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**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).

**Benzalacetophenone (Chalcone)** [94-41-7] M 208.3, m 56-58°, b 208°/25mm, pK<sup>25</sup> -5.73 (aq H<sub>2</sub>SO<sub>4</sub>). Crystd from EtOH warmed to 50° (about 5mL/g), iso-octane, or toluene/pet ether, or recrystd from MeOH, and then twice from hexane. SKIN IRRITANT.

**Benzaldehyde** [100-52-7] M 106.1, f -26°, b 62° (58°)/10mm, 179.0°/760mm, d 1.044, n 1.5455, pK<sup>25</sup> -7.1 (aq H<sub>2</sub>SO<sub>4</sub>). To diminish its rate of oxidation, benzaldehyde usually contains additives such as hydroquinone or catechol. It can be purified *via* its bisulfite addition compound but usually distn (under nitrogen at reduced pressure) is sufficient. Prior to distn it is washed with NaOH or 10% Na<sub>2</sub>CO<sub>3</sub> (until no more CO<sub>2</sub> is evolved), then with satd Na<sub>2</sub>SO<sub>3</sub> and H<sub>2</sub>O, followed by drying with CaSO<sub>4</sub>, MgSO<sub>4</sub> or CaCl<sub>2</sub>.

**anti-Benzaldoxime** [932-90-1] M 121.1, m 33-34°. Crystd from diethyl ether by adding pet ether (b 60-80°). The *syn*-isomer [622-32-2] has b 121-124°/12mm, m 34-36°.

**Benzamide** [55-21-0] M 121.1, m 129.5°, pK<sup>25</sup> -2.16 (aq H<sub>2</sub>SO<sub>4</sub>). Crystd from hot water (about 5mL/g), EtOH or 1,2-dichloroethane, and air dried. Crystd from dilute aqueous ammonia, water, acetone and then \*benzene (using a Soxhlet extractor). Dried in an oven at 110° for 8h and stored in a desiccator over 99% H<sub>2</sub>SO<sub>4</sub>. [Bates and Hobbs *J Am Chem Soc* 73 2151 1951.]

**Benzamidine** [618-39-3] M 120.2, m 64-66°, pK<sup>20</sup> 11.6. Liberated from chloride by treatment with 5M NaOH. Extracted into diethyl ether. Sublimed *in vacuo*.

**Benzanilide** [93-98-1] M 197.2, m 164°, pK<sup>55</sup> 1.26. Crystd from pet ether (b 70-90°) using a Soxhlet extractor, and dried overnight at 120°. Also crystd from EtOH.

**Benz[a]anthracene** [56-55-3] M 228.3, m 159-160°. Crystd from MeOH, EtOH or \*benzene (charcoal), then chromatographed on alumina from sodium-dried \*benzene (twice), using vacuum distn to remove \*benzene. Final purification was by vacuum sublimation.

**Benz[a]anthracene-7,12-dione** [2498-66-0] M 258.3, m 169.5-170.5°. Crystd from MeOH (charcoal).

**Benzanthrone** [82-05-3] M 230.3, m 170°, pK -3.2 (aq H<sub>2</sub>SO<sub>4</sub>). Crystd from EtOH or xylene.

**\*Benzene** [71-43-2] M 78.1, f 5.5°, b 80.1°, d 0.874, n 1.50110, n<sup>25</sup> 1.49790. For most purposes, \*benzene can be purified sufficiently by shaking with conc H<sub>2</sub>SO<sub>4</sub> until free from thiophene, then with H<sub>2</sub>O, dilute NaOH and water, followed by drying (with P<sub>2</sub>O<sub>5</sub>, sodium, LiAlH<sub>4</sub>, CaH<sub>2</sub>, 4X Linde molecular sieve, or CaSO<sub>4</sub>, or by passage through a column of silica gel, for a preliminary drying, CaCl<sub>2</sub> is suitable), and distn. A further purification step to remove thiophene, acetic acid and propionic acid, is crystn by partial freezing. The usual contaminants in dry thiophene-free \*benzene are non-benzenoid hydrocarbons such as cyclohexane, methylcyclohexane, and heptanes, together with naphthenic hydrocarbons and traces of toluene. Carbonyl-containing impurities can be removed by percolation through a Celite column impregnated with 2,4-dinitrophenylhydrazine, phosphoric acid and H<sub>2</sub>O. (Prepared by dissolving 0.5g DNPH in 6mL of 85% H<sub>3</sub>PO<sub>4</sub> by grinding together, then adding and mixing 4mL of distd H<sub>2</sub>O and 10g Celite.) [Schwartz and Parker *Anal Chem* 33 1396 1961.] \*Benzene has been freed from thiophene by refluxing with 10% (w/v) of Raney nickel for 15min, after which the nickel was removed by filtration or centrifugation.

Dry \*benzene was obtained by doubly distilling high purity \*benzene from a soln containing the blue ketyl formed by the reaction of sodium-potassium alloy with a small amount of benzophenone.

Thiophene has been removed from \*benzene (absence of bluish-green coloration when 3mL of \*benzene is shaken with a soln of 10mg of isatin in 10mL of conc H<sub>2</sub>SO<sub>4</sub>) by refluxing the \*benzene (1Kg) for several hours with 40g HgO (freshly pptd) dissolved in 40mL glacial acetic acid and 300mL of water. The ppte was filtered off, the aq phase was removed and the \*benzene was washed twice with H<sub>2</sub>O, dried and distd. Alternatively, \*benzene dried with CaCl<sub>2</sub> has been shaken vigorously for half an hour with anhydrous AlCl<sub>3</sub> (12g/L) at 25-35°, then decanted, washed with 10% NaOH, and water, dried and distd. The process was repeated, giving thiophene-free \*benzene. [Holmes and Beeman *Ind Eng Chem* 26 172 1934.]

After shaking successively for about an hour with conc  $\text{H}_2\text{SO}_4$ , distd water (twice), 6M NaOH, and distd water (twice), \*benzene was distd through a 3-ft glass column to remove most of the water. Abs EtOH was added and the \*benzene-alcohol azeotrope was distd. (This low-boiling distn leaves any non-azeotrope-forming impurities behind.) The middle fraction was shaken with distd water to remove EtOH, and again redistd. Final slow and very careful fractional distn from sodium, then  $\text{LiAlH}_4$  under  $\text{N}_2$ , removed traces of water and peroxides. [Peebles, Clarke and Stockmayer *J Am Chem Soc* **82** 2780 1960.] \*Benzene liquid and vapour are very **TOXIC and HIGHLY FLAMMABLE**, and all operations should be carried out in an efficient fume cupboard and in the absence of naked flames in the vicinity.

**Rapid purification:** To dry benzene, alumina,  $\text{CaH}_2$  or 4A molecular sieves (3% w/v) may be used (dry for 6h). Then benzene is distd, discarding the first 5% of distillate, and stored over molecular sieves (3A, 4A) or Na wire.

[ $^2\text{H}_6$ ]\*Benzene (\*benzene- $d_6$ ) [1076-43-3] M 84.2, b  $80^\circ/773.6\text{mm}$ ,  $70^\circ/562\text{mm}$ ,  $60^\circ/399\text{mm}$ ,  $40^\circ/186.3\text{mm}$ ,  $20^\circ/77.1\text{mm}$ ,  $10^\circ/49.9\text{mm}$ ,  $0^\circ/27.5\text{mm}$ , d 0.9488,  $d^{40}$  0.9257, n 1.4991,  $n^{40}$  1.4865. Hexadeuteriobenzene of 99.5% purity is refluxed over and distd from  $\text{CaH}_2$  onto Linde type 5A sieves under  $\text{N}_2$ .

**Benzeneazodiphenylamine (4-phenylazodiphenylamine)** [28110-26-1] M 273.3, m  $82^\circ$ ,  $\text{pK}^{22}$  1.52. Purified by chromatography on neutral alumina using anhydrous  $^*\text{C}_6\text{H}_6$  with 1% anhydrous MeOH. The major component, which gave a stationary band, was cut out and eluted with EtOH or MeOH. [Högfeldt and Bigeleisen *J Am Chem Soc* **82** 15 1960.] Crystd from pet ether or EtOH. See Sudan I.

**1-Benzeneazo-2-naphthol** [842-07-9] M 248.3, m  $134^\circ$ ,  $\text{pK}_{\text{Est}}$  ~9.5 (OH). Crystd from EtOH.

**1-Benzeneazo-2-naphthylamine (Yellow AB)** [85-84-7] M 247.3, m  $102-104^\circ$ ,  $\text{pK}_{\text{Est}}$  ~4.1. Crystd from glacial acetic acid, acetic acid/water or ethanol.

**1,2-Benzenedimethanol (1,2-bishydroxymethylbenzene)** [612-14-6] M 138.2, m  $61-64^\circ$ ,  $63-64^\circ$ ,  $64-65^\circ$ ,  $65-66.5^\circ$ , b  $145^\circ/3\text{mm}$ . Recrystd from  $^*\text{C}_6\text{H}_6$ ,  $\text{H}_2\text{O}$ , pet ether or pentane. It has been extracted in a Soxhlet with  $\text{Et}_2\text{O}$ , evaporated and recrystd from hot pet ether. Also dissolve in  $\text{Et}_2\text{O}$ , allow to evaporate till crystals are formed, filter off and wash the colourless crystals with warm pet ether or pentane. The diacetate has m  $35^\circ$ ,  $35-36^\circ$ . [*J Am Chem Soc* **69** 1197 1947, IR and UV: *J Am Chem Soc* **74** 441 1952.]

**m-Benzenedisulfonic acid** [98-48-6] M 238.2,  $\text{pK}_{\text{Est}}$  <0. Freed from  $\text{H}_2\text{SO}_4$  by conversion to the calcium or barium salts (using  $\text{Ca}(\text{OH})_2$  or  $\text{Ba}(\text{OH})_2$ , and filtering). The calcium salt was then converted to the potassium salt, using  $\text{K}_2\text{CO}_3$ . Both the potassium and the barium salts were recrystd from  $\text{H}_2\text{O}$ , and the acid was regenerated by passing through the  $\text{H}^+$  form of a strong cation exchange resin. The acid was recrystd twice from conductivity water and dried over  $\text{CaCl}_2$  at  $25^\circ$ . [Atkinson, Yokoi and Hallada *J Am Chem Soc* **83** 1570 1961.] It has also been crystd from  $\text{Et}_2\text{O}$  and dried in a vacuum oven.

**m-Benzenedisulfonyl chloride** [585-47-7] M 275.1, m  $63^\circ$ . Crystd from  $\text{CHCl}_3$  (EtOH free, by passing through an alumina column) and dried at 20mm pressure.

