# *Appendices*

1 APPENDIX 1

# *Tables of Unknowns and Derivatives*

More extensive tables of unknowns may be found in Z. Rappoport, ed. *Handbook of Tables for Organic Compound Identification*, 3rd ed. CRC Press: Boca Raton FL, 1967.

## ALDEHYDES

| Compound | BP | MP | Semi-carbazone* | 2,4-Dinitro-phenyl-hydrazone* |
|---|---|---|---|---|
| Ethanal (acetaldehyde) | 21 | — | 162 | 168 |
| Propanal (propionaldehyde) | 48 | — | 89 | 148 |
| Propenal (acrolein) | 52 | — | 171 | 165 |
| 2-Methylpropanal (isobutyraldehyde) | 64 | — | 125 | 187 |
| Butanal (butyraldehyde) | 75 | — | 95 | 123 |
| 3-Methylbutanal (isovaleraldehyde) | 92 | — | 107 | 123 |
| Pentanal (valeraldehyde) | 102 | — | — | 106 |
| 2-Butenal (crotonaldehyde) | 104 | — | 199 | 190 |
| 2-Ethylbutanal (diethylacetaldehyde) | 117 | — | 99 | 95 |
| Hexanal (caproaldehyde) | 130 | — | 106 | 104 |
| Heptanal (heptaldehyde) | 153 | — | 109 | 108 |
| 2-Furaldehyde (furfural) | 162 | — | 202 | 212 |
| 2-Ethylhexanal | 163 | — | 254 | 114 |
| Octanal (caprylaldehyde) | 171 | — | 101 | 106 |
| Benzaldehyde | 179 | — | 222 | 237 |
| Nonanal (nonyl aldehyde) | 185 | — | 100 | 100 |
| Phenylethanal (phenylacetaldehyde) | 195 | 33 | 153 | 121 |
| 2-Hydroxybenzaldehyde (salicylaldehyde) | 197 | — | 231 | 248 |
| 4-Methylbenzaldehyde (*p*-tolualdehyde) | 204 | — | 234 | 234 |
| 3,7-Dimethyl-6-octenal (citronellal) | 207 | — | 82 | 77 |
| Decanal (decyl aldehyde) | 207 | — | 102 | 104 |
| 2-Chlorobenzaldehyde | 213 | 11 | 229 | 213 |
| 3-Chlorobenzaldehyde | 214 | 18 | 228 | 248 |
| 3-Methoxybenzaldehyde (*m*-anisaldehyde) | 230 | — | 233 d. | — |
| 3-Bromobenzaldehyde | 235 | — | 205 | — |
| 4-Methoxybenzaldehyde (*p*-anisaldehyde) | 248 | 2.5 | 210 | 253 |
| *trans*-Cinnamaldehyde | 250 d. | — | 215 | 255 |
| 3,4-Methylenedioxybenzaldehyde (piperonal) | 263 | 37 | 230 | 266 d. |
| 2-Methoxybenzaldehyde (*o*-anisaldehyde) | 245 | 38 | 215 d. | 254 |
| 3,4-Dimethoxybenzaldehyde | — | 44 | 177 | 261 |
| 2-Nitrobenzaldehyde | — | 44 | 256 | 265 |
| 4-Chlorobenzaldehyde | — | 48 | 230 | 254 |
| 4-Bromobenzaldehyde | — | 57 | 228 | 257 |
| 3-Nitrobenzaldehyde | — | 58 | 246 | 293 |

## ALDEHYDES *(Cont.)*

| Compound | BP | MP | Semi-carbazone* | 2,4-Dinitro-phenyl-hydrazone* |
|---|---|---|---|---|
| 2,4-Dimethoxybenzaldehyde | — | 71 | — | — |
| 2,4-Dichlorobenzaldehyde | — | 72 | — | — |
| 4-Dimethylaminobenzaldehyde | — | 74 | 222 | 325 |
| 4-Hydroxy-3-methoxybenzaldehyde (vanillin) | — | 82 | 230 | 271 |
| 3-Hydroxybenzaldehyde | — | 104 | 198 | 259 |
| 5-Bromo-2-hydroxybenzaldehyde (5-bromosalicylaldehyde) | — | 106 | 297 d. | — |
| 4-Nitrobenzaldehyde | — | 106 | 221 | 320 d. |
| 4-Hydroxybenzaldehyde | — | 116 | 224 | 280 d. |
| (±)-Glyceraldehyde | — | 142 | 160 d. | 167 |

*Note: "d" indicates "decomposition."*

*See Appendix 2, "Procedures for Preparing Derivatives."

## KETONES

| Compound | BP | MP | Semi-carbazone* | 2,4-Dinitro-phenyl-hydrazone* |
|---|---|---|---|---|
| 2-Propanone (acetone) | 56 | — | 187 | 126 |
| 2-Butanone (methyl ethyl ketone) | 80 | — | 146 | 117 |
| 3-Buten-2-one (methyl vinyl ketone) | 81 | — | 140 | — |
| 3-Methyl-2-butanone (isopropyl methyl ketone) | 94 | — | 112 | 120 |
| 2-Pentanone (methyl propyl ketone) | 102 | — | 112 | 143 |
| 3-Pentanone (diethyl ketone) | 102 | — | 138 | 156 |
| 3,3-Dimethyl-2-butanone (pinacolone) | 106 | — | 157 | 125 |
| 4-Methyl-2-pentanone (isobutyl methyl ketone) | 117 | — | 132 | 95 |
| 2,4-Dimethyl-3-pentanone (diisopropyl ketone) | 124 | — | 160 | 86 |
| 3-Hexanone | 125 | — | 113 | 130 |
| 2-Hexanone (methyl butyl ketone) | 128 | — | 121 | 106 |
| 4-Methyl-3-penten-2-one (mesityl oxide) | 130 | — | 164 | 200 |
| Cyclopentanone | 131 | — | 210 | 146 |
| 5-Hexen-2-one | 131 | — | 102 | 108 |
| 2,3-Pentanedione | 134 | — | 122 (mono)<br>209 (di) | 209 |
| 5-Methyl-3-hexanone | 136 | — | — | — |
| 2,4-Pentanedione (acetylacetone) | 139 | — | 122 (mono) | 209 |

## KETONES *(Cont.)*

| Compound | BP | MP | Semi-carbazone* | 2,4-Dinitro-phenyl-hydrazone* |
|---|---|---|---|---|
| | | | 209 (di) | |
| 4-Heptanone (dipropyl ketone) | 144 | — | 132 | 75 |
| 5-Methyl-2-hexanone | 145 | — | — | — |
| 1-Hydroxy-2-propanone (hydroxyacetone, acetol) | 146 | — | 196 | 129 |
| 3-Heptanone | 148 | — | 101 | — |
| 2-Heptanone (methyl amyl ketone) | 151 | — | 123 | 89 |
| Cyclohexanone | 156 | — | 166 | 162 |
| 2-Methylcyclohexanone | 165 | — | 191 | 136 |
| 3-Octanone | 167 | — | — | — |
| 2,6-Dimethyl-4-heptanone (diisobutyl ketone) | 168 | — | 122 | 66 |
| 2-Octanone | 173 | — | 122 | 92 |
| Cycloheptanone | 181 | — | 163 | 148 |
| Ethyl acetoacetate | 181 | — | 129 d. | 93 |
| 5-Nonanone | 186 | — | 90 | — |
| 3-Nonanone | 187 | — | 112 | — |
| 2,5-Hexanedione (acetonylacetone) | 191 | –9 | 185 (mono)<br>224 (di) | 257 (di) |
| 2-Nonanone | 195 | -8 | 118 | — |
| Acetophenone (methyl phenyl ketone) | 202 | 20 | 198 | 238 |
| 2-Hydroxyacetophenone | 215 | 28 | 210 | 212 |
| 1-Phenyl-2-propanone (phenylacetone) | 216 | 27 | 198 | 156 |
| Propiophenone (1-phenyl-1-propanone) | 218 | 21 | 173 | 191 |
| Isobutyrophenone (2-methyl-1-phenyl-1-propanone) | 222 | — | 181 | 163 |
| 1-Phenyl-2-butanone | 226 | — | 135 | — |
| 4-Methylacetophenone | 226 | 28 | 205 | 258 |
| 3-Chloroacetophenone | 228 | — | 232 | — |
| 2-Chloroacetophenone | 229 | — | 160 | — |
| Butyrophenone (1-phenyl-1-butanone) | 230 | 12 | 187 | 190 |
| 2-Undecanone | 231 | 12 | 122 | 63 |
| 4-Chloroacetophenone | 232 | 12 | 204 | 231 |
| 4-Phenyl-2-butanone (benzylacetone) | 235 | — | 142 | 127 |
| 2-Methoxyacetophenone | 239 | — | 183 | — |
| 3-Methoxyacetophenone | 240 | — | 196 | — |
| Valerophenone (1-phenyl-1-pentanone) | 248 | — | 160 | 166 |
| 4-Chloropropiophenone | — | 36 | 176 | — |
| 4-Phenyl-3-buten-2-one (benzalacetone) | — | 37 | 187 | 227 |
| 4-Methoxyacetophenone | — | 38 | 198 | 220 |
| 3-Bromopropiophenone | — | 40 | 183 | — |
| 1-Indanone | — | 41 | 233 | 258 |

