

**Allene (prodiene)** [463-49-0] M 40.1, m -146°, b -32°. Frozen in liquid nitrogen, evacuated, then thawed out. This cycle was repeated several times, then the allene was frozen in a methyl cyclohexane-liquid nitrogen bath and pumped for some time. Also purified by HPLC. [Cripps and Kiefer *Org Synth* 42 12 1962.]

**(-)-Alloaromadendrene** [25246-27-9] M 204.4, b 96°/2mm, 265-267°/atm,  $[\alpha]_{\text{D}}^{25}$  -22° (neat),  $d_4^{20}$  0.923,  $n_{\text{D}}^{23}$  1.501. Fractionally distd from Na. IR has bands at 6.06 and 11.27 $\mu$  due to C=CH<sub>2</sub>. [*J Chem Soc* 715 1953; cf *J Am Chem Soc* 91 6473 1969.]

**neo-Allocimene (tc-2,6-dimethyl-2,4,6-octatriene)** [7216-56-0] M 136.2, b 80°/13mm, 196-198°/atm,  $d_4^{20}$  0.8161,  $n_{\text{D}}^{20}$  1.5437. Fractionally distd through an efficient column and stabilised with ca 0.1% of hydroquinone. UV:  $\lambda_{\text{max}}$  nm( $\epsilon$  M<sup>-1</sup>cm<sup>-1</sup>) 290 (32 500), 279 (41 900) and 270 (32 600). [*Justus Liebigs Ann Chem* 609 1 1957; *Anal Chem* 26 1726 1954.]

**5 $\alpha$ -Allopregnane-3 $\alpha$ ,20 $\alpha$ -diol** [566-58-5] M 320.5, m 248-248.5°,  $[\alpha]_{\text{D}} +17^\circ$  (c 0.15, EtOH). Crystd from EtOH.

**D-Allothreonine [2R,3R(-)-isomer]** [24830-94-2] M 119.1, m 272-273°(dec), 276°(dec),  $[\alpha]_{\text{D}}^{25}$  -9.1° (c 3.9, H<sub>2</sub>O),  $\text{pK}_1^{25}$  2.11,  $\text{pK}_2^{25}$  9.10. Recrystd from aqueous EtOH or 50% EtOH. [*J Chem Soc* 62 1950; *J Am Chem Soc* 194 455 1952; IR: Greenstein & Winitz *The Chemistry of the Amino Acids* J. Wiley, Vol 3 1961.]

**Alloxan [2,4,5,6(1H,3H)pyrimidine, tetrone]** [50-71-5] M 142.0, m -170°(dec),  $\text{pK}^{25}$  6.64. Crystn from water gives the tetrahydrate. Anhydrous crystals are obtained by crystn from acetone, glacial acetic acid or by sublimation *in vacuo*.

**Alloxan monohydrate** [2244-11-3] M 160.1, m 255°(dec),  $\text{pK}$  6.64. Recryst from H<sub>2</sub>O as the *tetrahydrate* in large prisms or rhombs. On heating at 100°, or on exposure to air, this is converted to the *monohydrate*. Dissolve it in its own weight of boiling H<sub>2</sub>O and cool for several days below 0° [the *tetrahydrate* crystallises from soln much more slowly when free from HNO<sub>3</sub>. It is less sol in HCO<sub>3</sub> solns than in H<sub>2</sub>O]. Drying the solid over H<sub>2</sub>SO<sub>4</sub> yields the *monohydrate*. The *anhydrous* crystals can be obtained by recrystn from dry Me<sub>2</sub>CO or AcOH followed by washing with dry Et<sub>2</sub>O or by sublimation in a vacuum. On heating it turns pink at 230° and decomposes at ca 256°. It is acidic to litmus. [*Org Synth Coll Vol III* 37 1955.] It forms a compound with urea which crystallises from H<sub>2</sub>O in yellow needles that become red at 170° and dec at 185-186°.

**Alloxantin** [76-24-4] M 286.2, m 253-255°(dec) (yellow at 225°). Crystd from water or EtOH and kept under nitrogen. Turns red in air.

**Allyl acetate** [591-87-7] M 100.1, b 103°, d 0.928,  $n_4$  1.40488,  $n_{\text{D}}^{27}$  1.4004. Freed from peroxides by standing with crystalline ferrous ammonium sulfate, then washed with 5% NaHCO<sub>3</sub>, followed by saturated CaCl<sub>2</sub> soln. Dried with Na<sub>2</sub>SO<sub>4</sub> and fractionally distd in an all-glass apparatus.

**Allylacetic acid (pent-4-enoic acid)** [591-80-0] M 100.1, m -22.5°, b 83-84°/12mm, 90°/15mm,  $d_4^{20}$  0.9877,  $n_{\text{D}}^{20}$  1.4280,  $\text{pK}^{25}$  4.68. Distil through an efficient column (allyl alcohol has b 95-97°). It is characterised as the *S-benzyl isothiuronium salt* m 155-158° (96% EtOH, aq EtOH) [*Acta Chem Scand* 9 1425 1955], *4-bromophenacyl ester* m 59.5-60.5° (from 90% EtOH). Solubility at 18°: in pyridine (57%), AcOH (7.3%), MeOH (5.4%), Me<sub>2</sub>CO (3.2%), MeOAc (2.8%), EtOH (5.4%), H<sub>2</sub>O (1.8%), PrOH (1.6%), isoPrOH (0.27%). [*J Am Chem Soc* 74 1894 1952.]

**Allyl alcohol** [107-18-6] M 58.1, b 98°,  $d_4$  0.857,  $n_{\text{D}}$  1.4134. Can be dried with K<sub>2</sub>CO<sub>3</sub> or CaSO<sub>4</sub>, or by azeotropic distn with \*benzene followed by distn under nitrogen. It is difficult to obtain peroxide free. Also reflux with magnesium and fractionally distd [Hands and Norman *Ind Chem* 21 307 1945].

**Allylamine** [107-11-9] M 57.1, b 52.9°, d 0.761, n 1.42051, pK<sup>25</sup> 9.49. Purified by fractional distn from calcium chloride. Causes sneezing and tears.

**1-Allyl-6-amino-3-ethyluracil** [642-44-4] M 195.2, m 143-144° (anhydr). Crystd from water (as monohydrate).

**Allyl bromide** [106-95-6] M 121, b 70°, d 1.398, n 1.46924. Washed with NaHCO<sub>3</sub> soln then distd water, dried (CaCl<sub>2</sub> or MgSO<sub>4</sub>), and fractionally distd. Protect from strong light. **LACHRYMATOR, HIGHLY TOXIC and FLAMMABLE.**

**Allyl butyl ether** [3739-64-8] M 114.2, b 64-65°/120mm, 117.8-118°/763mm, d<sub>4</sub><sup>20</sup> 1.4057, n<sub>D</sub><sup>20</sup> 0.7829. Check the IR for the presence of OH str vibrations, if so then wash well with H<sub>2</sub>O, dry with CaCl<sub>2</sub> and distil through a good fractionating column. **The liquid is an irritant.** [*J Org Chem* 23 1666 1958; *J Am Chem Soc* 73 3528 1951.]

**Allyl chloride** [107-05-1] M 76.5, b 45.1°, d 0.939, n 1.4130. Likely impurities include 2-chloropropene, propyl chloride, *i*-propyl chloride, 3,3-dichloropropane, 1,2-dichloropropane and 1,3-dichloropropane. Purified by washing with conc HCl, then with Na<sub>2</sub>CO<sub>3</sub> soln, drying with CaCl<sub>2</sub>, and distn through an efficient column [Oae and Vanderwerf *J Am Chem Soc* 75 2724 1953]. **LACHRYMATOR, TOXIC.**

**Allyl chloroformate** [2937-50-0] M 120.5, b 56°/97mm, 109-110°/atm, d<sub>4</sub><sup>20</sup> 1.14, n<sub>D</sub><sup>20</sup> 1.4223. Wash several times with cold H<sub>2</sub>O to remove alcohol and HCl and dry over CaCl<sub>2</sub>. It is **important** to dry well before distilling *in vacuo*. Note that the receiver should be cooled in ice to avoid loss of distillate into the trap and vacuum pump. The liquid is **highly TOXIC and flammable.** [*J Am Chem Soc* 72 1254 1950.]

**Allyl cyanide (3-butene nitrile)** [109-75-1] M 67.1, b -19.6°/1.0mm, 2.9°/5 mm, 14.1°/5mm, 26.6°/20mm, 48.8°/60mm, 60.2°/100mm, 98°/400mm, 119°/760mm, d<sub>4</sub><sup>20</sup> 0.8341, n<sub>D</sub><sup>20</sup> 1.406. It should be redistd at atmospheric pressure then distilled under a vacuum to remove final traces of HCN from the residue. Note that the residue from the first distiln may be difficult to remove from the flask and should be treated with conc HNO<sub>3</sub> then H<sub>2</sub>O and finally hot EtOH (**CARE**). Allyl cyanide has an onion-like odour and is stable to heat. It forms a complex with AlCl<sub>3</sub> (2:2) m 41°, and (3:2) m 120°. **All operations should be done in an efficient fume hood as the liquid is flammable and HIGHLY TOXIC.** [*Org Synth Coll Vol I* 46 1941.]

**Allyl disulfide (diallyl disulfide)** [2179-57-9] M 146.3, b 58-59°/5mm, 79-81°/20mm, 138-139°/atm, d<sub>4</sub><sup>20</sup> 1.01, n<sub>D</sub><sup>20</sup> 1.541. Purified by fractional distn until their molar refractivities are in uniformly good agreement with the calculated values [*J Am Chem Soc* 69 1710 1947]. Also purified by gas chromatography [retention times: *J Org Chem* 24 175 1959; UV: *J Chem Soc* 395 1949].

**RS- $\alpha$ -Allylglycine (2-aminopent-4-enoic acid).** [7685-44-1] M 115.1, m 250-255°(dec), pK<sub>Est(1)</sub> ~2.3, pK<sub>Est(2)</sub> ~9.6. Dissolve in absolute EtOH and ppt with pyridine, then recrystallise from aqueous EtOH [R<sub>F</sub> in BuOH:EtOH:NH<sub>3</sub>:H<sub>2</sub>O (4:4:1:1:) 0.37]. The *hydrobromide* has m 136-140° (from EtOAc) and the *phenylureido* derivative has m 159-161°. [*Monatsh Chem* 89 377 1958.]

**1-N-Allyl-3-hydroxymorphinan** [152-02-3] M 283.4, m 180-182°. Crystd from aqueous EtOH.

**Allyl iodide (3-iodopropene)** [556-56-9] M 167.7, b 103°, d<sup>12</sup> 1.848. Purified in a dark room by washing with aq Na<sub>2</sub>SO<sub>3</sub> to remove free iodine, then drying with MgSO<sub>4</sub> and distilling at 21mm pressure, to give a very pale yellow liquid. (This material, dissolved in hexane, was stored in a light-tight container at -5° for up to three months before free iodine could be detected, by its colour in the soln) [*Sibbett and Noyes J Am Chem Soc* 75 761 1953].

**5-Allyl-5-isobutylbarbituric acid** [77-26-9] M 224.3, m 139°, 139-140°, 140-142°, pK<sup>38</sup> 12.36. It can be recrystallised from H<sub>2</sub>O or dilute EtOH, and sublimes at 100-120°/8-12mm. It is soluble in \*C<sub>6</sub>H<sub>6</sub>, cyclohexane, tetralin and pet ether at 20°. [J Am Chem Soc 77 1486 1955.]

**Allylisocyanate** [1476-23-9] M 83.1, b 84°/atm, 87-89°/atm, d<sub>4</sub><sup>20</sup> 0.94, n<sub>D</sub><sup>20</sup> 1.417. Purify as for allylthiocyanate.

**Allylthiocyanate** [57-06-7] M 99.2, m -80°, b 84-85°/80mm, 150°/760mm, 151°/atm, d<sub>4</sub><sup>20</sup> 1.017, n<sub>D</sub><sup>20</sup> 1.5268. Fractionate using an efficient column, preferably in a vacuum. It is a yellow pungent irritating and TOXIC (suspected CARCINOGEN) liquid. Store in a sealed tube under N<sub>2</sub>. The *N'*-benzylthiourea derivative has m 94.5° (from aq EtOH) [J Am Chem Soc 74 1104 1952].

