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Bis-(β-chloroethyl) ether *[111-44-4]* **M 143.0, b 94°/33mm, 178.8°, d 1.220, n 1.45750.** Wash with conc H_2SO_4, then Na_2CO_3 soln, dry with anhydrous Na_2CO_3, and finally pass through a 50cm column of activated alumina before distn. Alternatively, wash with 10% ferrous sulfate soln to remove peroxides, then H_2O, dry with $CaSO_4$, and dist in vac. Add 0.2% of catechol to stabilise it. **VERY TOXIC.**

***N,N*-Bis-(2-chloroethyl)2-naphthylamine (chlornaphthazine)** *[494-03-1]* **M 268.3, m 54-56°, b 210°/5mm, pK_{Est} ~5.3.** Crystd from pet ether. **CARCINOGENIC.**

Bis-(chloromethyl)durene *[3022-16-0]* **M 231.2, m 197-198°.** Crystd three times from *benzene, then dried under vacuum in an Abderhalden pistol.

3,3'-Bis-(chloromethyl)oxacyclobutane *[78-71-7]* **M 155.0, m 18.9°.** Shaken with aqueous $NaHCO_3$ or $FeSO_4$ to remove peroxides. Separated, dried with anhydrous Na_2SO_4, then distd under reduced pressure from a little CaH_2 [Dainton, Ivin and Walmsley *Trans Faraday Soc* **65** 17884 *1960*].

2,2-Bis-(*p*-chlorophenyl)-1,1-dichloroethane (*p,p'*-DDD) *[72-54-8]* **M 320.1, m 109-111°, 111-112°.** Crystd from EtOH and dried in a vac. Purity checked by TLC. **TOXIC INSECTICIDE.**

2,2-Bis-(*p*-chlorophenyl)-1,1-dichloroethylene (*p,p'*-DDE) *[72-55-9]* **M 318.0, m 89-91°.** Crystd from EtOH and dried in a vac. Purity checked by TLC. **POSSIBLE CARCINOGEN.**

2,2-Bis-(4-chlorophenyl)-1,1,1-trichloroethane (*p,p'*-DDT, 1,1,1-trichloro-2,2-bis(*p*-chlorophenyl)ethane) *[50-29-3]* **M 354.5, m 108.5-109°, 108°.** Crystd from *n*-propyl alcohol (5mL/g), then dried in air or an air oven at 50-60°. Alternatively crystd from 95% EtOH, and checked by TLC.

2,2'-Bis-[di-(carboxymethyl)-amino]diethyl ether, $(HOOCCH_2)_2NCH_2CH_2OCH_2CH_2N(CH_2COOH)_2$ *[923-73-9]* **M 336.3, pK_1^{20} 1.8, pK_2^{20} 2.76, pK_3^{20} 8.84, K_4^{20} 9.47.** Crystd from EtOH.

4,4'-Bis-(diethylamino)benzophenone *[90-93-7]* **M 324.5, m 95-96°, $pK_{Est(1)}$~1.8, $pK_{Est(2)}$ ~3.3.** Crystd from EtOH (25mL/g) and dried under vacuum.

Bis-(4-dimethylaminobenzylidene)benzidine *[6001-51-0]* **M 454.5, m 318°, pK_{Est} ~0.** Crystd from nitrobenzene.

1,8-Bis-(dimethylamino)naphthalene (Proton sponge) *[20734-58-1]* **M 214.3, m 47-48°, pK 12.34 (pK_2 -10.5 from half protonation in 86% H_2SO_4).** Crystd from EtOH and dried in a vacuum oven. Stored in the dark. Also see *N,N,N',N'*-Tetramethyl-1,8-naphthalenediamine on p. 364.

Bis-(dimethylthiocarbamyl)disulfide (tetramethylthiuram disulfide, Thiram) *[137-26-8]* **M 240.4, m 155-156°.** See tetramethylthiuram disulfide on p. 365.

Bis-(4-fluoro-3-nitrophenyl) sulfone *[312-30-1]* **M 344.3, m 193-194°.** Recrystd from Me_2CO and H_2O (5:1). It should give a yellow colour in aqueous base. [*Chem Ber* **86** 172 *1953*.]

***N,N*-Bis-(2-hydroxyethyl)-2-aminoethanesulfonic acid (BES)** *[10191-18-1]* **M 213.3, m 150-155°, pK^{20} 7.17.** Crystd from aqueous EtOH.

Bis-(2-hydroxyethyl)amino-tris-(hydroxymethyl)methane (BIS-TRIS) *[6976-37-0]* **M 209.2, m 89°, pK^{20} 6.46.** Crystd from hot 1-butanol. Dried in a vacuum at 25°.

***N,N*-Bis-(2-hydroxyethyl)glycine** *[150-25-4]* **M 163.2, m 191-194°(dec).** See *N,N*-di-(hdyroxyethyl)glycine (BICINE) on p. 208.

3,4-Bis-(4-hydroxyphenyl)hexane *[5635-50-7]* **M 270.4, m 187°.** Freed from diethylstilboestrol by zone refining.

1,4-Bismethylaminoanthraquinone (Disperse Blue 14) *[2475-44-7]* **M 266.3, λmax 640 (594)nm.** Purified by thin-layer chromatography on silica gel plates, using toluene/acetone (3:1) as eluent. The main band was scraped off and extracted with MeOH. The solvent was evapd and the dye was dried in a drying pistol [Land, McAlpine, Sinclair and Truscott *J Chem Soc, Faraday Trans 1* **72** 2091 *1976*].

Bis-(1-naphthylmethyl)amine *[5798-49-2]* **M 329.4, m 62°, pK_{Est} ~8.4.** Crystd from pet ether.

***N,N'*-Bis-(nicotinic acid) hydrazide** *[840-78-8]* **M 227-228°, m dec 200°, pK_{Est} ~3.3.** Crystd from water.

Bis-(4-nitrophenyl) carbonate *[5070-13-3]* **M 304.3, m 142-143°.** Dissolve in $CHCl_3$, wash with 2N NaOH (3 x) and once with conc HCl, dry (Na_2SO_4), evaporate and crystallise from toluene (authors say 15 vols of *benzene, prisms). [*Helv Chim Acta* **46** 795 *1963*.]

Bis-(2-nitrophenyl) disulfide *[1155-00-6]* **M 308.3, m 192-195°, 195°, 194-197°, 198-199°.** Purified by recrystn from glacial AcOH or from $^*C_6H_6$ and the yellow needles are dried in an oven at 100° until the odour of the solvent is absent. It is sparingly soluble in EtOH and Me_2CO. [Bogert and Stull *Org Synth* Coll Vol I 220 *1941*; Bauer and Cymerman *J Chem Soc* 3434 *1949*.]

Bis-(4-nitrophenyl) ether *[101-63-3]* **M 260.2, m 142-143°.** Crystd twice from $^*C_6H_6$, and dried under vacuum.

Bis-(4-nitrophenyl) methane *[1817-74-9]* **M 258.2, m 183°.** Crystd twice from $^*C_6H_6$, and dried under vacuum.

Bisnorcholanic acid (pregnane-20-carboxylic acid) *[28393-20-6]* **M 332.5, m 214° (α-form), 242° (β-form), 210-211° (γ-form), 184° (δ-form), 181° (ε-form), pK_{Est} ~5.0.** Crystd from EtOH (α-form), or acetic acid (all forms).

3,3'-Bis-(phenoxymethyl)oxacyclobutane *[1224-69-7]* **M 270.3, m 67.5-68°.** Crystd from MeOH.

1,4-Bis-(2-pyridyl-2-vinyl)benzene *[20218-87-5]* **M 284.3, pK_{Est} ~5.4.** Recrystd from xylene, then chromatography (in the dark) on basic silica gel (60-80-mesh), using CH_2Cl_2 as eluent. Vacuum sublimed in the dark to a cold surface at 10^{-3} torr.

Bis-(trichloromethyl) carbonate (triphosgene) *[32315-10-9]* **M 296.8, m 79-83°, 81-83°, b 203-206°(slight decomp).** A good solid substitute for phosgene (using a third mol per mol). Cryst from pet ether and wash with anhydrous cold Et_2O, degas at 200mm then dry at 0.1mm (over H_2SO_4). It is a **lachrymator**, is **TOXIC** and should be handled with gloves and in an efficient fume hood. [Eckert and Forster *Angew Chem, Int Ed Engl* **26** 894 *1987*; *Aldrichimica Acta* **21** 47 *1988*.]

Bistrifluoroacetamide *[407-24-9]* **M 209.1, m 85°, b 135-136°/744mm, 141°/760mm.** Major impurity is trifluoroacetamide. Add trifluoroacetic anhydride, reflux for 2h and fractionate using a Vigreux column at atmospheric pressure. [*J Chromatogr* **78** 273 *1973*.]

Bis-(trifluoroacetoxy)iodobenzene *[2712-78-9]* **M 430.0, m 112-114° (dec), 120-121°, 124-126°.** Cryst from warm trifluoroacetic acid and dry over NaOH pellets. Recrystd from Me_2CO/pet ether. Melting point depends on heating rate. [*Synthesis* 445 *1975*.]

Biuret (allophanic acid amide, carbamoylurea) *[108-19-0]* **M 103.1, sinters at 218° and chars at 270°, pK_1^{25} -0.88, pK_2^{25}>4.** Crystd from EtOH.

Bixin (6,6'-diapo-ψ,ψ- carotenedioic acid monomethyl ester) *[6983-79-5]* **M 394.5, m 198°, 217°(dec), λmax ($CHCl_3$) 209, 475 and 443nm, pK_{Est} ~4.3.** Crystd from Me_2CO (violet prisms) [Pattenden et al. *J Chem Soc (C)* 235 *1970*].

Blue Tetrazolium *[1871-22-3]* **M 727.7, m 254-255°(dec).** Crystd from 95% EtOH/anhydrous diethyl ether, to constant absorbance at 254nm.

***R*-2-*endo*-Borneol** *[464-43-7]* **M 154.3, m 208° $[\alpha]_D^{20}$ +15.8° (in EtOH).** Crystd from boiling EtOH (charcoal).

(±)-Borneol *[6627-72-1]* **M 154.3, m 130°(dec).** Crystd from pet ether (b 60-80°).

Brazilin *[474-07-7]* **M 269.3, m 130°(dec), $pK_{Est(1)}$~9.3, $pK_{Est(2)}$ ~10.0, $pK_{Est(3)}$ ~12.5 (all phenolic).** Crystd from EtOH.

Brilliant Cresyl Blue *[4712-70-3]* **M 332.8, pK^{25} 3.2.** Crystd from pet ether.

Brilliant Green (4-dimethylaminotriphenyl carbinol) *[633-03-4]* **M 482.7, m 209-211°(dec), pK^{25} 4.75.** Purified by pptn as the perchlorate from aqueous soln (0.3%) after filtering, heating to 75° and adjustment to pH 1-2. Recrystd from EtOH/water (1:4) [Kerr and Gregory *Analyst (London)* **94** 1036 *1969*].

***N*-Bromoacetamide** *[79-15-2]* **M 138.0, m 102-105°, 107-109°, 108° (anhyd).** Possible contaminant is CH_3CONBr_2. Recrystd from $CHCl_3$/hexane (1:1, seed if necessary) or water and dried over $CaCl_2$. [Oliveto and Gerold *Org Synth* Coll Vol IV 104 *1963*).

4-Bromoacetanilide *[103-88-8]* **M 214.1, m 167°.** Crystd from aq MeOH or EtOH. Purified by zone refining.

Bromoacetic acid *[79-08-3]* **M 138.9, m 50°, b 118°/15mm, 208°/760mm, pK^{25} 2.92.** Crystd from pet ether (b 40-60°). Diethyl ether soln passed through an alumina column, and the ether evaporated at room temperature under vacuum. **LACHRYMATORY.**

Bromoacetone *[598-31-2]* **M 137.0, b 31.5°/8mm.** Stood with anhydrous $CaCO_3$, distd under low vacuum, and stored with $CaCO_3$ in the dark at 0°. **LACHRYMATORY.**

4-Bromoacetophenone *[99-90-1]* **M 199.1, m 54°.** Crystd from EtOH, MeOH or from pet ether (b 80-100°). [Tanner *J Org Chem* **52** 2142 *1987*.]

