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with metal filings (20 theoretical plates) at atmospheric pressure. [*Izv Akad Nauk SSSR Ser Khim* 1474 1957 and 767 1958.]

Milling Red SWB {1-[4-[4-[4-toluenesulfonyloxy]phenylazo](3,3'-dimethyl-1,1'-biphenyl)-4'-azo]-2-hydroxynaphthalene-6,8-disulfonic acid di-Na salt, Acid Red 114} [6459-94-5] M 830.8, m dec >250°, CI 23635, λ_{\max} ~514nm. Salted out three times with sodium acetate, then repeatedly extracted with EtOH. [McGrew and Schneider *J Am Chem Soc* 72 2547 1950.] See Solochrome Violet R on p. 352 in Chapter 4.

Milling Yellow G [51569-18-7]. Salted out three times with sodium acetate, then repeatedly extracted with EtOH. [McGrew and Schneider *J Am Chem Soc* 72 2547 1950.] See Solochrome Violet R on p. 352 in Chapter 4.

Molybdenum hexacarbonyl [13939-06-5] M 264.0, m 150°(dec), b 156°. Sublimed in a vacuum before use [Connor et al. *J Chem Soc, Dalton Trans* 511 1986].

Molybdenum hexafluoride [7783-77-9] M 209.9, b 35°/760mm. Purified by low-temperature trap-to-trap distillation over predried NaF. [Anderson and Winfield *J Chem Soc, Dalton Trans* 337 1986.]
Poisonous vapours.

Molybdenum trichloride [13478-18-7] M 202.3, m 1027°, d 3.74. Boiled with 12M HCl, washed with absolute EtOH and dried in a vacuum desiccator.

Molybdenum trioxide (molybdenum IV oxide, MoO₃) [1313-27-5] M 143.9, m 795°, d 4.5. Crystd from water (50mL/g) between 70° and 0°.

Monocalcium phosphate (2H₂O) (monobasic) [7789-77-7 (2H₂O); 7757-93-9 (anhydr)] M 154.1, m 200°(dec, loses H₂O at 100°), d 2.2. Crystd from a near-saturated soln in 50% aqueous reagent grade phosphoric acid at 100° by filtering through fritted glass and cooling to room temperature. The crystals were filtered off and this process was repeated three times using fresh acid. For the final crystn the solution was cooled slowly with constant stirring to give thin plate crystals that were filtered off on fritted glass, washed free of acid with anhydrous acetone and dried in a vacuum desiccator [Egan, Wakefield and Elmore, *J Am Chem Soc* 78 1811 1956].

Monoperoxyphthalic acid magnesium salt 6H₂O. (MMPP) [84665-66-7] M 494.7, m ~93°(dec). MMPP is a safer reagent than *m*-chloroperbenzoic acid because it is not as explosive and has advantages of solubility. It is sol in H₂O, low mol wt alcohols, *i*-PrOH and DMF. The product of reaction, Mg phthalate, is sol in H₂O. It has been used in aq phase to oxidise compds in e.g. CHCl₃ and using a phase transfer catalyst e.g. methyltrioctylammonium chloride [Brougham *Synthesis* 1015 1987]. The oxidising activity can be checked (as for perbenzoic acid in Silbert et al. *Org Synth Coll Vol V* 906 1973), and if found to be low it would be best to prepare afresh from phthalic anhydride (1mol), H₂O₂ (1mol) and MgO at 20-25° to give MMPP. [Hignett, European Pat Appl 27 693 1981, *Chem Abstr* 95 168810 1981.]

Naphthalene Scarlet Red 4R [1-(4-sulfonaphthalene-1-azo)-2-hydroxynaphthalene-6,8-disulfonic acid tri-Na salt, New Coccine, Acid Red 18] [2611-82-7] M 604.5, m >250°(dec), CI 16255, λ_{\max} 506nm. Dissolved in the minimum quantity of boiling water, filtered and enough EtOH was added to ppt ca 80% of the dye. This process was repeated until a soln of the dye in aqueous 20% pyridine had a constant extinction coefficient.

Naphthol Yellow S (citronin A, flavianic acid sodium salt, 8-hydroxy-5,7-dinitro-2-naphthalene sulfonic acid disodium salt) [846-70-8] M 358.2, m dec on heating. Greenish yellow powder soluble in H₂O. The *free sulfonic acid* can be recrystd from dil HCl (m 150°) or AcOH-EtOAc (m 148-149.5°). The disodium salt is then obtained by dissolving the acid in two equivalents of aqueous NaOH

and evaporating to dryness and drying the residue in a vacuum desiccator. The sodium salt can be recrystd from the minimum volume of H₂O or from EtOH [Dermer and Dermer *J Am Chem Soc* **61** 3302 1939].

1,2-Naphthoquinone-4-sulfonic acid sodium salt (3,4-dihydro-3,4-dioxo-1-naphthlene sulfonic acid sodium salt) [521-24-4] **M 260.2, pK_{Est} <0**. Yellow crystals from aqueous EtOH and dry at 80° *in vacuo*. Solubility in H₂O is 5% [Org Synth Coll Vol III 633 1955; Danielson *J Biol Chem* **101** 507 1933; UV: Rosenblatt et al. *Anal Chem* **27** 1290 1955].

1-Naphthyl phosphate disodium salt [2183-17-7] **M 268.1, pK₁²⁵ 0.97, pK₂²⁵ 5.85 (for free acid)**. The free acid has **m 157-158°** (from Me₂CO/*C₆H₆). The *free acid* is crystd several times by adding 20 parts of boiling *C₆H₆ to a hot solution of 1 part of *free acid* and 1.2 parts of Me₂CO. It has **m 157-158°**. [*J Am Chem Soc* **77** 4002 1955.] The *monosodium salt* was pptd from a soln of the acid phosphate in MeOH by addition of an equivalent of MeONa in MeOH. [*J Am Chem Soc* **72** 624 1950.] See entry on p.550 in Chapter 6.

2-Naphthyl phosphate monosodium salt [14463-68-4] **M 246.1, m 203-205°, pK₁²⁵ 1.25, pK₂²⁵ 5.83 (for free acid)**. Recrystd from H₂O (10mL) containing NaCl (0.4g). The salt is collected by centrifugation and dried in a vac desiccator, **m 203-205°** (partially resolidifies and melts at 244°). Crystd from MeOH (**m 222-223°**). The free acid is recrystd several times by addn of 2.5 parts of hot CHCl₃ to a hot soln of the free acid (1 part) in Me₂CO (1.3 parts), **m 177-178°**. [*J Am Chem Soc.* **73** 5292 1951, **77** 4002 1955.] See entry on p. 551 in Chapter 6.

Neodymium chloride 6H₂O [13477-89-9] **M 358.7, m 124°, pK₁²⁵ 8.43 (for Nd³⁺ hydrolysis)**. Forms large purple prisms from conc solns of dilute HCl. Soluble in H₂O (2.46 parts in 1 part of H₂O) and EtOH.

Neodymium nitrate (6H₂O) [16454-60-7] **M 438.4, m 70-72°**. Crystallises with 5 and 6 molecules of H₂O from conc solutions in dilute HNO₃ by slow evaporation; 1 part is soluble in 10 parts of H₂O.

Neodymium oxide [1313-97-9] **M 336.5, m 2320°**. Dissolved in HClO₄, pptd as the oxalate with doubly recrystd oxalic acid, washed free of soluble impurities, dried at room temperature and ignited in a platinum crucible at higher than 850° in a stream of oxygen [Tobias and Garrett *J Am Chem Soc* **80** 3532 1958].

Neon [7440-01-9] **M 20.2**. Passed through a copper coil packed with 60/80 mesh 13X molecular sieves which is cooled in liquid N₂, or through a column of Ascarite (NaOH-coated silica adsorbent).

Neopentoxylithium [3710-27-8] **M 94.1**. Recrystd from hexane [Kress and Osborn *J Am Chem Soc* **109** 3953 1987].

New Methylene Blue N (2,8-dimethyl-3,6-bis(ethylamino)phenothiazinium chloride 0.5 ZnCl₂) [6586-05-6] **M 416.1, m >200°(dec), pK₁ 3.54, pK₂ 4.82**. Crystd from *benzene/MeOH (3:1).

Nickel (II) acetate (4H₂O) [6018-89-9] **M 248.9, d 1.744, pK₁²⁵ 8.94 (from Ni²⁺ hydrolysis)**. Recryst from aqueous AcOH as the green tetrahydrate. Soluble in 6 parts of H₂O. It forms lower hydrates and should be kept in a well closed container. [*Z Anorg Allg Chem* **343** 92 1966.]

Nickel (II) acetylacetonate [3264-82-2] **M 256.9, m 229-230°, b 220-235°/11mm, d¹⁷ 1.455**. Wash the green solid with H₂O, dry in a vacuum desiccator and recrystallise from MeOH. [*J Phys Chem* **62** 440 1958.] The complex can be conveniently dehydrated by azeotropic distn with toluene and the crystals may be isolated by concentrating the toluene solution. [*J Am Chem Soc* **76** 1970 1954.]

Nickel bromide [13462-88-9] **M 218.5, m 963°(loses H₂O at ~ 200°)**. Crystd from dilute HBr (0.5mL/g) by partial evaporation in a desiccator.

Nickel chloride (6H₂O) [7791-20-0 (6H₂O); 69098-15-3 (xH₂O); 7718-54-9 (anhydr)] **M 237.7**. Crystd from dilute HCl.

Nickel nitrate (6H₂O) [13478-00-7] **M 290.8, m 57°**. Crystd from water (0.3mL/g) by partial evaporation in a desiccator.

Nickelocene [bis-(cyclopentadienyl)nickel II] [1271-28-9] **M 188.9, m 173-174°(under N₂)**. Dissolve in Et₂O, filter and evaporate in a vacuum. Purify rapidly by recrystn from pet ether using a solid CO₂-Me₂CO bath, **m 171-173°(in an evacuated tube)**. Also purified by vacuum sublimation. [*J Am Chem Soc* **76** 1970 1954; *J Inorg Nucl Chem* **295**, 110 1956.]

Nickel (II) phthalocyanine [14055-02-8] **M 571.3, m >300°**. Wash well with H₂O and boiling EtOH and sublime at high vacuum in a slight stream of CO₂. A special apparatus is used (see reference) with the phthalocyanine being heated to red heat. The sublimate is made of needles with an extremely bright red lustre. The powder is dull greenish blue in colour. [*J Chem Soc* 1719 1936.]

Nickel sulfate (7H₂O) [1010-98-1] **M 280.9, m loses 5H₂O at 100°, anhydr m at ~280°**. Crystd from warm water (0.25mL/g) by cooling.

Nickel 5,10,15,20-tetraphenylporphyrin [14172-92-0] **M 671.4, λ_{max} 414(525)nm**. Purified by chromatography on neutral (Grade I) alumina, followed by recrystn from CH₂Cl₂/MeOH [Yamashita *J Phys Chem* **91** 3055 1987].

