

## CHAPTER 5

# PURIFICATION OF INORGANIC AND METAL ORGANIC CHEMICALS

(Including Organic compounds of B, Bi, P, Se, Si, and ammonium and metal salts of organic acids)

The most common method of purification of inorganic species is by recrystallisation, usually from water. However, especially with salts of weak acids or of cations other than the alkaline and alkaline earth metals, care must be taken to minimise the effect of hydrolysis. This can be achieved, for example, by recrystallising acetates in the presence of dilute acetic acid. Nevertheless, there are many inorganic chemicals that are too insoluble or are hydrolysed by water so that no general purification method can be given. It is convenient that many inorganic substances have large temperature coefficients for their solubility in water, but in other cases recrystallisation is still possible by partial solvent evaporation.

Organo-metallic compounds, on the other hand, behave very much like organic compounds, e.g. they can be redistilled and may be soluble in organic solvents. A note of **caution** should be made about handling organo-metallic compounds, e.g. arsines, because of their **potential toxicities**, particularly when they are volatile. Generally the suppliers of such compounds provide details about their safe manipulation. These should be read carefully and adhered to closely. If in any doubt always assume that the materials are lethal and treat them with utmost care. The same **safety precautions** about the handling of substances as stated in Chapter 4 should be followed here (see Chapter 1).

For information on **ionization (pK)** see Chapter 1, p. 7, and Chapter 4, p. 80. In order to avoid repetition, the literature (or predicted) pK values of anionic and/or cationic species are usually reported at least once, and in several cases is entered for the free acid or free base, e.g.  $\text{Na}_2\text{SO}_4$  will have a pK value for  $\text{Na}^+$  at the entry for NaOH and the pK values for  $\text{SO}_4^{2-}$  at the entries for  $\text{H}_2\text{SO}_4$ . When the pK values of the organic counter-ions are not given in this Chapter, as in case of sodium benzoate, the reader is referred to the value(s) in Chapter 4, e.g. of benzoic acid.

**Abbreviations** of titles of periodical are defined as in the Chemical Abstracts Service Source Index (CASSI). A note on other abbreviations is in Chapter 1, p. 30.

**Benzene**, which has been used as a solvent successfully and extensively in the past for reactions and purification by chromatography and crystallisation is now considered a **very dangerous substance** so it has to be used with extreme care. We emphasised that an alternative solvent to benzene (e.g. toluene, toluene-petroleum ether, or a petroleum ether to name a few) should be used first. However, if benzene has to be used then all operations have to be performed in a well ventilated fumehood and precautions taken to avoid inhalation and contact with skin and eyes. Whenever benzene is mentioned in the text and asterisk e.g.  $^*\text{C}_6\text{H}_6$  or  $^*\text{benzene}$ , is inserted to remind the user that special precaution should be adopted.

**Organic dyes** which are *not* complexed or are salts of metals are included in Chapter 4 (use the CAS Registry Numbers to find them). Commercially available polymer supported reagents are indicated with § under the appropriate reagent.

**Acetarsol** see *N*-Acetyl-4-hydroxy-*m*-arsanilic acid.

**Acetyltriphenylphosphonium chloride** [1235-21-8] **M 354.8, m 237-238°, 244-246° (dec)**. Recrystd from  $\text{CHCl}_3 + *C_6H_6 + \text{pet ether}$  (b 60-80°) and by dissolving in  $\text{CHCl}_3$  and pouring it into dry  $\text{Et}_2\text{O}$ .  $\lambda_{\text{max}}^{\text{EtOH}}$  nm( $\epsilon$ ) 255(3,600), 262(3,700), 268(4,000) and 275(3,100). The *iodide salt* crystallises from  $\text{H}_2\text{O}$  and has **m 207-209°**. [*J Org Chem* 22 41 1957.] **IRRITANT and hygroscopic**. When shaken with a 10% aqueous soln of  $\text{Na}_2\text{CO}_3$  (8h) it gives **acetylmethylene triphenyl phosphorane** which is recrystd from  $\text{MeOH-H}_2\text{O}$  and after drying at 70°/0.1mm has **m 205-206°**. UV:  $\lambda_{\text{max}}$  nm( $\epsilon$ ) 268 (6600), 275 (6500) and 288 (5700); IR:  $\nu$  ( $\text{cm}^{-1}$ ) 1529 (s), 1470 (m), 1425 (s), 1374 (m), 1105 (s) and 978 (s). [*J Org Chem* 22 41, 44 1957.]

**3R,4R,1'R-4-Acetoxy-3-[1-(tert-butylmethylsilyloxy)ethyl]-2-azetinone** [76855-69-1] **M 287.4, m 107-108°,  $[\alpha]_{\text{D}}^{20} +55^\circ$  (c 0.5, toluene),  $[\alpha]_{\text{D}}^{20} +53.7^\circ$  (c 1.04,  $\text{CHCl}_3$ )**. Purified by chromatography on silica gel (3 x 14cm) for 50g of ester using 20%  $\text{EtOAc}$  in *n*-hexane. The eluate is evaporated and the residue recrystd from hexane as white fluffy crystals. [*Tetrahedron* 39 2505 1983.]

**Acetylenedicarboxylic acid monopotassium salt** [928-04-1] **M 152.2**. Very soluble in  $\text{H}_2\text{O}$ , but can be crystd from small volume of  $\text{H}_2\text{O}$  in small crystals. These are washed with  $\text{EtOH}$  and dried over  $\text{H}_2\text{SO}_4$  at 125°. [*Chem Ber* 10 841 1877; *Justus Liebigs Ann Chem* 272 133 1893.]

**Acetylferrocene (ferrocenyl methylketone)** [1271-55-2] **M 228.1, m 86°, 86-87°**. Orange-red crystals, recrystd from isooctane and sublimed at 100°/1mm. The *oxime* has **m 167-170°** (from  $\text{Et}_2\text{O}$  or aq  $\text{EtOH}$ ). The *semicarbazone* has **m 198-201°** (from  $\text{EtOH}$ ). [*J Am Chem Soc* 77 2022 3009 1955; *J Chem Soc* 650 1958.]

**N-Acetyl-4-hydroxy-m-arsanilic acid** [97-44-9] **M 275.1, pK<sub>1</sub> 3.73, pK<sub>2</sub> 7.9, pK<sub>3</sub> 9.3**. Crystd from water.

**Allyl trimethylsilane (2-propenyltrimethylsilane)** [762-72-1] **M 114.3, b 83.0-84.5°, 84-88°, 85.5-86.0°, d 0.713, n 1.405**. Fractionate through an efficient column at atm pressure. If impure dissolve in THF, shake with  $\text{H}_2\text{O}$  (2x), dry ( $\text{Na}_2\text{SO}_4$ ) and fractionate. [Cudlin and Chvalovský *Collect Czech Chem Commun* 27 1658 1962.]

**Allyl tri-n-butylstannane (allyl tributyl tin)** [24850-33-7] **M 331.1, b 88-92°/0.2mm, 115°/17mm, d 1.068, n 1.487**. A possible impurity is tributylchlorostannane — test for Cl as Cl ion after hydrolysing. Dissolve in  $*C_6H_6$  (or toluene), shake with dil aq  $\text{NaOH}$ , dry ( $\text{CaCl}_2$ ), and dist in a vac [Jones et al. *J Chem Soc* 1446 1947; *Aldrichimica Acta* 17 75 1984 and 20 45 1987].

**Alizarin Red S (3,4-dihydroxy-9,10-dioxo-2-anthracene sulfonic acid, Na salt.  $\text{H}_2\text{O}$ )** [130-22-3] **M 360.4, pK<sub>1</sub><sup>2.5</sup> <1, pK<sub>2</sub><sup>2.5</sup> 5.49, pK<sub>3</sub><sup>2.5</sup> 10.85 (11.01)**. Commercial samples contain large amounts of sodium and potassium chlorides and sulfates. It is purified by passing through a Sephadex G-10 column, followed by elution with water, then 50% aq  $\text{EtOH}$  [King and Pruden *Analyst (London)* 93 601 1968]. Finally dissolve in  $\text{EtOH}$  and ppt with  $\text{Et}_2\text{O}$  several times [*J Phys Chem* 54 829 1950; polarography *J Am Chem Soc* 70 3055 1948].

**Alumina (neutral)** [1344-28-1] **M 102.0 (anhyd.)**. Stirred with hot 2M  $\text{HNO}_3$ , either on a steam bath for 12h (changing the acid every hour) or three times for 30min, then washed with hot distilled water until the washings had pH 4, followed by three washings with hot  $\text{MeOH}$ . The product was dried at 270° [Angyal and Young *J Am Chem Soc* 81 5251 1959]. For the preparation of alumina for chromatography see Chapter 1.

**Aluminum acetylacetonate** [13963-57-0] **M 324.3, m 192-194°, 195°**. Crystd several times from  $*\text{benzene}$  or aqueous  $\text{MeOH}$ ,  $\lambda_{\text{max}}$  216 and 286nm. [*J Phys Chem* 62 440 1958.] It can be purified by sublimation and has the following solubilities in g per cent:  $*C_6H_6$  35.9 (20°), 47.6 (40°), toluene 15.9 (20°), 22.0 (40°) and acetylacetone 6.6 (20°), 10.4 (40°). [*Inorg Synth* 5 105 1957.]

**Aluminium ammonium sulfate (10H<sub>2</sub>O)** [7784-26-1] M 453.3, m 93°, pK<sub>1</sub><sup>25</sup> 4.89, pK<sub>2</sub><sup>25</sup> 5.43, pK<sub>3</sub><sup>25</sup> 5.86 (fAl<sup>3+</sup> aquo), pK<sub>4</sub><sup>25</sup> 11.22 [aluminate Al(OH)<sub>4</sub><sup>-</sup>]. Crystd from hot H<sub>2</sub>O and cool in ice.

**Aluminium bromide** [7727-15-3] M 266.7, m 97°, b 114°/10mm. Refluxed and then distilled from pure aluminium chips in a stream of nitrogen into a flask containing more of the chips. It was then distd under vacuum into ampoules [Tipper and Walker *J Chem Soc* 1352 1959]. Anhydrous conditions are essential, and the white to very light brown solid distillate can be broken into lumps in a dry-box (under nitrogen). Fumes in moist air.

**Aluminium caesium sulfate (12H<sub>2</sub>O)** [7784-17-0 (12H<sub>2</sub>O); 14284-36-7] M 568.2. Crystd from hot water (3mL/g).

**Aluminium chloride (anhydrous)** [7446-70-0] M 133.3, m 192.6°. Sublimed several times in an all glass system under nitrogen at 30-50mm pressure. Has also been sublimed in a stream of dry HCl and has been subjected to a preliminary sublimation through a section of granular aluminium metal [for manipulative details see Jensen *J Am Chem Soc* 79 1226 1957]. Fumes in moist air.