## KETONES *(Cont.)*

| Compound | BP | MP | Semicarbazone* | 2,4-Dinitrophenylhydrazone* |
|---|---|---|---|---|
| Benzophenone | — | 48 | 164 | 238 |
| 4-Bromoacetophenone | — | 51 | 208 | 230 |
| 3,4-Dimethoxyacetophenone | — | 51 | 218 | 207 |
| 2-Acetonaphthone (methyl 2-naphthyl ketone) | — | 53 | 234 | 262 d. |
| Desoxybenzoin (benzyl phenyl ketone) | — | 60 | 148 | 204 |
| 1,1-Diphenylacetone | — | 61 | 170 | — |
| 4-Chlorobenzophenone | — | 76 | — | 185 |
| 3-Nitroacetophenone | — | 80 | 257 | 228 |
| 4-Nitroacetophenone | — | 80 | — | — |
| 4-Bromobenzophenone | — | 82 | 350 | 230 |
| Fluorenone | — | 83 | — | 283 |
| 4-Hydroxyacetophenone | — | 109 | 199 | 210 |
| Benzoin | — | 136 | 206 | 245 |
| 4-Hydroxypropiophenone | — | 148 | — | 229 |
| (±)-Camphor | — | 179 | 237 | 164 |

Note: "d" indicates "decomposition."
*See Appendix 2, "Procedures for Preparing Derivatives."

## CARBOXYLIC ACIDS

| Compound | BP | MP | *p*-Toluidide* | Anilide* | Amide* |
|---|---|---|---|---|---|
| Methanoic acid (formic acid) | 101 | 8 | 53 | 47 | 43 |
| Ethanoic acid (acetic acid) | 118 | 17 | 148 | 114 | 82 |
| Propenoic acid (acrylic acid) | 139 | 13 | 141 | 104 | 85 |
| Propanoic acid (propionic acid) | 141 | — | 124 | 103 | 81 |
| 2-Methylpropanoic acid (isobutyric acid) | 154 | — | 104 | 105 | 128 |
| Butanoic acid (butyric acid) | 162 | — | 72 | 95 | 115 |
| 3-Butenoic acid (vinylacetic acid) | 163 | — | — | 58 | 73 |
| 2-Methylpropenoic acid (methacrylic acid) | 163 | 16 | — | 87 | 102 |
| Pyruvic acid | 165 d. | 14 | 109 | 104 | 124 |
| 3-Methylbutanoic acid (isovaleric acid) | 176 | — | 106 | 109 | 135 |
| 3,3-Dimethylbutanoic acid | 185 | — | 134 | 132 | 132 |
| Pentanoic acid (valeric acid) | 186 | — | 74 | 63 | 106 |
| 2-Chloropropanoic acid | 186 | — | 124 | 92 | 80 |

## CARBOXYLIC ACIDS *(Cont.)*

| Compound | BP | MP | *p*-Toluidide* | Anilide* | Amide* |
|---|---|---|---|---|---|
| Dichloroacetic acid | 194 | 6 | 153 | 118 | 98 |
| 2-Methylpentanoic acid | 195 | — | 80 | 95 | 79 |
| Hexanoic acid (caproic acid) | 205 | — | 75 | 95 | 101 |
| 2-Bromopropanoic acid | 205 d. | 24 | 125 | 99 | 123 |
| Heptanoic acid | 223 | — | 81 | 70 | 96 |
| 2-Ethylhexanoic acid | 228 | — | — | — | 102 |
| Cyclohexanecarboxylic acid | 233 | 31 | — | 146 | 186 |
| Octanoic acid (caprylic acid) | 237 | 16 | 70 | 57 | 107 |
| Nonanoic acid | 254 | 12 | 84 | 57 | 99 |
| Decanoic acid (capric acid) | — | 32 | 78 | 70 | 108 |
| 4-Oxopentanoic acid (levulinic acid) | — | 33 | 108 | 102 | 108 d. |
| Trimethylacetic acid (pivalic acid) | — | 35 | 120 | 130 | 155 |
| 3-Chloropropanoic acid | — | 40 | — | — | 101 |
| Dodecanoic acid (lauric acid) | — | 43 | 87 | 78 | 100 |
| 3-Phenylpropanoic acid (hydrocinnamic acid) | — | 48 | 135 | 98 | 105 |
| Bromoacetic acid | — | 50 | — | 131 | 91 |
| 4-Phenylbutanoic acid | — | 52 | — | — | 84 |
| Tetradecanoic acid (myristic acid) | — | 54 | 93 | 84 | 103 |
| Trichloroacetic acid | — | 57 | 113 | 97 | 141 |
| 3-Bromopropanoic acid | — | 61 | — | — | 111 |
| Hexadecanoic acid (palmitic acid) | — | 62 | 98 | 90 | 106 |
| Chloroacetic acid | — | 63 | 162 | 137 | 121 |
| Cyanoacetic acid | — | 66 | — | 198 | 120 |
| Octadecanoic acid (stearic acid) | — | 69 | 102 | 95 | 109 |
| *trans*-2-Butenoic acid (crotonic acid) | — | 72 | 132 | 118 | 158 |
| Phenylacetic acid | — | 77 | 136 | 118 | 156 |
| $\alpha$-Methyl-*trans*-cinnamic acid | — | 81 | — | — | 128 |
| 4-Methoxyphenylacetic acid | — | 87 | — | — | 189 |
| 3,4-Dimethoxyphenyl acetic acid | — | 97 | — | — | 147 |
| Pentanedioic acid (glutaric acid) | — | 98 | 218 (di) | 224 (di) | 176 (di) |
| Phenoxyacetic acid | — | 99 | — | 99 | 102 |
| 2-Methoxybenzoic acid (*o*-anisic acid) | — | 100 | — | 131 | 129 |
| 2-Methylbenzoic acid (*o*-toluic acid) | — | 104 | 144 | 125 | 142 |
| Nonanedioic acid (azelaic acid) | — | 106 | 201 (di) | 107 (mono)<br>186 (di) | 93 (mono)<br>175 (di) |
| 3-Methoxybenzoic acid (*m*-anisic acid) | — | 107 | — | — | 136 |
| 3-Methylbenzoic acid (*m*-toluic acid) | — | 111 | 118 | 126 | 94 |
| 4-Bromophenylacetic acid | — | 117 | — | — | 194 |
| (±)-Phenylhydroxyacetic acid (mandelic acid) | — | 118 | 172 | 151 | 133 |
| Benzoic acid | — | 122 | 158 | 163 | 130 |
| 2,4-Dimethylbenzoic acid | — | 126 | — | 141 | 180 |
| 2-Benzoylbenzoic acid | — | 127 | — | 195 | 165 |

