

2-Butyne-1,4-diol [110-65-6] M 86.1, m 54-57°, 56-58°, b 238°. Crystd from EtOAc.

***n*-Butyraldehyde** [123-72-8] M 72.1, b 74.8°, d 0.810, n 1.37911, n¹⁵ 1.38164. Dried with CaCl₂ or CaSO₄, then fractionally distd under N₂. Lin and Day [*J Am Chem Soc* 74 5133 1952] shook with batches of CaSO₄ for 10min intervals until a 5mL sample, on mixing with 2.5mL of CCl₄ containing 0.5g of aluminium isopropoxide, gave no ppt and caused the soln to boil within 2min. Water can be removed from *n*-butyraldehyde by careful distn as an azeotrope distilling at 68°. The aldehyde has also been purified through its bisulfite compound which, after decomposing with excess NaHCO₃ soln, was steam distd, extracted under N₂ into ether and, after drying, the extract was fractionally distd [Kyte, Jeffery and Vogel *J Chem Soc* 4454 1960].

Butyramide [514-35-5] M 87.1, m 115°, b 230°. Crystd from acetone, *benzene, CCl₄-pet ether, 20% EtOH or water. Dried under vacuum over P₂O₅, CaCl₂ or 99% H₂SO₄.

***n*-Butyric acid** [107-92-6] M 88.1, f -5.3°, b 163.3°, d 0.961, n²⁵ 1.396, pK²⁵ 2.82. Distd, mixed with KMnO₄ (20g/L), and fractionally redistd, discarding the first third [Vogel *J Chem Soc* 1814 1948].

***n*-Butyric anhydride** [106-31-0] M 158.2, b 198°, d 0.968. Dried by shaking with P₂O₅, then distd.

γ -Butyrolactone [96-48-0] M 86.1, b 83.8°/12mm, d 1.124. Dried with anhydrous CaSO₄, then fractionally distd. *Handle in a fume cupboard due to TOXICITY.*

Butyronitrile [109-74-0] M 69.1, b 117.9°, d 0.793, n 1.3846, n³⁰ 1.37954. Treated with conc HCl until the smell of the isonitrile had gone, then dried with K₂CO₃ and fractionally distd [Turner *J Chem Soc* 1681 1956]. Alternatively it was twice heated at 75° and stirred for several hours with a mixture of 7.7g Na₂CO₃ and 11.5g KMnO₄ per L of butyronitrile. The mixture was cooled, then distd. The middle fraction was dried over activated alumina. [Schoeller and Wiemann *J Am Chem Soc* 108 22 1986.]

Butyryl chloride (butanoyl chloride) [141-75-3] M 106.6, f -89°, b 101-102°/atm, d₄²⁰ 1.026, n_D²⁰ 1.412. Check IR to see if there is a significant peak at 3000-3500 cm⁻¹ (br) for OH. If OH is present then reflux with less than one mol equiv of SOCl₂ for 1h and distil directly. The fraction boiling between 85-100° is then refractionated at atm pressure. Keep all apparatus free from moisture and store the product in sealed glass ampoules under N₂. **LACHRYMATORY** - *handle in a good fume hood.* [*Org Synth Coll Vol I* 147 1941.]

Cacotheline (2,3-dihydro-4-nitro-2,3-dioxo-9,10-*secostrychnidin*-10-oic acid) [561-20-6] M 508.4, pK_{Est(1)} ~4.4 (CO₂H), pK_{Est(2)} ~10.2 (N). Yellow crystals from H₂O. It is then dried over H₂SO₄ which gives the *dihydrate*, and in a vacuum over H₂SO₄ at 105° to give the anhydrous compound. The *hydrochloride* separates as the hydrate (on heating in vacuum at 80°) in orange-yellow prisms or plates, m 250°(dec), and forms a *resorcinol complex* which gives brown crystals from EtOH, m 325°, and a *hydroquinone complex* as dark red crystals from EtOH, m 319°. [*Chem Ber* 43 1042 1910, 86 232, UV: 242 1953; complexes: Gatto *Gazz Chim Ital* 85 1441 1955.] Used in the titrimetric estimation of Sn²⁺ ions [Szrvas and Lantos *Talanta* 10 477 1963].

Caffeic (3,4-dihydroxycinnamic) acid [331-39-5] M 180.2, m 195°, 223-225°, pK₁²⁵ 4.62, pK₂²⁵ 9.07 Crystd from water.

Caffeine [58-08-2] M 194.2, m 237°, pK₁⁴⁰ -0.10, pK₂⁵⁵ 1.22. Crystd from water or absolute EtOH.

(+)-Calarene (+ β -gurjunen, 1,3,3,11-tetramethyltricyclo[5.4.0.0^{2,4}]undecan-7-ane, (1aR)-1,1,7c,7ac-tetramethyl-1a,2,3,5,6,7,7a,7b-octahydro-1H-cyclopropa[α]naphthalene, new name 1(10)aristolene) [17334-55-3] M 204.35, b 45-47°/0.008-0.01mm, 255-258°/atm, d₄²⁰ 0.9340, n_D²⁰ 1.55051, [α]_D²⁰ +58° (EtOH), +81.8° (neat). Purified by gas chromatography (7%

propylene glycol adipate on unglazed tile particles of size 0.2-0.3mm, 400 cm column length and 0.6 cm diameter, at 184°, with N₂ carrier gas at a flow rate of 0.54 mL/sec using a thermal detector). Also purified by chromatography on alumina (200 times the weight of calarene) and eluted with pet ether. UV: λ_{\max} 200 and 210 nm (ϵ 9560, 5480) in EtOH. [IR: *Sorm Collect Czech Chem Commun* **18** 512 1953, **29** 795 1964; *Tetrahedron Lett* 827 1962, 225 1963.]

Calcon carboxylic acid [3-hydroxy-4-(2-hydroxy-4-sulfo-1-naphthylazo)naphthalene-2-carboxylic acid] [3737-95-9] M 428.4, m 300°, λ_{\max} 560nm, pK₁ 1.2, pK₂ 3.8, pK₃ 9.26, pK₄ 13.14. Purified through its *p*-toluidinium salt. The dye was dissolved in warm 20% aq MeOH and treated with *p*-toluidine to ppt the salt after cooling. Finally recrystd from hot water. [Itoh and Ueno *Analyst (London)* **95** 583 1970.] Patton and Reeder (*Anal Chem* **28** 1026 1956) indicator and complexes with Ca in presence of Mg and other metal ions.

Calmagite [3147-14-6] M 358.4, m 300°, pK₁ 8.1, pK₂ 12.4. Crude sample was extracted with anhydrous diethyl ether [Lindstrom and Diehl *Anal Chem* **32** 1123 1960]. Complexes with Ca, Mg and Th.

Campesterol (24R-24-methylcholest-5-en-3 β -ol) [474-62-4] M 400.7, m 156-159°, 157-158°, $[\alpha]_D^{24}$ -35.1° (c 1.2, CHCl₃). Recryst twice from hexane and once from Me₂CO. The *benzoyl derivative* has m 158-160° $[\alpha]_D^{23}$ -8.6° (CHCl₃), the *acetyl derivative* has m 137-138° (from EtOH) and $[\alpha]_D^{23}$ -35.1° (c 2.9, CHCl₃) [*J Am Chem Soc* **63** 1155 1941].

1R,4S-(-)-Camphanic acid [13429-83-9] M 198.2, m 190-192°, 198-200°, $[\alpha]_{548}^{20}$ -22.5° (c 1, dioxane), -4.4° (c 8, EtOH), pK_{Est} ~3.8. Dissolve in CH₂Cl₂, dry (MgSO₄), filter, evaporate and residue is sublimed at 120°/0.5mm or 140°/1mm. [*Helv Chim Acta* **61** 2773 1978.]

1R,4S-(-)-Camphanic acid chloride [39637-74-6] M 216.7, m 65-66.5°, 70.5-71°, $[\alpha]_{548}$ -23° (c 2, CCl₄), -7.5° (c 0.67, *benzene). Soluble in toluene (50g/100mL at 0°) and crystals from pet ether (b 40-60°). It sublimes at 70°/5mm. Store dry at 0°, ν (CCl₄) 1805s and 1780m cm⁻¹. [*J Chem Soc, Dalton Trans* 2229 1976.]

RS-Camphene [565-00-4] M 136.2, m 51-52°, b 40-70°/10mm. Crystd twice from EtOH, then repeatedly melted and frozen at 30mm pressure. [Williams and Smyth *J Am Chem Soc* **84** 1808 1962.] Alternatively it is dissolved in Et₂O, dried over CaCl₂ and Na, evaporated and the residue sublimed in a vacuum [NMR: *Chem Ber* **111** 2527 1978].