**Aluminum ethoxide** [555-75-9] M 162.2, m 154-159°, 146-151°, b 187-190°/7mm, 210-214°/13mm. Crystd from CS<sub>2</sub> [m 139°, CS<sub>2</sub> complex] and distd in a vacuum. Molecular weight corresponds to [Al(OEt)<sub>3</sub>]<sub>4</sub> [*J Phys Chem* 39 1127 1935; *J Am Chem Soc* 69 2605 1947].

**Aluminium fluoride (anhydrous)** [7784-18-4] M 84.0, m 250°. Technical material may contain up to 15% alumina, with minor impurities such as aluminium sulfate, cryolite, silica and iron oxide. Reagent grade AlF<sub>3</sub> (hydrated) contains only traces of impurities but its water content is very variable (may be up to 40%). It can be dried by calcining at 600-800° in a stream of dry air (some hydrolysis occurs), followed by vacuum distn at low pressure in a graphite system, heated to approximately 925° (condenser at 900°) [Henry and Dreisbach *J Am Chem Soc* 81 5274 1959].

**Aluminium isopropoxide** [555-31-7] M 204.3, m 119°, b 94°/0.5mm, 135°/10mm. Distd under vacuum. *Hygroscopic*.

**Aluminium nitrate (9H<sub>2</sub>O)** [7784-27-2 (9H<sub>2</sub>O); 13473-90-0] M 375.1. Crystd from dilute HNO<sub>3</sub>, and dried by passing dry nitrogen through the crystals for several hours at 40°. After 2 recrystns of ACS grade it had S, Na and Fe at 2.2, 0.01 and 0.02 ppm resp.

**Aluminium potassium sulfate (12H<sub>2</sub>O, alum)** [7784-24-9] M 474.4, m 92°. Crystd from weak aqueous H<sub>2</sub>SO<sub>4</sub> (ca 0.5mL/g).

**Aluminium rubidium sulfate (12H<sub>2</sub>O)** [7784-29-4] M 496.2. Crystd from aq H<sub>2</sub>SO<sub>4</sub> (ca 2.5mL/g).

**Aluminium sulfate (anhydrous)** [10043-01-3] M 342.2, m 765°(dec); Al<sub>2</sub>O<sub>3</sub> 14-18 H<sub>2</sub>O [17927-65-0]; Al<sub>2</sub>O<sub>3</sub> 18 H<sub>2</sub>O [7784-31-8]. Crystd from hot dilute H<sub>2</sub>SO<sub>4</sub> (1 mL/g) by cooling in ice. When a soln of alumina (Al<sub>2</sub>O<sub>3</sub>) in conc H<sub>2</sub>SO<sub>4</sub> is slowly cooled, Al<sub>2</sub>SO<sub>4</sub> 17 or 18H<sub>2</sub>O deposits as a crystalline mass. Al<sub>2</sub>SO<sub>4</sub> 17H<sub>2</sub>O is the stable form in equilibrium with its saturated aqueous soln at 25° [Smith *J Am Chem Soc* 64 41 1942]. This is purified by dissolving in a small vol of H<sub>2</sub>O and adding EtOH until the sulfate readily crystallises from the oily supersaturated soln. It forms Al<sub>2</sub>O<sub>3</sub> 16H<sub>2</sub>O between 0-112°. On gradual heating the hydrate melts giving the anhydrous salt at ca 250°. Several hydrates up to 27H<sub>2</sub>O have been described. Further heating to red heat (~ 600-800) causes decomposition to Al<sub>2</sub>O<sub>3</sub> + SO<sub>3</sub> + SO<sub>2</sub> and O<sub>2</sub> [Cobb *J Soc Chem Ind* 29 250 1910]. ACS reagent is Al<sub>2</sub>O<sub>3</sub> 18H<sub>2</sub>O (98+%).

**Aluminum triethyl (triethyl aluminum)** [97-93-8] M 114.2, b 69°/1.5mm, 76°/2.5mm, 129-131°/55mm, d<sub>4</sub><sup>20</sup> 0.695, n<sub>D</sub><sup>20</sup> 1.394. Purified by fractionation in an inert atmosphere under vacuum in a 50cm column containing a heated nichrome spiral, taking the fraction 112-114°/27mm. It is very sensitive to H<sub>2</sub>O and should be stored under N<sub>2</sub>. It should not contain chloride which can be shown by hydrolysis and testing with AgNO<sub>3</sub>. [*J Am Chem Soc* 75 4828 5193 1953; NMR: *J Am Chem Soc* 81 3826 1959.]

**Aluminium tri-*tert*-butoxide** [556-91-2] M 246.3, m 208-210°(dec). Crystd from \*benzene and sublimed at 180°.

**Aluminium trimethanide (trimethyl aluminium)** [75-24-1] M 72.1, m 15.2°, b 111.5°/488.2mm, 124.5°/atm,  $d_4^{20}$  0.725. Distd through a 10-20 theoretical plates column under 1 atm of N<sub>2</sub> (better with very slow take-off). Attacks grease (use glass joints). Also vac distd over Al in absence of grease, into small glass vials and sealed under N<sub>2</sub>. Purity is measured by freezing point. Reacts with H<sub>2</sub>O, is non-conducting in \*C<sub>6</sub>H<sub>6</sub> and is **HIGHLY FLAMMABLE**. [*J Chem Soc* 4681946; *J Am Chem Soc* 68 2204 1946.]

**4-Aminophenylmercuric acetate** [6283-24-5] M 371.8, m 168°, 175°(dec), 180°(dec). Recrystd from hot dilute AcOH and dried in air. [*J Indian Chem Soc* 32 613 1955; *Justus Liebigs Ann Chem* 465 269 1928.]

**Ammonia (gas)** [7664-41-7] M 17.0, pK<sup>25</sup> 9.25. Major contaminants are water, oil and non-condensable gases. Most of these impurities are removed by passing the ammonia through a trap at -22° and condensing it at -176° under vacuum. Water is removed by distilling the ammonia into a tube containing a small lump of sodium. Also dried by passage through porous BaO, or over alumina followed by glass wool impregnated with sodium (prepared by soaking the glass wool in a solution of sodium in liquid ammonia, and evaporating off the ammonia). It can be rendered oxygen-free by passage through a soln of potassium in liquid ammonia.

**Ammonia (liquid)** [7664-41-7] M 17.0, m -77.7°, b -33.4°, n<sub>D</sub> 1.325, d 0.597,  $d^{-79}$  0.817g/mL. Dried, and stored, with sodium in a steel cylinder, then distd and condensed by means of liquid air, the non-condensable gases being pumped off. In order to obtain liquid NH<sub>3</sub> from a cylinder turn the cylinder up-side-down (i.e. with the valve at the bottom, use a metal stand to secure it in this position) and lead a plastic tube from the tap to a measuring cylinder placed in an efficient fume cupboard which is kept running. Turn the tap on and allow the ammonia to be released. At first, gas and liquid will splatter out (make sure that the plastic tube is secure) but soon the liquid will drip into the measuring cylinder. The high latent heat of evaporation will cool the ammonia so that the liquid will remain cool and not boil vigorously. If the ammonia is required dry the necessary precautions should be taken, i.e. the gas is allowed to flow through tubes packed with coarse CaO pellets.

**Ammonia (aqueous)** [7664-41-7] M 17.0 + H<sub>2</sub>O, d 0.90 (satd, 27% w/v, 14.3 N), pK<sup>25</sup> 9.25. Obtained metal-free by saturating distilled water, in a cooling bath, with ammonia (from tank) gas. Alternatively, can use isothermal distn by placing a dish of conc aq ammonia and a dish of pure water in an empty desiccator and leaving for several days. **AMMONIA (gas, liquid or aq soln) is very irritating and should not be inhaled in large volumes as it can lead to olfactory paralysis (temporary and partially permanent).**

**Ammonium acetate** [631-61-8] M 77.1, m 112-114°, d 1.04. Crystd twice from anhydrous acetic acid, dried under vacuum for 24h at 100° [Proll and Sutcliff *Trans Faraday Soc* 57 1078 1961].

**Ammonium benzoate** [1863-63-4] M 139.2, m 198°, 200°(dec), d 1.26. Crystd from EtOH.

**Ammonium bisulfate (ammonium hydrogen sulfate)** [7803-63-6] M 115.1°, m ~147°, d 1.79, pK<sup>25</sup> 1.96 (HSO<sub>4</sub><sup>-</sup>). Crystd from water at room temperature (1mL/g) by adding EtOH and cooling.

**Ammonium bromide** [12124-97-9] M 98.0, m 450°(sublimes), d 2.43. Crystd from 95% EtOH.

**Ammonium chloride** [12125-02-9] M 53.5, m 338°(sublime point, without melting), d 1.53. Crystd several times from conductivity water (1.5mL/g) between 90° and 0°. Sublimes. After one crystn, ACS grade had: metal(ppm) As (1.2), K (1), Sb (7.2), V (10.2).

**Ammonium chromate** [7788-98-9] M 152.1, m 185°(dec), d 1.81, pK<sub>1</sub><sup>25</sup> 0.74, pK<sub>2</sub><sup>25</sup> 6.49 (for H<sub>2</sub>CrO<sub>4</sub>). Crystd from weak aqueous ammonia (ca 2.5mL/g) by cooling from room temperature.

**Ammonium dichromate** [7789-09-5] M 252.1, m 170°(dec), d 1.26. Crystd from weak aq HCl (ca 1mL/g). (Possible carcinogen)

**Ammonium dihydrogen arsenate** [13462-93-6] M 159.0, m 300°(dec). Crystd from water (1mL/g).

**Ammonium dihydrogen orthophosphate** [7722-76-1] M 115.0, m 190°, d 1.80. Crystd from water (0.7mL/g) between 100° and 0°.

**Ammonium dodecylsulfate** [2235-54-3] M 283.4. Recrystd first from 90% EtOH and then twice from abs EtOH, finally dried in a vacuum.

**Ammonium ferric oxalate (3H<sub>2</sub>O)** [13268-42-3] M 428.1, m ~160°(dec), d 1.77. Crystd from hot water (0.5mL/g).

**Ammonium ferric sulfate (12H<sub>2</sub>O)** [7783-83-7 (12H<sub>2</sub>O); 10138-04-2 (anhydr)] M 482.2, m ~37°, d 1.71. Crystd from aqueous ethanol.

**Ammonium ferrous sulfate (6H<sub>2</sub>O)** [7783-85-9 (6H<sub>2</sub>O); 10045-89-3 (anhydr)] M 392.1, m 100°(dec), d 1.86. A soln in warm water (1.5mL/g) was cooled rapidly to 0°, and the resulting fine crystals were filtered at the pump, washed with cold distilled water and pressed between sheets of filter paper to dry.

**Ammonium formate** [540-69-2] M 63.1, m 116°, 117.3°, d<sub>4</sub><sup>45</sup> 1.280. Heat solid in NH<sub>3</sub> vapour and dry in vacuum till NH<sub>3</sub> odour is faint. Recryst from abs EtOH and then keep in a desiccator over 99% H<sub>2</sub>SO<sub>4</sub> *in vacuo*. It is very *hygroscopic*. Exists in two forms, stable needles and less stable plates. Also forms acid salts, i.e. HCO<sub>2</sub>NH<sub>4</sub>.3HCO<sub>2</sub>H and HCO<sub>2</sub>NH<sub>4</sub>.HCO<sub>2</sub>H. [*J Am Chem Soc* 43 1473 1921; 63 3124 1941 .]