## CARBOXYLIC ACIDS *(Cont.)*

| Compound | BP | MP | *p*-Toluidide* | Anilide* | Amide* |
|---|---|---|---|---|---|
| Maleic acid | — | 130 | 142 (di) | 198 (mono) | 172 (mono) |
| | | | | 187 (di) | 260 (di) |
| Decanedioic acid (sebacic acid) | — | 133 | 201 (di) | 122 (mono) | 170 (mono) |
| | | | | 200 (di) | 210 (di) |
| 3-Chlorocinnamic acid | — | 133 | 142 | 135 | 76 |
| 2-Furoic acid | — | 133 | 170 | 124 | 143 |
| *trans*-Cinnamic acid | — | 133 | 168 | 153 | 147 |
| 2-Acetylsalicylic acid (aspirin) | — | 138 | — | 136 | 138 |
| 5-Chloro-2-nitrobenzoic acid | — | 139 | — | 164 | 154 |
| 2-Chlorobenzoic acid | — | 140 | 131 | 118 | 139 |
| 3-Nitrobenzoic acid | — | 140 | 162 | 155 | 143 |
| 4-Chloro-2-nitrobenzoic acid | — | 142 | — | — | 172 |
| 2-Nitrobenzoic acid | — | 146 | — | 155 | 176 |
| 2-Aminobenzoic acid (anthranilic acid) | — | 146 | 151 | 131 | 109 |
| Diphenylacetic acid | — | 148 | 172 | 180 | 167 |
| 2-Bromobenzoic acid | — | 150 | — | 141 | 155 |
| Benzilic acid | — | 150 | 190 | 175 | 154 |
| Hexanedioic acid (adipic acid) | — | 152 | 239 | 151 (mono) | 125 (mono) |
| | | | | 241 (di) | 220 (di) |
| Citric acid | — | 153 | 189 (tri) | 198 (tri) | 210 (tri) |
| 4-Nitrophenylacetic acid | — | 153 | — | 198 | 198 |
| 2,5-Dichlorobenzoic acid | — | 153 | — | — | 155 |
| 3-Chlorobenzoic acid | — | 156 | — | 123 | 134 |
| 2,4-Dichlorobenzoic acid | — | 158 | — | — | 194 |
| 4-Chlorophenoxyacetic acid | — | 158 | — | 125 | 133 |
| 2-Hydroxybenzoic acid (salicylic acid) | — | 158 | 156 | 136 | 142 |
| 5-Bromo-2-hydroxybenzoic acid (5-bromosalicylic acid) | — | 165 | — | 222 | 232 |
| 3,4-Dimethylbenzoic acid | — | 165 | — | 104 | 130 |
| 2-Chloro-5-nitrobenzoic acid | — | 166 | — | — | 178 |
| Methylenesuccinic acid (itaconic acid) | — | 166 d. | — | 152 (mono) | 191 (di) |
| (+)-Tartaric acid | — | 169 | — | 180 (mono) | 171 (mono) |
| | | | | 264 (di) | 196 (di) |
| 5-Chlorosalicylic acid | — | 172 | — | — | 227 |
| 4-Methylbenzoic acid (*p*-toluic acid) | — | 180 | 160 | 145 | 160 |
| 4-Chloro-3-nitrobenzoic acid | — | 182 | — | 131 | 156 |
| 4-Methoxybenzoic acid (*p*-anisic acid) | — | 184 | 186 | 169 | 167 |
| Butanedioic acid (succinic acid) | — | 188 | 180 (mono) | 143 (mono) | 157 (mono) |
| | | | 255 (di) | 230 (di) | 260 (di) |
| 4-Ethoxybenzoic acid | — | 198 | — | 170 | 202 |
| Fumaric acid | — | 200 s. | — | 233 (mono) | 270 (mono) |
| | | | | 314 (di) | 266 (di) |

## CARBOXYLIC ACIDS *(Cont.)*

| Compound | BP | MP | *p*-Toluidide* | Anilide* | Amide* |
|---|---|---|---|---|---|
| 3-Hydroxybenzoic acid | — | 201 s. | 163 | 157 | 170 |
| 3,5-Dinitrobenzoic acid | — | 202 | — | 234 | 183 |
| 3,4-Dichlorobenzoic acid | — | 209 | — | — | 133 |
| Phthalic acid | — | 210 d. | 150 (mono) | 169 (mono) | 144 (mono) |
| | | | 201 (di) | 253 (di) | 220 (di) |
| 4-Hydroxybenzoic acid | — | 214 | 204 | 197 | 162 |
| 3-Nitrophthalic acid | — | 215 | 226 (di) | 234 (di) | 201 (di) |
| Pyridine-3-carboxylic acid (nicotinic acid) | — | 236 | 150 | 132 | 128 |
| 4-Nitrobenzoic acid | — | 240 | 204 | 211 | 201 |
| 4-Chlorobenzoic acid | — | 242 | — | 194 | 179 |
| 4-Bromobenzoic acid | — | 251 | — | 197 | 190 |

*Note:* "d" indicates "decomposition"; "s" indicates "sublimation."

*See Appendix 2, "Procedures for Preparing Derivatives."

## PHENOLS†

| Compound | BP | MP | α-Naphthyl-urethane* | Bromo Derivative* | | | |
|---|---|---|---|---|---|---|---|
| | | | | Mono | Di | Tri | Tetra |
| 2-Chlorophenol | 176 | 7 | 120 | 48 | 76 | — | — |
| 3-Methylphenol (*m*-cresol) | 203 | 12 | 128 | — | — | 84 | — |
| 2-Ethylphenol | 207 | — | — | — | — | — | — |
| 2,4-Dimethylphenol | 212 | 23 | 135 | — | — | — | — |
| 2-Methylphenol (*o*-cresol) | 191 | 32 | 142 | — | 56 | — | — |
| 2-Methoxyphenol (guaiacol) | 204 | 32 | 118 | — | — | 116 | — |
| 4-Methylphenol (*p*-cresol) | 202 | 35 | 146 | — | 49 | — | 198 |
| 3-Chlorophenol | 214 | 35 | 158 | — | — | — | — |
| 4-Methyl-2-nitrophenol | — | 35 | — | — | — | — | — |
| 2,4-Dibromophenol | 238 | 40 | — | 95 | — | — | — |
| Phenol | 181 | 42 | 133 | — | — | 95 | — |
| 4-Chlorophenol | 217 | 43 | 166 | 33 | 90 | — | — |
| 4-Ethylphenol | 219 | 45 | 128 | — | — | — | — |
| 2-Nitrophenol | 216 | 45 | 113 | — | 117 | — | — |
| 2-Isopropyl-5-methylphenol (thymol) | 234 | 51 | 160 | 55 | — | — | — |
| 4-Methoxyphenol | 243 | 56 | — | — | — | — | — |
| 3,4-Dimethylphenol | 225 | 64 | 141 | — | — | 171 | — |
| 4-Bromophenol | 238 | 64 | 169 | — | — | — | — |
| 4-Chloro-3-methylphenol | 235 | 66 | 153 | — | — | — | — |
| 3,5-Dimethylphenol | 220 | 68 | — | — | — | 166 | — |
| 2,6-Di-*tert*-butyl-4-methylphenol | — | 70 | — | — | — | — | — |

## PHENOLS† *(Cont.)*

| Compound | BP | MP | α-Naphthyl-urethane* | Bromo Derivative* | | | |
|---|---|---|---|---|---|---|---|
| | | | | Mono | Di | Tri | Tetra |
| 2,4,6-Trimethylphenol | 232 | 72 | — | — | — | — | — |
| 2,5-Dimethylphenol | 212 | 75 | 173 | — | — | 178 | — |
| 1-Naphthol (α-naphthol) | 278 | 94 | 152 | — | 105 | — | — |
| 2-Methyl-4-nitrophenol | 186 | 96 | — | — | — | — | — |
| 2-Hydroxyphenol (catechol) | 245 | 104 | 175 | — | — | — | 192 |
| 2-Chloro-4-nitrophenol | — | 106 | — | — | — | — | — |
| 3-Hydroxyphenol (resorcinol) | — | 109 | — | — | — | 112 | — |
| 4-Nitrophenol | — | 112 | 150 | — | 142 | — | — |
| 2-Naphthol (β-naphthol) | — | 123 | 157 | 84 | — | — | — |
| 3-Methyl-4-nitrophenol | — | 129 | — | — | — | — | — |
| 1,2,3-Trihydroxybenzene (pyrogallol) | — | 133 | — | — | 158 | — | — |
| 4-Phenylphenol | — | 164 | — | — | — | — | — |

*See Appendix 2, "Procedures for Preparing Derivatives."