ω-Bromoacetophenone (phenacyl bromide) *[70-11-1]* **M 199.1, m 57-58°.** Crystd from EtOH, MeOH or from pet ether (b 80-100°). [Tanner *J Org Chem* **52** 2142 *1987*.]

4-Bromoaniline *[106-40-1]* **M 172.0, m 66°, pK^{25} 3.86.** Crystd (with appreciable loss) from aqueous EtOH.

2-Bromoanisole *[578-57-4]* **M 187.0, f 2.5°, b 124°/40mm, d 1.513, n^{25} 1.5717.** Crystd by partial freezing (repeatedly), then distd under reduced pressure.

4-Bromoanisole *[104-92-7]* **M 187.0, f 13.4°, b 124°/40mm, d 1.495, n^{25} 1.5617.** Crystd by partial freezing (repeatedly), then distd under reduced pressure.

9-Bromoanthracene *[1564-64-3]* **M 257.1, m 98-100°.** Crystd from MeOH or EtOH followed by sublimation *in vacuo*. [Masnori et al. *J Am Chem Soc* **108** 126 *1986*.]

4-Bromobenzal diacetate *[55605-27-1]* **M 287.1, m 95°.** Crystd from hot EtOH (3mL/g).

Bromobenzene *[108-86-1]* **M 157.0, b 155.9°, d 1.495, n 1.5588, n^{15} 1.56252.** Washed vigorously with conc H_2SO_4, then 10% NaOH or $NaHCO_3$ solns, and H_2O. Dried with $CaCl_2$ or Na_2SO_4, or passed through activated alumina, before refluxing with, and distilling from, CaH_2, using a glass helix-packed column.

4-Bromobenzene diazonium tetrafluoroborate *[673-40-5]* **M 270.8, m 133° (dec), 135-140° (dec), 135° (dec).** Wash with Et_2O until the wash is colourless and allow to dry by blowing N_2 over it. Store at 0-4° in the dark. [*Chem Ber* **64** 1340 *1931.*]

4-Bromobenzenesulfonyl chloride *[98-58-8]* **M 255.5, m 73-75°, 74.3-75.1, 75-76°, 77°, b 153°/15mm, 150.6°/13mm.** Wash with cold water, dry and recryst from pet ether, or from ethyl ether cooled in powdered Dry-ice after the ether soln had been washed with 10% NaOH until colourless, then dried with anhydrous Na_2SO_4. Alternatively dissolve in $CHCl_3$, wash with H_2O, dry (Na_2SO_4), evaporate and crystallise. [*J Am Chem Soc* **62** 511 *1940.*] Test for the SO_2Cl group by dissolving in EtOH and boiling with NH_4CNS whereby a yellow amorphous ppte forms on cooling [*J Am Chem Soc* **25** 198 *1901*].

o-**Bromobenzoic acid** *[88-65-3]* **M 201.0, m 148.9°, pK^{20} 2.88.** Crystd from $*C_6H_6$ or MeOH.

m-**Bromobenzoic acid** *[585-76-2]* **M 201.0, m 155°, pK^{25} 3.81.** Crystd from acetone/water, MeOH or acetic acid.

p-**Bromobenzoic acid** *[586-76-5]* **M 201.0, m 251-252°, 254-256°, 257-258°, pK^{25} 3.96.** Crystd from MeOH, or MeOH/water mixture, 90% EtOH and Et_2O. The *methyl ester* has **m** 81° from Et_2O or dilute MeOH. [Male and Thorp *J Am Chem Soc* **35** 269 *1913*; Lamneck *J Am Chem Soc* **76** 406 *1954*, Vandenbelt et al. *Anal Chem* **26** 926 *1954.*]

p-**Bromobenzophenone** *[90-90-4]* **M 261.1, m 81°.** Crystd from EtOH.

p-**Bromobenzoyl chloride** *[586-75-4]* **M 219.5, m 36-39°, 39.8°, 41°, b 62°/0.1mm, 104.5°/6mm, 126.4-127.2°/14mm.** Check IR of a film to see if OH bands are present. If absent then recryst from pet ether and dry in a vacuum. If OH bands are weak then distil *in vacuo* and recryst if necessary. If OH bands are very strong then treat with an equal volume of redistilled $SOCl_2$ reflux for 2h then evaporate excess of $SOCl_2$ and distil residual oil or low melting solid. Store in the dark away from moisture. **LACHRYMATORY.** [Martin and Partington *J Chem Soc* 1175 *1936.*]

p-**Bromobenzyl bromide** *[589-15-1]* **M 249.9, m 60-61°.** Crystd from EtOH. **LACHRYMATORY.**

p-**Bromobenzyl chloride** *[589-17-3]* **M 205.5, m 40-41°, b 105-115°/12mm.** Crystd from EtOH. **LACHRYMATORY.**

p-**Bromobiphenyl** *[92-66-0]* **M 233.1, m 88.8-89.2°.** Crystd from abs EtOH and dried under vacuum.

2-Bromobutane *[78-76-2]* **M 137.0, b 91.2°, d 1.255, n 1.4367, n^{25} 1.4341.** Washed with conc HCl, water, 10% aqueous $NaHSO_3$, and then water. Dried with $CaCl_2$, Na_2SO_4 or anhydrous K_2CO_3, and fractionally distd through a 1m column packed with glass helices.

(+)-3-Bromocamphor-8-sulfonic acid *[5344-58-1]* **M 311.2, m 195-196°(anhydrous), $[\alpha]_D^{20}$ +88.3° (in H_2O), pK ~0.** Crystd from water.

***1R(endo,anti)*-3-Bromocamphor-8-sulfonic acid ammonium salt** see entry in Chapter 5.

(+)-3-Bromocamphor-10-sulfonic acid hydrate *[67999-30-8]* **M 329.2, m 119-121°, $[\alpha]_D^{20}$ +98.3° (in H_2O), pK ~0.** Crystd from water.

4-Bromo-4'-chlorobenzophenone *[27428-57-5]* **M 295.6, m 150°.** Crystd from EtOH or *C_6H_6 and further purified by zone refining (100 passes) [Grove and Turner *J Chem Soc* 509 *1929*; Lin and Hanson *J Phys Chem* **91** 2279 *1987*].

Bromocresol Green (3',3",5',5"-tetrabromo-*m*-cresolsulfonephthalein) *[76-60-8]* **M 698.0, m 218-219°(dec), 225°(dec), pK 4.51.** Crystd from glacial acetic acid or dissolved in aqueous 5% $NaHCO_3$ soln and ppted from hot soln by dropwise addition of aqueous HCl. Repeated until the extinction did not increase (λ_{max} 423nm). Indicator at pH 3.81 (yellow) and pH 5.4 (blue-green).

Bromocresol Purple (5',5"-dibromo-*o*-cresolsulfonephthalein) *[115-40-2]* **M 540.2, m 241-242°(dec), pK_1 -2.15, pK_2 6.3.** Dissolved in aqueous 5% $NaHCO_3$ soln and ppted from hot soln by dropwise addition of aqueous HCl. Repeated until the extinction did not increase (λ_{max} 419nm). Can also be crystd from *benzene. Indicator at pH 5.2 (yellow) and pH 6.8 (purple).

5-Bromocytosine *[2240-25-7]* **M 190.0, m 245-255°(dec), 250°(dec), pK_1^{25} 3.04, pK_2^{25} 10.33.** Recryst from H_2O or 50% aq EtOH. Alternatively, dissolve *ca* 3g in conc HCl (10mL) and evaporate to dryness. Dissolve the residual hydrochloride in the minimum volume of warm H_2O and make faintly alkaline with aq NH_3. Collect the crystals and dry in a vacuum at 100°. [*J Am Chem Soc* **56** 134 *1934*.]

***p*-Bromo-*N*,*N*-dimethylaniline** *[586-77-6]* **M 200.1, m 55°, b 264°, pK^{25} 4.23.** Refluxed for 3h with two equivalents of acetic anhydride, then fractionally distd under reduced pressure

1-Bromo-2,4-dinitrobenzene *[584-48-5]* **M 247.0, m 75°.** Crystd from ethyl ether, isopropyl ether, 80% EtOH or absolute EtOH.

2-(2-Bromoethyl)-1,3-dioxane *[33884-43-4]* **M 195.1, b 67-70°/2.8mm, 71-72°/4mm, 95°/15mm, d_4^{20} 1.44, n_D^{20} 1.4219.** Purify by vacuum fractionation. Also dissolve in Et_2O, wash with aqueous $NaHCO_3$, dry extract with Na_2SO_4, filter and fractionate. NMR in CCl_4 has δ 1.3 (m, 1H), 2.1 (m, 3H), 3.36 (t, 2H), 3.90 (m, 4H) and 4.57 (t, H). [*J Org Chem* **41** 560 *1976*; NMR, MS: *Tetrahedron* **35** 1969 *1979*; *J Pharm Sci* **60** 1250 *1971*.]

2-(2-Bromoethyl)-1,3-dioxolane *[18742-02-4]* **M 181.1, b 68-80°/8mm, 68-73°/10mm, 78-80°/20mm, d_4^{20} 1.510, n_D^{20} 1.479.** Dissolve in pentane, wash with 5% aqueous $NaHCO_3$, dry (Na_2SO_4), and evaporate. Distil the residue. [NMR: *J Org Chem* **34** 1122 *1969*; *J Pharm Sci* **60** 1250 *1971*.]

***N*-(2-Bromoethyl)phthalimide** *[574-98-1]* **M 254.1, m 81-83°, 82.5-83.5°.** The following is to be carried out in an efficient **FUME HOOD**. Dissolve the compound (180g) in CS_2 (500 mL) by refluxing for 15 min (to cause the separation of the most likely impurity, 1,2-diphthalimidoethane), filter and evaporate under reduced pressure. The product forms light tan crystals. (**m** 78-80°). Recryst from EtOH (charcoal) [the compound (50g) is dissolved in hot 75% EtOH (200mL), boiled for *ca* 10 min, carbon added (5g, Norite), filtered and cooled to 0°], as white crystals (40g) which can be recrystd (**m** 80-81°) and further recrystn gave **m** 82-83°. [*Org Synth* Coll Vol I 119 *1932*, *Synthesis* 389 *1976*; NMR: *Bull Soc Chim Fr* II-165 *1979*.]

Bromoform *[75-25-2]* **M 252.8, f 8.1°, 55-56°/35mm, 149.6°/760mm, d^{15} 2.9038, d^{30} 2.86460, n^{15} 1.60053, n 1.5988.** Storage and stability of bromoform and chloroform are similar. Ethanol, added as a stabilizer, is removed by washing with H_2O or with saturated $CaCl_2$ soln, and the $CHBr_3$, after drying with $CaCl_2$ or K_2CO_3, is fractionally distd. Prior to distn, $CHBr_3$ has also been washed with conc H_2SO_4 until the acid layer no longer became coloured, then dilute NaOH or $NaHCO_3$, and H_2O. A further purification step is fractional crystn by partial freezing.

3-Bromofuran *[22037-28-1]* **M 147.0, b 38.5°/40mm, 50°/110mm, 102.5-103°/atm, d 1.661, n 1.4970.** Purified by two steam distillations and dried over fresh CaO. It can be dried over Na metal (no obvious reaction) and fractionated. It is not very soluble in H_2O but soluble in organic solvents. Freshly distilled, it is a clear oil, but darkens on standing and eventually resinifies. It can be stored for long periods by covering the oil with an alkaline soln of hydroquinone and redistilled when required. It forms a characteristic

maleic anhydride adduct, **m** 131.5-132°. [*J Am Chem Soc* **52** 2083 *1930*, **53** 737 *1931*, adduct: **55** 430 *1933*.]