**Ammonium hexachloroiridate (IV)** [16940-92-4] M 441.0. Ppted several times from aqueous soln by saturation with ammonium chloride. This removes any palladium and rhodium. Then washed with ice-cold water and dried over conc H<sub>2</sub>SO<sub>4</sub> in a vacuum desiccator. If osmium or ruthenium is present, it can be removed as the tetroxide by heating with conc HNO<sub>3</sub>, followed by conc HClO<sub>4</sub>, until most of the acid has been driven off. (This treatment is repeated). The near-dry residue is dissolved in a small amount of water and added to excess NaHCO<sub>3</sub> soln and bromine water. On boiling, iridic (but not platonic) hydroxide is ppted. It is dissolved in HCl and ppted several times, then dissolved in HBr and treated with HNO<sub>3</sub> and HCl to convert the bromides to chlorides. Saturation with ammonium chloride and cooling precipitates ammonium hexachloroiridate which is filtered off and purified as above [Woo and Yost *J Am Chem Soc* 53 884 1931].

**Ammonium hexacyanoferrate II hydrate** [14481-29-9] M 284.1, m dec on heating. The pale yellow trihydrate powder can be washed with 10% aq NH<sub>3</sub>, fildt, then washed several times with EtOH and Et<sub>2</sub>O, and dried at room temp. Decomposes in vacuum above 100° and should be stored away from light and under N<sub>2</sub>. In light and air it decomposes by losing NH<sub>3</sub>. [*Handbook of Preparative Inorganic Chem (Ed. Brauer)* Vol II 1509 1965.]

**Ammonium hexafluorophosphate** [16941-11-0] M 163.0, d<sub>4</sub><sup>18</sup> 2.181, pK<sub>1</sub><sup>25</sup>~ 0.5, pK<sub>2</sub><sup>25</sup> 5.12 (for fluorophosphoric acid H<sub>2</sub>PO<sub>3</sub>F). Crystallises from H<sub>2</sub>O in square plates. Decomposes on heating before melting. Soluble in H<sub>2</sub>O at 20° (74.8% w/v), also very soluble in Me<sub>2</sub>CO, MeOH, EtOH and MeOAc and is decomposed by boiling acids. [*Chem Ber* 63 1063 1930.]

**Ammonium hexafluorosilicate** [16919-19-0] M 178.1, pK<sub>2</sub> 1.92 (for H<sub>2</sub>SiF<sub>6</sub>). Crystd from water (2mL/g). After 3 recrystns of Tech grade it had Li, Na, K and Fe at 0.3, 0.2, 0.1 and 1.0 ppm resp.

**Ammonium hypophosphite** [7803-65-8] M 83.0. Crystd from hot EtOH.

**Ammonium iodate** [13446-09-8] **M 192.9, pK<sup>25</sup> 0.79 (IO<sup>3+</sup>)**. Crystd from water (8mL/g) between 100° and 0°.

**Ammonium iodide** [12027-06-4] **M 144.9, sublimes with dec ~405°, d 2.51**. Crystd from EtOH by addition of ethyl iodide. Very *hygroscopic*. Stored in the dark.

**Ammonium ionophore I (Nonactin)** [6833-86-7] **M 736.9, m 147-148°, [α]<sub>D</sub><sup>20</sup> 0° (c 1.2, CHCl<sub>3</sub>)**. Crystd from MeOH in colourless needles and is dried at 20° in high vac. A selectophore with high sensitivity for NH<sub>4</sub><sup>+</sup> ions. [*Helv Chim Acta* **38** 1445 1955, **45** 129 1962, **55** 1371 1972; *Acta Cryst* **27B** 1680 1971.]

**Ammonium magnesium chloride (6H<sub>2</sub>O)** [60314-43-4] **M 256.8**. Crystd from water (6mL/g) by partial evapn in a desiccator over KOH (deliquescent).

**Ammonium magnesium sulfate (6H<sub>2</sub>O)** [20861-69-2] **M 360.6**. Crystd from water (1mL/g) between 100° and 0°.

**Ammonium manganous sulfate (6H<sub>2</sub>O)** [13566-22-8] **M 391.3**. Crystd from water (2mL/g) by partial evapn in a desiccator.

**Ammonium metavanadate** [7803-55-6] **M 117.0, m 200°(dec)**. See ammonium (meta) vanadate on p. 395.

**Ammonium molybdate** [13106-76-8] **M 196.0, pK<sub>1</sub><sup>25</sup> 0.9 (proton addition), pK<sub>2</sub><sup>25</sup> 3.57, pK<sub>3</sub><sup>25</sup> 4.08 (for H<sub>2</sub>MoO<sub>4</sub>)**. Crystd from water (2.5mL/g) by partial evapn in a desiccator.

**Ammonium nickel sulfate (6H<sub>2</sub>O)** [7785-20-8 (6H<sub>2</sub>O); 15699-18-0 (anhydr)] **M 395.0, d 1.923**. Crystd from water (3mL/g) between 90° and 0°.

**Ammonium nitrate** [6484-52-2] **M 80.0, m 210°(dec explosively), d 1.72**. Crystd twice from distilled water (1mL/g) by adding EtOH, or from warm water (0.5mL/g) by cooling in an ice-salt bath. Dried in air, then under vacuum. After 3 recrystns of ACS grade it contained Li and B at 0.03 and 0.74 ppm resp.

**Ammonium oxalate (H<sub>2</sub>O)** [6009-70-7] **M 142.1, d 1.50**. Crystd from water (10mL/g) between 50° and 0°.

**Ammonium perchlorate** [7790-98-9] **M 117.5, d 1.95, pK<sup>25</sup> -2.4 to -3.1 (for HClO<sub>4</sub>)**. Crystd twice from distilled water (2.5mL/g) between 80° and 0°, and dried in a vacuum desiccator over P<sub>2</sub>O<sub>5</sub>. Drying at 110° might lead to slow decomposition to chloride. **POTENTIALLY EXPLOSIVE**.

**Ammonium peroxydisulfate** [7727-54-0] **M 228.2, m dec when heated wet liberating oxygen, d 1.98**. Recrystd at room temperature from EtOH/water.

**Ammonium picrate** [131-74-8] **M 246.1, m EXPLODES above 200°**. Crystd from EtOH and acetone.

**Ammonium reineckate (Reineckate salt)** [13573-16-5] **M 345.5, m 270-273°(dec)**. Crystd from water, between 30° and 0°, working by artificial light. Solns of reineckate decompose slowly at room temperature in the dark and more rapidly at higher temperatures or in diffuse sunlight.

**Ammonium selenate** [7783-21-3] **M 179.0, d 2.19, m dec on heating**. Crystd from water at room temperature by adding EtOH and cooling.

**Ammonium sulfamate** [7773-06-0] **M 114.1, m 132-135°, dec at 160°**. Crystd from water at room temperature (1mL/g) by adding EtOH and cooling.

**Ammonium sulfate** [7783-20-2] M 132.1, m 230°(dec), 280°(dec), d 1.77. Crystd twice from hot water containing 0.2% EDTA to remove metal ions, then finally from distilled water. Dried in a desiccator for 2 weeks over Mg(ClO<sub>4</sub>)<sub>2</sub>. After 3 recrystns ACS grade had Ti, K, Fe, Na at 11, 4.4, 4.4, 3.2 ppm resp.

**Ammonium tetrafluoroborate** [13826-83-0] M 104.8, pK<sup>25</sup> 2.77 (for HBF<sub>4</sub>). Crystd from conductivity water (1mL/g) between 100° and 0°.

**Ammonium tetraphenylborate** [14637-34-4] M 337.3, m ca 220°(dec). Dissolve in aqueous Me<sub>2</sub>CO and allow crystn to proceed slowly otherwise very small crystals are formed. No trace of Me<sub>2</sub>CO was left after drying at 120° [*Trans Faraday Soc* 53 19 1957]. The salt was pptd from dilute AcOH soln of sodium tetraphenylborane in the presence of NH<sub>4</sub><sup>+</sup> ions. After standing for 5min, the ppte was filtered off onto a sintered porcelain crucible, washed with very dilute AcOH and dried at room temp for at least 24h [*Anal Chem* 28 1001 1956]. Alternatively a soln of sodium tetraphenylborane (5% excess) in H<sub>2</sub>O is added to NH<sub>4</sub>Cl soln. After 5min the ppte is collected, washed several times with H<sub>2</sub>O and recryst from aqueous Me<sub>2</sub>CO. [*Analyt Chim Acta* 19 342 1958.]

**Ammonium thiocyanate** [1762-95-4] M 76.1, m 138°(dec), 149°(dec), pK<sup>25</sup> -1.85 (for HSCN), 149. Crystd three times from dilute HClO<sub>4</sub>, to give material optically transparent at wavelengths longer than 270nm. Has also been crystd from absolute MeOH and from acetonitrile.

**Ammonium tungstate (VI)** [11120-25-5] M 283.9, pK<sub>1</sub><sup>25</sup> 2.20, pK<sub>2</sub><sup>25</sup> 3.70 (for tungstic acid, H<sub>2</sub>WO<sub>4</sub>). Crystd from warm water by adding EtOH and cooling.

**Ammonium (meta) vanadate** [7803-55-6] M 117.0, d<sub>10</sub><sup>20</sup> 2.326. Wash with H<sub>2</sub>O until free from Cl<sup>-</sup> and dry in air. It is soluble in H<sub>2</sub>O (5.18g/100mL at 15°, 10.4g/100mL at 32°) but is more soluble in dilute NH<sub>3</sub>. Crystd from conductivity water (20mL/g). When heated at relatively low temperatures it loses H<sub>2</sub>O and NH<sub>3</sub> to give vanadium oxide (V<sub>2</sub>O<sub>5</sub>) and at 210° it forms lower oxides. [*Inorg Synth* 3 117 1950.] After washing Tech grade with H<sub>2</sub>O it had Na, Mn and U at 0.06, 0.2 and 0.1 ppm resp.

**n-Amylmercuric chloride** [544-15-0] M 307.2, m 110°. Crystd from EtOH.

**Anthraquinone Blue B (Acid Blue 45, 1,5-diamino-4,8-dihydroxy-9,10-anthraquinone-3,7-disulfonic acid di-Na salt)** [2861-02-1] M 474.3, m >300°, CI 63010, λ<sub>max</sub> 595nm, pK<sub>Est(1)</sub> ~<0, pK<sub>Est(2)</sub> ~2, pK<sub>Est(3)</sub> ~9. Purified by salting out three times with sodium acetate, followed by repeated extraction with EtOH [McGrew and Schneider *J Am Chem Soc* 72 2547 1950].

