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L-Lysine *[56-87-1]* **M 146.2, m >210°(dec), pK_1 2.18, pK_2 8.95, pK_3 10.53.** Crystd from aqueous EtOH.

L-Lysine dihydrochloride *[657-26-1]* **M 219.1, m 193°, $[\alpha]_D^{25}$ +25.9° (5M HCl).** Crystd from MeOH, in the presence of excess HCl, by adding diethyl ether.

L-Lysine monohydrochloride *[657-27-2]* **M 182.7, [α] as above.** Likely impurities are arginine, D-lysine, 2,6-diaminoheptanedioic acid and glutamic acid. Crystd from water at pH 4-6 by adding 4 volumes of EtOH. Above 60% relative humidity it forms a dihydrate.

β-D-Lyxose *[1114-34-7]* **M 150.1, m 118-119°, $[\alpha]_D^{20}$ -14° (c 4, H_2O).** Crystd from EtOH or aqueous 80% EtOH. Dried under vacuum at 60°, and stored in a vacuum desiccator over P_2O_5 or $CaSO_4$.

Malachite Green (carbinol) *[510-13-4]* **M 346.4, m 112-114°, CI 42000, pK^{24} 6.84.** The oxalate was recrystd from hot water and dried in air. The carbinol was ppted from the oxalate (1g) in distd water (100mL) by adding M NaOH (10mL). The ppte was filtered off, recrystd from 95% EtOH containing a little dissolved KOH, then washed with ether, and crystd from pet ether. Dried in a vacuum at 40°. An acid soln (2 x 10^{-5}M in 6 x 10^{-5}M H_2SO_4) rapidly reverted to the dye. [Swain and Hedberg *J Am Chem Soc* **72** 3373 *1950*.]

Z-Maleamic acid (*cis*-maleic acid monoamide) *[557-24-4]* **M 115.1, m 158-161°, 172-173°(dec), pK_{Est} ~2.65.** Crystd from EtOH. **IRRITANT.**

Maleic acid *[110-16-7]* **M 116.1, m 143.5°, pK_1^{25} 1.91, pK_2^{25} 6.33.** Crystd from acetone/pet ether (b 60-80°) or hot water. Dried at 100°.

Maleic anhydride *[108-31-6]* **M 98.1, m 54°, b 94-96°/20mm, 199°/760mm.** Crystd from *benzene, $CHCl_3$, CH_2Cl_2 or CCl_4. Sublimed under reduced pressure. [Skell et al. *J Am Chem Soc* **108** 6300 *1986*.]

Maleic hydrazide *[123-33-1]* **M 112.1, m 144°(dec), pK_1^{25} 5.67, pK_2^{25} 13.3.** Crystd from water.

Maleimide (pyrrol-2,5-dione) *[541-59-3]* **M 97.1, m 91-93°, 92.6-93°, $d_D^{105.5}$ 1.2493, $n_D^{110.7}$ 1.49256.** Purified by sublimation in a vacuum. The UV has λ_{max} at 216 and 280nm in EtOH. [de Wolf and van de Straete *Bull Soc Chim Belg* **44** 288 *1935*; UV: Rondestvedt et al. *J Am Chem Soc* **78** 6115 *1956*; IR: Chiorboli and Mirone *Ann Chim (Rome)* **42** 681 *1952*.]

Maleuric acid *[105-61-3]* **M 158.1, m 167-168°(dec).** Crystd from hot water.

***dl*-Malic acid** *[617-48-1 and 6915-15-7]* **M 134.1, m 128-129°.** Crystd from acetone, then from acetone/CCl_4, or from ethyl acetate by adding pet ether (b 60-70°). Dried at 35° under 1mm pressure to avoid formation of the anhydride.

L-Malic acid *[97-67-6]* **M 134.1, m 104.5-106°, $[\alpha]_D^{20}$ -2.3° (c 8.5, H_2O), pK_1^{25} 3.46, pK_2^{25} 5.10.** Crystd (charcoal) from ethyl acetate/pet ether (b 55-56°), keeping the temperature below 65°. Or, dissolved by refluxing in fifteen parts of anhydrous diethyl ether, decanted, concentrated to one-third volume and crystd at 0°, repeatedly to constant melting point.

Malonamide *[108-13-4]* **M 102.1, m 170°.** Crystd from water.

Malonic acid *[141-82-2]* **M 104.1, m 136°, pK_1^{25} 2.58, pK_2^{25} 5.69.** Crystd from *benzene/diethyl ether (1:1) containing 5% of pet ether (b 60-80°), washed with diethyl ether, then recrystd from H_2O or acetone. Dried under vac over conc H_2SO_4.

Malononitrile *[109-77-3]* **M 66.1, m 32-34°, b 109°/20mm, 113-118°/25mm, 220°/760mm.** Crystd from water, EtOH, *benzene or chloroform. Distd in a vacuum from, and stored over, P_2O_5. [Bernasconi et al. *J Am Chem Soc* **107** 7692 *1985*; Gratenhuis *J Am Chem Soc* **109** 8044 *1987*].

Maltol (3-hydroxy-2-methyl-4-pyrone) *[118-71-8]* **M 126.1, m 161-162°.** Crystd from $CHCl_3$ or aqueous 50% EtOH. Volatile in steam. It can be readily sublimed in a vacuum.

Maltose (H_2O) *[6363-53-7]* **M 360.3, m 118°.** Purified by chromatography from aqueous soln on to a charcoal/Celite (1:1) column, washed with water to remove glucose and other monosaccharides, then eluted with aqueous 75% EtOH. Crystd from water, aqueous EtOH or EtOH containing 1% nitric acid. Dried as the monohydrate at room temperature under vacuum over H_2SO_4 or P_2O_5.

Mandelic acid (α-hydroxyphenylacetic acid) *[S-(+)- 17199-29-0; R-(-)- 611-71-2]* **M 152.2, m 130-133°, 133°, 133.1° (evacuated capillary), 133-133.5°, $[\alpha]_{546}^{20}$ (+) and (-) 188° (c 5, H_2O), $[\alpha]_D^{20}$ (+) and (-) 155° (c 5, H_2O) and (+) and (-) 158° (c 5, Me_2CO), pK^{25} 3.41.** Purified by recrystn from H_2O, *C_6H_6 or $CHCl_3$. [Roger *J Chem Soc* 2168 *1932*; Jamison and Turner *J Chem Soc* 611 *1942*.] They have solubilities in H_2O of *ca* 11% at 25°. [Banks and Davies *J Chem Soc* 73 *1938*.] The *S-benzylisothiuronium salt* has **m** 180° (from H_2O) and $[\alpha]_D^{25}$ (+) and (-) 57° (c 20, EtOH) [El Masri et al. *Biochem J* **68** 199 *1958*].

***RS*-(±)-Mandelic acid** *[61-72-3]* **M 152.2, m 118°, 120-121°.** Purified by Soxhlet extraction with *benzene (about 6mL/g), allowing the extract to crystallise. Also crystallises from $CHCl_3$. The *S-benzylisothiuronium salt* has **m** 169° (166°) (from H_2O). Dry at room temperature under vacuum.

D-Mannitol *[69-65-8]* **M 182.2, m 166.1°, $[\alpha]_{546}^{20}$ + 29° (c 10, after 1h in 8% borax soln).** Crystd from EtOH or distilled water and dried at 100°.

Mannitol hexanitrate *[15825-70-4]* **M 452.2, m 112-113°.** Crystd from EtOH. **EXPLOSIVE (on detonation).**

α-D-Mannose *[3458-28-4]* **M 180.2, m 132°, $[\alpha]_D^{20}$ +14.1° (c 4, H_2O).** Crystd repeatedly from EtOH or aq 80% EtOH, then dried under vacuum over P_2O_5 at 60°.

Meconic acid (3-hydroxy-γ-pyrone-2,6-dicarboxylic acid) *[497-59-6]* **M 200.1, m 100° (loses H_2O), pK_1^{25} 1.83, pK_2^{25} 2.3, pK_3^{25} 10.10.** Crystd from water and dried at 100° for 20min.

Melamine (2,4,6-triamino-1,3,5-triazine) *[108-78-1]* **M 126.1, m 353°, pK^{25} 5.00.** Crystd from water or dilute aqueous NaOH.

D(+)-Melezitose (H_2O) *[597-12-6]* **M 540.5, m 153-154°(dec), $2H_2O$ m 160°(dec), $[\alpha]_D^{20}$ +88° (c 4, H_2O).** Crystallises from water as the dihydrate, then dried at 110° (anhydrous).

D(+)-Melibiose ($2H_2O$) *[585-99-9, 66009-10-7]* **M 360.3, m 84-85°, $[\alpha]_D^{20}$+135° (c 5, after 10h H_2O).** Crystallises as a hydrate from water or aqueous EtOH.

(±)-Mellein [(±)-3,4-dihydro-8-hydroxy-3-methyl-2-benzopyran-1-one] *[1200-93-7]* **M 178.2, m 37-39°, 39°, pK_{Est} ~9.5.** Purified by recrystn from aqueous EtOH. It has UV max at 247 and 314nm. [Arakawa et al. *Justus Liebigs Ann Chem* 728 152 *1969*; Blair and Newbold *Chem Ind (London)* 93 *1955*, *J Chem Soc* 2871 *1955*.] The *methyl ether* has **m** 66-67° and UV: λmax 242nm (ε 7,400) and 305nm (ε 4,600).

Melphalan (4-[bis-{2-chloroethyl}amino]-L-phenylalanine) *[148-82-3]* **M 305.2, m 182-183° (dec), 183-185°, $[\alpha]_D^{25}$ +7.5° (c 1.33, 1.0 N HCl), $[\alpha]_D^{20}$ -28° (c 0.8, MeOH), pK_{Est} ~6.4.** Purified by recrystn from MeOH and its solubility is 5% in 95% EtOH containing one drop of 6N HCl.

It is soluble in EtOH and propylene glycol but is almost insoluble in H_2O. The *RS-form* has **m** 180-181° and the *R-form* crystallises from MeOH with a **m** 181.5-182° and $[\alpha]_D^{21}$ -7.5° (c 1.26, 1.0 N HCl). [Bergel and Stock *J Chem Soc* 2409 *1954*.]

(-)-Menthol *[2216-51-5]* **M 156.3, m 44-46.5°, $[\alpha]_D$ 50° (c 10, EtOH).** Crystd from $CHCl_3$, pet ether or EtOH/water.

1*R*-(-)-Menthyl chloride (1*S*,2*R*,4*R*-2-chloro-1-isopropyl-1-methylcyclohexane) *[16052-42-9]* **M 174.7, m -20.1° to -16.5°, b 88.5°/12.5mm, 101-105°/21mm, d_D^{20} 0.936, n_D^{20} 1.463(neat).** Dissolve in pet ether (b 40-60°), wash with H_2O, conc H_2SO_4 until no discoloration of the organic layer occurs (care with the use of conc H_2SO_4 during shaking in a separating funnel), again with H_2O and dry over $MgSO_4$. Evaporate the pet ether and dist the residual oil through a Claisen head with a Vigreux neck (head) of *ca* 40 cm length. [Smith and Wright *J Org Chem* **17** 1116 *1952*; Barton et al. *J Chem Soc* 453 *1952*.]

Meprobamate [2,2-di(carbamoyloxymethyl)pentane] *[57-53-4]* **M 246.3, m 104-106°.** Crystd from hot water. Could be an addictive drug.

2-Mercaptobenzimidazole *[583-39-1]* **M 150.2, m 302-304°, 312°, pK^{20} 10.24.** Crystd from aq EtOH, AcOH or aq ammonia.

2-Mercaptobenzothiazole *[149-30-4]* **M 167.2, m 182°, pK^{25} 7.5 (50% aq AcOH).** Crystd repeatedly from 95% EtOH, or purified by incomplete pptn by dilute H_2SO_4 from a basic soln, followed by several crystns from acetone/H_2O or *benzene. Complexes with Ag, Au, Bi, Cd, Hg, Ir, Pt, and Tl.

2-Mercaptoethanol *[60-24-2]* **M 78.1, b 44°/4mm, 53.5°/10mm, 58°/12mm, 68°/20mm, 78.5°/40mm, 96-97° (92°)/100mm, 157°/748mm, d_4^{20} 1.114, n_D^{20} 1.500, pK^{25} 9.72 (9.43).** Purified by distn in a vacuum. Distn at atmospheric pressure causes some oxidation and should be done in an inert atmosphere. [Woodward *J Chem Soc* 1892 *1948*.] **It has a foul odour, is irritating to the eyes, nose and skin — should be handled in an efficient fume cupboard.** It is miscible with H_2O, EtOH, Et_2O and *C_6H_6 and has a UV max at 235nm. The *2,4-dinitrophenyl thioether* has **m** 101-102°(from EtOH or aq MeOH) [Grogen et al. *J Org Chem* **20** 50 *1955*].

2-Mercaptoethylamine *[60-23-1]* **M 77.2.** See cysteamine p. 525 in Chapter 6.

2-Mercaptoimidazole *[872-35-5]* **M 100.1, m 221-222°, pK_1^{20} -1.6, pK_2^{20} 11.6.** Crystd from H_2O.

2-Mercapto-1-methylimidazole *[60-56-0]* **M 114.2, m 145-147°, pK_1^{20} -2.0, pK_2^{20} 11.9.** Crystd from EtOH.

6-Mercaptopurine (H_2O) *[6112-76-1]* **M 170.2, m >315°(dec), pK_1^{20} 0.5, pK_2^{20} 7.77, pK_3^{20} 10.8.** Crystd from pyridine (30mL/g), washed with pyridine, then triturated with water (25mL/g), adjusting to pH 5 by adding M HCl. Recrystd by heating, then cooling, the soln. Filtered, washed with water and dried at 110°. Has also been crystd from water (charcoal).

8-Mercaptoquinoline ($2H_2O$, thioxine) *[491-33-8]* **M 197.3, m 58-59°, pK_1^{25} 2.0, pK_2^{25} 8.40.** Easily oxidised in air to give diquinolyl-8,8'-disulfide (which is stable). It is more convenient to make 8-mercaptoquinoline by reduction of the material. [Nakamura and Sekido *Talanta* **17** 515 *1970*.]

Mesaconic acid (methylfumaric acid) *[498-24-8]* **M 130.1, m 204-205°, pK^{18} 4.82.** Crystd from water or EtOH [Katakis et al. *J Chem Soc, Dalton Trans* 1491 *1986*].

Mescaline sulfate [2-(3,4,5-trimethoxyphenyl)ethylamine sulfate] *[5967-42-0]* **M 309.3, m 183-184°, pK_{Est} ~9.7.** Crystd from water.