†Also check:

Salicylic acid (2-hydroxybenzoic acid)
Esters of salicylic acid (salicylates)
Salicylaldehyde (2-hydroxybenzaldehyde)
4-Hydroxybenzaldehyde
4-Hydroxypropiophenone
3-Hydroxybenzoic acid
4-Hydroxybenzoic acid
4-Hydroxybenzophenone

## PRIMARY AMINES†

| Compound | BP | MP | Benzamide* | Picrate* | Acetamide* |
|---|---|---|---|---|---|
| *t*-Butylamine | 46 | — | 134 | 198 | 101 |
| Propylamine | 48 | — | 84 | 135 | — |
| Allylamine | 56 | — | — | 140 | — |
| *sec*-Butylamine | 63 | — | 76 | 139 | — |
| Isobutylamine | 69 | — | 57 | 150 | — |
| Butylamine | 78 | — | 42 | 151 | — |
| Isopentylamine (ioamylamine) | 96 | — | — | 138 | — |
| Pentylamine (amylamine) | 104 | — | — | 139 | — |
| Ethylenediamine | 118 | — | 244 (di) | 233 (di) | 172 (di) |
| Hexylamine | 132 | — | 40 | 126 | — |
| Cyclohexylamine | 135 | — | 149 | — | 101 |
| 1,3-Diaminopropane | 140 | — | 148 (di) | 250 | 126 (di) |
| Furfurylamine | 145 | — | — | 150 | — |
| Heptylamine | 156 | — | — | 121 | — |

## PRIMARY AMINES† *(Cont.)*

| Compound | BP | MP | Benzamide* | Picrate* | Acetamide* |
|---|---|---|---|---|---|
| Octylamine | 180 | — | — | 112 | — |
| Benzylamine | 184 | — | 105 | 194 | 65 |
| Aniline | 184 | — | 163 | 180 | 114 |
| 2-Methylaniline (*o*-toluidine) | 200 | — | 144 | 213 | 110 |
| 3-Methylaniline (*m*-toluidine) | 203 | — | 125 | 200 | 65 |
| 2-Chloroaniline | 208 | — | 99 | 134 | 87 |
| 2,6-Dimethylaniline | 216 | 11 | 168 | 180 | 177 |
| 2,5-Dimethylaniline | 216 | 14 | 140 | 171 | 139 |
| 3,5-Dimethylaniline | 220 | — | 144 | 225 | — |
| 4-Isopropylaniline | 225 | — | 162 | — | 102 |
| 2-Methoxyaniline (*o*-anisidine) | 225 | 6 | 60 | 200 | 85 |
| 3-Chloroaniline | 230 | — | 120 | 177 | 74 |
| 2-Ethoxyaniline (*o*-phenetidine) | 231 | — | 104 | — | 79 |
| 4-Chloro-2-methylaniline | 241 | 29 | 142 | — | 140 |
| 4-Ethoxyaniline (*p*-phenetidine) | 250 | 2 | 173 | 69 | 137 |
| 3-Bromoaniline | 251 | 18 | 120 | 180 | 87 |
| 2-Bromoaniline | 250 | 31 | 116 | 129 | 99 |
| 2,6-Dichloroaniline | — | 39 | — | — | — |
| 4-Methylaniline (*p*-toluidine) | 200 | 43 | 158 | 182 | 147 |
| 2-Ethylaniline | 210 | 47 | 147 | 194 | 111 |
| 2,5-Dichloroaniline | 251 | 50 | 120 | 86 | 132 |
| 4-Methoxyaniline (*p*-anisidine) | — | 58 | 154 | 170 | 130 |
| 2,4-Dichloroaniline | 245 | 62 | 117 | 106 | 145 |
| 4-Bromoaniline | 245 | 64 | 204 | 180 | 168 |
| 4-Chloroaniline | — | 72 | 192 | 178 | 179 |
| 2-Nitroaniline | — | 72 | 110 | 73 | 92 |
| 2,4,6-Trichloroaniline | 262 | 75 | 174 | 83 | 204 |
| Ethyl *p*-aminobenzoate | — | 89 | 148 | — | 110 |
| *o*-Phenylenediamine | 258 | 102 | 301 (di) | 208 | 185 (di) |
| 2-Methyl-5-nitroaniline | — | 106 | 186 | — | 151 |
| 4-Aminoacetophenone | — | 106 | 205 | — | 167 |
| 2-Chloro-4-nitroaniline | — | 108 | 161 | — | 139 |
| 3-Nitroaniline | — | 114 | 157 | 143 | 155 |
| 4-Methyl-2-nitroaniline | — | 116 | 148 | — | 99 |
| 4-Chloro-2-nitroaniline | — | 118 | 133 | — | 104 |
| 2,4,6-Tribromoaniline | — | 120 | 200 | — | 232 |
| 2-Methyl-4-nitroaniline | — | 130 | — | — | 202 |
| 2-Methoxy-4-nitroaniline | — | 138 | 149 | — | 153 |
| *p*-Phenylenediamine | — | 140 | 128 (mono)<br>300 (di) | — | 162 (mono)<br>304 (di) |
| 4-Nitroaniline | — | 148 | 199 | 100 | 215 |
| 4-Aminoacetanilide | — | 162 | — | — | 304 |
| 2,4-Dinitroaniline | — | 180 | 202 | — | 120 |

*See Appendix 2, "Procedures for Preparing Derivatives."

†Also check 4-aminobenzoic acid and its esters.

## SECONDARY AMINES

| Compound | BP | MP | Benzamide* | Picrate* | Acetamide* |
|---|---|---|---|---|---|
| Diethylamine | 56 | — | 42 | 155 | — |
| Diisopropylamine | 84 | — | — | 140 | — |
| Pyrrolidine | 88 | — | Oil | 112 | — |
| Piperidine | 106 | — | 48 | 152 | — |
| Dipropylamine | 110 | — | — | 75 | — |
| Morpholine | 129 | — | 75 | 146 | — |
| Diisobutylamine | 139 | — | — | 121 | 86 |
| *N*-Methylcyclohexylamine | 148 | — | 85 | 170 | — |
| Dibutylamine | 159 | — | — | 59 | — |
| Benzylmethylamine | 184 | — | — | 117 | — |
| *N*-Methylaniline | 196 | — | 63 | 145 | 102 |
| *N*-Ethylaniline | 205 | — | 60 | 132 | 54 |
| *N*-Ethyl-*m*-toluidine | 221 | — | 72 | — | — |
| Dicyclohexylamine | 256 | — | 153 | 173 | 103 |
| *N*-Benzylaniline | 298 | 37 | 107 | 48 | 58 |
| Indole | 254 | 52 | 68 | — | 157 |
| Diphenylamine | 302 | 52 | 180 | 182 | 101 |
| *N*-Phenyl-1-naphthylamine | 335 | 62 | 152 | — | 115 |

*See Appendix 2, "Procedures for Preparing Derivatives."

## TERTIARY AMINES†

| Compound | BP | MP | Picrate* | Methiodide* |
|---|---|---|---|---|
| Triethylamine | 89 | — | 173 | 280 |
| Pyridine | 115 | — | 167 | 117 |
| 2-Methylpyridine ($\alpha$-picoline) | 129 | — | 169 | 230 |
| 2,6-Dimethylpyridine (2,6-lutidine) | 143 | — | 168 | 233 |
| 4-Methylpyridine (4-picoline) | 143 | — | 167 | — |
| 3-Methylpyridine ($\beta$-picoline) | 144 | — | 150 | 92 |
| Tripropylamine | 157 | — | 116 | 207 |
| *N*,*N*-Dimethylbenzylamine | 183 | — | 93 | 179 |
| *N*,*N*-Dimethylaniline | 193 | — | 163 | 228 d. |
| Tributylamine | 216 | — | 105 | 186 |
| *N*,*N*-Diethylaniline | 217 | — | 142 | 102 |
| Quinoline | 237 | — | 203 | 72/133 |

Note: "d" indicates "decomposition."