**Anthraquinone Blue RXO** [4403-89-8] M 445.5. Purified by salting out three times with sodium acetate, followed by repeated extraction with EtOH [McGrew and Schneider *J Am Chem Soc* 72 2547 1950].

**Anthraquinone Green G [Acid Green 25, Alizarin Cyanine Green F, 1,4-bis-(4-methyl-2-sulfophenyl-1-amino)-9,10-anthraquinone di-Na salt]** [4403-90-1] M 624.6, m 235-238°, CI 61570, λ<sub>max</sub> 642nm, pK >0. Purified by salting out three times with sodium acetate, followed by repeated extraction with EtOH [McGrew and Schneider *J Am Chem Soc* 72 2547 1950]. It is a green powder that slightly sol in Me<sub>2</sub>CO, EtOH and pyridine. Sol in conc H<sub>2</sub>SO<sub>4</sub> to give a blue soln which becomes turquoise on dilution. [Allen et al. *J Org Chem* 7 63 1942.]

**9,10-Anthraquinone-2,6-disulfonic acid (disodium salt)** [853-68-9] M 412.3, m >325°, pK<sub>Est</sub> ~<0 (for SO<sub>3</sub>H). Crystd three times from water, in the dark [Moore et al. *J Chem Soc. Faraday Transl* 82 745 1986].

**9,10-Anthraquinone-2-sulfonic acid (Na salt, H<sub>2</sub>O)** [131-08-8] M 328.3, pK<sub>Est</sub> ~<0 (SO<sub>3</sub>H). Crystd from H<sub>2</sub>O or MeOH (charcoal). [Costa and Bookfield *J Chem Soc, Faraday Trans 1* 82 991 1986].

**Antimony (V) pentafluoride** [7783-70-2] M 216.7, m 7.0°, 8.3°, b 141°, 150°, 148-150°, d 2.99, pK<sup>25</sup> 2.55 [for HSb(OH)<sub>6</sub> = Sb(OH)<sub>6</sub><sup>-</sup> + H<sup>+</sup>]. Purified by vacuum distillation preferably in a

quartz apparatus, and stored in quartz or aluminum bottles. It is a *hygroscopic* viscous liquid which reacts *violently* with H<sub>2</sub>O and is hydrolysed by alkalis. It is **POISONOUS** and attacks the skin. [*J Chem Soc* 2200 1950; *Handbook of Preparative Inorganic Chemistry* (Ed. Brauer) Vol I 200 1965.]

**Antimony trichloride** [10025-91-9] M 228.1, m 73°, b 283°, pK<sub>1</sub><sup>25</sup> 1.4, pK<sub>2</sub><sup>25</sup> 11.0 (11.8), pK<sub>3</sub><sup>25</sup> 12.95 (for Sb<sup>3+</sup> aquo). Dried over P<sub>2</sub>O<sub>5</sub> or by mixing with toluene or xylene and distilling (water is carried off with the organic solvent), then distd twice under dry nitrogen at 50mm, degassed and sublimed twice in a vacuum into ampoules. Can be crystd from CS<sub>2</sub>. Deliquescent. Fumes in moist air.

**Antimony trifluoride** [7783-56-4] M 178.8, m 292°. Crystd from MeOH to remove oxide and oxyfluoride, then sublimed under vacuum in an aluminium cup on to a water-cooled copper condenser [*Woolf J Chem Soc* 279 1955].

**Antimony triiodide** [7790-44-5] M 502.5, m 167°. Sublimed under vacuum.

**Antimony trioxide** [1309-64-4] M 291.5, m 656°. Dissolved in minimum volume of dilute HCl, filtered, and six volumes of water were added to ppte a basic antimonous chloride (free from Fe and Sb<sub>2</sub>O<sub>5</sub>). The ppte was redissolved in dilute HCl, and added slowly, with stirring, to a boiling soln (containing a slight excess) of Na<sub>2</sub>CO<sub>3</sub>. The oxide was filtered off, washed with hot water, then boiled and filtered, the process being repeated until the filtrate gave no test for chloride ions. The product was dried in a vacuum desiccator [Schuhmann *J Am Chem Soc* 46 52 1924]. After on cryst(pptn?), the oxide from a Chinese source had: metal (ppm) Al (8), Ag (0.2), As (56), Cr (6), Ge (0.4), Mn (0.2), Na (16), Ni (2.2) Pb (2.4), Sn (0.4) and V (32).

**Aqua regia**. This is prepared by adding slowly concentrated HNO<sub>3</sub> (1 vol) to concentrated hydrochloric acid (3 vols) in a glass container. This mixture is used to dissolve metals, including noble metals and alloys, as well as minerals and refractory substances. It is done by suspending the material and boiling (**EFFICIENT FUME CUPBOARD — EYE PROTECTION**) to dryness and repeating the process until the residue dissolves in H<sub>2</sub>O. If the aqua regia is to be stored for long periods it is advisable to dilute it with one volume of H<sub>2</sub>O which will prevent it from releasing chlorine and other chloro and nitrous compounds which are objectionable. Store cool in a fume cupboard. However, it is good laboratory practice to prepare it freshly and dispose of it down the fume cupboard sink with copious amounts of water.

**Argon** [7440-37-1] M 39.95, b -185.6°. Rendered oxygen-free by passage over reduced copper at 450°, or by bubbling through alkaline pyrogallol and H<sub>2</sub>SO<sub>4</sub>, then dried with CaSO<sub>4</sub>, Mg(ClO<sub>4</sub>)<sub>2</sub>, or Linde 5A molecular sieves. Other purification steps include passage through Ascarite (asbestos impregnated with sodium hydroxide), through finely divided uranium at about 800° and through a -78° cold trap. Alternatively the gas is passed over CuO pellets at 300° to remove hydrogen and hydrocarbons, over Ca chips at 600° to remove oxygen and, finally, over titanium chips at 700° to remove nitrogen. Also purified by freeze-pump-thaw cycles and by passage over sputtered sodium [Arnold and Smith *J Chem Soc, Faraday Trans 2* 77 861 1981].

**o-Arsanilic acid** [2045-00-3] M 216.1, m 153°, pK<sub>1</sub><sup>22</sup> 3.77 (AsO<sub>3</sub>H<sub>2</sub>), pK<sub>2</sub><sup>22</sup> 8.66 (AsO<sub>3</sub>H<sup>-</sup>). Crystd from water or ethanol/ether. **POISONOUS**.

**p-Arsanilic acid** [98-50-0] M 216.1, m 232°, pK<sub>1</sub><sup>22</sup> 4.05 (AsO<sub>3</sub>H<sub>2</sub>), pK<sub>2</sub><sup>22</sup> 8.66 (AsO<sub>3</sub>H<sup>-</sup>). Crystd from water or ethanol/ether. **POISONOUS**.

**Arsenazo I** [3(2-arsonophenylazo)-4,5-dihydroxy-2,7-naphthalenedisulfonic acid di Na salt] [66019-20-3] M 614.3, ε 2.6 x 10<sup>4</sup> at 500nm, pH 8.0; pK<sub>1</sub> 0.6(0.8), pK<sub>2</sub> 3.52, pK<sub>3</sub> 2.97(AsO<sub>3</sub>H<sub>2</sub>), pK<sub>4</sub> 8.20(AsO<sub>3</sub>H<sup>-</sup>), pK<sub>5</sub> 9.98(OH), pK<sub>6</sub> 15.0. A saturated aqueous soln of the free acid was slowly added to an equal volume of conc HCl. The orange ppte was filtered, washed with acetonitrile and dried for 1-2h at 110° [Fritz and Bradford *Anal Chem* 30 1021 1958].

**Arsenazo III** [3,6-bis(2-arsonophenylazo)-4,5-dihydroxy-2,7-naphthalenedisulfonic acid di Na salt] [62337-00-2] M 776.4, pK<sub>1</sub> -2.7, pK<sub>2</sub> -2.7, pK<sub>3</sub> 0.6, pK<sub>4</sub> 0.8, pK<sub>5</sub> 1.6, pK<sub>6</sub> 3.4,



**pK<sub>7</sub> 6.27, pK<sub>8</sub> 9.05, pK<sub>9</sub> 11.98, pK<sub>10</sub> 15.1.** Contaminants include monoazo derivatives, starting materials for synthesis and by-products. Partially purified by pptn of the dye from aqueous alkali by addition of HCl. More thorough purification by taking a 2g sample in 15-25mL of 5% aq NH<sub>3</sub> and filter. Add 10mL HCl (1:1) to the filtrate to ppt the dye. Repeat procedure and dissolve solid dye (0.5g) in 7mL of a 1:1:1 mixture of *n*-propanol:conc NH<sub>3</sub>:water at 50°. After cooling, filter soln and treat the filtrate on a cellulose column using 3:1:1 mixture of *n*-propanol:conc NH<sub>3</sub>:water as eluent. Collect the blue band and evaporate to 10-15mL below 80°, then add 10mL conc HCl to ppt pure Arsenazo III. Wash with EtOH and air-dry [Borak et al. *Talanta* 17 215 1970]. The purity of the dye can be checked by paper chromatography using M HCl as eluent.

**Arsenic** [7440-38-2] **M 74.9, m 816°.** Heated under vacuum at 350° to sublime oxides, then sealed in a Pyrex tube under vacuum and sublimed at 600°, the arsenic condensing in the cooler parts of the tube. Stored under vacuum [Shih and Peretti *J Am Chem Soc* 75 608 1953]. **POISONOUS.**

**Arsenic acid (arsenic pentoxide hydrate, arsenic V oxide hydrate, orthoarsenic acid)** [12044-50-7] **M 229.8 + xH<sub>2</sub>O, pK<sub>1</sub><sup>25</sup> 2.26, pK<sub>2</sub><sup>25</sup> 6.76, pK<sub>3</sub><sup>25</sup> 11.29 (H<sub>3</sub>AsO<sub>4</sub>).** Cryst from conc solns of boiling conc HNO<sub>3</sub> as rhombic crystals. Dried in vac to give hemihydrate (hygroscopic). Heating above 300° yields As<sub>2</sub>O<sub>5</sub>. [Thaler *Z Anorg Allg Chem* 246 19 1941.] **POISONOUS.**

**Arsenic tribromide** [7784-33-0] **M 314.6, m 31.1°, b 89°/11mm, 221°/760mm.** Distd under vacuum. **POISONOUS.**

**Arsenic trichloride (butter of arsenic)** [7784-34-1] **M 181.3, b 25°/11mm, 130.0°.** Refluxed with arsenic for 4h, then fractionally distd. The middle fraction was stored with sodium wire for two days, then again distd [Lewis and Sowerby *J Chem Soc* 336 1957]. Fumes in moist air and readily hydrolysed by H<sub>2</sub>O. **POISONOUS.**

**Arsenic triiodide** [7784-45-4] **M 455.6, m 146°, b 400°/atm.** Crystd from acetone, sublimes below 100°. **POISONOUS**

**Arsenic III oxide (arsenic trioxide, arsenious oxide)** [1327-53-3] **M 197.8, three forms: m ~200°(amorphous glass), m 275°(sealed tube, octahedral, common form, sublimes > 125° without fusion but melts under pressure), m ~312°, pK<sub>1</sub><sup>20</sup> 9.27, pK<sub>2</sub><sup>20</sup> 13.54, pK<sub>3</sub><sup>20</sup> 13.99 (for H<sub>3</sub>AsO<sub>3</sub>).** Crystd in octahedral form from H<sub>2</sub>O or from dil HCl (1:2), washed, dried and sublimed (193°/760mm). Analytical reagent grade material is suitable for use as an analytical standard after it has been dried by heating at 105° for 1-2h or has been left in a desiccator for several hours over conc H<sub>2</sub>SO<sub>4</sub>. **POISONOUS (particulary the vapour, handle in a ventilated fume cupboard).**

**Aurothioglucose (gold thioglucose)** [12192-57-3] **M 392.2.** Purified by dissolving in H<sub>2</sub>O (0.05g in 1mL) and ppting by adding EtOH. Yellow cryst with slight mercaptan odour. Decomposes slowly in H<sub>2</sub>O, sol in propylene glycol but insol in EtOH and other common organic solvents. [*FEBS Lett* 98 351 1970.]