**Benzene-1,2-dithiol** [17534-15-5] M 142.2, m  $24-25^\circ$ ,  $27-28^\circ$ , b  $110-112^\circ$ ,  $\text{pK}_{\text{Est}(1)}$  ~6.0,  $\text{pK}_{\text{Est}(2)}$  ~9.4. Likely impurities are the oxidation products, the disulfides which could be polymeric. Dissolve in aq NaOH until the soln is alkaline. Extract with  $\text{Et}_2\text{O}$  and discard the extract. Acidify with cold HCl (diluted 1:1 by vol with  $\text{H}_2\text{O}$ ) to Congo Red paper under  $\text{N}_2$  and extract three times with  $\text{Et}_2\text{O}$ . Dry the  $\text{Et}_2\text{O}$  with  $\text{Na}_2\text{SO}_4$ , filter, evaporate and distil residue under reduced press in an atmosphere of  $\text{N}_2$ . The distillate solidifies on cooling. [UV: *J Chem Soc* 3076 1958; *J Am Chem Soc* **81** 4939 1951; *Org Synth Coll Vol V* 419 1973.]

**Benzenesulfinic acid** [618-41-7] M 142.2, m  $84^\circ$ ,  $\text{pK}^{25}$  2.16 (2.74). The acid is purified by dissolving the Na salt in  $\text{H}_2\text{O}$ , acidifying to Congo Red paper with HCl and adding a concentrated soln of  $\text{FeCl}_3$  whereby Fe sulfinate ppts. Collect the salt, wash with a little  $\text{H}_2\text{O}$ , drain, suspend in  $\text{H}_2\text{O}$  and add a slight excess of 1.5M aq NaOH. The  $\text{Fe}(\text{OH})_3$  ppts, it is fild off, the sulfinic acid in the aq soln is extracted with

$\text{Et}_2\text{O}$ , the extract is dried ( $\text{Na}_2\text{SO}_4$ ) and evapd to give colorless crystals of benzenesulfonic acid **m** 84° which are stored under  $\text{N}_2$  in the dark, as it slowly oxidises in air to the sulfonic acid [see *Org Synth* **42** 62 1966].

**Benzenesulfonic acid** [98-11-3] **M** 158.2, **m** 43-44°, 50-55° (anhydrous), 65-66°, **pK**<sup>25</sup> -2.7, 0.70 (2.53?) Purified by dissolving in a small volume of distd  $\text{H}_2\text{O}$  and stirring with slightly less than the theoretical amount of  $\text{BaCO}_3$ . When effervescence is complete and the solution is still acidic, filter off the insoluble barium benzenesulfonate. The salt is collected and dried to constant weight *in vacuo*, then suspended in  $\text{H}_2\text{O}$  and stirred with a little less than the equivalent (half mol.) of sulfuric acid. The insoluble  $\text{BaSO}_4$  (containing a little barium benzenesulfonate) is filt'd off and the filtrate containing the free acid is evapd in a high vacuum. The oily residue will eventually crystallise when completely anhydrous. A 32% commercial acid was caused to fractionally cryst at room temp over  $\text{P}_2\text{O}_5$  in a vac desiccator giving finally colorless deliquescent plates **m** 52.5°. The anhydrous crystn acid is deliquescent and should be stored over anhyd  $\text{Na}_2\text{SO}_4$  in the dark and should be used in subdued sunlight as it darkens under sunlight. The main impurity is Fe which readily separates as the Fe salt in the early fractions [Taylor and Vincent *J Chem Soc* 3218 1952]. It is an IRRITANT to the skin and eyes. [see *Org Synth Coll Vol I* 84 1948; Michael and Adair *Chem Ber* **10** 585 1877.]

**Benzenesulfonic anhydride** [512-35-6] **M** 298.3, **m** 88-91°. Crystd from  $\text{Et}_2\text{O}$ .

**Benzenesulfonyl chloride** [98-09-9] **M** 176.6, **m** 14.5°, **b** 120°/10mm, 251.2°/760mm(dec), **d** 1.384. Distd, then treated with 3mole % each of toluene and  $\text{AlCl}_3$ , and allowed to stand overnight. The free benzenesulfonyl chloride was distd off at 1mm pressure, and then carefully fractionally distd at 10mm in an all-glass column. [Jensen and Brown *J Am Chem Soc* **80** 4042 1958.]

**Benzene-1,2,4,5-tetracarboxylic (pyromellitic) acid** [89-05-4] **M** 254.2, **m** 281-284°, **pK**<sub>1</sub><sup>25</sup> 1.87, **pK**<sub>2</sub><sup>25</sup> 2.72, **pK**<sub>3</sub><sup>25</sup> 4.30, **pK**<sub>4</sub><sup>25</sup> 5.52. See entry on p. 345.

**Benzene-1,2,3-tricarboxylic (hemimellitic) acid ( $\text{H}_2\text{O}$ )** [36362-97-7] **M** 210.1, **m** 190°(dec), **pK**<sub>1</sub><sup>25</sup> 2.62, **pK**<sub>2</sub><sup>25</sup> 3.82, **pK**<sub>3</sub><sup>25</sup> 5.51. Crystd from water.

**Benzene-1,3,5-tricarboxylic (trimesic or trimellitic) acid** [554-95-0] **M** 210.1, **m** 360°(dec), **pK**<sub>1</sub><sup>25</sup> 2.64, **pK**<sub>2</sub><sup>25</sup> 3.71, **pK**<sub>3</sub><sup>25</sup> 5.01. Crystd from water.

**1,2,4-Benzenetriol** [533-73-3] **M** 126.1, **m** 141°, **pK**<sub>1</sub><sup>20</sup> 9.08, **pK**<sub>2</sub><sup>20</sup> 11.82. Crystd from  $\text{Et}_2\text{O}$ .

**Benzethonium chloride** [121-54-0] **M** 448.1, **m** 164-166°. Crystd from 1:9 MeOH/ $\text{Et}_2\text{O}$  mixture.

**Benzhydrol (diphenylmethanol)** [91-01-0] **M** 184.2, **m** 69°, **b** 297°/748mm, 180°/20mm. Crystd from hot  $\text{H}_2\text{O}$  or pet ether (b 60-70°), pet ether containing a little \*benzene, from  $\text{CCl}_4$ , or EtOH (1mL/g). An additional purification step is passage of a \*benzene soln through an activated alumina column. Sublimes in a vacuum. Also crystd three times from MeOH/ $\text{H}_2\text{O}$  [Naguib *J Am Chem Soc* **108** 128 1986]. § A commercial polystyrene supported version is available.

**Benzidine (4,4'-diaminobiphenyl)** [92-87-5] **M** 184.2, **m** 128-129°, **pK**<sub>1</sub><sup>20</sup> 3.85, **pK**<sub>2</sub><sup>20</sup> 4.95. Its soln in \*benzene was decolorized by percolation through two 2-cm columns of activated alumina, then concentrated until benzidine crystd on cooling. Recrystd alternatively from EtOH and \*benzene to constant absorption spectrum [Carlin, Nelb and Odioso *J Am Chem Soc* **73** 1002 1951]. Has also been crystd from hot water (charcoal) and from diethyl ether. Dried under vac in an Abderhalden pistol. Stored in the dark in a stoppered container. **CARCINOGENIC**.

**Benzidine dihydrochloride** [531-85-1] **M** 257.2, **m** >250°(dec). Crystd by soln in hot  $\text{H}_2\text{O}$ , with addition of conc HCl to the slightly cooled soln. **CARCINOGENIC**.

**Benzil** [134-81-6] **M** 210.2, **m** 96-96.5°. Crystd from \*benzene after washing with alkali. (Crystn from EtOH did not free benzil from material reacting with alkali.) [Hine and Howarth *J Am Chem Soc* **80** 2274

1958.] Has also been crystd from  $\text{CCl}_4$ , diethyl ether or EtOH [Inoue et al. *J Chem Soc, Faraday Trans 1* **82** 523 1986].

**Benzilic acid (diphenylglycollic acid)** [76-93-7] M 228.3, m 150°, pK<sup>18</sup> 3.06. Crystd from \*benzene (ca 6mL/g), or hot H<sub>2</sub>O.

**Benzil monohydrazone** [5433-88-7] M 224.3, m 151°. Crystd from EtOH.

**$\alpha$ -Benzil monoxime** [14090-77-8], [E, 574-15-2], [Z, 574-16-3] M 105.1, m 140°. Crystd from \*C<sub>6</sub>H<sub>6</sub> (must not use animal charcoal).

**Benzimidazole** [51-17-2] M 118.1, m 172-173°, pK<sub>1</sub><sup>25</sup> 5.53, pK<sub>2</sub><sup>25</sup> 11.70. Crystd from water or aqueous EtOH (charcoal), and dried at 100° for 12h.

**2-Benzimidazolylacetonitrile** [4414-88-4] M 157.2, m 200-205° dec, 209.7-210.7°(corrected), 210°. Recrystd from aqueous EtOH. It has been recrystd from hot H<sub>2</sub>O using charcoal, and finally from aqueous EtOH. [*J Am Chem Soc* **65** 1072 1943].

**Benzo[b]biphenylene** [259-56-3] M 202.2, m dec >250°. Purified by sublimation under reduced pressure.

**Benzo-15-crown-5** [14098-44-3] M 268.3, m 78-80°. Recrystd from *n*-heptane. **IRRITANT.**

**Benzo-18-crown-6** [14098-24-9] M 312.2, m 42-45°, 43-43.5°. Purified by passage through a DEAE cellulose column in cyclohexane. Recryst from *n*-hexane. Its complex with thiourea has m 127° [5-6 mol of urea to ether, *J Org Chem* **36** 1690 1971]. The stability constants of Na<sup>+</sup>, K<sup>+</sup>, Rb<sup>+</sup>, Cs<sup>+</sup>, Tl<sup>+</sup> and Ba<sup>2+</sup> are in *Inorg Chim Acta* **28** 73 1978] [NMR: *J Am Chem Soc* **98** 3769 1976]. **IRRITANT.**

**Benzo[3,4]cyclobuta[1,2-*b*]quinoxaline** [259-57-4] M 204.2, m dec >250°. Purified by sublimation under reduced pressure.

**Benzofuran (coumarone)** [271-89-6] M 118.1, b 62-63°/15mm, 97.5-99.0°/80mm, 170-173°/atm, 173-175°(169)/760mm, d<sub>4</sub><sup>20</sup> 1.0945, n<sub>D</sub><sup>20</sup> 1.565. Steam distil, dissolve in Et<sub>2</sub>O, wash with 5% aqueous NaOH, saturated NaCl, dry (Na<sub>2</sub>SO<sub>4</sub>), evaporate and distil. UV:  $\lambda_{\text{max}}$  245, 275, 282nm (log  $\epsilon$  4.08, 3.45, 3.48). The *picrate* has m 102-103°. [*Org Synth Coll Vol V* 251 1973; NMR: Black and Heffernan *Aust J Chem* **18** 353 1965.]