Mesitylene (1,3,5-trimethylbenzene) *[108-67-8]* **M 120.2, m -44.7°, b 99.0-99.8°/100mm, 166.5-167°/760mm, n^{25} 1.4967, d 0.865.** Dried with $CaCl_2$ and distd from Na in a glass helices packed column. Treated with silica gel and redistd. Alternative purifications include vapour-phase chromatography, or fractional distn followed by azeotropic distn with 2-methoxyethanol (which is subsequently washed out with H_2O), drying and fractional distn. More exhaustive purification uses sulfonation by dissolving in two volumes of conc H_2SO_4, precipitating with four volumes of conc HCl at 0°, washing with conc HCl and recrystallising from $CHCl_3$. The mesitylene sulfonic acid is hydrolysed with boiling 20% HCl and steam distd. The separated mesitylene is dried ($MgSO_4$ or $CaSO_4$) and distilled. It can also be fractionally crystd from the melt at low temperatures.

Mesityl oxide *[141-79-7]* **M 98.2, b 112°/760mm, n^{24} 1.4412, d 0.854, pK^{20} -5.36 (H$_0$ scale, aq H_2SO_4).** Purified *via* the *semicarbazone* (**m** 165°). [Erskine and Waight *J Chem Soc* 3425 *1960.*]

Metalphthalein (H_2O) (*o*-cresolcomplexon) *[2411-89-4]* **M 636.6, m 186°(dec).** See *o*-cresolphthalein complexone on p. 173.

Metanilic acid (3-aminobenzenesulfonic acid) *[121-47-1]* **M 173.2, m <300°(dec), pK$_1^{25}$ < 1, pK$_2^{25}$ 3.74.** Crystd from water (as the hydrate), under CO_2 in a semi-darkened room. (The soln is photosensitive.) Dried over 90% H_2SO_4 in a vac desiccator.

α-Methacraldehyde *[78-85-3]* **M 68.1, b 68.4°, d 0.849, n 1.416.** Fractionally distd under nitrogen through a short Vigreux column. Stored in sealed ampoules. (Slight polymerisation may occur.)

Methacrylamide *[79-39-0]* **M 85.1, m 111-112°.** Crystd from *benzene or ethyl acetate and dried under vacuum at room temperature.

Methacrylic acid *[79-41-4]* **M 86.1, b 72°/14mm, 160°/760mm, d 1.015, n 1.431, pK 4.65.** Aq methacrylic acid (90%) was satd with NaCl (to remove the bulk of the water), then the organic phase was dried with $CaCl_2$ and distd under vacuum. Polymerisation inhibitors include 0.25% *p*-methoxyphenol, 0.1% hydroquinone, or 0.05% *N,N'*-diphenyl-*p*-phenylenediamine.

Methacrylic anhydride *[760-93-0]* **M 154.2, b 65°/2mm, d 1.040, n 1.454.** Distd at 2mm pressure, immediately before use, in the presence of hydroquinone.

Methacrylonitrile *[126-98-7]* **M 67.1, b 90.3°, d 0.800, n 1.4007, n^{30} 1.3954.** Washed (to remove inhibitors such as *p-tert*-butylcatechol) with satd aq $NaHSO_3$, 1% NaOH in saturated NaCl and then with saturated NaCl. Dried with $CaCl_2$ and fractionally distd under nitrogen to separate from impurities such as methacrolein and acetone.

Methane *[74-82-8]* **M 16.0, m -184°, b -164°/760mm, -130°/6.7atm, d^{-164} 0.466 (air 1).** Dried by passage over $CaCl_2$ and P_2O_5, then passed through a Dry-ice trap and fractionally distd from a liquid-nitrogen trap. Oxygen can be removed by prior passage in a stream of hydrogen over reduced copper oxide at 500°, and higher hydrocarbons can be removed by chlorinating about 10% of the sample: the hydrocarbons, chlorides and HCl are readily separated from the methane by condensing the sample in the liquid-nitrogen trap and fractionally distilling it. Methane has also been washed with conc H_2SO_4, then solid NaOH and then 30% NaOH soln. It was dried with $CaCl_2$, then P_2O_5, and condensed in a trap at liquid air temp, then transferred to another trap cooled in liquid nitrogen. CO_2, O_2, N_2 and higher hydrocarbons can be removed from methane by adsorption on charcoal. [Eiseman and Potter *J Res Nat Bur Stand* **58** 213 *1957.*] **HIGHLY FLAMMABLE.**

Methanesulfonic acid *[76-75-2]* **M 96.1, m 20°, b 134.5-135°/3mm, d 1.483, n 1.432, pK^{25} -1.86 (-1.2).** Dried, either by azeotropic removal of water with *benzene or toluene, or by stirring 20g of P_2O_5 with 500mL of the acid at 100° for 0.5h. Then distd under vacuum and fractionally crystd by partial freezing. Sulfuric acid, if present, can be removed by prior addition of $Ba(OH)_2$ to a dilute soln, filtering off the $BaSO_4$ and concentrating under reduced pressure, and is sufficiently pure for most applications.

Methanesulfonyl chloride *[124-63-0]* **M 114.5. b 55°/11mmm, d 1.474, n 1.452.** Distd from P_2O_5 under vacuum.

Methanol *[67-56-1]* **M 32.0, b 64.5°, d^{15} 0.79609, d^{25} 1.32663, n^{15} 1.33057, n^{25} 1.32663, pK^{25} 15.5.** Almost all methanol is now obtained synthetically. Likely impurities are water, acetone, formaldehyde, ethanol, methyl formate and traces of dimethyl ether, methylal, methyl acetate, acetaldehyde, carbon dioxide and ammonia. Most of the water (down to about 0.01%) can be removed by fractional distn. Drying with CaO is unnecessary and wasteful. Anhydrous methanol can be obtained from "absolute" material by passage through Linde type 4A molecular sieves, or by drying with CaH_2, $CaSO_4$, or with just a little more sodium than required to react with the water present; in all cases the methanol is then distd. Two treatments with sodium reduces the water content to about 5 x 10^{-5}%. [Friedman, Gill and Doty *J Am Chem Soc* **83** 4050 *1961*.] Lund and Bjerrum [*Chem Ber* **64** 210 *1931*] warmed clean dry magnesium turnings (5g) and iodine (0.5g) with 50-75mL of "absolute" methanol in a flask until the iodine disappeared and all the magnesium was converted to methoxide. Up to 1L of methanol was added and, after refluxing for 2-3h, it was distd off, excluding moisture from the system. Redistn from tribromobenzoic acid removes basic impurities and traces of magnesium oxides, and leaves conductivity-quality material. The method of Hartley and Raikes [*J Chem Soc* **127** 524 *1925*] gives a slightly better product. This consists of an initial fractional distn, followed by distn from aluminium methoxide, and then ammonia and other volatile impurities are removed by refluxing for 6h with freshly dehydrated $CuSO_4$ (2g/L) while dry air is passed through: the methanol is finally distd. (The aluminium methoxide is prepared by warming with aluminium amalgam (3g/L) until all the aluminium has reacted. The amalgam is obtained by warming pieces of sheet aluminium with a soln of $HgCl_2$ in dry methanol). This treatment also removes aldehydes.

If acetone is present in the methanol, it is usually removed prior to drying. Bates, Mullaly and Hartley [*J Chem Soc* 401 *1923*] dissolved 25g of iodine in 1L of methanol and then poured the soln, with constant stirring, into 500mL of M NaOH. Addition of 150mL of water ppted iodoform. The soln was stood overnight, filtered, then boiled under reflux until the odour of iodoform disappeared, and fractionally distd. (This treatment also removes formaldehyde.) Morton and Mark [*Ind Eng Chem (Anal Edn)* **6** 151 *1934*] refluxed methanol (1L) with furfural (50mL) and 10% NaOH soln (120mL) for 6-12h, the refluxing resin carrying down with it the acetone and other carbonyl-containing impurities. The alcohol was then fractionally distd. Evers and Knox [*J Am Chem Soc* **73** 1739 *1951*], after refluxing 4.5L of methanol for 24h with 50g of magnesium, distd off 4L of it, which they then refluxed with $AgNO_3$ for 24h in the absence of moisture or CO_2. The methanol was again distd, shaken for 24h with activated alumina before being filtered through a glass sinter and distd under nitrogen in an all-glass still. Material suitable for conductivity work was obtained.

Variations of the above methods have also been used. For example, a sodium hydroxide soln containing iodine has been added to methanol and, after standing for 1day, the soln has been poured slowly into about a quarter of its volume of 10% $AgNO_3$, shaken for several hours, then distd. Sulfanilic acid has been used instead of tribromobenzoic acid in Lund and Bjerrum's method. A soln of 15g of magnesium in 500mL of methanol has been heated under reflux, under nitrogen, with hydroquinone (30g), before degassing and distilling the methanol, which was subsequently stored with magnesium (2g) and hydroquinone (4g per 100mL). Refluxing for about 12h removes the bulk of the formaldehyde from methanol: further purification has been obtained by subsequent distn, refluxing for 12h with dinitrophenylhydrazine (5g) and H_2SO_4 (2g/L), and again fractionally distilling.

Rapid purification: Methanol purification is the same as for Ethanol.

Another simple purification procedure consists of adding 2g of $NaBH_4$ to 1.5L methanol, gently bubbling with argon and refluxing for a day at 30°, then adding 2g of freshly cut sodium (washed with methanol) and refluxing for 1day before distilling. The middle fraction is taken. [Jou and Freeman *J Phys Chem* **81** 909 *1977*.]

***dl*-Methionine (*RS*-α-aminohexanoic acid)** *[59-51-8]* **M 149.2, m 281°(dec).** Crystd from hot water.

L-Methionine *[63-68-3]* **M 149.2, m 283°(dec), $[\alpha]_D^{25}$ +21.2° (0.2M HCl) pK_1^{25} 2.13, pK_2^{25} 9.73.** Crystd from aqueous EtOH.

***dl*-Methionine sulfoxide** *[454-41-1, 62697-73-8]* **M 165.2, m >240°(dec).** Likely impurities are *dl*-methionine sulfone and *dl*-methionine. Crystd from water by adding EtOH in excess.

Methoxyacetic acid *[625-45-6]* **M 90.1, b 97°/13-14mm, d 1.175, n 1.417, pK^{25} 3.57.** Fractionally crystd by repeated partial freezing, then fractionally distd under vacuum through a vacuum-jacketed Vigreux column 20cm long.

***p*-Methoxyacetophenone** *[100-06-1]* **M 150.2, m 39°, b 139°/15mm, 264°/736mm.** Crystd from diethyl ether/pet ether.

Methoxyamine hydrochloride *[593-56-6]* **M 83.5, m 151-152°, pK^{25} 4.60.** Crystd from absolute EtOH or EtOH by addition of diethyl ether. [Kovach et al. *J Am Chem Soc* **107** 7360 *1985*.]

***p*-Methoxyazobenzene** *[2396-60-3]* **M 212.3, m 54-56°.** Crystd from EtOH.

3-Methoxybenzanthrone *[3688-79-7]* **M 274.3, m 173°.** Crystd from *benzene, EtOH or Me$_2$CO as yellow needles.

***m*-Methoxybenzoic acid (*m*-anisic acid)** *[586-38-9]* **M 152.2, m 110°, pK^{25} 4.09.** Crystd from EtOH/water.

***p*-Methoxybenzoic acid (*p*-anisic acid)** *[100-09-4]* **M 152.2, m 184.0-184.5°, pK^{25} 4.51.** Crystd from EtOH, water, EtOH/water or toluene.

4-Methoxybenzyl chloride (anisyl chloride) *[824-94-2]* **M 156.6, m -1°, b 76°/0.1mm, 95°/5mm, 110°/10mm, 117-117/5°/14mm, 117°/18mm, d$_4^{20}$ 1.15491, n$_D^{20}$ 1.55478.** Purified by fractional distn under vacuum and the middle fraction is redistd at 10^{-6} mm at room temperature by intermittent cooling of the receiver in liquid N_2, and the middle fraction is collected. [Mohammed and Kosower *J Am Chem Soc* **93** 2709 *1971*.]

3-Methoxycarbonyl-2,5-dihydrothiophen-1,1-dioxide *[67488-50-0]* **M 176.1, m 57-58°, 60-62°.** If IR show CO bands then dissolve in $CHCl_2$, wash with aqueous Na_2CO_3 and H_2O, dry over $MgSO_4$, filter, evaporate and wash the residue with cold Et_2O and dry *in vacuo*. NMR ($CDCl_3$): δ 7.00 (m 1H), 3.98 (bs 4H) and 3.80 (s Me). [Mcintoch and Sieber *J Org Chem* **43** 4431 *1978*.]

"Methoxychlor", 1,1-Bis(*p*-methoxyphenyl)-2,2,2-trichloroethane (dimorphic) *[72-43-5]* **M 345.7, m 78-78.2°, or 86-88°.** Freed from 1,1-bis(*p*-chlorophenyl)-2,2,2-trichloroethane by crystn from EtOH.

***trans-p*-Methoxycinnamic acid** *[830-09-1, 943-89-5 (trans)]* **M 178.2, m 173.4-174.8°, pK^{25} 4.54.** Crystd from MeOH to constant melting point and UV spectrum.

2-Methoxyethanol (methylcellosolve) *[109-86-4]* **M 76.1, b 124.4°, d 0.964, n 1.4017, pK^{25} 14.8.** Peroxides can be removed by refluxing with stannous chloride or by filtration under slight pressure through a column of activated alumina. 2-Methoxyethanol can be dried with K_2CO_3, $CaSO_4$, $MgSO_4$ or silica gel, with a final distn from sodium. Aliphatic ketones (and water) can be removed by making the solvent 0.1% in 2,4-dinitrophenylhydrazine and allowing to stand overnight with silica gel before fractionally distilling.

2-Methoxyethoxymethylchloride (MEMCl) *[3970-21-6]* **M 124.6, b 50-52°/13mm, 140-145°(dec)/atm, d 1.092, n 1.427.** Possible impurites are methoxyethanol (**b** 124°/atm), HCHO and HCl which can be removed below the **b** of MEMCl. Purify by fractional distn in a vacuum. If too impure, prepare from methoxyethanol (152g) and *s*-trioxane (66g) by bubbling a stream of dry HCl (with stirring) until a clear mixt is obtained. Dilute with pentane (900mL), dry (3h over 100g $MgSO_4$, at 5°), evaporate and the residue is distd in a vac. It is MOISTURE SENSITIVE and **TOXIC.** The *MEM.NEt$_3^+$Cl$^-$* salt, prepared by reactn with

1.3 equivs of Et_3N (16h/25°) and dried in vac has **m** 58-61°, and is moisture sensitive. [Corey et al. *Tetrahedron Lett* 809 *1976*.]