**Barium (metal)** [7440-39-3] **M 137.3, m 727°.** Cleaned by washing with diethyl ether to remove adhering paraffin, then filed in an argon-filled glove box, washed first with ethanol containing 2% conc HCl, then with dry ethanol. Dried under vacuum and stored under argon [Addison, Coldrey and Halstead *J Chem Soc* 3868 1962]. Has also been purified by double distn under 10mm argon pressure.

**Barium acetate** [543-80-6] **M 255.4.** Crystd twice from anhydrous acetic acid and dried under vacuum for 24h at 100°.

**Barium bromate** [13967-90-3] **M 265.3.** Crystd from hot water (20mL/g). The monohydrate melts at 260°(dec).

**Barium bromide (2H<sub>2</sub>O)** [7791-28-8] M 333.2, m at 75° loses first H<sub>2</sub>O and at 120° loses the second H<sub>2</sub>O. Crystd from water (1mL/g) by partial evaporation in a desiccator.

**Barium chlorate (H<sub>2</sub>O)** [10294-38-9 (hydrate); 13477-00-4 (anhydr)] M 322.3, m 414°. Crystd from water (1mL/g) between 100° and 0°.

**Barium chloride (2H<sub>2</sub>O)** [10326-27-9] M 244.3, m ~120°(dec, hydrate), 963° (anhyd). Twice crystd from water (2mL/g) and oven dried to constant weight.

**Barium dithionate (2H<sub>2</sub>O)** [13845-17-5] M 333.5, m >150° loses SO<sub>2</sub>, pK<sup>25</sup> 0.49 (for H<sub>2</sub>S<sub>2</sub>O<sub>6</sub>, theory pK<sub>1</sub> -3.4, pK<sub>2</sub> -0.2). Crystd from water.

**Barium ferrocyanide (6H<sub>2</sub>O)** [13821-06-2] M 594.8, m 80°(dec), pK<sub>3</sub><sup>25</sup> 2.57, pK<sub>4</sub><sup>25</sup> 4.35 (for ferrocyanide). Crystd from hot water (100mL/g).

**Barium fluoride** [7787-32-8] M 175.3, m 1353°, 1368°, b 2260°, d 4.83. Washed well with distd H<sub>2</sub>O and dried in vacuum Sol in H<sub>2</sub>O [1.6g (10°), 1.6g (20°) and 1.62g (30°) per L], mineral acids and aq NH<sub>4</sub>Cl. May be stored in glass bottles. [*Handbook of Preparative Inorganic Chemistry* (Ed. Brauer) Vol I 234 1963.]

**Barium formate** [541-43-5] M 277.4, pK<sup>25</sup> 3.74 (for HCO<sub>2</sub>H). Crystd from warm water (4mL/g) by adding EtOH and cooling.

**Barium hydroxide (8H<sub>2</sub>O)** [12230-71-6] M 315.5, m 78°, pK<sub>1</sub><sup>25</sup> 13.13, pK<sub>2</sub><sup>25</sup> 13.36. Crystd from water (1mL/g).

**Barium hypophosphite (H<sub>2</sub>O)** [14871-79-5] M 285.4. Pptd from aq soln (3mL/g) by adding EtOH.

**Barium iodate (H<sub>2</sub>O)** [7787-34-0] M 487.1, m 130°(loses H<sub>2</sub>O), 476°(dec). Crystd from a large volume of hot water by cooling.

**Barium iodide (2H<sub>2</sub>O)** [7787-33-9 (2H<sub>2</sub>O); 13718-50-8 (anhydr)] M 427.2, m 740°(dec). Crystd from water (0.5mL/g) by partial evapn in a desiccator. **POISONOUS.**

**Barium ionophore I** [*N,N,N',N'*-tetracyclohexyloxy-bis-(*o*-phenyleneoxy)diacetamide] [96476-01-6] M 644.9, m 156-158°. Purified by chromatography on a Kieselgel column and eluted with CH<sub>2</sub>Cl<sub>2</sub>-EtOAc (5:1), and recryst from EtOH-Me<sub>2</sub>CO as colourless crystals. It is an electrically neutral ionophore with high selectivity for Ba<sup>2+</sup> ions and with high lipophilicity. [*Chem Ber* 118 1071 1985.]

**Barium manganate (barium permanganate)** [7787-35-1] M 256.3, d 3.77. Wash with conductivity H<sub>2</sub>O by decantation until the supernatant gives a faint test for Ba<sup>2+</sup>. Remove excess H<sub>2</sub>O in vac (IMPORTANT), then heat at 100° and the last traces of H<sub>2</sub>O are removed in a vac desiccator over P<sub>2</sub>O<sub>5</sub>. Store over KOH. It disproportionates in hot H<sub>2</sub>O or dil acid to Ba(MnO<sub>2</sub>)<sub>2</sub> and MnO<sub>2</sub>, and is a mild oxidant. [*J Am Chem Soc* 44 1965 1924; *Inorg Synth* 11 56 1960.]

**Barium nitrate** [10022-31-8] M 261.4, m 593°(dec). Crystd twice from water (4mL/g) and dried overnight at 110°. **POISONOUS.**

**Barium nitrite (H<sub>2</sub>O)** [7787-38-4] M 247.4, m 217°(dec). Crystd from water (1mL/g) by cooling in an ice-salt bath. **POISONOUS.**

**Barium perchlorate** [13465-95-7] M 336.2, m 505°, pK<sup>25</sup> -2.4 to -3.1 (for HClO<sub>4</sub>). Crystd twice from water.

**Barium propionate (H<sub>2</sub>O)** [5908-77-0] M 301.5, pK<sup>24</sup> 4.88 (for propionic acid). Crystd from warm water (50mL/g) by adding EtOH and cooling.

**Barium sulfate** [7722-43-7] M 233.4, m >1580°. Washed five times by decantation with hot distilled water, dialysed against distd water for one week, then freeze-dried and oven dried at 105° for 12h.

**Barium tetrathionate** [82203-66-5] M 361.6. Purified by dissolution in a small volume of water and ppted with EtOH below 5°. After drying the salt was stored in the dark at 0°.

**Barium thiocyanate (2 H<sub>2</sub>O)** [2092-17-3] M 289.6, pK<sup>25</sup> -1.85 (for HSCN). Crystd from water (2.5mL/g) by partial evaporation in a desiccator.

**Barium thiosulfate** [35112-53-9] M 249.5, m 220°(dec), pK<sub>1</sub><sup>25</sup> 0.6, pK<sub>2</sub><sup>25</sup> 1.74 (for H<sub>2</sub>S<sub>2</sub>O<sub>3</sub>). Very slightly soluble in water. Washed repeatedly with chilled water and dried in air at 40°.

**Benzaldehyde-2-sulfonic acid sodium salt** [1008-72-6] M 208.2, m dec on heating. Forms prisms or plates by extracting with boiling EtOH, filtering, evaporate to dryness and recrystallise the Na salt from a small volume of H<sub>2</sub>O. The *N*-phenylhydrazone sodium salt recrystd from H<sub>2</sub>O, m 174.5°. [Gnehm and Schüle *Justus Liebigs Ann Chem* 299 363 1898.]

**Benzenechromium tricarbonyl** [12082-08-5] M 214.1, m 163-166°. Purified by sublimation *in vacuo*.

**Benzeneselenenyl bromide (phenylselenenyl bromide)** [34837-55-3] M 236.0, m 58-62°, 60°, 62°, b 107-108°/15mm, 134°/35mm. Dist in a vac, recryst from pet ether, CHCl<sub>3</sub> (EtOH free), or Et<sub>2</sub>O (cooling mixture) as dark red or orange crystals, sublimes at 25°/0.001mm [Behaghel et al. *Chem Ber* 65 815 1932; Pitteloud and Petrzilka *Helv Chim Acta* 62 1319 1979]. **HIGHLY TOXIC**

**Benzeneselenenyl chloride (benzeneselenenyl chloride, phenylselenenyl chloride)** [5707-04-0] M 191.5, m 59-60°, 64-65°, b 92°/5mm, 120°/20mm. Purified by distn in vac and recrystn (orange needles) from hexane [Foster *J Am Chem Soc* 55 822 1933, Foster et al. *Recl Trav Chim, Pays-Bas* 53 405, 408 1934; Behaghel and Seibert *Chem Ber* 66 714 1933.] **HIGHLY TOXIC.**

**Benzeneseleninic acid** [6996-92-5] M 189.1, m 122-124°, pK<sup>25</sup> 4.70. Add 10% excess of 15M NH<sub>3</sub> to the solid acid and stir until the solid dissolves, filter, decolorise with charcoal (2x, Norite) and acidify by slow addn of 6M HCl, filter solid and wash with H<sub>2</sub>O. Dissolve the acid in the minimum vol of MeOH and this soln is added dropwise to boiling H<sub>2</sub>O until cloudiness appears. At this point add 25% more boiling H<sub>2</sub>O, filter hot (decolorise if necessary) and cool rapidly with scratching to 0°. After 30min the solid is filt'd off and recryst as before but with very slow cooling. The colorless needles are filtered off and dried in a vac desiccator (CaCl<sub>2</sub>) before the melting point is measured [McCullough and Gould *J Am Chem Soc* 71 674 1949].