**2-Benzofurancarboxylic acid** [496-41-3] M 162.1, m 192-193°, pK<sub>Est</sub> ~3.2. Crystd from water.

**Benzofurazan** [273-09-6] M 120.1, m 55°. Purified by crystn from EtOH and sublimed.

**Benzoic acid** [65-85-0] M 122.1, m 122.6-123.1°, pK<sup>25</sup> 4.12. For use as a volumetric standard, analytical reagent grade benzoic acid should be carefully fused to ca 130° (to dry it) in a platinum crucible, and then powdered in an agate mortar. Benzoic acid has been crystd from boiling water (charcoal), aq acetic acid, glacial acetic acid, \*C<sub>6</sub>H<sub>6</sub>, aq EtOH, pet ether (b 60-80°), and from EtOH soln by adding water. It is readily purified by fractional crystn from its melt and by sublimation in a vacuum at 80°.

***o*-Benzoic acid sulfimide (saccharin, 1,2-benzisothiazol-3(2*H*)-one 1,1-dioxide)** [81-07-2] M 183.2, m 227-229°, 229°, 228.8-229.7°, pK<sup>25</sup> 1.31, pK<sup>25</sup> 12.8. Purified by recrystn from Me<sub>2</sub>CO [solubility 7.14% at 0°, 14.4% at 50°], or aqueous isoPrOH to give a fluorescent soln. [*Am J Pharm* **41** 17 1952.]

**Benzoic anhydride** [93-97-0] M 226.2, m 42°. Freed from benzoic acid by washing with NaHCO<sub>3</sub>, then water, and drying. Crystd from \*benzene (0.5mL/g) by adding just enough pet ether (b 40-60°), to cause cloudiness, then cooling in ice. Can be distd at 210-220°/20mm.

(±)-**Benzoin (2-hydroxy-2-phenylacetophenone)** [119-53-9] **M 212.3, m 137°**. Crystd from CCl<sub>4</sub>, hot EtOH (8mL/g), or 50% acetic acid. Crystd from high purity \*benzene, then twice from high purity MeOH, to remove fluorescent impurities [Elliott and Radley *Anal Chem* 33 1623 1961]. Sublimes.

(±)-**α-Benzoinoxime** [441-38-3] **M 227.3, m 151°**. Crystd from diethyl ether.

**Benzonitrile** [100-47-0] **M 103.1, f -12.9°, b 191.1°, d 1.010, n 1.528**. Dried with CaSO<sub>4</sub>, CaCl<sub>2</sub>, MgSO<sub>4</sub> or K<sub>2</sub>CO<sub>3</sub>, and distd from P<sub>2</sub>O<sub>5</sub> in an all-glass apparatus, under reduced pressure (**b 69°/10mm**), collecting the middle fraction. Distn from CaH<sub>2</sub> causes some decomposition of solvent. Isonitriles can be removed by preliminary treatment with conc HCl until the smell of isonitrile has gone, followed by preliminary drying with K<sub>2</sub>CO<sub>3</sub>. (This treatment also removes amines).

Steam distd (to remove small quantities of carbylamine). The distillate was extracted into ether, washed with dil Na<sub>2</sub>CO<sub>3</sub>, dried overnight with CaCl<sub>2</sub>, and the ether removed by evaporation. The residue was distd at 40mm (**b 96°**) [Kice, Perham and Simons *J Am Chem Soc* 82 834 1960].

Conductivity grade benzonitrile (specific conductance  $2 \times 10^{-8}$  mho) was obtained by treatment with anhydrous AlCl<sub>3</sub>, followed by rapid distn at 40-50° under vacuum. After washing with alkali and drying with CaCl<sub>2</sub>, the distillate was vac distd several times at 35° before being fractionally crystd several times by partial freezing. It was dried over finely divided activated alumina from which it was withdrawn as required [Van Dyke and Harrison *J Am Chem Soc* 73 402 1951].

**Benzo[ghi]perylene (1,12-benzoperylene)** [191-24-2] **M 276.3, m 273°, 277-278.5°, 278-280°**. Purified as light green crystals by recrystn from \*C<sub>6</sub>H<sub>6</sub> or xylene and sublimes at 320-340° and 0.05mm [UV *Helv Chim Acta* 42 2315 1959; *Chem Ber* 65 846 1932; Fluoresc. Spectrum: *J Chem Soc* 3875 1954]. *1,3,5-Trinitrobenzene complex* **m 310-313°** (deep red crystals from \*C<sub>6</sub>H<sub>6</sub>); *picrate* **m 267-270°** (dark red crystals from \*C<sub>6</sub>H<sub>6</sub>); *styphnate (2,4,6-trinitroresorcinol complex)* **m 234°** (wine red crystals from \*C<sub>6</sub>H<sub>6</sub>). It recrystallises from propan-1-ol [*J Chem Soc* 466 1959].

**3,4-Benzophenanthrene** [195-19-7] **M 228.3, m 68°**. Crystd from EtOH, pet ether, or EtOH/Me<sub>2</sub>CO.

**Benzophenone** [119-61-9] **M 182.2, m 48.5-49°, pK -6.0 (aq H<sub>2</sub>SO<sub>4</sub>)**. Crystd from MeOH, EtOH, cyclohexane, \*benzene or pet ether, then dried in a current of warm air and stored over BaO or P<sub>2</sub>O<sub>5</sub>. Also purified by zone melting and by sublimation [Itoh *J Phys Chem* 89 3949 1985; Naguib et al. *J Am Chem Soc* 108 128 1986; Gorman and Rodgers *J Am Chem Soc* 108 5074 1986; Ohamoto and Teranishi *J Am Chem Soc* 108 6378 1986; Naguib et al. *J Phys Chem* 91 3033 1987].

**Benzophenone oxime** [574-66-3] **M 197.2, m 142°, pK 11.18**. Crystd from MeOH (4mL/g).

**Benzopinacol** [464-72-2] **M 366.5, m 170-180° (depends on heating rate)**. Crystd from EtOH.

**Benzo[a]pyrene (3,4 benzpyrene)** [50-32-8] **M 252.3, m 177.5-178°, 179.0-179.5°**. A soln of 250mg in 100mL of \*benzene was diluted with an equal volume of hexane, then passed through a column of alumina, Ca(OH)<sub>2</sub> and Celite (3:1:1). The adsorbed material was developed with a 2:3 \*benzene/hexane mixture. (It showed as an intensely fluorescent zone.) The main zone was eluted with 3:1 acetone/EtOH, and was transferred into 1:1 \*benzene-hexane by adding H<sub>2</sub>O. The soln was washed, dried with Na<sub>2</sub>SO<sub>4</sub>, evaporated and crystd from \*benzene by the addition of MeOH [Lijinsky and Zechmeister *J Am Chem Soc* 75 5495 1953]. Alternatively it can be chromatographed on activated alumina, eluted with a cyclohexane-\*benzene mixture containing up to 8% \*benzene, and the solvent evapd under reduced pressure [Cahnmann *Anal Chem* 27 1235 1955], and recrystd from EtOH [Nithipatikom and McGown *Anal Chem* 58 3145 1986]. **CARCINOGENIC.**

**Benzo[e]pyrene (1,2-benzpyrene)** [192-97-2] **M 252.3, m 178-179°, 178-180°**. Purified by passage through an Al<sub>2</sub>O<sub>3</sub> column (Woelm, basic, activity I) and eluted with \*C<sub>6</sub>H<sub>6</sub> and recrystd from 2 volumes of EtOH-\*C<sub>6</sub>H<sub>6</sub> (4:1). Forms colourless or light yellow prisms or needles. [*J Chem Soc* 3659 1954; *Justus Liebigs Ann Chem* 705 190 1967.] *1,3,5-Trinitrobenzene complex* **m 253-254°** (orange needles from

EtOH); the *picrate* prepared by mixing 20mg in 1mL of  $^*C_6H_6$  with 20mg of picric acid in 2mL  $^*C_6H_6$ , collecting the deep red crystals, and recrystallising from  $^*C_6H_6$  m 228-229° [Synth J Chem Soc 398 1967; NMR: J Chem Phys 47 2020 1967]. **CARCINOGEN.**

**3,4-Benzoquinoline (phenanthridine)** [229-87-8] M 179.2, m 108-109°, b 350°, pK<sup>20</sup> 4.61. Chromatographed on activated alumina from  $^*$ benzene soln, with diethyl ether as eluent. Evapn of ether gave crystalline material which was freed from residual solvent under vacuum, then further purified by fractional crystn under N<sub>2</sub>, from its melt. Sublimes in vacuo. See also p. 324.

**5,6-Benzoquinoline** [85-02-9] M 179.0, m 93°, b 350°, pK<sup>20</sup> 5.11. As 3,4-benzoquinoline above.

**7,8-Benzoquinoline** [230-27-3] M 179.0, m 52.0-52.5°, pK<sup>20</sup> 4.21. As 3,4-benzoquinoline above.

**p-Benzoquinone** [106-51-4] M 108.1, m 115.7°. Usually purified in one or more of the following ways: steam distn, followed by filtration and drying (e.g. in a desiccator over CaCl<sub>2</sub>); crystn from pet ether (b 80-100°),  $^*$ benzene (with, then without, charcoal), water or 95% EtOH; sublimation under vacuum (e.g. from room temperature to liquid N<sub>2</sub>). It slowly decomposes, and should be stored, refrigerated, in an evacuated or sealed glass vessel in the dark. It should be resublimed before use. [Wolfenden et al. J Am Chem Soc 109 463 1987.]

**1-Benzosuberone (6,7,8,9-tetrahydrobenzocyclohepten-5-one)** [826-73-3] M 160.2, b 80-85°/0.5mm, 90-93°/1mm, 138-139°/12mm, 154°/15mm, 175-175°/40mm, d<sub>4</sub><sup>20</sup> 1.086, n<sub>D</sub><sup>20</sup> 1.5638. Purified by dissolving in toluene, washing with aqueous 5% NaOH, then brine, dried (MgSO<sub>4</sub>), and distd. *2,4-Dinitrophenylhydrazone* has m 210.5°, 207-208° (from CHCl<sub>3</sub> + MeOH). *Z-O-Picryloxime* has m 156-157° (from Me<sub>2</sub>CO+MeOH); the *E-O-picryloxime* has m 107°. The *oxime* has m 106.5-107.5°. [UV J Am Chem Soc 73 1411 1951, 75 3744 1953; Chem Ber 90 1844 1957.]

