

Chapter 3. Compounds derived from aminoacetic acids

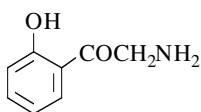
3.1. Compounds derived from aminoacetic acid

2-Amino-1-(2-hydroxyphenyl)ethanone

[72481-17-5]

C₈H₉NO₂

mol.wt. 151.17



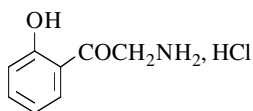
Syntheses

-Obtained by treatment of 3-nitro-4-hydroxycoumarin — m.p. 177° (d) — with refluxing in a mixture of 58% hydriodic acid solution and acetic acid for 15 min. The iodine produced during the reaction was reduced with hypophosphorous acid [664].
-Also refer to: [572] [1426].

2-Amino-1-(2-hydroxyphenyl)ethanone (Hydrochloride)

C₈H₉NO₂, HCl

mol.wt. 187.63



Synthesis

-Preparation by treatment of 3-nitro-4-hydroxycoumarin — m.p. 177° (d) — with refluxing in a mixture of 58% hydriodic acid solution and acetic acid for 15 min. The iodine produced during the reaction was reduced with hypophosphorous acid. Then, recrystallisation of the obtained base from concentrated hydrochloric acid (66%) [664].

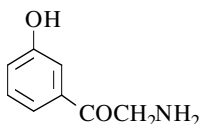
m.p. 229-230° [664].

2-Amino-1-(3-hydroxyphenyl)ethanone

[90005-54-2]

C₈H₉NO₂

mol.wt. 151.17



Syntheses

-Obtained by adding ammonia to an aqueous solution of its hydrochloride (63%) [226].
-Also refer to: [219] [220] [355] [572] [850].

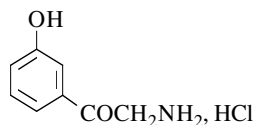
m.p. 217-220° [220], 215-235° [226].

2-Amino-1-(3-hydroxyphenyl)ethanone (Hydrochloride)

[14665-75-9]

C₈H₉NO₂, HCl

mol.wt. 187.63



Syntheses

-Preparation by hydrolysis of m-(benzoyloxy)-α-amino-acetophenone hydrochloride (SM) (m.p. 202-205°) [220], (m.p. 206°) [226],
*with refluxing 10% hydrochloric acid (quantitative yield) [226], for 2 h (80%) [220];

- *with 37% hydrochloric acid in chlorobenzene at 90° for 3 h (90%) [355]. SM was obtained by reaction of hexamethylenetetramine with m-(benzoyloxy)- α -bromoacetophenone (m.p. 162°) in ethanol in the presence of 37% hydrochloric acid for 6 h at r.t. (75%) [355].
- Also obtained by hydrolysis of 3,6-bis(3-hydroxyphenyl)-2,5-dihydropyrazine in aqueous suspension with hydrochloric acid at r.t. [1047].
 - Also obtained by reaction of 3-acetoxy- α -bromoacetophenone (m.p. 71-72°) with hexamethylenetetramine in chloroform, followed by acetoxy group elimination in the obtained compound with hydrochloric acid [1270].
 - Also obtained by reaction of 3-hydroxy- α -iodoacetophenone with hexamethylenetetramine, followed by transformation of the obtained iodo derivative (m.p. 138-139°) into hydrochloride salt [1269].
 - Also refer to: [219].

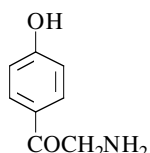
m.p. 221-222° [1047] [1269] [1270], 219-220° [226],
218-220° (d) [355], 217-220° [220].

2-Amino-1-(4-hydroxyphenyl)ethanone

[77369-38-1]

C₈H₉NO₂

mol.wt. 151.17



Syntheses

- Obtained by oxidation of the biogenic amine 1-(4-hydroxyphenyl)-2-aminoethanol at high pH [929].
- Also obtained by hydrogenation of p-hydroxyisonitrosoacetophenone — so called p-hydroxy- α -(hydroximino)-acetophenone — over Pd/C in acetic acid at a temperature < 60° (91%) [1426].
- Also obtained from the corresponding hydrochloride aqueous solution with ammonia [963].
- Also refer to: [327] [572] [689] [865] [1035] [1505].