Niobium (V) chloride [10026-12-7] **M 270.2, m 204.7-209.5°, b ~250°(begins to sublime at 125°), d 2.75**. Yellow very deliquescent crystals which decompose in moist air to give HCl. Should be kept in a dry box flushed with N₂ in the presence of P₂O₅. Wash with CCl₄ and dry over P₂O₅. The yellow crystals usually contain a few small dirty white pellets among the yellow needles. These should be easily picked out. Upon grinding in a dry box, however, they turn yellow. NbCl₅ has been sublimed and fractionated in an electric furnace. [*Inorg Synth* **7** 163 1963; *J Chem Soc* suppl 233 1949.]

Nitric acid [7697-37-2] **M 63.0, m -42°, b 83°, d₂₅ 1.5027, [Constant boiling acid has composition 68% HNO₃ + 32% H₂O, b 120.5°, d 1.41], pK²⁵ -1.27 (1.19)**. Obtained colourless (approx. 92%) by direct distn of fuming HNO₃ under reduced pressure at 40-50° with an air leak at the head of the fractionating column. Stored in a desiccator kept in a refrigerator. Nitrite-free HNO₃ can be obtained by vac distn from urea.

Nitric oxide [10102-43-9] **M 30.0, b -151.8°**. Bubbling through 10M NaOH removes NO₂. It can also be freed from NO₂ by passage through a column of Ascarite followed by a column of silica gel held at -197°K. The gas is dried with solid NaOH pellets or by passing through silica gel cooled at -78°, followed by fractional distillation from a liquid N₂ trap. This purification does not eliminate nitrous oxide. Other gas scrubbers sometimes used include one containing conc H₂SO₄ and another containing mercury. It is freed from traces of N₂ by a freeze and thaw method. **TOXIC**.

p-Nitrobenzenediazonium fluoroborate [456-27-9] **M 236.9**. Crystd from water. **Can be EXPLOSIVE when dry**.

Nitrogen [7727-37-9] **M 28.0, b -195.8°**. Cylinder N₂ can be freed from oxygen by passage through Fieser's soln [which comprises 2g sodium anthraquinone-2-sulfonate and 15g sodium hydrosulfite dissolved in 100mL of 20% KOH [Fieser, *J Am Chem Soc* **46** 2639 1924] followed by scrubbing with saturated lead acetate soln (to remove any H₂S generated by the Fieser soln), conc H₂SO₄ (to remove moisture), then soda-lime (to remove any H₂SO₄ and CO₂). Alternatively, after passage through Fieser's solution, N₂ can be dried by washing with a soln of the metal ketyl from benzophenone and Na wire in absolute diethyl ether. [If ether vapour in N₂ is undesirable, the ketyl from liquid Na-K alloy under xylene can be used.]

Another method for removing O₂ is to pass the nitrogen through a long tightly packed column of Cu turnings, the surface of which is constantly renewed by scrubbing it with ammonia (sg 0.880) soln. The gas is then

passed through a column packed with glass beads moistened with conc H_2SO_4 (to remove ammonia), through a column of packed KOH pellets (to remove H_2SO_4 and to dry the N_2), and finally through a glass trap packed with chemically clean glass wool immersed in liquid N_2 . Nitrogen has also been purified by passage over Cu wool at 723°K and Cu(II) oxide [prepared by heating $\text{Cu}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ at 903°K for 24h] and then into a cold trap at 77°K .

A typical dry purification method consists of a mercury bubbler (as trap), followed by a small column of silver and gold turnings to remove any mercury vapour, towers containing anhydrous CaSO_4 , dry molecular sieves or $\text{Mg}(\text{ClO}_4)_2$, a tube filled with fine Cu turnings and heated to 400° by an electric furnace, a tower containing soda-lime, and finally a plug of glass wool as filter. Variations include tubes of silica gel, traps containing activated charcoal cooled in a Dry-ice bath, copper on Kieselguhr heated to 250° , and Cu and Fe filings at 400° .

2-Nitrophenol-4-arsonic acid (4-hydroxy-3-nitrophenylarsonic acid) [121-19-7] M 263.0, $\text{pK}_{\text{Est}(1)} \sim 4.4$ $\text{As}(\text{O})-(\text{OH})-(\text{O}^-)$, $\text{pK}_{\text{Est}(2)} \sim 7.4$ (phenolic OH), $\text{pK}_{\text{Est}(3)} \sim 7.7$ ($\text{As}(\text{O})-2(\text{O}^-)$). Crystd from water.

1-Nitroso-2-naphthol-3,6-disulfonic acid, di-Na salt, hydrate (Nitroso-R-salt) [525-05-3] M 377.3, m $>300^\circ$, $\text{pK}_{\text{Est}(1)} < 0$ (SO_3^-), $\text{pK}_{\text{Est}(2)} \sim 7$ (OH). Purified by dissolution in aqueous alkali and precipitation by addition of HCl.

Nitrosyl chloride [2696-92-6] M 65.5, b -5.5° . Fractionally distilled at atmospheric pressure in an all-glass, low temperature still, taking the fraction boiling at -4° and storing it in sealed tubes.

Nitrous oxide [10024-97-2] M 44.0, b -88.5° . Washed with conc alkaline pyrogallol solution, to remove O_2 , CO_2 , and NO_2 , then dried by passage through columns of P_2O_5 or Drierite, and collected in a dry trap cooled in liquid N_2 . Further purified by freeze-pump-thaw and distn cycles under vacuum [Ryan and Freeman *J Phys Chem* 81 1455 1977].

Nuclear Fast Red (1-amino-2,4-dihydroxy-5,10-anthraquinone-3-sulfonic acid Na Salt) [6409-77-4] M 357.3, m $>290^\circ(\text{dec})$, λ_{max} 518nm. A soln of 5g of the dye in 250mL of warm 50% EtOH was cooled to 15° for 36h, then filtered on a Büchner funnel, washed with EtOH until the washings were colourless, then with 100mL of diethyl ether and dried over P_2O_5 . [Kingsley and Robnett *Anal Chem* 33 552 1961.]

Octadecyl isonicotinate see hydrogen ionophore IV, ETH 1778 on p. 430.

Octadecyl trichlorosilane [112-04-9] M 387.9, b $159-162^\circ/13\text{mm}$, $185-199^\circ/2-3\text{mm}$, d_4^{30} 0.98. Purified by fractional distillation. [*J Am Chem Soc* 69 2916 1947.]

Octadecyl trimethylammonium bromide [1120-02-1] M 392.5, m $\sim 250^\circ\text{dec}$, $230-240^\circ(\text{dec})$. Cryst from EtOH or H_2O (sol 1 in 1000parts). Very soluble in Me_2CO . [*J Am Chem Soc* 68 714 1946.]

Octamethyl cyclotetrasiloxane [556-67-2] M 296.6, m $17-19^\circ$, 17.58° , 18.5° , b $74^\circ/20\text{mm}$, $176.4^\circ/760\text{mm}$, $d_4^{29.3}$ 0.9451, n_D^{30} 1.3968. Solid has two forms, m 16.30° and 17.65° . Dry over CaH_2 and distil. Further fractionation can be effected by repeated partial freezing and discarding the liquid phase. [*J Am Chem Soc* 76 399 1954, 75 6313 1954.]

Octamethyl trisiloxane [107-51-7] M 236.5, m -80° , b $151.7^\circ/747\text{mm}$, $153^\circ/760\text{mm}$. Distil twice, the middle fraction from the first distillation is again distilled, and the middle fraction of the second distillation is used. [*J Am Chem Soc* 68 358, 691 1946, *J Chem Soc* 1908 1953.]

Octaphenyl cyclotetrasiloxane [546-56-5] M 793.2, m $201-202^\circ$, $203-204^\circ$, b $330-340^\circ/1\text{mm}$. Recryst from AcOH, EtOAc, $^*\text{C}_6\text{H}_6$ or $^*\text{C}_6\text{H}_6/\text{EtOH}$. It forms two stable polymorphs and both

forms as well as the mixture melt at 200-201°. There is a metastable form which melts at 187-189°. [*J Am Chem Soc* 67 2173 1945, 69 488 1947.]

Octyl trichlorosilane [5283-66-9] M 247.7, b 96.5°/10mm, 112°/15mm. 119°/28mm, 229°/760mm, d 1.0744, n 1.4453. Purified by repeated fractionation using a 15-20 theoretical plates glass column packed with glass helices. This can be done more efficiently using a spinning band column. The purity can be checked by analysing for Cl [ca 0.5-1g of sample is dissolved in 25mL of MeOH, diluted with H₂O and titrated with standard alkali. [*J Am Chem Soc* 68 475 1946, 80 1737 1958.]

Orange I [tropaeolin 000 Nr1, 4-(4-hydroxy-1-naphthylazo)benzenesulfonic acid sodium salt] [523-44-4] M 350.3, m >260°(dec). Purified by dissolving in the minimum volume of H₂O, adding, with stirring, a large excess of EtOH. The salt separates as orange needles. It is collected by centrifugation or filtration, washed with absolute EtOH (3 x) and Et₂O (2x) in the same way and dried in a vacuum desiccator over KOH. The free acid can be recrystallised from EtOH. [*Chem Ber* 64 86 1931.] The purity can be checked by titration with titanium chloride [*J Am Chem Soc* 68 2299 1946].

Orange II [tropaeolin 000 Nr2, 4-(2-hydroxy-1-naphthylazo)benzenesulfonic acid sodium salt] [633-96-5] M 350.3. Purification is as for Orange I. The solubility in H₂O is 40g/L at 25°. [*Helv Chim Acta* 35 2579 1952.] Also purified by extracting with a small volume of water, then crystd by dissolving in boiling water, cooling to ca 80°, adding two volumes of EtOH and cooling. When cold, the ppte is filtered off, washed with a little EtOH and dried in air. It can be salted out from aqueous solution with sodium acetate, then repeatedly extracted with EtOH. Meggy and Sims [*J Chem Soc* 2940 1956], after crystallising the sodium salt twice from water, dissolved it in cold water (11mL/g) and conc HCl added to ppte the dye acid which was separated by centrifugation, redissolved and again ppted with acid. After washing the ppte three times with 0.5M acid it was dried over NaOH, recrystd twice from absolute EtOH, washed with a little Et₂O, dried over NaOH and stored over conc H₂SO₄ in the dark.

Orange G (1-phenylazo-2-naphthol-6,8-disulfonic acid di-Na salt) [1936-15-8] M 452.4, pK_{Est}~ 9. Recryst from 75% EtOH, dry for 3h at 110° and keep in a vacuum desiccator over H₂SO₄. The free acid crystallises from EtOH or conc HCl in deep red needles with a green reflex. [*J Am Chem Soc* 48 2483 1923, *J Chem Soc* 292 1938.]

Orange RO {acid orange 8, 1,8-[bis(4-n-propyl-3-sulfophenyl-1-amino)]anthra-9,10-quinone di-Na salt} [5850-86-2] M 364.4, CI 15575, λ_{max} 490nm. Salted out three times with sodium acetate, then repeatedly extracted with EtOH.