*See Appendix 2, "Procedures for Preparing Derivatives."

†Also check nicotinic acid and its esters.

## ALCOHOLS

| Compound | BP | MP | 3,5-Dinitrobenzoate* | Phenylurethane* |
|---|---|---|---|---|
| Methanol | 65 | — | 108 | 47 |
| Ethanol | 78 | — | 93 | 52 |
| 2-Propanol (isopropyl alcohol) | 82 | — | 123 | 88 |
| 2-Methyl-2-propanol (*t*-butyl alcohol) | 83 | 26 | 142 | 136 |
| 3-Buten-2-ol | 96 | — | 54 | — |
| 2-Propen-1-ol (allyl alcohol) | 97 | — | 49 | 70 |
| 1-Propanol | 97 | — | 74 | 57 |
| 2-Butanol (*sec*-butyl alcohol) | 99 | — | 76 | 65 |
| 2-Methyl-2-butanol (*t*-pentyl alcohol) | 102 | -8.5 | 116 | 42 |
| 2-Methyl-3-butyn-2-ol | 104 | — | 112 | — |
| 2-Methyl-1-propanol (isobutyl alcohol) | 108 | — | 87 | 86 |
| 3-Buten-1-ol | 113 | — | 59 | 25 |
| 3-Methyl-2-butanol | 114 | — | 76 | 68 |
| 2-Propyn-1-ol (propargyl alcohol) | 114 | — | — | — |
| 3-Pentanol | 115 | — | 101 | 48 |
| 1-Butanol | 118 | — | 64 | 61 |
| 2-Pentanol | 119 | — | 62 | — |
| 3,3-Dimethyl-2-butanol | 120 | — | 107 | 77 |
| 2,3-Dimethyl-2-butanol | 121 | — | 111 | 65 |
| 2-Methyl-2-pentanol | 123 | — | 72 | — |
| 3-Methyl-3-pentanol | 123 | — | 96 | 43 |
| 2-Methoxyethanol | 124 | — | — | (113)† |
| 2-Methyl-3-pentanol | 128 | — | 85 | 50 |
| 2-Chloroethanol | 129 | — | 95 | 51 |
| 3-Methyl-1-butanol (isoamyl alcohol) | 132 | — | 61 | 56 |
| 4-Methyl-2-pentanol | 132 | — | 65 | 143 |
| 2-Ethoxyethanol | 135 | — | 75 | (67)† |
| 3-Hexanol | 136 | — | 97 | — |
| 1-Pentanol | 138 | — | 46 | 46 |
| 2-Hexanol | 139 | — | 39 | (61)† |
| 2,4-Dimethyl-3-pentanol | 140 | — | — | 95 |
| Cyclopentanol | 140 | — | 115 | 132 |
| 2-Ethyl-1-butanol | 146 | — | 51 | — |
| 2,2,2-Trichloroethanol | 151 | — | 142 | 87 |
| 1-Hexanol | 157 | — | 58 | 42 |
| 2-Heptanol | 159 | — | 49 | (54)† |
| Cyclohexanol | 160 | — | 113 | 82 |
| 3-Chloro-1-propanol | 161 | — | 77 | 38 |
| (2-Furyl)-methanol (furfuryl alcohol) | 170 | — | 80 | 45 |
| 1-Heptanol | 176 | — | 47 | 60 |
| 2-Octanol | 179 | — | 32 | 114 |
| 2-Ethyl-1-hexanol | 185 | — | — | (61)† |
| 1-Octanol | 195 | — | 61 | 74 |

## ALCOHOLS *(Cont.)*

| Compound | BP | MP | 3,5-Dinitrobenzoate* | Phenylurethane* |
|---|---|---|---|---|
| 3,7-Dimethyl-1,6-octadien-3-ol (linalool) | 196 | — | — | 66 |
| 2-Nonanol | 198 | — | 43 | (56)† |
| Benzyl alcohol | 204 | — | 113 | 77 |
| 1-Phenylethanol | 204 | 20 | 92 | 95 |
| 1-Nonanol | 214 | — | 52 | 62 |
| 1,3-Propanediol | 215 | — | 178 (di) | 137 (di) |
| 2-Phenylethanol | 219 | — | 108 | 78 |
| 1-Decanol | 231 | 7 | 57 | 59 |
| 3-Phenylpropanol | 236 | — | 45 | 92 |
| 1-Dodecanol (lauryl alcohol) | — | 24 | 60 | 74 |
| 3-Phenyl-2-propen-1-ol (cinnamyl alcohol) | 250 | 34 | 121 | 90 |
| $\alpha$-Terpineol | 221 | 36 | 78 | 112 |
| 1-Tetradecanol (myristyl alcohol) | — | 39 | 67 | 74 |
| (–)-Menthol | 212 | 41 | 158 | 111 |
| 1-Hexadecanol (cetyl alcohol) | — | 49 | 66 | 73 |
| 2,2-Dimethyl-1-propanol (neopentyl alcohol) | 113 | 56 | — | 144 |
| 4-Methylbenzyl alcohol | 217 | 59 | 117 | 79 |
| 1-Octadecanol (stearyl alcohol) | — | 59 | 77 | 79 |
| Diphenylmethanol (benzhydrol) | — | 68 | 141 | 139 |
| 4-Nitrobenzyl alcohol | — | 93 | 157 | — |
| Benzoin | — | 136 | — | 165 |
| Cholesterol | — | 147 | — | 168 |
| Triphenylmethanol | — | 161 | — | — |
| (+)-Borneol | — | 208 | 154 | 138 |

*See Appendix 2, "Procedures for Preparing Derivatives."
†$\alpha$-Naphthylurethane.

## ESTERS

| Compound | BP | MP | Compound | BP | MP |
|---|---|---|---|---|---|
| Methyl formate | 32 | — | Ethyl chloroformate | 93 | — |
| Ethyl formate | 54 | — | Methyl isobutyrate (methyl 2-methylpropanoate) | 93 | — |
| Methyl acetate | 57 | — | | | |
| Isopropyl formate | 71 | — | 2-Propenyl acetate (isopropenyl acetate) | 94 | — |
| Vinyl acetate | 72 | — | *tert*-Butyl acetate (1,1-dimethylethyl acetate) | 98 | — |
| Ethyl acetate | 77 | — | | | |
| Methyl propionate (methyl propanoate) | 80 | — | Ethyl propionate (ethyl propanoate) | 99 | — |
| | | | Methyl methacrylate (methyl 2-methylpropenoate) | 100 | — |
| Methyl acrylate | 80 | — | | | |
| Propyl formate | 81 | — | Methyl pivalate (methyl trimethyl acetate) | 101 | — |
| Isopropyl acetate | 89 | — | | | |