**1,2,3-Benzothiadiazole** [273-77-8] M 136.2, m 35°, pK<sub>Est</sub> ~<0. Crystd from pet ether.

**2,1,3-Benzothiadiazole** [272-13-2] M 136.2, m 44°, b 206°/760mm, pK<sub>Est</sub> <0. Crystd from pet ether.

**1-Benzothiophene (benzo[b]thiophene, thianaphthene)** [95-15-8] M 134.2, m 29-32°, 30°, 31-32°, 32°, b 100°/16mm, 103-105°/20mm, 221-222°/760mm, d<sub>4</sub><sup>32.2</sup> 1.1484, n<sub>D</sub><sup>39</sup> 1.6306. It has the odour of naphthalene. If the IR spectrum is not very good then suspend in a faintly alkaline aqueous soln and steam distil. Extract the distillate with Et<sub>2</sub>O, dry the extract with CaCl<sub>2</sub>, filter, evaporate the solvent and fractionate the residue. Distillate sets solid. The *sulfoxide* has m 142°, the *picrate* has m 148-149° (yellow crystals from EtOH) and the *stypnate* has m 136-137°. [J Org Chem 10, 381 1945; Chem Ber 52B 1249 1919, 53 1551 1920; The Chemistry of Heterocyclic Compounds Hartough and Weisel eds, Interscience Publ, NY, p23, 28, 1954.]

**1,2,3-Benzotriazole** [95-14-7] M 119.1, m 96-97°, 98.5°, 100°, b 159°/0.2mm, 204°/15mm, pK<sub>1</sub><sup>20</sup> 1.6, pK<sub>2</sub><sup>20</sup> 8.64. Crystd from toluene, CHCl<sub>3</sub>, Me<sub>2</sub>NCHO or satd aq soln, and dried at room temperature or in a vacuum oven at 65°. Losses are less if material is distd in a vacuum. **CAUTION: may EXPLODE during vac distn, necessary precautions must be taken.** [Org Synth Coll Vol III 106 1955.]

**O-Benzotriazol-1-yl-N,N,N',N'-tetramethyluronium hexafluorophosphate (HBTU)** [94790-37-1] M 379.2, m 200° (dec), 250°, 254°(dec). Wash with H<sub>2</sub>O (3 x), CH<sub>2</sub>Cl<sub>2</sub> (3 x), dry and recryst from MeCN. Dry in a vacuum and store cold in the dark [Dourtoglou et al. Tetrahedron Lett 1269 1978, NMR: Synthesis 572 1984].

**Benzoylacetone (1-phenyl-1,3-butanedione)** [93-91-4] M 162.2, m 58.5-59.0°. Crystd from Et<sub>2</sub>O or MeOH and dried under vacuum at 40°.

**2-Benzoylbenzoic acid** [85-52-9] M 226.2, m 126-129°, 129.2, 130°, pK<sup>25</sup> 3.54. Recrystd from \*C<sub>6</sub>H<sub>6</sub> or cyclohexane, but is best recrystallised by dissolving in a small volume of hot toluene and then adding just enough pet ether to cause pptn and cool. Dry in a low vacuum at 80°. It can be sublimed at 230-240°/0.3mm [J Chem Soc 265 1957]. The *S*-benzylthiuronium salt has m 177-178° (from EtOH). [J Am Chem Soc 75 4087 1953; Chem Ber 90 1208 1957.]

**3-Benzoylbenzoic acid** [579-18-0] M 226.2, m 164-166°, pK<sub>Est</sub>~3.5. Cryst from EtOH; vac subl.

**4-Benzoylbenzoic acid** [611-95-0] M 226.2, m 196.5-198°, 197-200°, pK<sub>Est</sub> ~3.7. Dissolve in hot H<sub>2</sub>O by adding enough aqueous KOH soln till distinctly alkaline, filter and then acidify with drops of conc HCl. Filter off, wash solid with cold H<sub>2</sub>O, dry at 100°, and recrystallise from EtOH. [J Am Chem Soc 55 2540 1933.]

**(S +) and (R -) 1-Benzoyl-2-tert-butyl-3-methyl-4-imidazolinone** [R- 101055-57-6] [S-101055-56-5] M 260.3, m 142-143°, 145.6-146.6°, 145-147°, [α]<sub>546</sub><sup>20</sup> (+) and (-) 155°, [α]<sub>D</sub><sup>20</sup> (+) and (-) 133° (c 1, CHCl<sub>3</sub>). Recrystd from boiling EtOH (sol 1.43g/mL) or better by dissolving in CH<sub>2</sub>Cl<sub>2</sub> and adding pentane, filter and dry for at least 12h at 60°/0.1mm and sublimed at 135°/0.01mm. It has also been purified by flash column chromatography with Merck silica gel at 0.04-0.063mm and using Et<sub>2</sub>O/pet ether/MeOH (60:35:5) as eluent. It is then recrystd from EtOH/pet ether. [IR, NMR: *Helv Chim Acta* 70 237 1987; *Angew Chem, Int Ed Engl* 25 345 1986.] The *racemate* is purified in a similar manner and has m 104-105° [NMR: *Helv Chim Acta* 68 949 1985].

**Benzoyl chloride** [98-88-4] M 140.6, b 56°/4mm, 196.8°/745mm, d 1.2120, n<sup>10</sup> 1.5537.

A soln of benzoyl chloride (300mL) in \*C<sub>6</sub>H<sub>6</sub> (200mL) was washed with two 100mL portions of cold 5% NaHCO<sub>3</sub> soln, separated, dried with CaCl<sub>2</sub> and distd [Oakwood and Weisgerber *Org Synth* III 113 1955]. Repeated fractional distn at 4mm Hg through a glass helices-packed column (avoiding porous porcelain or silicon-carbide boiling chips, and hydrocarbon or silicon greases on the ground joints) gave benzoyl chloride that did not darken on addition of AlCl<sub>3</sub>. Further purification was achieved by adding 3 mole% each of AlCl<sub>3</sub> and toluene, standing overnight, and distilling off the benzoyl chloride at 1-2mm [Brown and Jenzen *J Am Chem Soc* 80 2291 1958]. Refluxing for 2h with an equal weight of thionyl chloride before distn, has also been used. **Strong IRRITANT.** Use in a fume cupboard.

**Benzoylformic acid (phenylglyoxylic acid)** [611-73-4] M 150.14, m 62-65°, 64.5-65.5°, 67°, b 84°/0.1mm, 163-167°/15mm, pK<sup>25</sup> 1.39 (1.79). If the sample is oily then it may contain H<sub>2</sub>O. In this case dry in a vacuum desiccator over P<sub>2</sub>O<sub>5</sub> or KOH until crisp. For further purification dissolve 5.5g in hot CCl<sub>4</sub> (750mL), add charcoal (2g, this is necessary otherwise the acid may separate as an oil), filter, cool in ice-water until crystallisation is complete. Filter the acid, and the solvent on the crystals is removed by keeping the acid (4.5g) in a vacuum desiccator for 2 days. Slightly yellow crystals are obtained. It can be recrystd also from \*C<sub>6</sub>H<sub>6</sub>/pet ether, and can be distilled in vacuum. The acid is estimated by titration with standard NaOH. The *phenylhydrazone* is recrystallised from EtOH, m 163-164°; the *semicarbazone acid* has m 259°(dec) (from EtOH). The *methyl ester* distils at 137°/14mm, 110-111°/2mm, n<sub>D</sub><sup>20</sup> 1.5850. [J Am Chem Soc 67 1482 1945; J Org Chem 24 1825 1959.]

**Benzoyl glycine (hippuric acid)** [495-69-2] M 179.2, m 188°, pK<sup>40</sup> 3.59. Crystd from boiling H<sub>2</sub>O. Dried over P<sub>2</sub>O<sub>5</sub>.

**Benzoyl isothiocyanate** [532-55-8] M 163.2, m 25.5-26°, b 72.5-73°/6mm, 88-91°/20mm, 94-96°/21mm, 202.5-204°/724mm, 250-255°/atm, d<sub>4</sub><sup>20</sup> 1.213, n<sub>D</sub><sup>20</sup> 1.637. Distil over a small amount of P<sub>2</sub>O<sub>5</sub>, whereby the distillate crystallises in prisms. It is readily hydrolysed by H<sub>2</sub>O to give benzamide and benzoylurea, but with NH<sub>3</sub> it gives *benzoylurea* m 210° which can be recrystd from EtOH. [J Am Chem Soc 62 1595 1940, 76 580 1954; *Org Synth Coll Vol* III 735 1955.]

**Benzoyl peroxide** [94-36-0] M 242.2, m 95°(dec). Dissolved in CHCl<sub>3</sub> at room temperature and ppted by adding an equal volume of MeOH or pet ether. Similarly ppted from acetone by adding two volumes of distilled water. Has also been crystd from 50% MeOH, and from diethyl ether. Dried under vacuum at room

temperature for 24h. Stored in a desiccator in the dark at 0°. When purifying in the absence of water it can be **EXPLOSIVE** and it should be done on a very small scale with adequate protection. Large amounts should be kept moist with water and stored in a refrigerator. [Kim et al. *J Org Chem* **52** 3691 1987.]

***p*-Benzoylphenol (4-hydroxybenzophenone)** [1137-42-4] **M 198.2, m 133.4-134.8°, pK<sup>25</sup> 7.95.** Dissolved in hot EtOH (charcoal), crystd once from EtOH/H<sub>2</sub>O and twice from \*benzene [Grunwald *J Am Chem Soc* **73** 4934 1951; Dryland and Sheppard *J Chem Soc Perkin Trans 1* 125 1986].

***N*-Benzoyl-*N*-phenylhydroxylamine** [304-88-1] **M 213.2, m 121-122°.** Recrystd from hot water, \*benzene or acetic acid.

**2-Benzoylpyridine** [91-02-1] **M 183.2, m 41-43°, 48-50°, 72°/0.02mm, 104-105°/0.01, n<sub>D</sub><sup>24</sup> 1.6032, pK<sub>Est</sub> ~2.4.** Dissolve in Et<sub>2</sub>O, shake with aqueous NaHCO<sub>3</sub>, H<sub>2</sub>O, dry over MgSO<sub>4</sub>, it solidifies on cooling. The solid can be recrystd from pet ether. Its *hydrochloride* crystallises from Me<sub>2</sub>CO, **m 126-127°**, and the *2,4-dinitrophenylhydrazone* has **m 193-195°.** [*J Organomet Chem* **24** 623 1970.]