Osmium tetroxide (osmic acid) [20816-12-0] M 524.2, m 40.6°, b 59.4°/60mm, 71.5°/100mm, 109.3°/400mm, 130°/760mm, d 5.10, pK₁^{2.5} 7.2, pK₂^{2.5} 12.2, pK₃^{2.5} 13.95, pK₄^{2.5} 14.17 (H₄OsO₆). It is VERY TOXIC and should be manipulated in a very efficient fume cupboard. It attacks the eyes severely (use also face protection) and is a good oxidising agent. It is volatile and has a high vapour pressure (11mm) at room temp. It sublimes and dists well below its boiling point. It is sol in *C₆H₆, H₂O (7.24% at 25°), CCl₄ (375% at 25°), EtOH and Et₂O. It is estimated by dissolving a sample in a glass stoppered flask containing 25mL of a solution of KI (previously saturated with CO₂) and acidified with 0.35M HCl. After gentle shaking in the dark for 30min, the solution is diluted to 200mL with distilled H₂O satd with CO₂ and titrated with standard thiosulfate using Starch indicator. This method is not as good as the gravimetric method. Hydrazine hydrochloride (0.1 to 0.3g) is dissolved in 3M HCl (10mL) in a glass stoppered bottle. After warming to 55-65°, a weighed sample of OsO₄ solution is introduced, and the mixture is digested on a water bath for 1h. The mixture is transferred to a weighed glazed crucible and evaporated to dryness on a hot plate. A stream of H₂ is started through the crucible and the crucible is heated over a burner for 20-30 min. The stream of H₂ is continued until the crucible is cooled to room temperature, and then the H₂ is displaced by CO₂ in order to avoid rapid combustion of H₂. Finally the crucible is weighed. [*Handbook of Preparative Inorganic Chemistry* (Ed. Brauer) Vol II 1603 1965; *J Am Chem Soc* 60 1822 1938.]

§ Available commercially on a polymer support.

Oxygen [7782-44-7] M 32.00, m -218.4°, b -182.96°, d-183 1.149, d-252.5 1.426. Purified by passage over finely divided platinum at 673°K and Cu(II) oxide (see under nitrogen) at 973°, then condensed in liquid N₂-cooled trap. **HIGHLY EXPLOSIVE in contact with organic matter.**

Palladium (II) acetate [3375-31-3] M 244.5, m 205°dec, pK₁²⁵ 1.0, pK₂²⁵ 1.2 (for Pd₂²⁺). Recrystd from CHCl₃ as purple crystals. It can be washed with AcOH and H₂O and dried in air. Large crystals can be obtained by dissolving in *C₆H₆ and allowing to evaporate slowly at room temp. It forms green adducts with nitrogen donors, dissolved in KI soln but is insoluble in aqueous saturated NaCl, and NaOAc. Soluble in HCl to form PdCl₄²⁻. [*Chem Ind (London)* 544 1964; *J Chem Soc* 658 1970.]

Palladium (II) acetyl acetone [14024-61-4] M 304.6. Recrystd from *C₆H₆-pet ether and sublimed *in vacuo*. It is soluble in heptane, *C₆H₆ (1.2% at 20°, 2.2 at 40°), toluene (0.56% at 20°, 1.4% at 40°) and acetylacetone (1.2% at 20°, 0.05% at 40°). [*J Inorg Nucl Chem* 5 295 1957/8; *Inorg Synth* 5 105 1957.]

Palladium (II) chloride [7647-10-1] M 177.3, m 678-680°. The anhydrous salt is insoluble in H₂O and dissolves in HCl with difficulty. The dihydrate forms red *hygroscopic* crystals that are readily reduced to Pd. Dissolve in conc HCl through which dry Cl₂ was bubbled. Filter this solution which contains H₂PdCl₄ and H₂PdCl₆ and on evaporation yields a residue of pure PdCl₂. [*Handbook of Preparative Inorganic Chemistry (Ed Brauer)* Vol 2 1582 1965; *Org Synth Coll Vol III* 685 1955.]

Palladium (II) cyanide [2035-66-7] M 158.1. A yellow solid, wash well with H₂O and dry in air. [*Inorg Chem* 2 245 1946]. **POISONOUS.**

Palladium (II) trifluoroacetate [42196-31-6] M 332.4, m 210°(dec). Suspend in trifluoroacetic acid and evaporate on a steam bath a couple of times. The residue is then dried in vacuum (40-80°) to a brown powder. [*J Chem Soc* 3632 1965; *J Am Chem Soc* 102 3572 1980.]

Pentafluorophenyl dimethylchlorosilane (Flophemesyl chloride) [20082-71-7] M 260.7, b 89-90°/10mm, d₄³⁰ 1.403, n_D³⁰ 1.447. If goes turbid on cooling due to separation of some LiCl, then dissolve in Et₂O, filter and fractionate. [*J Chromatogr* 89 225 1974, 132 548 1977.]

Perchloric acid [7601-90-3] M 100.5, d 1.665, pK²⁵ -2.4 to -3.1 (HClO₄). The 72% acid has been purified by double distn from silver oxide under vacuum: this frees the acid from metal contamination. Anhydrous acid can be obtained by adding gradually 400-500mL of oleum (20% fuming H₂SO₄) to 100-120mL of 72% HClO₄ in a reaction flask cooled in an ice-bath. The pressure is reduced to 1mm (or less), with the reaction mixture at 20-25°. The temperature is gradually raised during 2h to 85°, the distillate being collected in a receiver cooled in Dry-ice. For further details of the distillation apparatus [see Smith *J Am Chem Soc* 75 184 1953]. **HIGHLY EXPLOSIVE, a strong protective screen should be used at all times.**

Phenylarsonic acid (benzenearsonic acid) [98-05-5] M 202.2, m 155-158°(dec), pK₁²⁵ 3.65, pK₂²⁵ 8.77. Crystd from H₂O (3mL/g) between 90° and 0°.

Phenylboric acid (benzeneboronic acid) [98-80-6] M 121.9, m ~43°, 215-216° (anhydride), 217-220°, pK₁²⁵ 8.83. It recrystallises from H₂O, but can convert spontaneously to benzeneboronic anhydride or phenylboroxide on standing in dry air. Possible impurity is dibenzeneborinic acid which can be removed by washing with pet ether. Heating in an oven at 110°/760mm 1h converts it to the *anhydride* m 214-216°. Its solubility in H₂O is 1.1% at 0° and 2.5% at 25° and in EtOH it is 10% (w/v). [Gilman and Moore *J Am Chem Soc* 80 3609 1958.] If the acid is required, not the anhydride, the acid (from recrystallisation in H₂O) is dried in a slow stream of air saturated with H₂O. The anhydride is converted to the acid by recrystallisation from H₂O. The acid gradually dehydrates to the anhydride if left in air at room temperature with 30-40% relative humidity. The melting point is usually that of the anhydride because the acid dehydrates before it melts [Washburn et al. *Org Synth Coll Vol IV* 68 1963].

Phenyl dimethyl chlorosilane (DMPCl, chlorodimethylphenylsilane) [768-33-2] M 170.7, b 79°/15mm, 85-87°/32mm, 196°/760mm, d 1.017, n 1.509. Fractionate through a 1.5 x 18 inch column packed with stainless steel helices; or a spinning band column. [*J Am Chem Soc* 74 386 1952; 70 1115 1948; *J Chem Soc* 494 1953.] Used for standardising MeLi or MeMgBr which form Me₃PhSi, estimated by GC [Mienthal et al. *J Am Chem Soc* 76 6392 1954; House and Respass *J Organomet Chem* 4 95 1965.] **TOXIC** and **MOISTURE SENSITIVE**.

1,2-Phenylenephosphorochloridate (2-chloro-1,3,2-benzodioxaphosphole-2-oxide) [1499-17-8] M 190.5, m 52°, 58-59°, 59-61°, b 80-81°/1-2mm, 118°/10mm, 122°/12mm, 125°/16mm, 155°/33mm. Distil in a vacuum, sets to a colourless solid. It is soluble in pet ether, *benzene and slightly soluble in Et₂O. [*J Chem Soc (C)* 2092 1970; *Justus Liebigs Ann Chem* 454 109 1927.]

Phenylmercuric hydroxide [100-57-2] M 294.7, m 195-203°. Crystd from dilute aqueous NaOH.

Phenylmercuric nitrate [8003-05-2] M 634.4, m 178-188°. Crystd from water.

Phenylphosphinic acid [benzenephosphinic acid, PhPH(O)(OH)] [1779-48-2] M 142.1, m 70°, 71°, 83-85°, 86°, pK₁²⁵ 1.75. Cryst from H₂O (sol 7.7% at 25°). Purified by placing the solid in a flask covered with dry Et₂O, and allowed to stand for 1 day with intermittent shaking. Et₂O was decanted off and the process repeated. After filtration, excess Et₂O was removed in vacuum. [*Justus Liebigs Ann Chem* 181 265 1876; *Anal Chem* 29 109 1957; NMR: *J Am Chem Soc* 78 5715 1956.]

Phenylphosphonic acid [1571-33-1] M 158.1, m 164.5-166°, pK₂²⁵ 7.43 (7.07). Best recryst from H₂O by concentrating an aqueous soln to a small volume and allowing to crystallise. Wash the crystals with ice cold H₂O and dry in a vacuum desiccator over H₂SO₄. [*J Am Chem Soc* 78 1045 1954.] pK²⁵ values in H₂O are 7.07, and in 50% EtOH 8.26. [*J Am Chem Soc* 75 2209 1953.] [IR: *Anal Chem* 23 853 1951.]

Phenylphosphonic dichloride (P,P-dichlorophenyl phosphine oxide) [824-72-6] M 195.0, b 83-84°/1mm, 135-136°/23mm, d₄³⁰ 1.977, n_D³⁰ 1.5578. Fractionally distilled using a spinning band column. [*J Am Chem Soc* 76 1045 1954; NMR: *J Am Chem Soc* 78 3557, 5715 1956; IR: *Anal Chem* 23 853 1951.]

Phenylphosphonous acid [PhP(OH)₂] [121-70-0] M 141.1, m 71°, pK_{Est} <0, pK¹⁷ 2.1. Crystd from hot H₂O.

Phenylphosphonous dichloride (P,P-dichloro phenyl phosphine) [644-97-3] M 179.0, b 68-70°/1mm, 224-226°/atm, d₄³⁰ 1.9317, n_D³⁵ 1.5962. Vacuum distilled by fractionating through a 20cm column packed with glass helices (better use a spinning band column) [*J Am Chem Soc* 73 755 1951; NMR: *J Am Chem Soc* 78 3557 1956; IR: *Anal Chem* 23 853 1951]. It forms a yellow Ni complex: Ni(C₆H₅Cl₂P)₄ (m 91-92°, from H₂O) [*J Am Chem Soc* 79 3681 1957] and a yellow complex with molybdenum carbonyl: Mo(CO)₃.(C₆H₅Cl₂P)₃ (m 106-110°dec) [*J Chem Soc* 2323 1959].

Phenyl phosphoro chloridate (diphenyl phosphoryl chloride) [2524-64-3] M 268.6, b 141°/1mm, 194°/13mm, 314-316°/272mm, d₄³⁰ 1.2960, n_D³⁵ 1.5490. Fractionally distd in a good vac, better use a spinning band column. [*J Am Chem Soc* 81 3023 1959; IR: *J Chem Soc* 475, 481 1952.]