(-)-Camphene (1S-2,2-dimethyl-3-methylene norbornane) [5794-04-7] M 136.2, m 49.2-49.6°, 49-50°, b 79-80°/58mm, 91.5°/100mm, d_4^{54} 0.8412, n_D^{54} 1.4564, $[\alpha]_D^{25}$ -106.2° (c 40, *C₆H₆), -117.5° (c 19, toluene), -113.5° (c 9.7, Et₂O). Purified by fractionation through a Stedman column (see p. 441) at 100mm in a N₂ atmosphere, crystallised from EtOH and sublimed in a vacuum below its melting point. It is characterised by its *camphenilone semicarbazone*, m 217-218.5°, or *camphor semicarbazone*, m 236-238°. [NMR: *Chem Ber* **111** 2527 1978; *Justus Liebigs Ann Chem* **623** 217 1959; Bain et al. *J Am Chem Soc* **72** 3124 1950]

Camphor (1R-bornan-2-one) [R-(+)- 464-49-3]; S-(-)- 464-48-2] M 136.2, m 178.8°, 179.97°(open capillary), b 204°/atm, $[\alpha]_{546}^{35}$ (+) and (-) 59.6° (in EtOH), $[\alpha]_D^{20}$ (+) and (-) 44.3° (c 10, EtOH), $[\alpha]_{579}^{179}$ (+) and (-) 70.85° (melt). Crystd from EtOH, 50% EtOH/water, MeOH, or pet ether or from glacial acetic acid by addition of water. It can be sublimed (50°/14mm) and also fractionally crystd from its own melt. It is steam volatile. It should be stored in tight containers as it is appreciably volatile at room temperature. The solubility is 0.1% (H₂O), 100% (EtOH), 173% (Et₂O) and 300% (CHCl₃). The *R-oxime* (from Et₂O, CHCl₃, or dil EtOH) m 119° $[\alpha]_D^{20}$ -42.4° (c 3, EtOH); the \pm *oxime* has m 118-119°. [*Chem Ber* **67** 1432 1934; Allan and Rodgers *J Chem Soc (B)* 632 1971; UV, NMR: Fairley et al. *J Chem Soc, Perkin Trans 1* 2109 1973; *J Am Chem Soc* **62** 8 1940.]

Camphoric acid (1,2,2-trimethyl-cyclopentan-1r,3c-dicarboxylic acid) [1R,2S)-(+)- 124-83-4; 1S,2R)-(-)- 560-09-8] M 200.2, m 186-188°, 187°, 186.5-189°, $[\alpha]_{546}^{20}$ (+) and (-) 57° (c 1,

EtOH), $[\alpha]_D^{20}$ (+) and (-) 47.7° (c 4, EtOH), pK_1^{25} 4.71, pK_2^{25} 5.83 (for + isomer). Purified by reprecipitation from an alkaline solution by HCl, filtered, and recrystallized from water several times, rejecting the first crop. It forms leaflets from EtOH and Me₂CO and H₂O and is insoluble in CHCl₃. Soluble in H₂O is 0.8% at 25° and 10% at 100°; 50% (EtOH) and 5% in ethylene glycol. The (±)-acid has m 202-203°. The (+)-1-methyl ester had m 86° (from petroleum ether) $[\alpha]_D^{20}$ +45° (c 4, EtOH), and the (+)-3-methyl ester has m 77° (from petroleum ether) $[\alpha]_D^{17.5}$ +53.9° (c 3, EtOH). [*J Am Chem Soc* 53 1661 1931; *Helv Chim Acta* 30 933 1947; *Acta Chem Scand* 2 597 1948; *J Am Chem Soc* 80 6316 1958.]

(±)-Camphoric anhydride [595-30-2] M 182.2, transition temp 135°, m 223.5°. Crystallized from EtOH.

Camphorquinone (borna-2,3-dione) [1R(-)- 10334-26-6; 1S(+)- 2767-84-2] M 166.2, m 198.7°, 198-199°, 197-201°, $[\alpha]_D^{25}$ (-) and (+) 101.1° (c 2, EtOH). It can be purified by steam distillation, recrystallized (yellow prisms) from EtOH, C₆H₆ or Et₂O-petroleum ether and can be sublimed in a vacuum. The (±)-quinone forms needles from EtOH, m 197-198°, 203°. [*Helv Chim Acta* 13 1026; *Chem Ber* 67 1432 1934.]

RS-Camphorquinone [10373-78-1] M 166.2, m 199-202°. Purification is same as for above isomers.

(1R)-(-)-Camphor-10-sulfonic acid [35963-20-3] M 232.3, m 197.4-198°(dec), 197-198°, $[\alpha]_D^{20}$ -20.7° (c 5.4, H₂O), pK_{Est} ~-1. Forms prisms from AcOH or EtOAc, and is deliquescent in moist air. Store in tightly stoppered bottles. The NH₄ salt forms needles from H₂O $[\alpha]_D^{16}$ ±20.5° (c 5, H₂O). [*J Chem Soc* 127 279 1925; *J Am Chem Soc* 78 3063 1956.]

(1S)-(+)-Camphor-10-sulfonic acid [3144-16-9] M 232.3, m 193°(dec), 197-198°, $[\alpha]_{546}^{20}$ +27.5° (c 10, H₂O), $[\alpha]_D^{20}$ +43.5° (c 4.3, EtOH), pK_{Est} ~-1. Crystallized from ethyl acetate and dried under vacuum.

Camphor-10-sulfonyl chloride [1S(+)- 21286-54-4; 1R(-)- 39262-22-1] M 250.7, m 67-68°, 70°, $[\alpha]_D^{20}$ (+) and (-) 32.2° (c 3, CHCl₃). If free from OH bands in the IR then recrystallized from Et₂O or petroleum ether, otherwise treat with SOCl₂ at 50° for 30min, evaporate, dry residue over KOH in a vacuum and recrystallize. The (±)-acid chloride has m 85°. Characterized as the amide (prisms from EtOH) m 132°, $[\alpha]_D^{17}$ (+) and (-) 1.5° (EtOH). [Read and Storey *J Chem Soc* 2761 1930; *J Am Chem Soc* 58 62 1936.]

2,10-Camphorsultam [1R(+)- 108448-77-7; 1S(-)- 94594-90-8] M 215.3, m 181-183°, 185-187°, $[\alpha]_D^{20}$ (+) and (-) 32° (c 5, CHCl₃). The (-)-enantiomer is recrystallized from 95% EtOH. It dissolves in dilute aqueous NaOH and can be precipitated without hydrolysis by acidifying. It forms the N-Na salt in EtOH (by addition of Na to the EtOH solution) and the salt can be methylated with MeI to give the (-)-N-Me lactam with m 80° after recrystallization from hot H₂O and has $[\alpha]_D^{25}$ -59.6° (c 5, CHCl₃) [Shriner et al. *J Am Chem Soc* 60 2794 1938].

S-Canavanine [543-38-4] M 176.2, m 184°, $[\alpha]_D^{17}$ +19.4° (c 2, H₂O), pK_1^{25} 2.43, pK_2^{25} 9.41. Crystallized from aqueous EtOH.

S(L)-Canavanine sulfate [2219-31-0] M 274.3, m 172°(dec). See L-canavanine sulfate on p. 518 in Chapter 6.

Cannabinol [521-35-7] M 310.4, m 76-77°, b 185°/0.05mm. Crystallized from petroleum ether. Sublimed.

Canthaxanthin (trans) [514-78-3] M 564.9, m 211-212°, $A_{1cm}^{1\%}$ 2200 (470nm) in cyclohexane. Purified by chromatography on a column of deactivated alumina or magnesium oxide, or on a thin layer of silica gel G (Merck), using dichloromethane/diethyl ether (9:1) to develop the chromatogram. Stored in the dark and in an inert atmosphere at -20°.

Capric acid (decanoic acid) [334-48-5] M 172.3, m 31.5°, b 148°/11mm, d 0.886, n_D^{25} 1.424, pK_{Est} ~4.9. Purified by conversion to its methyl ester, b 114.0°/15mm (using excess MeOH, in the presence of H₂SO₄). After removal of the H₂SO₄ and excess MeOH, the ester was distilled under vacuum through a 3ft

column packed with glass helices. The acid was then obtained from the ester by saponification. [Trachtman and Miller *J Am Chem Soc* **84** 4828 1962].

***n*-Caproamide (*n*-hexanamide)** [628-02-4] M 115.2, m 100°. Crystd from hot water.

Caproic acid (hexanoic acid) [142-62-1] M 116.2, b 205.4°, d 0.925, n 1.417, pK²⁵ 4.85. Dried with MgSO₄ and fractionally distilled from CaSO₄.

ϵ -Caprolactam (azepan-2-one, aza-2-cycloheptanone, 2-oxohexamethyleneimine) [105-60-2] M 113.2, m 70°, 70.5-71.5°, 70-71°, 262.5°/760mm. Distd at reduced pressure, crystd from acetone or pet ether and redistd. Purified by zone melting. Very *hygroscopic*. Discolours in contact with air unless small amounts (0.2g/L) of NaOH, Na₂CO₃ or NaBO₂ are present. Crystd from a mixture of pet ether (185mL of b 70°) and 2-methyl-2-propanol (30mL), from acetone, or pet ether. Distd under reduced pressure and stored under nitrogen. [*Synthesis* 614 1978.]

Capronitrile (hexanenitrile) [124-12-9] M 125.2, b 163.7°, n 1.4069, n²⁵ 1.4048. Washed twice with half-volumes of conc HCl, then with saturated aqueous NaHCO₃, dried with MgSO₄, and distilled.