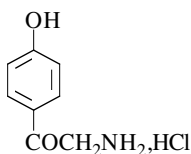
N.B.: For the acetate [172417-70-8], refer to: [1504] [1505]; pK_B [555].

2-Amino-1-(4-hydroxyphenyl)ethanone (Hydrochloride)

[19745-72-3]

C₈H₉NO₂, HCl

mol.wt. 187.63



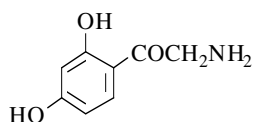
Syntheses

- Preparation by treatment of α -amino-p-hydroxyacetophenone with hydrogen chloride in DMF (70%) [1426].
- Preparation by hydrogenation of p-hydroxy- α -(hydroximino)acetophenone (SM) over Pd/C in DMF (70%). SM was obtained by adding tert-butyl nitrite to a mixture of p-hydroxyacetophenone, hydrogen chloride and DMF at 40-45° [1425].
- Preparation from α -amino-p-benzoyloxyacetophenone hydrochloride with refluxing 20% hydrochloric acid solution for 7 h (80%) [327].
- Preparation by condensation of phenol with aminoacetonitrile hydrochloride (Houben-Hoesch reaction) (51%) [89].
- Also obtained by demethylation of α -amino-p-methoxyacetophenone (m.p. 197°) with 38% hydrochloric acid at 160-170° for 2 h [963].
- Also refer to: [236].

m.p. 249-251° [89], 242° [963], 241-245° (d) [327].

2-Amino-1-(2,4-dihydroxyphenyl)ethanoneC₈H₉NO₃

mol.wt. 167.16

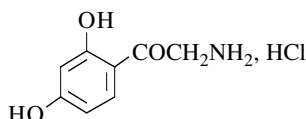
**Syntheses**

- Obtained from its hydriodide (m.p. 258°) or its hydrochloride (m.p. 280°) by addition of a hot concentrated solution of sodium carbonate [1482].
- Also refer to: [1121] [1555].

m.p. 310° (d) [1482].

2-Amino-1-(2,4-dihydroxyphenyl)ethanone (Hydrochloride)C₈H₉NO₃, HCl

mol.wt. 203.61

**Syntheses**

- Obtained by refluxing a mixture of 2,4-dihydroxy- α -[(ethoxycarbonyl)amino]acetophenone (m.p. 156-157°) and hydrochloric acid (1:1) for 2 h [1380].
- Also obtained by addition of concentrated hydrochloric acid to an alcoholic solution of the corresponding hydriodide (SM). SM — m.p. 128° (d) — was prepared from 2,4-dimethoxy- α -phthaliminoacetophenone (m.p. 188°) with boiling concentrated hydriodic acid containing some acetic acid [1482].
- Also obtained by treatment of 3-acetamido-4,7-dihydroxycoumarin (m.p. 268°) with 10% hydrochloric acid for 1 h [1121].
- Also refer to: [1555].

m.p. 280° (d) [1482], 271° [1121], 257° [1380].

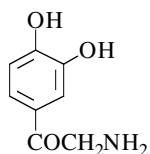
One of the reported melting points is obviously wrong.

2-Amino-1-(3,4-dihydroxyphenyl)ethanone (Arterenone; Noradrenalone; ART)

[499-61-6]

C₈H₉NO₃

mol.wt. 167.16

**Syntheses**

- Preparation by reaction of 35% aqueous ammonia with 3,4-dihydroxy- α -chloroacetophenone in methanol or in ethanol [874], (71-73%) [1233], (67%) [1404].
- Also obtained by adding ammonia to an aqueous solution of the corresponding hydrochloride [555] [797], (60-75%) [963].
- Also obtained by adding sodium carbonate to an aqueous solution of its hydriodide (m.p. 247-248°) (SM). SM was prepared from m,m',p,p'-tetramethoxy-2,5-diphenylpyrazine by boiling for 2 h with a mixture of acetic acid and concentrated hydriodic acid [1482].
- Preparation by hydrogenolysis of α -dibenzylamino-3,4-dihydroxyacetophenone hydrochloride in water in the presence of Pd/C under hydrogen atmosphere for 5 h. Then, treatment of the concentrated solution with 28% ammonia (85%) [1363].
- Also refer to: [357] [572] [1047] [1092].