**Benzeneseleninic anhydride** [17697-12-0] M 360.1, m 124-126°, 164-165°, 170-173°. When the anhydride is recrystd from \*C<sub>6</sub>H<sub>6</sub> it has m 124-126° but when this is heated at 140°/1h in a vac or at 90°/2h it had m 164-165° and gives a solid m 124-126° when recrystd from \*C<sub>6</sub>H<sub>6</sub>. Both depress the melting point of the acid PhSeO<sub>2</sub>H. If the high melting anhydride is dissolved in \*C<sub>6</sub>H<sub>6</sub> and seeded with the high melting anhydride, the high melting anhydride crystallises out. It readily absorbs H<sub>2</sub>O to form the acid (PhSeO<sub>2</sub>H, m 122-124°). Because of this the commercial anhydride could contain up to 30% of the acid. Best purified by converting to the HNO<sub>3</sub> complex (m 112°) and heating this *in vacuo* at 120°/72h to give the anhydride as a white powder m 164-165°. Alternatively heat the anhydride *in vacuo* at 120°/72 h until IR shows no OH band. [Ayvrey et al. *J Chem Soc* 2089 1962; Barton et al. *J Chem Soc, Perkin Trans 1* 567 1977.] **TOXIC** solid.

**Benzeneselenol (phenylselenol, selenophenol)** [645-96-5] M 157.1, b 57-59°/8mm, 71-72°/18mm, 84-86°/25mm, d 1.480, n 1.616. Dissolve in aq N NaOH, acidify with conc HCl and extract with Et<sub>2</sub>O, dry over CaCl<sub>2</sub>, filter, evap on a steam bath and distil from a Claisen flask or through a short

column collecting the middle fraction and seal immediately in a glass vial, otherwise the colourless liquid becomes yellow. The alkali insol materials consist of diphenylselenide (**b** 167°/16mm) and diphenyldiselenide, **m** 63° (from EtOH). **TOXIC**, use rubber gloves. It has a foul odour. [Foster *Org Synth Coll Vol III* 771 1955.]

**Benzeneselenonic acid (benzeneselenoic acid)** [39254-48-3] **M 205.1, m 64°, pK<sup>25</sup> 4.79.** Purified by dissolving in H<sub>2</sub>O and passing through a strong cation exchange resin (H<sup>+</sup> form). Evap under reduced pressure and dry in a high vac to give colourless hygroscopic crystals [Dostal et al. *Z Chem* 6 153 1966 and IR: *Chem Ber* 104 2044 1971].

**Benzenestibonic acid** [535-46-6] **M 248.9, m >250°(dec).** Crystd from acetic acid, or from EtOH-CHCl<sub>3</sub> mixture by addition of water.

**Benzenesulfinic acid Na salt** [873-55-2] **M 164.2, m >300°, pK<sup>25</sup> 2.16 (2.74; for PhSO<sub>2</sub>H).** Dissolve in the minimum vol of O<sub>2</sub> free H<sub>2</sub>O (prepared by bubbling N<sub>2</sub> through for 2 h) and adding O<sub>2</sub> free EtOH (prepared as for H<sub>2</sub>O), set aside at 4° overnight under N<sub>2</sub>, filt'd, washed with abs EtOH, then Et<sub>2</sub>O and dried in a vac. The Na salt is relatively stable to air oxidation, but is best kept under N<sub>2</sub> in the dark. Also recrystd from EtOH and dried at 120° for 4h in a vacuum [Kornblum and Wade *J Org Chem* 52 5301 1987].

**Benzopurpurin 4B {3,3'-[(3,3'-dimethyl[1,1'-biphenyl]-4,4'-diyl)bis(azo)]bis[4-amino-1-naphthalenesulfonic acid di-Na salt, Direct red 2}** [992-59-6] **M 724.7, λ<sub>max</sub> 500nm, CI 23500, pK<0.** Crystd from H<sub>2</sub>O. It is a biological stain that is violet at pH 1.2 and red at pH 4.0 and is used for detecting Al, Mg, Hg, Au and U.

**Benzotriazol-1-yloxytris(dimethylamino)phosphonium hexafluorophosphate (BOP reagent)** [56602-33-6] **M 442.29, m > 130° (dec), 147-149° (dec).** Dissolve in CH<sub>2</sub>Cl<sub>2</sub>, dry (MgSO<sub>4</sub>), filter, conc under vac then add dry Et<sub>2</sub>O and filter off first crop. Add CH<sub>2</sub>Cl<sub>2</sub> to the filtrate and concentrate again to give a second crop. Solid is washed with dry Et<sub>2</sub>O and dried in vac. Also recryst from dry Me<sub>2</sub>CO/Et<sub>2</sub>O and check purity by NMR. Store in the dark. [Castro et al. *Synthesis* 751 1976.]

**Benzylidene-bis-(tricyclohexylphosphine) dichlororuthenium (Grubbs catalyst)** [172222-30-9] **M 823.0.** Repeatedly wash with Me<sub>2</sub>CO and MeOH and dry in vac. Alternatively dissolve in CH<sub>2</sub>Cl<sub>2</sub> concentrate to half vol, filter, add MeOH to ppt it as purple microcrystals. Filter off, wash several times with Me<sub>2</sub>CO and MeOH and dry in a vac for several hours. [Scwab, Grubbs and Ziller *J Am Chem Soc* 118 100 1996; Miller, Blackwell and Grubbs *J Am Chem Soc* 118 9606 1966.]

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**Benzyl Orange [4-(4-benzylaminophenylazo)benzenesulfonic acid potassium salt]** [589-02-6] **M 405.5, pK<sub>Est(1)</sub>~<0, pK<sub>Est(2)</sub>~3.8.** Crystd from H<sub>2</sub>O.

**Benzyltriphenylphosphonium chloride** [1100-88-5] **M 388.9, m 280° (sintering), 287-288°.** Wash with Et<sub>2</sub>O and crystallise from EtOH (six sided plates). *Hygroscopic* and forms crystals with one mol H<sub>2</sub>O. [Justus Liebigs *Ann Chem* 229 320 1885; *Chem Ber* 83 291 1950.]

**Beryllium acetate (basic) [Be<sub>4</sub>O(OAc)<sub>6</sub>]** [1332-52-1] **M 406.3, m 285-286°.** Crystd from chloroform.

**Beryllium potassium fluoride** [7787-50-0] **M 105.1.** Crystd from hot water (25mL/g).

**Beryllium sulfate (4H<sub>2</sub>O)** [7787-56-6] **M 177.1, m ~100°(dec), pK<sub>1</sub><sup>25</sup> 3.2, pK<sub>2</sub><sup>25</sup> ~6.5 (Be<sup>2+</sup>).** Crystd from weak aqueous H<sub>2</sub>SO<sub>4</sub>.

**Bicyclo[2.2.1]hepta-2,5-diene rhodium (I) chloride dimer (norbornadiene rhodium chloride complex dimer)** [12257-42-0] **M 462, m 240°(dec).** Recrystd from hot CHCl<sub>3</sub>-pet ether as fine crystals soluble in CHCl<sub>3</sub> and \*C<sub>6</sub>H<sub>6</sub> but almost insoluble in Et<sub>2</sub>O or pet ether. [*J Chem Soc* 3178 1959.]

**R-(-)-1,1'-Binaphthyl-2,2'-diylhydrogen phosphate** [39648-67-4] M 348.3, m 217°,  $[\alpha]_D^{20}$  -608° (c 1, MeOH), pK<sup>20</sup> 0.74. Recrystallise from EtOH. Reflux for 3h in N NaOH is required to hydrolyse the cyclic phosphate. [*Tetrahedron Lett* 4617 1971 ; *Tetrahedron Lett* 24, 343 1983.]

**S-(+)-1,1'-Binaphthyl-2,2'-diylhydrogen phosphate** [35193-64-7] M 348.3,  $[\alpha]_D^{20}$  +608° (c 1, MeOH), pK<sup>20</sup> 0.74. Recrystallise from EtOH. Reflux for 3h in N NaOH is required to hydrolyse the cyclic phosphate. [*Tetrahedron Lett* 4617 1971 ; *Tetrahedron Lett* 24, 343 1983.]

**2-Biphenyl diphenyl phosphate** [132-29-6] M 302.4, n<sup>25</sup> 1.5925. Vacuum distd, then percolated through an alumina column. Passed through a packed column maintained at 150° to remove residual traces of volatile materials by a counter-current stream of nitrogen at reduced pressure. [Dobry and Keller *J Phys Chem* 61 1448 1957.]

**2,2'-Bipyridinium chlorochromate** [76899-34-8] M 292.6. Washed with cold conc HCl then H<sub>2</sub>O (sintered glass funnel) and dried in vacuum (CaCl<sub>2</sub>) to a free flowing yellow-brown powder. Stored in the dark. [*Synthesis* 691 1980; *Synth Commun* 10 951 1980.] **SUSPECTED CARCINOGEN.**

**2,2'-Biquinolin-4,4'-dicarboxylic acid dipotassium salt** [63451-34-3] M 420.51. Recryst from H<sub>2</sub>O. The Cu salt has  $\lambda_{\max}$  at 562nm. [*Anal Biochem* 56 4409 1973.]

**Bis-(p-tert-butylphenyl)phenyl phosphate** [115-87-7] M 438.5, b 281°/5mm, n<sup>25</sup> 1.5412. Same as for 2-biphenyl diphenyl phosphate (above).

**Bis-(2-chlorophenyl) phenyl phosphate** [597-80-8] M 395, b 254°/4mm, n<sup>25</sup> 1.5767. Same as for 2-biphenyl diphenyl phosphate above.

**Bis-(1,5-cyclooctadiene)nickel (0)** [1295-35-8] M 275.0, m 142° (dec). Available in sealed ampoules under N<sub>2</sub>. All procedures should be carried out in a dry box and in an atmosphere of N<sub>2</sub> or Argon in subdued light because the complex is light and oxygen sensitive and flammable. The solid is washed with dry Et<sub>2</sub>O (under Ar) and separates from toluene as yellow crystals. Filter under Ar gas pressure, place the crystals in a container and dry under a vac of 0.01 mm to remove adhered toluene, flush with Ar and seal under Ar or N<sub>2</sub> in glass ampoules. [Semmelhack *Org Reactions* 19 115 and 178 1972; Wilke et al. *Justus Liebigs Ann Chem* 699 1 1966.] **SUSPECTED CARCINOGEN.**

**Bis(2,9-dimethyl-1,10-phenanthroline) copper(I) perchlorate** [54816-44-5] M 579.6, pK<sup>25</sup> -2.4 to -3.1 (for HClO<sub>4</sub>). Crystd from acetone.

**2,2'-Bis-(diphenylphosphino)-1,1'-binaphthyl (BINAP)** [RS 98327-87-8] M 622.7, m 283-286°, [R-(+)-76189-55-4] m 241-242°, [S-(-)-76189-56-5] m 241-242°,  $[\alpha]_D^{20}$  (+) and (-) 233° (c 0.3 toluene). Dissolve the individual enantiomers in toluene, wash with 30% aq NaOH, three times with H<sub>2</sub>O, dry (Na<sub>2</sub>SO<sub>4</sub>), evap to ~15% of its vol and add an equal vol of degassed MeOH. Collect the solid, wash with MeOH and dry at 80°/0.005mm for 6h. Recryst from 1:1 mixt of toluene-EtOH to optical purity (m 241-242°)[Takaya et al. *Org Synth* 67 20 1989].