Caprylolactam (azanon-2-one, azacyclononan-2-one, 8-aminooctanoic acid lactam) [935-30-8] M 141.2, m 72°, 73°, 74-76°, 75°, 76-77°, b 119-122°/0.7mm, 150-151°/7-8mm, 164°/14mm, d₄⁷³ 1.009, n_D⁷³ 1.489, pK²⁵ 0.55 (AcOH). Dissolve in CHCl₃, decolorise with charcoal, evaporate to dryness and recrystallise from CHCl₃-hexane. Sublime at high vacuum. The *oxime* has m 117° (from *C₆H₆ or pet ether). [*J Med Chem* **14** 501 1971; *Justus Liebigs Ann Chem* **607** 67 1957.]

Capsaicin (*E-N*-[(4-hydroxy-3-methoxyphenyl)-methyl]-8-methyl-6-nonenamide) [404-86-4] M 305.4, m 64-66°, 65°, 66.1°, b 210-220°/0.01mm. Recrystd from pet ether (b 40-60°), or pet ether-Et₂O (9:1). Also purified by chromatography on neutral Al₂O₃ (grade V) and eluted successively with *C₆H₆, *C₆H₆-EtOAc (17:3) and *C₆H₆-EtOAc (7:3), and distilled at 120°/10⁻⁵mm, and repeatedly recrystd from isopropanol (charcoal), needles. [*J Chem Soc* 11025 1955, *J Chem Soc(C)* 442 1968.]

Capsorubin (3,3'-dihydroxy- κ,κ -carotene-6,6'dione) [470-38-2] M 604.9, m 218°, λ_{\max} 443, 468, 503 nm, in hexane. Possible impurities: zeaxanthin and capsanthin. Purified by chromatography on a column of CaCO₃ or MgO. Crystd from *benzene/pet ether or CS₂.

Captan (*N*-trichloromethylmercapto-cyclohex-4-ene-1,2-dicarboxamide) [133-06-2] M 300.5, m 172-173°. Crystd from CCl₄. Large quantities internally cause diarrhoea and vomiting.

Captopril (*S*-1-[3-mercapto-2-methyl-1-oxopropyl]-L-proline) [62571-86-2] M 217.3, m 103-104°(polymorphic unstable form m 86°, melts at 87-88° solidifies and then melts again at 104-105°), [α]_D²² -131° (c 1.7, EtOH), pK₁ 3.7, pK₂ 9.8. Purified by recrystn from EtOAc-hexane. Also purified by dissolving in EtOAc and chromatographed on a column of Wakogel C200 using a linear gradient of MeOH in EtOAc (0-100°) and fractions which give a positive nitroprusside test (for SH) are combined, evap and recrystd from EtOAc-hexane (1:1), white crystals [α]_D²⁰ -128.2° (c 2.0, EtOH). [*Nam J Pharm Sci* **73** 1843 1984]. Alternatively, dissolve in H₂O, apply to a column of AG-50Wx2 (BioRad) and eluted with H₂O. The free acid is converted to the dicyclohexylamine salt in MeCN by addition until the pH is 8-9 (moist filter paper). The salt is converted to the free acid by shaking with EtOAc and 10% aq KHSO₄ or passage through an AG50Wx2 column. The EtOAc soln is dried (MgSO₄) and recrystd as above from EtOAc-hexane [*Biochem J* **16** 5484 1977; NMR and IR: Horii and Watanabe *Yakugaku Zasshi (J Pharm Soc Japan)* **81** 1786 1961].

4-(Carbamoylmethoxy)acetanilide [14260-41-4] M 208.2, m 208°. Crystd from water.

3-Carbamoyl-1-methylpyridinium chloride (1-methylnicotinamide chloride, Trigonellamide) [1005-24-9] M 172.6, m 240°(dec). Crystd from MeOH.

Carbanilide (*sym*-diphenylurea) [102-07-8] M 212.3, m 242°. Crystd from EtOH or a large volume (40mL/g) of hot water.

9-Carbazolacetic acid [524-80-1] M 225.2, m 215°, pK_{Est} ~3.5. Crystd from ethyl acetate.

Carbazole [86-74-8] M 167.2, m 240-243°, pK <0. Dissolved (60g) in conc H₂SO₄ (300mL), extracted with three 200mL portions of *benzene, then stirred into 1600mL of an ice-water mixture. The ppt was filtered off, washed with a little water, dried, crystd from *benzene and then from pyridine/*benzene. [Feldman, Pantages and Orchin *J Am Chem Soc* 73 4341 1951]. Has also been crystd from EtOH or toluene, sublimed in vacuum, zone-refined, and purified by TLC.

Carbazole-9-carbonyl chloride [73500-82-0] M 300.0, m 100-103°, 103.5-104.5°. Recrystd from *C₆H₆. If it is not very pure (presence of OH or NH bands in the IR) dissolve in pyridine, shake with phosgene in toluene, evaporate and recrystallise the residue. Carry out this experiment in a good fume cupboard as COCl₂ is very TOXIC, and store the product in the dark. It is moisture sensitive. The *amide* has m 246.5-247°, and the *dimethylaminoethylamide hydrochloride* has m 197-198°. [Weston et al. *J Am Chem Soc* 75 4006 1953.]

4-Carboethoxy-3-methyl-2-cyclohexen-1-one (Hagemann's ester) [487-51-4] M 182, b 79-80°/0.2mm, 121-123°/4mm, 142-144°/15mm, d₄²⁰ 1.038. Dissolve in ether, shake with solid K₂CO₃, aqueous saturated NaHCO₃, dry (MgSO₄) and distil. *Semicarbazone* has m 165-167° (169°). [*J Am Chem Soc* 65, 631, 1943.]

1-Carboethoxy-4-methylpiperazine hydrochloride [532-78-5] M 204.7, m 168.5-169°, pK 7.31. Crystd from absolute EtOH.

N-Carboethoxyphthalimide (*N*-ethoxycarbonylphthalimide) [22509-74-6] M 219.2, m 87-89°, 90-92°. Crystd from toluene-pet ether (or *benzene-pet ether). Partly soluble in Et₂O, *benzene and CHCl₃. [*Chem Ber* 54 1112 1921.]

γ-Carboline {9*H*-pyrido[3,4-*b*]indole} [244-69-9] M 168.2, m 225°, pK~0. Crystd from water.

Carbon Black Leached for 24h with 1:1 HCl to remove oil contamination, then washed repeatedly with distd water. Dried in air, and eluted for one day each with *benzene and acetone. Again dried in air at room temp, then heated in a vacuum for 24h at 600° to remove adsorbed gases. [Tamamushi and Tamaki *Trans Faraday Soc* 55 1007 1959.]

Carbon disulfide [75-15-0] M 76.1, b 46.3°, d 1.264, n 1.627. Shaken for 3h with three portions of KMnO₄ soln (5g/L), twice for 6h with mercury (to remove sulfide impurities) until no further darkening of the interface occurred, and finally with a soln of HgSO₄ (2.5g/L) or cold, satd HgCl₂. Dried with CaCl₂, MgSO₄, or CaH₂ (with further drying by refluxing with P₂O₅), followed by fractional distn in diffuse light. **Alkali metals cannot be used as drying agents.** Has also been purified by standing with bromine (0.5mL/L) for 3-4h, shaking with KOH soln, then copper turnings (to remove unreacted bromine), and drying with CaCl₂. CS₂ is highly TOXIC and highly FLAMMABLE. *Work in a good fumehood.* Small quantities of CS₂ have been purified (including removal of hydrocarbons) by mechanical agitation of a 45-50g sample with a soln of 130g of sodium sulfide in 150mL of H₂O for 24h at 35-40°. The aqueous sodium thiocarbonate soln was separated from unreacted CS₂, then pptd with 140g of copper sulfate in 350g of water, with cooling. After filtering off the copper thiocarbonate, it was decomposed by passing steam into it. The distillate was separated from H₂O and distd from P₂O₅. [Ruff and Golla *Z Anorg Chem* 138 17 1924.]

Carbon tetrabromide [558-13-4] M 331.7, m 92.5°. Reactive bromide was removed by refluxing with dilute aqueous Na₂CO₃, then steam distd, crystd from EtOH, and dried in the dark under vacuum. [Sharpe and Walker *J Chem Soc* 157 1962.] Can be sublimed at 70° at low pressure.