**Benzoyl sulfide** [644-32-6] **M 174.4, m 131.2-132.3°.** About 300mL of solvent was blown off from a filtered soln of benzoyl disulfide (25g) in acetone (350mL). The remaining acetone was decanted from the solid which was recrystd first from 300mL of 1:1 (v/v) EtOH/ethyl acetate, then from 300mL of EtOH, and finally from 240mL of 1:1 (v/v) EtOH/ethyl acetate. Yield about 40% [Pryor and Pickering *J Am Chem Soc* **84** 2705 1962]. *Handle in a fume cupboard because of TOXICITY and obnoxious odour.*

**2,1-Benzoxathiol-3-one-1,1-dioxide (sulfobenzoic acid anhydride)** [81-08-3] **M 184.2, m 116-124°, 126-127°, 128°, b 184-186°/18mm.** Purified by distn in a vacuum and readily solidifies to a crystalline mass on cooling. [*J Am Chem Soc* **34** 1594 1912.] Alternatively purified by dissolving in the minimum vol of toluene and reflux for 2h using a Dean-Stark trap. Evaporate under reduced pressure and distil the anhydride at 18mm. It can then be recrystd three times from its own weight of dry \*C<sub>6</sub>H<sub>6</sub>. It is sensitive to moisture and should be stored in the dark in a dry atmosphere. The *O-methyl oxime* has **m 110-112°** [*Tetrahedron Lett* 3289 1972]. [*Org Synth Coll Vol I* 495 1941.] (See also p. 568 in Chapter 6.)

**Benzoxazolinone** [59-49-4] **M 135.1, m 137-139°, 142-143°(corrected), b 121-213°/17mm, 335-337°/760mm.** It can be purified by recrystn from aqueous Me<sub>2</sub>CO then by distn at atm pressure then in a vacuum. The *methyl mercury salt* recryst from aq EtOH has **m 156-158°.** [*J Am Chem Soc* **67** 905 1945.]

***N*-Benzoyl-*o*-tolylhydroxylamine** [1143-74-4] **M 227.3, m 104°.** Recrystd from aqueous EtOH.

**Benzyl-2-acetamido-4,6-*O*-benzylidene-2-deoxy- $\alpha$ -D-glucopyranoside** [13343-63-0] **M 399.4, m 256-261°, 263-264°, [ $\alpha$ ]<sub>D</sub><sup>26</sup> +120° (c 1, pyridine).** Wash with cold isoPrOH and crystallise from dioxane/isoPrOH. [*J Org Chem* **32** 2759 1967.]

**Benzyl acetate** [140-11-4] **M 150.2, m -51°, b 92-93°/10mm, 134°/102mm, 214.9°/760mm, d<sub>4</sub><sup>20</sup> 1.0562, n<sub>D</sub><sup>25</sup> 1.4994.** Purified by fractional distn, preferably in a good vacuum. Values of n<sub>D</sub><sup>25</sup> of 1.5232-1.5242 seem too high and should be 1.4994. [*J Org Chem* **26** 5180 1961.]

**Benzyl acetoacetate** [5396-89-4] **M 192.2, b 130°/2mm, 156-157°/10mm, 162-167°/15mm, 275-277°/atm, d<sub>4</sub><sup>20</sup> 1.114, n<sub>D</sub><sup>20</sup> 1.514.** Fractionate and collect fractions of expected physical properties. Otherwise add *ca* 10% by weight of benzyl alcohol and heat in an oil bath (160-170°, open vessel) for 30min during which time excess of benzyl alcohol will have distd off, then fractionate. [*J Org Chem* **17** 77 1952.]

**4'-Benzylacetophenone** [782-92-3] **M 210.3, m 73°.** Crystd from EtOH (*ca* 1mL/g).

**Benzyl alcohol** [100-51-6] **M 107.2, f -15.3°, b 205.5°, 93°/10mm, d 0.981, n 1.54033, pK<sup>25</sup> 15.4.** Usually purified by careful fractional distn at reduced pressure in the absence of air. Benzaldehyde, if present, can be detected by UV absorption at 283nm. Also purified by shaking with aq KOH and extracting with peroxide-free diethyl ether. After washing with water, the extract was treated with satd NaHS sol, filtered,

washed and dried with CaO and distd under reduced pressure [Mathews *J Am Chem Soc* **48** 562 1926]. Peroxy compounds can be removed by shaking with a soln of Fe(II) followed by washing the alcohol layer with distd water and fractionally distd.

**Benzylamine** [100-46-9] M 107.2, b 178°/742mm, 185°/768mm, d 0.981, n 1.5392, pK<sup>25</sup> 9.33. Dried with NaOH or KOH, then distd under N<sub>2</sub>, through a column packed with glass helices, taking the middle fraction. Has also been distd from zinc dust under reduced pressure.

**Benzylamine hydrochloride** [3287-99-8] M 143.6, m 248° (rapid heating). Crystd from water.

**N-Benzylaniline (N-phenylbenzylamine)** [103-32-2] M 183.4, m 36°, b 306-307°, d 1.061, pK<sup>25</sup> 4.04. Crystd from pet ether (b 60-80°) (ca 0.5mL/g).

**1-Benzyl-1-aza-12-crown-4 (10-benzyl-1,4,7-trioxa-10-azacyclododecane)** [84227-47-4] M 265.4, 122-125°/0.03mm, 140-143°/0.05mm, d<sub>4</sub><sup>20</sup> 1.09, n<sub>D</sub><sup>20</sup> 1.52, pK<sub>Est</sub> ~ 7.7. Dissolve in CH<sub>2</sub>Cl<sub>2</sub> or CCl<sub>4</sub> (1g in 30mL) wash with H<sub>2</sub>O (30mL), brine (30mL), H<sub>2</sub>O (30 mL) again, dry over MgSO<sub>4</sub> or Na<sub>2</sub>SO<sub>4</sub> and evaporate. The residue in CH<sub>2</sub>Cl<sub>2</sub> is chromatographed through Al<sub>2</sub>O<sub>3</sub> (eluting with 10% EtOAc in hexane), evaporate, collect the correct fractions and distil (Kügelrohr). Log K<sub>Na</sub> in dry MeOH at 25° for Na<sup>+</sup> complex is 2.08. [*Tetrahedron Lett* **26** 151 1985; *J Org Chem* **53** 5652 1988.]

**Benzyl bromide** [100-39-0] M 171.0, m -4°, b 85°/12mm, 192°/760mm, d 1.438, n 1.575. Washed with conc H<sub>2</sub>SO<sub>4</sub> (CARE), water, 10% Na<sub>2</sub>CO<sub>3</sub> or NaHCO<sub>3</sub> soln, and again with water. Dried with CaCl<sub>2</sub>, Na<sub>2</sub>CO<sub>3</sub> or MgSO<sub>4</sub> and fractionally distd in the dark, under reduced pressure. It has also been thoroughly degassed at 10<sup>-6</sup> mm and redistd in the dark. This gave material with λ<sub>max</sub> (MeCN): 226nm (ε 8200) [Mohammed and Kosower *J Am Chem Soc* **93** 2709 1971]. Handle in a fume cupboard, extremely LACHRYMATORY.

**Benzyl bromoacetate** [5437-45-6] M 229.1, b 96-98°/0.1mm, 146°/12mm, 166-170°/22mm, d<sub>4</sub><sup>20</sup> 1.444, n<sub>D</sub><sup>25</sup> 1.5412. Dilute with Et<sub>2</sub>O, wash with 10% aqueous NaHCO<sub>3</sub>, H<sub>2</sub>O, dry (MgSO<sub>4</sub>) and fractionate using a Fenske (glass helices packing) column. [*J Chem Soc* 1521 1956.] LACHRYMATORY

**N-Benzyl-tert-butylamine (N-tert-butylbenzylamine)** [3378-72-1] M 163.3, b 91°/12mm, 109-110°/25mm, 218-220°/atm, d<sub>4</sub><sup>20</sup> 0.899, n<sub>D</sub><sup>25</sup> 1.4942., pK<sup>25</sup> 10.19. Dissolve in Et<sub>2</sub>O, dry over KOH pellets, filter and fractionate in a N<sub>2</sub> atmosphere to avoid reaction with CO<sub>2</sub> from the air. The hydrochloride has m 245-246°(dec) (from MeOH + Me<sub>2</sub>CO) and the perchlorate has m 200-201°. [*J Am Chem Soc* **80** 4320 1958.]

**Benzyl carbamate** [621-84-1] M 151.2, m 86°, 86-88°, 90-91°. If it smells of NH<sub>3</sub> then dry in a vac desiccator and recryst from 2 vols of toluene and dry in a vac desiccator again. It forms glistening plates from toluene, and can be recrystd from H<sub>2</sub>O [*J Org Chem* **6** 878 1941; *Org Synth Coll Vol III* 168 1955].

**Benzyl chloride** [100-44-7] M 126.6, m 139°, b 63°/8mm, d 1.100, n 1.538. Dried with MgSO<sub>4</sub> or CaSO<sub>4</sub>, or refluxed with fresh Ca turnings, then fractionally distd under reduced pressure, collecting the middle fraction and storing with CaH<sub>2</sub> or P<sub>2</sub>O<sub>5</sub>. Has also been purified by passage through a column of alumina. Alternatively it is dried over MgSO<sub>4</sub> and distd in a vacuum. The middle fraction is degassed by several freeze-thaw cycles and then fractionated in an 'isolated fractionating column' (which has been evacuated and sealed off at ~10<sup>-6</sup> mm) over a steam bath. The middle fraction is retained. The final samples were vacuum distd from this sample and again retaining the middle fraction. The purity is >99.9% (no other peaks are visible on GLC and the NMR spectrum is consistent with the structure. [Mohammed and Kosower *J Am Chem Soc* **93** 1709 1971.] IRRITANT and strongly LACHRYMATORY.

**N-Benzyl-β-chloropropionamide** [24752-66-7] M 197.7, m 94°. Crystd from MeOH.

**Benzyl cinnamate** [103-41-3] M 238.3, m 34-35°, 39°, b 154-157°/0.5mm, 228-230°/22mm. Recrystd to constant melting point from 95% EtOH and has the odour of balsam. Alternatively dissolve in

Et<sub>2</sub>O, wash with 10% aqueous Na<sub>2</sub>CO<sub>3</sub>, H<sub>2</sub>O, dry (Na<sub>2</sub>SO<sub>4</sub>), evaporate and fractionate under reduced press using a short Vigreux column. It decomposes when boiled at atm press. [*J Am Chem Soc* **74** 547 1952; **84** 2550 1962.]