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**1,4-Bis-(diphenylphosphino)butane** [7688-25-7] M 426.5, m 135-136°. Recrystd from EtOH [Trippett *J Chem Soc* 4263 1961].

**2R,3R-(+)-2,3-Bis(diphenylphosphino)butane (R,R-CHIRAPHOS)** [74839-84-2], **2S,3S-(-)-2,3-bis(di-phenylphosphino)butane (S,S-CHIRAPHOS)** [64896-28-2] M 426.5, m 108-109°,  $[\alpha]_D^{20}$  (+) and (-) 200° (c 1.5 CHCl<sub>3</sub>). Recrystd from abs EtOH (~6g in 60mL) as colorless plates [Fryzuk and Bosnich *J Am Chem Soc* 99 6262 1977 and 101 3043 1979].

**1,2-Bis-(diphenylphosphino)ethane (DIPHOS)** [1663-45-2] **M 398.4, m 139-140°, 140-142°, 143-144°,  $pK_{Est} \sim 4.5$** . Recrystd from aq EtOH or  $^*C_6H_6$ . The *dimethiodide* recrystd from MeOH has **m 305-307°** and the *dioxide* recrystd from toluene or DMF (needles), or  $^*C_6H_6$  (plates) has **m 252-254° (276-278°)** [Isslieb et al. *Chem Ber* **92** 3175 1959; NMR: Aquiar et al. *J Org Chem* **29** 1660 1964; Bäckvall et al. *J Org Chem* **52** 5430 1987].

**1,1'-Bis-(diphenylphosphino)ferrocene** [12150-46-8] **M 554.4, m 181-183°, 184-194°**. Wash with distilled  $H_2O$  and dry in a vacuum. Dissolve in *ca* 5 parts of hot dioxane and cool to give orange crystals **m 181-183°**. Recrystn from  $^*C_6H_6$ -heptane (1:2) gives product with **m 183-184°**. [*J Organomet Chem* **27** 241 1971.]

**Bis-(2-ethylhexyl) 2-ethylhexyl phosphonate** [25103-23-5] **M 434.6,  $n^{25} 1.4473$** . Purified by stirring an 0.4M soln in  $^*$ benzene with an equal volume of 6M HCl at *ca* 60° for 8h. The  $^*$ benzene layer was then shaken successively with equal volumes of water (twice), aqueous 5%  $Na_2CO_3$  (three times), and water (eight times), followed by evaporation of the  $^*$ benzene and distilled under reduced pressure at room temperature (using a rotating evacuated flask). Stored in dry, dark conditions [Peppard et al. *J Inorg Nucl Chem* **24** 1387 1962]. Vacuum distilled, then percolated through an alumina column before finally passed through a packed column maintained at 150° where residual traces of volatile materials were removed by a counter-current stream of  $N_2$  at reduced pressure [Dobry and Keller *J Phys Chem* **61** 1448 1957].

**Bis-(2-ethylhexyl) phosphoric acid** [298-07-7] **M 322.4**. See di-(2-ethylhexyl) phosphoric acid on p. 418.

**Bis(ethyl)titanium(IV) chloride** [2247-00-9] **M 177.0**. Crystd from boiling toluene.

**Bis(ethyl)zirconium(IV) chloride** [92212-70-9] **M 220.3**. Crystd from boiling toluene.

**2,4-Bis-(methylthio)-1,3,2 $\lambda^5$ ,4 $\lambda^5$ -dithiadiphosphetane-2,4-dithione (Davy's reagent)** [82737-61-9] **M 284.4, m 160°**. Recrystd from  $^*C_6H_6$  in yellow plates or from hot trichlorobenzene. The low **m** observed in the literature (112° with gradual softening at 68-102°) has been attributed to the presence of elemental sulfur in the crystals. [*Tetrahedron* **40** 2663 1984; *J Org Chem* **22** 789 1957.]

**Bismuth** [7440-69-9] **M 209.0, m 271-273°**. Melted in an atmosphere of dry helium and filtered through dry Pyrex wool to remove any bismuth oxide present [Mayer, Yosim and Topol *J Phys Chem* **64** 238 1960].

**Bismuthiol I (2,5-dimercapto-1,3,4-thiadiazole) potassium salt** [4628-94-8] **M 226.4, m 275-276°(dec),  $pK_{Est(1)} \sim 4.1$** . Usually contaminated with disulfide. Purified by crystn from EtOH. Reagent for detection of Bi, Cu, Pb and Sb.

**Bismuth trichloride** [7787-60-2] **M 315.3, m 233.6°,  $pK^{25} 1.58$  ( $Bi_3^+ = BiOH_2^+ + H^+$ )**. Sublimed under high vacuum, or dried under a current of HCl gas, followed by fractional distn, once under HCl and once under argon.

***N,N'*-Bis-(salicylidene)ethylenediamine cobalt (II) [Co(SALEN)<sub>2</sub>, salcomine]** [14167-18-1] **M 325.2**. The powder should have an oxygen capacity of 4.7-4.8% as measured by the increase in wt under  $O_2$  at 100 pounds pressure at *ca* 20°. The  $O_2$  is expelled on heating the material to 65°. Recryst from pyridine,  $CHCl_3$  or  $^*C_6H_6$ , and the solvent may be removed by heating at 120° in a vac. However this heating may mean reduced  $O_2$  capacity. In the dry state it absorbs  $O_2$  turning from maroon colour to black. [Diehl and Hack *Inorg Synth* **3** 196 1950.]

**Bis-(tetrabutylammonium) dichromate** [56660-19-6] **M 700.9, m 139-142°**. Wash with water and dry in a vacuum. Crystallises from hexane (**m 79-80°**). [*Synth Commun* **10** 75 1980.] (Possible CARCINOGEN).

**Bis-[4-(1,1,3,3-tetramethylbutyl)phenyl]phosphate calcium salt (Selectophore)** [40835-97-0] **M 987.3**. The Ca diester salt is washed with H<sub>2</sub>O (x3) and MeOH (x3) alternately and dried in a vacuum oven at 50°. If the Ca salt is contaminated with much Ca salt of the monoester then it (10g) is converted to the free acid by adding 6N HCl (*ca* 10vols) and Et<sub>2</sub>O (> 50vols) to it and stirred vigorously to form the free acids. When no white ppte remained (*ca* 5min), the Et<sub>2</sub>O is separated, washed with H<sub>2</sub>O (2 x > 50 mL) and dried by filtering through a bed of anhydrous Na<sub>2</sub>SO<sub>4</sub> (11 x 5 cm) which is then washed with Et<sub>2</sub>O (2 x > 50 mL). Evapn gives an oil (TLC R<sub>F</sub> 0.81 for diester and 0.50 for monoester). The oil is dissolved in \*benzene (*ca* 25mL) and extracted with ethane-1,2-diol (25mL, 10x). After ten washings, a small sample of the \*benzene layer is washed twice with H<sub>2</sub>O to remove the diol and showed that it is pure bis-[4-(1,1,3,3-tetramethylbutyl)phenyl]phosphoric acid by TLC, i.e. no monophosphate. To form the Ca salt the oil is dissolved in MeOH and to it is added the equivalent amount of CaCl<sub>2</sub> together with aq NaOH to keep the pH >10. The resulting white ppte is collected washed alternately with 3 batches of H<sub>2</sub>O and MeOH and dried in a vacuum oven at 50°. [*J Inorg Nucl Chem* **40** 1483 1978.]

**2,4-Bis-(*p*-tolylthio)-1,3,2λ<sup>5</sup>,4λ<sup>5</sup>-dithiadiphosphetane-2,4-dithione (Heimgartner's reagent)** [114234-09-2] **M 436.6, m 175-176°**. Recrystallise from toluene (light yellow solid), wash with Et<sub>2</sub>O and dry in a vacuum. [*Helv Chim Acta* **70** 1001 1987.]

***N,O*-Bis-(trimethylsilyl)acetamide (BSA)** [10416-59-8] **M 203.4, b 71-73°/35mm, d 0.836, 1.4150**. Fractionate through a spinning band column and collect liquid **b 71-73°/35mm**, and not higher because the main impurity MeCONHSiMe<sub>3</sub> distills at **b 105-107°/35mm**. Used for derivatising alcohols and sugars [Klebe et al. *J Am Chem Soc* **88** 3390 1966, see *Carbohydr Res* **241** 209 1993 and **237** 313 1992]. It is **FLAMMABLE** and **TOXIC**.

**Bis-(trimethylsilyl)acetylene** [14630-40-1] **M 170.4, m 26°, b 134-136°/atm**. Dissolve in pet ether, wash with ice-cold dilute HCl. The pet ether extract is dried (MgSO<sub>4</sub>), evaporated and fractionated at atmospheric pressure. [*J Organomet Chem* **37** 45 1972.]

**Bis-(trimethylsilyl) sulfide (hexamethyldisilathiane)** [3385-94-2] **M 178.5, b 65-67°/16mm, 162.5-163.5°/750mm corr, 164°/760mm, d 0.85, n 1.4598**. Dissolve in pet ether (*b ca* 40°), remove solvent and distilled. Redistilled under atmospheric pressure of dry N<sub>2</sub>. It is collected as a colourless liquid which solidifies to a white solid in Dry-ice. On standing for several days it turns yellow possibly due to liberation of sulfur. Store below 4° under dry N<sub>2</sub>. [*J Chem Soc* 3077 1950.]

**Bis-(triphenylphosphine)nickel(II) chloride** [14264-16-5] **M 654.2, m 225°(dec)**. Wash with glacial AcOH and dry in vac over H<sub>2</sub>SO<sub>4</sub> and KOH until AcOH is removed. [*J Chem Soc* 719 1958.]

**Boric acid (boracic acid)** [10043-35-3] **M 61.8, m 171°, pK<sup>25</sup> 9.23**. Crystd three times from H<sub>2</sub>O (3mL/g) between 100° and 0°, after filtering through sintered glass. Dried to constant weight over metaboric acid in a desiccator. It is steam volatile. After 2 recrystns of ACS grade it had Ag at 0.2 ppm.

**9-Borabicyclo[3.3.1]nonane (9BBN)** [monomer 280-64-8] [dimer 21205-91-4 or 70658-61-6] [1:1 coordination compound with tetrahydrofuran 76422-63-4] **M 122.0 (monomer), 244.0 (dimer), m 141-143° (monomer), 150-152°, 154-155° (dimer), b 195°/12mm**. Available as the solid dimer or in tetrahydrofuran soln. The solid is relatively stable and can be purified by distn in a vacuum (as dimer) and by recrystn from tetrahydrofuran (solubility at room temp is 9.5%, 0.78M), filter solid under N<sub>2</sub> wash with dry pentane and dry *in vacuo* at *ca* 100°. The solid is a dimer (IR 1567cm<sup>-1</sup>), stable in air (for *ca* 2 months), and can be heated for 24h at 200° in an inert atmosphere without loss of hydride activity. It is a dimer in tetrahydrofuran soln also (IR 1567cm<sup>-1</sup>). It is sensitive to H<sub>2</sub>O and air (O<sub>2</sub>) in soln. Concentration in soln can be determined by reaction with MeOH and measuring the vol of H<sub>2</sub> liberated, or it can be oxidised to *cis*-cyclooctane-1,5-diol (**m 73.5-74.5°**). [IR: *J Am Chem Soc* **90** 5280 1968, **96** 7765 1974; *J Org Chem* **41** 1778 1976, **46** 3978 1981.]