Phenyl phosphoryl dichloride [770-12-7] M 211.0, m -1°, b 103-104°/2mm, 110-111°/10mm, 130-134°/21mm, 241-243°/atm, d₄³⁰ 1.4160, n_D³⁰ 1.5216. Fractionally distilled under as good a vacuum as possible using an efficient fractionating column or a spinning band column. It should be redistilled if the IR is not very good [IR: *J Chem Soc* 475, 481 1952; *J Am Chem Soc* 60 750 1938, 80 727 1958]. **HARMFUL VAPOURS**.

Phenylthio trimethylsilane (trimethyl phenylthio silane) [4551-15-9] M 182.4, b 95-99°/12mm, d₄³⁰ 0.97. Purification is as for phenyl trimethyl silylmethyl sulfide on p. 450.

Phenyl trimethoxysilane (trimethoxysilyl benzene) [2996-92-1] **M 198.3, b 103°/20mm, 130.5-131°/45mm, d_4^{35} 1.022, n_D^{35} 1.4698.** Fractionate through an efficient column but note that it forms an azeotrope with MeOH which is a likely impurity. [*J Am Chem Soc* **75** 2712 1953; *J Gen Chem USSR (Engl Transl)* **25** 1079 1955.]

Phenyl trimethylsilane (trimethylphenylsilane) [768-32-1] **M 150.3, b 67.3°/20mm, 98-99°/80mm, 170.6°/738mm, d_4^{25} 0.8646.** See trimethylphenylsilane on p. 489.

Phenyl trimethylsilylmethyl sulfide [(phenylthiomethyl)trimethylsilane] [17873-08-4] **M 196.4, b 48°/0.04mm, 113-115°/12mm, 158.5°/52mm, d_4^{30} 0.9671, n_D^{30} 1.5380.** If the sample is suspect then add H₂O, wash with 10% aqueous NaOH, H₂O again, dry (anhydrous CaCl₂) and fractionally distil through a 2ft column packed with glass helices. [*J Am Chem Soc* **76** 3713 1954.]

Phosgene [75-44-5] **M 98.9, b 8.2°/756mm.** Dried with Linde 4A molecular sieves, degassed and distilled under vacuum. This should be done in a closed system such as a vacuum line. **HIGHLY TOXIC, should not be inhaled. If it is inhaled operator should lie still and made to breath ammonia vapour which reacts with phosgene to give urea.**

Phosphine [7803-51-2] **M 34.0, m -133°, b -87.7°, pK -14, pK_b 28.** Best purified in a gas line (in a vacuum) in an efficient fume cupboard. It is spontaneously flammable, has a strong odour of decayed fish and is **POISONOUS**. The gas is distd through solid KOH towers (two), through a Dry ice-acetone trap (-78°, to remove H₂O, and P₂H₄ which causes spontaneous ignition with O₂), then through two liquid N₂ traps (-196°), followed by distn into a -126° trap (Dry ice-methylcyclohexane slush), allowed to warm in the gas line and then seal in ampoules preferably under N₂. IR: ν 2327 (m), 1121 (m) and 900 (m) cm⁻¹. [Klement in *Handbook of Preparative Inorganic Chemistry (Ed. Brauer)* Vol I, pp. 525-530 1963; Gokhale and Jolly *Inorg Synth* **9** 56 1967.] PH₃ has also been absorbed into a soln of cuprous chloride in hydrochloric acid (when CuCl.PH₃ is formed). PH₃ gas is released when the soln is heated and the gas is purified by passage through KOH pellets and over then P₂O₅. The solubility is 0.26mL/1 mL of H₂O at 20° and a crystalline hydrate is formed on releasing the pressure on an aq soln.

Phosphonitrilic chloride (tetramer) [1832-07-1] **M 463.9.** Purified by zone melting, then crystd from pet ether (b 40-60°) or *n*-hexane. [van der Huizen et al. *J Chem Soc, Dalton Trans* 1317 1986.]

Phosphonitrilic chloride (trimer) (hexachlorocyclotriphosphazine) [940-71-6] **M 347.7, m 112.8°, 113-114°.** Purified by zone melting, by crystallisation from pet.ether, *n*-hexane or *benzene, and by sublimation. [van der Huizen et al. *J Chem Soc, Dalton Trans* 1311 1986; Meirovitch et al. *J Phys Chem* **88** 1522 1984; Alcock et al. *J Am Chem Soc* **106** 5561 1984; Winter and van de Grampel *J Chem Soc, Dalton Trans* 1269 1986.]

Phosphoric acid [7664-38-2] **M 98.0, m 42.3°, pK₁²⁵ 2.15, pK₂²⁵ 7.21, pK₃²⁵ 12.33.** Pyrophosphate can be removed from phosphoric acid by diluting with distilled H₂O and refluxing overnight. By cooling to 11° and seeding with crystals obtained by cooling a few millilitres in a Dry-ice/acetone bath, 85% orthophosphoric acid crystallises as H₃PO₄.H₂O. The crystals are separated using a sintered glass filter. It has pKa²⁵ values of 2.15, 7.20 and 12.37 in H₂O.

Phosphorus (red) [7723-14-0] **M 31.0, m 590°/43atm, ignites at 200°, d 2.34.** Boiled for 15min with distilled H₂O, allowed to settle and washed several times with boiling H₂O. Transferred to a Büchner funnel, washed with hot H₂O until the washings are neutral, then dried at 100° and stored in a desiccator.

Phosphorus (white) [7723-14-0] **M 31.0, m 590, d 1.82.** Purified by melting under dilute H₂SO₄⁻ dichromate (possible **carcinogen**) mixture and allowed to stand for several days in the dark at room temperature. It remains liquid, and the initial milky appearance due to insoluble, oxidisable material gradually disappears. The phosphorus can then be distilled under vacuum in the dark [Holmes *Trans Faraday Soc* **58** 1916

1962]. Other methods include extraction with dry CS₂ followed by evaporation of the solvent, or washing with 6M HNO₃, then H₂O, and drying under vacuum. **POISONOUS.**

Phosphorus oxychloride [10025-87-3] **M 153.3, b 105.5°, n 1.461, d 1.675.** Distilled under reduced pressure to separate from the bulk of the HCl and the phosphoric acid, the middle fraction being distilled into ampoules containing a little purified mercury. These ampoules are sealed and stored in the dark for 4-6 weeks with occasional shaking to facilitate reaction of any free chloride with the mercury. The POCl₃ is then again fractionally distd and stored in sealed ampoules in the dark until used [Herber *J Am Chem Soc* **82** 792 1960]. Lewis and Sowerby [*J Chem Soc* 336 1957] refluxed their distilled POCl₃ with Na wire for 4h, then removed the Na and again distilled. *Use Na only with almost pure POCl₃ to avoid explosions.* **HARMFUL VAPOURS.**

Phosphorus pentabromide [7789-69-7] **M 430.6, m <100°, b 106°(dec).** Dissolved in pure nitrobenzene at 60°, filtering off any insoluble residue on to sintered glass, then crystallised by cooling. Washed with dry Et₂O and removed the ether in a current of dry N₂. (All manipulations should be performed in a dry-box.) [Harris and Payne *J Chem Soc* 3732 1958]. Fumes in moist air because of hydrolysis. **HARMFUL VAPOURS.**

Phosphorus pentachloride [10026-13-8] **M 208.2, m 179-180°(sublimes).** Sublimed at 160-170° in an atmosphere of chlorine. The excess chlorine was then displaced by dry N₂ gas. All subsequent manipulations were performed in a dry-box [Downs and Johnson *J Am Chem Soc* **77** 2098 1955]. Fumes in moist air. **HARMFUL VAPOURS.**

Phosphorus pentasulfide [1314-80-3] **M 444.5, m 277-283°.** Purified by extraction and crystallisation with CS₂, using a Soxhlet extractor. Liberates H₂S in moist air. **HARMFUL VAPOURS.**

Phosphorus pentoxide [1314-56-3] **M 141.9, m 562°, b 605°.** Sublimed at 250° under vacuum into glass ampoules. Fumes in moist air and reacts violently with water. **HARMFUL VAPOURS and attacks skin.**

Phosphorus sesquisulfide P₄S₃ [1314-85-8] **M 220.1, m 172°.** Extracted with CS₂, filtered and evapd to dryness. Placed in H₂O, and steam was passed through for an hour. The H₂O was then removed, the solid was dried, followed by crystallisation from CS₂ [Rogers and Gross *J Am Chem Soc* **74** 5294 1952].

Phosphorus sulfochloride (phosphorus thiochloride) [3982-91-0] **M 169.4, m -35°, b 122-124°, 125°(corr), d₄³⁰ 1.64, n_D³⁰ 1.556.** Possible impurities are PCl₅, H₃PO₄, HCl and AlCl₃. Gently mix with H₂O to avoid a heavy emulsion, the product decolorises immediately and settles to the bottom layer. **HARMFUL VAPOURS.**

Phosphorus tribromide [7789-60-8] **M 270.7, m -41.5°, b 168-170°/725mm, 171-173°/atm, 172.9°/760mm(corr), d₄³⁰ 2.852.** It is decomposed by moisture, should be kept dry and is *corrosive*. Purified by distillation through an efficient fractionating column (see Whitmore and Lux *J Am Chem Soc* **54** 3451) in a slow stream of dry N₂, i.e. under strictly dry conditions. [*Inorg Synth* **2** 147 1946; *Org Synth Col Vol II* 358 1943.] Dissolve in CCl₄, dry over CaCl₂, filter and distil. [*Handbook of Preparative Inorganic Chemistry* (Ed. Brauer) vol I 532 1963.] Store in sealed ampoules under N₂ and kept away from light. **HARMFUL VAPOURS.**

Phosphorus trichloride [7719-12-2] **M 137.3, b 76°, n 1.515, d 1.575.** Heated under reflux to expel dissolved HCl, then distilled. It has been further purified by vacuum fractionation several times through a -45° trap into a receiver at -78°. **HARMFUL VAPOURS.**

Phosphorus triiodide [13455-01-1] **M 411.7, m 61°.** Decomposes in moist air and must be kept in a desiccator over CaCl₂. It is crystallised from sulfur-free CS₂ otherwise the **m** decreases to *ca* 55°. It is best prepared freshly. [*J Am Chem Soc* **49** 307 1927; *Handbook of Preparative Inorganic Chemistry* (Ed. Brauer) vol I 541 1963.] **HARMFUL VAPOURS.**

12-Phosphotungstic acid [12501-23-4] M 2880.2, m -96° . A few drops of conc HNO_3 were added to 100g of phosphotungstic acid dissolved in 75mL of water, in a separating funnel, and the soln was extracted with diethyl ether. The lowest of the three layers, which contained a phosphotungstic acid-ether complex, was separated, washed several times with 2M HCl, then with water and again extracted with ether. Evaporation of the ether, under vacuum with mild heating on a water bath gave crystals which were dried under vacuum and ground [Matijevec and Kerker, *J Am Chem Soc* **81** 1307 1959].