(±)-2-Bromohexadecanoic acid (2-bromopalmitic acid) *[18263-25-7]* **M 335.3, m 51-53°, 52.3-52.5°, 53°, pK_{Est} ~3.2.** Recrystd from pet ether (b 60-80°, charcoal) and finally from EtOH. The *ethyl ester* has **b** 177-178°/2mm, d_{28}^{28} 1.0484, n_D^{20} 1.4560. [IR: *J Org Chem* **21** 1426 *1956*.]

5-Bromoindole *[10075-50-0]* **M 196.1, m 90.5-91°, 90-92°, pK 16.13 (NH).** Purified by steam distn from a faintly alkaline soln. Cool the aqueous distillate, collect the solid, dry in a vacuum desiccator over P_2O_5 and recryst from aqueous EtOH (35% EtOH) or pet ether-Et_2O. λ_{max} in MeOH: 279, 287 and 296 (log ε 3.70, 3.69 and 3.53. The *picrate* has **m** 137-138°(dec) (from Et_2O-pet ether). [UV: *Chem Ber* **95** 2205 *1962*; UV and NMR: *Bull Soc Chim Fr* 4091 *1970*.]

5-Bromoisatin *[87-48-9]* **M 226.0, m 245°(dec), 251-153°, 255-256°.** Forms red prisms or needles from EtOH. The *N-acetate* crystallises as yellow prisms from *C_6H_6, **m** 170-172°, and the *N-methyl* derivative form orange-red needles from MeOH, **m** 172-173°. [*Chem Ber* **47** 360 *1914*, **53** 1545 *1920*; *Recl Trav Chim Pays-Bas* **73** 197 *1954*; *Tetrahedron Lett* 215 *1978*.]

6-Bromoisatin *[6326-79-0]* **M 226.0, m 270°, pK 10.35.** Recrystd from AcOH (yellow needles). It is a plant growth substance. [Sadler *J Org Chem* **21** 169 *1956*.]

2-Bromomethylanthraquinone *[7598-10-9]* **M 301.1, m 200-202°.** Recrystd from AcOH, the crystals are washed with a little Et_2O, dried in air and then in vac at 100°. It is prepared by bromination of 2-methylanthraquinone with $Br_2/PhNO_2$ at 145-150°, or *N*-bromosuccinimide in CCl_4 containing a trace of $(PhCOO)_2$.

2-(Bromomethyl)benzonitrile *[22115-41-9]* **M 195.1, m 72-73°, 79°, b 152-155°/15mm.** Purified by steam distn. Extract the distillate with Et_2O, dry extract (Na_2SO_4), evap and distil residue. The solidified distillate can be recrystd from pet ether or cyclohexane. NMR ($CDCl_3$) δ: 7.8-7.2 (m 4H), 4.62 (s, 2H); IR ν: 2238 cm^{-1}. **LACHRYMATORY** [*Chem Ber* **24** 2570 *1891*, **74** 675 *1934*; *Aust J Chem* **22** 577 *1969*.]

***S*-(+)-1-Bromo-2-methylbutane** *[534-00-9]* **M 151.1, b 38.2°/39mm, 49°/62mm, 60.8°(57-58°)/100mm, 65-65.6°/140mm, 116-122°/atm, d_4^{20} 1.2232, n_D^{20} 1.4453, $[\alpha]_D^{20}$ +5.1° (neat, +5.8° (c 5, $CHCl_3$).** Wash with ice-cold H_2O, dried by freezing, shake twice with an equal vol of H_2SO_4 at 0°, and twice with an equal volume of H_2O at 0°. Freeze dried and kept over freshly heated (and then cooled) K_2CO_3, and distd through a vacuum jacketed column of broken glass. Alternatively, dissolve in pet ether (b 40-60°), wash with 5% NaOH, conc H_2SO_4 (at 0°), then H_2O, dry ($CaCl_2$), evaporate and distil. [*J Am Chem Soc* **74** 4858 *1952*, **81** 2779 *1959*; *J Chem Soc* 1413 *1959*, 2685 *1950*.]

2-Bromo-3-methylindole (2-bromoskatole) *[1484-28-2]* **M 210.1, m 102-104°, pK_{Est} <0.** Purified by chromatography on silica gel in $CHCl_3$/pet ether (1:2) followed by crystn from aqueous EtOH. [Phillips and Cohen *J Am Chem Soc* **108** 2023 *1986*.]

4-(Bromomethyl)-7-methoxycoumarin *[35231-44-8]* **M 269.1, m 208-209°, 213-215°, 216-218°.** Cryst from boiling AcOH, crystals are washed with AcOH, EtOH and dried in a vacuum, NMR (TFA) δ 3.97s, 4.57s, 6.62s, 6.92-7.19m and 7.80d. [*Biochem Biophys Res Commun* **45** 1262 *1971*.]

2-(Bromomethyl)-naphthalene *[939-26-4]* **M 221.1, m 52-54°, 56°, 56-57°, b 133-136°/0.8mm, 214°/100mm.** Dissolve in toluene, wash with saturated aqueous $NaHCO_3$, dry ($MgSO_4$), evaporate and fractionally distil the residue and recrystallise the distillate from EtOH. [*J Chem Soc* 5044, *1952*; *Bull Soc Chim Fr* 566 *1953*.]

2-Bromo-2-methylpropane *[507-19-7]* **M 137.0, b 71-73°, d 1.218, n 1.429.** Neutralised with K_2CO_3, distd, and dehydrated using molecular sieves (5A), then vacuum distd and degassed by freeze-pump-thaw technique. Sealed under vacuum.

1-Bromonaphthalene *[90-11-9]* **M 207.1, b 118°/6mm, d 1.489.** Purified by passage through activated alumina, and three vacuum distns.

2-Bromonaphthalene *[580-13-2]* **M 207.1, m 59°.** Purified by fractional elution from a chromatographic column. Crystd from EtOH.

1-Bromo-2-naphthol *[573-97-7]* **M 223.1, m 76-78°, pK_{Est} ~8.0.** Crystd from EtOH.

6-Bromo-2-naphthol *[15231-91-1]* **M 223.1, m 122-126°, pK_{Est} ~9.1.** Crystd from EtOH.

5-Bromonicotinic acid *[20826-04-4]* **M 202.0, m 178-182°, 189-190°, pK_{Est} ~4.4, pK^{25} 4.02 (50% aq EtOH).** Recryst from H_2O and then from EtOH using charcoal. The *amide* has **m** 219-219.5° (from aq EtOH) and the *methyl ester* prepared by addition of ethereal diazomethane can be purified by sublimation in a vacuum and has **m** 98-99°, the *acid chloride* also can be sublimed in *vacuo* and has **m** 74-75° and gives the methyl ester in MeOH. [*J Prakt Chem* **138** 244 *1933*; *J Am Chem Soc* **70** 2381 *1948*; **82** 4430 *1960*; *J Chem Soc* 35 *1978*.]

ω-Bromo-4-nitroacetophenone *[99-81-0]* **M 244.1, m 98°.** Crystd from *C_6H_6-pet ether.

***o*-Bromonitrobenzene** *[577-19-5]* **M 202.1, m 43°.** Crystd twice from pet ether, using charcoal before the first crystn.

***m*-Bromonitrobenzene** *[585-79-5]* **M 202.1, m 55-56°.** Crystd twice from pet ether, using charcoal before the first crystn.

***p*-Bromonitrobenzene** *[586-78-7]* **M 202.1, m 127°.** Crystd twice from pet ether, using charcoal before the first crystn.

1-Bromooctadecane *[112-89-0]* **M 333.4, m 26°, 27.3°, 28-30°, b 178-179°/2mm, 214-218°/15mm, d^{20} 0.976, n_D^{20} 1.461.** Twice recrystd from the melt then distilled under vacuum three times and using the middle cut. Alternatively, wash the oil with aqueous Na_2SO_4, then conc H_2SO_4 (cool) and again with aqueous Na_2SO_4 and then fractionate. [*J Am Chem Soc* **55** 1574 *1933*, **72** 171 *1950*; IR: *Aust J Chem* **12** 743 *1959*; IR: *Bull Soc Chim Fr* 516 *1957*.]

(±)-2-Bromopentane *[107-81-3]* **M 151.1, b 117.2°/753mm, 116-117°/atm, 117.5°/740mm, d_4^{20} 1.2190, n_D^{20} 1.4401.** Dry over K_2CO_3 and distil through a short Vigreux column. [IR: *J Am Chem Soc* **74** 4063 *1952*, **78** 2199 *1956*.]

***p*-Bromophenacyl bromide** *[99-73-0]* **M 277.9, m 110-111°.** Crystd from EtOH (*ca* 8mL/g).

***o*-Bromophenol** *[95-56-7]* **M 173.0, b 194°, d 1.490, pK^{25} 8.45.** Purified by at least two passes through a chromatographic column.

***p*-Bromophenol** *[106-41-2]* **M 173.0, m 64°, pK^{25} 9.36.** Crystd from $CHCl_3$, CCl_4, pet ether (b 40-60°), or water and dried at 70° under vacuum for 2h.

Bromophenol Blue (3,3',5,5'-tetrabromophenolsulfonephthalein) *[115-39-9]* **M 670.0, m 270-271°(dec), 273°(dec), λmax 422max, pK 3.62.** Crystd from *benzene or acetone/glacial acetic acid, and air dried. Indicator at pH 3.0 (yellow) and pH 4.6 (purple).

(4-Bromophenoxy)acetic acid *[1878-91-7]* **M 231.1, m 158°, pK^{25} 3.13.** Crystd from EtOH.

3-(4-Bromophenoxy)propionic acid *[93670-18-9]* **M 247.1, m 146°, pK_{Est} ~4.2.** Crystd from EtOH.

4-Bromophenylacetic acid *[1878-68-8]* **M 215.1, m 112-113°, 113-115°, 114°, pK 4.19.** Recrystd from H_2O as needles. The *acid chloride* has **b** 238°/atm, **m** 50°, and the *anilide* has **m** 174-175°. [*J Chem Soc* 161 *1934, 1251* 1948; *J Org Chem* **11** 798 *1946*.]

4-Bromophenylhydrazine *[589-21-9]* **M 187.1, m 108-109°, pK^{20} -5.6 (aq H_2SO_4), pK^{25} 5.05.** Crystd from H_2O.

4-Bromophenyl isocyanate *[2492-02-9]* **M 189.0, m 41-42°.** Crystd from pet ether (b 30-40°).

4-Bromophenyl isothiocyanate *[1985-12-2]* **M 214.1, m 56-58°.** Recryst from boiling *n*-hexane. Any insoluble material is most probably the corresponding urea. It can be purified by steam distn, cool the receiver, add NaCl and extract in Et_2O, wash extract with N H_2SO_4; dry ($MgSO_4$), evaporate and recrystallise the residual solid. [*Org Synth* Coll Vol IV 700 *1963*; Coll Vol I 447 *1941*.]

Bromopicrin (tribromonitromethane) *[464-10-8]* **M 297.8, m 10.2-10.3°, b 85-87°/16mm, d 2.788, n 1.579.** Steam distd, dried with anhydrous Na_2SO_4 and vacuum distd. **TOXIC.**

***R*-(+)-2-Bromopropionic acid** *[10009-70-8]* **M 153.0, b 78°/4mm, $[\alpha]_D^{25}$ +27.2° (neat), pK^{25}4.07.** Dissolve in Et_2O, dry ($CaCl_2$), evap and distil through a short column. Distillation through a Podbielniak column led to decomposition. **[Podbielniak column.** A plain tube containing "Heli-Grid" Nichrome or Inconel wire packing. This packing provides a number of passage-ways for the reflux liquid, while the capillary spaces ensure very even spreading of the liquid, so that there is a very large area of contact between liquid and vapour while, at the same time, channelling and flooding are minimised. A column 1m high has been stated to have an efficiency of 200-400 theoretical plates (for further details, see Podbielniak *Ind Eng Chem (Anal Ed)* **13** 639 *1941*; Mitchell and O'Gorman *Anal Chem* **20** 315 *1948*)]. Store in the dark under N_2, preferably in sealed ampoules. Even at -10° it slowly decomposes. [*J Am Chem Soc* **76** 6054 *1954*.]