**Benzyl cyanide** [140-29-4] **M 117.1, b 100°/8mm, 233.5°/760mm, d 1.015, n 1.523.** Benzyl isocyanide can be removed by shaking vigorously with an equal volume of 50% H<sub>2</sub>SO<sub>4</sub> at 60°, washing with satd aq NaHCO<sub>3</sub>, then half-saturated NaCl soln, drying and fractionally distilling under reduced pressure. Distn from CaH<sub>2</sub> causes some decomposition of this compound: it is better to use P<sub>2</sub>O<sub>5</sub>. Other purification procedures include passage through a column of highly activated alumina, and distn from Raney nickel. *Precautions should be taken because of possible formation of free TOXIC cyanide; use an efficient fume cupboard.*

**N-Benzyl dimethylamine** [103-83-3] **M 135.2, b 66-67°/15mm, 83-84°/30mm, 98-99°/24mm, d<sub>4</sub><sup>20</sup> 0.898, n<sub>D</sub><sup>20</sup> 1.516, pK<sup>25</sup> 8.91.** Dry over KOH pellets and fractionate over Zn dust in a CO<sub>2</sub>-free atmosphere. It has a pK<sup>25</sup> of 8.25 in 45% aq EtOH. Store under N<sub>2</sub> or in a vacuum. The *picrate* has **m 94-95°**, and the *picrolonate* has **m 151°** (from EtOH). [*Chem Ber* **63** 34 1930; *J Am Chem Soc* **55** 3001 1933; *J Chem Soc* 2845 1957.] The *tetraphenyl borate salt* has **m 182-185°**. [*Anal Chem* **28** 1794 1956.]

**Benzyl dimethyloctadecylammonium chloride** [122-19-0] **M 442.2, m 63°.** Crystd from acetone.

**2-Benzyl-1,3-dioxolane** [101-49-5] **M 164.2, b 98-99°/1mm, 110°/5mm, 137-138°/34mm, 240-242°/atm, d<sub>4</sub><sup>20</sup> 1.087, n<sub>D</sub><sup>20</sup> 1.532.** Dissolve in CH<sub>2</sub>Cl<sub>2</sub>, wash well with 1M NaOH, dry over K<sub>2</sub>CO<sub>3</sub>, filter, evaporate and distil through a short path still (Kügelrohr). It has also been purified by preparative gas chromatography. [*Synthesis* 808 1974; *J Org Chem* **34** 3949 1969.]

**Benzyl ether** [103-50-4] **M 198.3, b 298°, 158-160°/0.1mm, d 1.043, n 1.54057.** Refluxed over sodium, then distd under reduced pressure. Also purified by fractional freezing.

**N-Benzyl-N-ethylaniline** [92-59-1] **M 221.3, b 212-222°/54mm, 285-286°/710mm, 312-313°/atm (dec), d<sub>4</sub><sup>20</sup> 1.029, n<sub>D</sub><sup>20</sup> 1.595, pK<sub>Est</sub> ~4.6.** Dry over KOH pellets and fractionate. The *picrate* crystallises from \*C<sub>6</sub>H<sub>6</sub> as yellow lemon crystals **m 126-128°** (softening at 120°). [*J Chem Soc* 303 1951; IR: *J Chem Soc* 760 1958.]

**Benzyl ethyl ether** [539-30-0] **M 136.2, b 186°, 65°/10mm, d 0.949, n 1.4955.** Dried with CaCl<sub>2</sub> or NaOH, then fractionally distd. [*J Am Chem Soc* **78** 6079 1956.]

**Benzyl ethyl ketone (1-phenylbutan-2-one)** [1007-32-5] **M 148.2, b 49-49.5°/0.01mm, 66-69°/1mm, 83-85°/5mm, 101-102°/10mm, 229-233°/atm, d<sub>4</sub><sup>20</sup> 0.989, n<sub>D</sub><sup>25</sup> 1.5015.** Purified by fractionation using an efficient column. It can be converted into the *oxime* and distd, **b 117-118°/2mm, 145-146°/15mm, d<sub>25</sub><sup>25</sup> 1.036, n<sub>D</sub><sup>25</sup> 1.5363,** decompose oxime and the ketone is redistilled. It can also be purified *via* the *semicarbazone* which has **m 154 155°**. [*J Am Chem Soc* **77** 5655 1955; *J Org Chem* **15** 8 1950.]

**S-(+)- and R-(-)- Benzyl glycidyl ether (1-benzyloxyoxirane)** [*S*:14618-80-5] [*R*:16495-13-9] **M 164.2, b 68°/10<sup>-4</sup> mm, 105°/0.4mm, d<sub>4</sub><sup>20</sup> 1.072, n<sub>D</sub><sup>20</sup> 1.517, [α]<sub>546</sub><sup>20</sup> (+) and (-) 5.5°, [α]<sub>D</sub><sup>20</sup> (+) and (-) 5.1° (c 5, toluene), [α]<sub>D</sub><sup>20</sup> (+) and (-) 1.79° (c 5.02, CHCl<sub>3</sub>), [α]<sub>D</sub><sup>21</sup> (+) and (-) 15.3° (neat).** The ether in EtOAc is dried (Na<sub>2</sub>SO<sub>4</sub>) then purified by flash chromatography using pet ether/EtOAc (5:1) as eluent. The ether is then distd through a short path dist apparatus (Kügelrohr) as a colourless liquid. Alternatively, dissolve in CHCl<sub>3</sub>, wash with H<sub>2</sub>O, dry (Na<sub>2</sub>SO<sub>4</sub>), evaporate and purify through silica gel chromatography. [*J Chem Soc* 1021 1967; *Heterocycles* **16** 381 1981; *Org Synth* **69** 82 1990; *Synthesis* 539 1989; *Chem Pharm Bull Jpn* **39** 1385 1991.]

**3-Benzyl-5-(2-hydroxyethyl)-4-methylthiazolinium chloride** [4568-71-2] **M 269.8, m 142-144°, 145-147°.** Purified by recrystn from EtOH or H<sub>2</sub>O. If placed in a bath at 125° and heated at 2°/min the **m** is 140.5-141.4°. [*J Biol Chem* **167** 699 1947, *J Am Chem Soc* **79** 4386 1957.]

**O-Benzylhydroxylamine hydrochloride** [2687-43-6] M 159.6, m 234-238°(sublimes),  $pK_{Est}$  ~5.9. Recrystd from H<sub>2</sub>O or EtOH.

**N-Benzylideneaniline** [538-51-2] M 181.2, m 48° (54°), b 300°/760mm. Steam volatile and crystd from \*benzene or 85% EtOH.

**Benzyl isocyanate** [3173-56-6] M 133.2, b 82-84°/10mm, 87°/14mm, 95°/17mm, 101-104°/33mm,  $d_4^{20}$  1.08,  $n_D^{20}$  1.524. Purified by fractionation through a two-plate column. It is a viscous liquid and is TOXIC. [J Chem Soc 182 1947; J Am Chem Soc 81 4838 1959; IR: *Monatsh Chem* 88 35 1957.]

**Benzyl isothiocyanate** [622-78-6] M 149.2, b 123-124°/1mm, 138-140°/20mm, 255-260°/atm,  $d_4^{20}$  1.1234,  $n_D^{20}$  1.6039. Dissolve in Et<sub>2</sub>O, filter, if there is any solid, and distil through an efficient column at 1mm with bath temperature at ca 150°. Characterise by reacting (0.5mL) in EtOH (1mL) with 50% NH<sub>2</sub>NH<sub>2</sub>.H<sub>2</sub>O (2 mL) to give 4-benzylthiosemicarbazide as colourless needles which are recrystallised from EtOH, m 130°. [J Chem Soc 1582 1950; *Justus Liebigs Ann Chem* 612 11 1958; IR and UV: *Acta Chem Scand* 13 442 1959.]

**S-Benzyl-isothiuronium chloride** [538-28-3] M 202.7, two forms, m 150° and 175°,  $pK_{Est}$  ~9.8 (free base). Crystd from 0.2M HCl (2mL/g) or EtOH and dried in air.

**Benzylmalonic acid** [616-75-1] M 194.2, m 121°,  $pK_1^{25}$  2.91,  $pK_2^{25}$  5.87. Crystd from \*C<sub>6</sub>H<sub>6</sub>.

**Benzylidene malononitrile** [2700-22-3] M 154.2, m 83-84°. Recrystd from EtOH [Bernasconi et al. *J Am Chem Soc* 107 3612 1985].

**Benzyl mercaptan** [100-53-8] M 124.2, b 70.5-70.7°/9.5mm, d 1.058, n 1.5761,  $pK^{25}$  9.43. Purified via the mercury salt [see Kern *J Am Chem Soc* 75 1865 1953], which was crystd from \*benzene as needles (m 121°), and then dissolved in CHCl<sub>3</sub>. Passage of H<sub>2</sub>S gas regenerated the mercaptan. The HgS ppte was filtered off, and washed thoroughly with CHCl<sub>3</sub>. The filtrate and washings were evaporated to remove CHCl<sub>3</sub>, then residue was fractionally distd under reduced pressure [Mackle and McClean, *Trans Faraday Soc* 58 895 1962].

**(-)-N-Benzyl-N-methylephedrinium bromide [benzyl(2-hydroxy-1-methyl-2-phenethyl) dimethylammonium bromide]** [58648-09-2] M 350.3, m 209-211°, 212-214°,  $[\alpha]_D^{25}$  -3.8° (c 1.45, MeOH),  $[\alpha]_D^{20}$  -5.3° (c 1.45, MeOH). Recrystd from MeOH/Et<sub>2</sub>O. [*Justus Liebigs Ann Chem* 710 1978.] The chloride is recrystd from EtOAc/n-hexane, m 198-199°  $[\alpha]_D^{25}$  -8.67° (c 1.45, MeOH). [*J Chem Soc, Perkin Trans 1* 574 1981.]

**Benzyl 4-nitrophenyl carbonate** [13795-24-9] M 273.2, m 78-80°. Dissolve in Et<sub>2</sub>O, wash with H<sub>2</sub>O (3x) and satd aq NaCl, dry (MgSO<sub>4</sub>), evap in vac and recryst residue from a small vol of MeOH, m 78-79°. Alternatively dissolve in Et<sub>2</sub>O, wash with N HCl (2x), 0.5N NaHCO<sub>3</sub> (4x) then H<sub>2</sub>O, dry (Na<sub>2</sub>SO<sub>4</sub>), evap Et<sub>2</sub>O and recryst residue from \*C<sub>6</sub>H<sub>6</sub>-pet ether, m 79-80°. [Khosla et al. *Indian J Chem* 5 279 1967; Wolman et al. *J Chem Soc (C)* 596 1976.]

**Benzylloxyacetyl chloride** [19810-31-2] M 184.6, b 81°/0.2mm, 84-87°/0.4mm, 105-107°/5mm,  $d_4^{20}$  1.19,  $n_D^{20}$  1.523. Check IR to see if there are OH bands. If so then it may be contaminated with free acid formed by hydrolysis. Add oxalyl chloride (amount depends on contamination and needs to be judged, ca 3mols) heat at 50° in the absence of moisture for 1h and fractionate twice, b 81°/0.2mm (with bath temp at 81°). Excessive heating results in decomposition to give benzyl chloride. The anilide is formed by adding aniline in CHCl<sub>3</sub> soln, m 49°. [*Helv Chim Acta* 16 1130 1933.]