β-Methoxyethylamine *[109-85-3]* **M 75.1, b 94°, d 0.874, n 1.407, pK^{25} 9.40.** An aqueous 70% soln was dehydrated by azeotropic distn with *benzene or methylene chloride and the amine was distilled twice from zinc dust. Store in a tight container as it absorbs CO_2 from the atmosphere.

6-Methoxy-1-indanone *[13623-25-1]* **M 162.2, m 151-153°.** Crystd from MeOH, then sublimed in a high vacuum.

5-Methoxyindole *[1006-94-6]* **M 147.2, m 55°, 57°, b 176-178°/17mm, pK$_{Est}$ ~0.** Crystd from cyclohexane pet ether or pet ether/Et_2O.

1-Methoxynaphthalene *[2216-69-5]* **M 158.2, b 268.4-268.5°.** See methyl 1-naphthyl ether on p. 295.

2-Methoxynaphthalene *[93-04-9]* **M 158.2, m 73.0-73.6°, b 273°/760mm.** Fractionally distd under vacuum. Crystd from absolute EtOH, aqueous EtOH, *benzene or *n*-heptane, and dried under vacuum in an Abderhalden pistol or distd *in vacuo*. [Kikuchi et al. *J Phys Chem* **91** 574 *1987*.]

1-Methoxy-4-nitronaphthalene *[4900-63-4]* **M 203.2, m 85°.** Purified by chromatography on silica gel and recrystd from MeOH. [Bunce et al. *J Org Chem* **52** 4214 *1987*.]

***p*-Methoxyphenol** *[150-76-5]* **M 124.1, m 54-55°, b 243°, pK^{25} 10.21.** Crystd from *benzene, pet ether or H_2O, and dried under vacuum over P_2O_5 at room temp. Sublimes *in vacuo*. [Wolfenden et al. *J Am Chem Soc* **109** 463 *1987*.]

α-Methoxyphenylacetic acid (*O*-methyl mandelic acid), *[R-(-)- 3966-32-3; S-(+)- 26164-26-1]* **M 166.2, m 62.9°, 62-65°, 65-66°, $[\alpha]^{20}_{546}$ (-) and (+) 179° (169.8°), $[\alpha]^{20}_D$ (-) and (+) 150.7° (148°) (c 0.5, EtOH), pK$_{Est}$ ~3.1.** Purified by recrystn from $*C_6H_6$-pet ether (b 80-100°). [Neilson and Peters *J Chem Soc* 1519 *1962*; Weizmann et al. *J Am Chem Soc* **70** 1153 *1948*; Pirie and Smith *J Chem Soc* 338 *1932*; NMR: Dale and Mosher *J Am Chem Soc* **95** 512 *1973*; for resolution: Roy and Deslongchamps *Can J Chem* **63** 651 *1985;* Trost et al. *J Am Chem Soc* **108** 4974 *1986*.] The *racemic mixture* has **m** 72°, **b** 121-122°/0.4mm, 165°/18mm (from pet ether) [Braun et al. *Chem Ber* **63** 2847 *1930*].

***o*-Methoxyphenylacetic acid** *[93-25-4]* **M 166.2, m 71.0-71.2°, pK$_{Est}$ ~4.4.** Crystd from H_2O, EtOH or aq EtOH and dried in a vacuum desiccator over Sicapent.

***m*-Methoxyphenylacetic acid** *[1798-09-0]* **M 166.2, m 71.0-71.2°, pK$_{Est}$ ~4.3.** Crystd from H_2O, or aq EtOH.

***p*-Methoxyphenylacetic acid** *[104-01-8]* **M 166.2, m 85-87°, pK^{25} 4.36.** Crystd from EtOH/water.

5-(*p*-Methoxyphenyl)-1,2-dithiole-3-thione *[42766-10-9]* **M 240.2, m 111°.** Crystd from butyl acetate.

***N*-(*p*-Methoxyphenyl)-*p*-phenylenediamine** *[101-64-4]* **M 214.3, m 102°, b 238°/12mm, pK 6.6 (5.9).** Crystd from ligroin.

8-Methoxypsoralen see xanthotoxin p. 577 in Chapter 6.

α-Methoxy-α-trifluoromethylphenylacetic acid (MTPA, Mosher's acid) *[R-(+)- 20445-31-2; S-(-)- 17257-71-5]* **M 234.2, m 43-45°, 90°/0.1mm, 105-107°/1mm, $[\alpha]^{20}_{546}$ (+) and (-) 87°, $[\alpha]^{20}_D$ (+) and (-) 73° (c 2, MeOH), pK$_{Est}$ ~2.5.** A likely impurity is phenylethylamine from the resolution. Dissolve acid in ether-*benzene (3:1), wash with 0.5N H_2SO_4, then water, dry over magnesium sulfate, filter, evaporate and distil. [Dale et al. *J Org Chem* **34** 2543 *1969, J Am Chem Soc* **75** 512 *1973.*]

α-Methoxy-α-trifluoromethylphenylacetyl chloride *[R-(-)- 39637-99-5; S-(+)- 20445-33-4]* **M 252.6, b 54-56°/1mm, 213-214°/atm, d_4^{20} 1.353, n_D^{20} 1.468, $[\alpha]_{546}^{20}$ (-) and (+) 167°, $[\alpha]_D^{20}$ (-) and (+) 137° (c 4, CCl_4), $[\alpha]_D^{24}$ (-) and (+)10.0° (neat).** The most likely impurity is the free acid due to hydrolysis and should be checked by IR. If free from acid then distil taking care to keep moisture out of the apparatus. Otherwise add $SOCl_2$ and reflux for 50h and distil. Note that shorter reflux times resulted in a higher boiling fraction (**b** 130-155°/1mm) which has been identified as the anhydride. [Dale et al. *J Org Chem* **34** 2543 *1969*; for enantiomeric purity see *J Am Chem Soc* **97** 512 *1973.*]

***N*-Methylacetamide** *[79-16-3]* **M 73.1, m 30°, b 70-71°/2.5-3mm, pK_1^{25} -3.70, pK_2^{25} -0.42.** Fractionally distd under vacuum, then fractionally crystd twice from its melt. Impurities include acetic acid, methyl amine and H_2O. For detailed purification procedure, see Knecht and Kolthoff, *Inorg Chem* **1** 195 *1962.* Although *N*-methylacetamide is commercially available it is often extensively contaminated with acetic acid, methylamine, water and an unidentified impurity. The recommended procedure is to synthesise it in the laboratory by direct reaction. The gaseous amine is passed into hot glacial acetic acid, to give a partially aq soln of methylammonium acetate which is heated to *ca* 130° to expel water. Chemical methods of purificatn such as extractn by pet ether, treatment with H_2SO_4, K_2CO_3 or CaO can be used but are more laborious.
Tests for purity include the Karl Fischer titration for water; this can be applied directly. Acetic acid and methylamine can be detected polarographically.
In addition to the above, purification of *N*-methylacetamide can be achieved by fractional freezing, including zone melting, repeated many times, or by chemical treatment with vacuum distn under reduced pressures. For details of zone melting techniques, see Knecht in *Recommended Methods for Purification of Solvents and Tests for Impurities*, Coetzee Ed. Pergamon Press *1982.*

***N*-Methylacetanilide** *[579-10-2]* **M 149.2, m 102-104°.** Crystd from water, ether or pet ether (b 80-100°).

Methyl acetate *[79-20-9]* **M 74.1, b 56.7-57.2°, d 0.934. n 1.36193, n^{25} 1.3538, pK^{20} -7.28 (H_0 scale, aq H_2SO_4).** Methanol in methyl acetate can be detected by measuring solubility in water. At 20°, the solubility of methyl acetate in water is *ca* 35g per 100mL, but 1% MeOH confers miscibility. Methanol can be removed by conversion to methyl acetate, using refluxing for 6h with acetic anhydride (85mL/L), followed by fractional distn. Acidic impurities can be removed by shaking with anhydrous K_2CO_3 and distilling. An alternative treatment is with acetyl chloride, followed by washing with conc NaCl and drying with CaO or $MgSO_4$. (Solid $CaCl_2$ cannot be used because it forms a crystalline addition compound.) Distn from copper stearate destroys peroxides. Free alcohol or acid can be eliminated from methyl acetate by shaking with strong aq Na_2CO_3 or K_2CO_3 (three times), then with aq 50% $CaCl_2$ (three times), satd aq NaCl (twice), drying with K_2CO_3 and distn from P_2O_5.

Methyl acetimidate hydrochloride *[14777-27-6]* **M 109.6, m 93-95°, 105°(dec), pK_{Est} ~ 5.5.** Crystd from methanol by adding dry ether to a ratio of 1:1 and cooled at 0°. Filter off the crystals in a cold room, wash with methanol/ether (1:2), then dry in a vacuum. [Hunter and Ludwig *J Am Chem Soc* **84** 3491 *1962.*] The *free base* has **b** 90-91°/765mm, **d** 0.867, **n** 1.403 [Hunter and Ludwig *Methods Enzymol* **25** 585 *1973.*]

***p*-Methylacetophenone** *[122-00-9]* **M 134.2, m 22-24°, b 93.5°/7mm, 110°/14mm, d 1.000, n 1.5335.** Impurities, including the *o*- and *m*-isomers, were removed by forming the semicarbazone which, after repeated crystn, was hydrolysed to the ketone. [Brown and Marino *J Am Chem Soc* **84** 1236 *1962.*] Also purified by distn under reduced pressure, followed by low temperature crystn from isopentane.

Methyl acrylate *[96-33-3]* **M 86.1, b 80°, d 0.9535, n 1.4040.** Washed repeatedly with aqueous NaOH until free from inhibitors (such as hydroquinone), then washed with distd water, dried ($CaCl_2$) and fractionally distd under reduced pressure in an all-glass apparatus. Sealed under nitrogen and stored at 0° in the dark. [Bamford and Han *J Chem Soc, Faraday Trans 1* **78** 855 *1982.*]

1-Methyladamantane *[768-91-2]* **M 150.2, m 103°.** Purified by zone melting and sublimes at 90-95°/12mm.

2-Methyladamantane *[700-56-1]* **M 150.2.** Purified by zone melting.

Methylamine (gas) *[74-89-5]* **M 31.1, b -7.55°/719mm, pK^{25} 10.62.** Dried with sodium or BaO.

Methylamine hydrochloride *[593-51-1]* **M 67.5, m 231.8-233.4°, b 225-230°/15mm, pK^{25} 10.62.** Crystd from *n*-butanol, absolute EtOH or MeOH/$CHCl_3$. Washed with $CHCl_3$ to remove traces of dimethylamine hydrochloride. Dried under vacuum first with H_2SO_4 then P_2O_5. Deliquescent, stored in a desiccator over P_2O_5.

1-Methylaminoanthraquinone *[82-38-2]* **M 237.3, m 166.5°, pK_{Est}~2.** Crystd to constant melting point from butan-1-ol, then crystd from EtOH. It can be sublimed under vacuum.

***N*-Methyl-*o*-aminobenzoic acid (*N*-methylanthranilic acid)** *[119-68-6]* **M 151.2, m 178.5°, pK_1^{25} 1.97, pK_2^{25} 5.34.** Crystd from water or EtOH.

***p*-Methylaminophenol sulfate** *[55-55-0]* **M 344.4, m 260°(dec), pK^{25} 5.9.** Crystd from MeOH.

6-Methylaminopurine *[443-72-1]* **M 149.2, m >300°, 312-314° (dec), pK_1^{20}<1, pK_2^{20} 4.15, pK_3^{20} 10.02.** Best purified by recrystallising 2g from 50mL of H_2O and 1.2g of charcoal. [UV: Albert and Brown *J Chem Soc* 2060 *1954*; UV: Mason *J Chem Soc* 2071 *1954*; see also Elion et al. *J Am Chem Soc* **74** 411 *1952*.] The *picrate* has **m** 265°(257°) [Bredereck et al. *Chem Ber* **81** 307 *1948*].

Methyl 3-aminopyrazine-2-carboxylate *[16298-03-6]* **M 153.1, m 169-172°, 172°.** Forms yellow needles from H_2O (100 parts using charcoal). If it contains the free acid then dissolve in CH_2Cl_2 wash with saturated aqueous Na_2CO_3, brine, dry over $MgSO_4$ filter, evaporate and recrystallise the residue. The *free acid* has **m** 203-204° (dec) [UV: Brown and Mason *J Chem Soc* 3443 *1956*] and pK_1 <1 and pK_2 3.70. The *ammonium salt* has **m** 232° (dec) (from aq Me_2CO) and the *amide* has **m** 239.2° (from H_2O) [Ellingson et al. *J Am Chem Soc* **67** 1711 *1945*].

***N*-Methylaniline** *[100-61-8]* **M 107.2, b 57°/4mm, 81-82°/14mm, d 0.985, n 1.570, pK^{25} 4.56.** Dried with KOH pellets and fractionally distd under vacuum. Acetylated and the acetyl derivative was recrystd to constant melting point (**m** 101-102°), then hydrolysed with aqueous HCl and distd from zinc dust under reduced pressure. [Hammond and Parks *J Am Chem Soc* **77** 340 *1955*.]

***N*-Methylaniline hydrochloride** *[2739-12-0]* **M 143.7, m 123.0-123.1°.** Crystd from dry *benzene/$CHCl_3$ and dried under vacuum.

Methyl *p*-anisate *[121-98-2]* **M 166.2, m 48°.** Crystd from EtOH.

4-Methyl anisole *[104-93-8]* **M 122.2, b 175-176°, d_{15}^{15} 0.9757, n 1.512.** Dissolved in diethyl ether, washed with M NaOH, water, dried (Na_2CO_3), evaporated and the residue distd under vacuum.

2-Methylanthracene *[613-12-7]* **M 192.3, m 204-206°** Chromatographed on silica gel with cyclohexane as eluent and recrystd from EtOH [Werst *J Am Chem Soc* **109** 32 *1987*].

4-Methylanthracene *[779-02-2]* **M 192.3, m 77-79°, b 196-197°/12mm, d 1.066.** Chromatographed on silica gel with cyclohexane as eluent and recrystd from EtOH [Werst *J Am Chem Soc* **109** 32 *1987*].

2-Methylanthraquinone *[84-54-8]* **M 222.3, m 176°.** Crystd from EtOH, then sublimed.

Methylarenes (see also pentamethyl- and hexamethyl- benzenes). Recrystd from EtOH and sublimed in vacuum [Schlesener et al. *J Am Chem Soc* **106** 7472 *1984*].

