, if purified in this way $Zn(CN)_2$ is not reactive in the Gattermann synthesis. For this the salt should contain at least 0.33 mols of KCl or NaCl which will allow the reaction to proceed faster. [*J Am Chem Soc* **45** 2375 *1923*, **60** 1699 *1938*; *Org Synth* Coll Vol III 549 *1955*.]

Zinc diethyldithiocarbamate *[14324-55-1]* **M 561.7, pK^{25} 3.04 (for $Et_2NCS_2^-$).** Crystd several times from hot toluene or from hot $CHCl_3$ by addition of EtOH.

Zinc dimethyldithiocarbamate *[137-30-4]* **M 305.8, m 248-250°, pK^{25} 3.36 (for $Me_2NCS_2^-$).** Crystd several times from hot toluene or from hot $CHCl_3$ by addition of EtOH.

Zinc ethylenebis[dithiocarbamate] *[12122-67-7]* **M 249.7.** Crystd several times from hot toluene or from hot $CHCl_3$ by addition of EtOH.

Zinc fluoride *[7783-49-5]* **M 103.4, m 872°, b 1500°, d^{25} 5.00.** Possible impurity is H_2O which can be removed by heating at 100° or by heating to 800° in a dry atmosphere. Heating in the presence of NH_4F produces larger crystals. It is sparingly sol in H_2O (1.51g/100mL) but more sol in HCl, HNO_3 and NH_4OH. It can be stored in glass bottles. [*Handbook of Preparative Inorganic Chemistry (Ed. Brauer)* Vol I 242 *1963*.]

Zinc formate ($2H_2O$) *[557-41-5]* **M 191.4, m 140°(loses H_2O), d 2.21.** Crystd from water (3mL/g).

Zinc iodide *[10139-47-6]* **M 319.2, m 446, b 624°(dec), d 4.74.** Heated to 300° under vacuum (2 x 10^{-2}mm) for 1h, then sublimed.

Zinc *RS*-lactate ($3H_2O$) *[554-05-2; 16039-53-5 (L)]* **M 297.5.** Crystd from water (6mL/g).

Zincon (*o*-[1-(2-hydroxy-5-sulfo)-3-phenyl-5-formazono]-benzoic acid) *[135-52-4]* **M 459.4.** Main impurities are inorganic salts which can be removed by treatment with dilute acetic acid. Organic contaminants are removed by refluxing with ether. It can be recrystd from dilute H_2SO_4. [Fichter and Schiess *Chem Ber* **33** 751 *1900*.]

Zincon disodium salt (*o*-[1-(2-hydroxy-5-sulfo)-3-phenyl-5-formazono]-benzoic acid di-Na salt) *[135-52-4; 56484-13-0]* **M 484.4, m ~250-260° (dec).** Zincon soln is prepared by dissolving 0.13g of the powder in aqueous N NaOH (2mL diluted to 100mL with H_2O). This gives a deep red colour which is stable for one week. It is a good reagent for zinc ions but also forms stable complexes with transition metal ions. [UV-VIS: Bush and Yoe *Anal Chem* **26** 1345 *1954*; Hunter and Roberts *J Chem Soc* 820 *1941*; Platte and Marcy *Anal Chem* **31** 1226 *1959*] The free acid has been recrystd from dilute H_2SO_4. [Fichter and Scheiss *Chem Ber* **33** 751 *1900*.]

Zinc perchlorate ($6H_2O$) *[13637-61-1]* **M 372.4, m 105-107°, pK^{25} -2.4 to -3.1 (for $HClO_4$).** Crystd from water.

Zinc phenol-*o*-sulfonate ($8H_2O$) *[127-82-2]* **M 555.8.** Crystd from warm water by cooling to 0°.

Zinc phthalocyanine *[14320-04-8]* **M 580.9.** Sublimed repeatedly in a flow of oxygen-free N_2.

Zinc sulfate ($7H_2O$) *[7446-20-0]* **M 287.5, m 100°(dec), 280°(loses all $7H_2O$), >500(anhydr), d 1.97.** Crystd from aqueous EtOH.