**Allyl Phenyl sulfide** [5296-64-0] M 150.2, b 59-60°/1.5mm, 79-80°/3mm, 114-114.3°/23.5mm, 225-226°/740mm, 215-218°/750mm, d<sub>4</sub><sup>20</sup> 1.0275, n<sub>D</sub><sup>20</sup> 1.5760. Dissolve in Et<sub>2</sub>O, wash with alkali, H<sub>2</sub>O, dry over CaCl<sub>2</sub>, evaporate and fractionally distil, preferably under vacuum. It should not give a ppte with an alcoholic soln of Pb(OAc)<sub>2</sub>. [J Am Chem Soc 52 3356 1930, 74 48 1952.]

***N*-Allylthiourea (thiosinamine)** [109-57-9] M 116.2, m 70-73°, 78°. Recrystd from H<sub>2</sub>O. Soluble in 30 parts of cold H<sub>2</sub>O, soluble in EtOH but insoluble in \*C<sub>6</sub>H<sub>6</sub>. Also recrystd from acetone, EtOH or ethyl acetate, after decolorising with charcoal. The white crystals have a bitter taste with a slight garlic odour and are TOXIC. [Anal Chem 21 421 1949.]

***N*-Allylurea** [557-11-9] M 100.1, m 85°. Crystd from EtOH, EtOH/ether, EtOH/chloroform or EtOH/toluene.

**Aloin [10-glucopyranosyl-1,8-dihydroxy-3-(hydroxymethyl)-9(10*H*)anthracenone, Barbaloin]** [8015-61-0] M 418.4, m 148-148.5°, 148-150°. Lemon yellow crystals from H<sub>2</sub>O (450g/1.5L) as the *monohydrate* which has a lower m (70-80°). [J Chem Soc 2573 1932, 3141 1956.]

**D-Altrose** [1990-29-0] M 180.2, m 103-105°, [α]<sub>546</sub> +35° (c 7.6, H<sub>2</sub>O). Crystd fom aq EtOH.

**Amberlite IRA-904 Anion exchange resin (Rohm and Haas)** [9050-98-0]. Washed with 1M HCl, CH<sub>3</sub>OH (1:10) and then rinsed with distilled water until the washings were neutral to litmus paper. Finally extracted successively for 24h in a Soxhlet apparatus with MeOH, \*benzene and cyclohexane [Shue and Yan Anal Chem 53 2081 1981]. Strongly basic resin also used for base catalysis [Fieser & Fieser Reagents for Org Synth 1 511, Wiley 1967].

**Aminoacetaldehyde dimethyl acetal (2,2-dimethoxyethylamine)** [22483-09-6] M 105.1, m <-78°, b 139.5°/768mm, 137-139°/atm, d<sub>4</sub><sup>20</sup> 0.9676 n<sub>D</sub><sup>20</sup> 1.4144. Dry over KOH pellets and distil through a 30cm vac jacketed Vigreux column. [J Am Chem Soc 75 3398 1953, 77 6640 1955.]

***p*-Aminoacetanilide** [122-80-5] M 150.2, m 162-163°. Crystd from water.

**Aminoacetic acid (Glycine)** [56-40-6] M 75.1, m 262° (dec, goes brown at 226°, sublimes at 200°/0.1mm), pK<sub>1</sub><sup>25</sup> 2.35, pK<sub>2</sub><sup>25</sup> 9.78. Crystd from distilled water by dissolving at 90-95°, filtering, cooling to about -5°, and draining the crystals centrifugally. Alternatively, crystd from distilled water by addition of MeOH or EtOH (e.g. 50g dissolved in 100mL of warm water, and 400mL of MeOH added). The crystals can be washed with MeOH or EtOH, then with diethyl ether. Likely impurities are ammonium glycinate, iminodiacetic acid, nitrilotriacetic acid, ammonium chloride.

**Aminoacetonitrile bisulfate** [151-63-3] M 154.1, m 188°(dec) Crystd from aqueous EtOH.

**Aminoacetonitrile hydrochloride** [6011-14-9] M 92.5, m 166-167°, 172-174°, pK<sup>25</sup> 5.34. Recrystd from dil EtOH *hygroscopic* leaflets. Best to crystallise from absolute EtOH-Et<sub>2</sub>O (1:1) and then recryst from absolute EtOH. The m recorded range from 144° to 174°. The free base has b 58°/15mm with

partial decomposition. [*J Prakt Chem* [2] **65** 189 1902; *J Am Chem Soc* **56** 2197 1934; *J Chem Soc* 1371 1947.]

**2-Aminoacetophenone hydrochloride** [5468-37-1] **M 171.6, m 188°(dec), 194°(dec), pK<sup>25</sup> 5.34.** Crystd from acetone/EtOH or 2-propanol [Castro *J Am Chem Soc* **108** 4179 1986].

***m*-Aminoacetophenone** [99-03-6] **M 135.2, m 98-99°, pK<sup>25</sup> 3.56.** Recrystd from EtOH.

***p*-Aminoacetophenone** [99-92-3] **M 135.2, m 104-106°, 105-107°, b 293°/atm, pK<sup>25</sup> 2.19** Recryst from CHCl<sub>3</sub>, \*C<sub>6</sub>H<sub>6</sub> or H<sub>2</sub>O. Soluble in hot H<sub>2</sub>O. UV (EtOH) has λ<sub>max</sub> 403nm (log ε 4.42) [*J Am Chem Soc* **75** 2720 1953]. [*Anal Chem* **26** 726 1954.] The *2,4-dinitrophenylhydrazone* has **m 266-267°** (from CHCl<sub>3</sub> or EtOH), and the *semicarbazone* has **m 193-194°(dec)**(from MeOH) and the *hydrochloride* has **m 98°(dec)**(from H<sub>2</sub>O).

**α-Amino acids** see Chapter 6.

**9-Aminoacridine [9-acridineamine]** [90-45-9] **M 194.2, m 241°, pK<sup>20</sup> 9.95.** Crystd from EtOH or acetone and sublimes at 170-180°/0.04mm [Albert and Ritchie *Org Synth Coll Vol III* 53 1955; for hydrochloride see Chapter 6.]

***dl*-α-Aminoadipic acid (hydrate)** [542-32-5] **M 161.2, m 196-198°, pK<sub>Est(1)</sub> ~2.0, pK<sub>Est(2)</sub> ~4.5, pK<sub>Est(3)</sub> ~9.8.** Crystd from water.

**2-Amino-4-anilino-*s*-triazine** [537-17-7] **M 168.2, m 235-236°, pK<sub>Est</sub> ~5.5.** Crystd from dioxane or 50% aqueous EtOH.

**1-Aminoanthraquinone-2-carboxylic acid** [82-24-6] **M 276.2, m 295-296°.** Crystd from nitrobenzene.

**4-Aminoantipyrine** [83-07-8] **M 203.3, m 109°.** Crystd from EtOH or EtOH/ether.

***p*-Aminoazobenzene (*p*-phenylazoaniline)** [60-09-3] **M 197.2, m 126°, pK<sup>25</sup> ~2.82.** Crystd from EtOH, CCl<sub>4</sub>, pet ether/\*benzene, or a MeOH/water mixture.

***o*-Aminoazotoluene (Fast Garnet GBC base, 4'-amino-2,3'-dimethylazobenzene)** [97-56-3] **M 225.3, m 101.4-102.6°, CI 11160, pK<sub>Est</sub> ~2.8.** Crystd twice from EtOH, once from \*benzene, then dried in an Abderhalden drying apparatus [Cilento *J Am Chem Soc* **74** 968 1952]. **CARCINOGENIC.**

**2-Aminobenzaldehyde** [529-23-7] **M 121.1, m 39-40°, pK<sup>20</sup> 1.36.** Distd in steam and crystd from water or EtOH/ether.

**2-Aminobenzaldehyde phenylhydrazone (Nitrin)** [63363-93-9] **M 211.3, m 227-229°.** Crystd from acetone. [Knöpfer *Monatsh Chem* **31** 97 1910.]

**3-Aminobenzaldehyde** [29159-23-7] **M 121.1, m 28-30°, pK<sub>Est</sub> ~2.0.** Crystd from ethyl acetate.

**4-Aminobenzamide hydrochloride** [59855-11-7] **M 199.6, m 284-285°, pK<sub>Est</sub> ~1.7.** Recrystd from EtOH.

***p*-Aminobenzeneazodimethylaniline** [539-17-3] **M 240.3, m 182-183°.** Crystd from aqueous EtOH.

***o*-Aminobenzoic acid (anthranilic acid)** [118-92-3] **M 137.1, m 145°, pK<sub>1</sub><sup>25</sup> 2.94, pK<sub>2</sub><sup>25</sup> 4.72.** Crystd from water (charcoal). Has also been crystd from 50% aqueous acetic acid. Can be vacuum sublimed.

***m*-Aminobenzoic acid** [99-05-8] M 137.1, m 174°, pK<sub>1</sub><sup>25</sup> 3.29, pK<sub>2</sub><sup>25</sup> 5.10. Crystd from water.

***p*-Aminobenzoic acid** [150-13-0] M 137.1, m 187-188°, pK<sub>1</sub><sup>25</sup> 2.45, pK<sub>2</sub><sup>25</sup> 4.85. Purified by dissolving in 4-5% aqueous HCl at 50-60°, decolorising with charcoal and carefully precipitating with 30% Na<sub>2</sub>CO<sub>3</sub> to pH 3.5-4 in the presence of ascorbic acid. It can be crystd from water, EtOH or EtOH/water mixtures.

***p*-Aminobenzonitrile** [873-74-5] M 118.1, m 86-86.5°, 85-87°, pK<sup>25</sup> 1.74. Crystd from water, 5% aqueous EtOH or EtOH and dried over P<sub>2</sub>O<sub>5</sub> or dried *in vacuo* for 6h at 40°. [Moore et al. *J Am Chem Soc* 108 2257 1986; Edidin et al. *J Am Chem Soc* 109 3945 1987.]

**4-Aminobenzophenone** [1137-41-3] M 197.2, m 123-124°, pK<sup>25</sup> 2.17. Dissolved in aq acetic acid, filtered and ppted with ammonia. Process repeated several times, then recrystd from aqueous EtOH.

**2-Aminobenzothiazole** [136-95-8] M 150.2, m 132°, pK<sup>20</sup> 4.48. Crystd from aqueous EtOH.

**6-Aminobenzothiazole** [533-30-2] M 150.2, m 87°, pK<sub>Est</sub> ~3. Crystd from aqueous EtOH.

***N*-(*p*-Aminobenzoyl)-L-glutamic acid** [4271-30-1] M 266.3, m 173° (L-form), [α]<sub>546</sub> -17.5° (c 2, 0.1m HCl); 197° (DL), pK<sub>Est(1)</sub> ~1.7, pK<sub>Est(2)</sub> ~3.4, pK<sub>Est(3)</sub> ~4.3. Crystd from H<sub>2</sub>O.

**3-*o*-Aminobenzyl-4-methylthiazolium chloride hydrochloride** [534-94-1] M 277.4, m 213°(dec). Crystd from aqueous EtOH.

**4-Amino-1-benzylpiperidine** [50541-93-0] M 190.3, b ~180°/20mm, d 0.933, n 1.543, pK<sub>Est(1)</sub> ~ 8.3 pK<sub>Est(2)</sub> ~ 10.4. Purified by distn *in vacuo*, and stored under N<sub>2</sub>, because it absorbs CO<sub>2</sub>. The *dihydrochloride salt* [1205-72-7] has m 270-273° (255°) after recrystn from MeOH + EtOAc or EtOH. [*J Chem Soc* 3165, 3172 1957.] The *4-methylamino-1-benzylpiperidine* derivative has b 168-172°/17mm, n 1.5367 [*J Am Chem Soc* 70 4009 1948]. The *1-(1-benzyl-4-piperidinyl)-3-cyano-2-methylisothiourea* derivative has m 160° from CHCl<sub>3</sub>/Et<sub>2</sub>O [Prepn, IR, NMR: Ried et al. *Chem Ber* 116 1547 1983].