Carbon tetrachloride [56-23-5] **M 153.8, b 76.8°, d²⁵ 1.5842.** For many purposes, careful fractional distn gives adequate purification. Carbon disulfide can be removed by shaking vigorously for several hours with saturated KOH, separating, and washing with water: this treatment is repeated. The CCl₄ is shaken with conc H₂SO₄ until there is no further coloration, then washed with water, dried with CaCl₂ or MgSO₄ and distd (from P₂O₅ if desired). **It must not be dried with sodium.** An initial refluxing with mercury for 2h removes sulfides. Other purification steps include passage of dry CCl₄ through activated alumina, and distn from KMnO₄. Carbonyl containing impurities can be removed by percolation through a Celite column impregnated with 2,4-dinitrophenylhydrazine (DNPH), H₃PO₄ and water. (Prepared by dissolving 0.5g DNPH in 6mL of 85% H₃PO₄ by grinding together, then mixing with 4mL of distd water and 10g Celite.) [Schwartz and Parks *Anal Chem* **33** 1396 1961]. Photochlorination of CCl₄ has also been used: CCl₄ to which a small amount of chlorine has been added is illuminated in a glass bottle (e.g. for 24h with a 200W tungsten lamp near it), and, after washing out the excess chlorine with 0.02M Na₂SO₃, the CCl₄ is washed with distd water and distd from P₂O₅. It can be dried by passing through 4A molecular sieves and distd. Another purification procedure is to wash CCl₄ with aq NaOH, then repeatedly with water and N₂ gas bubbled through the liquid for several hours. After drying over CaCl₂ it is percolated through silica gel and distd under dry N₂ before use [Klassen and Ross *J Phys Chem* **91** 3664 1987].

Rapid purification: Distil, discarding the first 10% of distillate or until the distillate is clear. The distilled CCl₄ is then stored over 5A molecular sieves.

Carbon tetrafluoride [75-73-0] **M 88.0, b -15°.** Purified by repeated passage over activated charcoal at solid-CO₂ temperatures. Traces of air were removed by evacuating while alternately freezing and melting. Alternatively, liquefied by cooling in liquid air and then fractionally distilled under vacuum. (The chief impurity originally present was probably CF₃Cl).

Carbon tetraiodide [507-25-5] **M 519.6, m 168°(dec).** Sublimed *in vacuo*.

N,N'-Carbonyldiimidazole [530-62-1] **M 162.2, m 115.5-116°.** Crystd from *benzene or tetrahydrofuran, in a dry-box.

1,1'-Carbonyldi(1,2,4-triazole) [41864-22-6] **M 164.1, m 134-136°, 145-150°.** Dissolve in tetrahydrofuran and evaporate at 10mm until it crystallises. Wash crystals with cold tetrahydrofuran and dry in a vacuum desiccator over P₂O₅ in which it can be stored for months. [*Recl Trav Chim Pays-Bas* **80** 1372 1961; Potts *J Org Chem* **27** 2631 1962; Staab *Justus Liebigs Ann Chem* **106** 75 1957.]

Carbonyl sulfide [463-58-1] **M 60.1.** See carbonyl sulfide entry on p. 409 in Chapter 5.

***o*-Carboxyphenylacetonitrile** [6627-91-4] **M 161.2, m 114-115°.** Crystd (with considerable loss) from *benzene or glacial acetic acid.

(-)-Caryophyllene oxide (1-S-5c-6t-epoxy-6c,10,10-trimethyl-2-methylene-1r,9t-bicyclo-[7.2.0]undecane) [1139-30-6] **M 220.4, m 62-63°, 63.5-64°, 64°, b 114-117°/1.8mm, 141-142°/11mm, d₄²⁰ 0.9666, n_D²⁰ 1.49564, [α]_D²⁰ -79° (c 2,CHCl₃), [α]_D²⁰ -68° (supercooled melt).** Purified by TLC on silica gel with EtOAc-pet ether (b 60-80°) (15:85), and recrystallised from MeOH or *C₆H₆. [NMR: Warnhoff *Can J Chem* **42** 1664 1964, Ramage and Whitehead *J Chem Soc* 4336 1954.]

(±)-Catechin [7295-85-4] **M 272.3, m 177° (anhyd).** Crystd from hot water. Dried at 100°.

Catechol (1,2-dihydroxybenzene, pyrocatechol) [120-80-9] **M 110.1, m 105°, pK₁²⁵ 9.45, pK₂²⁵ 12.8.** Crystd from *benzene or toluene. Sublimed under vacuum. [Rozo et al. *Anal Chem* **58** 2988 1986.]

Cation exchange resin. Conditioned before use by successive washing with water, EtOH and water, and taken through two H⁺-Na⁺-H⁺ cycles by successive treatment with M NaOH, water and M HCl then washed with water until neutral.

(+)-Cedrol (octahydro-3,6,8,8-tetramethyl-1-3a,7-methanoazulen-6-ol, 8a*S*-6*c*-hydroxy-3*c*,6*t*,8,8-tetramethyl[8*ar*-*H*]-octahydro-3*H*,3*at*,7*t*-methanoazulene), [77-53-2] **m 82-86°**, 86-87°, $[\alpha]_D^{28} +10.5^\circ$ (c 5, CHCl₃), $[\alpha]_D^{18} +13.1^\circ$ (c 5.5, EtOH), $[\alpha]_D^{18} +14.3^\circ$ (c 10, dioxane). Purified by recrystn from aqueous MeOH. It is estimated colorimetrically with H₃PO₄ in EtOH followed by vanillin and HCl [Hayward and Seymour *Anal Chem* 20 572 1948]. The 3,5-dinitrobenzoyl derivative has **m 92-93°**. [*J Am Chem Soc* 83 3114 1961.]

β-Cellobiose [528-50-7] **M 342.3**, **m 228-229°(dec)**, $[\alpha]_D^{25} +33.3^\circ$ (c 2, water). Crystd from 75% aqueous EtOH.

Cellulose triacetate [9012-09-3] **M 72,000-74,000**. Extracted with cold EtOH, dried in air, washed with hot distd water, again dried in air, then dried at 50° for 30min. [Madorsky, Hart and Straus *J Res Nat Bur Stand* 60 343 1958.]

Cerulenin (helicocerin, 2*R*,3*S*-2,3-epoxy-4-oxo-7*E*,10*E*-dodecadienamide) [17397-89-6] **M 223.3**, **m 93-94°**, 93-95°, **b 120°/10⁻⁸mm**, $[\alpha]_D^{16} +63^\circ$ (c 2, MeOH). White needles from *C₆H₆. Also purified by repeated chromatography from Florisil and silica gel. It is soluble in EtOH, MeOH, *C₆H₆, slightly soluble in H₂O and pet ether. The dl-form has **m 40-42°** (from *C₆H₆-hexane), and the 2*R*,3*S*-tetrahydrocerulenin has **m 86-87°**, $[\alpha]_D^{20} +44.4$ (c 0.25, MeOH after 24h). [*Tetrahedron Lett* 2095 1978, 2039 1979; *J Am Chem Soc* 99 2805 1977; *J Org Chem* 47 1221 1982.]

Cetyl acetate [629-70-9] **M 284.5**, **m 18.3°**. Vacuum distd twice, then crystd several times from diethyl ether/MeOH.

Cetyl alcohol (1-hexadecanol) [36653-82-4] **M 242.5**, **m 49.3°**. Crystd from aqueous EtOH or from cyclohexane. Purified by zone refining. Purity checked by gas chromatography.

Cetylamine [629-54-9] **M 255.4**, **m 106-107°**, **b 235-236°/12mm**. Crystd from thiophene-free *benzene and dried under vacuum over P₂O₅.

Cetylamine (1-hexadecylamine) [143-27-1] **M 241.5**, **m 48°**, **b 162-165°/5.2mm**, **pK²⁵ 10.60**. Crystd from thiophene-free *benzene and dried under vacuum over P₂O₅.

Cetylammonium chloride [1602-97-7] **M 278.0**, **m 178°**. Crystd from MeOH.

Cetyl bromide (1-bromohexadecane) [112-82-3] **M 305.4**, **m 15°**, **b 193-196°/14mm**. Shaken with H₂SO₄, washed with water, dried with K₂CO₃ and fractionally distd.

Cetyl ether [4113-12-6] **M 466.9**, **m 54°**. Vacuum distd then crystd several times from MeOH/*benzene.

Cetylpyridinium chloride (H₂O) [6004-24-6] **M 358.0**, **m 80-83°**. Crystd from MeOH or EtOH/diethyl ether and dried *in vacuo*. [Moss et al. *J Am Chem Soc* 108 788 1986; Lennox and McClelland *J Am Chem Soc* 108 3771 1986.]

Cetyltrimethylammonium bromide (cetrimonium bromide, CTAB) [57-09-0] **M 364.5**, **m 227-235°(dec)**. Crystd from EtOH, EtOH/*benzene or from wet acetone after extracting twice with pet ether. Shaken with anhydrous diethyl ether, filtered and dissolved in a little hot MeOH. After cooling in the refrigerator, the ppt was filtered at room temperature and redissolved in MeOH. Anhydrous ether was added and, after warming to obtain a clear soln, it was cooled and crystalline material was filtered. [Dearden and Wooley *J Phys Chem* 91 2404 1987; Hakemi et al. *J Am Chem Soc* 91 120 1987.]

Cetyltrimethylammonium chloride [112-02-7] **M 320.0**. Crystd from acetone/ether mixture, EtOH/ether, or from MeOH. [Moss et al. *J Am Chem Soc* 109 4363 1987.]

Charcoal. Charcoal (50g) was added to 1L of 6M HCl and boiled for 45min. The supernatant was discarded, and the charcoal was boiled with two more lots of HCl, then with distilled water until the supernatant no longer gave a test for chloride ion. The charcoal (which was now phosphate-free) was filtered on a sintered-glass funnel and air dried at 120° for 24h. [Lippin, Talbert and Cohn *J Am Chem Soc* **76** 2871 1954.] The purification can be carried out using a Soxhlet extractor (without cartridge), allowing longer extraction times. Treatment with conc H₂SO₄ instead of HCl has been used to remove reducing substances.