Methyl benzoate *[93-58-3]* **M 136.2, b 104-105°/39mm, 199.5°/760mm, d 1.087, n^{15} 1.52049, n 1.51701, pK^{20} -8.11, -6.51 (H$_0$ scale, aq H_2SO_4).** Washed with dilute aqueous $NaHCO_3$, then water, dried with Na_2SO_4 and fractionally distd under reduced pressure.

p-**Methylbenzophenone** *[134-84-9]* **M 196.3, m 57°.** Crystd from MeOH and pet ether.

Methyl-1,4-benzoquinone *[553-97-9]* **M 122.1, m 68-69°.** Crystd from heptane or EtOH, dried rapidly (vacuum over P_2O_5) and stored under vacuum.

Methyl benzoylformate *[15206-55-0]* **M 164.2, m 246-248°.** Purified by radial chromatography (diethyl ether/hexane, 1:1), and dried at 110-112° at 6mm pressure. [Meyers and Oppenlaender *J Am Chem Soc* **108** 1989 *1986*.]

2-Methyl-3,4-benzphenanthrene *[652-04-0]* **M 242.3, m 70°.** Crystd from EtOH.

dl-**α-Methylbenzyl alcohol** *[13323-81-4]* **M 122.2, b 60.5-61.0°/3mm.** See *dl*-1-phenylethanol on p. 330.

***R*-(+)-α-Methylbenzylamine** *[R(+) 3886-69-9, RS 618-36-0]* **M 121.2, b 187-188°/atm, [α]$^{20}_{546}$ +35° (c 10, EtOH), [α]$^{25}_{D}$ +39.7° (neat), pK 9.08 (for *RS*).** Dissolve in toluene, dry over NaOH and distd, fraction boiling at 187-188°/atm is collected. Store under N_2 to avoid forming the carbamate and urea. Similarly for the *S-(-) enantiomer [2627-86-3]*. [*Org Synth* Coll Vol II 503 *1943*.]

p-**Methylbenzyl bromide** *[104-81-4]*. See α-bromo-*p*-xylene on p. 143.

p-**Methylbenzyl chloride** *[104-82-5]* **M 140.6, b 80°/2mm, d 1.085, n 1.543.** Dried with $CaSO_4$ and fractionally distd under vacuum.

Methylbixin *[26585-94-4]* **M 408.5, m 163°.** Crystd from EtOH/$CHCl_3$.

Methyl bromide *[74-83-9]* **M 94.9, b 3.6°.** Purified by bubbling through conc H_2SO_4, followed by passage through a tube containing glass beads coated with P_2O_5. Also purified by distn from $AlBr_3$ at -80°, by passage through a tower of KOH pellets and by partial condensation.

Methyl *o*-**bromobenzoate** *[610-94-6]* **M 215.1, b 122°/17mm, 234-244°/760mm.** Soln in ether is washed with 10% aqueous Na_2CO_3, water, then dried and distd.

Methyl *p*-**bromobenzoate** *[619-42-1]* **M 215.1, m 79.5-80.5°.** Crystd from MeOH.

2-Methylbutane (isopentane) *[78-78-4]* **M 72.2, b 27.9°, d 0.621, n 1.35373, n^{25} 1.35088.** Stirred for several hours in the cold with conc H_2SO_4 (to remove olefinic impurities), then washed with H_2O, aqueous Na_2CO_3 and H_2O again. Dried with $MgSO_4$ and fractionally distd using a Todd column packed with glass helices (see p. 174). Material transparent down to 180nm was obtained by distilling from sodium wire, and passing through a column of silica gel which had previously been dried in place at 350° for 12h before use. [Potts *J Phys Chem* **20** 809 *1952*].

2-Methyl-1-butanol *[137-32-6; RS 34713-94-5; S(-)- 1565-80-6]* **M 88.2, b 130°(*RS*), 128.6°(*S*), [α]$^{25}_{D}$ -5.8° (neat), d 0.809, n^{52} 1.4082.** Refluxed with CaO, distd, refluxed with magnesium and again fractionally distd. A small sample of highly purified material was obtained by fractional crystn after conversion into a suitable ester such as the trinitrophthalate or the 3-nitrophthalate. The latter was converted to the cinchonine salt in acetone and recrystd from $CHCl_3$ by adding pentane. The salt was saponified, extracted with ether, and fractionally distd. [Terry et al. *J Chem Eng Data* **5** 403 *1960*.]

3-Methyl-1-butanol *[123-51-3]* **M 88.2, b 128°/750mm, 132°/760mm, d^{15} 0.8129, n^{15} 1.4085, n 1.4075.** Dried by heating with CaO and fractionally distilling, then heating with BaO and redistilling. Alternatively, boiled with conc KOH, washed with dilute H_3PO_4, and dried with K_2CO_3, then anhydrous $CuSO_4$, before fractionally distilling. If very dry alcohol is required, the distillate can be refluxed with the appropriate alkyl phthalate or succinate as described for *ethanol.* It is separated from 2-methyl-1-butanol by fractional distn, fractional crystn and preparative gas chromatography.

3-Methyl-2-butanol *[598-75-4]* **M 88.2, b 111.5°, d 0.807, n 1.4095, n^{25} 1.4076.** Refluxed with magnesium, then fractionally distd.

3-Methyl-2-butanone (methyl isopropyl ketone) *[563-80-4]* **M 86.1, b 93-94°/752mm, d 0.818, n 1.410, pK^{25} -7.1 (aq H_2SO_4).** Refluxed with a little $KMnO_4$. Fractionated on a spinning-band column, dried with $CaSO_4$ and distd.

2-Methyl-2-butene *[513-35-9]* **M 70.1, f -133.8°, b 38.4°/760mm, d^{15} 0.66708, d 0.6783, d^{25} 0.65694, n^{15} 1.3908.** Distd from sodium.

Methyl *n*-butyrate *[623-42-7]* **M 102.1, b 102.3°/760mm, d 0.898, n 1.389.** Treated with anhydrous $CuSO_4$, then distd under dry nitrogen.

***S*-(+)-2-Methylbutyric acid** *[1730-91-2]* **M 102.1, b 64°/2mm, 78°/15mm, 90-94°/23mm, 174-175°/atm, d_4^{20} 0.938, n_D^{20} 1.406, $[\alpha]_{546}^{20}$ +23°, $[\alpha]_D^{20}$+19.8° (neat), $[\alpha]_D^{13}$+18.3° (c 6, EtOH), pK^{25} 4.76 (for *RS*).** Purified by distn *in vacuo* [Sax and Bergmann *J Am Chem Soc* **77** 1910 *1955*; Doering and Aschner *J Am Chem Soc* **75** 393 *1953*]. The *methyl ester* is formed by addition of diazomethane and has **b** 112-115°/atm, $[\alpha]_D^{27}$ +21.1° (c 1.7, MeOH).

Methyl carbamate *[598-55-0]* **M 75.1, m 54.4-54.8°.** Crystd from *benzene.

9-Methylcarbazole *[1484-12-4]* **M 181.2, m 89°.** Purified by zone melting.

4-Methylcatechol *[452-86-8]* **M 124.1.** See 3,4-dihydroxytoluene on p. 208.

Methyl chloride *[74-87-3]* **M 50.5, b -24.1°.** Bubbled through a sintered-glass disc dipping into conc H_2SO_4, then washed with water, condensed at low temperature and fractionally distd. Has been distd from $AlCl_3$ at -80°. Alternatively, passed through towers containing $AlCl_3$, soda-lime and P_2O_5, then condensed and fractionally distd. Stored as a gas.

Methyl chloroacetate *[96-34-4]* **M 108.5, b 129-130°, d 1.230, n 1.423.** Shaken with satd aq Na_2CO_3 (three times), aq 50% $CaCl_2$ (three times), satd aq NaCl (twice), dried (Na_2SO_4) and fractionally distd.

***R*-(+) Methyl 2-chloropropionate** *[77287-29-7]* **M 122.6, b 49-50°/35mm, 78-80°/120mm, 132-134°/760mm, d_4^{20} 1.152, n_D^{20} 1.417, $[\alpha]_D^{20}$ +26° (19.0°) (neat).** Purified by repeated distillation [Walker *J Chem Soc* **67** 916 *1895*; Walden *Chem Ber* **28** 1293 *1985*; see also Gless *Synth Commun* **16** 633 *1986*].

3-Methylcholanthrene *[56-49-5]* **M 268.4, m 179-180°.** Crystd from *benzene and diethyl ether. **CARCINOGEN.**

Methyl cyanoacetate *[105-34-0]* **M 99.1, f -13°, b 205°, d 1.128, n 1.420.** Purified by shaking with 10% Na_2CO_3 soln, washing well with water, drying with anhydrous Na_2SO_4, and distilling.

Methyl cyanoformate *[17640-15-2]* **M 85.1, b 81°/47mm, 97°/751mm, 100-101°/760mm, d_4^{20}1.072, n_D^{20} 1.37378.** Purified by fractionation through a 45cm glass helices packed column and with a 30cm spinning band column. [Sheppard *J Org Chem* **27** 3756 *1962*.] It has been distd through a short Vigreux column, and further purified by recrystn from Et_2O at -40° as white crystals which melt at room temperature. NMR: δ 4.0 (CH_3), and IR: 2250 (CN) and 1750 (CO) cm^{-1}. [Childes and Weber *J Org Chem* 41 3486 *1976*.]

Methylcyclohexane *[108-87-2]* **M 98.2, b 100.9°, d^{25} 0.7650, n 1.4231, n^{52} 1.42058.** Passage through a column of activated silica gel gives material transparent down to 220nm. Also purified by passage through a column of activated basic alumina, or by azeotropic distn with MeOH, followed by washing out the MeOH with H_2O, drying and distilling. Methylcyclohexane can be dried with $CaSO_4$, CaH_2 or sodium. Has also been purified by shaking with a mixture of conc H_2SO_4 and HNO_3 in the cold, washing with H_2O, drying with $CaSO_4$ and fractionally distilling from potassium. Percolation through a Celite column impregnated with 2,4-dinitrophenylhydrazine (DNPH), phosphoric acid and H_2O (prepared by grinding 0.5g DNPH with 6mL 85% H_3PO_4, then mixing with 4mL of distilled H_2O and 10g of Celite) removes carbonyl-containing impurities.

2-Methylcyclohexanol *[583-59-5]* **M 114.2, b 65°/20mm, 167.6°/760mm, d 0.922, n 1.46085.** Dried with Na_2SO_4 and distd under vacuum.

***cis-* and *trans-*3-Methylcyclohexanol** *[591-23-1]* **M 114.2, b 69°/16mm, 172°/760mm, d 0.930, n 1.45757, $n^{25.5}$ 1.45444.** Dried with Na_2SO_4 and distd under vacuum.

4-Methylcyclohexanone *[589-92-4]* **M 112.2, b 165.5°/743mm, d 0.914, n 1.44506.** Dried with $CaSO_4$, then fractionally distd.

1-Methylcyclohexene *[591-49-1]* **M 96.2, b 107.4-108°/atm, 110-111°/760mm, d 0.813, n 1.451.** Freed from hydroperoxides by passing through a column containing basic alumina or refluxing with cupric stearate, filtered and fractionally distd from sodium.

Methylcyclopentane *[96-37-7]* **M 84.2, b 71.8°, d 0.749, n 1.40970, n^{25} 1.40700.** Purification procedures include passage through columns of silica gel (prepared by heating in nitrogen to 350° prior to use) and activated basic alumina, distn from sodium-potassium alloy, and azeotropic distn with MeOH, followed by washing out the methanol with water, drying and distilling. It can be stored with CaH_2 or sodium.

3'-Methyl-1,2-cyclopentenophenanthrene *[549-38-2]* **M 232.3, m 126-127°.** Crystd from AcOH.

S-Methyl-L-cysteine *[1187-84-4]* **M 135.2, m 207-211°, $[\alpha]_D^{26}$ -32.0° (c 5, H_2O), pK_1^{25} 1.94 (COOH), pK_2^{25} 8.73 (NH_2, 8.97).** Likely impurities are cysteine and S-methyl-*dl*-cysteine. Crystd from water by adding 4 volumes of EtOH.

5-Methylcytosine [4-amino-5-methylpyrimidin-2(1*H*)-one] *[554-01-8]* **M 125.1, m 270°(dec), pK_1 4.6, pK_2 12.4.** Crystd from water (sol 3.4%).

Methyl decanoate *[110-42-9]* **M 186.3, b 114°/15mm, 224°/760mm, d 0.874, n 1.426.** Passed through alumina before use.

Methyl 2,4-dichlorophenoxyacetate *[1928-38-7]* **M 235.1, m 43°, b 119°/11mm.** Crystd from MeOH.

***m*-Methyl-*N,N*-dimethylaniline** *[121-72-2]* **M 135.2, b 72-74°/5mm, 215°/760mm, pK^{25} 5.22.** Refluxed for 3h with 2 molar equivalents of acetic anhydride, then fractionally distd under reduced pressure. Also dried over BaO, distd and stored over KOH. Methods described for *N,N*-dimethylaniline are applicable.

***p*-Methyl-*N,N*-dimethylaniline** *[99-97-8]* **M 135.2, b 76.5-77.5°/4mm, 211°/760mm, pK^{25} 4.76.** Refluxed for 3h with 2 molar equivalents of acetic anhydride, then fractionally distd under reduced pressure. Also dried over BaO, distd and stored over KOH. Methods described for *N,N*-dimethylaniline are applicable.

2-Methyl-1,3-dithiane *[6007-26-7]* **M 134.3, b 53-54°/1.1mm, 66°/5mm, 79-80°/8-10mm, 85°/12mm, d_4^{20} 1.121, n_D^{20} 1.560.** Wash with H_2O, 2.5 M aqueous NaOH, H_2O, brine, dried over K_2CO_3 (use toluene as solvent if volume of reagent is small), filter, evaporate and distil the colourless residue. IR film: 1455, 1371 and 1060 (all medium and CH_3), 1451m, 1422s, 1412m, 1275m, 1236m, 1190m, 1171w, 918m and 866w (all dithiane) cm^{-1} [Corey and Erickson *J Org Chem* **36** 3553 *1971*; Seebach and Corey *J Org Chem* **40** 231 *1975*].

Methyl dodecanoate *[111-82-0]* **M 214.4, m 5°, b 141°/15mm, d 0.870, n^{50} 1.4199.** Passed through alumina before use.

***N*-Methyleneaminoacetonitrile** *[109-82-0]* **M 68.1, m 129°.** Crystd from EtOH or acetone.

***p,p'*-Methylene-bis-(*N,N*-dimethylaniline)** *[101-61-1]* **M 254.4, m 89.5°.** See *p,p'*-tetramethyldiaminodiphenylmethane on p. 364.