***o*-Aminobiphenyl** [90-41-5] M 169.2, m 49.0°, pK<sup>18</sup> 3.83. Crystd from aqueous EtOH (charcoal).

***p*-Aminobiphenyl** [92-67-1] M 169.2, m 53°, b 191°/16mm, pK<sup>18</sup> 4.38. Crystd from water or EtOH. CARCINOGENIC.

**2-Amino-5-bromotoluene** [583-75-5] M 186.1, m 59°, pK<sup>25</sup> 3.58. Steam distd, and crystd from EtOH.

***RS*-2-Aminobutyric acid** [2835-81-6] M 103.1, m 303°(dec), pK<sub>1</sub><sup>25</sup> 2.29, pK<sub>2</sub><sup>25</sup> 9.83. Crystd from water.

***S*-2-Aminobutyric acid** [1492-24-6] M 103.1, m 292°(dec), [α]<sub>D</sub> + 20.4° (c 2, 2.5N HCl). Crystd from aqueous EtOH.

**3-Aminobutyric acid** [2835-82-7] M 103.1, m 193-194°, pK<sub>Est(1)</sub> ~3.5, pK<sub>Est(2)</sub> ~10.3. Crystd form aqueous EtOH or MeOH + Et<sub>2</sub>O.

**4-Aminobutyric acid (GABA)** [56-12-2] M 103.1, m 202°(dec), pK<sub>1</sub><sup>25</sup> 4.14, pK<sub>2</sub><sup>25</sup> 10.55. Crystd form aqueous EtOH or MeOH + Et<sub>2</sub>O.

**2-Amino-5-chlorobenzoic acid** [635-21-1] M 171.6, m 100°, pK<sub>1</sub><sup>25</sup> 1.69, pK<sub>2</sub><sup>25</sup> 4.35. Crystd from water, EtOH or chloroform.

**3-Amino-4-chlorobenzoic acid** [2840-28-0] M 171.6, m 216-217°, pK<sub>Est(1)</sub> ~2.7, pK<sub>Est(2)</sub> ~2.9. Crystd from water.

**4-Amino-4'-chlorobiphenyl** [135-68-2] M 203.5, m 134°, pK<sub>Est</sub> ~4.0. Crystd from pet ether.

**2-Amino-4-chloro-6-methylpyrimidine** [5600-21-5] M 143.6, m 184-186°, pK<sub>Est</sub> ~1.0. Crystd from EtOH.

**2-Amino-5-chloropyridine** [1072-98-6] M 128.6, m 135-136°, pK 4.38. Crystd from pet ether, sublimes at 50°/0.5mm.

**1-Amino-1-cyclopentanecarboxylic acid (cycloleucine)** [52-52-8] M 129.2, m 330°(dec), pK<sub>Est(1)</sub> ~2.5 pK<sub>Est(2)</sub> ~10.3. Crystd from aq EtOH.

**2-Amino-3,5-dibromopyridine** [35486-42-1] M 251.9, m 103-104°, pK<sub>Est</sub> ~2.4. Steam distd and crystd from aqueous EtOH or pet ether.

**2-Amino-4,6-dichlorophenol** [527-62-8] M 175.0, m 95-96°, pK<sub>Est(1)</sub> ~3.1, pK<sub>Est(2)</sub> ~6.8. Crystd from CS<sub>2</sub> or \*benzene.

**3-Amino-2,6-dichloropyridine** [62476-56-6] M 164.0, m 119°, b 110°/0.3mm, pK<sub>Est</sub> ~2.0. Crystd from water.

**4-Amino-N,N-diethylaniline hydrochloride** [16713-15-8] M 200.7, m 233.5°, pK<sup>22</sup> 6.61. Crystd from EtOH.

**4-Amino-3,5-diiodobenzoic acid** [2122-61-4] M 388.9, m >350°, pK<sub>Est(1)</sub> 0.4, pK<sub>Est(2)</sub> ~1.6. Purified by soln in dilute NaOH and pptn with dilute HCl. Air dried.

**2-Amino-4,6-dimethylpyridine** [5407-87-4] M 122.2, m 69-70.5°, pK 7.84. Crystd from hexane, ether/pet ether or \*benzene. Residual \*benzene was removed over paraffin-wax chips in an evacuated desiccator.

**2-Amino-4,6-dimethylpyrimidine** [767-15-7] M 123.2, m 152-153°, pK<sup>25</sup> 4.95. Crystn from water gives m 197°, and crystn from acetone gives m 153°.

**2-Aminodiphenylamine** [534-85-0] M 184.2, m 79-80°, pK<sub>Est(1)</sub> ~3.8 (NH<sub>2</sub>), pK<sub>Est(2)</sub> <~0. Crystd from H<sub>2</sub>O.

**4-Aminodiphenylamine** [101-54-2] M 184.2, b 155°/0.026mm, pK<sup>25</sup> 5.20. Crystn from EtOH gives m 66°, and crystn from ligroin gives m 75°.

**2-Amino-1,2-diphenylethanol** [530-36-9] M 213.3, m 165°, pK<sub>Est(1)</sub> ~7.5. Crystd from EtOH.

**2-Aminodiphenylmethane** [28059-64-5] M 183.3, m 52°, b 172°/12mm and 190°/22mm, pK<sub>Est(1)</sub> ~4.2. Crystd from ether.

**2-Aminoethanethiol** see cysteamine in Chapter 6.

**2-Aminoethanol (ethanolamine)** [141-43-5] M 61.1, f 10.5°, b 72-73°/12mm, 171.1°/760mm, d 1.012, n 1.14539, pK<sup>25</sup> 9.51. Decomposes slightly when distd at atmospheric pressure, with the formation of conducting impurities. Fractional distn at about 12mm pressure is satisfactory. After distn, 2-aminoethanol was further purified by repeated washing with ether and crystn from EtOH (at low temperature). After fractional distn in the absence of CO<sub>2</sub>, it was twice crystd by cooling, followed by distn.

*Hygroscopic.* [Reitmeier, Silvertz and Tartar *J Am Chem Soc* **62** 1943 1940.] It can be dried by azeotropic distn with dry \*benzene.

**2-Aminoethanol hydrochloride** [2002-24-6] M 97.6, m 75-77°. Crystd from EtOH. It is deliquescent.

**2-Aminoethyl hydrogen sulfate (sulfuric acid mono-2-aminoethyl ester)** [926-39-6] M 141.1, m 285-287° (chars at 275°). Crystd from water or dissolved in water and EtOH added.

**S-(2-Aminoethyl)isothiuronium bromide hydrobromide** [56-10-0] M 281.0, m 194-195°. Crystd from absolute EtOH/ethyl acetate. It is *hygroscopic*.

**(2-Aminoethyl)trimethylammonium chloride hydrochloride (chloramine chloride hydrochloride)** [3399-67-5] M 175.1, m 260°(dec). Crystd from EtOH. (Material is very soluble in H<sub>2</sub>O).

**2-Aminofluorene** [153-78-6] M 181.2, m 127.8-128.8°, 132-133°, pK<sup>25</sup> 4.64. Wash well with H<sub>2</sub>O and recrystd from Et<sub>2</sub>O or 50% aqueous EtOH (25g with 400mL), and dry in a vacuum. Store in the dark. [*Org Synth Coll Vol II* 447 1943; *Coll Vol V* 30 1973].

**4-Amino hippuric acid** [61-78-9] M 194.2, m 198-199°, pK<sub>Est(1)</sub>~1.7(NH<sub>2</sub>), pK<sub>Est(2)</sub>~3.4 (CO<sub>2</sub>H). Crystd from H<sub>2</sub>O.

**4-Amino-3-hydrazino-5-mercapto-1,2,4-triazole (Purpald)** [1750-12-5] M 146.2, m 228-230°(dec), 234-235°(dec), pK<sub>Est(1)</sub>~2, pK<sub>Est(2)</sub>~3 (NH<sub>2</sub>), pK<sub>Est(3)</sub>~8 (SH). Crystd from H<sub>2</sub>O (0.6g in 300-400mL). The *benzylidene deriv* has m 245-246°(dec) from *i*-PrOH [Hogarth *J Chem Soc* 4817 1952].

**1-Amino-4-hydroxyanthraquinone** [116-85-8] M 293.2, m 207-208°, pK<sub>Est(1)</sub>~2.6 (NH<sub>2</sub>), pK<sub>Est(2)</sub>~9.0 (OH). Purified by TLC on SiO<sub>2</sub> gel plates using toluene/acetone (9:1) as eluent. The main band was scraped off and extracted with MeOH. The solvent was evaporated and the dye was dried in a drying pistol [Land, McAlpine, Sinclair and Truscott *J Chem Soc, Faraday Trans 1* 72 2091 1976]. Crystd from aq EtOH.

***dl*-4-Amino-3-hydroxybutyric acid** [924-49-2] M 119.1, m 225°(dec), pK<sub>1</sub><sup>25</sup>~3.80 (CO<sub>2</sub>H), pK<sub>Est(2)</sub>~9.3. Crystd from H<sub>2</sub>O or aqueous EtOH.

**5-Amino-8-hydroxyquinoline hydrochloride** [3881-33-2] M 196.7, pK<sub>1</sub><sup>20</sup> 5.67, pK<sub>2</sub><sup>20</sup> 11.24. Dissolved in minimum of MeOH, then Et<sub>2</sub>O was added to initiate pptn. Ppte was filtered off and dried [Lovell et al. *J Phys Chem* **88** 1885 1984].

**3-Amino-4-hydroxytoluene** [95-84-1] M 123.2, m 137-138°, pK<sub>Est(1)</sub>~4.7(NH<sub>2</sub>), pK<sub>Est(2)</sub>~9.6 (OH). Crystd from H<sub>2</sub>O or toluene.

**4-Amino-5-hydroxytoluene** [2835-98-5] M 123.2, m 159°, pK<sub>Est(1)</sub>~5.4 (NH<sub>2</sub>), pK<sub>Est(2)</sub>~10.2 (OH). Crystd from H<sub>2</sub>O, 50% EtOH, or toluene.

**6-Amino-3-hydroxytoluene** [2835-99-6] M 123.2, m 162°(dec), pK<sub>Est(1)</sub>~5.4 (NH<sub>2</sub>), pK<sub>Est(2)</sub>~10.4 (OH). Crystd from 50% EtOH.

**4-Aminoimidazole-5-carboxamide hydrochloride (AICAR HCl)** [72-40-2] M 162.6, m 255-256°(dec), pK<sub>Est(1)</sub>~3.5, pK<sub>Est(2)</sub>~9.4. Recrystd from EtOH.

**5-Aminoindane** [24425-40-9] M 133.2, m 37-38°, b 131°/15mm, 146-147°/25mm, 247-249°/745mm, pK<sup>16</sup> 5.31. Distd and then crystd from pet ether.

**6-Aminoindazole** [6967-12-0] M 133.2, m 210°, pK<sup>25</sup> 3.99. Crystd from H<sub>2</sub>O or EtOH and sublimed in a vacuum.

**2-Amino-5-iodotoluene** [13194-68-8] M 233.0, m 87°, pK<sub>Est</sub> ~3.6. Crystd from 50% EtOH.

**α-Aminoisobutyric acid** [62-57-7] M 103.1, m sublimes at 280°, pK<sub>1</sub><sup>25</sup> 2.36, pK<sub>2</sub><sup>25</sup> 10.21. Crystd from aqueous EtOH and dried at 110°.

**RS- β-Aminoisobutyric acid (α-methyl-β-alanine)** [10569-72-9] M 103.1, m 176-178°, 178-180°, 181-182°, R (-)- isomer [144-90-1] m 183°, [α]<sub>D</sub><sup>25</sup> -21° (c 0.43, H<sub>2</sub>O), pK<sub>Est(1)</sub> ~ 3.7, pK<sub>Est(2)</sub> ~ 10.2. Colorless prisms from hot H<sub>2</sub>O, were powdered and dried *in vacuo*. The purity is checked by paper chromatography (Whatman 1) using ninhydrin spray to visualise the amino acid; R<sub>F</sub> values in 95% MeOH and *n*-PrOH/5N HCOOH (8:2) are 0.36 and 0.50 respectively. [Kupiecki and Coon *Biochem Prep* 7 20 1960; Pollack *J Am Chem Soc* 65 1335 1943.] The *R*-enantiomer, isolated from iris bulbs or human urine was crystd from H<sub>2</sub>O and sublimed *in vacuo* [Asen et al. *J Biol Chem* 234 343 1959]. The *RS*-hydrochloride was recrystd from EtOH/Et<sub>2</sub>O m 128-129°, 130° [Böhme et al. *Chem Ber* 92 1258, 1260, 1261 1959].