Chaulmoogric acid [(13-cyclopent-2-enyl)tridecanoic acid] [29106-32-9] **M 280.4, m 68.5°, b 247-248°/20mm**, $[\alpha]_D^{20} +60^\circ$ (c 4, CHCl₃), **pK_{Est} ~5.0**. Crystd from pet ether or EtOH. The *Me ester* [24828-59-9] has **m 22°, b 227°/20mm** and $[\alpha]_D^{15} +50^\circ$ (c 5, CHCl₃).

Chelerythrine [34316-15-9] **M 389.4, m 207°**. Crystd from CHCl₃ by addition of MeOH.

Chelex 100 [11139-85-8]. Washed successively with 2M ammonia, water, 2M nitric acid and water. Chelex 100 may develop an odour on long standing. This can be removed by heating to 80° for 2h in 3M ammonia, then washing with water. [Ashbrook *J Chromatogr* **105** 151 1975.]

Chelidonic acid (4-oxopyran-2,6-dicarboxylic acid) [99-32-1] **M 184.1, m 262°, pK₂²⁵ 2.36**. Crystd from aqueous EtOH.

Chenodesoxycholic acid [474-25-9] **M 392.6, m 143°**. See 3 α ,7 α -dihydroxycholanolic acid on p. 207.

Chimyl alcohol (1-O-n-hexadecylglycerol) [(±) 506-03-6; 10550-58-0 (*chimyl alcohol*)] **M 316.5, m 64°**. Crystd from hexane.

Chloral [75-87-6; 302-17-0 (*hydrate*)] **M 147.4, b 98°, pK²⁵ 10.04**. Distd, then dried by distilling through a heated column of CaSO₄.

Chloralacetone chloroform [512-47-0] **M 324.9, m 65°**. Crystd from *benzene.

α -Chloralose (R-1,2-O-[2,2,2-trichloroethylidene]- α -D-glucofuranose) [15879-93-3] **M 309.5, m 180-182°, 187°, 186-188°, $[\alpha]_D^{26} +19.5^\circ$ (c 11, pyridine)**. Recrystd from EtOH, 38% aqueous EtOH, Et₂O, H₂O or CHCl₃. The solubility is 0.44% in H₂O at 15°, 0.83% in H₂O at 37°, 6.7% in EtOH at 25°. [Whiton and Hixon *J Am Chem Soc* **55** 2438 1933; *Helv Chim Acta* **6** 621 1923.] The β -isomer is less soluble in H₂O, EtOH or Et₂O and has **m 237.5-238°** [*J Am Chem Soc* **59** 1955 1937; *Acta Chem Scand* **19** 359 1965].

2-Chloroacetophenone [532-27-4] **M 154.6, m 54-56°**. Crystd from MeOH [Tanner *J Org Chem* **52** 2142 1987].

p-Chloranil (2,3,5,6-tetrachloro-1,4-benzoquinone) [118-75-2] **M 245.9, m 290°, 294.2-294.6° (sealed tube)**. Crystd from acetic acid, acetone, *benzene, EtOH or toluene, drying under vac over P₂O₅, or from acetic acid, drying over NaOH in a vacuum desiccator. It can be sublimed under vacuum at 290°. Sample may contain significant amounts of the *o*-chloranil isomer as impurity. Purified by triple sublimation under vacuum. Recrystd before use. **It is a skin and mucous membrane irritant.** [UV: *Rec Trav Chim Pays Bas* **276** 684 1924; Brook *J Chem Soc* 5040 1952.]

Chloranilic acid (2,5-dichloro-3,6-dihydroxy-1,4-benzoquinone) [87-88-7] **M 209.0, m 283-284° pK₁²⁵ 1.22, pK₂²⁵ 3.01**. A soln of 8g in 1L of boiling water was filtered while hot, then extracted twice at about 50° with 200mL portions of *benzene. The aq phase was cooled in ice-water. The crystals were filtered off, washed with three 10mL portions of water, and dried at 115°. It can be sublimed in vacuum. [*J Phys Chem* **61** 765 1957.] The *diacetate* has **m 182-185°** [*J Am Chem Soc* **46** 1866 1924; Thamer and Voight *J Phys Chem* **56** 225 1952].

Chlorendic anhydride (1,4,5,6,7,7,-hexachloro-5-norbornene-2,3-dicarboxylic anhydride) [115-27-5] M 370.9, m 234-236°. 235-237°, 238°. Steam distn or recrystn from H₂O yields the diacid. The purified diacid yields the anhydride with Ac₂O. [Prill *J Am Chem Soc* 69 62 1947.]

Chloroacetaldehyde dimethyl acetal [97-97-2] M 124.6, m -34.4°, b 64°/23mm, 71-72°/35mm, d₄²⁰ 1.0172, n_D²⁰ 1.4175. Purified by fractional distillation. [Melhotra *J Indian Chem Soc* 36 4405 1959; *Bull Soc Chim Belg* 61 393 1952.]

α-Chloroacetamide [79-07-2] M 93.5, m 121°, b 224-225°/743mm. Crystd from acetone and dried under vacuum over P₂O₅.

p-Chloroacetanilide [539-03-7] M 169.6, m 179°. Crystd from EtOH or aqueous EtOH.

Chloroacetic acid [79-11-8] M 94.5, m 62.8°, b 189°, pK²⁵ 2.87. Crystd from CHCl₃, CCl₄, *benzene or water. Dried over P₂O₅ or conc H₂SO₄ in a vacuum desiccator. Further purification by distn from MgSO₄, and by fractional crystn from the melt. Stored under vac or under dry N₂. [Bernasconi et al. *J Am Chem Soc* 107 3621 1985.]

Chloroacetic anhydride [541-88-8] M 171.0, m 46°, d 1.5494. Crystd from *benzene.

Chloroacetone [78-95-5] M 92.5, b 119°/763mm, d 1.15. Dissolved in water and shaken repeatedly with small amounts of diethyl ether which extracts, preferentially, 1,1-dichloroacetone present as an impurity. The chloroacetone was then extracted from the aqueous phase using a large amount of diethyl ether, and distd at slightly reduced pressure. It was dried with CaCl₂ and stored at Dry-ice temperature. Alternatively, it was stood with CaSO₄, distd and stored over CaSO₄. **LACHRYMATORY.**

Chloroacetonitrile [107-14-2] M 75.5, b 125°. Refluxed with P₂O₅ for one day, then distd through a helices-packed column. Also purified by gas chromatography. **LACHRYMATOR, HIGHLY TOXIC.**

o-Chloroaniline [95-51-2] M 127.6, m -1.9°, b 208.8°, d 1.213, n 1.588, pK²⁵ 2.66. Freed from small amounts of the *p*-isomer by dissolving in one equivalent of H₂SO₄ and steam distilling. The *p*-isomer remains behind as the sulfate. [Sidgwick and Rubie *J Chem Soc* 1013 1921.] An alternative method is to dissolve in warm 10% HCl (11mL/g of amine) and on cooling, the hydrochloride of *o*-chloroaniline separates out. The latter can be recrystd until the acetyl derivative has a constant melting point. (In this way, yields are better than for the recrystn of the picrate from EtOH or of the acetyl derivative from pet ether.) [King and Orton *J Chem Soc* 1377 1911].

p-Chloroaniline [106-47-8] M 127.6, m 70-71°, pK²⁵ 3.98. Crystd from MeOH, pet ether (b 30-60°), or 50% aq EtOH, then *benzene/pet ether (b 60-70°), then dried in a vacuum desiccator. Can be distd under vacuum (b 75-77°/33mm).

p-Chloroanisole [623-12-1] M 142.6, b 79°/11.5mm, 196.6°/760mm, d 1.164, n^{25.5} 1.5326. Washed with 10% (vol) aqueous H₂SO₄ (three times), 10% aqueous KOH (three times), and then with water until neutral. Dried with MgSO₄ and fractionally distd from CaH₂ through a glass helices-packed column under reduced pressure.

9-Chloroanthracene [716-53-0] M 212.9, m 105-107°. Crystd from EtOH. [Masnori *J Am Chem Soc* 108 1126 1986.]

10-Chloro-9-anthraldehyde [10527-16-9] M 240.7, m 217-219°. Crystd from EtOH.

o-Chlorobenzaldehyde [89-98-5] M 140.6, m 11°, b 213-214°, d 1.248, n 1.566. Washed with 10% Na₂CO₃ soln, then fractionally distd in the presence of a small amount of catechol.

3-Chlorobenzaldehyde [587-04-2] M 140.6, m 18°, b 213-214°, d 1.241, n 1.564. Purified by low temperature crystn from pet ether (b 40-60°).

4-Chlorobenzaldehyde [104-88-1] M 140.6, m 47°. Crystd from EtOH/water (3:1), then sublimed twice at 2mm pressure at a temperature slightly above the melting point.