## ESTERS *(Cont.)*

| Compound | BP | MP | Compound | BP | MP |
|---|---|---|---|---|---|
| Ethyl acrylate (ethyl propenoate) | 101 | — | Ethyl heptanoate | 187 | — |
| Propyl acetate | 102 | — | Heptyl acetate | 192 | — |
| Methyl butyrate (methyl butanoate) | 102 | — | Dimethyl succinate | 196 | — |
| Ethyl isobutyrate | | | Phenyl acetate | 197 | — |
| (ethyl 2-methylpropanoate) | 110 | — | Diethyl malonate | 199 | — |
| Isopropyl propionate | | | Methyl benzoate | 199 | — |
| (isopropyl propanoate) | 110 | — | Dimethyl maleate | 204 | — |
| 2-Butyl acetate (*sec*-butyl acetate) | 111 | — | Ethyl levulinate | 206 | — |
| Methyl isovalerate | 117 | — | Ethyl octanoate | 208 | — |
| (methyl 3-methylbutanoate) | | | Ethyl cyanoacetate | 208 | — |
| Isobutyl acetate | | | Ethyl benzoate | 212 | — |
| (2-methylpropyl acetate) | 117 | — | Benzyl acetate | 217 | — |
| Ethyl pivalate | | | Diethyl succinate | 217 | — |
| (ethyl 2,2-dimethylpropanoate) | 118 | — | Diethyl fumarate | 219 | — |
| Methyl crotonate (methyl 2-butenoate) | 119 | — | Methyl phenylacetate | 220 | — |
| Ethyl butyrate (ethyl butanoate) | 121 | — | Methyl salicylate | 224 | — |
| Propyl propionate (propyl propanoate) | 123 | — | Diethyl maleate | 224 | — |
| Butyl acetate | 126 | — | Ethyl phenylacetate | 228 | — |
| Methyl valerate (methyl pentanoate) | 128 | — | Propyl benzoate | 231 | — |
| Methyl methoxyacetate | 130 | — | Ethyl salicylate | 234 | — |
| Methyl chloroacetate | 130 | — | Dimethyl suberate | 268 | — |
| Ethyl isovalerate | | | Ethyl cinnamate | 271 | — |
| (ethyl 3-methylbutanoate) | 134 | — | Dimethyl phthalate | 284 | — |
| Ethyl crotonate (ethyl 2-butenoate) | 138 | — | Diethyl phthalate | 298 | — |
| Isopentyl acetate | | | Methyl cinnamate | — | 36 |
| (3-methylbutyl acetate) | 142 | — | Ethyl 2-furoate | — | 36 |
| 2-Methoxyethyl acetate | 145 | — | Methyl stearate | — | 39 |
| Ethyl chloroacetate | 145 | — | Dimethyl itaconate | — | 39 |
| Ethyl valerate (ethyl pentanoate) | 146 | — | Phenyl salicylate | — | 42 |
| Ethyl $\alpha$-chloropropanoate | 146 | — | Diethyl terephthalate | — | 44 |
| Pentyl acetate | 147 | — | Methyl 4-chlorobenzoate | — | 44 |
| Methyl hexanoate | 151 | — | Ethyl 3-nitrobenzoate | — | 47 |
| Ethyl lactate | 154 | — | Methyl mandelate | — | 53 |
| Butyl butyrate | 167 | — | Ethyl 4-nitrobenzoate | — | 56 |
| Ethyl hexanoate | 168 | — | Dimethyl isophthalate | — | 68 |
| Hexyl acetate | 169 | — | Phenyl benzoate | — | 69 |
| Methyl acetoacetate | 170 | — | Methyl 3-nitrobenzoate | — | 78 |
| Methyl heptanoate (methyl enanthlate) | 172 | — | Methyl 4-bromobenzoate | — | 81 |
| Furfuryl acetate | 176 | — | Ethyl 4-aminobenzoate | — | 89 |
| Methyl 2-furoate | 181 | — | Methyl 4-nitrobenzoate | — | 96 |
| Dimethyl malonate | 181 | — | Dimethyl fumarate | — | 102 |
| Ethyl acetoacetate | 181 | — | Cholesterol acetate | — | 114 |
| Diethyl oxalate | 185 | — | Ethyl 4-hydroxybenzoate | — | 116 |

2 APPENDIX 2

# *Procedures for Preparing Derivatives*

**CAUTION**

**Some of the chemicals used in preparing derivatives are suspected carcinogens. Before beginning any of these procedures, consult the list of suspected carcinogens on pp. 561–562. Exercise care in handling these substances.**

## ALDEHYDES AND KETONES

### Semicarbazones

Place 0.5 mL of a 2M stock solution of semicarbazide hydrochloride (or 0.5 mL of a solution prepared by dissolving 1.11 g of semicarbazide hydrochloride [*MW* = 111.5] in 5 mL of water) in a small test tube. Add 0.15 g of the unknown compound to the test tube. If the unknown does not dissolve in the solution or if the solution becomes cloudy, add enough methanol (maximum of 2 mL) to dissolve the solid and produce a clear solution. If a solid or cloudiness remains after adding 2 mL of methanol, do not add any more methanol and continue this procedure with the solid present. Using a Pasteur pipet, add 10 drops of pyridine and heat the mixture in a hotwater bath (about 60°C) for about 10–15 minutes. By that time, the product should have begun to crystallize. Collect the product by vacuum filtration. The product can be recrystallized from ethanol if necessary.

### Semicarbazones (Alternative Method)

Dissolve 0.25 g of semicarbazide hydrochloride and 0.38 g of sodium acetate in 1.3 mL of water. Then dissolve 0.25 g of the unknown in 2.5 mL of ethanol. Mix the two solutions together in a 25-mL Erlenmeyer flask and heat the mixture to boiling for about 5 minutes. After heating the mixture, place the reaction flask in a beaker of ice and scratch the sides of the flask with a glass rod to induce crystallization of the derivative. Collect the derivative by vacuum filtration and recrystallize it from ethanol.

### 2, 4-Dinitrophenylhydrazones

Place 10 mL of a solution of 2, 4-dinitrophenylhydrazine (prepared as described for the classification test in Experiment 54D) in a test tube and add 0.15 g of the unknown compound. If the unknown is a solid, it should be dissolved in the minimum amount of 95% ethanol or 1,2-dimethoxyethane before it is added. If crystallization is not immediate, gently warm the solution for a minute in a hotwater bath (90°C) and then set it aside to crystallize. Collect the product by vacuum filtration.

## CARBOXYLIC ACIDS

Working in a hood, place 0.50 g of the acid and 2 mL of thionyl chloride into a small round-bottom flask. Add a magnetic stir bar, and attach a water-jacketed condenser and a drying tube packed with calcium chloride to the flask. While stirring, heat the reaction mixture to boiling for 30 minutes on a hot plate. Allow the mixture to cool

to room temperature. Use this mixture to prepare the amide, anilide, or *p*-toluidide derivatives by one of the following three procedures.

**Amides**

Working in a hood, add the thionyl chloride/carboxylic acid mixture dropwise from a Pasteur pipet into a beaker containing 5 mL of ice-cold concentrated ammonium hydroxide. The reaction is very exothermic. Stir the mixture vigorously after the addition for about 5 minutes. When the reaction is complete, collect the product by vacuum filtration and recrystallize it from water or from water–ethanol, using the mixed-solvents method (See Technique 11, Section 11.10).

**Anilides**

Dissolve 0.5 g of aniline in 13 mL of methylene chloride in a 50-mL Erlenmeyer flask. Using a Pasteur pipet, carefully add the mixture of thionyl chloride/carboxylic acid to this solution. Warm the mixture for an additional 5 minutes on a hot plate, unless a significant color change occurs. *If a color change occurs,* discontinue heating, add a magnetic stir bar, and stir the mixture for 20 minutes at room temperature. Then transfer the methylene chloride solution to a small separatory funnel and wash it sequentially with 2.5 mL of water, 2.5 mL of 5% hydrochloric acid, 2.5 mL of 5% sodium hydroxide, and a second 2.5-mL portion of water (the methylene chloride solution should be the bottom layer). Dry the methylene chloride layer over a small amount of anhydrous sodium sulfate. Decant the methylene chloride layer away from the drying agent into a small flask and evaporate the methylene chloride on a warm hot plate in the hood. Use a stream of air or nitrogen to speed up the evaporation. Recrystallize the product from water or from ethanol–water, using the mixed-solvents method (See Technique 11, Section 11.10).

***p*-Toluidides**

Use the same procedure as that described in preparing anilides, but substitute *p*-toluidine for aniline.

## PHENOLS

**α-Naphthylurethanes**

Follow the procedure given later for preparing phenylurethanes from alcohols, but substitute α-naphthylisocyanate for phenylisocyanate.