**5-Aminolaevulinic acid hydrochloride** [5451-09-2] M 167.6, m 156-158°(dec), pK<sub>1</sub><sup>22</sup> 4.05, pK<sub>2</sub><sup>22</sup> 8.90. Dried in a vacuum desiccator over P<sub>2</sub>O<sub>5</sub> overnight then crystd by dissolving in cold EtOH and adding dry Et<sub>2</sub>O.

**Aminomalonitrile toluene-4-sulfonate** [5098-14-6] M 253.4, m 168-170°, 172°(dec), pK<sub>Est</sub> ~ 1.3. Colourless crystals on recrystn from MeCN (1.8g in 100mL) using activated charcoal. Wash the crystals with dry Et<sub>2</sub>O and dry at 25°/1mm. Recovery of ~80%. [Ferris et al. *Org Synth Coll Vol V* 32 1973.]

**3-Amino-5-mercapto-1,2,4-triazole** [16691-43-3] M 116.1, m 298°, pK<sub>Est(1)</sub> ~ 3.0, pK<sub>Est(2)</sub> ~ 9. Recrystd from H<sub>2</sub>O and dried *in vacuo*. The *acetyl derivative* has m 325°(dec) after recrystn from H<sub>2</sub>O. [Beilstein 26, 3rd/4th Suppl p. 1351.] Also recrystd from EtOH/H<sub>2</sub>O (3:1, 1g in 50 mL, 50% recovery), m 300-302° dec subject to heating rate (λ<sub>max</sub> 263nm, log ε 4.12), and *S-Benzyl derivative* when crystd from \*C<sub>6</sub>H<sub>6</sub>/EtOH (20:1), or CHCl<sub>3</sub>/Et<sub>2</sub>O has m 109-111° [Godfrey and Kruzer *J Chem Soc* 3437 1960].

**2-Amino-4-methoxy-6-methylpyrimidine** [7749-47-5] M 139.2, m 157-159°, 158-158.5°, 158-160°, pK<sub>Est</sub> ~ 6.0. Recrystd from H<sub>2</sub>O. The *picrate* has m 220-221°(dec). [Baker et al. *J Am Chem Soc* 69 3072, 3075 1947; Sirakawa et al. *Yakugaku Zasshi* 73 598 1953; Backer and Grevenstuk *Recl Trav Chim, Pays-Bas* 61 291 1942.]

**8-Amino-6-methoxyquinoline** [90-52-8] M 174.2, m 41-42°, 51°, b 137-138°/1mm, pK<sup>70.1</sup> 3.38. Distd under N<sub>2</sub> and high vac, then recrystd several times from MeOH (0.4mL/g). It remains colourless for several months when purified in this way [Elderfield and Rubin *J Am Chem Soc* 75 2963 1953].

**1-Amino-4-methylaminoanthraquinone** [1220-94-6] M 252.3, pK<sub>Est(1)</sub> ~1, pK<sub>Est(2)</sub> <~4. Purified by TLC on silica gel plates using toluene/acetone (3:1) as eluent. The main band was scraped off and extracted with MeOH. The solvent was evaporated and the residue dried in a drying pistol [Land, McAlpine, Sinclair and Truscott *J Chem Soc, Faraday Trans 1* 72 2091 1976].

**4-Aminomethylbenzenesulfonamide hydrochloride** [138-37-4] M 222.3, m 265-267°, pK<sub>1</sub><sup>20</sup> 8.18 (NH<sub>2</sub>), pK<sub>2</sub><sup>20</sup> 10.23 (SONH<sub>2</sub>). Crystd from dilute HCl and dried in a vacuum at 100°.

**S-2-Amino-3-methyl-1-butanol (S-valinol)** [2026-48-4] M 103.2, m 31-32°, b 88°/11mm, d 0.92, [α]<sub>546</sub> + 16.5° (c 6.32, l = 2 H<sub>2</sub>O), [α]<sub>D</sub> + 15.6° (EtOH), pK<sub>Est</sub> ~10.4. Purified by vacuum distn using short Vigreux column. Alternatively it is purified by steam distn. The steam distillate is acidified with HCl, the aq layer is collected and evapd. The residue is dissolved in butan-1-ol, filtered and dry Et<sub>2</sub>O added to cryst the hydrochloride salt (*hygroscopic*), m 113°. The free base can be obtained by suspending the salt in Et<sub>2</sub>O adding small vols of satd K<sub>2</sub>CO<sub>3</sub> until effervescence is complete and the mixture is distinctly alkaline. At this stage the aqueous layer should appear as a white sludge. The mixture is heated to boiling and refluxed for 30 min (more Et<sub>2</sub>O is added if necessary). The Et<sub>2</sub>O is decanted off from the white sludge, the



sludge is extracted twice with Et<sub>2</sub>O (by boiling for a few minutes), the combined organic layers are dried (KOH pellets), evapd and the residue distd in a vacuum.

**7-Amino-4-methylcoumarin** [26093-31-2] M 175.2, m 221-442°(dec), pK<sub>Est</sub> ~3.2. Dissolved in 5% HCl, filtered and basified with 2M ammonia. The ppt is dried in a vacuum, and crystd from dilute EtOH. It yields a blue soln and is light sensitive.

**4-Amino-2-methyl-1-naphthol hydrochloride** [130-24-5] M 209.6, m 283°(dec), pK<sub>Est(1)</sub>~5.6 (NH<sub>2</sub>), pK<sub>Est(2)</sub> ~10.4 (OH). Crystd from dilute HCl.

**2-Amino-2-methyl-1,3-propanediol** [115-69-5] M 105.1, m 111°, b 151-152°/10mm, pK<sup>25</sup> 8.80. Crystd three times from MeOH, dried in a stream of dry N<sub>2</sub> at room temp, then in a vacuum oven at 55°. Stored over CaCl<sub>2</sub> [Hetzer and Bates *J Phys Chem* 66 308 1962].

**2-Amino-2-methyl-1-propanol (β-aminoisobutanol)** [124-68-5] M 89.4, m 24°, 31°, b 67°/10mm, 164-166°/760mm, d 0.935, n 1.45, pK<sup>25</sup> 9.71. Purified by distn and fractional freezing. The *hydrochloride* has m 204°-206°.

**2-Amino-3-methylpyridine** [1603-40-3] M 108.1, m 33.2°, b 221-222°, pK<sup>25</sup> 7.24. Crystd three times from \*benzene, most of the residual \*benzene being removed from the crystals over paraffin wax chips in an evacuated desiccator. The amine, transferred to a separating funnel under N<sub>2</sub>, was left in contact with NaOH pellets for 3h with occasional shaking. It was then placed in a vacuum distilling flask where it was refluxed gently in a stream of dry N<sub>2</sub> before being fractionally distd [Mod, Magne and Skau *J Phys Chem* 60 1651 1956].

**2-Amino-4-methylpyridine** [695-34-1] M 108.1, m 99.2°, b 230°, pK<sup>25</sup> 7.48. Crystd from EtOH or a 2:1 \*benzene/acetone mixture, and dried under vacuum.

**2-Amino-5-methylpyridine** [1603-41-4] M 108.1, m 76.5°, b 227°, pK<sup>25</sup> 7.22. Crystd from acetone.

**2-Amino-6-methylpyridine** [1824-81-3] M 108.1, m 44.2°, b 208-209°, pK<sup>25</sup> 7.41. Crystd three times from acetone, dried under vacuum at ca 45°. After leaving in contact with NaOH pellets for 3h, with occasional shaking, it was decanted and fractionally distd [Mod, Magne and Skau *J Phys Chem* 60 1651 1956]. Also recrystd from CH<sub>2</sub>Cl<sub>2</sub> by addition of pet ether. [Marzilli et al. *J Am Chem Soc* 108 4830 1986.]

**2-Amino-5-methylpyrimidine** [50840-23-8] M 109.1, m 193.5°, pK<sub>Est</sub> ~4.0. Crystd from water and \*benzene. Sublimes at 50°/0.5mm.

**4-Amino-2-methylquinoline** [6628-04-2] M 158.2, m 168°, b 333°/760mm, pK<sup>20</sup> 9.42. Crystd from \*benzene/pet ether.

**2-Aminonaphthalene (β-naphthylamine)** [91-59-8] M 143.2, m 111-113°, pK<sup>25</sup> 4.20. See entry on p. 306.

**3-Amino-2-naphthoic acid** [5959-52-4] M 187.2, m 214°(dec), pK<sub>Est(1)</sub>~1.5 pK<sub>Est(2)</sub> ~4.0. Crystd from aqueous EtOH.

**4-Amino-5-naphthol-2,7-disulfonic acid** [90-20-0] M 320.3, pK<sub>1</sub><sup>25</sup> 3.63, pK<sub>2</sub><sup>25</sup> 8.83. Sufficient Na<sub>2</sub>CO<sub>3</sub> (ca 22g) to make the soln slightly alkaline to litmus was added to a soln of 100g of the dry acid in 750mL of hot distd water, followed by 5g of activated charcoal and 5g of Celite. The suspension was stirred for 10min and filtered by suction. The acid was pptd by adding ca 40mL of conc HCl (soln blue to Congo Red), then filtered by suction through sharkskin filter circular sheet (or hardened filter paper) and washed with 100mL of distd water. The purification process was repeated. The acid was dried overnight in an oven at 60° and stored in a dark bottle [Post and Moore *Anal Chem* 31 1872 1959].

**1-Amino-2-naphthol hydrochloride** [1198-27-2] M 195.7, m 250°(dec),  $pK_{Est(1)} \sim 3.7$  (NH<sub>2</sub>),  $pK_{Est(2)} \sim 9.9$  (OH). Crystd from the minimum volume of hot water containing a few drops of stannous chloride in an equal weight of hydrochloric acid (to reduce atmospheric oxidation).

**1-Amino-2-naphthol-4-sulfonic acid** [116-63-2] M 239.3, m 295°(dec),  $pK_{Est(1)} < 0$ ,  $pK_{Est(2)} \sim 2.8$  (NH<sub>2</sub>),  $pK_{Est(2)} \sim 8.8$ . Purified by warming 15g of the acid, 150g of NaHSO<sub>3</sub> and 5g of Na<sub>2</sub>SO<sub>3</sub> (anhydrous) with 1L of water to ca 90°, shaking until most of the solid had dissolved, then filtering hot. The precipitate obtained by adding 10mL of conc HCl to the cooled filtrate was collected, washed with 95% EtOH until the washings were colourless, and dried under vacuum over CaCl<sub>2</sub>. It was stored in a dark coloured bottle, in the cold [Chanley, Gindler and Sobotka *J Am Chem Soc* 74 4347 1952].

**6-Aminonicotinic acid** [3167-49-5] M 138.1, m 312°(dec),  $pK_{Est(1)} \sim 2.2$  (CO<sub>2</sub>H),  $pK_{Est(2)} \sim 6.5$ . Crystd from aq acetic acid.

**2-Amino-4-nitrobenzoic acid** [619-17-0] M 182.1, m 269°(dec),  $pK_1^{25} 0.65$ ,  $pK_2^{25} 3.70$ . Crystd from water or aq EtOH.

**5-Amino-2-nitrobenzoic acid** [13280-60-9] M 182.1, m 235°(dec),  $pK_{Est(1)} \sim 1.1$ ,  $pK_{Est(2)} \sim 1.2$ . Crystd from water.

**1-Amino-4-nitronaphthalene** [776-34-1] M 188.2, m 195°,  $pK^{20} 0.54$ . Crystd from EtOH or ethyl acetate.

**2-Amino-4-nitrophenol** [99-57-0] M 154.1, m 80-90° (hydrate), 142-143° (anhydr),  $pK_{Est(1)} \sim 3.9$  (NH<sub>2</sub>),  $pK_{Est(2)} \sim 9.2$ . Crystd from water.