3-Bromopropionic acid *[590-92-1]* **M 153.0, m 62.5°, 62.5-63.5°, 63-64°.** Crystallises as plates from CCl_4. It is soluble in organic solvents and H_2O. It has a pKa^{25} in H_2O of 4.01, and its *methyl ester* has **b** 65°/18mm and 80°/27mm. The *S-benzylisothiouronium salt* has **m** 136°. [*Org Synth* Coll Vol I 134 *1948*; *Justus Liebigs Ann Chem* **599** 140 *1956*.]

***N*-(3-Bromopropyl)phthalimide** *[5460-29-7]* **M 268.1, m 72-74°, 74°.** Place in a Soxhlet and extract with Et_2O, whereby the bis-phthalimido impurity is not extracted. Evaporate the Et_2O and recryst from EtOH or aqueous EtOH or pet ether. [*Chem Ber* **21** 2669 1888; *Justus Liebigs Ann Chem* **614** 83 *1958*; *Can J Chem* **31** 1060 *1953*.]

2-Bromopyridine *[109-04-6]* **M 158.0, b 49.0°/2.7mm, d 1.660, n 1.5713, pK^{25} 0.90.** Dried over KOH for several days, then distd from CaO under reduced pressure, taking the middle fraction.

Bromopyrogallol Red (5,5'-dibromopyrogallolsulfonephthalein) *[16574-43-9]* **M 576.2, m 300°, λmax 538nm (ε 54,500 H_2O pH 5.6-7.5), pK_1 2.9, pK_2 4.39, pK_3 9.15, pK_4 11.72.** Crystd from 50% EtOH, or aq alkaline soln by acid [Suk *Collect Czech Chem Commun* **31** 3127 *1966*].

Bromopyruvic acid *[1113-59-3]* **M 167.0, m 79-82°, pK_{Est} ~1.6.** Dried by azeotropic distn (toluene), and then recrystd from dry $CHCl_3$. Dried for 48h at 20° (0.5 Torr) over P_2O_5. Stored at 0°. [Labandiniere et al. *J Org Chem* **52** 157 *1987*].

5-Bromosalicyl hydroxamic acid *[5798-94-7]* **M 210.1, m 232°(dec), $pK_{Est(1)}$~ 1.5, $pK_{Est(2)}$~ 7.0, $pK_{Est(3)}$~ 8.7.** Crystd from EtOH.

4-Bromostyrene *[2039-82-9]* **M 183.1, b 49.5-50°/2.5mm, 87-88°/12mm, 102-104°/20mm, d 1.3984, n 1.5925.** It polymerises above 75° in the presence of benzoyl peroxide. To purify, if it has not gone to a solid resin, dissolve in Et_2O, dry ($MgSO_4$), add *ca* 0.1g of 4-*tert*butylcatechol (polymerisation inhibitor) per 100g of bromostyrene. Filter, evap under reduced press (use as high a vac as possible) and distil. Store in dark bottles in the presence of the inhibitor (concn as above). [*Org Synth* Coll Vol III 204 *1955.*]

***N*-Bromosuccinimide** *[128-08-5]* **M 178.0, m 183-184°(dec).** *N*-Bromosuccinimide (30g) was dissolved rapidly in 300mL of boiling water and filtered through a fluted filter paper into a flask immersed in an ice bath, and left for 2h. The crystals were filtered, washed thoroughly with *ca* 100mL of ice-cold water and drained on a Büchner funnel before drying under vac over P_2O_5 or $CaCl_2$ [Dauben and McCoy *J Am Chem Soc* **81** 4863 *1959*]. Has also been crystd from acetic acid or water (10 parts, washed in water and dried *in vacuo*, [Wilcox et al. *J Am Chem Soc* **108** 7693 *1986;* Shell et al. *J Am Chem Soc* **108** 121 *1986*; Phillips and Cohen *J Am Chem Soc* **108** 2013 *1986.*]

Bromotetronic acid *[21151-51-9]* **M 179.0, m 183°(dec), pK^{25} 2.23.** Decolorised, and free bromine was removed by charcoal treatment of an ethyl acetate soln, then recrystd from ethyl acetate [Schuler, Bhatia and Schuler *J Phys Chem* **78** 1063 *1974*].

Bromotheophylline *[10381-75-6]* **M 259.1, m 309°, 315-320° (with browning and dec), $pK_{Est(1)}$~5.5, $pK_{Est(2)}$ ~9.2.** It is purified by dissolving in the minimum volume of dilute NaOH (charcoal), filter and acidify to pH *ca* 3.5-4 and the solid that separates is collected, dried *in vacuo* at 100° and stored in a dark container. [*J Prakt Chem* [2] **118** 158 *1928*; *Chem Ber* **28** 3142 *1895.*]

Bromothymol Blue (3',3"-dibromothymolsulfonephthalein) *[76-59-5]* **M 624.4, m 201-203°, pK_1 -0.66, pK_2 6.99.** Dissolved in aq 5% $NaHCO_3$ soln and ppted from the hot soln by dropwise addn of aq HCl. Repeated until the extinction did not increase (λ_{max} 420nm). Indicator at pH 6.0 (yellow) and 7.6 (blue).

***p*-Bromotoluene** *[106-38-7]* **M 171.0, m 28°, b 184°, d 1.390.** Crystd from EtOH [Taylor and Stewart *J Am Chem Soc* **108** 6977 *1986*].

α-Bromo-4-toluic acid *[6232-88-8]* **M 215.1, m 229-230°, pK_{Est} ~3.2.** Crystd from Me_2CO.

Bromotrichloromethane *[75-62-7]* **M 198.5, f -5.6°, m 21°, b 104.1°, d 2.01, n 1.5061.** Washed with aq NaOH soln or dilute Na_2CO_3, then with H_2O, and dried with $CaCl_2$, BaO, $MgSO_4$ or P_2O_5 before distilling in diffuse light and storing in the dark. Has also been purified by treatment with charcoal and by fractional crystn by partial freezing. Purified also by vigorous stirring with portions of conc H_2SO_4 until the acid did not discolour during several hours stirring. Washed with Na_2CO_3 and water, dried with $CaCl_2$ and then illuminated with a 1000W projection lamp at 15cm for 10h, after making it 0.01M in bromine. Passed through a 30 x 1.5cm column of activated alumina and fractionally redistilling through a 12-in Vigreux column. [Firestone and Willard *J Am Chem Soc* **83** 3511 *1961*; see also Cadogan and Duell *J Chem Soc* 4154 *1962.*]

1-Bromo-3,3,3-trifluoroethane *[421-06-7]* **M 163.0, m -94°, b 26-27°, d 1.788, n 1.332.** Washed with water, dried ($CaCl_2$) and distd.

Bromotrifluoromethane (Freon 13B1) *[75-63-8]* **M 148.9, b -59°, d 1.590.** Passed through a tube containing P_2O_5 on glass wool into a vac system where it was frozen out in a quartz sample tube and degassed by a series of cycles of freezing, evacuating and thawing.

5-Bromouracil *[51-20-7]* **M 191.0, m 293°, 303-305°, 312°(dec), pK_1^{25} -7.25, pK_2^{25} 7.83.** Purified by dissolving in 2N NaOH (charcoal), filter and acidify with HCl. The ppte is dried *in vacuo* at 100° and recryst (prisms) twice from H_2O. [*J Am Chem Soc* **56** 134 *1934*, UV: *J Am Chem Soc* **81** 3786 *1959*; *J Org Chem* **23** 1377 *1958.*]

5-Bromovaleric (γ–bromopentanoic) acid *[2067-33-6]* **M 181.0, m 40°, pK_{Est} ~4.6.** Crystd from pet ether.

α-Bromo-*p*-xylene *[104-81-4]* **M 185.1, m 35°, b 218-220°/740mm.** Crystd from EtOH or pentane.

Bromural [*N*-(aminocarbonyl)-2-bromo-3-methylbutanamide, bromisovalum] *[496-67-3]* **M 223.1, m 154-155°.** Crystd from toluene, and air dried.

Bufotenine hydrogen oxalate *[2963-79-3]* **M 294.3, m 96.5°.** Crystd from Et_2O.

1,3-Butadiene *[106-99-0]* **M 54.1, b -2.6°.** Dried by condensing with a soln of triethylaluminium in decahydronaphthalene; then flash distd. Also dried by passage over anhydrous $CaCl_2$ or distd from $NaBH_4$. Also purified by passage through a column packed with molecular sieves (4A), followed by cooling in Dry-ice/MeOH bath overnight, filtering off the ice and drying over CaH_2 at -78° and distd in a vacuum line.

***n*-Butane** *[106-97-8]* **M 58.1, m -135°, b -0.5°.** Dried by passage over anhydrous $Mg(ClO_4)_2$ and molecular sieves type 4A. Air was removed by prolonged and frequent degassing at -107°.

1,4-Butanediol (tetramethylene glycol) *[110-63-4]* **M 90.1, f 20.4°, b 107-108°/4mm, 127°/20mm, d 1.02, n 1.4467.** Distd and stored over Linde type 4A molecular sieves, or crystd twice from anhydrous diethyl ether/acetone, and redistd. Also purified by recrystn from the melt and doubly distd *in vacuo* in the presence of Na_2SO_4.

***meso*-2,3-Butanediol** *[513-85-9]* **M 90.1, m 25°.** Crystd from isopropyl ether.

***threo*-2,3-butanediol** *[R,R(-): 24347-58-8] [S,S (+):19132-06-0]* **M 90.1, m 16-19°, 19.7°, b 77,5-78°/10mm, 179-180°/atm, $[\alpha]_D^{20}$ (-) or (+) 13.1° (neat).** Purified by fractional distn. The *bis-(4-nitrobenzoate)* has **m** 141-142° and $[\alpha]_D^{25}$± 52° (c 4 $CHCl_3$). [*J Am Chem Soc* **79** 734 *1957*, **74** 425 *1952*, *Can J Res* **27** 457 *1949*.]

1-Butanesulfonyl chloride *[2386-60-9]* **M 156.6, b 75-76°/7mm, 98°/13mm, d_4^{20}1.2078, n_D^{20} 1.4559**. It has a pungent odour and is **LACHRYMATORY.** If IR shows OH bands then dissolve in Et_2O, wash with cold saturated aq $NaHCO_3$ (care since CO_2 will be generated) then H_2O, dry over solid Na_2SO_4, filter evaporate and distil the residue twice. Characterised by shaking a soln in Et_2O or *C_6H_6 with aq NH_3, collect the solid and recryst from $CHCl_3$, CCl_4 or Et_2O-pet ether, **m** 48°. [*J Am Chem Soc* **60** 1488 *1938*; *J Org Chem* **5** 83 *1940*.]

1-Butanethiol *[109-79-5]* **M 90.2, b 98.4°, d^{25} 0.837, n 1.443, n^{25} 1.440, pK_{Est} ~11.3.** Dried with $CaSO_4$ or Na_2SO_4, then refluxed from magnesium; or dried with, and distd from CaO, under nitrogen [Roberts and Friend *J Am Chem Soc* **108** 7204 *1986*.] Has been separated from hydrocarbons by extractive distn with aniline.
Dissolved in 20% NaOH, extracted with a small amount of *C_6H_6, then steam distd, until clear. The soln was then cooled and acidified slightly with 15% H_2SO_4. The thiol was distd out, dried with $CaSO_4$ or $CaCl_2$, and fractionally distd under N_2 [Mathias and Filho *J Phys Chem* **62** 1427 *1958*]. Also purified by pptn as lead mercaptide from alcoholic soln, with regeneration by adding dilute HCl to the residue after steam distn. *All operations should be carried out in a fume cupboard due to the* **TOXICITY** *and obnoxious odour of the thiol.*

2-Butanethiol *[513-53-1]* **M 90.2, b 37.4°/134mm, d^{25} 0.846, n^{25} 1.4338, pK_{Est} ~11.4.** Purified as for 1-butanethiol.