Chlorobenzene [108-90-7] M 112.6, b 131.7°, d 1.107, n 1.52480. The main impurities are likely to be chlorinated impurities originally present in the *benzene used in the synthesis of chlorobenzene, and also unchlorinated hydrocarbons. A common purification procedure is to wash several times with conc H₂SO₄ then with aq NaHCO₃ or Na₂CO₃, and water, followed by drying with CaCl₂, K₂CO₃ or CaSO₄, then with P₂O₅, and distn. It can also be dried with Linde 4A molecular sieve. Passage through, and storage over, activated alumina has been used to obtain low conductance material. [Flaherty and Stern *J Am Chem Soc* 80 1034 1958.]

4-Chlorobenzenesulfonyl chloride [98-60-2] M 211.1, m 53°, b 141°/15mm. Crystd from ether in powdered Dry-ice, after soln had been washed with 10% NaOH until colourless and dried with Na₂SO₄.

4-Chlorobenzhydrazide [536-40-3] M 170.6, m 164°. Crystd from water.

2-Chlorobenzoic acid [118-91-2] M 156.6, m 139-140°, pK²⁵ 2.91. Crystd successively from glacial acetic acid, aq EtOH, and pet ether (b 60-80°). Other solvents include hot water or toluene (ca 4mL/g). Crude material can be given an initial purification by dissolving 30g in 100mL of hot water containing 10g of Na₂CO₃, boiling with 5g of charcoal for 15min, then filtering and adding 31mL of 1:1 aq HCl: the ppte is washed with a little water and dried at 100°.

3-Chlorobenzoic acid [535-80-8] M 156.6, m 154-156°, 158°, d₄²⁵ 1.496, pK²⁵ 3.82 (5.25 in 50% dimethylacetamide). Crystd successively from glacial acetic acid, aqueous EtOH and pet ether (b 60-80°). It also recrystd from *C₆H₆ or Et₂O-hexane, and sublimes at 55° in a vacuum. [*Anal Chem* 26 726 1954] The methyl ester has m 21°, b 231°/atm. The *S*-benzyl thiuronium salt has m 164-165° (from EtOH) [*Acta Chem Scand* 9 1425 1955; *J Chem Soc* 1318 1960].

4-Chlorobenzoic acid [74-11-3] M 156.6, m 238-239°, pK²⁵ 3.99. Same as for *m*-chlorobenzoic acid. Has also been crystd from hot water, and from EtOH.

2-Chlorobenzonitrile [873-32-5] M 137.6, m 45-46°. Crystd to constant melting point from *benzene/pet ether (b 40-60°).

4-Chlorobenzophenone [134-85-0] M 216.7, m 75-76°. Recrystd for EtOH. [Wagner et al. *J Am Chem Soc* 108 7727 1986.]

2-Chlorobenzothiazole [615-20-3] M 169.6, m 21°, 90-91.4°/4mm, 135-136°/28mm, d₄²⁰ 1.303, n_D²⁰ 1.6398. It is purified by fractional distn *in vacuo*. The 2-chloro-3-methylbenzothiazolinium 2,4-dinitrobenzenesulfonate crystallises from Ac₂O, m 162-163° (dec). [*J Am Chem Soc* 73 4773 1951; *J Org Chem* 19 1830 1954; *J Chem Soc* 2190 1930.]

***o*-Chlorobenzotrifluoride** [88-16-4] M 180.6, b 152.3°. Dried with CaSO₄, and distd at high reflux ratio through a silvered vacuum-jacketed glass column packed with one-eighth inch glass helices [Potter and Saylor *J Am Chem Soc* 73 90 1951].

***m*-Chlorobenzotrifluoride** [98-15-7] M 180.6, b 137.6°. Same as for *o*-chlorobenzotrifluoride above.

***p*-Chlorobenzotrifluoride** [98-56-6] M 180.6, b 138.6°. Same as for *o*-chlorobenzotrifluoride above.

2-Chlorobenzoxazole [615-18-9] M 153.6, b 95-96°/20mm, 198-202°/atm, d_4^{20} 1.331, n_D^{20} 1.570. Purified by fractional distn, preferably in a vacuum. [Siedel *J Prakt Chem* (2) 42 456 1890; *J Am Chem Soc* 75 712 1953.]

p-Chlorobenzyl chloride [104-83-6] M 161.0, m 28-29°, b 96°/15mm. Dried with CaSO₄, then fractionally distd under reduced pressure. Crystd from heptane or dry diethyl ether. **LACHRYMATORY.**

p-Chlorobenzylisothiuronium chloride [544-47-8] M 237.1, m 197°, pK_{Est} ~9.6 (free base). Crystd from conc HCl by addition of water.

2-Chlorobutane [78-86-4] M 92.6, b 68.5°, d 0.873, n^{25} 1.3945. Purified in the same way as *n*-butyl chloride.

2-(4-Chlorobutyl)-1,3-dioxolane [118336-86-0] M 164.6, b 56-58°/0.1mm, d_4^{20} 1.106, n_D^{20} 1.457. If the IR has a CHO band then just distil in vacuum. If it is present then dissolve in Et₂O, wash with H₂O, then saturated NaHCO₃, dry over MgSO₄, evaporate and distil. [*J Am Chem Soc* 73 1365 1951.]

N-Chlorocarbonyl isocyanate [27738-96-1] M 105.5, m -68°, b 63.6°/atm, d_4^{20} 1.310. Fractionally distd at atmospheric pressure using a 40cm column. **TOXIC vapour use a good fume hood.** Store dry, ν 2260 (NCO), 1818 (CO) and 1420 (NCO sym) cm⁻¹. [*Chem Ber* 106 1752 1975.]

trans-4-Chlorocinnamic acid [1615-02-7] M 182.6, m 243°, 248-250°, 249-251°, pK^{25} 4.41. Recrystd from EtOH or aq EtOH (charcoal). [*Org Synth Coll Vol IV* 731 1963, Walling and Wolfstin *J Am Chem Soc* 69 852 1947.]

Chlorocyclohexane [542-18-7] M 118.6, b 142.5°, d 1.00, n^{25} 1.46265. Washed several times with dilute NaHCO₃, then repeatedly with distilled water. Dried with CaCl₂ and fractionally distd.

4-Chloro-2,6-diaminopyrimidine (2,4-diamino-6-chloropyrimidine) [156-83-2] M 144.6, m 198°, 199-202°, pK^{25} 3.57. Purified by recrystn from boiling H₂O (charcoal) as needles; also crystallises from Me₂CO. [Büttner *Chem Ber* 36 2232 1903; Roth *J Am Chem Soc* 72 1914 1950; UV: *J Chem Soc* 3172 1962.]

4-Chloro-3,5-dimethylphenol [88-04-0] M 156.6, m 115.5°, pK^{25} 9.70. Crystd from *benzene or toluene.

1-Chloro-2,4-dinitrobenzene [97-00-7] M 202.6, m 48-50°, 51°, 52-54°, 54°, b 315°/atm, d_4^{22} 1.697. Usually crystd from EtOH or MeOH. Has also been crystd from Et₂O, *C₆H₆, *C₆H₆-pet ether or isopropyl alcohol. A preliminary purification step has been to pass its soln in *benzene through an alumina column. Also purified by zone refining. It exists in three forms: one stable and two unstable. The stable form crysts as yellow needles from Et₂O, m 51°, b 315°/atm with some dec, and is sol in EtOH. The labile forms also crystallises from Et₂O, m 43°, and is more soluble in organic solvents. The second labile form has m 27°. [Hoffman and Dame, *J Am Chem Soc* 41 1015 1919, Welsh *J Am Chem Soc* 63 3276 1941; *J Chem Soc* 2476 1957.]

4-Chloro-3,5-dinitrobenzoic acid [118-97-8] M 246.6, m 159-161°, pK_{Est} ~2.5. Crystd from EtOH/water, EtOH or *benzene.

2-Chloro-3,5-dinitropyridine [2578-45-2] M 203.5, m 62-65°, 63-65°, 64°, pK_{Est} <-5. Dissolve in CHCl₃, shake with saturated NaHCO₃, dry (MgSO₄), evaporate and apply to an Al₂O₃ column, elute with pet ether (b 60-80°), evaporate and recryst from *C₆H₆ or pet ether. [*Chem Pharm Bull Jpn* 8 28 1960; *Recl Trav Chim Pays-Bas* 72 573 1953.]

2-Chloroethanol (ethylene chlorohydrin) [107-07-3] M 80.5, b 51.0°/31 mm, 128.6°/760mm, d 1.201, n¹⁵ 1.444. Dried with, then distd from, CaSO₄ in the presence of a little Na₂CO₃ to remove traces of acid.

2-Chloroethyl bromide (1-bromo-2-chloroethane) [107-04-0] M 143.4, b 106-108°. Washed with conc H₂SO₄, water, 10% Na₂CO₃ soln, and again with water, then dried with CaCl₂ and fractionally distd before use.

2-Chloroethyl chloroformate [627-11-2] M 143.0, b 52-54°/12mm, 153°/760mm, d₄¹⁸ 1.3760, n_D²⁰ 1.446. Purified by fractional distn, preferably in a vacuum and stored in dry atmosphere. [*J Chem Soc* 2735 1957.]