**2-Amino-5-nitrophenol** [121-88-0] M 154.1, m 207-208°,  $pK_{Est(1)} \sim 3.8$ ,  $pK_{Est(2)} \sim 9.3$ . Crystd from water.

**6-Aminopenicillanic acid** [551-16-6] M 216.2, m 208-209°,  $[\alpha]_{546} +327^\circ$  (in 0.1M HCl),  $pK_1^{25} 2.30$ ,  $pK_2^{25} 4.90$ . Crystd from water.

**2-Aminoperimidine hydrobromide** [40835-96-9] M 264.1, m 299°,  $pK_{Est} \sim 7.9$  (free base). Purified by boiling a saturated aqueous soln with charcoal, filtering and leaving the salt to crystallise. Stored in a cool, dark place.

**2-Aminophenol** [95-55-6] M 109.1, m 175-176°,  $pK_1^{25} 4.65$ ,  $pK_2^{25} 9.75$ . Purified by soln in hot water, decolorised with activated charcoal, filtered and cooled to induce crystn. Maintain an atmosphere of N<sub>2</sub> over the hot phenol soln to prevent its oxidation [Charles and Freiser *J Am Chem Soc* 74 1385 1952]. Can also be crystd from EtOH.

**3-Aminophenol** [591-27-5] M 109.1, m 122-123°,  $pK_1^{25} 4.25$ ,  $pK_2^{25} 9.90$ . Crystd from hot water or toluene.

**4-Aminophenol** [123-30-8] M 109.1, m 190° (under N<sub>2</sub>),  $pK_1^{25} 5.38$ ,  $pK_2^{25} 10.4$ . Crystd from EtOH, then water, excluding oxygen. Can be sublimed at 110°/0.3mm. Has been purified by chromatography on alumina with a 1:4 (v/v) mixture of absolute EtOH/\*benzene as eluent.

**4-Aminophenol hydrochloride** [51-78-5] M 145.6, m 306°(dec). Purified by treating an aqueous soln with saturated Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub>, filtering under an inert atmosphere, then recrystd from 50% EtOH twice and once from absolute EtOH [Livingston and Ke *J Am Chem Soc* 72 909 1950].

**4-Aminophenylacetic acid** [1197-55-3] M 151.2, m 199-200°(dec),  $pK_1^{20} 3.60$ ,  $pK_2^{20} 5.26$ . Crystd from hot water (60-70mL/g).

**2-Amino-1-phenylbutan-1-ol** [ $\alpha$ -( $\alpha$ -aminopropyl)benzyl alcohol] [( $\pm$ )-*threo* 5897-76-7] M 165.1, m 79-80°, pK<sub>Est</sub> ~9.7. Crystd from \*benzene/pet ether.

**S-(-)-2-Amino-3-phenyl-1-propanol** (L-phenylalaninol) [3182-95-4] M 151.2, m 95°. See phenylalaninol on p. 327.

**N-Aminophthalimide** [1875-48-5] M 162.2, m 200-202°, pK<sub>Est</sub> ~0. It has been recrystd from 96% EtOH (sol ~2% at boiling temperature) to form a yellow solution. It sublimes *in vacuo* at ca 150°. Resolidifies after melting, and remelts at 338-341°.

**4-Aminopropiophenone** [70-69-9] M 163.1, m 140°, pK<sub>Est</sub> ~2.2. Crystd from water or EtOH.

**4-(2-Aminopropyl)phenol** [103-86-6] M 151.2, m 125-126°, pK<sub>Est(1)</sub> ~9.4 (OH), pK<sub>Est(2)</sub> ~9.7(NH<sub>2</sub>). Crystd from \*benzene.

**1-Aminopyrene** [1606-67-3] M 217.3, m 117-118°, pK<sub>1</sub><sup>25</sup> 2.91 (50% aq EtOH), pK<sub>2</sub><sup>25</sup> 2.77 (50% aq EtOH). Crystd from hexane.

**2-Aminopyridine** [504-29-0] M 94.1, m 58°, b 204-210°, pK<sub>1</sub><sup>25</sup> -7.6, pK<sub>2</sub><sup>25</sup> 6.71. Crystd from \*benzene/pet ether (b 40-60°) or CHCl<sub>3</sub>/pet ether.

**3-Aminopyridine** [462-08-8] M 94.1, m 64°, b 248°, pK<sub>1</sub><sup>25</sup> -1.5, pK<sub>2</sub><sup>25</sup> 6.03. Crystd from \*benzene, CHCl<sub>3</sub>/pet ether (b 60-70°), or \*benzene/pet ether (4:1).

**4-Aminopyridine** [504-24-5] M 94.1, m 160°, b 180°/12-13mm, pK<sub>1</sub><sup>25</sup> -6.55, pK<sub>2</sub><sup>25</sup> 9.11 (9.18). Crystd from \*benzene/EtOH, then recrystd twice from water, crushed and dried for 4h at 105° [Bates and Hetzer *J Res Nat Bur Stand* 64A 427 1960]. Has also been crystd from EtOH, \*benzene, \*benzene/pet ether, toluene and sublimes in vacuum.

**2-Aminopyrimidine** [109-12-6] M 95.1, m 126-127.5°, pK<sup>20</sup> 3.45. Crystd from \*C<sub>6</sub>H<sub>6</sub>, EtOH or H<sub>2</sub>O.

**4-Aminopyrimidine** [591-54-8] M 95.1, m 149-151°, 154-156°, pK<sup>25</sup> 5.69. Recryst 10.6g from hot EtOAc (200mL), 7.4g colorless needles, first crop, evap to 25mL gave 1.7g of second crop. The *Hydriodide* has m 180°. *Picrate* has m 225°. [Brown *J Soc Chem Ind* (London) 69 353 1950.]

**5-Aminopyrimidine** [591-55-9] M 95.1, m 171-172° (with sublimation), pK<sup>25</sup> 2.52. Purified by conversion to the MgCl<sub>2</sub> complex in a small vol of H<sub>2</sub>O. The complex (~ 5g) is dissolved in the minimum vol of hot H<sub>2</sub>O, passed through a column of activated Al<sub>2</sub>O<sub>3</sub> (200g) and the column washed with EtOH. Evapn of the EtOH gives a colorless residue of the aminopyrimidine which is recrystd from \*C<sub>6</sub>H<sub>6</sub> (toluene could also be used) which forms needles at first then prisms. It melts with sublimation. Acetylation yields 5-*acetamidopyrimidine* which crystals from \*C<sub>6</sub>H<sub>6</sub>, m 148-149°. [Whittaker *J Chem Soc* 1565 1951.]

**Aminopyrene** (4-dimethylaminoantipyrene) [58-15-1] M 231.3, m 107-109°, pK<sub>1</sub><sup>25</sup> -2.22, pK<sub>2</sub><sup>25</sup> 4.94. Crystd from pet ether.

**3-Aminoquinoline** [580-17-6] M 144.2, m 93.5°, pK<sup>20</sup> 4.94. Crystd from \*C<sub>6</sub>H<sub>6</sub>.

**4-Aminoquinoline** [578-68-7] M 144.2, m 158°, pK<sub>1</sub><sup>20</sup> -7.11, pK<sub>2</sub><sup>20</sup> 9.13. Purified by zone refining.

**5-Aminoquinoline** [611-34-7] M 144.2, m 110°, b 184°/10mm, 310°/760mm, pK<sub>1</sub><sup>20</sup> 0.97, pK<sub>2</sub><sup>20</sup> 5.42. Crystd from pentane, then from \*benzene or EtOH.

**6-Aminoquinoline** [580-15-4] M 144.2, m 117-119°, pK<sub>1</sub><sup>20</sup> 1.63, pK<sub>2</sub><sup>20</sup> 5.59. Purified by column chromatography on a SiO<sub>2</sub> column using CHCl<sub>3</sub>/MeOH (4:1) as eluent. It is an irritant.

**8-Aminoquinoline** [578-66-5] M 144.2, m 70°, pK<sup>20</sup> 3.95. Crystd from EtOH or ligroin.

**4-Aminosalicylic acid** [65-49-6] M 153.1, m 150-151°(dec), pK<sub>1</sub><sup>25</sup> 1.78 (CO<sub>2</sub>H), pK<sub>2</sub><sup>25</sup> 3.63 (NH<sub>2</sub>), pK<sup>20</sup> 13.74 (OH). Cryst from EtOH.

**5-Aminosalicylic acid (5-amino-2-hydroxybenzoic acid)** [89-57-6] M 153.1, m 276-280°, 283°(dec), pK<sub>1</sub><sup>25</sup> 2.74 (CO<sub>2</sub>H), pK<sub>2</sub><sup>25</sup> 5.84 (NH<sub>2</sub>). Cryst as needles from H<sub>2</sub>O containing a little NaHSO<sub>3</sub> to avoid aerial oxidation to the quinone-imine. The *Me ester* gives needles from \*C<sub>6</sub>H<sub>6</sub>, m 96°, and the *hydrazide* has m 180-182° (From H<sub>2</sub>O). [Fallab et al. *Helv Chim Acta* 34 26 1951, Shavel *J Amer Pharm Assoc* 42 402 1953.]

**2-Amino-5-sulfanylthiazole** [473-30-3] M 238.3, m 219-221°(dec), pK<sub>Est</sub> ~4.5 (OH). Crystd from EtOH.

**4-Amino-2-sulfobenzoic acid** [527-76-4] M 217.1. Crystd from water.

**2-Aminothiazole** [96-50-4] M 108.1, m 93°, b 140°/11mm, pK<sup>20</sup> 5.36. Crystd from pet ether (b 100-120°), or EtOH.

**1-Amino-1,2,4-triazole** [24994-60-3] M 84.1, m 91-93°, pK<sub>Est</sub> ~2. Crystd from water. [Barszez et al. *J Chem Soc, Dalton Trans* 2025 1986.]

**3-Amino-1,2,4-triazole** [61-82-5] M 84.1, m 159°, pK<sub>1</sub><sup>20</sup> 4.04, pK<sub>2</sub><sup>20</sup> 11.08. Crystd from EtOH (charcoal), then three times from dioxane [Williams, McEwan and Henry *J Phys Chem* 61 261 1957].

**4-Amino-1,2,4-triazole** [584-13-4] M 84.1, m 80-81°, pK 3.23. Crystd from water. [Barszez et al. *J Chem Soc, Dalton Trans* 2025 1986.]

**7-Amino-4-(trifluoromethyl)coumarin**, [53518-15-3] M 229.1, m 222°, pK<sub>Est</sub> ~3.1. Purified by column chromatography on a C18 column, eluted with acetonitrile/0.01M aq HCl (1:1), and crystd from isopropanol. Alternatively, it is eluted from a silica gel column with CH<sub>2</sub>Cl<sub>2</sub>, or by extracting a CH<sub>2</sub>Cl<sub>2</sub> solution (4g/L) with 1M aq NaOH (3 x 0.1L), followed by drying (MgSO<sub>4</sub>), filtration and evaporation. [Bissell *J Org Chem* 45 2283 1980.]

**9-Aminotryptcene** [793-41-9] M 269.3, m 223.5-224.5°. Recrystd from ligroin [Imashiro et al. *J Am Chem Soc* 109 729 1987].

**5-Amino-*n*-valeric acid (5-aminopentanoic acid)** [660-88-8] M 117.2, m 157-158°, pK<sub>1</sub><sup>25</sup> 4.25, pK<sub>2</sub><sup>25</sup> 10.66. Crystd by dissolving in H<sub>2</sub>O and adding EtOH.

**5-Amino-*n*-valeric acid hydrochloride** [627-95-2] M 153.6, m 103-104°. Crystd from CHCl<sub>3</sub>.

**Amodiaquin** [4-(3-dimethylaminomethyl-4-hydroxyanilino)-7-chloroquinoline] [86-42-0] M 287.5, m 208°. Crystd from 2-ethoxyethanol.

**D-Amygdalin** [29883-15-6] M 457.4, m 214-216°, [α]<sub>D</sub><sup>22</sup> -38° (c 1.2, H<sub>2</sub>O). Crystd from water.