***n*-Butanol** *[71-36-3]* **M 74.1, b 117.7°, d^{25} 0.80572, n 1.39922, n^{15} 1.40118.** Dried with $MgSO_4$, CaO, K_2CO_3, Ca or solid NaOH, followed by refluxing with, and distn from, calcium, magnesium activated with iodine, aluminium amalgam or sodium. Can also dry with molecular sieves, or by refluxing with *n*-butyl phthalate or succinate. (For method, see *Ethanol.*) *n*-Butanol can also be dried by efficient fractional distn, water passing over in the first fractn as a binary azeotrope (contains about 37% water). An ultraviolet-

transparent distillate has been obtained by drying with magnesium amd distilling from sulfanilic acid. To remove bases, aldehydes and ketones, the alcohol has been washed with dil H_2SO_4, then $NaHSO_4$ soln; esters were removed by boiling for 1.5h with 10% NaOH.
Also purified by adding 2g $NaBH_4$ to 1.5L butanol, gently bubbling with argon and refluxing for 1 day at 50°. Then added 2g of freshly cut sodium (washed with butanol) and refluxed for 1 day. Distd and the middle fraction collected [Jou and Freeman *J Phys Chem* **81** 909 *1977*].

2-Butanone (methyl ethyl ketone, MEK) *[78-93-0]* **M 72.1, b 79.6°, d 0.853, n 1.37850, n^{25} 1.37612, pK^{25} -7.2 (aq H_2SO_4).** In general, purification methods are the same as for acetone. Aldehydes can be removed by refluxing with $KMnO_4$ + CaO, until the Schiff aldehyde test is negative, prior to distn. Shaking with satd K_2CO_3, or passage through a small column of activated alumina, removes cyclic impurities. The ketone can be dried by careful distn (an azeotrope containing 11% water boils at 73.4°), or by $CaSO_4$, P_2O_5, Na_2SO_4, or K_2CO_3, followed by fractional distn. Purification as the bisulfite addition compound is achieved by shaking with excess satd Na_2SO_3, cooled to 0°, filtering off the ppte, washing with a little ethyl ether and drying in air; this is followed by decomposition with a slight excess of Na_2CO_3 soln and steam distn, the distillate being satd with K_2CO_3 so that the ketone can be separated, dried with K_2CO_3, filtered, and distd. Purification as the *NaI addition compound* (**m** 73-74°) is more convenient. (For details, see *Acetone*.) Small quantities of 2-butanone can be purified by conversion to the semicarbazone, recrystn to constant melting point, drying under vac over $CaCl_2$ and paraffin wax, refluxing for 30min with excess oxalic acid, followed by steam distn, salting out, drying and distilling [Cowan, Jeffery and Vogel *J Chem Soc* 171 *1940*].

***cis*-2-Butene** *[590-18-1]* **M 56.1, b 2.95-3.05°/746mm.** The gas is dried with CaH_2. Purified by gas chromatography. **HIGHLY FLAMMABLE.**

***trans*-2-Butene** *[624-64-6]* **M 56.1, b 0.3-0.4°/744mm.** The gas is dried with CaH_2. Purified by gas chromatography. **HIGHLY FLAMMABLE.**

2-Butene-1,4-dicarboxylic acid (*trans*-3-hexenedioic acid, *trans*-ß-hydromuconic acid) *[4436-74-2]* **M 144.1, m 194-197°, 195-196°, $pK_{Est(1)}$~4.2, $pK_{Est(2)}$ ~5.00.** Crystd from boiling water, then dried at 50-60° in a vacuum oven.

But-3-en-2-one (methyl vinyl ketone) *[78-94-4]* **M 70.1, b 79-80°/760mm, d 0.842.** See entry on p.302.

2-*tert*-Butoxycarbonyloxyimino-2-phenylacetonitrile (BOC-ON) *[58632-95-4]* **M 246.3, m 87-89°.** Triturate solid with 90% aq MeOH, filter, wash with 90% aq MeOH and dry in a vac. Recryst from MeOH (needles or plates), but use warm MeOH and cool to cryst, *do not boil as it decomposes slowly.* IR has ν 1785 (C=O) cm^{-1} and NMR ($CDCl_3$) usually shows two *tert*-butyl singlets for *syn* and *anti* isomers. Store in a brown bottle (fridge). It evolves CO_2 at room temp (stoppered bottle can explode!), but can be stored over silica gel which can extend its useful life to more than a year. [Itoh et al. *Org Synth* **59** 95 *1980*.]

2-Butoxyethanol (butyl cellosolve) *[111-76-2]* **M 118.2, b 171°/745mm, d 0.903, n 1.4191.** Peroxides can be removed by refluxing with anhydrous $SnCl_2$ or by passage under slight pressure through a column of activated alumina. Dried with anhydrous K_2CO_3 and $CaSO_4$, filtered and distd, or refluxed with, and distd from NaOH.

4-Butoxyphenylacetic acid *[4547-57-3]* **M 208.3, m 86-87°, 88.5°, pK_{Est} ~4.4.** Purified by recrystn from pet ether (b 40-60°). [*J Am Chem Soc* **68** 2592 *1946*.]

***n*-Butyl acetate** *[123-86-4]* **M 116.2, b 126.1°, d 0.882, n 1.394.** Distd, refluxed with successive small portions of $KMnO_4$ until the colour persisted, dried with anhydrous $CaSO_4$, filtered and redistd.

***tert*-Butyl acetate** *[540-88-5]* **M 116.2, b 97-98°, d 0.72.** Washed with 5% Na_2CO_3 soln, then saturated aqueous $CaCl_2$, dried with $CaSO_4$ and distd.

***tert*-Butyl acetoacetate** *[1694-31-1]* **M 158.2, b 71°/10mm, 85°/20mm, d_4^{20} 0.954, n_4^{20} 1.42.** Dist under reduced press through a short column. [*Org Synth* **42** 28 *1962*.] **HARMFUL VAPOUR.**

***tert*-Butylacetylchloride** *[7065-46-5]* **M 134.6, b 68-71°/100mm, 81°/180mm, 128-132°/atm, d_4^{20} 0.964, n_D^{20} 1.423.** Distil under vacuum. If IR shows OH group then treat with thionyl chloride or oxalyl chloride at *ca* 50° for 30min, evap and fractionate using a short column. Strongly **LACHRYMATORY**, use a good fume hood. [*J Am Chem Soc* **72** 222 *1950*; *J Org Chem* **22** 1551 *1957*.]

Butyl acrylate *[141-32-2]* **M 128.2, b 59°/25mm, d 0.894, n^{12} 1.4254.** Washed repeatedly with aqueous NaOH to remove inhibitors such as hydroquinone, then with distilled water. Dried with $CaCl_2$. Fractionally distd under reduced pressure in an all-glass apparatus. The middle fraction was sealed under nitrogen and stored at 0° in the dark until used [Mallik and Das *J Am Chem Soc* **82** 4269 *1960*].

(±)-*sec*-Butyl alcohol *[15892-23-6]* **M 74.1, b 99.4°, d 0.808.** Purification methods are the same as for *n*-Butanol. These include drying with K_2CO_3 or $CaSO_4$, followed by filtration and fractional distn, refluxing with CaO, distn, then refluxing with magnesium and redistn; and refluxing with, then distn from CaH_2. Calcium carbide has also been used as a drying agent. Anhydrous alcohol is obtained by refluxing with *sec*-butyl phthalate or succinate. (For method see *Ethanol*.) Small amounts of alcohol can be purified by conversion to the alkyl hydrogen phthalate and recrystn [Hargreaves, *J Chem Soc* 3679 *1956*]. For purification of optical isomers, see Timmermans and Martin [*J Chem Phys* **25** 411 *1928*].

***tert*-Butyl alcohol** *[75-65-0]* **M 74.1, m 23-25°, 25.7°, b 28.3°/60mm, 43.3°/123.8mm, 61.8°/315mm, 72.5°/507mm, 82.45°/760mm, d_4^{20} 0.7858, n_D^{20} 1.3878.** Synthesised commercially by the hydration of 2-methylpropene in dilute H_2SO_4. Dried with CaO, K_2CO_3, $CaSO_4$ or $MgSO_4$, filtered and fractionally distd. Dried further by refluxing with, and distilling from, either magnesium activated with iodine, or small amounts of calcium, sodium or potassium, under nitrogen. Passage through a column of type 4A molecular sieve is another effective method of drying. So, also, refluxing with *tert*-butyl phthalate or succinate. (For method see *Ethanol*.) Other methods include refluxing with excess aluminium *tert*-butylate, or standing with CaH_2, and distilling as needed. Further purification is achieved by fractional crystn by partial freezing, taking care to exclude moisture. *tert*-Butyl alcohol samples containing much water can be dried by adding *benzene, so that the water distils off as a tertiary azeotrope, b 67.3°. Traces of isobutylene have been removed from dry *tert*-butyl alcohol by bubbling dry pre-purified nitrogen through for several hours at 40-50° before using. It form azeotropic mixtures with a large number of compounds. It has also been purified by distn from CaH_2 into Linde 4A molecular sieves which had been activated at 350° for 24h [Jaeger et al. *J Am Chem Soc* **101** 717 *1979*].
Rapid purification: Dry *tert*-butanol with CaH_2 (5% w/v), distil and store over 3A molecular sieves.

***n*-Butylamine** *[109-73-9]* **M 73.1, b 77.8°, d 0.740, n 1.4009, n^{25} 1.399, pK^{25} 10.66.** Dried with solid KOH, K_2CO_3, $LiAlH_4$, CaH_2 or $MgSO_4$, then refluxed with, and fractionally distd from P_2O_5, CaH_2, CaO or BaO. Further purified by pptn as the *hydrochloride*, **m** 213-213.5°, from ether soln by bubbling HCl gas into it. Re-ppted three times from EtOH by adding ether, followed by liberation of the free amine using excess strong base. The amine was extracted into ether, which was separated, dried with solid KOH, the ether removed by evapn and then the amine was distd. It was stored in a desiccator over solid NaOH [Bunnett and Davis *J Am Chem Soc* **82** 665 *1960*; Lycan et al. *Org Synth* Coll Vol II 319 *1943*]. **SKIN IRRITANT.**

***R*-(-)-*sec*-Butylamine** *[13250-12-9]* **M 73.1, b 61-63°/atm, 62.5°/atm, d_4^{20} 0.731, n_D^{20} 1.393, $[\alpha]_D^{20}$ +7.5° (neat), pK 10.56.** Dry over solid NaOH overnight and fractionate through a short helices packed column. The L-*hydrogen tartrate salt* has **m** 139-140° (from H_2O), the *1H_2O* has **m** 96° $[\alpha]_D^{21}$ +18.1° (c 11, H_2O); the *hydrochloride* has **m** 152° $[\alpha]_D^{21}$ -1.1° (c 13, H_2O) and the *benzoyl derivative* crystallises from EtOH as needles **m** 97°, $[\alpha]_D^{21}$ -34.9° (c 11, H_2O). [*J Chem Soc* 921 *1956*; *Acta Chem Scand* **11** 898 *1957*.]

***tert*-Butylamine** *[75-64-9]* **M 73.1, b 42°, d 0.696, pK 10.68.** Dried with KOH or $LiAlH_4$. Distd from CaH_2 or BaO.

***n*-Butyl *p*-aminobenzoate** *[94-25-7]* **M 193.2, m 57-59°, pK_{Est} ~2.5.** Crystd from EtOH.

***tert*-Butylammonium bromide** *[60469-70-7]* **M 154.1, m >250°(dec).** Recrystd several times from absolute EtOH and thoroughly dried at 105°.