Methylene Blue [3,7-bis-(dimethylamino)phenothiazin-5-ium chloride *[61-73-4]* **M 319.9, CI 52015, ε_{654} 94,000 (EtOH), ε_{664} 81,000 (H_2O), pK^{25} 3.8.** Crystd from 0.1M HCl (16mL/g), the crystals were separated by centrifugation, washed with chilled EtOH and diethyl ether and dried under vacuum. Crystd from 50% aqueous EtOH, washed with absolute EtOH, and dried at 50-55° for 24h. Also crystd from *benzene-MeOH (3:1). Salted out with NaCl from a commercial conc aqueous soln, then crystd from water, dried at 100° in an oven for 8-10h.

3,4-Methylenedioxyaniline *[14268-66-7]* **M 137.1, m 45-46°, b 144°/14mm, pK_{Est} ~3.8.** Crystd from pet ether.

3,4-Methylenedioxycinnamic acid *[2373-80-0]* **M 192.2, m 243-244°(dec), pK_{Est} ~4.6.** Crystd from glacial acetic acid.

5,5'-Methylenedisalicylic acid *[122-25-8]* **M 372.3, m 238°(dec).** Crystd from acetone and *benzene.

Methylene Green [3,7-bis-(dimethylamino)-4-nitrophenothiazin-5-ium chloride] *[2679-01-8]* **M 364.9, m >200°(dec), CI 52020, pK^{25} 3.2.** Crystd three times from water (18mL/g).

***N*-Methylephedrine (2-dimethylamino-1-phenylpropanol)** *[1S,2R-(+)- 42151-56-4; 1R,2S-(-)- 552-79-4]* **M 179.3, m 85-86°, 87-87.5°, 90°, b 115°/2mm, $[\alpha]_{546}^{20}$ (+) and (-) 35°, $[\alpha]_D^{20}$ (+) and (-) 30° (c 4.5, MeOH), pK^{26} 9.22.** It has been recrystd from Et_2O, pet ether, of aq EtOH or aq MeOH and has been distilled under reduced pressure. [Smith *J Chem Soc* 2056 *1927* ; Tanaka and Sugawa *Yakugaku Zasshi (J Pharm Soc Japan) 72* 1548 *1952* (*Chem Abstr* **47** 8682 *1953*); Takamatsu *Yakugaku Zasshi (J Pharm Soc Japan)* **76** 1227 *1956* ,*Chem Abstr* **51** 4304 *1957*.] The *hydrochloride* has **m** 192-193° and $[\alpha]_D^{20}$ +30° (c 5,H_2O)[Prelog and Hüfliger *Helv Chim Acta* **33** 2021 *1950*].

Methyl ether (dimethyl ether) *[115-10-6]* **M 46.1, b -63.5°/96.5mm.** Dried by passing over alumina and then BaO, or over CaH_2, followed by fractional distn at low temperatures.

***N*-Methyl ethylamine hydrochloride** *[624-60-2]* **M 95.6, m 126-130°, pK 10.9 (free base).** Crystd from absolute EtOH or diethyl ether.

***N*-Methyl formamide** *[123-39-7]* **M 59.1, m -3.5°, b 100.5°/25mm, d 1.005., n^{52} 1.4306** Dried with molecular sieves for 2days, then distd under reduced pressure through a column packed with glass helices. Fractionally crystd by partial freezing and the solid portion was vac distd.

Methyl formate *[107-31-3]* **M 60.1, b 31.5°, d 0.971, n^{15} 1.34648, n 1.34332.** Washed with strong aq Na_2CO_3, dried with solid Na_2CO_3 and distd from P_2O_5. (Procedure removes free alcohol or acid.)

2-Methylfuran *[534-22-5]* **M 82.1, b 62.7-62.8°/731mm, d 0.917, n 1.436.** Washed with acidified satd ferrous sulfate soln (to remove peroxides), separated, dried with $CaSO_4$ or $CaCl_2$, and fractionally distd from KOH immediately before use. To reduce the possibility of spontaneous polymerisation, addition of about one-third of its volume of heavy mineral oil to 2-methylfuran prior to distn has been recommended.

Methyl gallate *[99-24-1]* **M 184.2, m 202°.** Crystd from MeOH.

***N*-Methylglucamine** *[6284-40-8]* **M 195.2, m 128-129°, $[\alpha]^{20}_{546}$ -19.5°(c 2, H_2O), pK^{28} 9.62.** Crystd from MeOH.

Methyl α-D-glucosamine *[97-30-3]* **M 194.2, m 165°, $[\alpha]^{25}_{D}$ +157.8° (c 3.0, H_2O), pK^{30} 7.1.** Crystd from MeOH.

α-Methylglutaric acid *[18069-17-5]* **M 146.1, m 79°, pK_1^{25} 4.36, pK_2^{25} 5.37.** Crystd from distd water, then dried under vacuum over conc H_2SO_4.

β-Methylglutaric acid *[626-51-7]* **M 146.1, m 87°, pK_1^{25} 4.35, pK_2^{25} 5.44.** Crystd from distd water, then dried under vacuum over conc H_2SO_4.

Methylglyoxal *[78-98-8]* **M 72.1, b *ca* 72°/760mm.** Commercial 30% (w/v) aqueous soln was diluted to about 10% and distd twice, taking the fraction boiling below 50°/20mm Hg. (This treatment does not remove lactic acid).

Methyl Green *[82-94-0, 7114-03-6 ($ZnCl_2$ salt)]* **M 458.5, m >200°(dec).** Crystd from hot water.

1-Methylguanine *[938-85-2]* **M 165.2, m >300°(dec), pK_1^{20} 3.13, pK_2^{20} 10.54.** Crystd from 50% aqueous acetic acid.

7-Methylguanine *[578-76-7]* **M 165.2, pK_1^{20} 3.50, pK_2^{20} 9.95.** Crystd from water.

2-Methylhexane *[591-76-4]* **M 100.2, b 90.1°, d 0.678, n 1.38485, n^{25} 1.38227.** Purified by azeotropic distn with MeOH, then washed with water (to remove the MeOH), dried over type 4A molecular sieves and distd.

3-Methylhexane *[589-34-4]* **M 100.2, b 91.9°, d 0.687, n 1.38864, n^{25} 1.38609.** Purification as for 2-methylhexene.

Methyl hexanoate *[106-70-7]* **M 130.2, b 52°/15mm, 150°/760mm, d 0.885, n 1.410.** Passed through alumina before use.

Methylhydrazine *[60-34-4]* **M 46.1, b 87°/745mm, d 0.876, n 1.436, pK^{30} 7.87.** Dried with BaO, then vacuum distd. Stored under nitrogen.

Methyl hydrazinocarboxylate *[6294-89-9]* **M 90.1, m 70-73°.** To remove impurities, the material was melted and pumped under vacuum until the vapours were spectroscopically pure [Caminati et al. *J Am Chem Soc* **108** 4364 *1986*].

Methyl 4-hydroxybenzoate *[99-76-3]* **M 152.2, m 127.5°, pK_{Est} ~9.3.** Fractionally crystd from its melt, recrystd from *benzene, then from *benzene/MeOH and dried over $CaCl_2$ in a vacuum desiccator.

Methyl 3-hydroxy-2-naphthoate *[883-99-8]* **M 202.2, m 73-74°, pK_{Est} ~9.0.** Crystd from MeOH (charcoal) containing a little water.

***N*-Methylimidazole** *[616-47-7]* **M 82.1, b 81-84°/27mm, 197-198°/760mm, d 1.032, n 1.496, pK^{25} 7.25.** Dried with sodium metal and then distd. Stored at 0° under dry argon.

2-Methylimidazole *[693-98-1]* **M 82.1, m 140-141°, b 267°/760mm, pK^{25} 7.86.** Recrystd from *benzene or pet ether.

4-Methylimidazole *[822-36-6]* **M 82.1, m 47-48°, b 263°/760mm, pK^{25} 7.61.** Recrystd from *benzene or pet ether.

2-Methylindole *[95-20-5]* **M 131.2, m 61°, pK^{25} -0.28 (C-3 protonation, aq H_2SO_4).** Crystd from *benzene. Purified by zone melting.

3-Methylindole (skatole) *[83-34-1]* **M 131.2, m 95°, pK^{25} -4.55 (C-3-protonation, aq H_2SO_4).** Crystd from *benzene. Purified by zone melting.

Methyl iodide *[74-88-4]* **M 141.9, b 42.8°, d 2.281, n 1.5315.** Deteriorates rapidly with liberation of iodine if exposed to light. Usually purified by shaking with dilute aqueous $Na_2S_2O_3$ or $NaHSO_3$ until colourless, then washed with water, dilute aqueous Na_2CO_3, and more water, dried with $CaCl_2$ and distd. It is stored in a brown bottle away from sunlight in contact with a small amount of mercury, powdered silver or copper. (Prolonged exposure of mercury to methyl iodide forms methylmercuric iodide.) Methyl iodide can be dried further using $CaSO_4$ or P_2O_5. An alternative purification is by percolation through a column of silica gel or activated alumina, then distn. The soln can be degassed by using a repeated freeze-pump-thaw cycle.

***O*-Methylisourea hydrogen sulfate (2-methylpseudourea sulfate)** *[29427-58-5]* **M 172.2, m 114-118°, 119°.** Recrystd from MeOH-Et_2O (327g of salt dissolved in 1L of MeOH and 2.5L of Et_2O is added) [Fearing and Fox *J Am Chem Soc* **76** 4382 *1954*]. The *picrate* has **m** 192° [Odo et al. *J Org Chem* **23** 1319 *1958*].

***N*-Methyl maleimide** *[930-88-1]* **M 111.1, m 94-96°.** Crystd three times from diethyl ether.

Methylmalonic acid *[516-05-2]* **M 118.1, m 135°(dec), pK$_1^{25}$ 3.05, pK$_2^{25}$ 5.76.** Crystallises as the hydrate from water.

3-Methylmercaptoaniline *[1783-81-9]* **M 139.2, b 101.5-102.5°/0.3mm, 163-165°/16mm, d$_4^{20}$ 1.147, n$_D^{20}$ 1.641, pK^{25} 4.05.** Purified by fractional distn in an inert atmostphere. It has UV max at 226 and 300. [Bordwell and Cooper *J Am Chem Soc* **74** 1058*1952*.] The *N-acetyl* derivative has **m** 78-78.5° (after recrystn from aq EtOH).

4-Methylmercaptoaniline *[104-96-1]* **M 139.2, b 140°/15mm, 151°/25mm, 155°/23mm, d$_4^{20}$ 1.137, n$_D^{20}$ 1.639, pK^{25} 4.40.** Purified by fractional distn in an inert atmosphere. [Lumbroso and Passerini *Bull Soc Chim Fr* 311 *1957*; Mangini and Passerini *J Chem Soc* 4954 *1956*.]

Methyl methacrylate *[80-62-6]* **M 100.1, f -50°, b 46°/100mm, d 0.937, n 1.4144.** Washed twice with aqueous 5% NaOH (to remove inhibitors such as hydroquinone) and twice with water. Dried with $CaCl_2$, Na_2CO_3, Na_2SO_4 or $MgSO_4$, then with CaH_2 under nitrogen at reduced pressure. The distillate is stored at low temperatures and redistd before use. Prior to distn, inhibitors such as ß-naphthylamine (0.2%) or di-β-naphthol are sometimes added. Also purified by boiling aqueous H_3PO_4 soln and finally with saturated NaCl soln. It was dried for 24h over anhydrous $CaSO_4$, distd at 0.1mm Hg at room temperature and stored at -30° [Albeck et al. *J Chem Soc, Faraday Trans 1* **1** 1488 *1978*].

Methyl methanesulfonate *[66-27-3]* **M 110.3, b 59°/0.6mm, 96-98°/19mm, d 1.300, n 1.4140.** Purified by careful fractionation and collecting the middle fraction. Suspected **CARCINOGEN.** Note that $MeSO_3H$ has **b** 134.5-135°, 167-167.5°/10mm and methanesulfonic anhydride has **b** 138°/10mm)—both are possible impurities.

Methyl methanethiolsulfonate *[2949-92-0]* **M 126.2, b 69-71°/0.4mm, 96-97°/4.5mm, 104-105°/10mm, 119°/16mm, d 1.226, n 1.515.** Purified by fractional distn uner reduced pressure, IR: ν 1350, 750 cm^{-1}. [Applegate et al. *J Org Chem* **38** 943 *1973.*]

α-Methylmethionine *[562-48-1]* **M 163.0, m 283-284°, pK^{30} 9.45.** Crystd from aqueous EtOH.

S-Methyl-L-methionine chloride (Vitamin U) *[1115-84-0]* **M 199.5, $[\alpha]_D^{23}$ +33° (0.2M HCl), pK$_1$ 1.9, pK$_2$ 7.9.** Likely impurities are methionine, methionine sulfoxide and methionine sulfone. Crystd from water by adding a large excess of EtOH. Stored in a cool, dry place, protected from light.

***N*-Methylmorpholine** *[109-02-4]* **M 101.2, b 116-117°/764mm, d 0.919, n 1.436, pK^{25} 7.38.** Dried by refluxing with BaO or sodium, then fractionally distd through a helices-packed column.

4-Methylmorpholine-4-oxide monohydrate *[7529-22-8]* **M 135.2, m 71-73°.** When dried for 2-3h at high vacuum it dehydrates. Add MeOH to the oxide and distil off the solvent under vacuum until the temp is *ca* 95°. Then add Me_2CO at reflux then cool to 20°. The crystals are filtered off washed with Me_2CO and dry. The degree of hydration may vary and may be important for the desired reactions. [van Rheenan et al. *Tetrahedron Lett* 1973 1076; Schneider and Hanze *US Pat 2 769 823*; see also Sharpless et al. *Tetrahedron Lett* 2503 *1976.*]

1-Methylnaphthalene *[90-12-0]* **M 142.2, f -30°, b 244.6°, d 1.021, n 1.6108.** Dried for several days with $CaCl_2$ or by prolonged refluxing with BaO. Fractionally distd through a glass helices-packed column from sodium. Purified further by soln in MeOH and pptn of its picrate complex by adding to a saturated soln of picric acid in MeOH. The picrate, after crystn to constant melting point (**m** 140-141°) from MeOH, was dissolved in *benzene and extracted with aqueous 10% LiOH until the extract was colourless. Evaporation of the *benzene under vacuum gave 1-methylnaphthalene [Kloetzel and Herzog *J Am Chem Soc* **72** 1991 *1950*]. However, neither the picrate nor the styphnate complexes satisfactorily separates 1- and 2-methylnaphthalenes. To achieve this, 2-methylnaphthalene (10.7g) in 95% EtOH (50mL) has been ppted with 1,3,5-trinitrobenzene (7.8g) and the complex has been crystd from MeOH to **m** 153-153.5° (**m** of the 2-methyl isomer is 124°). [Alternatively, 2,4,7-trinitrofluorenone in hot glacial acetic acid could be used, and the derivative (**m** 163-164°) recrystd from glacial acetic acid]. The 1-methylnaphthalene was regenerated by passing a soln of the complex in dry *benzene through a 15-in column of activated alumina and washing with *benzene/pet ether (b 35-60°) until the coloured band of the nitro compound had moved down near the end of the column. The complex can also be decomposed using tin and acetic-hydrochloric acids, followed by extraction with diethyl ether and *benzene; the extracts were washed successively with dilute HCl, strongly alkaline sodium hypophosphite, water, dilute HCl and water. [Soffer and Stewart *J Am Chem Soc* **74** 567 *1952.*] It can be purified from anthracene by zone melting.