***n*-Amyl acetate** [628-63-7] M 130.2, b 149.2°, d 0.876, n 1.40228. Shaken with saturated NaHCO<sub>3</sub> soln until neutral, washed with water, dried with MgSO<sub>4</sub> and distd.

***n*-Amyl alcohol (1-pentanol)** [71-41-0] M 88.2, b 138.1°, d<sup>15</sup> 0.818, n 1.4100. Dried with anhydrous K<sub>2</sub>CO<sub>3</sub> or CaSO<sub>4</sub>, filtered and fractionally distd. Has also been treated with 1-2% of sodium and

heated at reflux for 15h to remove water and chlorides. Traces of water can be removed from the near-dry alcohol by refluxing with a small amount of sodium in the presence of 2-3% *n*-amyl phthalate or succinate followed by distn (see *ethanol*).

Small amounts of amyl alcohol have been purified by esterifying with *p*-hydroxybenzoic acid, recrystallising the ester from CS<sub>2</sub>, saponifying with ethanolic-KOH, drying with CaSO<sub>4</sub> and fractionally distilling [Olivier *Recl Trav Chim Pays-Bas* 55 1027 1936].

***tert*-Amyl alcohol** [75-85-4] M 88.2, b 102.3°, d<sup>15</sup> 0.8135, n 1.4058. Refluxed with anhydrous K<sub>2</sub>CO<sub>3</sub>, CaH<sub>2</sub>, CaO or sodium, then fractionally distd. Near-dry alcohol can be further dried by refluxing with magnesium activated with iodine, as described for *ethanol*. Further purification is possible using fractional crystn, zone refining or preparative gas chromatography.

***n*-Amylamine [1-aminopentane]** [110-58-7] M 87.2, b 105°, d 0.752, pK<sup>25</sup> 10.63. Dried by prolonged shaking with NaOH pellets, then distd.

***n*-Amyl bromide (*n*-pentylbromide)** [110-53-2] M 151.1, b 129.7°, d 1.218, n 1.445. Washed with conc H<sub>2</sub>SO<sub>4</sub>, then water, 10% Na<sub>2</sub>CO<sub>3</sub> soln, again with water, dried with CaCl<sub>2</sub> or K<sub>2</sub>CO<sub>3</sub>, and fractionally distd just before use.

***n*-Amyl chloride** [543-59-9] M 106.6, b 107.8°, d 0.882, n 1.41177. Same as *sec*-amyl chloride.

***sec*-Amyl chloride (1-chloro-2-methylbutane)** [616-13-7] M 106.6, b 96-97°. Purified by stirring vigorously with 95% H<sub>2</sub>SO<sub>4</sub>, replacing the acid when it became coloured, until the layer remained colourless after 12h stirring. The amyl chloride was then washed with satd Na<sub>2</sub>CO<sub>3</sub> soln, then distd water, and dried with anhydrous MgSO<sub>4</sub>, followed by filtration, and distn through a 10-in Vigreux column. Alternatively a stream of oxygen containing 5% ozone was passed through the amyl chloride for three times as long as it took to cause the first coloration of starch iodide paper by the exit gas. Washing the liquid with NaHCO<sub>3</sub> soln hydrolyzed ozonides and removed organic acids prior to drying and fractional distn [Chien and Willard *J Am Chem Soc* 75 6160 1953].

***tert*-Amyl chloride** [594-36-5] M 106.6, b 86°, d 0.866. Methods of purification commonly used for other alkyl chlorides lead to decomposition. Unsatd materials were removed by chlorination with a small amount of chlorine in bright light, followed by distn [Chien and Willard *J Am Chem Soc* 75 6160 1953].

**Amyl ether** [693-65-2] M 158.3, b 186.8°, d 0.785, n 1.41195. Repeatedly refluxed over sodium and distd.

***p*-*tert*-Amylphenol** [80-46-6] M 146.3, m 93.5-94.2°, pK<sub>Est</sub> ~10.2. Purified *via* its benzoate, as for phenol. After evaporating the solvent from its soln in ether, the material was crystd (from the melt) to constant melting point [Berliner, Berliner and Nelidow *J Am Chem Soc* 76 507 1954].

**2-*n*-Amylpyridine** [2294-76-0] M 149.2, b 63.0°/2mm, n<sup>26</sup> 1.4861, pK<sup>25</sup> 6.00. Dried with NaOH for several days, then distd from CaO under reduced pressure, taking the middle fraction and redistilling it.

**4-*n*-Amylpyridine** [2961-50-4] M 149.2, b 78.0°/2.5mm, n 1.4908, pK<sub>Est</sub> ~6.1. Dried with NaOH for several days, then distd from CaO under reduced pressure, taking the middle fraction and redistilling it.

**α-Amyrin** [638-95-9] M 426.7, m 186°. Crystd from EtOH.

**β-Amyrin** [508-04-3] M 426.7, m 197-197.5°. Crystd from pet ether or EtOH.

**Androstane** [24887-75-0] M 260.5, m 50-50.5°. Crystd from acetone/MeOH.

***epi*-Androsterone** [481-29-8] M 290.4, m 172-173°, [α]<sub>546</sub> +115° (c 1, MeOH). Crystd from aq EtOH.

*cis*-Androsterone [53-41-8] M 290.4, m 185-185.5°. Crystd from acetone/Et<sub>2</sub>O.

Angelic acid [565-63-9] M 100.1, m 45°, pK<sup>18</sup> 4.29. Steam distd, then crystd from H<sub>2</sub>O.

Aniline [62-53-3] M 93.1, f -6.0°, b 68.3/10mm, 184.4°/760mm, d 1.0220, n 1.585, n<sup>25</sup> 1.5832, pK<sup>25</sup> 4.60. Aniline is *hygroscopic*. It can be dried with KOH or CaH<sub>2</sub>, and distd at reduced pressure. Treatment with stannous chloride removes sulfur-containing impurities, reducing the tendency to become coloured by aerial oxidn. Can be crystd from Et<sub>2</sub>O at low temps. More extensive purifications involve preparation of derivatives, such as the double salt of aniline hydrochloride and cuprous chloride or zinc chloride, or *N*-acetylaniline (m 114°) which can be recrystd from water.

Recrystd aniline was dropped slowly into an aqueous soln of recrystd oxalic acid. Aniline oxalate was filtered off, washed several times with water and recrystd three times from 95% EtOH. Treatment with satd Na<sub>2</sub>CO<sub>3</sub> soln, regenerated aniline which was distd from the soln, dried and redistd under reduced pressure [Knowles *Ind Eng Chem* 12 881 1920].

After refluxing with 10% acetone for 10h, aniline was acidified with HCl (Congo Red as indicator) and extracted with Et<sub>2</sub>O until colourless. The hydrochloride was purified by repeated crystn before aniline was liberated by addition of alkali, then dried with solid KOH, and distd. The product was sulfur-free and remained colourless in air [Hantzsch and Freese *Chem Ber* 27 2529, 2966 1894].

Non-basic materials, including nitro compounds were removed from aniline in 40% H<sub>2</sub>SO<sub>4</sub> by passing steam through the soln for 1h. Pellets of KOH were added to liberate the aniline which was steam distd, dried with KOH, distd twice from zinc dust at 20mm, dried with freshly prepared BaO, and finally distd from BaO in an all-glass apparatus [Few and Smith *J Chem Soc* 753 1949]. Aniline is absorbed by skin and is **TOXIC**

Aniline hydrobromide [542-11-0] M 174.0, m 286°. Crystd from water or EtOH and dried at 5mm over P<sub>2</sub>O<sub>5</sub>. Crystd four times from MeOH containing a few drops of conc HCl by addition of pet ether (b 60-70°), then dried to constant weight over paraffin chips, under vacuum [Gutbezahl and Grunwald *J Am Chem Soc* 75 559 1953]. It was pptd from EtOH soln by addition of Et<sub>2</sub>O, and the filtered solid was recrystd from EtOH and dried *in vacuo*. [Buchanan et al. *J Am Chem Soc* 108 1537 1986.]

Aniline hydrochloride [142-04-1] M 129.6, m 200.5-201°. Same as aniline HBr above.

Aniline hydroiodide [45497-73-2] M 220.0, m dec on heating. Same as aniline HBr, store in the dark.

*m*-Anisaldehyde [591-31-1] M 136.2, b 143°/50mm, d 1.119. Washed with saturated aq NaHCO<sub>3</sub>, then H<sub>2</sub>O, dried with anhydrous MgSO<sub>4</sub> and distd at reduced pressure under N<sub>2</sub>. Stored under N<sub>2</sub> in glass sealed ampoules.

*p*-Anisaldehyde (*p*-methoxybenzaldehyde) [123-11-5] M 136.2, m -1°, b 249°/atm, 89-90°/2mm, d 1.119, n 1.576. Washed with saturated aq NaHCO<sub>3</sub>, then H<sub>2</sub>O, steam distd, extracted distillate with Et<sub>2</sub>O, dried (MgSO<sub>4</sub>) and distd under vac and N<sub>2</sub>. Store in glass ampoules under N<sub>2</sub> in the dark.

*o*-Anisidine [2-methoxyaniline] [90-04-0] M 123.2, m ~5°, b 109°/17mm, 119°/21mm, 225°/atm, d 1.096, n 1.575, pK<sup>25</sup> 4.52. It is separated from the *m*- and *p*- isomers by steam distn. It is also separated from its usual synthetic precursor *o*-nitroanisole by dissolving in dil HCl (pH <2.0) extracting the nitro impurity with Et<sub>2</sub>O, adjusting the pH to ~8.0 with NaOH extracting the amine in Et<sub>2</sub>O or steam distg. Extract the distillate with Et<sub>2</sub>O, dry extract (Na<sub>2</sub>SO<sub>4</sub>), evaporate and fractionate the residual oil. Protect the almost colorless oil from light which turns it yellow in color. [Biggs and Robinson *J Chem Soc* 3881961; Nodzu et al. *Yakugaku Zasshi (J Pharm Soc Japan)* 71 713, 715 1951.]

*m*-Anisidine [3-methoxyaniline] [536-90-3] M 123.2, m ~5°, b 79°/1mm, 128°/17mm, 251°/atm, d 1.101, n 1.583, pK<sup>25</sup> 4.20. *o*-Isomer impurity can be removed by steam distn. Possible impurity is the precursor 3-nitroanisole which can be removed as for the preceding *o*-isomer and fractionated using an efficient column. Yellow liquid. [Gilman and Kyle *J Am Chem Soc* 74 3027 1952; Bryson *J Am Chem Soc* 82 4858 1960; Kadaba and Massie *J Org Chem* 22 333 1957.]

***p*-Anisidine [4-methoxyaniline]** [104-94-9] M 123.2, m 57°, pK<sup>25</sup> 5.31. Crystd from H<sub>2</sub>O or aqueous EtOH. Dried in a vacuum oven at 35° for 6h and stored in a dry box. [More et al. *J Am Chem Soc* 108 2257 1986.] Purified by vacuum sublimation [Guarr et al. *J Am Chem Soc* 107 5104 1985].

**Anisole** [100-66-3] M 108.1, f -37.5°, b 43°/11mm, 153.8°/760mm, d<sup>15</sup> 0.9988, n<sup>25</sup> 1.5143, pK<sup>0</sup> -6.61 (aq H<sub>2</sub>SO<sub>4</sub>). Shaken with half volume of 2M NaOH, and emulsion allowed to separate. Repeated 3 times, then washed twice with water, dried over CaCl<sub>2</sub>, filtered, dried over sodium wire and finally distd from fresh sodium under N<sub>2</sub>, using a Dean-Stark trap, samples in the trap being rejected until free from turbidity [Caldin, Parbov, Walker and Wilson *J Chem Soc, Faraday Trans 1* 72 1856 1976].

Dried with CaSO<sub>4</sub> or CaCl<sub>2</sub>, or by refluxing with sodium or BaO with crystalline FeSO<sub>4</sub> or by passage through an alumina column. Traces of phenols have been removed by prior shaking with 2M NaOH, followed by washing with water. Can be purified by zone refining.