4-*tert*-Butylaniline *[769-92-6]* **M 149.2, m 14.5-15°, 15-16°, b 98.5-99°/3mm, 122°/20mm, d_4^{20} 0.945, n_D^{20} 1.538, pK^{25} 4.95.** Isolate as sulfate salt then liberate the free base with 10% aqueous NaOH, separate layers, dry over solid KOH and dist twice from Zn dust in a vacuum and store in brown containers. It has pKa^{25} (H_2O) 4.95 and (50% aq EtOH) 4.62. [*J Am Chem Soc* **76** 2349 *1954*.] The *anilide* has **m** 171.5-172.3°, and the *hydrochloride* has **m** 270-274°. [*J Chem Soc* 680 *1952*; *J Am Chem Soc* **76** 6179 *1954*.]

2-*tert*-Butylanthracene *[13719-97-6]* **M 234.3, m 148-149°.** Recrystd from EtOH and finally purified by TLC.

***n*-Butylbenzene** *[104-51-8]* **M 134.2, b 183.3°, d 0.860, n 1.4897, n^{25} 1.487.** Distd from sodium. Washed with small portions of conc H_2SO_4 until the acid was no longer coloured, then with water and aqueous Na_2CO_3. Dried with anhydrous $MgSO_4$, and distd twice from Na, collecting the middle fraction [Vogel *J Chem Soc* 607 *1948*].

***tert*-Butylbenzene** *[98-06-6]* **M 134.2, b 169.1°, d 0.867, n 1.493, n^{25} 1.490.** Washed with cold conc H_2SO_4 until a fresh portion of acid was no longer coloured, then with 10% aqueous NaOH, followed by distd water until neutral. Dried with $CaSO_4$ and distd in a glass helices-packed column, taking the middle fraction.

4-*tert*-Butyl benzoyl chloride *[1710-98-1]* **M 196.7, b 135°/10mm, 149.9-150.5°/14mm, 266-268°(dec), d_4^{20} 1.082, n_D^{20} 1.536.** Distil under vac. If IR shows OH group then treat with thionyl chloride or oxalyl chloride at *ca* 50° for 30min, evap and fractionate in a vac using a short column. Strongly **LACHRYMATORY**, use a good fume hood. [*Bull Chem Soc Jpn* **32** 960 *1959*; *J Am Chem Soc* **72** 5433 *1950*.]

***n*-Butyl bromide** *[109-65-9]* **M 137.0, b 101-102°, d^{25} 1.2678, n 1.4399, n^{25} 1.4374.** Washed with conc H_2SO_4, water, 10% Na_2CO_3 and again with H_2O. Dried with $CaCl_2$, $CaSO_4$ or K_2CO_3, and distd. Redistd after drying with P_2O_5, or passed through two columns containing 5:1 silica gel/Celite mixture and stored with freshly activated alumina.

***tert*-Butyl bromoacetate** *[5292-43-3]* **M 195.1, b 52°/10mm, 74-76°/25mm, d_4^{20} 1.324, n_D^{25} 1.4162.** Dissolve in Et_2O, wash well with ice cold 10% aqueous K_2CO_3, dry over $CaCl_2$, filter and evaporate the Et_2O then fractionate through a Vigreux column in a vacuum. **LACHRYMATORY** [*Org Synth* **34** 28 *1954*, Coll Vol III 144 *1955*; *J Am Chem Soc* **64** 2274 *1942*, **65** 986 *1943*.]

4-*tert*-Butylcalix[4]arene *[60705-62-6]* **M 648.9, m >300° (dec), 380° (dec), 344-346°.** Recrystd from $CHCl_3$ in large solvated prisms (**m** 380° dec) effloresces on drying in air; *tetra-acetate* crysts from Ac_2O in colourless prisms **m** 332-333° dec. Crysts from CCl_4 or chlorobenzene + EtOH (**m** >300°) and *tetra-acetate* cryst from $CHCl_3$ + EtOH **m** >290° dec. Crysts from toluene in white plates with toluene of crystallisation **m** 344-346° (330-332°); the *tetra-acetate* crystallises with 1AcOH of crystallisation **m** 383-386° (softening at 330-340°, also **m** 283-286°), but acetylation with Ac_2O-NaOAc gives *triacetate* which recrysts from AcOH with 1AcOH of crystn **m** 278-281°. 4-*tert*-Butylcalix[4]arene (100mg) is unchanged after boiling for 4h with 10N KOH (0.04mL) in xylene (4mL). [*Br J Pharmacol* **10** 73 *1955*; *Monatsh Chem* **109** 767 *1978*; *J Am Chem Soc* **103** 3782 *1981*; see also J.Vicens and V.Böhner eds,*Calixarenes*, Kluawer Academic Publ., Boston, 1991.]

4-*tert*-Butylcalix[6]arene *[78092-53-2]* **M 972.3, m >300°, 380-381°.** Recryst from $CHCl_3$ or $CHCl_3$ - MeOH as a white solid from the mother liquors of the calix[8]arene preparation. The *hexa-acetate* (Ac_2O-H_2SO_4) crystallises from $CHCl_3$-MeOH **m** 360-362° dec, and the $(SiMe_3)_6$ derivative crystallises from

$CHCl_3$-MeOH **m** 410-412°. Stability in KOH-xylene is same as for the 4-*tert*-butylcalix[4]arene. [*J Am Chem Soc* **103** 3782 *1981*; see also J.Vicens and V.Böhner eds,*Calixarenes*, Kluawer Academic Publ., Boston, 1991.]

4-*tert*-Butylcalix[8]arene *[68971-82-4]* **M 1297.8, m 411-412°.** Recryst from $CHCl_3$ in fine colourless glistening needles. It melts sharply between 400-401° and 411-412° depending on the sample and is sensitive to traces of metal ions. TLC on silica gel (250μm thick) and elution with $CHCl_3$-hexane (3:4); it has R_F 0.75. The *octa-acetate* is prepared from 8g in Ac_2O (50mL) and 2 drops of conc H_2SO_4 refluxed for 2h. On cooling a colourless ppte separates and is recrystd from Ac_2O (1.2g 48%) **m** 353-354°. The $(SiMe_3)_8$ is prepared from 4-*tert*-butylcalix[8]arene (0.65g) in pyridine (4mL) with excess of hexamethyldisilazane (1mL) and trimethylchlorosilane (0.5mL) and refluxed under N_2 for 2h. Cool, evaporate the pyridine, triturate gummy residue with MeOH. Chromatography on silica gel using hexane-CH_2Cl_2 gave 0.5g (61%) with one spot on TLC. Crystallises from hexane-Me_2CO as colourless needles **m** 358-360°. [*J Am Chem Soc* **103** 3782 *1981*; *J Org Chem* **43** 4905 1978; **44** 3962 *1979*; *J Chem Soc, Chem Commun* 533 *1981*; see also J.Vicens and V.Böhner eds,*Calixarenes*, Kluawer Academic Publ., Boston, 1991.]

***tert*-Butyl carbazate** *[870-46-2]* **M 132.2, m 41-42°, b 64°/0.01mm, 55-57°/0.4mm.** Dist in a Claisen flask with a water or oil bath at *ca* 80°. After a couple of drops have distd the carbazate is collected as an oil which solidifies to a snow white solid. It can be crystd with 90% recovery from a 1:1 mixt of pet ether (b 30-60°) and pet ether (b 60-70°). [*Org Synth* **44** 20 *1964*.]

4-*tert*-Butylcatchol *[98-29-3]* **M 166.22, m 47-48°, 55-56°, 75°, b 265°/atm, $pK_{Est(1)}$~9.5, $pK_{Est(2)}$ ~13.0.** Vacuum distd and recrystd from pentane or pet ether (or $*C_6H_6$).

***n*-Butyl chloride** *[109-69-3]* **M 92.6, b 78°, d 0.886, n 1.4021.** Shaken repeatedly with conc H_2SO_4 (until no further colour developed in the acid), then washed with water, aq $NaHCO_3$ or Na_2CO_3, and more water. Dried with $CaCl_2$, or $MgSO_4$ (then with P_2O_5 if desired), decanted and fractionally distd. Alternatively, a stream of oxygen continuing *ca* three times as long as was necessary to obtain the first coloration of starch iodide paper by the exit gas. After washing with $NaHCO_3$ soln to hydrolyze ozonides and to remove the resulting organic acid, the liquid was dried and distd [Chien and Willard *J Am Chem Soc* **75** 6160 *1953*].

***tert*-Butyl chloride** *[507-20-0]* **M 92.6, f -24.6°, b 50.4°, d 0.851, n 1.38564.** Purification methods commonly used for other alkyl halides lead to decomposition. Some impurities can be removed by photochlorination with a small amount of chlorine prior to use. The liquid can be washed with ice water, dried with $CaCl_2$ or $CaCl_2$ + CaO and fractionally distd. It has been further purified by repeated fractional crystn by partial freezing.

***tert*-Butyl chloroacetate** *[107-59-5]* **M 150.6, b 48-49°/11mm, 60.2°/15mm, 155°/atm (dec), d_4^{25} 1.4204, n_D^{20} 1.4259.** Check the NMR spectrum, if satisfactory then dist in a vac, if not then dissolve in Et_2O, wash with H_2O, 10% H_2SO_4 until the acid extract does not become cloudy when made alkaline with NaOH. Wash the organic layer again with H_2O, then satd aq $NaHCO_3$, dry over Na_2SO_4, evap and fractionate through a carborundum-packed column or a 6-inch Widmer column (*see tert-butyl ethyl malonate for precautions to avoid decomposition during distn*). [*J Chem Soc* 940 *1940*; *J Am Chem Soc* **75** 4995 *1953*; *Org Synth* Coll Vol 144 *1944*.]

6-*tert*-Butyl-1-chloro-2-naphthol *[525-27-9]* **M 232.7, m 76°, b 185°/15mm, pK_{Est} ~8.0.** Crystd from pet ether.

***tert*-Butyl cyanide (trimethylacetonitrile)** *[630-18-2]* **M 83.1, m 16-18°, d 0.765, b 104-106°.** Purified by a two stage vac distn and degassed by freeze-pump-thaw technique. Stored under vac at 0°. **TOXIC,** use efficient fume hood.

***tert*-Butyl cyanoacetate** *[1116-98-9]* **M 141.2, b 40-42°/0.1mm, 54-56°/0.3mm, 90°/10mm, 107-108°/23mm, d_4^{20} 0.989, n_D^{20}1.4198.** The IR spectrum of a film should have bands at 1742 (ester

CO) and 2273 (C≡N) but not OH band (*ca* 3500 broad) cm^{-1}. If it does not have the last named band then fractionally dist, otherwise dissolve in Et_2O, wash with satd aq $NaHCO_3$, dry over K_2CO_3, evap Et_2O, and dist residue under a vacuum (*see tert-butyl ethyl malonate for precautions to avoid decomposition during distn*). [*J Chem Soc* 423 *1955*; *Helv Chim Acta* **42** 1214 *1959*].

4-*tert*-Butyl-1-cyclohexanone *[98-53-3]* **M 154.3, m 49-50°.** Crystd from pentane.

***n*-Butyl disulfide** *[629-45-8]* **M 178.4, b 110-113°/15mm, d 0.938, n^{22} 1.494.** Shaken with lead peroxide, filtered and distd in vacuum under N_2.

***n*-Butyl ether (di-*n*-butyl ether)** *[142-96-1]* **M 130.2, b 52-53°/26mm, 142.0°/760mm, d 0.764, n 1.39925, n^{25} 1.39685, pK^{25} -5.40 (aq H_2SO_4).** Peroxides (detected by the liberation of iodine from weakly acid (HCl) solns of 2% KI) can be removed by shaking 1L of ether with 5-10mL of a soln comprising 6.0g of ferrous sulfate and 6mL conc H_2SO_4 and 110mL of water, with aq Na_2SO_3, or with acidified NaI, water, then $Na_2S_2O_3$. After washing with dil NaOH, KOH, or Na_2CO_3, then water, the ether is dried with $CaCl_2$ and distd. It can be further dried by distn from CaH_2 or Na (after drying with P_2O_5), and stored in the dark with Na or NaH. The ether can also be purified by treating with CS_2 and NaOH, expelling the excess sulfide by heating. The ether is then washed with water, dried with NaOH and distd [Kusama and Koike *J Chem Soc Japan, Pure Chem Sect* **72** 229 *1951*]. Other purification procedures include passage through an activated alumina column to remove peroxides, or through a column of silica gel, and distn after adding about 3% (v/v) of a 1M soln of MeMgI in *n*-butyl ether.