1-(2-Chloroethyl)pyrrolidine hydrochloride [7250-67-1] M 170.1, m 167-170°, 173.5-174°, pK_{Est} ~8.5 (free base). Purified by recrystn from isopropanol-di-isopropyl ether (charcoal) and recrystallised twice more. The free base, b 55-56°/11mm, 60-63°/23mm and 90°/56mm, is relatively unstable and should be converted to the hydrochloride immediately, by dissolving in isopropanol and bubbling dry HCl through the soln at 0°, and filtering off the hydrochloride and recrystallising it. The picrate has m 107.3-107.8° (from EtOH) [*Cason J Org Chem* 24 247 1959; *J Am Chem Soc* 70 3098 1948].

2-Chloroethyl vinyl ether [110-75-8] M 106.6, b 109°/760mm, d 1.048, n 1.437. Washed repeatedly with equal volumes of water made slightly alkaline with KOH, dried with sodium, and distd under vacuum. TOXIC.

Chloroform [67-66-3] M 119.4, b 61.2°, d¹⁵ 1.49845, d¹⁰ 1.47060, n¹⁵ 1.44858. Reacts slowly with oxygen or oxidising agents, when exposed to air and light, giving, mainly, phosgene, Cl₂ and HCl. Commercial CHCl₃ is usually stabilized by addn of up to 1% EtOH or of dimethylaminoazobenzene. Simplest purifications involve washing with water to remove the EtOH, drying with K₂CO₃ or CaCl₂, refluxing with P₂O₅, CaCl₂, CaSO₄ or Na₂SO₄, and distilling. It must not be dried with sodium. The distd CHCl₃ should be stored in the dark to avoid photochemical formation of phosgene. As an alternative purification, CHCl₃ can be shaken with several small portions of conc H₂SO₄, washed thoroughly with water, and dried with CaCl₂ or K₂CO₃ before filtering and distilling. EtOH can be removed from CHCl₃ by passage through a column of activated alumina, or through a column of silica gel 4-ft long by 1.75-in diameter at a flow rate of 3mL/min. (The column, which can hold about 8% of its weight of EtOH, is regenerated by air drying and then heating at 600° for 6h. It is pre-purified by washing with CHCl₃, then EtOH, leaving in conc H₂SO₄ for about 8hr, washing with water until the washings are neutral, then air drying, followed by activation at 600° for 6h. Just before use it is reheated for 2h to 154°.) [McLaughlin, Kaniecki and Gray *Anal Chem* 30 1517 1958].

Carbonyl-containing impurities can be removed from CHCl₃ by percolation through a Celite column impregnated with 2,4-dinitrophenylhydrazine, phosphoric acid and water. (Prepared by dissolving 0.5g DNPH in 6mL of 85% H₃PO₄ by grinding together, then mixing with 4mL of distilled water and 10g of Celite.) [Schwartz and Parks *Anal Chem* 33 1396 1961]. Chloroform can be dried by distn from powdered type 4A Linde molecular sieves. For use as a solvent in IR spectroscopy, chloroform is washed with water (to remove EtOH), then dried for several hours over anhydrous CaCl₂ and fractionally distd. This treatment removes material absorbing near 1600 cm⁻¹. (Percolation through activated alumina increases this absorbing impurity). [Goodspeed and Millson *Chem Ind (London)* 1594 1967].

Rapid purification: Pass through a column of basic alumina (Grade I, 10g/mL of CHCl₃), and either dry by standing over 4A molecular sieves, or alternatively, distil from P₂O₅ (3% w/v). Use immediately.

Chlorogenic [3-(3,4-dihydroxycinnamoyl)quinic] acid [327-97-9] M 354.3, m 208°, [α]_D²⁵ -36° (c 1, H₂O), pK₁²⁵ 3.59, pK₂²⁵ 8.59. Crystd from water. Dried at 110°.

Chlorohydroquinone (2-chloro-1,4-dihydroxybenzene) [615-67-8] M 144.6, m 106°, b 263°, pK₁²⁵ 8.81, pK₂²⁵ 10.78. Crystd from CHCl₃ or toluene.

5-Chloro-8-hydroxy-7-iodoquinoline (vioform) [130-26-7] M 305.5, m 178-179°, pK_{Est(1)} ~2.6, pK_{Est(2)} ~7.0. Crystd from abs EtOH.

5-Chloroindole [17422-32-1] M 151.6, m 69-71°, 72-73°, b 120-130°/0.4mm, pK_{Est} <0 It is distd at high vacuum and recrystallises from pet ether (b 40-60°) or (b 80-100°) as glistening plates. The *picrate* has m 147° (146.5-147.5°)(from *C₆H₆). [*J Chem Soc* 3493 1955; *J Org Chem* 44 578 1979].

4-Chloriodobenzene [637-87-6] M 238.5, m 53-54°. Crystd from EtOH.

2,3-Chloromaleic anhydride [1122-17-4] M 167.0, m 121-121.5°. See 2,3-dichloromaleic anhydride on p. 198.

5-Chloro-2-methoxyaniline (2-amino-4-chloroanisole) [95-03-4] M 157.6, m 81-83°, 82-84°, 84°, pK²⁵ 3.56. Purified by steam distn and recrystn from H₂O or 40% aqueous EtOH. The *N*-acetate forms needles from hot H₂O m 104°; the *N*-benzoyl derivative forms needles from aq EtOH m 77-78°; the *picrate* has m 194° dec. [*J Am Chem Soc* 48 2657 1926.]

9-Chloromethyl anthracene [24463-19-2] M 226.7, m 141-142° dec, 141-142.5°. If it is free from OH in the IR then recryst from hexane-*C₆H₆ or *C₆H₆ as needles. If OH is present then some solvolysis has occurred. In this case treat 8.5g with SOCl₂ (4.8g) in dioxane (60mL) and reflux for 5h, then evaporate to dryness and wash the residue with cold *C₆H₆ and recrystallise. With KI/Me₂CO it forms the *iodomethyl* derivative. [Martin et al. *Helv Chim Acta* 38 2009 1955; *J Org Chem* 21 1512 1956.]

2-Chloro-3-methylindole (2-chloroskatole) [51206-73-6] M 165.6, m 114.5-115.5°, pK_{Est} <0. Purified by chromatography on silica gel in CH₂Cl₂/pet ether (1:2), followed by recrystn from aqueous EtOH or aqueous acetic acid. [Phillips and Cohen *J Am Chem Soc* 108 2023 1986.]

Chloromethyl methyl ether (MOMCl) [107-30-2] M 80.5, b 55-57°, d 1.060, n 1.396. If suspect (check IR), shake with satd aq CaCl₂ soln, dry over CaCl₂ and fractionally distil taking middle fraction. [Marvel and Porter *Org Synth Coll Vol I* 377 1941.] **VERY TOXIC and CARCINOGENIC.**

4-Chloro-2-methylphenol [1570-64-5] M 142.6, m 49°, pK²⁵ 9.71. Purified by zone melting.

4-Chloro-3-methylphenol [59-50-7] M 142.6, m 66°, pK²⁵ 9.55. Crystd from pet ether.

4-Chloro-2-methylphenoxyacetic acid (MCPA) [94-74-6] M 200.6, m 113-117°, 120°, 122-123°, pK²⁰ 3.62 (3.05). It is insoluble in H₂O (sol 0.55g/L at 20°), and recrystallises from *C₆H₆ or chlorobenzene as plates [*Acta Chem Scand* 6 993 1952]. The *S*-benzylthiuronium salt has m 164-165°, and the Cu²⁺ salt has m 247-249°dec [Armarego et al. *Nature* 183 1176 1959; UV: Duvaux and Grabe *Acta Chem Scand* 4 806 1950; IR: Jöberg *Acta Chem Scand* 4 798 1950].

Chloromethyl phenyl sulfide [7205-91-6] M 158.7, b 63°/0.1mm, 98°/12mm, 113-115°/20mm. Dissolve in CH₂Cl₂ or CCl₄ and dry over CaCl₂, or pass through a tube of CaCl₂ and fractionally distil using a fractionating column. *Harmful vapours*. It gives the *sulfone* (b 130°/1mm and m 53° from EtOH) on oxidation with permonophthalic acid. [*Justus Liebigs Ann Chem* 563 54 64 1949.]

***N*-(Chloromethyl)phthalimide** [17564-64-6] M 195.6, m 131-135°, 134-135°, 136.5°. Purified by recrystn from EtOAc or CCl₄ [*J Am Chem Soc* 70 2822 1948; Böhme et al. *Chem Ber* 92 1258 1959].

4-(Chloromethyl)pyridine hydrochloride [1822-51-1] M 164.0, m 170-175°, 172-173°, pK_{Est} ~5.6. Purified by recrystn from EtOH or EtOH-dry Et₂O. It melts between 171° and 175° and the clear melt resolidifies on further heating at 190° and turns red to black at 280° but does not melt again. The *picrate-hydrochloride* (prepared in EtOH) has m 146-147°. The free base is an oil, [Mosher and Tessieri *J Am Chem Soc* 73 4925 1951.]