2-Methylnaphthalene *[91-57-6]* **M 142.2, m 34.7-34.9°, b 129-130°/25mm.** Fractionally crystd repeatedly from its melt, then fractionally distd under reduced pressure. Crystd from *benzene and dried under vacuum in an Abderhalden pistol. Purified *via* its picrate (**m** 114-115°) as described for 1-methylnaphthalene.

6-Methyl-2-naphthol *[17579-79-2]* **M 158.2, m 128-129°, pK$_{Est}$ ~9.8.** Crystd from EtOH or ligroin. Sublimed *in vacuo.*

7-Methyl-2-naphthol *[26593-50-0]* **M 158.2, m 118°, pK$_{Est}$ ~9.7.** Crystd from EtOH or ligroin. Sublimed *in vacuo.*

Methyl 1-naphthyl ether *[2216-69-5]* **M 158.2, b 90-91°/2mm, d 1.095, n^{26} 1.6210.** Steam distd from alkali. The distillate was extracted with diethyl ether. After drying ($MgSO_4$) the extract and evaporating diethyl ether, the methyl naphthyl ether was then fractionated under reduced pressure from CaH_2.

Methyl nitrate *[598-58-3]* **M 77.0, b 65°/760mm, d^5 1.2322, d^{15} 1.2167, d^{25} 1.2032.** Distd at -80°. The middle fraction was subjected to several freeze-pump-thaw cycles. **VAPOUR EXPLODES ON HEATING.**

Methyl nitrite *[624-91-9]* **M 61.0, b -12°, d^{15} (liq) 0.991.** Condensed in a liquid nitrogen trap. Distd under vacuum, first trap containing dry Na_2CO_3 to free it from acid impurities then into further Na_2CO_3 traps before collection.

***N*-Methyl-4-nitroaniline** *[100-15-2]* **M 152.2, m 152.2°, pK^{25} 0.55.** Crystd from aqueous EtOH.

2-Methyl-5-nitroaniline *[99-55-8]* **M 152.2, m 109°, pK^{25} 2.35.** Acetylated, and the acetyl derivative crystd to constant melting point, then hydrolysed with 70% H_2SO_4 and the free base regenerated by treatment with ammonia [Bevan, Fayiga and Hirst *J Chem Soc* 4284 *1956*].

4-Methyl-3-nitroaniline *[119-32-4]* **M 152.2, m 81.5°, pK^{25} 3.02.** Crystd from hot water (charcoal), then ethanol and dried in a vacuum desiccator.

Methyl 3-nitrobenzoate *[618-95-1]* **M 181.2, m 78°.** Crystd from MeOH (1g/mL).

Methyl 4-nitrobenzoate *[619-50-1]* **M 181.2, m 95-95.5°.** Dissolved in diethyl ether, then washed with aqueous alkali, the ether was evaporated and the ester was recrystd from EtOH.

2-Methyl-2-nitro-1,3-propanediol *[77-49-6]* **M 135.1, m 145°.** Crystd from *n*-butanol.

2-Methyl-2-nitro-1-propanol *[76-39-1]* **M 119.1, m 87-88°.** Crystd from pet ether.

***N*-Methyl-4-nitrosoaniline** *[10595-51-4]* **M 136.2, m 118°.** Crystd from *benzene.

***N*-Methyl-*N*-nitroso-*p*-toluenesulfonamide (diazald)** *[80-11-5]* **M 214.2, m 62°.** Crystd from *benzene by addition of pet ether, store in a refrigerator.

Methylnorbornene-2,3-dicarboxylic anhydride (5-methylnorborn-5-ene-2-endo-3-endo-dicarboxylic anhydride) *[25134-21-8]* **M 178.2, m 88.5-89°.** Purified by thin layer chromatography on Al_2O_3 (previously boiled in EtOAc) and eluted with hexane-*C_6H_6 (1:2) then recrystd from *C_6H_6-hexane. The free acid has **m** 118.5-119.5°. [Miranov et al. *Tetrahedron* **19** 1939 *1963*.]

3-Methyloctane *[2216-33-3]* **M 128.3, b 142-144°/760mm, d 0.719, n 1.407.** Passed through a column of silica gel [Klassen and Ross *J Phys Chem* **91** 3668 *1987*].

Methyl octanoate (methyl caprylate) *[111-11-5]* **M 158.2, b 83°/15mm, 193-194°/760mm, d 0.877, n 1.419.** Passed through alumina before use.

Methyl oleate *[112-62-9]* **M 296.5, f -19.9°, b 217°/16mm, d 0.874, n 1.4522.** Purified by fractional distn under reduced pressure, and by low temperature crystn from acetone.

3-Methyl-2-oxazolidone *[19836-78-3]* **M 101.1, m 15°, b 88-91°/1mm, d 1.172, n 1.455.** Purified by successive fractional freezing, then dried in a dry-box over 4A molecular sieves for 2 days.

3-Methyl-3-oxetanemethanol (3-hydroxymethyl-3-methyloxetane) *[3143-02-0]* **M 102.1, b 80°/4mm, 92-93°/12mm, d_4^{20} 1.033, n_D^{25} 1.4449.** Purified by fractionation through a glass column [Pattison *J Am Chem Soc* **79** 3455 *1957*].

Methylpentane (mixture of isomers). Passage through a long column of activated silica gel (or alumina) gave material transparent down to 200nm by UV.

2-Methylpentane *[107-83-5]* **M 86.2, b 60.3°, d 0.655, n 1.37145, n^{25} 1.36873.** Purified by azeotropic distn with MeOH, followed by washing out the MeOH with water, drying ($CaCl_2$, then sodium), and distn. [Forziati et al. *J Res Nat Bur Stand* **36** 129 *1946*.]

3-Methylpentane *[96-14-0]* **M 86.2, b 63.3°, d 0.664, n 1.37652, n^{25} 1.37384.** Purified by azeotropic distn with MeOH, as for 2-methylpentane. Purified for ultraviolet spectroscopy by passage through columns of silica gel or alumina activated by heating for 8h at 210° under a stream of nitrogen. Has also been treated with conc (or fuming) H_2SO_4, then washed with water, aqueous 5% NaOH, water again, then dried ($CaCl_2$, then sodium), and distd through a long, glass helices-packed column.

2-Methyl-2,4-pentanediol *[107-41-5]* **M 118.2, b 107.5-108.5°/25mm, d 0.922, n^{25} 1.4265.** Dried with Na_2SO_4, then CaH_2 and fractionally distd under reduced pressure through a packed column, taking precautions to avoid absorption of water.

2-Methyl-1-pentanol *[105-30-6]* **M 102.2, b 65-66°/60mm, 146-147°/760mm, d 0.827, n 1.420.** Dried with Na_2SO_4 and distd.

4-Methyl-2-pentanol *[108-11-2]* **M 102.2, b 131-132°, d 0.810, n 1.413.** Washed with aqueous $NaHCO_3$, dried and distd. Further purified by conversion to the phthalate ester by adding 120mL of dry pyridine and 67g of phthalic anhydride per mole of alcohol, purifying the ester and steam distilling it in the presence of NaOH. The distillate was extracted with ether, and the extract was dried and fractionally distd. [Levine and Walti *J Biol Chem* **94** 367 *1931*].

3-Methyl-3-pentanol carbamate (Emylcamate) *[78-28-4]* **M 145.2, m 56-58.5°.** Crystd from 30% EtOH.

4-Methyl-2-pentanone (methyl isobutyl ketone) *[108-10-1]* **M 100.2, b 115.7°, d 0.801, n 1.3958, n^{25} 1.3938.** Refluxed with a little $KMnO_4$, washed with aqueous $NaHCO_3$, dried with $CaSO_4$ and distd. Acidic impurities were removed by passage through a small column of activated alumina.

2-Methyl-1-pentene *[763-29-1]* **M 84.2, b 61.5-62°, d 0.680, n 1.395.** Water was removed, and peroxide formation prevented by several vacuum distns from sodium, followed by storage with sodium-potassium alloy.

***cis*-4-Methyl-2-pentene** *[691-38-3]* **M 84.2, m -134.4°, b 57.7-58.5°, d 0.672, n 1.388.** Dried with CaH_2, and distd.

***trans*-4-Methyl-2-pentene** *[674-76-0]* **M 84.2, m -140.8°, b 58.5°, d 0.669, n 1.389.** Dried with CaH_2, and distd.

5-Methyl-1,10-phenanthroline *[3002-78-6]* **M 194.2, m 113°(anhydr), pK^{25} 5.28.** Crystd from *benzene/pet ether.

***N*-Methylphenazonium methosulfate** see 5-methylphenazinium methyl sulfate on p. 547 in Chapter 6.

***N*-Methylphenothiazine** *[1207-72-3]* **M 213.2, α-form m 99.3° and b 360-365°, ß-form m 78-79°.** Recrystn (three times) from EtOH gave α-form (prisms). Recrystn from EtOH/*benzene gave the ß-form (needles). Also purified by vacuum sublimation and carefully dried in a vacuum line. Also crystd from toluene and stored in the dark [Guarr et al. *J Am Chem Soc* **107** 5104 *1985;* Olmsted et al. *J Am Chem Soc* **109** 3297 *1987*.]

4-Methylphenylacetic acid *[622-47-9]* **M 150.2, m 94°, pK^{25} 4.37.** Crystd from heptane or water.

1-Methyl-1-phenylhydrazine sulfate *[33008-18-3]* **M 218.2, pK^{25} 4.98 (free base).** Crystd from hot H_2O by addition of hot EtOH.

3-Methyl-1-phenyl-5-pyrazolone *[89-25-8]* **M 174.2, m 127°.** Crystd from hot H_2O, or EtOH/water (1:1).

***N*-Methylphthalimide** *[550-44-7]* **M 161.1, m 133.8°.** Recrystd from absolute EtOH.

2-Methylpiperazine *[109-07-9]* **M 100.2, m 61-62°, 66°, b 147-150°/739mm, pK_1^{25} 5.46, pK_2^{25} 9.90.** Purified by zone melting and by distn.

3-Methylpiperidine *[626-56-2]* **M 99.2, b 125°/763mm, d 0.846, n^{25} 1.4448, pK^{25} 11.07.** Purified *via* the *hydrochloride* (**m** 172°). [Chapman, Isaacs and Parker *J Chem Soc* 1925 *1959*.]

4-Methylpiperidine *[626-58-4]* **M 99.2, b 124.4°/755mm, d 0.839, n^{25} 1.4430, pK^{25} 10.78.** Purified *via* the *hydrochloride* (**m** 189°). Freed from 3-methylpyridine by zone melting.

1-Methyl-4-piperidone *[1445-73-4]* **M 113.2, b 53-56°/0.5mm, 54-56°/9mm, 68-71°/17mm, 85-87°/45mm, d_4^{20} 0.972, n_D^{25} 1.4588, pK^{25} 7.9.** It is best purified by fractional distn. The *hydrochloride* of the hydrate (4-diol) has **m** 94.7-95.5°, but the anhydrous *hydrochloride* which crystallises from $CHCl_3$-Et_2O and has **m** 165-168° (164-167°) and can also be obtained by sublimation at 120°/2mm. The *oxime* has **m** 130-132° (from Me_2CO). The *methiodide* crystallises from MeOH and the crystals with 1MeOH has **m** 189-190°, and the solvent-free *iodide* has **m** 202-204° dec. [Lyle et al. *J Org Chem* **24** 342 *1959*; Bowden and Greeen *J Chem Soc* 1164 *1952*; Tomita *Yakugaku Zasshi (J Pharm Soc Japan)* **71** 1053 *1951*.]

2-Methylpropane-1,2-diamine (1,2-diamino-2-methylpropane) *[811-93-8]* **M 88.2, b 47-48°/17mm, pK_1^{25} 6.25 (6.18), pK_2^{25} 9.82 (9.42).** Dried with sodium for 2 days, then distd under reduced pressure from sodium.

2-Methylpropane-1-thiol *[513-44-0]* **M 90.2, b 41.2°/142mm, n^{25} 1.43582, pK_{Est} ~10.8.** Dissolved in EtOH, and added to 0.25M $Pb(OAc)_2$ in 50% aqueous EtOH. The ppted lead mercaptide was filtered off, washed with a little EtOH, and impurities were removed from the molten salt by steam distn. After cooling, dilute HCl was added dropwise to the residue, and the mercaptan was distd directly from the flask. Water was separated from the distillate, and the mercaptan was dried (Na_2CO_3) and distd under nitrogen. [Mathias *J Am Chem Soc* **72** 1897 *1950*.]

2-Methylpropane-2-thiol *[75-66-1]* **M 90.2, b 61.6°/701mm, d^{25} 0.79426, n^{25} 1.41984, pK^{25} 11.22.** Dried for several days with CaO, then distd from CaO. Purified as for *2-methylpropane-1-thiol.*

2-Methyl-1-propanol (isobutanol) *[78-83-1]* **M 74.1, b 107.9°, d 0.804, n^{15} 1.39768, n^{25} 1.3939.** Dried by refluxing with CaO and BaO for several hours, followed by treatment with calcium or aluminium amalgam, then fractional distn from sulfanilic or tartaric acids. More exhaustive purifications involve formation of phthalate or borate esters. Heating with phthalic anhydride gives the *acid phthalate* which, after crystn to constant melting point (**m** 65°) from pet ether, is hydrolysed with aqueous 15% KOH. The alcohol is distd as the water azeotrope and dried with K_2CO_3, then anhydrous $CuSO_4$, and finally magnesium turnings, followed by fractional distn. [Hückel and Ackermann *J Prakt Chem* **136** 15 *1933*.] The borate ester is formed by heating the dried alcohol for 6h in an autoclave at 160-175° with a quarter of its weight of boric acid. After fractional distns under vac the ester is hydrolysed by heating for a short time with aq alkali and the alcohol is dried with CaO and distd. [Michael, Scharf and Voigt *J Am Chem Soc* **38** 653 *1916*.] (see p. 271).