***n*-Butyl ethyl ether** *[628-81-9]* **M 102.2, b 92.7°, d 0.751, n 1.38175, n^{25} 1.3800.** Purified by drying with $CaSO_4$, by passage through a column of activated alumina (to remove peroxides), followed by prolonged refluxing with Na and then fractional distn.

***tert*-Butyl ethyl ether** *[637-92-3]* **M 102.2, b 71-72°, d 0.741.** Dried with $CaSO_4$, passed through an alumina column, and fractionally distd.

***tert*-Butyl ethyl malonate** *[32864-38-3]* **M 188.2, b 83-85°/8mm, 93-95°/17mm, 107-109°/24mm, d_4^{25} 0.994, n_D^{24} 1.4150.** Likely impurity is monoethyl malonate, check IR for OH bands at 3330 br. To *ca* 50g of ester add ice cold NaOH (50g in 200mL of H_2O and 200g of ice). Swirl a few times (filter off ice if necessary), place in a separating funnel and extract with 2 x 75mL of Et_2O. Dry extract ($MgSO_4$) (since traces of acid decompose the *t*-Bu group of the ester, the distillation flask has to be washed with aq NaOH, rinsed with H_2O and allowed to dry). Addition of some K_2CO_3 or MgO before distilling is recommended to inhibit decomposition. Distil under reduced press through a 10 cm Vigreux column. *Decomposition is evidenced by severe foaming due to autocatalytic decomposition and cannot be prevented from accelerating except by stopping the distillation and rewashing the distillation flask with alkali again.* [*J Am Chem Soc* **66** 1287 *1944*, **64** 2714 *1942*; *Org Synth* Coll Vol IV 417 *1963*; *Org Synth* **37** 35 *1957*.]

***n*-Butyl formate** *[592-84-7]* **M 102.1, b 106.6°, d 0.891, n 1.3890.** Washed with satd $NaHCO_3$ soln in the presence of satd NaCl, until no further reaction occurred, then with saturated NaCl soln, dried ($MgSO_4$) and fractionally distd.

Butyl glycolate *[7397-62-8]* **M 132.2, b 191-192°/755mm, 187-190°/atm, d_4^{20} 1.019, n_D^{20} 1.4263.** Dissolve in $CHCl_3$ (EtOH-free), wash with 5% $KHCO_3$ until effervescence ceases (if free acid is present), dry over $CaCl_2$, filter, evaporate and distil through a short column. [Bøhme and Opfer *Z Anal Chem* **139** 255 *1953*; *cf J Am Chem Soc* **73** 5265 *1951*.]

***tert*-Butyl hydroperoxide (TBHP)** *[75-91-2]* **M 90.1, f 5.4°, m 0.5-2.0°, b 38°/18mm, d 0.900, n 1.4013, pK^{20} 12.8.** *Care should be taken when handling this peroxide because of the possibility of* **EXPLOSION. It explodes when heating over an open flame.** Alcoholic and volatile impurities can be removed by prolonged refluxing at 40° under reduced pressure, or by steam distn. For example, Bartlett, Benzing and Pincock [*J Am Chem Soc* **82** 1762 *1960*] refluxed at 30mm pressure in an azeotropic separation apparatus until two phases no longer separated, and then distilled at 41°/23mm. Pure

material is stored under N_2, in the dark at 0°. Crude commercial material has been added to 25% NaOH below 30°, and the crystals of the sodium salt have been collected, washed twice with *benzene and dissolved in distd water. After adjusting the pH of the soln to 7.5 by adding solid CO_2, the peroxide was extracted into pet ether, from which, after drying with K_2CO_3, it was recovered by distilling off the solvent under reduced pressure at room temperature [O'Brien, Beringer and Mesrobian *J Am Chem Soc* **79** 6238 *1957*]. **The temperatures should be kept below 75°.** It has also been distilled through a helices packed column (*ca* 15 plates) and material collected had **b** 34-35°/20 mm. Similarly, a soln in pet ether has been extracted with cold aq NaOH, and the hydroperoxide has been regenerated by adding at 0°, $KHSO_4$ at a pH not higher than 4.5, then extracted into diethyl ether, dried with $MgSO_4$, filtered and the ether evapd in a rotary evaporator under reduced pressure [Milac and Djokic *J Am Chem Soc* **84** 3098 *1962*].
A 3M soln of TBHP in CH_2Cl_2 is prepared by swirling 85mL (0.61mol) of commercial TBHP (70% TBHP-30% H_2O, **d** 0.935 *ca* 7.2mmol/mL) with 140mL of CH_2Cl_2 in a separating funnel. The milky mixture is allowed to stand until the phases separate (*ca* 30min). The organic (lower) layer (*ca* 200mL) containing 0.60mole of TBHP was separated from the aqueous layer (*ca* 21mL) and used without further drying. TBHP is assayed by iodometric titration. With 90% grade TBHP (w/w, d 0.90, *ca* 9.0mmole/mL) no separation of layers occurs; i.e. when TBHP (66.67mL, 0.60mole) is added to CH_2Cl_2 (140mL) the resulting soln (*ca* 200mL) is clear. [*J Am Chem Soc* **77** 60032 *1955*, **74** 4742 *1952*; Akashi, Palermo and Sharpless *J Org Chem* ***43*** 2063 *1978* states quality of available grades, handling and compatibility for reactions.]

2-*tert*-Butyl hydroquinone *[1948-33-0]* **M 166.2, m 125-127°, 127-128°, 129°, $pK_{Est(1)}$ ~10.5. $pK_{Est(2)}$ ~11.6.** Recrysts from H_2O or MeOH and dried in a vacuum at 70°. Store in a dark container. [*Angew Chem* **69** 699 *1957*.]

***n*-Butyl iodide (1-iodobutane)** *[542-69-8]* **M 184.0, b 130.4°, d 1.616, n^{25} 1.44967.** Dried with $MgSO_4$ or P_2O_5, fractionally distd through a column packed with glass helices, taking the middle fraction and storing with calcium or mercury in the dark. Also purified by prior passage through activated alumina or by shaking with conc H_2SO_4 then washing with Na_2SO_3 soln. It has also been treated carefully with sodium to remove free HI and H_2O, before distilling in a column containing copper turnings at the top. Another purification consisted of treatment with bromine, followed by extraction of free halogen with $Na_2S_2O_3$, washing with H_2O, drying and fractional distn.

***tert*-Butyl iodide** *[558-17-8]* **M 184.0, b 100°(dec), d 1.544.** Vacuum distn has been used to obtain a distillate which remained colourless for several weeks at -5°. More extensive treatment has been used by Boggs, Thompson and Crain [*J Phys Chem* **61** 625 *1957*] who washed with aq $NaHSO_3$ soln to remove free iodine, dried for 1h with Na_2SO_3 at 0°, and purified by four or five successive partial freezings of the liquid to obtain colourless material which was stored at -78°.

***tert*-Butyl isocyanate** *[1609-86-5]* **M 99.1, m 10.5-11.5°, b 30.5-32°/10mm, 64°/52mm, d_{25}^{25} 0.9079, n_D^{25} 1.470.** It is **LACHRYMATORY** and **TOXIC**, and should have IR with 2251 (C≡N) cm^{-1} and no OH bands. The NMR should have one band at 1.37 ppm from TMS. Purified by fractional distn under reduced pressure. [*J Org Chem* **36** 3056 *1971*; *J Prakt Chem.* **125** 152 *1930*.]

***tert*-Butyl isocyanide** *[7188-38-7]* **M 83.1, b 91-92°/730mm, 90°/758mm, d^{20} 0.735.** Dissolve in pet ether (b 40-60°) wash with H_2O, dry (Na_2SO_4), remove pet ether under slight vacuum, dist using a vacuum-jacketed Vigreux column at atmospheric pressure, IR: ν 2134 cm^{-1}. [*Chem Ber* **93** 239 *1960*.]

***tert*-butyl isocyanoacetate** *[2769-72-4]* **M 141.2, b 50°/0.1mm, 49-50°/10mm, 63-65°/15mm, d_4^{20} 0.970, n_D^{20} 1.420.** If it contains some free acid (OH bands in IR) then dissolve in Et_2O, shake with 20% Na_2CO_3, dry over anhydrous K_2CO_3, evaporate and distil. [*Chem Ber* **94** 2814 *1961*.]

***n*-Butyl methacrylate** *[97-88-1]* **M 142.2, b 49-52°/0.1mm, d 0.896, n 1.424.** Purified as for butyl acrylate.

***tert*-Butyl methacrylate** *[585-07-9]* **M 142.2, f -48°, b 135-136°/760mm, d 0.878, n 1.415.** Purified as for butyl acrylate.

2-*tert*-Butyl-4-methoxyphenol (2-*tert*-butyl-4-hydroxyanisole) *[121-00-6]* **M 180.3, m 64.1°, pK_{Est} ~10.8.** Fractionally distd *in vacuo*, then passed as a soln in $CHCl_3$ through alumina, and the solvent evaporated from the eluate. Recrystd from pet ether.

***n*-Butyl methyl ether** *[628-28-4]* **M 88.2, b 70°, d 0.744, pK -3.50 (aq H_2SO_4).** Dried with $CaSO_4$, passed through an alumina column to remove peroxides, and fractionally distd.

***tert*-Butyl methyl ether** *[1634-04-4]* **M 88.2, b 56°, n 1.369.** Same as for *n*-butyl methyl ether.

***tert*-Butyl methyl ketone** *[75-97-8]* **M 100.2, b 105°/746mm, 106°/760mm, d 0.814, n 1.401.** Refluxed with a little $KMnO_4$. Dried with $CaSO_4$ and distd.

8-*sec*-Butylmetrazole *[25717-83-3]* **M 194.3, m 70°.** Crystd from pet ether, and dried for 2 days under vacuum over P_2O_5.

***tert*-Butyl nitrite** *[540-80-7]* **M 103.1, b 34°/250mm, 61-63°/atm, d_4^{20} 0.8671, n_D^{25} 1.3660.** If it is free from OH bands (IR) then distil through a 12inch helices packed column under reduced pressure, otherwise wash with aq 5% $NaHCO_3$ (**effervescence**), then H_2O, dry (Na_2SO_4) and fractionate through a 10 theoretical plates column at *ca* 10mm pressure. [*J Chem Soc* 1968 *1954*, *J Am Chem Soc* **70** 1516 *1948*; UV: *J Org Chem* **21** 993 *1956*; IR: *Bull Soc Chim Belg* **60** 240 *1951*.]

***p*-*tert*-Butylnitrobenzene** *[3282-56-2]* **M 179.2, m 28.4°.** Fractionally crystd three times by partially freezing a mixture of the mono-nitro isomers, then recryst from MeOH twice and dried under vacuum [Brown *J Am Chem Soc* **81** 3232 *1959*].

***N*-(*n*-Butyl)-5-nitro-2-furamide** *[14121-89-2]* **M 212.2, m 89-90°.** Recrystd twice from EtOH/water mixture.

Butyloxirane (1-hexene oxide) *[1436-34-6]* **M 100.2, b 116-117°/atm, 116-119°/atm, d_4^{20} 0.833, n_D^{20} 1.44051.** Purified by fractional distn through a 2ft helices packed column at atmospheric pressure in a N_2 atm. [*J Org Chem* ***30*** 1271 *1965*; *J Chem Soc* 2433 *1927* ; ^{13}C NMR *J Chem Soc Perkin Trans 2* 861 *1975*.]