**Bromo Derivatives**

First, if a stock brominating solution is not available, prepare one by dissolving 0.75 g of potassium bromide in 5 mL of water and adding 0.5 g of bromine. Dissolve 0.1 g of the phenol in 1 mL of methanol or 1,2-dimethoxyethane; then add 1 mL of water. Add 1 mL of the brominating mixture to the phenol solution and swirl the mixture vigorously. Then continue adding the brominating solution dropwise while swirling, until the color of the bromine reagent persists. Finally, add 3–5 mL of water and shake the mixture vigorously. Collect the precipitated product by vacuum filtration and wash it well with water. Recrystallize the derivative from methanol–water, using the mixed-solvents method (See Technique 11, Section 11.10).

## AMINES

**Acetamides**

Place 0.15 g of the amine and 0.5 mL of acetic anhydride in a small Erlenmeyer flask. Heat the mixture for about 5 minutes; then add 5 mL of water and stir the solution vigorously to precipitate the product and hydrolyze the excess acetic anhydride. If the product does not crystallize, it may be necessary to scratch the

walls of the flask with a glass rod. Collect the crystals by vacuum filtration and wash them with several portions of cold 5% hydrochloric acid. Recrystallize the derivative from methanol–water, using the mixed-solvents method (See Technique 11, Section 11.10).

Aromatic amines, or those amines that are not very basic, may require pyridine (2 mL) as a solvent and a catalyst for the reaction. If pyridine is used, a longer period of heating is required (up to 1 hour), and the reaction should be carried out in an apparatus equipped with a reflux condenser. After reflux, the reaction mixture must be extracted with 5–10 mL of 5% sulfuric acid to remove the pyridine.

### Benzamides

Using a centrifuge tube, suspend 0.15 g of the amine in 1 mL of 10% sodium hydroxide solution and add 0.5 g of benzoyl chloride. Cap the tube and shake the mixture vigorously for about 10 minutes. After shaking the mixture, add enough dilute hydrochloric acid to bring the pH of the solution to pH 7 or 8. Collect the precipitate by vacuum filtration, wash it thoroughly with cold water, and recrystallize it from ethanol–water, using the mixed-solvents method (See Technique 11, Section 11.10).

### Benzamides (Alternative Method)

In a small round-bottom flask, dissolve 0.25 g of the amine in a solution of 1.2 mL of pyridine and 2.5 mL of toluene. Add 0.25 mL of benzoyl chloride to the solution, and heat the mixture under reflux for about 30 minutes. Pour the cooled reaction mixture into 25 mL of water, and stir the mixture vigorously to hydrolyze the excess benzoyl chloride. Separate the toluene layer and wash it, first with 1.5 mL of water, and then with 1.5 mL of 5% sodium carbonate. Dry the toluene over granular anhydrous sodium sulfate, decant the toluene into a small Erlenmeyer flask, and remove the toluene by evaporation on a hot plate in the hood. Use a stream of air or nitrogen to speed up the evaporation. Recrystallize the benzamide from ethanol or ethanol–water, using the mixed-solvents method (See Technique 11, Section 11.10).

### Picrates

In an Erlenmeyer flask, dissolve 0.2 g of the unknown in about 5 mL of ethanol and add 5 mL of a saturated solution of picric acid in ethanol. Heat the solution to boiling and then allow it to cool slowly. Collect the product by vacuum filtration and rinse it with a small amount of cold ethanol.

**CAUTION**

**Great care must be taken when working with saturated solutions of picric acid. Picric acid may detonate when heated above 300°C. It is also known to explode when hearted rapidly. For this reason, it is strongly recommended that you check with your instructor before preparing this derivation.**

### Methiodides

Mix equal-volume quantities of the amine and methyl iodide in a small round-bottom flask (about 0.25 mL is sufficient) and allow the mixture to stand for several minutes. Then heat the mixture gently under reflux for about 5 minutes. The methiodide should crystallize on cooling. If it does not, you can induce crystallization by scratching the walls of the flask with a glass rod. Collect the product by vacuum filtration and recrystallize it from ethanol or ethyl acetate.

# ALCOHOLS

## 3,5-Dinitrobenzoates

**Liquid Alcohols**

Dissolve 0.25 g of 3,5-dinitrobenzoyl chloride in 0.25 mL of the alcohol and heat the mixture for about 5 minutes[1]. Allow the mixture to cool and add 1.5 mL of a 5% sodium carbonate solution and 1 mL of water. Stir the mixture vigorously and crush any solid that forms. Collect the product by vacuum filtration, and wash it with cold water. Recrystallize the derivative from ethanol–water, using the mixed-solvents method (See Technique 11, Section 11.10).

## Solid Alcohols

Dissolve 0.25 g of the alcohol in 1.5 mL of dry pyridine and add 0.25 g of 3, 5-dinitrobenzoyl chloride. Heat the mixture under reflux for 15 minutes. Pour the cooled reaction mixture into a cold mixture of 2.5 mL of 5% sodium carbonate and 2.5 mL of water. Keep the solution cooled in an ice bath until the product crystallizes, and stir it vigorously during the entire period. Collect the product by vacuum filtration, wash it with cold water, and recrystallize it from ethanol–water, using the mixed-solvents method (See Technique 11, Section 11.10).

## Phenylurethanes

Place 0.25 g of the *anhydrous* alcohol in a dry test tube and add 0.25 mL of phenylisocyanate ($\alpha$-naphthylisocyanate for a phenol). If the compound is a phenol, add 1 drop of pyridine to catalyze the reaction. If the reaction is not spontaneous, heat the mixture in a hot-water bath (90°C) for 5–10 minutes. Cool the test tube in a beaker of ice, and scratch the tube with a glass rod to induce crystallization. Decant the liquid from the solid product or, if necessary, collect the product by vacuum filtration. Dissolve the product in 2.5–3 mL of hot ligroin or hexane, and filter the mixture by gravity (preheat funnel) to remove any unwanted and insoluble diphenylurea present. Cool the filtrate to induce crystallization of the urethane. Collect the product by vacuum filtration.

# ESTERS

We recommend that esters be characterized by spectroscopic methods whenever possible. A derivative of the alcohol part of an ester can be prepared with the following procedure. For other derivatives, consult a comprehensive textbook. Several are listed in Experiment 55I.

## 3,5-Dinitrobenzoates

Place 1.0 mL of the ester and 0.75 g of 3,5-dinitrobenzoic acid in a small round-bottom flask. Add 2 drops of concentrated sulfuric acid and a magnetic stir bar to the flask and attach a condenser. If the boiling point of the ester is above 150°C, heat at reflux while stirring for 30–45 minutes. If the boiling point of the ester is above 150°C, heat the mixture at about 150°C for 30–45 minutes. Cool the mixture, and transfer it to a small separatory funnel. Add 10 mL of ether. Extract the ether layer 2 times with 5 mL of 5% aqueous sodium carbonate (save the ether layer). Wash the organic layer with 5 mL of water, and dry the ether solution over magnesium sulfate. Evaporate the ether in a hot-water bath in the hood. Use a stream of air or

[1] 3,5-Dinnitrobenzoyl chloride is an acid chloride and hydrolysis readily. The purity of this reagent should be checked before its use by determining its melting point (mp 69–71°C). When the carboxylic acid is present, the melting point will be high.

nitrogen to speed the evaporation. Dissolve the residue, usually an oil, in 2 mL of boiling ethanol and add water dropwise until the mixture becomes cloudy. Cool the solution to induce crystallization of the derivative.

**Preparation of a Solid Carboxylic Acid from an Ester.**

An excellent derivative of an ester can be prepared by a basic hydrolysis of an ester when it yields a solid carboxylic acid. A procedure is provided in Experiment 55I. Melting points for solid carboxylic acids are included in the Carboxylic Acids Table in Appendix 1.