Phthalocyanine [574-93-6] M 514.6. Purified by sublimation (two to three times) in an argon flow at 300-400Pa. Similarly for the Cu(II), Ni(II), Pb(II), VO(II) and Zn(II) phthalocyanine complexes.

Platinum (II) acetylacetonate [15170-57-7] M 393.3, m 249-252 $^{\circ}$. Recrystd from $^*\text{C}_6\text{H}_6$ as yellow crystals and dried in air or in a vacuum desiccator. [*Chem Ber* **34** 2584 1901.]

Platinum (II) chloride [10025-65-7] M 266.0, d 5.87. It is purified by heating at 450 $^{\circ}$ in a stream of Cl_2 for 2h. Some sublimation occurs because the PtCl_2 sublimes completely at 560 $^{\circ}$ as red (almost black) needles. This sublimate can be combined to the bulk chloride and while still at ca 450 $^{\circ}$ it should be transferred to a container and cooled in a desiccator. A probable impurity is PtCl_4 . To test for this add a few drops of H_2O (in which PtCl_4 is soluble) to the salt, filter and add an equal volume of saturated aqueous NH_4Cl to the filtrate. If no ppt is formed within 1 min then the product is pure. If a ppt appears then the whole material should be washed with small volumes of H_2O until the soluble PtCl_4 is removed. The purified PtCl_2 is partly dried by suction and then dried in a vacuum desiccator over P_2O_5 . It is insoluble in H_2O but soluble in HCl to form chloroplatinic acid (H_2PtCl_4) by disproportionation. [*Inorg Synth* **6** 209 1960.]

Polystyrenesulfonic acid sodium salt (-CH₂CH(C₆H₄SO₃Na)-) [25704-18-1]. Purified by repeated pptn of the sodium salt from aqueous soln by MeOH, with subsequent conversion to the free acid by passage through an Amberlite IR-120 ion-exchange resin. [Kotin and Nagasawa *J Am Chem Soc* **83** 1026 1961.] Recrystd from EtOH. Also purified by passage through cation and anion exchange resins in series (Rexyn 101 cation exchange resin and Rexyn 203 anion exchange resin), then titrated with NaOH to pH 7. The sodium form of polystyrenesulfonic acid ppted by addition of 2-propanol. Dried in a vac oven at 80 $^{\circ}$ for 24h, finally increasing to 120 $^{\circ}$ prior to use. [Kowblansky and Ander *J Phys Chem* **80** 297 1976.]

Pontacyl Carmine 2G (Acid Red 1, Amido Naphthol Red G, Azophloxine, 1-acetamido-8-hydroxy-7-phenylazonaphthalene-3,7-disulfonic acid di-Na salt) [3734-67-6] M 510.4, CI 18050, λ_{max} 532nm. Salted out three times with sodium acetate, then repeatedly extracted with EtOH. See Solochrome Violet R on p. 352 in Chapter 4. [McGrew and Schneider *J Am Chem Soc* **72** 2547 1950.]

Pontacyl Light Yellow GX [Acid Yellow 17, 1-(2,5-dichloro-4-sulfophenyl)-3-methyl-4-(4-sulfophenylazo)-5-hydroxypyrazole di-Na Salt] [6359-98-4] M 551.3, CI 18965, λ_{max} 400nm. Purification as for Pontacyl Carmine 2G above.

Potassium (metal) [7440-09-7] M 39.1, m 62.3 $^{\circ}$, d 0.89. Oil was removed from the surface of the metal by immersion in *n*-hexane and pure Et_2O for long periods. The surface oxide was next removed by scraping under ether, and the potassium was melted under vacuum. It was then allowed to flow through metal constrictions into tubes that could be sealed, followed by distillation under vacuum in the absence of mercury vapour (see Sodium). **EXPLOSIVE IN WATER.**

Potassium acetate [127-08-2] M 98.2, m 292 $^{\circ}$, d 1.57, pK^{25} 16 (for aquo K^+). Crystd three times from water-ethanol (1:1) dried to constant weight in a vacuum oven, or crystd from anhydrous acetic acid and pumped dry under vacuum for 30h at 100 $^{\circ}$.

Potassium 4-aminobenzoate [138-84-1] M 175.2. Crystd from EtOH.

Potassium antimonyltartrate (H₂O) [28300-74-5] M 333.9, $[\alpha]_{\text{D}}$ +141 $^{\circ}$ (c 2, H₂O). Crystd from water (3mL/g) between 100 $^{\circ}$ and 0 $^{\circ}$. Dried at 100 $^{\circ}$.

Potassium benzoate [582-25-2] M 160.2. Crystd from water (1mL/g) between 100° and 0°.

Potassium bicarbonate [298-14-6] M 100.1. Crystd from water at 65-70° (1.25mL/g) by filtering, then cooling to 15°. During all operations, CO₂ is passed through the stirred mixture. The crystals, sucked dry at the pump, are washed with distilled water, dried in air and then over H₂SO₄ in an atmosphere of CO₂.

Potassium biiodate [13455-24-8] M 389.9. Crystd three times from hot water (3mL/g), stirred continuously during each cooling. After drying at 100° for several hours, the crystals are suitable for use in volumetric analysis.

Potassium bisulfate [7646-93-7] M 136.2, m 214°. Crystd from H₂O(1mL/g) between 100° and 0°.

Potassium borohydride [13762-51-1] M 53.9, m ~500°(dec). Crystd from liquid ammonia.

Potassium bromate [7758-01-2] M 167.0, m 350°(dec at 370°), d 3.27. Crystd from distilled H₂O(2mL/g) between 100° and 0°. To remove bromide contamination, a 5% soln in distilled H₂O, cooled to 10°, has been bubbled with gaseous chlorine for 2h, then filtered and extracted with reagent grade CCl₄ until colourless and odourless. After evaporating the aqueous phase to about half its volume, it was cooled again slowly to about 10°. The crystalline KBrO₃ was separated, washed with 95% EtOH and vacuum dried [Boyd, Cobble and Wexler *J Am Chem Soc* 74 237 1952]. Another way to remove Br⁻ ions was by stirring several times in MeOH and then dried at 150° [Field and Boyd *J Phys Chem* 89 3767 1985].

Potassium bromide [7758-02-3] M 119.0, m 734°, d 2.75. Crystd from distilled water (1mL/g) between 100° and 0°. Washed with 95% EtOH, followed by Et₂O. Dried in air, then heated at 115° for 1h, pulverised and heated in a vacuum oven at 130° for 4h. Has also been crystd from aqueous 30% EtOH, or EtOH, and dried over P₂O₅ under vacuum before heating in an oven.

Potassium tert-butoxide [865-47-4] M 112.2. It sublimes at 220°/1 Torr. Last traces of *tert*-BuOH are removed by heating at 150-160°/2mm for 1h. It is best prepared fresh; likely impurities are *tert*-BuOH, KOH and K₂CO₃ depending on exposure to air. Its solubility at 25°-26° in hexane, toluene, Et₂O, and THF is 0.27%, 2.27%, 4.34% and 25.0% respectively. [*J Am Chem Soc* 78 5938, 4364 1956.]

Potassium carbonate [584-08-7] M 138.2, m 898°, d 2.3. Crystd from water between 100° and 0°. After 2 recrystns tech grade had B, Li and Fe at 1.0, 0.04 and 0.01 ppm resp.

Potassium chlorate [3811-04-9] M 122.6, m 368°. Crystd from water (1.8mL/g) between 100° and 0°, and the crystals are filtered onto sintered glass.

Potassium chloride [7447-40-7] M 74.6, m 771°, d 1.98. Dissolved in conductivity water, filtered, and saturated with chlorine (generated from conc HCl and KMnO₄). Excess chlorine was boiled off, and the KCl was pptd by HCl (generated by dropping conc HCl into conc H₂SO₄). The ppte was washed with water, dissolved in conductivity water at 90-95°, and crystd by cooling to about -5°. The crystals were drained at the centrifuge, dried in a vacuum desiccator at room temperature, then fused in a platinum dish under N₂, cooled and stored in desiccator. Potassium chloride has also been sublimed in a stream of prepurified N₂ gas and collected by electrostatic discharge [Craig and McIntosh *Can J Chem* 30 448 1952].

Potassium chromate [7789-00-6] M 194.2, m 975°, d 2.72, pK₁²⁵ 0.74, pK₂²⁵ 6.49 (for H₂CrO₄). Crystd from conductivity water (0.6g/mL at 20°), and dried between 135° and 170°.

Potassium cobalticyanide [13963-58-1] M 332.4, m dec on heating, d 1.91. Crystd from water to remove traces of HCN.

Potassium cyanate [590-28-3] M 81.1, d 2.05, pK²⁵ 3.46 (for HCNO). Common impurities include ammonia and bicarbonate ion (from hydrolysis). Purified by preparing a saturated aqueous solution at

50°, neutralising with acetic acid, filtering, adding two volumes of EtOH and keeping for 3-4h in an ice bath. (More EtOH can lead to co-precipitation of KHCO_3 .) Filtered, washed with EtOH and dried rapidly in a vacuum desiccator (P_2O_5). The process is repeated [Vanderzee and Meyers *J Chem Soc* **65** 153 1961].

Potassium cyanide [151-50-8] **M 65.1, m 634°, d 1.52**. A saturated solution in H_2O -ethanol (1:3) at 60° was filtered and cooled to room temperature. Absolute EtOH was added, with stirring, until crystallisation ceased. The solution was again allowed to cool to room temperature (during 2-3h) then the crystals were filtered off, washed with absolute EtOH, and dried, first at 70-80° for 2-3h, then at 105° for 2h [Brown, Adisesh and Taylor *J Phys Chem* **66** 2426 1962]. Also purified by vacuum melting and zone refining. **HIGHLY POISONOUS**.

Potassium dichromate [7778-50-9] **M 294.2, m 398°(dec), d 2.68**. Crystd from water (1mL/g) between 100° and 0° and dried under vacuum at 156°. (Possible **CARCINOGEN**).

Potassium dihydrogen citrate [866-83-1] **M 230.2**. Crystd from water. Dried at 80°, or in a vacuum desiccator over Sicapent.

Potassium dihydrogen phosphate [7778-77-0] **M 136.1**. Dissolved in boiling distilled water (2mL/g), kept on a boiling water-bath for several hours, then filtered through paper pulp to remove any turbidity. Cooled rapidly with constant stirring, and the crystals were separated on to hardened filter paper, using suction, washed twice with ice-cold water, once with 50% EtOH, and dried at 105°. Alternative crystns are from water, then 50% EtOH, and again water, or from conc aqueous solution by addition of EtOH. Freed from traces of Cu by extracting its aqueous solution with diphenylthiocarbazon in CCl_4 , followed by repeated extraction with CCl_4 to remove traces of diphenylthiocarbazon.

Potassium dithionate [13455-20-4] **M 238.3, pK_{Est(1)} -3.4, pK₂^{2.5} 0.49 (for dithionic acid)**. Crystd from water (1.5mL/g) between 100° and 0°.