2-Chloro-1-methylpyridinium iodide [14338-32-0] M 255.5, m 203-205°, 205-206°(dec), 207°. Purified by dissolving in EtOH and adding dry Et₂O. The solid is washed with Me₂CO and dried at

20°/0.35mm. Store in the dark. Attempted recrystn from Me₂CO-EtOH-pet ether (b 40-60°) caused some exchange of the Cl substituent by I. The *picrate* has *m* 106-107°, and the *perchlorate* has *m* 212-213°. [UV and solvolysis: Barlin and Benbow *J Chem Soc, Perkin Trans 2* 790 1974.]

1-Chloronaphthalene [90-13-1] *M* 162.6, *f* -2.3°, *b* 136-136.5°/20mm, 259.3°/760mm, *d* 1.194, *n* 1.6326. Washed with dilute NaHCO₃, then dried with Na₂SO₄ and fractionally distd under reduced pressure. Alternatively, before distn, it was passed through a column of activated alumina, or dried with CaCl₂, then distd from sodium. It can be further purified by fractional crystn by partial freezing or by crystn of its picrate to constant melting point (132-133°) from EtOH, and recovering from the picrate.

2-Chloronaphthalene [91-58-7] *M* 162.6, *m* 61°, *b* 264-266°. Crystd from 25% EtOH/water and dried under vacuum.

1-Chloro-2-naphthol [633-99-8] *M* 178.6, *m* 70°, *pK*_{Est} ~8.3. Cryst from pet ether. *Acetate* has *m* 42-43°.

2-Chloro-1-naphthol [606-40-6] *M* 178.6, *m* 64-65°, *pK*_{Est} ~7.9. Crystd from pet ether.

4-Chloro-1-naphthol [604-44-4] *M* 178.6, *m* 116-117°, 120-121°, *pK*²⁵ 8.86. Crystd from EtOH or chloroform.

6-Chloronicotinic acid [5326-23-8] *M* 157.6, *m* 190-193°, 198-199°(dec), *pK*²⁵ 4.22 (50% aq EtOH). Purified by recrystn from hot H₂O and is sublimed in a vacuum. [Pechmann and Welsch *Chem Ber* 17 2384 1884; Herz and Murty *J Org Chem* 26 122 1961.]

4-Chloro-2-nitroaniline [89-63-4] *M* 172.6, *m* 116-116.5°, *pK*²⁵ -0.99. Crystd from hot water or EtOH/water and dried for 10h at 60° under vacuum.

2-Chloro-4-nitrobenzamide [3011-89-0] *M* 200.6, *m* 172°. Crystd from EtOH.

2-Chloro-1-nitrobenzene [88-73-3] *M* 157.6, *m* 32.8-33.2°. Crystd from EtOH, MeOH or pentane (charcoal).

3-Chloro-1-nitrobenzene [121-73-3] *M* 157.6, *m* 45.3-45.8°. Crystd from MeOH or 95% EtOH (charcoal), then pentane.

4-Chloro-1-nitrobenzene [100-00-5] *M* 157.6, *m* 80-83°, 83.5-84°, *b* 113°/8mm, 242°/atm, *d*^{100.5} 1.2914. Crystd from 95% EtOH (charcoal) and sublimes in a vacuum. [Emmons *J Am Chem Soc* 76⁴ 3470 1954; Newman and Forres *J Am Chem Soc* 69 1221 1947.]

4-Chloro-7-nitrobenzofurazane (7-chloro-4-nitrobenzoxadiazole) [10199-89-0] *M* 199.6, *m* 96.5-97°, 97°, 99-100°. Wash the solid with H₂O and recrystallise from aqueous EtOH (1:1) as pale yellow needles. It sublimes in a vacuum [UV, NMR: Bolton, Gosh and Katritzky *J Chem Soc* 1004 1966].

1-Chloro-2-nitroethane [625-47-8] *M* 109.5, *b* 37-38°/20mm, *n* 1.4224, *n*²⁵ 1.4235. Dissolved in alkali, extracted with ether (discarded), then the aqueous phase was acidified with hydroxylamine hydrochloride, and the nitro compound fractionally distd under reduced pressure. [Pearson and Dillon *J Am Chem Soc* 75 2439 1953.]

2-Chloro-3-nitropyridine [5470-18-8] *M* 158.5, *m* 100-103°, 101-102°, 103-104° (sublimes), *pK*²⁰ -2.6. Forms needles from H₂O. Purified by continuous sublimation over a period of 2 weeks at 50-60°/0.1mm [Barlin *J Chem Soc* 2150 1964]. The *N-oxide* has *m* 99-100°(from CH₂Cl₂-Et₂O). [Taylor and Driscoll *J Org Chem* 25 1716 1960; Ochiai and Kaneko *Chem Pharm Bull Jpn* 8 28 1960.]

2-Chloro-5-nitropyridine [4548-45-2] M 158.5, m 108°, pK_{Est} ~-2.6. Crystd from *benzene or *benzene/pet ether.

3-Chloroperbenzoic acid [937-14-4] M 172.6, m 92-94°(dec), pK²⁵ 7.57. Recrystd from CH₂Cl₂ [Traylor and Mikzta *J Am Chem Soc* 109 2770 1987]. Peracid of 99+% purity can be obtained by washing commercial 85% material with phosphate buffer pH 7.5 and drying the residue under reduced pressure. Alternatively the peracid can be freed from *m*-chlorobenzoic acid by dissolving 50g/L of *benzene and washing with an aq soln buffered at pH 7.4 (NaH₂PO₄/NaOH) (5 x 100mL). The organic layer was dried over MgSO₄ and carefully evaporated under vacuum. *Necessary care should be taken in case of EXPLOSION.* The solid was recrystd twice from CH₂Cl₂/Et₂O and stored at 0° in a plastic container as glass catalyses the decomposition of the peracid. The acid is assayed iodometrically. [*J Org Chem* 29 1976 1964; Bortolini et al. *J Org Chem* 52 5093 1987.]

2-Chlorophenol [95-57-8] M 128.6, m 8.8°, b 61-62°/10mm, 176°/atm, pK²⁵ 8.34. Passed at least twice through a gas chromatograph column. Also purified by fractional distn.

3-Chlorophenol [108-43-0] M 128.6, m 33°, b 44.2°/1mm, 214°/atm, pK²⁵ 9.13. Could not be obtained solid by crystn from pet ether. Purified by distn under reduced pressure.

4-Chlorophenol [106-48-9] M 128.6, m 43°, 100-101°/10mm, pK²⁵ 9.38. Distd, then crystd from pet ether (b 40-60°) or hexane, and dried under vacuum over P₂O₅ at room temp. It has pK_a 9.38 at 20° in water. [Bernasconi and Paschalis *J Am Chem Soc* 108 2969 1986.]

Chlorophenol Red (3,3'-dichlorophenolsulfonephthalein) [4430-20-0] M 423.3, m dec on heating, λ_{max} 573nm, pK²⁵ 5.96. Crystd from glacial acetic acid. It is yellow at pH 4.8 and violet at pH 6.7.

4-Chlorophenoxyacetic acid [122-88-3] M 186.6, m 157°, pK²⁰ 3.00. Crystd from EtOH.

α-4-Chlorophenoxypropionic acid [3307-39-9] M 200.6, m 116°, pK_{Est} ~3.2. Crystd from EtOH.

β-4-Chlorophenoxypropionic acid [3284-79-5] M 200.6, m 138°, pK_{Est} ~4.2. Crystd from EtOH.

3-Chlorophenylacetic acid [1878-65-5] M 170.6, m 74°, pK²⁵ 4.11. Crystd from EtOH/water, or as needles from *C₆H₆ or H₂O (charcoal). The *acid chloride* (prepared by boiling with SOCl₂) has b 127-129°/15mm. [Dippy and Williams *J Chem Soc* 161 1934; Misra and Shukla *J Indian Chem Soc* 28 480 1951.]

4-Chlorophenylacetic acid [1878-66-6] M 170.6, m 105°, 106°, pK²⁵ 4.12. Same as for 3-chlorophenylacetic acid.

4-Chloro-1-phenylbutan-1-one [939-52-6] M 182.7, m 19-20°, b 134-137°/5mm, d₄²⁰ 1.149, n_D²⁰ 1.55413. Fractionate several times using a short column. It can be recrystd from anhydrous pet ether at -20° as glistening white rosettes and filtered at 0° and dried in a vacuum desiccator over H₂SO₄. The *semicarbazone* has m 136-137°. [*J Am Chem Soc* 46 1882 1924, 51 1174 1929, Hart and Curtis *J Am Chem Soc* 79 931 1957.]

1-(2-Chlorophenyl)-1-(4-chlorophenyl)-2,2-dichloroethane (Mitotane, *o,p'*-DDD) [53-19-0] M 320.1, m 75.8-76.8°, 76-78°. Purified by recrystallisation from pentane and from MeOH or EtOH. It is sol in isooctane and CCl₄. [Haller et al. *J Am Chem Soc* 67 1600 1945.]

3-(4-Chlorophenyl)-1,1-dimethylurea (monuron) [150-68-5] M 198.7, m 171°. Crystd from MeOH.