Zinc 5,10,15,20-tetraphenylporphyrin *[14074-80-7]* **M 678.1, λ_{max} 418(556)nm.** Purified by chromatography on neutral (Grade I) alumina, followed by recrystallisation from CH_2Cl_2/MeOH [Yamashita et al. *J Phys Chem* **91** 3055 *1987*].

Zinc trifluoromethanesulfonate *[54010-75-2]* **M 363.5, m >300°.** It should be dried at 125° for 2h at 3mm. It is soluble in CH_2Cl_2 but insoluble in pet ether. [*Tetrahedron Lett* **24** 169 *1983*.]

Zirconium (IV) propoxide *[23519-77-9]* **M 327.6, b 198°/0.03mm, 208°/0.1mm, d_4^{20} 1.06, n_D^{20} 1.454.** Although it was stated that it could not be crystallised or sublimed even at 150°/10^{-4}mm [*J Chem Soc* 280 *1951*], the propoxide has, when properly prepared, been purifed by distn in a high vacuum [*J Chem Soc* 2025 *1953*].

Zirconium tetrachloride *[10026-11-6]* **M 233.0, m 300°(sublimes), pK_1^{25} -0.32, pK_2^{25} 0.06, pK_3^{25} 0.35, pK_4^{25} 0.46 (for hydrolysis of aquo Zr^{4-}).** Crystd repeatedly from conc HCl.

Zirconocene chloride hydride (bis[cyclopentadienyl]zirconium hydride chloride) (Schwartz reagent) *[37342-97-5]* **M 257.9.** It is a moisture and light sensitive compound. Its purity can be determined by reaction with a slight excess of Me_2CO whereby the active H reacts to produce $Cp_2ZrClOPr^i$ and the integrals of the residual Me_2CO in the ^1H NMR will show how pure the sample is. The presence of Cp_2ZrH_2 can be determined because it forms $Cp_2Zr(OPr^i)_2$. For very active compound it is best to prepare freshly from the dichloride by reduction with Vitride $[LiAl(OCH_2CH_2OH)_2H_2]$, the white ppte is filtered off, washed with tetrahydrofuran, $^*C_6H_6$, Et_2O, dried in vacuum and stored under anhydrous conditions and in the dark. [IR: *J Chem Soc, Chem Commun* 1105 *1969*; *J Am Chem Soc* **96** 8115 *1974*, **101** 3521 *1979*; *Synthesis* 1 *1988*.]

Zirconocene dichloride (bis[cyclopentadienyl]zirconium dichloride) *[1291-32-3]* **M 292.3, m 242-245°, 248°.** Purified by recrystn from $CHCl_3$ or xylene, and dried in vacuum. ^1H NMR ($CDCl_3$) δ: 6.52 from Me_4Si. Store in the dark under N_2 as it is moisture sensitive. [IR, NMR, MS: *Aust J Chem* **18** 173 *1965*; method of *J Am Chem Soc* **81** 1364 *1959*; and references in the previous entry.]

Zirconyl chloride ($6H_2O$) *[7699-43-6]* **M 286.2, m 150°(loses $6H_2O$).** Crystd repeatedly from 8M HCl as $ZrOCl_2.8H_2O$. On drying $ZrOCl_2.6H_2O$ **m** 150°. The product was not free from hafnium.

Zirconyl chloride ($8H_2O$) *[13520-92-8]* **M 322.3, m 150°(loses $6H_2O$), 210°(loses all H_2O). 400°(anhydr dec), d 1.91.** Recrystd several times from water [Ferragina et al. *J Chem Soc, Dalton Trans* 265 *1986*]. Recrystn from 8M HCl gives the octahydrate as white needles on concentrating. It is also formed by hydrolysing $ZrCl_4$ with water. After one recryst from H_2O, 99+% grade had Ag, Al, As, Cd, Cu, Hf, Mg, Na, Sc and V at 20, 1.8, 0.6, 0.6, 0.4, 8.4, 0.4, 2.4, 80 and 3 ppm resp.