**Borane pyridine complex** [110-51-0] **M 92.9, m 8-10°, 10-11°, b 86°/7mm, 100-101°/12mm, d<sub>4</sub><sup>20</sup> 0.785**. Dissolve in Et<sub>2</sub>O and wash with H<sub>2</sub>O in which it is insol. Evap Et<sub>2</sub>O and distil

(gives better than 99.8% purity). Its vap pressure is less than 0.1mm at room temp. [*J Am Chem Soc* **77** 1506 1955.]

**Borane triethylamine complex** [1722-26-5] **M 115.0, b 76°/4mm, 97.0°/12mm,  $d_4^{20}$  0.78.** Distil in a vacuum using a 60cm glass helices packed column. [*J Am Chem Soc* **64** 325 1942, **84** 3407 1962; *Tetrahedron Lett* 4703 1968.]

**Borane trimethylamine complex** [75-22-9] **M 73.0, m 94-94.5°, b 171°/atm.** Sublimed using equipment described in *J Am Chem Soc* **59** 780 1937. Its vapour pressure is 86mm at 100°. Colourless hexagonal crystals varying from needles to short lumps, slightly soluble in H<sub>2</sub>O (1.48% at 30°), EtOH (1%), hexane (0.74%) but very soluble in Et<sub>2</sub>O, \*C<sub>6</sub>H<sub>6</sub> and AcOH. Stable at 125°. [*J Am Chem Soc* **59** 780 1939, **104** 325 1942.]

**Boron trichloride (trichloroborane)** [10294-34-5] **M 117.2, b 0°/476mm.** Purified (from chlorine) by passage through two mercury-filled bubblers, then fractionally distd under vacuum. In a more extensive purification the nitrobenzene addition compound is formed by passage of the gas over nitrobenzene in a vacuum system at 10°. Volatile impurities are removed from the crystalline yellow solid by pumping at -20°, and the BCl<sub>3</sub> is recovered by warming the addition compound at 50°. Passage through a trap at -78° removes entrained nitrobenzene; the BCl<sub>3</sub> finally condensing in a trap at -112° [Brown and Holmes *J Am Chem Soc* **78** 2173 1956]. Also purified by condensing into a trap cooled in acetone/Dry-ice, where it was pumped for 15min to remove volatile impurities. It was then warmed, recondensed and again pumped.

**Boron trifluoride** [7637-07-2] **M 67.8, b -101°/760mm.** The usual impurities - bromine, BF<sub>5</sub>, HF and non-volatile fluorides - are readily separated by distn. Brown and Johannesen [*J Am Chem Soc* **72** 2934 1950] passed BF<sub>3</sub> into benzonitrile at 0° until the latter was satd. Evacuation to 10<sup>-5</sup>mm then removed all traces of SiF<sub>4</sub> and other gaseous impurities. [A small amount of the BF<sub>3</sub>-benzonitrile addition compound sublimed and was collected in a U-tube cooled to -80°]. Pressure was raised to 20mm by admitting dry air, and the flask containing the BF<sub>3</sub> addition compound was warmed with hot water. The BF<sub>3</sub> evolved was passed through a -80° trap (to condense any benzonitrile) into a tube cooled in liquid air. The addition compound with anisole can also be used. For drying, BF<sub>3</sub> can be passed through H<sub>2</sub>SO<sub>4</sub> saturated with boric oxide. Fumes in moist air. [Commercially available as a 1.3M soln in MeOH or PrOH.]

**Boron trifluoride diethyl etherate** [109-63-7] **M 141.9, b 67°/43mm, b 126°/760mm, d 1.154, n 1.340.** Treated with a small quantity of diethyl ether (to remove an excess of this component), and then distd under reduced pressure, from CaH<sub>2</sub>. Fumes in moist air. **TOXIC.**

**Bromine** [7726-95-6] **M 159.8, b 59°, d 3.102, n 1.661.** Refluxed with solid KBr and distd, dried by shaking with an equal volume of conc H<sub>2</sub>SO<sub>4</sub>, then distd. The H<sub>2</sub>SO<sub>4</sub> treatment can be replaced by direct distn from BaO or P<sub>2</sub>O<sub>5</sub>. A more extensive purification [Hildenbrand et al. *J Am Chem Soc* **80** 4129 1958] is to reflux about 1L of bromine for 1h with a mixture of 16g of CrO<sub>3</sub> in 200mL of conc H<sub>2</sub>SO<sub>4</sub> (to remove organic material). The bromine is distd into a clean, dry, glass-stoppered bottle, and chlorine is removed by dissolving ca 25g of freshly fused CsBr in 500mL of the bromine and standing overnight. To remove HBr and water, the bromine was then distd back and forth through a train containing alternate tubes of MgO and P<sub>2</sub>O<sub>5</sub>. **HIGHLY TOXIC.**

**Bromine pentafluoride** [7789-30-2] **M 174.9, m -60.5°, b 41.3°,  $d_4^{25}$  2.466.** Purified *via* its KF complex, as described for chlorine trifluoride. **HIGHLY TOXIC.**

**2-Bromoallyltrimethylsilane** [81790-10-5] **M 193.2, b 64-66°/10mm, 82-85°/58-60mm,  $d_4^{20}$  1.13.** Fractionally distd through an efficient column. It is **flammable**. [*J Am Chem Soc* **104** 3733 6879 1982.]

**2-Bromo-1,3,2-benzodioxaborole** [51901-85-0] **M 198.8, m 47°, 51-53°, b 76°/9mm.** Keep at 20°/15mm for some time and then fractionally distil. [*J Chem Soc* 1529 1959.]



**IR(endo,anti)-3-Bromocamphor-8-sulfonic acid ammonium salt** [55870-50-3] M 328.2, m 284-285°(dec),  $[\alpha]_D^{25} +84.8^\circ$  (c 4, H<sub>2</sub>O). Passage of a hot aqueous soln through an alumina column removed water-soluble coloured impurities which remained on the column when the ammonium salt was eluted with hot water. The salt was crystd from water and dried over CaCl<sub>2</sub> [Craddock and Jones *J Am Chem Soc* 84 1098 1962; Kauffmann *J Prakt Chem* 33 295 1966].

**Bromopyrogallol Red** [16574-43-9] M 576.2,  $\epsilon$  5.45 x 10<sup>4</sup> at 538nm (water pH 5.6-7.5). See Bromopyrogallol Red (5,5'-dibromopyrogallolsulfonephthalein) on p. 141 in Chapter 4.

**Bromosulfalein (phenoltetrabromophthalein 3',3'-disulfonic acid disodium salt)** [71-67-0] M 838.0. Purified by TLC on silica Gel G (Merck 250 $\mu$  particle size) in two solvent systems (BuOH-AcOH-H<sub>2</sub>O 30:7.5:12.5 v/v; and BuOH-propionic acid-H<sub>2</sub>O 30:20:7.5 v/v). When the solvent reached a height of 10cm the plate was removed, dried in air and developed with NH<sub>3</sub> vapour giving blue coloured spots. Also the dye was chromatographed on MN Silica Gel with *t*-BuOH-H<sub>2</sub>O-*n*-BuOH (32:10:5 v/v and visualised with a dilute KOH (or NaOH if the Na salt is required) spray. The product corresponding to bromosulfalein was scraped off and eluted with H<sub>2</sub>O, filtered and evap to dryness in a vacuum. It was dissolved in H<sub>2</sub>O and filtered through Sephadex G-25 and evaporated to dryness. [UV and IR identification: *J Pharm Sci* 57 819 1968; NMR: *Chem Pharm Bull Jpn* 20 581 1972; *Anal Biochem* 83 75 1977.]

**Bromtrimethylsilane (trimethylbromosilane, trimethylsilyl bromide)** [2857-97-8] M 153.1, m -43.5° to -43.2°; b 40.5°/200mm, 77.3°/735mm, 79°/744mm, 79.8-79.9°/754mm,  $d_4^{20}$  1.1805,  $d_4^{20}$  1.190,  $n_D^{20}$  1.422. Purified by repeated fractional distillation and stored in sealed ampoules in the dark. [*J Am Chem Soc* 75 1583 1953.] Also fractionally distd through a 15 plate column (0.8 x 32cm packed with 1/16in single turn helices from Pt-Ir wire). [*J Am Chem Soc* 68 1161 1946; 70 433 1948.]

**tert-Butyldiphenylchlorosilane (TBDPSCI, tert-butylchlorodiphenylsilane)** [58479-61-1] M 274.9, b 90°/0.015mm, d 1.057, n 1.568. Purified by repeated fractional distn. It is soluble in DMF and pentane [Hanessian and Lavalee *Can J Chem* 53 2975 1975; Robl et al. *J Med Chem* 34 2804 1991].

**n-Butylmercuric chloride** [543-63-5] M 293.1, m 130°. Crystd from EtOH.

**n-Butylphenyl n-butylphosphonate** [36411-99-1] M 270.3. Crystd three times from hexane as its compound with uranyl nitrate. See *tri-n-butyl phosphate* below.

**tert-Butyldimethylsilyl chloride (TBDMSCl)** [18162-48-6] M 150.7, m 87-89°, 92.5°, b 125°/760mm. Fractionally distd at atmospheric pressure. [*J Am Chem Soc* 76 1030 1954; 94 6190 1972.]

**p-tert-Butylphenyl diphenyl phosphate** [981-40-8] M 382.4, b 261°/6mm,  $n^{25}$  1.5522. Purified by vacuum distn, and percolation through an alumina column, followed by passage through a packed column maintained at 150° to remove residual traces of volatile materials in a counter-current stream of N<sub>2</sub> at reduced pressure [Dobry and Keller *J Phys Chem* 61 1448 1957].

**n-Butylstannic acid [PhSn(OH)<sub>3</sub>, trihydroxy-n-butylstannane]** [22719-01-3] M 208.8. Purified by adding excess KOH in CHCl<sub>3</sub> to remove *n*-BuSn(OH)Cl<sub>2</sub> and *n*-BuSn(OH)<sub>2</sub>Cl, and isolated by acidification [Holmes et al. *J Am Chem Soc* 109 1408 1987].

**Cacodylic acid (dimethylarsinic acid)** [75-60-5] M 138.0, m 195-196°, pK<sup>25</sup> 6.15 [Me<sub>2</sub>As(O)OH]. Crystd from warm EtOH (3mL/g) by cooling and filtering. Dried in vacuum desiccator over CaCl<sub>2</sub>. Has also been twice recrystd from propan-2-ol. [Koller and Hawkrigde *J Am Chem Soc* 107 7412 1985.]