**2-*p*-Anisyl-1,3-indanone** [117-37-3] M 252.3, m 156-157°, pK<sup>20</sup> 4.09. Crystd from acetic acid or EtOH.

**Anserine [N,β-alanyl-1-methylhistidine]** [584-85-0] M 240.3, m 238-239°, [α]<sub>D</sub> +11.3° (H<sub>2</sub>O), pK<sub>1</sub><sup>25</sup> 2.64, pK<sub>2</sub><sup>25</sup> 7.04, pK<sub>3</sub><sup>25</sup> 9.49. Crystd from aqueous EtOH. It is *hygroscopic*.

***S*-Anserine nitrate** [5937-77-9] M 303.3, m 225°(dec), [α]<sub>D</sub><sup>30</sup> +12.2°. Likely impurities: 1-methylimidazole-5-alanine, histidine. Crystd from aqueous MeOH.

**Antheraxanthin** [68831-78-7] M 584.8, m 205°, λ<sub>max</sub> 460.5, 490.5nm, in CHCl<sub>3</sub>. Likely impurities: violaxanthin and mutatoxanthin. Purified by chromatography on columns of Ca(OH)<sub>2</sub> and of ZnCO<sub>3</sub>. Crystd from \*C<sub>6</sub>H<sub>6</sub>/MeOH as needles or thin plates. Stored in the dark, in an inert atmosphere, at -20°.

**Anthracene** [120-12-7] M 178.2, m 218°, pK -7.4 (aq H<sub>2</sub>SO<sub>4</sub>). Likely impurities are anthraquinone, anthrone, carbazole, fluorene, 9,10-dihydroanthracene, tetracene and bianthryl. Carbazole is removed by continuous-adsorption chromatography [see Sangster and Irvine *J Phys Chem* 24 670 1956] using a neutral alumina column and passing *n*-hexane. [Sherwood in *Purification of Inorganic and Organic Materials*, Zief (ed), Marcel Dekker, New York, 1969.] The solvent is evaporated and anthracene is sublimed under vacuum, then purified by zone refining, under N<sub>2</sub> in darkness or non-actinic light.

Has been purified by co-distillation with ethylene glycol (boils at 197.5°), from which it can be recovered by additn of water, followed by crystn from 95% EtOH, \*benzene, toluene, a mixture of \*benzene/xylene (4:1), or Et<sub>2</sub>O. It has also been chromatographed on alumina with pet ether in a dark room (to avoid photo-oxidation of adsorbed anthracene to anthraquinone). Other purification methods include sublimation in a N<sub>2</sub> atmosphere (in some cases after refluxing with sodium), and recrystd from toluene [Gorman et al. *J Am Chem Soc* 107 4404 1985].

Anthracene has also been crystd from EtOH, chromatographed through alumina in hot \*benzene (*fume hood*) and then vac sublimed in a pyrex tube that has been cleaned and baked at 100°. (For further details see Craig and Rajikan *J Chem Soc, Faraday Trans 1* 74 292 1978; and Williams and Zboinski *J Chem Soc, Faraday Trans 1* 74 611 1978.) It has been chromatographed on alumina, recrystd from *n*-hexane and sublimed under reduced pressure. [Saltiel *J Am Chem Soc* 108 2674 1986; Masnori et al. *J Am Chem Soc* 108 1126 1986.] Alternatively, it was recrystd from cyclohexane, chromatographed on alumina with *n*-hexane as eluent, and recrystd two more times [Saltiel et al. *J Am Chem Soc* 109 1209 1987].

**Anthracene-9-carboxylic acid** [723-62-6] M 222.2, m 214°(dec), pK<sup>20</sup> 3.65. Crystd from EtOH.

**9-Anthraldehyde** [642-31-9] M 206.2, m 104-105°. Crystd from acetic acid or EtOH. [Masnori et al. *J Am Chem Soc* 108 1126 1986.]

**Anthranol** [529-86-2] M 196.2, m 160-170°(dec). Crystd from glacial acetic acid or aqueous EtOH.

**Anthranthrone** [641-13-4] M 306.3, m 300°, pK -7.9 (aq H<sub>2</sub>SO<sub>4</sub>). Crystd from chlorobenzene or nitrobenzene.

**Anthraquinone** [84-65-1] M 208.2, m 286°, pK<sup>25</sup> -8.27 (aq H<sub>2</sub>SO<sub>4</sub>). Crystd from CHCl<sub>3</sub> (38mL/g), \*benzene, or boiling acetic acid, washing with a little EtOH and drying under vacuum over P<sub>2</sub>O<sub>5</sub>.

**Anthrarufin** [1,5-dihydroxy-9,10-anthraquinone] [117-12-4] M 240.1, m 280°(dec), pK<sub>1</sub><sup>25</sup> 9.90, pK<sub>2</sub><sup>25</sup> 11.05. Purified by column chromatography on silica gel with CHCl<sub>3</sub>/Et<sub>2</sub>O as eluent, followed by recrystn from acetone. Alternatively recrystd from glacial acetic acid [Flom and Barbara *J Phys Chem* 89 4489 1985].

**1,8,9-Anthratrionol** [480-22-8] M 226.2, m 176-181°, pK<sub>Est</sub> ~9.5. Crystd from pet ether.

**Anthrimide** [1,1'-imino-bis-anthraquinone] [82-22-4] M 429.4, m >250°(dec). Crystd from chlorobenzene (red needles) or nitrobenzene (red rhombs)

**Anthrone** [90-44-8] M 194.2, m 155°, pK -5.5 (aq H<sub>2</sub>SO<sub>4</sub>). Crystd from a 3:1 mixture of \*benzene/pet ether (b 60-80°) (10-12mL/g), or successively from \*benzene then EtOH. Dried under vacuum.

**Antipyrine** [2,3-dihydro-1,5-dimethyl-3-oxo-2-phenylpyrazole] [60-80-0] M 188.2, m 114°, b 319°, pK<sup>25</sup> 1.45. Crystd from EtOH/water mixture, \*benzene, \*benzene/pet ether or hot water (charcoal), and dried under vacuum.

**β-Apo-4'-carotenal, β-Apo-8'-carotenal, β-Apo-8'-carotenoic acid ethyl ester, β-Apo-8'-carotenoic acid methyl ester, Apocodeine, Apomorphine** see entries in Chapter 6.

**β-L-Arabinose (natural)** [87-72-9] M 150.1, m 158°, [α]<sub>D</sub> +104° (c 4, H<sub>2</sub>O after 24h). Crystd slowly twice from 80% aq EtOH, then dried under vacuum over P<sub>2</sub>O<sub>5</sub>.

**D-Arabinose** [10323-20-3, 28697-53-2 (pyranoside)] M 150.1, m 164°, [α]<sub>546</sub> -123° (c 10, H<sub>2</sub>O after 24h), pK<sup>25</sup> 12.54. Crystd three times from EtOH, vacuum dried at 60° for 24h and stored in a vacuum desiccator.

**L-Arabitol** [7643-75-6] M 152.2, m 102°, [α]<sub>546</sub> -16° (c 5, 8% borax soln). Crystd from 90% EtOH.

**DL-Arabitol** [2152-56-9] M 152.2, m 105-106°. Crystd from 90% EtOH.

**Arachidic (eicosanoic C<sub>20</sub>) acid** [506-30-9] M 312.5, m 77°, pK<sub>Est</sub> ~5.0. Crystd from abs EtOH.

**Arachidic alcohol (1-eicosanol)** [629-96-9] M 298.6, m 65.5° (71°), b 200°/3mm. Crystd from \*benzene or \*benzene/pet ether.

**p-Arbutin** [497-76-7] M 272.3, m 163-164°. Crystd from water.

**S-Arginine** [74-79-3] M 174.2, m 207°(dec), [α]<sub>D</sub> +26.5° (c 5, in 5M HCl), [α]<sub>546</sub> +32° (c 5, in 5M HCl), pK<sub>1</sub><sup>25</sup> 2.18, pK<sub>2</sub><sup>25</sup> 9.36, pK<sub>3</sub><sup>25</sup> 11.5. Crystd from 66% EtOH.

**S-Arginine hydrochloride** [1119-34-2] M 210.7, m 217°(dec), [α]<sub>D</sub><sup>20</sup> +26.9° (c 6, M HCl). Likely impurity is ornithine. Crystd from water at pH 5-7, by adding EtOH to 80% (v/v).

**S-Argininosuccinic acid** [2387-71-5] M 290.3, [α]<sub>D</sub><sup>24</sup> +16.4° (H<sub>2</sub>O). Likely impurity is fumaric acid. In neutral or alkaline soln it readily undergoes ring closure to the 'anhydride'. Crystd from water by adding 1.5 vols of EtOH. Barium salt is stable at 0-5° if dry. [Westfall *Biochem J* 77 135 1960.]



**S-Argininosuccinic anhydride** [28643-94-9] M 272.3,  $[\alpha]_D^{23} -10^\circ$  ( $H_2O$  for anhydride formed at neutral pH). Crystd from water by adding two volumes of EtOH. An isomeric anhydride is formed if the free acid is allowed to stand at acid pH. In soln, the mixture of anhydrides and free acid is formed [see above entry].

**L(+)-Ascorbic acid** [50-81-7] M 176.1, m 193°(dec),  $[\alpha]_{546} +23^\circ$  (c 10,  $H_2O$ ),  $pK_1^{25} 4.04$ ,  $pK_2^{25} 11.34$ . Crystd from MeOH/Et<sub>2</sub>O/pet ether [Herbert et al. *J Chem Soc* 1270 1933].

**S-Asparagine** [70-47-3] M 150.1, m 234-235°, (monohydrate) [5794-13-8]  $[\alpha]_D +32.6^\circ$  (0.1M HCl),  $pK_1^{25} 1.98$ ,  $pK_2^{25} 8.84$ . Likely impurities are aspartic acid and tyrosine. Crystd from H<sub>2</sub>O or aqueous EtOH. Slowly effloresces in dry air.

**Aspartic acid** M 133.1, m 338-339° (RS, [617-45-8]); m 271° (S, requires heating in a sealed tube [56-84-8]),  $[\alpha]_D^{25} +25.4^\circ$  (3M HCl),  $pK_1^{25} 1.99$ ,  $pK_2^{25} 3.90$ . Likely impurities are glutamic acid, cystine and asparagine. Crystd from water by adding 4 volumes of EtOH and dried at 110°.

**L-Aspartic acid β-methyl ester hydrochloride** [16856-13-6] M 183.6, m 194°,  $pK^{25} 8.62$ . Recrystd from MeOH by using anhydrous diethyl ether [Bach et al. *Biochem Prep* 13 20 1971].

**DL-Aspartic acid dimethyl ester hydrochloride** [14358-33-9] M 197.7, 116-117°. Crystd from absolute MeOH. [Kovach et al. *J Am Chem Soc* 107 7360 1985.] Diethyl ester has  $pK^{25} 6.4$ .

**Aspergillic acid** [490-02-8] M 224.3, m 97-99°, pK 5.5. Sublimed at 80°/10<sup>-3</sup>mm. Crystd from MeOH.

**Astacin** (β,β-carotene-3,3',4,4'-tetraone) [514-76-1] M 592.8, m 228°, 240-243°(evacuated tube),  $\epsilon_{1cm}^{1\%} 550,000$  at 498mm (pyridine). Probable impurity is astaxanthin. Purified by chromatography on alumina/fibrous clay (1:4) or sucrose, or by partition between pet ether and MeOH (alkaline). Crystd from pyridine/water. Stored in the dark under N<sub>2</sub> at -20°. [Davis and Weedon *J Chem Soc* 182 1960.]

**Atrolactic acid (0.5H<sub>2</sub>O) (2-hydroxy-2-phenylpropionic acid)** [515-30-0] M 166.2, m 94.5° (anhydr), 88-91° (0.5H<sub>2</sub>O),  $pK^{18} 3.53$ . Crystd from water and dried at 55°/0.5mm.

**Atropine** [51-55-8] M 289.4, m 114-116°,  $pK^{18} 9.85$ . Crystd from acetone or hot water.

**Auramine O** (4,4'-bis-dimethylaminobenzophenone imine hydrochloride) [2465-27-2] M 321.9,  $pK^{25} 10.71$  (free base), 9.78 (carbinolamine). Crystd from EtOH as hydrochloride, very slightly soluble in CHCl<sub>3</sub>, UV:  $\lambda_{max}$  434 (370) nm. The free base has m 136° after crystn from \*benzene. [*J Chem Soc* 1724 1949; *Biochemistry* 9 1540 1970].