Methyl propiolate *[922-67-8]* **M 84.1, b 100°/atm, 102°/atm, 103-105°/atm, d 0.945, n 1.4080.** Purified by fractional distn and collecting the middle fraction; note that propiolic acid has a high **b** [144°(dec)/atm]. LACHRYMATORY.

***N*-Methylpropionamide** *[1187-58-2]* **M 87.1, f -30.9°, b 103°/12-13mm, d 0.934, n^{25} 1.4356.** A colourless, odourless, neutral liquid at room temperature with a high dielectric constant. The amount of water present can be determined directly by Karl Fischer titration; GLC and NMR have been used to detect unreacted propionic acid. Commercial material of high quality is available, probably from the condensation of anhydrous methylamine with 50% excess of propionic acid. Rapid heating to 120-140° with stirring favours the reaction by removing water either directly or as the ternary xylene azeotrope. The quality of the distillate improves during the distn.

The propionamide can be dried over CaO. H_2O and unreacted propionic acid were removed as their xylene azeotropes. It was vacuum dried. Material used as an electrolyte solvent (specific conductance less than 10^{-6} ohm^{-1} cm^{-1}) was obtained by fractional distn under reduced pressure, and stored over BaO or molecular sieves because it readily absorbs moisture from the atmosphere on prolonged storage. [Hoover *Pure Appl Chem* **37** 581 *1974*; *Recommended Methods for Purification of Solvents and Tests for Impurities,* Coetzee Ed., Pergamon Press, *1982*.]

Methyl propionate *[554-12-1]* **M 88.1, b 79.7°.** Washed with satd aq NaCl, then dried with Na_2CO_3 and distd from P_2O_5. (This removes any free acid and alcohol.) It has also been dried with anhydrous $CuSO_4$.

Methyl *n*-propyl ether *[557-17-5]* **M 74.1, b 39°, d 0.736, n^{14} 1.3602, pK^{25} -3.79 (aq H_2SO_4).** Dried with $CaSO_4$, then passed through a column of alumina (to remove peroxides) and fractionally distd.

Methyl *n*-propyl ketone *[107-87-9]* **M 86.1, b 102.4°, d 0.807, n 1.3903.** Refluxed with a little $KMnO_4$, dried with $CaSO_4$ and distd. It was converted to its bisulfite addition compound by shaking with excess saturated aqueous $NaHSO_3$ at room temperature, cooling to 0°, filtering, washing with diethyl ether and drying. Steam distillation gave a distillate from which the ketone was recovered, washed with aq $NaHCO_3$ and distd water, dried (K_2CO_3) and fractionally distd. [Waring and Garik *J Am Chem Soc* **78** 5198 *1956*.]

3-Methyl-1-propyn-3-ol carbamate *[302-66-9]* **M 141.2, m 55.8-57°.** Crystd from ether/pet ether or cyclohexane.

2-Methylpyrazine *[109-08-0]* **M 94.1, b 136-137°, d 1.025, n 1.505, pK_1^{25} -5.25 (aq H_2SO_4), pK_2^{25} 1.47.** Purified *via* the picrate. [Wiggins and Wise *J Chem Soc* 4780 *1956*.]

2-Methylpyridine (2-picoline) *[109-06-8]* **M 93.1, b 129.4°, d 0.9444, n 1.50102, pK^{25} 5.96.** Biddiscombe and Handley [*J Chem Soc* 1957 *1954*] steam distd a boiling soln of the base in 1.2 equivalents of 20% H_2SO_4 until about 10% of the base had been carried over, along with non-basic impurities. Excess aqueous NaOH was then added to the residue, the free base was separated, dried with solid NaOH and fractionally distd.

2-Methylpyridine can also be dried with BaO, CaO, CaH_2, $LiAlH_4$, sodium or Linde type 5A molecular sieves. An alternative purification is *via* the $ZnCl_2$ adduct, which is formed by adding 2-methylpyridine (90mL) to a soln of anhydrous $ZnCl_2$ (168g) and 42mL conc HCl in absolute EtOH (200mL). Crystals of the complex are filtered off, recrystd twice from absolute EtOH (to give **m** 118.5-119.5°), and the free base is liberated by addition of excess aqueous NaOH. It is steam distd, and solid NaOH added to the distillate to form two layers, the upper one of which is then dried with KOH pellets, stored for several days with BaO and fractionally distd. Instead of $ZnCl_2$, $HgCl_2$ (430g in 2.4L of hot water) can be used. The complex, which separates on cooling, can be dried at 110° and recrystd from 1% HCl (to **m** 156-157°).

3-Methylpyridine (3-picoline) *[108-99-6]* **M 93.1, m -18.5°, b 144°/767mm, d 0.957, n 1.5069, pK^{25} 5.70.** In general, the same methods of purification that are described for *2-methylpyridine* can be used. However, 3-methylpyridine often contains 4-methylpyridine and 2,6-lutidine, neither of which can be removed satisfactorily by drying and fractionation, or by using the $ZnCl_2$ complex. Biddiscombe and Handley [*J Chem Soc* 1957 *1954*], after steam distn as for *2-methylpyridine*, treated the residue with urea to remove 2,6-lutidine, then azeotropically distd with acetic acid (the azeotrope had **b** 114.5°/712mm), and recovered the base by adding excess of aqueous 30% NaOH, drying with solid NaOH and carefully fractionally distilling. The distillate was then fractionally crystd by slow partial freezing. An alternative treatment [Reithof et al. *Ind Eng Chem (Anal Edn)* **18** 458 *1946*] is to reflux the crude base (500mL) for 20-24h with a mixture of acetic anhydride (125g) and phthalic anhydride (125g) followed by distn until phthalic anhydride begins to pass over. The distillate was treated with NaOH (250g in 1.5L of water) and then steam distd. Addition of solid NaOH (250g) to this distillate (*ca* 2L) led to the separation of 3-methylpyridine which was removed, dried (K_2CO_3, then BaO) and fractionally distd. (Subsequent fractional freezing would probably be advantageous.)

4-Methylpyridine (4-picoline) *[108-89-4]* **M 93.1, m 4.25°, b 145.0°/765mm, d 0.955, n 1.5058, pK^{25} 4.99.** Can be purified as for *2-methylpyridine*. Biddescombe and Handley's method for 3-methylpyridine is also applicable. Lidstone [*J Chem Soc* 242 *1940*] purified *via* the *oxalate* (**m** 137-138°) by heating 100mL of 4-methylpyridine to 80° and adding slowly 110g of anhydrous oxalic acid, followed by 150mL of boiling EtOH. After cooling and filtering, the ppte was washed with a little EtOH, then recrystd from EtOH, dissolved in the minimum quantity of water and distd with excess 50% KOH. The distillate was dried with solid KOH and again distd. Hydrocarbons can be removed from 4-methylpyridine by converting the latter to its hydrochloride, crystallising from EtOH/diethyl ether, regenerating the free base by adding alkali and distilling. As a final purification step, 4-methylpyridine can be fractionally crystd by partial freezing to effect a separation from 3-methylpyridine. Contamination by 2,6-lutidine is detected by its strong absorption at 270nm.

4-Methylpyridine 1-oxide *[1003-67-4]* **M 109.1, m 182-184°.** See 4-picoline-*N*-oxide on p. 335.

***N*-Methylpyrrole** *[96-54-8]* **M 81.1, b 115-116°/756mm, d 0.908, n 1.487, pK -3.4 (-2.90).** Dried with $CaSO_4$, then fractionally distd from KOH immediately before use.

1-Methyl-2-pyrrolidinone *[872-50-4]* **M 99.1, f -24.4, b 65-76°/1mm, 78-79°/12mm, 94-96°/20mm, 202°/760mm, d_4^{20} 1.0328, n_D^{20} 1.4678, pK -0.17 (also -0.92, and 0.2).** Dried by removing water as *benzene azeotrope. Fractionally distd at 10 torr through a 100-cm column packed with glass helices. [Adelman *J Org Chem* **29** 1837 *1964*; McElvain and Vozza *J Am Chem Soc* **71** 896 *1949*.] The *hydrochloride* has **m** 86-88° (from EtOH or Me_2CO-EtOH) [Reppe et al. *Justus Liebigs Ann Chem* **596** 1 *1955*].

2-Methylquinoline (quinaldine) *[91-63-4]* **M 143.2, b 86-87°/1mm, 155°/14mm, 246-247°/760mm, d 1.058, n 1.6126, pK^{25} 5.65.** Dried with Na_2SO_4 or by refluxing with BaO, then fractionally distd under reduced pressure. Redistd from zinc dust. Purified by conversion to its *phosphate* (**m** 220°) or *picrate* (**m** 192°) from which after recrystn, the free base was regenerated. [Packer, Vaughan and Wong *J Am Chem Soc* **80** 905 *1958*.] Its $ZnCl_2$ complex can be used for the same purpose.

4-Methylquinoline (lepidine) *[491-35-0]* **M 143.2, b 265.5°, d 1.084, n 1.61995, pK^{25} 5.59.** Refluxed with BaO, then fractionally distd. Purified *via* its recrystd *dichromate salt* (**m** 138°). [Cumper, Redford and Vogel *J Chem Soc* 1176 *1962*.]

6-Methylquinoline *[91-62-3]* **M 143.2, b 258.6°, d 1.067, n 1.61606, pK^{25} 4.92.** Refluxed with BaO, then fractionally distd. Purified *via* its recrystd *$ZnCl_2$ complex* (**m** 190°). [Cumper, Redford and Vogel *J Chem Soc* 1176 *1962*.]

7-Methylquinoline *[612-60-2]* **M 143.2, m 38°, b 255-260°, d 1.052, n 1.61481, pK^{25} 5.29.** Purified *via* its *dichromate complex* (**m** 149°, after five recrystns from water). [Cumper, Redford and Vogel *J Chem Soc* 1176 *1962*.]

8-Methylquinoline *[611-32-5]* **M 143.2, b 122.5°/16mm, 247.8°/760mm, d 1.703, n 1.61631, pK^{25} 4.60.** Purified as for 2-methylquinoline. The *phosphate* and *picrate* have **m** 158° and **m** 201° respectively.

Methyl Red (4-dimethylaminoazobenzene-2'-carboxylic acid) *[493-52-7]* **M 269.3, m 181-182°, CI 13020, pK$_1^{25}$ 2.30, pK$_2^{25}$ 4.82.** The acid is extracted with boiling toluene using a Soxhlet apparatus. The crystals which separated on slow cooling to room temperature are filtered off, washed with a little toluene and recrystd from glacial acetic acid, *benzene or toluene followed by pyridine/water. Alternatively, dissolved in aq 5% $NaHCO_3$ soln, and ppted from hot soln by dropwise addition of aq HCl. Repeated until the extinction coefficients did not increase.

Methyl salicylate (methyl 2-hydroxybenzoate) *[119-36-8]* **M 152.2, m -8.6°, b 79°/6mm, 104-105°/14mm, 223.3°/atm, d_4^{20} 1.1149, n_D^{20} 1.5380, pK^{25} 10.19.** Dilute with Et_2O, wash with satd $NaHCO_3$ (it may effervesce due to the presence of free acid), brine, dry $MgSO_4$, filter, evaporate and distil.

Its solubility is 1g/1.5L of H_2O. The *benzoyl* derivative has **m** 92° (b 270-280°/120mm), and the *3,5-dinitrobenzoate* has **m** 107.5°, and the *3,5-dinitrocarbamoyl* derivative has **m** 180-181°. [Hallas *J Chem Soc* 5770 *1965*.]

Methyl stearate *[122-61-8]* **M 298.5, m 41-43°, b 181-182°/4mm.** Crystd from pet ether or distd.

α-Methylstyrene (monomer) *[98-83-9]* **M 118.2, b 57°/15mm, d 0.910, n 1.5368.** Washed three times with aqueous 10% NaOH (to remove inhibitors such as quinol), then six times with distd water, dried with $CaCl_2$ and distd under vacuum. The distillate is kept under nitrogen, in the cold, and redistd if kept for more than 48h before use. It can also be dried with CaH_2.

***trans*-ß-Methylstyrene** *[873-66-5]* **M 118.2, b 176°/760mm, d 0.910, n 1.5496.** Distd under nitrogen from powdered NaOH through a Vigreux column, and passed through activated neutral alumina before use [Wong et al. *J Am Chem Soc* **109** 3428 *1987*].

4-Methylstyrene *[622-97-9]* **M 118.2, b 60°/12mm, 106°/10mm, d_4^{20} 0.9173, n_D^{20} 1.542.** Purified as the above styrenes and add a small amount of antioxidant if it is to be stored, UV in EtOH λmax 285nm (log ε 3.07), and in EtOH + HCl 295nm (log ε 2.84) and 252nm (log ε 4.23). [Schwartzman and Carson *J Am Chem Soc* **78** 322 *1956*; Joy and Orchin *J Am Chem Soc* **81** 305 *1959*; Buck et al. *J Chem Soc* 2377*1949*.]

Methylsuccinic acid *[498-21-5]* **M 132.1, m 115.0°, pK_1^{25} 3.88, pK_2^{25} 5.35.** Crystd from water.

(±)-3-Methylsulfolane (3-methyl-tetrahydrothiophene-1,1-dioxide) *[872-93-5]* **M 134.2, m 0.5°, b 101°/2mm, 125-130°/12mm, 278-282°/763.5mm, d_4^{20} 1.1885, n_D^{20} 1.4770.** Distil under vacuum and recryst from Et_2O at -60° to -70°. IR film has strong bands at 570 and 500 cm^{-1}. [Eigenberger *J Prakt Chem [2]* **131** 289 *1931*; Freaheller and Katon *Spectrochim Acta* **20** 1099*1964*.]

17α-Methyltestosterone *[58-18-4]* **M 302.5, m 164-165°, $[\alpha]_{546}^{20}$ +87° (c 1, dioxane).** Crystd from hexane/*benzene.

Methyl tetradecanoate (methyl myristate) *[124-10-7]* **M 382.7, m 18.5°, b 155-157°/7mm.** Passed through alumina before use.