***tert*-Butyl peracetate** *[107-71-1]* **M 132.2, b 23-24°/0.5mm, n^{25} 1.4030.** Washed with $NaHCO_3$ from a *benzene soln, then redistd to remove *benzene [Kochi *J Am Chem Soc* **84** 774 *1962*]. *Handle with adequate protection due to possible* **EXPLOSIVE** *nature.*

***tert*-Butylperoxy isobutyrate** *[109-13-7]* **M 160.2, f -45.6°.** After diluting 90mL of the material with 120mL of pet ether, the mixture was cooled to 5° and shaken twice with 90mL portions of 5% NaOH soln (also at 5°). The non-aqueous layer, after washing once with cold water, was dried at 0° with a mixture of anhydrous $MgSO_4$ and $MgCO_3$ containing *ca* 40% MgO. After filtering, this material was passed, twice, through a column of silica gel at 0° (to remove *tert*-butyl hydroperoxide). The soln was evapd at 0°/0.5-1mm to remove the solvent, and the residue was recrystd several times from pet ether at -60°, then subjected to high vac to remove traces of solvent [Milos and Golubovic *J Am Chem Soc* **80** 5994 *1958*]. *Handle with adequate protection due to possible* **EXPLOSIVE** *nature.*

***tert*-Butyl perphthalic acid** *[15042-77-0]* **M 238.2, pK_{Est} ~6.2.** Crystd from Et_2O and dried over H_2SO_4. *Possibly* **EXPLOSIVE**.

***p*-*tert*-Butylphenol** *[98-54-4]* **M 150.2, m 99°, pK^{25} 10.39.** Crystd to constant melting point from pet ether (b 60-80°). It sublimes. Also purified *via* its benzoate, as for phenol.

p-tert-**Butylphenoxyacetic acid** *[1798-04-5]* **M 208.3, m 88-89°, pK_{Est} ~2.9.** Crystd from pet ether/*C_6H_6 mixture.

tert-**Butyl phenyl carbonate** *[6627-89-0]* **M 194.2, b 74-78°/0.5mm, 83°/0.6mm, d_4^{20} 1.05, n_D^{20} 1.480.** If IR is free from OH then purify by redistillation, otherwise, dissolve in Et_2O, wash with 5% HCl, then H_2O, dry over $MgSO_4$, evap and distil through a Claisen head under vacuum. Care should be taken in the distillation as distn of large quantities can lead to decomposition with liberation of CO_2 and isobutylene, **use the necessary precautions.** [*J Am Chem Soc* **79** 98 *1957*.]

n-**Butyl phenyl ether** *[1126-79-0]* **M 150.2, b 210.5°, d 0.935.** Dissolved in diethyl ether, washed first with 10% aq NaOH to remove traces of phenol, then repeatedly with distilled water, followed by evaporation of the solvent and distn under reduced pressure [Arnett and Wu *J Am Chem Soc* **82** 5660 *1960*].

N-tert-**Butyl α-phenyl nitrone** *[3376-24-7]* **M 177.2, m 73-74°.** Crystd from hexane.

Butyl phthalate *[84-74-2]* **M 278.4, f -35°, b 340°/760mm, d 1.043.** Freed from alcohol by washing with H_2O, or from acids and butyl hydrogen phthalate by washing with dilute NaOH. Distd at 10torr or less. (See also p. 195.)

4-*tert*-**Butyl pyridine** *[3978-81-2]* **M 135.2, f -44.4°, b 194-197°atm, 197°/765mm, d_4^{20} 0.923, n_D^{20} 1.495, pK^{25} 5.82.** It is dried over solid KOH and is purified by fractional distn through an efficient column under dry N_2. Its *picrate* has **m** 153.9-154°, and the *hydrochloride* has **m** 151.7-154.8° (from Me_2CO). [*J Am Chem Soc* **73** 3308, 3310 *1951*, IR: *J Am Chem Soc* **100** 214 *1978*; *J Chem Soc* 4454 *1960*.]

Butyl stearate *[123-95-5]* **M 340.6, m 26.3°, d 0.861.** Acidic impurities removed by shaking with 0.05M NaOH or a 2% $NaHCO_3$ soln, followed by several water washes, then purified by fractional freezing of the melt and fractional crystn from solvents with boiling points below 100°.

S-*tert*-**Butyl thioacetate** *[999-90-6]* **M 132.2, b 31-32°/11mm, 38°/14mm, 44-45°/28mm, 67°/54mm, 135.6-135.9°/773mm, d_4^{25} 0.9207, n_D^{20} 1.4532.** Dissolve in $CHCl_3$ (EtOH-free), wash with H_2O, 10% H_2SO_4, saturated aqueous $NaHCO_3$ (care CO_2 liberated), H_2O again, dried over Drierite and anhydrous K_2CO_3, and fractionate under reduced pressure. [*J Am Chem Soc* **72** 3021 *1950*.]

p-tert-**Butyltoluene** *[98-51-1]* **M 148.3, f -53.2°, b 91°/28mm, d 0.854, n 1.4920.** A sample containing 5% of the *meta*-isomer was purified by selective mercuration. Fractional distn of the solid arylmercuric acetate, after removal from the residual hydrocarbon, gave pure *p-tert*-butyltoluene [Stock and Brown *J Am Chem Soc* **81** 5615 *1959*].

tert-**Butyl 2,4,6-trichlorophenyl carbonate** *[16965-08-5]* **M 297.6, m 64-66°.** Crystd from a mixture of MeOH (90mL) and water (6mL) using charcoal [Broadbent et al. *J Chem Soc (C)* 2632 *1967*].

N-tert-**Butyl urea** *[1118-12-3]* **M 116.2, m 182°, 185°(dec).** Possible impurity is *N,N'*-di-*tert*-butyl urea which is quite insol in H_2O. Recrystd from hot H_2O, filter off insol material, and cool to 0° to -5° with stirring. Dry in vac at room temp over KOH or H_2SO_4. If dried at higher temperatures it sublimes slowly. It can be recrystd from EtOH as long white needles or from 95% aq EtOH as plates. During melting point determination the bath temp has to be raised rapidly as the urea sublimes slowly above 100° at 760mm. [*Org Synth* Coll Vol III 151 *1955*.]

n-**Butyl vinyl ether** *[111-34-2]* **M 100.2, b 93.3°, d 0.775.** After five washings with equal volumes of water to remove alcohols (made slightly alkaline with KOH), the ether was dried with sodium and distd under vacuum, taking the middle fraction [Coombes and Eley *J Chem Soc* 3700 *1957*]. Stored over KOH.

2-Butyne *[503-17-3]* **M 54.1, b 0°/253mm, d 0.693.** Stood with sodium for 24h, then fractionally distd under reduced pressure.

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

***n*-Butyraldehyde** *[123-72-8]* **M 72.1, b 74.8°, d 0.810, n 1.37911, n^{15} 1.38164.** Dried with $CaCl_2$ or $CaSO_4$, then fractionally distd under N_2. Lin and Day [*J Am Chem Soc* **74** 5133 *1952*] shook with batches of $CaSO_4$ for 10min intervals until a 5mL sample, on mixing with 2.5mL of CCl_4 containing 0.5g of aluminium isopropoxide, gave no ppte and caused the soln to boil within 2min. Water can be removed from *n*-butyraldehyde by careful distn as an azeotrope distilling at 68°. The aldehyde has also been purified through its bisulfite compound which, after decomposing with excess $NaHCO_3$ soln, was steam distd, extracted under N_2 into ether and, after drying, the extract was fractionally distd [Kyte, Jeffery and Vogel *J Chem Soc* 4454 *1960*].

Butyramide *[514-35-5]* **M 87.1, m 115°, b 230°.** Crystd from acetone, *benzene, CCl_4-pet ether, 20% EtOH or water. Dried under vacuum over P_2O_5, $CaCl_2$ or 99% H_2SO_4.

***n*-Butyric acid** *[107-92-6]* **M 88.1, f -5.3°, b 163.3°, d 0.961, n^{25} 1.396, pK^{25} 2.82.** Distd, mixed with $KMnO_4$ (20g/L), and fractionally redistd, discarding the first third [Vogel *J Chem Soc* 1814 *1948*].

***n*-Butyric anhydride** *[106-31-0]* **M 158.2, b 198°, d 0.968.** Dried by shaking with P_2O_5, then distd.

γ-Butyrolactone *[96-48-0]* **M 86.1, b 83.8°/12mm, d 1.124.** Dried with anhydrous $CaSO_4$, then fractionally distd. *Handle in a fume cupboard due to* **TOXICITY.**

Butyronitrile *[109-74-0]* **M 69.1, b 117.9°, d 0.793, n 1.3846, n^{30} 1.37954.** Treated with conc HCl until the smell of the isonitrile had gone, then dried with K_2CO_3 and fractionally distd [Turner *J Chem Soc* 1681 *1956*]. Alternatively it was twice heated at 75° and stirred for several hours with a mixture of 7.7g Na_2CO_3 and 11.5g $KMnO_4$ per L of butyronitrile. The mixture was cooled, then distd. The middle fraction was dried over activated alumina. [Schoeller and Wiemann *J Am Chem Soc* **108** 22 *1986*.]

Butyryl chloride (butanoyl chloride) *[141-75-3]* **M 106.6, f -89°, b 101-102°/atm, d_4^{20} 1.026, n_D^{20} 1.412.** Check IR to see if there is a significant peak at 3000-3500 cm^{-1} (br) for OH. If OH is present then reflux with less than one mol equiv of $SOCl_2$ for 1h and distil directly. The fraction boiling between 85-100° is then refractionated at atm pressure. Keep all apparatus free from moisture and store the product in sealed glass ampoules under N_2. **LACHRYMATORY** - *handle in a good fume hood.* [*Org Synth* Coll Vol I 147 *1941*.]

Cacotheline

(2,3-dihydro-4-nitro-2,3-dioxo-9,10-*seco*strychnidin-10-oic acid) *[561-20-6]* **M 508.4, $pK_{Est(1)}$~4.4 (CO_2H), $pK_{Est(2)}$ ~10.2 (N).** Yellow crystals from H_2O. It is then dried over H_2SO_4 which gives the *dihydrate*, and in a vacuum over H_2SO_4 at 105° to give the anhydrous compound. The *hydrochloride* separates as the hydrate (on heating in vacuum at 80°) in orange-yellow prisms or plates, **m** 250°(dec), and forms a *resorcinol complex* which gives brown crystals from EtOH, **m** 325°, and a *hydroquinone complex* as dark red crystals from EtOH, **m** 319°. [*Chem Ber* **43** 1042 *1910*, **86** 232, UV: 242 *1953*; complexes: Gatto *Gazz Chim Ital* **85** 1441 *1955*.] Used in the titrimetric estimation of Sn^{2+} ions [Szrvas and Lantos *Talanta* **10** 477 *1963*].

Caffeic (3,4-dihydroxycinnamic) acid *[331-39-5]* **M 180.2, m 195°, 223-225°, pK_1^{25} 4.62, pK_2^{25} 9.07** Crystd from water.

Caffeine *[58-08-2]* **M 194.2, m 237°, pK_1^{40} -0.10, pK_2^{55} 1.22.** Crystd from water or absolute EtOH.

(+)-Calarene (+ β-gurjunen, 1,3,3,11-tetramethyltricyclo[5.4.0.$0^{2,4}$]undecan-7-ane, (1a*R*)-1,1,7c,7ac-tetramethyl-1a,2,3,5,6,7,7a,7b-octahydro-1*H*-cyclopropa[α]naphthalene, new name 1(10)aristolene) *[17334-55-3]* **M 204.35, b 45-47°/0.008-0.01mm, 255-258°/atm, d_4^{20} 0.9340, n_D^{20} 1.55051, $[\alpha]_D^{20}$ +58° (EtOH), +81.8° (neat).** Purified by gas chromatography (7%

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