**Benzylloxybutan-2-one** [6278-91-7] M 178.2, b 90-92°/0.1mm, 88-91°/0.5mm, 121-126°/5mm,  $d_4^{20}$  1.0275,  $n_D^{20}$  1.5040. Dissolve in CHCl<sub>3</sub>, wash with H<sub>2</sub>O, aqueous saturated NaHCO<sub>3</sub>, H<sub>2</sub>O, dry (MgSO<sub>4</sub>), evaporate the CHCl<sub>3</sub>, and fractionate. [*J Am Chem Soc* 79 2316 1957.]

**Benzyloxycarbonyl chloride (Cbz-Cl, benzyl chloroformate) [501-53-1] M 170.6, b 103°/20mm, d 1.195, n 1.5190.** Commercial material is better than 95% pure and may contain some toluene, benzyl alcohol, benzyl chloride and HCl. After long storage (e.g. two years at 4°, Greenstein and Winitz [*The Chemistry of the Amino Acids Vol 2* p. 890, J Wiley and Sons NY, 1961] recommended that the liquid should be flushed with a stream of dry air, filtered and stored over sodium sulfate to remove CO<sub>2</sub> and HCl which are formed by decomposition. It may further be distilled from an oil bath at a temperature below 85° because Thiel and Dent [*Annalen* 301 257 1898] stated that benzyloxycarbonyl chloride decarboxylates to benzyl chloride slowly at 100° and vigorously at 155°. Redistillation at higher vac below 85° yields material which shows no other peaks than those of benzyloxycarbonyl chloride by NMR spectroscopy. **LACHRYMATORY and TOXIC.**

**N-Benzyloxycarbonylglycyl-L-alaninamide [17331-79-2] M 279.3, m dec >200°.** Recrystd from EtOH/Et<sub>2</sub>O.

**N-Benzyloxycarbonyl-N'-methyl-L-alaninamide [33628-84-1] M 236.3, m dec >200°.** Recrystd from EtOAc.

**5-Benzyloxyindole [1215-59-4] M 223.3, m 96-97°; 100-103°, 104-106°, pK <0.** Recrystd from \*C<sub>6</sub>H<sub>6</sub>-pet ether or pet ether. The *picrate*, red crystals from \*C<sub>6</sub>H<sub>6</sub>, has m 142-143°. [*Chem Ind (London)* 1035 1953; *J Am Chem Soc* 76 5579 1954; fluorescence: *Biochem J* 107 225 1968.]

**p-(Benzyloxy)phenol [103-16-2] M 200.2, m 122.5°, pK<sub>Est</sub> ~10.1.** Crystd from EtOH or water, and dried over P<sub>2</sub>O<sub>5</sub> under vacuum. [Walter et al. *J Am Chem Soc* 108 5210 1986.]

**S-(-)-3-Benzyloxypropan-1,2-diol [17325-85-8] M 182.2, m 24-26°, b 117-118°/10<sup>-4</sup>mm, 115-116°/0.02mm, 121-123°/0.2mm, d<sub>4</sub><sup>20</sup> 1.1437, n<sub>D</sub><sup>22</sup> 1.5295, [α]<sub>D</sub><sup>25</sup> -5.9° (neat).** Purified by repeated fractional distn. [*J Biol Chem* 193 835 1951, 230 447 1958.]

**2-Benzylphenol [28994-41-4] M 184.2, m 54.5°, b 312°/760mm, 175°/18mm, pK<sub>Est</sub> ~10.0** Crystd from EtOH, stable form has m 52° and unstable form has m 21°.

**4-Benzylphenol (α-Phenyl-p-cresol) [101-53-1] M 184.2, m 84°, pK<sub>Est</sub> ~10.2.** Crystd from water.

**1-Benzyl-4-piperidone [3612-20-2] M 189.3, b 107-108°/0.2mm, 114-116°/0.3mm, 143-146°/5mm, 157-158°/11mm, d 1.059, n 1.538.** If physical properties show contamination then dissolve in the minimum volume of H<sub>2</sub>O, made strongly alkaline with aqueous KOH, extract with toluene several times, dry the extract with K<sub>2</sub>CO<sub>3</sub>, filter, evaporate and distil the residue at high vacuum using a bath temp of 160-190°, and redistil. [*J Chem Soc* 3173 1957, *J Am Chem Soc* 53 1030 1930.] The *hydrochloride* has m 159-161° (from Me<sub>2</sub>CO + Et<sub>2</sub>O), and the *picrate* has m 174-182° (from Me<sub>2</sub>CO + Et<sub>2</sub>O). [*Helv Chim Acta* 41 1184 1958.]

**2-Benzylpyridine [101-82-6] M 169.2, b 98.5°/4mm, d 1.054, n<sup>26</sup> 1.5771, pK<sup>25</sup> 5.13.** Dried with NaOH for several days, then distd from CaO under reduced pressure, redistilling the middle fraction.

**4-Benzylpyridine [2116-65-6] M 169.2, b 110.0°/6mm, d 1.065, n<sup>26</sup> 1.5814, pK<sup>25</sup> 5.59.** Dried with NaOH for several days, then distd from CaO under reduced pressure, redistilling the middle fraction.

**4-N-Benzylsulfanilamide [1709-54-2] M 262.3, m 175°.** Crystd from dioxane/H<sub>2</sub>O.

**Benzyl sulfide [538-74-9] M 214.3, m 50°.** See dibenzylsulfide on p. 192.

**Benzylthiocyanate [3012-37-1] M 149.2, m 43°, b 256°(dec).** Crystd from EtOH or aqueous EtOH.

**Benzyl toluene-*p*-sulfonate** [1024-41-5] M 162.3, m 58°. Crystd from pet ether (b 40-60°).

**Benzyltributylammonium bromide** [25316-59-0] M 356.4, m 169-171°, 174-175°. Recrystd from EtOAc/EtOH and EtOH/Et<sub>2</sub>O. [*J Am Chem Soc* 73 4122 1951, 81 3264 1959.]

**Benzyl 2,2,2-trichloroacetimidate** [81927-55-1] M 252.5, b 106°/0.5mm, m 3°, d 1.349, n 1.545. Purify by distn to remove up to 1% of PhCH<sub>2</sub>OH as stabiliser. A soln in hexane can be stored for up to 2 months without decompn. It is hygroscopic and has to be stored dry. [Wessel et al. *J Chem Soc, Perkin Trans I* 2247 1985.]

**Benzyltrimethylammonium chloride** [56-93-9] M 185.7, m 238-239°(dec). A 60% aq soln was evapd to dryness under vac on a steam bath, and then left in a vac desiccator containing a suitable dehydrating agent. The solid residue was dissolved in a small amount of boiling absolute EtOH and pptd by adding an equal volume of diethyl ether and cooling. After washing, the ppte was dried under vac [Karusch *J Am Chem Soc* 73 1246 1951].

**Benzyltrimethylammonium hydroxide (Triton B)** [100-85-6] M 167.3, d 0.91. A 38% soln (as supplied) was decolorized (charcoal), then evaporated under reduced pressure to a syrup, with final drying at 75° and 1mm pressure. Prepared anhydrous by prolonged drying over P<sub>2</sub>O<sub>5</sub> in a vacuum desiccator.

**Berbamine** [478-61-5] M 608.7, m 197-210°, [α]<sub>D</sub><sup>20</sup> +115° (CHCl<sub>3</sub>), pK<sup>20</sup> 7.33. Crystd from pet ether.

**Berberine** [2086-83-1] M 336.4, m 145°, pK<sub>1</sub><sup>20</sup> 2.47, pK<sub>2</sub><sup>20</sup> 11.73 (pseudobase?). Crystd from pet ether or ether as yellow needles.

**Berberine hydrochloride (2H<sub>2</sub>O)** [633-65-8] M 407.9, m 204-206°(dec), pK 2.47. Crystn from water gives the dihydrate. The anhydrous salt may be obtained by recrystn from EtOH/Et<sub>2</sub>O, wash with Et<sub>2</sub>O and dry in a vacuum. The *iodide* has m 250°(dec) (from EtOH). [*J Chem Soc* 113 503 1918; *J Chem Soc* 2036 1969.]

**Betaine** [107-43-7] M 117.1, m 301-305°(dec) (anhydrous), pK<sup>25</sup> 1.83. Crystd from aq EtOH.

**Betamethasone (9α-fluoro-11β,17α,21-trihydroxy-16β-methylpregna-1,4-diene-3,20-dione)** [378-44-9] M 392.5, m 231-136°(dec), 235-237°(dec), [α]<sub>D</sub><sup>20</sup> +108° (c 1, Me<sub>2</sub>CO). Crystd from ethyl acetate, and has λ<sub>max</sub> 238nm (log ε 4.18) in MeOH.

**Biacetyl (butan-2,3-dione)** [431-03-8] M 86.1, b 88°, d 0.981, n<sup>18.5</sup> 1.3933. Dried with anhydrous CaSO<sub>4</sub>, CaCl<sub>2</sub> or MgSO<sub>4</sub>, then vacuum distd under nitrogen, taking the middle fraction and storing it at Dry-ice temperature in the dark (to prevent polymerization).

**Bibenzyl** [103-29-7] M 182.3, m 52.5-53.5°. Crystd from hexane, MeOH, or 95% EtOH. It has also been sublimed under vacuum, and further purified by percolation through columns of silica gel and activated alumina.

**Bicuculline** [485-49-4] M 367.4, m 215° (196°, 177°), [α]<sub>546</sub><sup>20</sup> +159° (c 1, CHCl<sub>3</sub>), pK 4.84. See bicuculline entry on p. 515 in Chapter 6.

**Bicyclohexyl** [92-51-3] M 166.3, b 238° (*cis-cis*), 217-219° (*trans-trans*). Shaken repeatedly with aqueous KMnO<sub>4</sub> and with conc H<sub>2</sub>SO<sub>4</sub>, washed with water, dried, first from CaCl<sub>2</sub> then from sodium, and distd. [Mackenzie *J Am Chem Soc* 77 2214 1955.]

**Bicyclo[3.2.1]octane** [6221-55-2] M 110.2, m 141°. Purified by zone melting.

**Biguanide** [56-03-1] M 101.1, m 130° pK<sub>1</sub><sup>25</sup> 3.1, pK<sub>2</sub><sup>25</sup> 12.8. Crystd from EtOH.

**Bilirubin** [635-65-4] M 584.7,  $\epsilon_{450\text{nm}}$  55,600 in CHCl<sub>3</sub>, pK<sub>Est</sub> ~3.0. An acyclic tetrapyrrole bile pigment with impurities which can be eliminated by successive Soxhlet extraction with diethyl ether and MeOH. It crystallises from CHCl<sub>3</sub> as deep red-brown rhombs, plates or prisms, and is dried to constant weight at 80° under vacuum. [Gray et al. *J Chem Soc* 2264, 2276 1961.]