Potassium ethylxanthate [140-89-6] **M 160.3, m > 215°(dec)**. Crystd from absolute EtOH, ligroin-ethanol or acetone by addition of Et_2O . Washed with ether, then dried in a desiccator.

Potassium ferricyanide [13746-66-2] **M 329.3, pK^{2.5} <1 (for ferricyanide)**. Crystd repeatedly from hot water (1.3mL/g). Dried under vacuum in a desiccator.

Potassium ferrocyanide (3H₂O) [14459-95-1] **M 422.4, pK₃^{2.5} 2.57, pK₄^{2.5} 4.35 (for ferrocyanide)** Crystd repeatedly from distilled water, never heating above 60°. Prepared anhydrous by drying at 110° over P_2O_5 in a vacuum desiccator. To obtain the trihydrate, it is necessary to equilibrate in a desiccator over saturated aqueous soln of sucrose and NaCl. Can also be ppted from a saturated solution at 0° by adding an equal volume of cold 95% EtOH, standing for several hours, then centrifuging and washing with cold 95% EtOH. Finally sucked air dry with a water-pump. The anhydrous salt can be obtained by drying in a platinum boat at 90° in a slow stream of N_2 [Loftfield and Swift *J Am Chem Soc* **60** 3083 1938].

Potassium fluoroborate [14075-53-7] **M 125.9, m 530°**. See potassium tetrafluoroborate on p. 458.

Potassium fluorosilicate [16871-90-2] **M 220.3, d 2.3, pK 1.92 (for H₂SiF₆)**. Crystd several times from conductivity water (100mL/g) between 100° and 0°.

Potassium hexachloroiridate (IV) [16920-56-2] **M 483.1**. Crystd from hot aqueous solution containing a few drops of HNO_3 .

Potassium hexachloroosmate (IV) [16871-60-6] **M 481.1**. Crystd from hot dilute aqueous HCl.

Potassium hexachloroplatinate (IV) [16921-30-5] **M 486.0, m 250°(dec)**. Crystd from water (20mL/g) between 100° and 0°.

Potassium hexacyanochromate (III) (3H₂O) [13601-11-1] M 418.5. Crystd from water.

Potassium hexafluorophosphate [17084-13-8] M 184.1, pK₁^{2.5} ~ 0.5, pK₂⁵ 5.12 (for fluorophosphoric acid H₂PO₃F). Crystd from alkaline aqueous solution, using polyethylene vessels, or from 95% EtOH, and dried in a vacuum desiccator over KOH.

Potassium hexafluorozirconate (K₂ZrF₆) [16923-95-8] M 283.4, d 3.48. Recrystd from hot water (solubility is 0.78% at 2° and 25% at 100°).

Potassium hydrogen fluoride [7789-29-9] M 78.1. Crystd from water.

Potassium hydrogen D-glucarate [18404-47-2] M 248.2, m 188°(dec). Crystd from water.

Potassium hydrogen malate [4675-64-3] M 172.2. A saturated aqueous solution at 60° was decolorised with activated charcoal, and filtered. The filtrate was cooled in water-ice bath and the salt was ppted by addition of EtOH. After being crystallised five times from ethanol-water mixtures, it was dried overnight at 130° in air [Eden and Bates *J Res Nat Bur Stand* 62 161 1959].

Potassium hydrogen oxalate (H₂O) [127-95-7] M 137.1. Crystd from water by dissolving 20g in 100mL water at 60° containing 4g of potassium oxalate, filtering and allowing to cool to 25°. The crystals, after washing three or four times with water, are allowed to dry in air.

Potassium hydrogen phthalate [877-24-7] M 204.2. Crystd first from a dilute aqueous solution of K₂CO₃, then H₂O(3mL/g) between 100° and 0°. Before being used as a standard in volumetric analysis, analytical grade potassium hydrogen phthalate should be dried at 120° for 2h, then allowed to cool in a desiccator.

Potassium hydrogen d-tartrate [868-14-4] M 188.2, [α]₅₄₆²⁰ +37.5° (c 10, M NaOH). Crystd from water (17mL/g) between 100° and 0°. Dried at 110°.

Potassium hydroxide (solution) [1310-58-3] M 56.1, pK²⁵ 16 (for aquo K⁺). Its carbonate content can be reduced by rinsing KOH sticks rapidly with water prior to dissolving them in boiled out distilled water. Alternatively, a slight excess of saturated BaCl₂ or Ba(OH)₂ can be added to the soln which, after shaking well, is left so that the BaCO₃ ppte will separate out. Davies and Nancollas [Nature 165 237 1950] rendered KOH solutions carbonate free by ion exchange using a column of Amberlite IR-100 in the OH⁻ form.

Potassium iodate [7758-05-6] M 214.0, pK²⁵ 0.80 (for HIO₃). Crystd twice from distilled water (3mL/g) between 100° and 0°, dried for 2h at 140° and cooled in a desiccator. Analytical reagent grade material dried in this way is suitable for use as an analytical standard.

Potassium iodide [7681-11-0] M 166.0, pK²⁵ -8.56 (for HI). Crystd from distilled water (0.5mL/g) by filtering the near-boiling soln and cooling. To minimise oxidation to iodine, the crystn can be carried out under N₂ and the salt is dried under vacuum over P₂O₅ at 70-100°. Before drying, the crystals can be washed with EtOH or with acetone followed by pet ether. Has also been recrystallised from water/ethanol. After 2 recrystns ACS/USP grade had Li and Sb at <0.02 and <0.01 ppm resp.

Potassium ionophore I (valinomycin) [2001-95-8] M 111.3, m 186-187°, 190°, [α]_D²⁰ +31.0° (c 1.6, *C₆H₆). See valinomycin on p. 573 in Chapter 6.

Potassium isoamyl xanthate [61792-26-5] M 202.4, pK 1.82 (pK⁰ 2.8 free acid). Crystd twice from acetone-diethyl ether. Dried in a desiccator for two days and stored under refrigeration.

Potassium laurate [10124-65-9] M 338.4. Recrystd three times from EtOH [Neto and Helene *J Phys Chem* 91 1466 1987].

Potassium nickel sulfate (6H₂O) [13842-46-1] **M 437.1**. Crystd from H₂O (1.7mL/g) between 75° and 0°.

Potassium nitrate [7757-79-1] **M 101.1, m 334°**. Crystd from hot H₂O (0.5mL/g) by cooling (*cf* KNO₂ below). Dried for 12h under vacuum at 70°. After 2 recrystns tech grade had < 0.001 ppm of metals.

Potassium nitrite [7758-09-0] **M 85.1, m 350°(dec), pK²⁰ 3.20 (for HNO₂)**. A saturated solution at 0° can be warmed and partially evaporated under vacuum, the crystals so obtained being filtered from the warm solution. (This procedure is designed to reduce the level of nitrate impurity and is based on the effects of temperature on solubility. The solubility of KNO₃ in water is 13g/100mL at 0°, 247g/100mL at 100°; for KNO₂ the corresponding figures are 280g/100mL and 413g/100mL.)

Potassium nitrosodisulfonate (Fremy's Salt) [14293-70-0] **M 268.3**. Yellow needles (dimeric) which dissolve in H₂O to give the violet monomeric free radical. Purified by dissolving (~12g) in 2M KOH (600mL) at 45°, filtering the blue soln and keeping it in a refrigerator overnight. The golden yellow crystals (10g) are filt'd off, washed with MeOH (3x), then Et₂O and stored in a glass container in a vac over KOH. It is stable indefinitely when dry. [Cram and Reeves *J Org Chem* **80** 3094 1958; Schenk *Handbook of Preparative Inorganic Chemistry* (Ed. Brauer) Vol I p. 505 1963.]

Potassium nonafluorobutane sulfonate [29420-49-3] **M 338.2**. Wash with H₂O and dry in vacuum. The K salt when distilled with 100% H₂SO₄ gives the free acid which can be distilled (**b** 105°/22mm, 210-212°/760mm) and then converted to the K salt. [*J Chem Soc* 2640 1957.]

Potassium oleate [143-18-0] **M 320.6**. Crystd from EtOH (1mL/g).

Potassium osmate (VI) dihydrate [19718-36-6] **M 368.4**. **Hygroscopic POISONOUS** crystals which are soluble in H₂O but insol in EtOH and Et₂O. It decomposes slowly in H₂O to form the tetroxide which attacks the eyes. The solid should be kept dry and in this form it is relatively safe. [*Synthesis* 610 1972.]

Potassium oxalate [6487-48-5] **M 184.2, m 160°(dec), d 2.13**. Crystd from hot water.

Potassium perchlorate [7778-74-7] **M 138.6, m 400(dec), d 2.52, pK²⁵ -2.4 to -3.1 (for HClO₄)**. Crystd from boiling water (5mL/g) by cooling. Dried under vacuum at 105°.

Potassium periodate (potassium metaperiodate) [7790-21-8] **M 230.0, m 582°, d 3.62**. Crystd from distilled water.

Potassium permanganate [7722-64-7] **M 158.0, m 240(dec), d 2.7, pK²⁵ -2.25 (for HMnO₄)**. Crystd from hot water (4mL/g at 65°), then dried in a vacuum desiccator over CaSO₄. Phillips and Taylor [*J Chem Soc* 4242 1962] cooled an aqueous solution of KMnO₄, saturated at 60°, to room temperature in the dark, and filtered through a No.4 porosity sintered-glass filter funnel. The solution was allowed to evaporate in air in the dark for 12h, and the supernatant liquid was decanted from the crystals, which were dried as quickly as possible with filter paper.

Potassium peroxydisulfate (potassium persulfate) [7727-21-1] **M 270.3**. Crystd twice from distilled water (10mL/g) and dried at 50° in a vacuum desiccator.

Potassium peroxymonosulfate (Oxone, potassium monopersulfate triple salt; 2KHSO₅·KHSO₄·K₂SO₄), [37222-66-5, triple salt] [70693-62-8] **M 614.8**. This is a stable form of Caro's acid and should contain >4.7% of active oxygen. It can be used in EtOH/H₂O and EtOH/AcOH/H₂O solutions. If active oxygen is too low it is best prepared afresh from 1mole of KHSO₅, 0.5moles of KHSO₄ and 0.5moles of K₂SO₄. [Kennedy and Stock *J Org Chem* **25** 1901 1960; Stephenson US Patent 2,802,722 1957.] A rapid prepn of *Caro's acid* is made by stirring finely powdered potassium persulfate (M 270.3) into ice cold conc H₂SO₄ (7mL) and when homogeneous add ice (40-50g). It is stable for several days if kept cold.

Keep away from organic matter as it is a **STRONG OXIDANT**. A detailed prepn of **Caro's acid** (*hypersulfuric acid*, H_2SO_5 , [7722-86-3]) in crystalline form $m \sim 45^\circ$ from H_2O_2 and chlorosulfonic acid was described by Fehér in *Handbook of Preparative Inorganic Chemistry* (Ed. Brauer) Vol I p. 388 1963.

Potassium perrhenate (KReO_4) [10466-65-6] **M 289.3**, $\text{pK}^{25} -1.25$ (for HReO_4). Crystd from water (7mL/g), then fused in a platinum crucible in air at 750° .