**Aurin tricarboxylic acid** [4431-00-9] M 422.4, m 300°. The acid is dissolved in aqueous NaOH, NaHSO<sub>3</sub> solution is added until the colour is discharged and then the tricarboxylic acid is ppted with HCl [*Org Synth Coll Vol I* 54 1947]. Do not extract the acid with hot water because it softens forming a viscous mass. Make a solution by dissolving in aqueous NH<sub>3</sub>. See **Aluminon** for the ammonium salt.

**8-Azaadenine** [1123-54-2] M 136.1, m 345°(dec),  $pK_1^{20} 2.65$ ,  $pK_2^{20} 6.29$ . Crystd from H<sub>2</sub>O.

**2-Azacyclotridecanone (lauro lactam)** [947-04-6] M 197.3, m 152°. Crystd from CHCl<sub>3</sub>, stored over P<sub>2</sub>O<sub>5</sub> in a vacuum desiccator.

**8-Azaguanine** [134-58-7] M 152.1, m >300°,  $pK_1^{20} 1.04$ ,  $pK_2^{20} 6.29$ . Dissolved in hot M NH<sub>4</sub>OH, filtered, and cooled; recrystd, and washed with water.

**7-Azaindole** [271-63-6] M 118.1, m 105-106°,  $pK^{20} 4.57$ . Repeatedly recrystd from EtOH, then vacuum sublimed [Tokumura et al. *J Am Chem Soc* 109 1346 1987].

**1-Azaindolizine** [274-76-0] **M 118.1, b 72-73°/1mm, pK<sup>20</sup> 1.43.** Purified by distn or gas chromatography.

**Azaserine** [115-02-6] **M 173.1, m 146-162°(dec), [ $\alpha$ ]<sub>D</sub><sup>27.5</sup> -0.5° (c 8.5, H<sub>2</sub>O, pH 5.2), pK<sub>Est(1)</sub>~4.53, pK<sub>Est(2)</sub> ~5.40.** Crystd from 90% EtOH.

**8-Azapurine (1*H*-1,2,3-triazolo[4,5-*d*]pyrimidine, 1,2,3,4,6[3*H*]penta-azaindene)** [273-40-5] **M 121.1, m 174-175° (effervescence, m depends on heating rate), pK<sub>1</sub><sup>20</sup> 2.05 (equilib with covalent hydrate), pK<sub>2</sub><sup>20</sup> 4.84.** Sublimed at 120-130°/0.01mm and recryst from 3 parts of EtOH. [Albert *J Chem Soc(B)* 427 1966.]

**Azelaic acid** [123-99-9] **M 188.2, m 105-106°.** Crystd from H<sub>2</sub>O (charcoal) or thiophene-free \*benzene. The material cryst from H<sub>2</sub>O was dried by azeotropic distn in toluene, the residual toluene soln was cooled and filtered, the ppte being dried in a vacuum oven. Also purified by zone refining or by sublimation onto a cold finger at 10<sup>-3</sup> torr.

**Azetidine (trimethyleneimine)** [503-29-7] **M 57.1, b 61-62°, d 0.846, n 1.432, pK<sup>25</sup> 11.29.** It is a flammable, hygroscopic liquid smelling of ammonia, which absorbs CO<sub>2</sub> from air and should be kept under Argon. Purified by drying over solid KOH and distd through a short Vigreux column at atm pressure (under Argon) and keeping the pot temp below 210°. [Searles et al. *J Am Chem Soc* 78 4917 1956.]

**Aziridine (ethyleneimine)** [151-56-4] **M 43.1, b 55-56°/756mm, 56°/760mm, d<sup>24</sup> 0.8321, pK<sup>25</sup> 8.00.** Redistd in an Ar or N<sub>2</sub> atmosphere in a fume hood, and stored over KOH in sealed bottles in a refrigerator. Commercial aziridine has been dried over sodium and distd from the metal through an efficient column before use [Jackson and Edwards *J Am Chem Soc* 83 355 1961; Wenker *J Am Chem Soc* 57 2328 1935]. It is a weaker base than Me<sub>2</sub>NH (pK 10.87) but is caustic to the skin. It should not be inhaled, causes inflammation of the eyes, nose and throat and one may become sensitised. It is sol in H<sub>2</sub>O and has an ammoniacal smell and reacts with CO<sub>2</sub>. Pure aziridine is comparatively stable but polymerises in the presence of traces of H<sub>2</sub>O and is occasionally explosive in the presence of acids. CO<sub>2</sub> is sufficiently acidic to cause polymerisation (forms linear polymers) which is not free radical promoted. It is stable in the presence of bases. The violet 2:1 Cu complex crystd from EtOH containing a few drops of Aziridine and adding Et<sub>2</sub>O has m 142°(decomp). The picrate has m 142°. [O'Rourke et al. *J Am Chem Soc* 78 2159 1956.] It has also been dried with BaO, and distd from sodium under nitrogen. **TOXIC.**

**Azobenzene** [103-33-3] **M 182.2, m 68°, pK<sup>25</sup> 2.48.** Ordinary azobenzene is nearly all in the *trans*-form. It is partly converted into the *cis*-form on exposure to light [for isolation see Hartley *J Chem Soc* 633 1938, and for spectra of *cis*- and *trans*-azobenzenes, see Winkel and Siebert *Chem Ber* 74B 6701941]. *trans*-Azobenzene is obtained by chromatography on alumina using 1:4 \*benzene/heptane or pet ether, and crystd from EtOH (after refluxing for several hours) or hexane. All operations should be carried out in diffuse red light or in the dark.

**1,1'-Azobis(cyclohexane carbonitrile)** [2094-98-6] **M 244.3, m 114-114.5°,  $\epsilon_{350nm}$  16.0.** Crystd from EtOH.

**$\alpha,\alpha'$ -Azobis(isobutyronitrile) (AIBN)** [78-61-1] **M 164.2, m 103°(dec).** Crystd from acetone, Et<sub>2</sub>O, CHCl<sub>3</sub>, aq EtOH or MeOH. Has also been crystd from abs EtOH below 40° in subdued light. Dried under vacuum at room temp over P<sub>2</sub>O<sub>5</sub> and stored under vacuum in the dark at <-10° until used. Also crystd from CHCl<sub>3</sub> soln by addn of pet ether (b <40°). [Askham et al. *J Am Chem Soc* 107 7423 1985; Ennis et al. *J Chem Soc, Dalton Trans* 2485 1986; Inoue and Anson *J Phys Chem* 91 1519 1987; Tanner *J Org Chem* 52 2142 1987].

**Azolitmin B** [1395-18-2] **M ~3300, m >250°(dec).** Crystd from water as dark violet scales, or ppted from H<sub>2</sub>O by addtn of EtOH as a red powder. It is an indicator which is red at pH 4.5 and blue at pH 8.3.

**Azomethane** [503-28-6] M 58.1, m  $-78^{\circ}$ , b  $1.5^{\circ}$ . Purified by vacuum distn and stored in the dark at  $-80^{\circ}$ . Can be **EXPLOSIVE**.

***p,p'*-Azoxyanisole (4,4'-dimethoxyazoxybenzene)** [1562-94-3] M 258.3, transition temps: 118.1-118.8 $^{\circ}$ , 135.6-136.0 $^{\circ}$ ,  $pK^{25}$  -5.23 (20% aq EtOH + 80% aq H<sub>2</sub>SO<sub>4</sub>). Crystd from absolute or 95% EtOH, or acetone, and dried by heating under vacuum or sublimed in a vac onto a cold finger.

**Azoxybenzene** [495-48-7] M 198.2, m  $36^{\circ}$ ,  $pK^{25}$  -6.16 (20% aq EtOH + 80% aq H<sub>2</sub>SO<sub>4</sub>). Crystd from EtOH or MeOH, and dried for 4h at  $25^{\circ}$  and  $10^{-3}$ mm. Sublimed before use.

***p,p*-Azoxyphenetole** [4792-83-0] M 286.3, m 137-138 $^{\circ}$  (turbid liquid clarifies at 167 $^{\circ}$ ). Crystd from toluene or EtOH.

**Azulene** [275-51-4] M 128.2, m 98.5-99 $^{\circ}$ ,  $pK^{25}$  -1.65 (aq H<sub>2</sub>SO<sub>4</sub>). Crystd from EtOH.

**Azuleno(1,2-b)thiophene** [25043-00-9] M 184.2. Crystd from cyclohexane, then sublimed *in vacuo*.

**Azuleno(2,1-b)thiophene** [248-13-5] M 184.2. Crystd from cyclohexane, then sublimed *in vacuo*.

**Azure A (3-amino-7-dimethylaminophenazin-5-ium chloride)** [531-53-3] M 291.8, CI 52005, m > 290 $^{\circ}$ (dec),  $\lambda_{max}$  633nm, pK 7.2. Twice recrystd from H<sub>2</sub>O, and dried at 100 $^{\circ}$ /1h in an oven.

**Azure B (3-dimethylamino-7-methylaminophenazin-5-ium chloride)** [531-55-5] M 305.8, CI 52010, m > 201 $^{\circ}$ (dec),  $\lambda_{max}$  648nm, pK 7.4. Twice recrystd from H<sub>2</sub>O, and dried at 100 $^{\circ}$ /1h in an oven.

**Azure C (3-amino-7-methylaminophenazin-5-ium chloride)** [531-57-7] M 277.8,  $\lambda_{max}$  616nm, pK 7.0. Twice recrystd from H<sub>2</sub>O, and dried at 100 $^{\circ}$ /1h in an oven.

**B.A.L.** (British Anti-Lewesite) see 1,2-dimercapto-3-propanol.

**Barbituric acid [6-hydroxypyrimidin-2,4-dione]** [67-52-7] M 128.1, m 250 $^{\circ}$ (dec),  $pK_1^{25}$  3.99,  $pK_2^{25}$  12.5. Crystd twice from H<sub>2</sub>O, then dried for 2 days at 100 $^{\circ}$ .

**Bathophenanthroline (4,7-diphenyl-1,10-phenanthroline)** [1662-01-7] M 332.4, m 215-216 $^{\circ}$ , 218-220 $^{\circ}$ ,  $pK^{25}$  4.67. Best purified by recrystn from \*C<sub>6</sub>H<sub>6</sub> or toluene. Its solubility (per L): H<sub>2</sub>O (1mg), M HCl (20mg), heptane (110mg), Et<sub>2</sub>O (530mg), Me<sub>2</sub>CO (2.3g), dioxane (3.4g), MeOH (6.0g), EtOH (10.5g), isoPrOH (10.0g), *n*-pentanol (18.7g), \*C<sub>6</sub>H<sub>6</sub> (12.2g), pyridine (33g), nitrobenzene (44.7g), CHCl<sub>3</sub> (78g) and AcOH (450.4g). [UV: *Bull Soc Chim Fr* 371 1972.] For di-Na salt 3H<sub>2</sub>O see entry in Chapter 5.

**Batyl alcohol** [544-62-7] M 344.6, m 70.5-71 $^{\circ}$ . Crystd from aq Me<sub>2</sub>CO, EtOH or pet ether (b 40-60 $^{\circ}$ ).

**Behenoyl chloride (docosanoyl chloride)** [21132-76-3] M 359.0, m 40 $^{\circ}$ . If the IR shows OH bands then it should be dissolved in oxalyl chloride in \*C<sub>6</sub>H<sub>6</sub> soln and warmed at 35 $^{\circ}$  for 24h in the absence of moisture, evaporated and distd in a vacuum of  $10^{-5}$ mm. It is sol in \*C<sub>6</sub>H<sub>6</sub> and Et<sub>2</sub>O. It is moisture sensitive and is **LACHRYMATORY**. [*J Chem Soc* 1001 1937; *J Biol Chem* 59 905 1924.]

**Benzalacetone (trans-4-phenyl-3-buten-2-one)** [122-57-6] M 146.2, m 42 $^{\circ}$ . Crystd from pet ether (b 40-60 $^{\circ}$ ), or distd (b 137-142 $^{\circ}$  /16mm).