**Biliverdine** [114-25-0] M 582.6, m >300°, pK 3.0. The precursor of bilirubin (above) and forms dark green plates or prisms, with a violet reflection, from MeOH. [Gray et al. *J Chem Soc* 2264 1961; Sheldrick *J Chem Soc, Perkin Trans 2* 1457 1976.]

(±)-1,1'-Bi-(2-naphthol) [1,1'-di-(2-naphthol)] [602-09-5; 41024-90-2] M 286.3, m 215-217°, 218°, pK<sub>Est(1)</sub>~7.1, pK<sub>Est(2)</sub>~11.2. Crystd from toluene or \*benzene (10mL/g). When crystd from chlorobenzene it had m 238°. Sol in dioxane is 5%.

1,1'-Bi-(2-naphthol) [1,1'-di-(2-naphthol)] [*R*(+)- 18531-94-7], [*S*(-)- 18531-99-2] M 286.3, m 207.5-208.5°, 209-211°, [ $\alpha$ ]<sub>D</sub><sup>20</sup> (+) and (-) 37.4.0° (c 0.5, THF), [ $\alpha$ ]<sub>546</sub><sup>25</sup> (+) and (-) 51° (c 0.1, THF), pK as above. Dissolve in cold 2.5N NaOH, extract with CH<sub>2</sub>Cl<sub>2</sub>, and acidify with 5% HCl. Collect the white ppte and recryst from aq EtOH and dry in a vacuum [*Tetrahedron* 27 5999 1971]. Optically stable in dioxane-water (100°/24h). *Racemisation*: 72% in 1.2N HCl at 100°/24h and 68% in 0.67M KOH in BuOH at 118°/23h [*J Am Chem Soc* 95 2693 1973]. Cryst from \*C<sub>6</sub>H<sub>6</sub> (sol 1%) using Norite or aq EtOH after chromatography through silica gel, eluting with Me<sub>2</sub>CO-\*C<sub>6</sub>H<sub>6</sub>. [Kyba et al. *J Org Chem* 42 4173 1977; see also Brussee and Jansen *Tetrahedron Lett* 24 3261 1983; Akimoto and Yamada *Tetrahedron* 27 5999 1971.]

1,1'-Binaphthyl [ $\pm$  32507-32-7 and 604-53-5; *R*(-)- 24161-30-6; *S*(+)- 734-77-0] M 254.3, m 145°, 159° ( $\pm$ , 2 forms), 153-154° (+ and -), [ $\alpha$ ]<sub>D</sub><sup>20</sup> (-) and (+) ~220° (\*C<sub>6</sub>H<sub>6</sub>). Purified through a silica gel column with Me<sub>2</sub>CO-\*C<sub>6</sub>H<sub>6</sub> [or Al<sub>2</sub>O<sub>3</sub> with 10% \*C<sub>6</sub>H<sub>6</sub>/pet ether (b 30-60°)] and recrystd from EtOH, pentane, or slow evap of \*C<sub>6</sub>H<sub>6</sub>, Me<sub>2</sub>CO or Et<sub>2</sub>O solns. Half life ~10h at 25° in various solvents. [Wilson and Pincock *J Am Chem Soc* 97 1474 1975; Akimoto and Yamada *Tetrahedron* 27 5999 1971.]

2,2'-Binaphthyl ( $\beta$ ,  $\beta'$ -binaphthyl) [61-78-2] M 254.3, m 188°. Crystd from \*benzene.

**Biphenyl** [92-52-4] M 154.2, m 70-71°, b 255°, d 0.992. Crystd from EtOH, MeOH, aq MeOH, pet ether (b 40-60°) or glacial acetic acid. Freed from polar impurities by passage through an alumina column in \*benzene, followed by evapn. A in CCl<sub>4</sub> has been purified by vac distn and by zone refining. Treatment with maleic anhydride removed anthracene-like impurities. Recrystd from EtOH followed by repeated vacuum sublimation and passage through a zone refiner. [Taliani and Bree *J Phys Chem* 88 2351 1984.]

*p*-Biphenylamine [92-67-1] M 169.2, m 53°, b 191°/15mm, pK<sup>18</sup> 4.38. See *p*-aminobiphenyl entry on p. 104.

**4-Biphenylcarbonyl chloride** [14002-51-8] M 216.7, m 114-115°. Dissolve in a large volume of pet ether (10 x, b 50-70°), filter through a short column of neutral alumina, evaporate to dryness *in vacuo* and recrystd from pet ether (b 60-80°). **LACHRYMATORY.**

**Biphenyl-2-carboxylic (2-phenylbenzoic) acid** [947-84-2] M 198.2, m 114°, b 343-344°, pK 3.46. Crystd from \*C<sub>6</sub>H<sub>6</sub>-pet ether or aq EtOH.

**Biphenyl-4-carboxylic (4-phenylbenzoic) acid** [92-92-2] M 198.2, m 228°, pK<sup>25</sup> 5.66 (in 50% 2-butoxyethanol). Crystd from \*C<sub>6</sub>H<sub>6</sub>-pet ether or aq EtOH.

**2,4'-Biphenyldiamine** [492-17-1] M 184.2, m 45°, b 363°/760mm, pK<sub>Est(1)</sub>~4.8, pK<sub>Est(2)</sub>~3.9. Crystd from aqueous EtOH.

**Biphenylene** [259-79-0] M 152.2, m 152°. Recrystd from cyclohexane then sublimed in vacuum.

$\alpha$ -(4-Biphenyl)butyric acid [959-10-4] M 240.3, m 175-177°, pK<sub>Est</sub> ~4.5. Crystd from MeOH.

$\gamma$ -(4-Biphenyl)butyric acid [6057-60-9] M 240.3, m 118°, pK<sub>Est</sub> ~4.8. Crystd from MeOH.

2,2'-Bipyridyl [366-18-7] M 156.2, m 70.5°, b 273°, pK<sub>1</sub><sup>25</sup> -0.52, pK<sub>2</sub><sup>25</sup> 4.44. Crystd from hexane, or EtOH, or (after charcoal treatment of a CHCl<sub>3</sub> soln) from pet ether. Also pptd from a conc soln in EtOH by addition of H<sub>2</sub>O. Dried in a vacuum over P<sub>2</sub>O<sub>5</sub>. Further purification by chromatography on Al<sub>2</sub>O<sub>3</sub> or by sublimation. [Airoldi et al. *J Chem Soc, Dalton Trans* 1913 1986.]

4,4'-Bipyridyl [553-26-4] M 156.2, m 73°(hydrate), 114° (171-171°)(anhydrous), b 305°/760mm, 293°/743mm, pK<sub>1</sub><sup>20</sup> 3.17, pK<sub>2</sub><sup>20</sup> 4.82. Crystd from water, \*benzene/pet ether, ethyl acetate and sublimed *in vacuo* at 70°. Also purified by dissolving in 0.1M H<sub>2</sub>SO<sub>4</sub> and twice pptd by addition of 1M NaOH to pH 8. Recrystd from EtOH. [Man et al. *J Chem Soc, Faraday Trans 1* 82 869 1986; Collman et al. *J Am Chem Soc* 109 4606 1987.]

2,2'-Bipyridylamine [1202-34-2] M 171.2, m 95.1°, pK<sub>Est</sub> ~5.0. Crystd from Me<sub>2</sub>CO.

2,2'-Biquinolin-4,4'-dicarboxylic (2,2'-bicinchoninic) acid [1245-13-2] M 344.3, m 367°, pK<sub>Est(1)</sub> ~1.5, pK<sub>Est(2)</sub> ~4.0. Dissolve in dilute NaOH and ppte with acetic acid, filter, wash well with H<sub>2</sub>O and dry at 100° in a vacuum oven. Attempts to form a picrate failed. The *methyl ester* (SOCl<sub>2</sub>-MeOH) has m 165.6-166°. [*J Am Chem Soc* 64 1897 1942; 68 2705 1946.] For di-K salt see entry in Chapter 5.

2,2'-Biquinolyl ( $\alpha,\alpha'$ -diquinolyl) [119-91-5] M 256.3, m 196°, pK<sub>Est</sub> ~4.2. Decolorised in CHCl<sub>3</sub> soln (charcoal), then crystd to constant melting point from EtOH or pet ether [Cumper, Ginman and Vogel *J Chem Soc* 1188 1962].

Bis-acrylamide (*N,N'*-methylene bisacrylamide) [110-26-9] M 154.2, m >300°. Recrystd from MeOH (100g dissolved in 500mL boiling MeOH) and filtered without suction in a warmed funnel. Allowed to stand at room temperature and then at -15°C overnight. Crystals collected with suction in a cooled funnel and washed with cold MeOH). Crystals air-dried in a warm oven. TOXIC.

Bis-(4-aminophenyl)methane [101-77-9] M 198.3, m 92-93°, b 232°/9mm, pK<sub>Est</sub> ~4.9. See 4,4'-diaminodiphenylmethane on p. 189.

2,5-Bis-(4-aminophenyl)-1,3,4-oxadiazole (BAO) [2425-95-8] M 252.3, m 252-255°, 254-255°. Recrystd from EtOH using charcoal and under N<sub>2</sub> to avoid oxidation.

2,5-Bis(2-benzothiazolyl)hydroquinone [33450-09-8] M 440.3, m dec >200°. Purified by repeated crystn from dimethylformamide followed by sublimation in vacuum [Erusting et al. *J Phys Chem* 91 1404 1987].

Bis-(*p*-bromophenyl)ether [53563-56-7] M 328.0, m 60.1-61.7°. Crystd twice from EtOH, once from \*benzene and dried under vac [Purcell and Smith *J Am Chem Soc* 83 1063 1961].

Bis-*N*-tert-butylloxycarbonyl-L-cystine, [10389-65-8] M 440.5, m 144.5-145°, [ $\alpha$ ]<sub>D</sub><sup>20</sup> -133.2° (c 1, MeOH), pK<sub>Est</sub> ~2.9. Crystd from in EtOAc by adding hexane [Ferraro *Biochem Prep* 13 39 1971].

2*R*,3*R*-(+)-1,4-Bis-(4-chlorobenzoyl)-2,3-butanediol [85362-86-3] and 2*S*,3*S*-(-)-1,4-Bis-(4-chlorobenzoyl)-2,3-butanediol [85362-85-2] M 371.3, m 76-77°, [ $\alpha$ ]<sub>D</sub><sup>20</sup> (+) and (-) 6.4° (c 3.11 CHCl<sub>3</sub>). Recrystd from toluene-hexane. [*Tetrahedron* 40 4617 1984.]

Bis-( $\beta$ -chloroethyl)amine hydrochloride [821-48-7] M 178.5, m 214-215°, pK<sub>Est</sub> ~5.8 (free base). Crystd from Me<sub>2</sub>CO.