Potassium phenol-4-sulfonate (**4-hydroxybenzene-1-sulfonic acid K salt**) [30145-40-5] **M 212.3**. Crystd several times from distilled water at 90° , after treatment with charcoal, by cooling to *ca* 10° . Dried at $90\text{-}100^\circ$.

Potassium phthalimide (**phthalimide K salt**) [1074-82-4] **M 185.2**, $m >300^\circ$. The solid may contain phthalimide and K_2CO_3 from hydrolysis. If too much hydrolysis has occurred (this can be checked by extraction with cold Me_2CO in which the salt is insoluble, evaporation of the Me_2CO and weighing the residue) it would be better to prepare it afresh. If little hydrolysis had occurred then recryst from a large volume of EtOH, and wash solid with a little Me_2CO and dry in a continuous vacuum to constant weight. [Salzerg and Supriawski *Org Synth Coll Vol I* 119 1941; Raman and IR: Hase *J Mol Struct* **48** 33 1978; Dykman *Chem Ind (London)* 40 1972; IR, NMR: Assef et al. *Bull Soc Chim Fr* II-167 1979.]

Potassium picrate [573-83-1] **M 267.2**. Crystd from water or 95% EtOH, and dried at room temperature in vacuum. It is soluble in 200 parts of cold water and 4 parts of boiling water. **THE DRY SOLID EXPLODES WHEN STRUCK OR HEATED.**

Potassium propionate [327-62-8] **M 112.2**. Crystd from water (30mL/g) or 95% EtOH.

Potassium reineckate [34430-73-4] **M 357.5**. Crystd from KNO_3 soln, then from warm water [Adamson *J Am Chem Soc* **80** 3183 1958].

Potassium (VI) ruthenate [31111-21-4] **M 243.3**. Dissolve in H_2O and evaporate until crystals are formed. The crystals are iridescent green prisms which appear red as thin films. Possible impurity is RuO_4 ; in this case wash with CCl_4 (which dissolves RuO_4). The concn of an aqueous solution of RuO_4^{2-} (orange colour) can be estimated from the absorbance at 385nm (ϵ 1030 $\text{M}^{-1} \text{cm}^{-1}$), or at 460nm (ϵ 1820 $\text{M}^{-1} \text{cm}^{-1}$). [*Can J Chem* **50** 3741 1972; *J Am Chem Soc* **74** 5012 1952; *Handbook of Preparative Inorganic Chemistry* (Ed. Brauer) Vol II 1600 1965].

Potassium selenocyanate [3425-46-5] **M 144.1**. Dissolved in acetone, filtered and ppted by adding Et_2O .

Potassium sodium tartrate ($4\text{H}_2\text{O}$) [6381-59-5 ($4\text{H}_2\text{O}$); 304-59-6 (*R,R*)] **M 282.3**. Crystd from distilled water (1.5mL/g) by cooling to 0° .

Potassium sulfate [7778-80-5] **M 174.3**, m 1069 $^\circ$, d 2.67 Crystd from distilled water (4mL/g at 20° ; 8mL/g at 100°) between 100° and 0° .

Potassium *d*-tartrate (H_2O) [921-53-9 , 6381-59-5] **M 235.3**, m loses H_2O at 150° , d 1.98. Crystd from distilled water (solubility: 0.4mL/g at 100° ; 0.7mL/g at 14°).

Potassium tetrachloroplatinate(II) [10025-99-7] **M 415.1**, m 500 $^\circ$ (dec). Crystd from aqueous 0.75M HCl (20mL/g) between 100° and 0° . Washed with ice-cold water and dried.

Potassium tetracyanopalladate (II) $3\text{H}_2\text{O}$ [10025-98-6] **M 377.4**. All operations should be carried out in an efficient fume cupboard - **Cyanide is very POISONOUS** Dissolve the complex (*ca* 5g) in a solution of KCN (4g) in H_2O (75mL) with warming and stirring and evaporate hot till crystals appear. Cool, filter off the crystals and wash with a few drops of cold H_2O . Further concentration of the mother liquors provides more crystals. The complex is recrystallised from H_2O as the colourless *trihydrate*. It effloresces in

dry air and dehydrates at 100° to the *monohydrate*. The *anhydrous salt* is obtained by heating at 200°, but at higher temperatures it decomposes to $(\text{CN})_2$, Pd and KCN. [*Inorg Synth* 2 245 1946.]

Potassium tetrafluoroborate (potassium borofluoride) [14075-53-7] M 125.9, m 530°, d_4^{30} 2.505, pK^{25} -4.9 (for HBF_4). Cryst from H_2O (sol % (temp): 0.3 (3°), 0.45 (20°), 1.4 (40°), 6.27 (100°), and dry under vacuum. Non-hygroscopic salt. A 10% solution is transparent blue at 100°, green at 90° and yellow at 60°. [*Chem Ber* 65 535 1932; *Handbook of Preparative Inorganic Chemistry* (Ed. Brauer) Vol 1 223 1963.]

Potassium tetraoxalate ($2\text{H}_2\text{O}$) [oxalic acid hemipotassium salt] [6100-20-5 ($2\text{H}_2\text{O}$); 127-96-8 (*anhydr*)] M 254.2. Crystd from water below 50°. Dried below 60° at atmospheric pressure.

Potassium tetraphenylborate [3244-41-5] M 358.3. Ppted from a soln of KCl acidified with dilute HCl, then crystallised twice from acetone, washed thoroughly with water and dried at 110° [Findeis and de Vries *Anal Chem* 28 1899 1956]. It has also been recrystd several times from conductivity water.

Potassium thiocyanate [333-20-0] M 97.2, m 172°, pK^{25} -1.85 (for HSCN). Crystd from H_2O if much chloride ion is present in the salt, otherwise from EtOH or MeOH (optionally by addition of Et_2O). Filtered on a Büchner funnel without paper, and dried in a desiccator at room temperature before being heated for 1h at 150°, with a final 10-20min at 200° to remove the last traces of solvent [Kolthoff and Lingane *J Am Chem Soc* 57 126 1935]. Stored in the dark.

Potassium thiosulfate hydrate [13446-67-8; 10294-66-3 (75% aq soln)] M 190.3, pK_1^{25} 0.6, pK_2^{25} 1.74 (for $\text{H}_2\text{S}_2\text{O}_3$) Crystd from warm water (0.5mL/g) by cooling in an ice-salt mixture.

Potassium thiotosylate [28519-50-8] M 226.4. Recrystallise from absolute EtOH and dry at 130°. In wet EtOH the *monohydrate* can be obtained. [*J Gen Chem USSR (Engl Transl)* 28 1345 1958.]

Potassium trifluoroacetate [2923-16-2] M 152.1, m 140-142°, pK^{25} 0.52 (for $\text{CF}_3\text{CO}_2\text{H}$). To purify dissolve the salt in trifluoroacetic acid with ca 2% of trifluoroacetic anhydride, filter and evaporate carefully to dryness (avoid over heating), and finally dry in a vacuum at 100°. It can be recrystallised from trifluoroacetic acid (solubility in the acid is ca 50.1%). [*J Am Chem Soc* 74 4746 1952, 76 4285 1954; *J Inorg Nucl Chem* 9 166 1959.]

Potassium trimethylsilanolate (trimethylsilanol K salt) [10519-96-7] M 128.3, m 131-135° (cubic form), d^{25} 1.11, 125°dec (orthorhombic form). Recryst from H_2O and dried at 100°/1-2mm. [*J Am Chem Soc* 75 5615 1953; IR: *J Org Chem* 17 1555 1952.]

Potassium tungstate (ortho $2\text{H}_2\text{O}$) [37349-36-3; 7790-60-5] M 362.1, m 921°, d 3.12, pK_1^{25} 2.20, pK_2^{25} 3.70 (for H_2WO_4). Crystd from hot water (0.7mL/g).

Praseodymium acetate [6192-12-7] M 318.1. Recrystd several times from water [Ganapathy *J Am Chem Soc* 109 3159 1986].

Praseodymium trichloride ($6\text{H}_2\text{O}$) [10361-79-2] M 355.4, pK_1^{25} 8.55 (for Pr^{3+} hydrol). Its 1M soln in 6M HCl was passed twice through a Dowex-1 anion-exchange column. The eluate was evaporated in a vac desiccator to about half its vol and allowed to crystallise [Katzin and Gulyas *J Phys Chem* 66 494 1962].

Praseodymium oxide (Pr_6O_{11}) [12037-29-5] M 1021.4. Dissolved in acid, ppted as the oxalate and ignited at 650°.

Propargyl triphenyl phosphonium bromide [2091-46-5] M 381.4, m 179°. Recrystallises from 2-propanol as white plates. Also crystallises from EtOH, m 156-158°. IR has ν 1440, 1110 cm^{-1} (P-C str). [*Justus Liebigs Ann Chem* 682 62 1965; *J Org Chem* 42 200 1977].

Propenyloxy trimethylsilane [1833-53-0] M 130.3, b 93-95°/atm, d 0.786. Purified by fractional distillation using a very efficient column at atmospheric pressure. Usually contains 5% of hexamethyldisiloxalane which boils at 99-101°, but is generally non-reactive and need not be removed. [*J Am Chem Soc* 71 5091 1952.] It has been distilled under N₂ through a 15cm column filled with glass helices. Fraction b 99-104° is further purified by gas chromatography through a Carbowax column (Autoprep A 700) at a column temperature of 87°, retention time is 9.5min. [*J Organometal Chem* 1 476 1963-4.]

1-Propenyltrimethylsilane (cis and trans mixture) [17680-01-2] M 114.3, b 85-88°, n_D²⁰ 1.4121. Dissolve (~ 20g) in THF (200mL), shake with H₂O (2x 300 mL), dry (Na₂SO₄) and fractionate. This is a mixture of *cis* and *trans* isomers which can be separated by gas chromatography on an AgNO₃ column (for prep: see Seyferth and Vaughan *J Organomet Chem* 1 138 1963) at 25° with He as carrier gas at 9psi. The *cis*-isomer has n_D²⁵ 1.4105 and the *trans*-isomer has n_D²⁵ 1.4062. [Seyferth et al. *Pure Appl Chem* 13 159 1966.]

Pyridinium chlorochromate [26299-14-9] M 215.6, m 205°(dec). Dry in a vacuum for 1h. It is not hygroscopic and can be stored for extended periods at room temp without change. If very suspect it can be readily prepared. [*Tetrahedron Lett* 2647 1975; *Synthesis* 245 1982.]

§ Available commercially on a polymer support.

Pyridinium dichromate [20039-37-6] M 376.2, m 145-148°, 152-153°. Dissolve in the minimum volume of H₂O and add 5 volumes of cold Me₂CO and cool to -20°. After 3h the orange crystals are collected, washed with a little cold Me₂CO and dried in a vacuum. It is soluble in dimethylformamide (0.9g/mL at 25°), and in H₂O, and has a characteristic IR with ν 930, 875, 765 and 730cm⁻¹. [*Tetrahedron Lett* 399 1979; *Chem Ind (London)* 1594 1969.] (Possible carcinogen).