2-Methyltetrahydrofuran *[96-47-9]* **M 86.1, b 80.0°, d_4^{20} 0.856, n_D^{20} 1.4053.** Likely impurities are 2-methylfuran, methyldihydrofurans and hydroquinone (stabiliser, which is removed by distn under reduced pressures). It was washed with 10% aqueous NaOH, dried, vacuum distd from CaH_2, passed through freshly activated alumina under nitrogen, and refluxed over sodium metal under vacuum. Stored over sodium. [Ling and Kevan *J Phys Chem* **80** 592 *1976*.] Vacuum distd from sodium, and stored with sodium-potassium alloy. (Treatment removes water and prevents the formation of peroxides.) Alternatively, it can be freed from peroxides by treatment with ferrous sulfate and sodium bisulfate, then solid KOH, followed by drying with, and distilling from, sodium, or type 4A molecular sieves under argon. It may be difficult to remove *benzene if it is present as an impurity (can be readily detected by its ultraviolet absorption in the 249-268nm region). [Ichikawa and Yoshida *J Phys Chem* **88** 3199 *1984*.] It has also been purifed by percolating through Al_2O_3 and fractionated collecting fraction **b** 79.5-80°. After degassing, the material was distd onto degassed molecular sieves, then distd onto anthracene and a sodium mirror. The solvent was distd from the green soln onto potassium mirror or sodium-potassium alloy, from which it was distilled again. [Mohammad and Kosower *J Am Chem Soc* **93** 2713 *1971*.] It should be stored in the presence of 0.1% of hydroquinone as stabiliser. **HARMFUL VAPOURS.**

***N*-Methylthioacetamide** *[5310-10-1]* **M 89.1, m 59°.** Recrystd from *benzene.

3-Methylthiophene *[616-44-4]* **M 98.2, b 111-113°, d 1.024, n 1.531.** Dried with Na_2SO_4, then distd from sodium.

6(4)-Methyl-2-thiouracil *[56-04-2]* **M 142.2, m 330°(dec), 299-303° (dec), 323-324° (dec), pK 8.1.** Crystd from a large volume of H_2O. Purified by dissolving in base adding charcoal, filtering and acidifying with AcOH. Suspend the wet solid (*ca* 100g) in boiling H_2O (1L), stir and add AcOH (20mL), stir and refrigerate. Collect the product, wash with cold H_2O (4 x 200mL), drain for several hours then place in an oven at 70° to constant weight. [IR: Short and Thompson *J Chem Soc* 168 *1952*; Foster and Snyder *Org Synth* Coll Vol IV 638 *1063*.]

Methyl 4-toluenesulfonate *[80-48-8]* **M 186.2, m 25-28°, 28°, b 144.6-145.2°/5mm, 168-170°/13mm, d_4^{20} 1.23.** It is purified by distn *in vacuo* and could be crystd from pet ether or Et_2O-pet ether at low temperature. It is a powerful methylating agent and is **TOXIC** and a **skin irritant**, so it is better to purify by repeated distn. [IR: Schreiber *Anal Chem* **21** 1168 *1949*; Buehler et al. *J Org Chem* **2** 167 *1937*; Roos et al. *Org Synth* Coll Vol I 145 *1948*.]

4-Methyl-1,2,4-triazoline-3,5-dione (MTAD) *[13274-43-6]* **M 113.1, m 103-104°, m 107-109°.** Obtained as pink needles by sublimation at 40-50°/0.1mm (see 4-phenyl-1,2,4-triazoline-3,5-dione, PTAD below). [Cookson et al. *Org Synth 51* 121 *1971*; Cheng et al. *J Org Chem* **49** 2910 *1984*.]

2-Methyltricycloquinazoline *[2642-52-6]* **M 334.4, m >300°.** Purified by vac sublimation. **CARCINOGEN.**

Methyl trifluoromethanesulfonate (methyl triflate) *[333-27-7]* **M 164.1, b 97-97.5°/736mm, 99°/atm, 100-102°/atm, d_4^{20} 1.496, n_D^{25} 1.3238.** It is a strong methylating agent but is corrosive and **POISONOUS**. Fractionate carefully and collecting the middle fraction (use efficient fume cupboard) and keep away from moisture. It is **POWERFUL ALKYLATING AGENT** and a strong **IRRITANT.** [IR: Gramstad and Haszeldine *J Chem Soc* 173 *1956*, 4069 *1957*.] *Trifluoromethanesulfonic acid* (triflic acid) *[1493-13-6]* M 151.1, boils higher (**b** 162°/atm), has a **pKa** of 3.10, and is **TOXIC** and hygroscopic. [Hansen *J Org Chem* **30** 4322 *1965*; Kurz and El-Nasr *J Am Chem Soc* **104** 5823 *1982*.]

***N*-Methyltryptophan (L-abrine)** *[526-31-8]* **M 218.3, m 295°(dec), $[\alpha]_D^{21}$ +44.4° (c 2.8, 0.5M HCl), $pK_{Est(1)}$~2.3, $pK_{Est(2)}$~9.7.** Crystd from water.

***dl*-5-Methyltryptophan** *[951-55-3]* **M 218.3, m 275°(dec) [pK see tryptophan].** Crystd from aqueous EtOH. *Picrate* has **m** 202° (dec).

6-Methyluracil *[626-48-2]* **M 126.1, m 270-280°(dec), λ_{max} 260_{nm} logε 3.97, pK_1 ~1.1, pK_2 9.8.** Crystd from EtOH or acetic acid.

3-Methyluric acid *[39717-48-1]* **M 182.1, m >350°, pK_1 5.75 (6.2), pK_2 >12.** Crystd from water.

7-Methyluric acid *[30409-21-3]* **M 182.1, m >380°, pK_1 5.6, pK_2 10.3.** Crystd from water.

9-Methyluric acid *[30345-24-5]* **M 182.1, m >400°.** Crystd from water.

Methyl vinyl ketone *[78-94-4]* **M 70.1, b 62-68°/400mm, 79-80°/760mm, d 0.845, n 1.413.** Forms an 85% azeotrope with water. After drying with K_2CO_3 and $CaCl_2$ (with cooling), the ketone is distd at low pressures.

Methyl vinyl sulfone *[3680-02-2]* **M 106.1, b 116-118°/20mm, d 1.215, n 1.461.** Passed through a column of alumina, then degassed and distd on a vacuum line and stored at -190° until required.

Methyl Violet 2B [4,4'-bis-(diethylamino)-4"-methyliminotriphenylmethyl hydrochloride) *[8004-87-3]* **M 394.0, m 137°(dec), CI 42535, max ~580nm.** Crystd from absolute EtOH by pptn with diethyl ether during cooling in an ice-bath. Filtered off and dried at 105°.

1-Methylxanthine *[6136-37-4]* **M 166.1, m >360° pK_1^{20} 7.90, pK_2^{20} 12.23.** Crystd from water.

3-Methylxanthine *[1076-22-8]* **M 166.1, m >360° pK_1^{20} 8.45, pK_2^{20} 11.92.** Crystd from water.

7-Methylxanthine *[552-62-5]* **M 166.1, m >380°(dec) pK_1^{20} 8.42, pK_2^{20} >13.** Crystd from water.

8-Methylxanthine *[17338-96-4]* **M 166.1, m 292-293°(dec).** Crystd from water.

9-Methylxanthine *[1198-33-0]* **M 166.1, m 384°(dec), pK_1^{20} 2.0, pK_2^{20} 6.12, pK_3^{20} 10.5 (>13).** Crystd from water.

Metrazol (Cardiazol, Leptazol, 3a,4,5,6,7,8-hexahydro-1,2,3,3a-tetraaza-azulene, 1,5-pentamethylene-1,2,3,4-tetrazole) *[54-95-5]* **M 138.2, m 61°, b 194°/12mm, pK_{Est} ~<0.** Crystd from diethyl ether. Dried under vacuum over P_2O_5.

Michler's ketone [4,4'-bis(dimethylamino)benzophenone] *[90-94-8]* **M 268.4, m 179°, pK^{25} 9.84.** Dissolved in dilute HCl, filtered and ppted by adding ammonia (to remove water-insoluble impurities such as benzophenone). Then crystd from EtOH or pet ether. [Suppan *J Chem Soc, Faraday Transl* **71** 539 *1975*.] It was also purified by dissolving in *benzene, then washed with water until the aqueous phase was colourless. The *benzene was evaporated off and the residue recrystd three times from *benzene and EtOH [Hoshino and Kogure *J Phys Chem* **72** 417 *1988*].

Monensin *[17090-79-8]* **M 670.9, m 103-105° (1 H_2O), $[\alpha]_D$ +47.7°, pK_{Est} ~ 4.6, pK 6.6 (66% Me_2NCHO).** Purified by chromatography, stable in aq alkaline soln. Slightly sol in H_2O but sol in EtOH, EtOAc and Et_2O.

***N*-Monobutyl urea** *[592-31-4]* **M 116.2, m 96-98°.** Crystd from EtOH/water, then dried under vacuum at room temperature.

***N*-Monoethyl urea** *[625-52-5]* **M 88.1, m 92-95°.** Crystd from EtOH/water, then dried under vacuum at room temperature.

***N*-Monomethyl urea** *[598-50-5]* **M 74.1, m 93-95°.** Crystd from EtOH/water, then dried under vacuum at room temperature.

Monopropyl urea *[627-06-5]* **M 102.1, m 110°.** Crystd from EtOH.

Morin (hydrate) (2',3,4',5,7-pentahydroxyflavone) *[480-16-0]* **M 302.2, m 289-292°, pK_1 5.3, pK_2 8.74.** Stirred at room temperature with ten times its weight of absolute EtOH, then left overnight to settle. Filtered, and evaporated under a heat lamp to one-tenth its volume. An equal volume of water was added, and the ppted morin was filtered off, dissolved in the minimum amount of EtOH and again ppted with an equal volume of water. The ppte was filtered, washed with water and dried at 110° for 1h. (Yield *ca* 2.5%.) [Perkins and Kalkwarf *Anal Chem* **28** 1989 *1956*.] Complexes with W and Zr.

Morphine (H_2O) *[57-27-2]* **M 302.2, m 230°(dec), $[\alpha]_D^{23}$ -130.9° (MeOH), pK_1 8.31, pK_2 9.51.** Crystd from MeOH.

Morpholine *[110-91-8]* **M 87.1, f -4.9°, b 128.9°, d 1.0007, n 1.4540, n^{25} 1.4533, pK^{25} 8.33.** Dried with KOH, fractionally distd, then refluxed with Na, and again fractionally distd. Dermer and Dermer [*J Am Chem Soc* **59** 1148 *1937*] ppted as the oxalate by adding slowly to slightly more than 1 molar equivalent of oxalic acid in EtOH. The ppte was filtered and recrystd twice from 60% EtOH. Addition of the oxalate to conc aq NaOH regenerated the base, which was separated and dried with solid KOH, then sodium, before being fractionally distd.

§ A polystyrene supported morpholine is commercially available.

2-(*N*-Morpholino)ethanesulfonic acid (MES) *[4432-31-9]* **M 213.3, m >300°(dec), pK^{20} 6.15.** Crystd from hot EtOH containing a little water.

Mucochloric acid (2,3-dichloro-4-oxo-2-butenoic acid) *[87-56-9]* **M 169.0, m 124-126°, pK^{25} 4.20.** Crystd twice from water (charcoal).

***trans,trans*-Muconic acid (hexa-2,4-dienedioic acid)** *[3588-17-8]* **M 142.1, m 300°, pK^{25} 4.51, for *cis,cis* pK^{25} 4.49.** Cryst from H_2O.

Muramic acid (H_2O) (3-*O*-α-carboxyethyl-D-glucosamine) *[1114-41-6]* **M 251.2, m 152-154°(dec).** See muramic acid on p. 549 in Chapter 6.

Murexide (ammonium purpurate) *[3051-09-0]* **M 284.2, m >300°, λ_{max} 520nm (ε 12,000), pK_2 9.2, pK_3 10.9.** The sample may be grossly contaminated with uramil, alloxanthine, etc. Difficult to purify. It is better to synthesise it from pure alloxanthine [Davidson *J Am Chem Soc* **58** 1821 *1936*]. Crystd from water.

Myristic acid (tetradecanoic acid) *[544-63-8]* **M 228.4, m 58°, pK^{20} 6.3 (50% EtOH), pK_{Est} ~4.9 (H_2O).** Purified *via* the *methyl ester* (b 153-154°/10mm, n^{25} 1.4350), as for capric acid. [Trachtman and Miller *J Am Chem Soc* **84** 4828 *1962*.] Also purified by zone melting. Crystd from pet ether and dried in a vacuum desiccator containing shredded wax.

Naphthacene (benz[b]anthracene, 2,3-benzanthracene, rubene) *[92-24-0]* **M 228.3, m >300°, 341° (open capillary), 349°, 357°.** Crystd from EtOH or *benzene. Dissolved in sodium-dried *benzene and passed through a column of alumina. The *benzene was evaporated under vacuum, and the chromatography was repeated using fresh *benzene. Finally, the naphthacene was sublimed under vacuum. [Martin and Ubblehode *J Chem Soc* 4948 *1961*.] Also recrysts in orange needles from xylene and sublimes *in vacuo* at 186°. [UV: *Chem Ber* **65** 517 *1932*, **69** 607 *1936*; IR: *Spectrochim Acta* **4** 373 *1951*.]

2-Naphthaldehyde *[66-99-9]* **M 156.2, m 59°, b 260°/19mm, pK^{20} -7.04 (aq H_2SO_4).** Distilled with steam and crystd from water or EtOH.

Naphthalene *[91-20-3]* **M 128.2, m 80.3°, b 87.5°/10mm, 218.0°/atm, d 1.0253, d^{100} 0.9625, n^{85} 1.5590.** Crystd one or more times from the following solvents: EtOH, MeOH, CCl_4, *benzene, glacial acetic acid, acetone or diethyl ether, followed by drying at 60° in an Abderhalden drying apparatus. Also purified by vacuum sublimation and by fractional crystn from its melt. Other purification procedures include refluxing in EtOH over Raney Ni, and chromatography of a CCl_4 soln on alumina with *benzene as eluting solvent. Baly and Tuck [*J Chem Soc* 1902 *1908*] purified naphthalene for spectroscopy by heating with conc H_2SO_4 and MnO_2, followed by steam distn (repeating the process), and formation of the picrate which, after recrystallisation, was decomposed and the naphthalene was steam distd. It was then crystd from dilute EtOH. It can be dried over P_2O_5 under vacuum. Also purified by sublimation and subsequent crystn from cyclohexane. Alternatively, it has been washed at 85° with 10% NaOH to remove phenols, with 50% NaOH to remove nitriles, with 10% H_2SO_4 to remove organic bases, and with 0.8g $AlCl_3$ to remove thianaphthalenes and various alkyl derivatives. Then it was treated with 20% H_2SO_4, 15% Na_2CO_3 and finally distd. [Gorman et al. *J Am Chem Soc* **107** 4404 *1985*.]
Zone refining purified naphthalene from anthracene, 2,4-dinitrophenylhydrazine, methyl violet, benzoic acid, methyl red, chrysene, pentacene and indoline.

Naphthalene-2,5-disulfonic acid *[92-41-1]* **M 288.2, pK_{Est} <0.** Crystd from conc HCl.

Naphthalene-1-sulfonic acid *[85-47-2]* **M 208.2, m ($2H_2O$) 90°, (anhydrous) 139-140°, pK^{20} -0.17.** Crystd from conc HCl and twice from water.

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