3 APPENDIX 3

# *Index of Spectra*

## INFRARED SPECTRA

## $^{1}$H NMR SPECTRA



## $^{13}$C NMR SPECTRA



## MASS SPECTRA

## ULTRAVIOLET–VISIBLE SPECTRA



## MIXTURES

# *Index*

## C

## D

## E



## F

## G



## H

## N

## O



## P

## Q



## R



## S

## T



## U

## V



## W



## X



## Y



## Z

Common Organic Solvents

| Solvent | Boiling Point (°C) | Density (g/mL) |
|---|---|---|
| Acetic acid | 118 | 1.05 |
| Acetic anhydride | 140 | 1.08 |
| Acetone | 56 | 0.79 |
| Benzene* | 80 | 0.88 |
| Carbon tetrachloride* | 77 | 1.59 |
| Chloroform* | 61 | 1.48 |
| Cyclohexane | 81 | 0.78 |
| Dimethylformamide (DMF) | 153 | 0.94 |
| Dimethyl sulfoxide (DMSO) | 189 | 1.10 |
| Ethanol | 78 | 0.80 |
| Ether (diethyl) | 35 | 0.71 |
| Ethyl acetate | 77 | 0.90 |
| Heptane | 98 | 0.68 |
| Hexane | 69 | 0.66 |
| Ligroin | 60–90 | 0.68 |
| Methanol | 65 | 0.79 |
| Methylene chloride | 40 | 1.32 |
| Pentane | 36 | 0.63 |
| Petroleum ether | 30–60 | 0.63 |
| 1-Propanol | 98 | 0.80 |
| 2-Propanol | 82 | 0.79 |
| Pyridine | 115 | 0.98 |
| Tetrahydrofuran (THF) | 65 | 0.99 |
| Toluene | 111 | 0.87 |
| Xylenes | 137–144 | 0.86 |

Solvents indicated in boldface type are flammable.

*Suspected carcinogen.

Atomic Mass Values for Selected Elements

| | |
|---|---|
| Aluminum | 26.98 |
| Boron | 10.81 |
| Bromine | 79.90 |
| Carbon | 12.01 |
| Chlorine | 35.45 |
| Fluorine | 18.99 |
| Hydrogen | 1.008 |
| Iodine | 126.9 |
| Lithium | 6.941 |
| Magnesium | 24.30 |
| Nitrogen | 14.01 |
| Oxygen | 15.99 |
| Phosphorus | 30.97 |
| Potassium | 39.09 |
| Silicon | 28.09 |
| Sodium | 22.99 |
| Sulfur | 32.07 |

Concentrated Acids and Bases

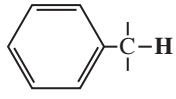
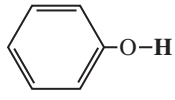
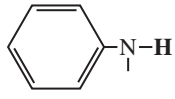
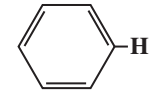
| **Reagent** | **HCI** | **$HNO_3$** | **$H_2SO_4$** | **HCOOH** | **$CH_3COOH$** | **$NH_3(NH_4OH)$** |
|---|---|---|---|---|---|---|
| Density (g/mL) | 1.18 | 1.41 | 1.84 | 1.20 | 1.06 | 0.90 |
| % Acid or base (by weight) | 37.3 | 70.0 | 96.5 | 90.0 | 99.7 | 29.0 |
| Molecular weight | 36.47 | 63.02 | 98.08 | 46.03 | 60.05 | 17.03 |
| Molarity of concentrated acid or base | 12 | 16 | 18 | 23.4 | 17.5 | 15.3 |
| Normality of concentrated acid or base | 12 | 16 | 36 | 23.4 | 17.5 | 15.3 |
| Volume of concentrated reagent required to prepare 1 L of 1 M solution (ml) | 83 | 64 | 56 | 42 | 58 | 65 |
| Volume of concentrated reagent required to prepare 1 L of 10% solution (ml)* | 227 | 101 | 56 | 93 | 95 | 384 |
| Molarity of a 10% solution* | 2.74 | 1.59 | 1.02 | 2.17 | 1.67 | 5.87 |

*Percent solutions by weight.

Infrared Absorption Bands

| | | Type of Vibration | Frequency ($cm^{21}$) | Intensity |
|---|---|---|---|---|
| C—H | Alkanes | (stretch) | 3000–2850 | s |
| | —$CH_3$ | (bend) | 1450 and 1375 | m |
| | —$CH_2$— | (bend) | 1465 | m |
| | Alkenes | (stretch) | 3100–3000 | m |
| | | (out-of-plane bend) | 1000–650 | s |
| | Aromatics | (stretch) | 3150–3050 | s |
| | | (out-of-plane bend) | 900–690 | s |
| | Alkyne | (stretch) | ca. 3300 | s |
| | Aldehyde | | 2900–2800 | w |
| | | | 2800–2700 | w |
| O—H | Alcohol, phenols | | | |
| | Free | | 3650–3600 | m |
| | H-bonded | | 3400–3200 | m |
| | Carboxylic acids | | 3400–2400 | m |
| N—H | Primary and secondary amines and amides | | | |
| | (stretch) | | 3500–3100 | m |
| | (bend) | | 1640–1550 | m–s |
| C≡C | Alkyne | | 2250–2100 | m–w |
| C≡N | Nitriles | | 2260–2240 | m |
| C=C | Alkene | | 1680–1600 | m–w |
| | Aromatic | | 1600 and 1475 | m–w |
| N=O | Nitro (R—$NO_2$) | | 1550 and 1350 | s |
| C=O | Aldehyde | | 1740–1720 | s |
| | Ketone | | 1725–1705 | s |
| | Carboxylic acid | | 1725–1700 | s |
| | Ester | | 1750–1730 | s |
| | Amide | | 1680–1630 | s |
| | Anhydride | | 1810 and 1760 | s |
| | Acid chloride | | 1800 | s |
| C—O | Alcohols, ethers, esters, carboxylic acids, anhydrides | | 1300–1000 | s |
| C—N | Amines | | 1350–1000 | m–s |
| C—X | Fluoride | | 1400–1000 | s |
| | Chloride | | 785–540 | s |
| | Bromide, iodide | | $< 667$ | s |

## NMR Chemical Shift Ranges (ppm) for Selected Protons

| | | |
|---|---|---|
| $R-CH_3$ | | 0.7–1.3 |
| $R-CH_2-R$ | | 1.2–1.4 |
| $R_3CH$ | | 1.4–1.7 |
| $R-C=C-C-H$ | | 1.6–2.6 |
| $R-C(=O)-C-H$, $H-C(=O)-C-H$ | | 2.1–2.4 |
| $RO-C(=O)-C-H$, $HO-C(=O)-C-H$ | | 2.1–2.5 |
| $N\equiv C-C-H$ | | 2.1–3.0 |
|  | | 2.3–2.7 |
| $R-C\equiv C-H$ | | 1.7–2.7 |
| $R-S-H$ | var | 1.0–4.0[a] |
| $R-N(-)-H$ | var | 0.5–4.0[a] |
| $R-O-H$ | var | 0.5–5.0[a] |
|  | var | 4.0–7.0[a] |
|  | var | 3.0–5.0[a] |
| $R-C(=O)-N(-)-H$ | var | 5.0–9.0[a] |
| $R-N(-)-C-H$ | | 2.2–2.9 |
| $R-S-C-H$ | | 2.0–3.0 |
| $I-C-H$ | | 2.0–4.0 |
| $Br-C-H$ | | 2.7–4.1 |
| $Cl-C-H$ | | 3.1–4.1 |
| $R-S(=O)(=O)-O-C-H$ | | ca. 3.0 |
| $RO-C-H$, $HO-C-H$ | | 3.2–3.8 |
| $R-C(=O)-O-C-H$ | | 3.5–4.8 |
| $O_2N-C-H$ | | 4.1–4.3 |
| $F-C-H$ | | 4.2–4.8 |
| $R-C=C-H$ | | 4.5–6.5 |
|  | | 6.5–8.0 |
| $R-C(=O)-H$ | | 9.0–10.0 |
| $R-C(=O)-OH$ | | 11.0–12.0 |

*Note:* For those hydrogens shown as —C(—)—H, if that hydrogen is part of a methyl group ($CH_3$), the shift is generally at the low end of the range given; if the hydrogen is in a methylene group (—$CH_2$—), the shift is intermediate; and if the hydrogen is in a methine group (—CH(—)—), the shift is typically at the high end of the range given.

[a] The chemical shift of these groups is variable, depending on the chemical environment in the molecule and on concentration, temperature, and solvent.