§ Available commercially on a polymer support.

3-(2-Pyridyl)-5,6-diphenyl-1,2,4-triazine-*p,p'*-disulfonic acid, monosodium salt (H₂O) [63451-29-6] M 510.5. Purified by recrystn from water or by dissolving in the minimum volume of water, followed by addition of EtOH to ppt the pure salt.

Pyrocatechol Violet (tetraphenolictriphenylmethanesulfonic acid Na salt) [115-41-3] M 386.4, ϵ 1.4 x 10⁴ at 445nm in acetate buffer pH 5.2-5.4, pK_{Est(1)}>0 (SO₃H), pK_{Est(2)}~ 9.4, pK_{Est(3)}~ 13. It was recrystd from glacial acetic acid. Very *hygroscopic*. Indicator standard for metal complex titrations. [Mustafin et al. *Zh Anal Khim* 22 1808 1967.]

Pyrogallol Red (tetraphenolic xanthyliumphenylsulfonate) [32638-88-3] M 418.4, m >300°(dec), ϵ 4.3 x 10⁴ at 542nm, pH 7.9-8.6, pK as above. Recrystd from aqueous alkaline solution (Na₂CO₃ or NaOH) by precipitation on acidification [Suk *Collect Czech Chem Commun* 31 3127 1966].

Pyronin B [di-(3,6-bis(diethylamino)xanthylium chloride) diFeCl₅ complex] [2150-48-3] M 358.9 (Fe free), m 176-178° (diFe complex), CI 45010, λ_{max} 555nm, pK²⁵ 7.7. Crystd from EtOH. Forms Fe stain.

Quinolinium chlorochromate [108703-35-1] M 265.6, m 127-130°. A yellow-brown solid which is stable in air for long periods. If it has deteriorated or been kept for too long, it is best to prepare it freshly. Add freshly distilled quinoline (13mL) to a mixture of chromic acid (CrO₃) (10g) and ~ 5M HCl (11mL of conc HCl and 10mL of H₂O) at 0°. A yellow-brown solid separates, it is filtered off on a sintered glass funnel, dried for 1h in a vacuum, and can be stored for extended periods without serious loss in activity. It is a good oxidant for primary alcohol in CH₂Cl₂. [Singh et al. *Chem Ind (London)* 751 1986; method of Corey and Suggs *Tetrahedron Lett* 2647 1975.]

Reinecke salt

see ammonium reineckate on p. 394.

Resorufin (7-hydroxy-3H-phenoxazine-3-one Na salt) [635-78-9] **M 213.2**, **pK₁³⁰ 6.93**, **pK₂³⁰ 9.26**, **pK₃³⁰ 10.0**. Washed with water and recrystd from EtOH several times.

Rhodium (II) acetate dimer (2H₂O) [15956-28-2] **M 478.0**. Dissolve 5g in boiling MeOH (*ca* 600mL) and filter. Concentrate to 400mL and chill overnight at *ca* 0° to give dark green crystals of the MeOH adduct. Conc'n of the mother liquors gives a further crop of [Rh(OAc)₂]₂·2MeOH. The adduct is then heated at 45° in vacuum for 2h (all MeOH is lost) to leave the emerald green crystals of the acetate. [*J Chem Soc (A)* 3322 1970.] Alternatively dissolve in glacial AcOH and reflux for a few hs to give an emerald green soln. Evaporate most of the AcOH on a steam bath then heat the residue at 120°/1h. Extract the residue with boiling Me₂CO. Filter, concentrate to half its volume and keep at 0°/18h. Collect the crystals, wash with ice cold Me₂CO and dry at 110°. It is soluble in most organic solvents with which it forms adducts including NMe₃ and Me₂S and give solutions with different colours varying from green to orange and red. [UV: *Inorg Synth* 2 960 1963.]

Rhodium (III) chloride [10049-07-7] **M 209.3**, **m >100°(dec)**, **b 717°**. Probable impurities are KCl and HCl. Wash solid well with small volumes of H₂O to remove excess KCl and KOH and dissolve in the minimum volume of conc HCl. Evaporate to dryness on a steam bath to give wine-red coloured RhCl₃·3H₂O. Leave on the steam bath until odour of HCl is lost - do not try to dry further as it begins to decompose above 100° to the oxide and HCl. It is not soluble in H₂O but soluble in alkalis or CN solns and forms double salts with alkali chlorides. [*Inorg Synth* 7 214 1063.]

Rhodizonic acid sodium salt (5,6-dihydroxycyclohex-5-ene-1,2,3,4-tetraone di-Na salt) [523-21-7] **M 214.0**, **pK₁³⁰ 4.1 (4.25)**, **pK₂³⁰ 4.5 (4.72)**. The free acid, obtained by acidifying and extracting with Et₂O, drying (MgSO₄), filtering, evaporating and distilling in vacuum (**b** 155-160°/14mm). The *free acid* solidifies on cooling and the colourless crystals can be recrystd from tetrahydrofuran-pet ether or *C₆H₆. It forms a *dihydrate* **m** 130-140°. The pure di Na salt is formed by dissolving in 2 equivs of NaOH and evaporating in a vacuum. It forms violet crystals which give an orange soln in H₂O that is unstable for extended periods even at 0°, and should be prepared freshly before use. Salts of rhodizonic acid cannot be purified by recrystn without great loss due to conversion to croconate, so that the original material must be prepared pure. It can be washed with NaOAc soln then EtOH to remove excess NaOAc dried under vacuum and stored in the dark. [UV and tautomerism: Schwarzenbach and Suter *Helv Chim Acta* 24 617 1941; Polarography: Preisler and Berger *J Am Chem Soc* 64 67 1942; Souchay and Taibouet *J Chim Phys* 49 C108 1952.]

Rose Bengal [Acid Red 94, 4,5,6,7-tetrachloro-2'.4',5',7'-tetraiodofluorescein di-Na or di-K salt] [*di-Na salt* 632-69-9] **M 1017.7 (di-Na salt)** [*di-K salt* 11121-48-5] **M 1049.8 (di-K salt)**. This biological stain can be purified by chromatography on silica TLC using a 35:65 mix of EtOH/acetone as eluent.

Rubidium bromide [7789-39-1] **M 165.4**, **m 682°**, **b 1340°**, **d 3.35**. A white crystalline powder which crystallises from H₂O (solubility: 50% in cold and 67% in boiling H₂O to give a neutral soln). Also crystd from near-boiling water (0.5mL/g) by cooling to 0°.

Rubidium chlorate [13446-71-4] **M 168.9**, **d 3.19**. Crystd from water (1.6mL/g) by cooling from 100°.

Rubidium chloride [7791-11-9] **M 120.9**, **m 715°**, **d 2.80**. Crystd from water (0.7mL/g) by cooling to 0° from 100°.

Rubidium nitrate [13126-12-0] **M 147.5**, **m 305°**, **d 3.11**. Crystd from hot water (0.25mL/g) by cooling to room temperature.

Rubidium perchlorate [13510-42-4] M 184.9, d 2.80, pK_1^{25} -2.4 to -3.1 (for $HClO_4$). Crystd from hot water (1.6mL/g) by cooling to 0°.

Rubidium sulfate [7488-54-2] M 267.0, m 1050°, d 6.31. Crystd from water (1.2mL/g) between 100° and 0°.

Ruthenium (III) acetylacetonate [14284-93-6] M 398.4, m 240°(dec). Purified by recrystn from *benzene. [*J Am Chem Soc* 74 6146 1952.]

Ruthenium (III) chloride (2H₂O) (β-form) [14898-67-0] M 207.4 + H₂O, m >500°(dec), d 3.11, pK_1^{25} 3.40 (for aquo Rh^{3+} hydrolysis). Dissolve in H₂O, filter and concentrate to crystallise in the absence of air to avoid oxidation. Evaporate the solution in a stream of HCl gas while being heated just below its boiling point until a syrup is formed and finally to dryness at 80-100° and dried in a vacuum over H₂SO₄. When heated at 700° in the presence of Cl₂ the insoluble α-form is obtained [*Handbook of Preparative Inorganic Chemistry* (Ed. Brauer) Vol II 1598 1965; *J Org Chem* 46 3936 1981].

Ruthenium (IV) oxide [12036-10-1] M 133.1, d 6.97. Freed from nitrates by boiling in distilled water and filtering. A more complete purification is based on fusion in a KOH-KNO₃ mix to form the soluble ruthenate and perruthenate salts. The melt is dissolved in water, and filtered, then acetone is added to reduce the ruthenates to the insoluble hydrate oxide which, after making a slurry with paper pulp, is filtered and ignited in air to form the anhydrous oxide [*Campbell, Ortner and Anderson Anal Chem* 33 58 1961].

Ruthenocene [bis-(cyclopentadienyl)ruthenium] [1287-13-4] M 231.2, m 195.5°, 199-210°. Sublime in high vacuum at 120°. Yellow crystals which can be recrystallised from CCl₄ as transparent plates. [*J Am Chem Soc* 74 6146 1952].

Samarium (II) iodide [32248-43-4] M 404.2, m 520°, b 1580. Possible impurity is SmI₃ from which it is made. If present, grind solid to a powder and heat in a stream of pure H₂. The temperature (~ 500-600°) should be below the m (~ 628°) of SmI₃, since the molten compounds react very slowly. [*Wetzel in Handbook of Preparative Inorganic Chemistry* (Ed. Brauer) Vol II pp. 1149, 1150 1965.]

Selenious acid [7783-00-8] M 129.0, m 70°(dec), d 3.0, pK_1^{25} 2.62, pK_2^{25} 8.32 (H₂SeO₃). Crystd from water. On heating it loses water and SeO₂ sublimes.

Selenium [7782-49-2] M 79.0, m 217.4°, d 4.81. Dissolved in small portions in hot conc HNO₃ (2mL/g) filtered and evaporated to dryness to give selenious acid which was then dissolved in conc HCl. Passage of SO₂ into the solution pptd selenium (but not tellurium) which was filtered off and washed with conc HCl. This purification process was repeated. The selenium was then converted twice to the selenocyanate by treating with a 10% excess of 3M aqueous KCN, heating for half an hour on a sand-bath and filtering. Addition of an equal weight of crushed ice to the cold solution, followed by an excess of cold, conc HCl, with stirring (in a well ventilated fume hood because HCN is evolved) pptd selenium powder, which, after washing with water until colourless, and then with MeOH, was heated in an oven at 105°, then by fusion for 2h under vacuum. It was cooled, crushed and stored in a desiccator [*Tideswell and McCullough J Am Chem Soc* 78 3036 1956].

Selenium dioxide [7446-08-4] M 111.0, m 340°. Purified by sublimation, or by solution in HNO₃, pptn of selenium which, after standing for several hours or boiling, is filtered off, then re-oxidised by HNO₃ and cautiously evaporated to dryness below 200°. The dioxide is dissolved in water and again evaporated to dryness.

Selenopyronine [85051-91-8] M 365.8, λ_{max} 571nm (ϵ 81,000). Purified as the hydrochloride from hydrochloric acid [*Fanghanel et al. J Phys Chem* 91 3700 1987].