Isolation from natural sources

- From insect cuticle [47] [50].
- Also obtained by mild acid hydrolysis of sclerotized cuticles from locusts (*Schistocerca gregaria*) and beetles (*Pachynoda sinuata*) [45].
- From acid hydrolysates of insect sclerotized cuticle in refluxing 1 N formic acid for 1 h or in boiling methanolic hydrochloric acid. The cuticle used was obtained from the desert locust *Schistocerca gregaria* [46].
- Also obtained by hydrolysis of 2-(3',4'-dihydroxyphenyl)-3-acetylamino-6 (or 7)-(N-acetyl-2''-aminoethyl)-2,3-dihydro-1,4-benzodioxin (SM) with 6 N hydrochloric acid at 110° for 3 h. SM was formed by incubation of N-acetyldopamine with locust cuticle [48].
- ART was the major identified catechol recovered from strong acid hydrolysates of tanning pharate pupae cuticle from *Manduca sexta* [1120].

m.p. 300° (d) [1404], 235° (d) [1363] [1482], >200° (d) (not melted) [797] [963];

One note a very large dispersion of the various melting points.

¹H NMR [48], UV [45] [46], MS [45] [1242];

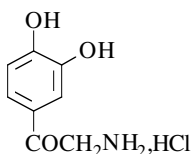
HPLC [1120]; pK_B [555]; column chromatography [45]; TLC [45].

2-Amino-1-(3,4-dihydroxyphenyl)ethanone (Hydrochloride)

[5090-29-9]

C₈H₉NO₃, HCl

mol.wt. 203.61



Syntheses

- Preparation by demethylation of α -amino-3,4-dimethoxyacetophenone on heating with 37% hydrochloric acid for 2.5 h at 160-165° under carbon dioxide (85%) [797].
- Preparation by dissolving the corresponding base in a mixture of concentrated hydrochloric acid/methanol and allowing to stand several hours at -10° (82%) [874].
- Also obtained by hydrogenation of 3,4-dihydroxy- α -azidoacetophenone (m.p. 132°) in an ethanol and concentrated hydrochloric acid solution under hydrogen in the presence of 4% Pd/C for 7 h (65%) [226].
- Also obtained from the addition compound (SM) of 3,4-diacetoxy- α -chloroacetophenone and hexamethylene tetramine in chloroform at r.t. for 24 h (40%). SM in ethanolic solution was treated with 38% hydrochloric acid at r.t. for 3 days [963].
- Also obtained from hydrolysis of 3,6-bis(3,4-dihydroxyphenyl)-2,5-dihydropyrazine — m.p. 250° (d) — in aqueous suspension with hydrochloric acid at r.t. [1047].
- Also refer to: [1233].

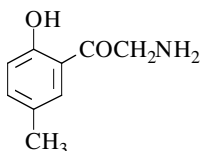
m.p. 270° [1047], 260° [1404], 259° [555], 256° (d) [226] [797], 255° [874], 252° [963].

One note a very large dispersion of the various melting points.

2-Amino-1-(2-hydroxy-5-methylphenyl)ethanone

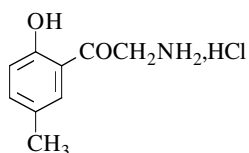
C₉H₁₁NO₂

mol.wt. 165.19



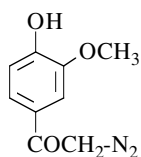
Synthesis

- Obtained by hydrogenation of the complex formed by addition of 2-(benzyloxy)-5-methyl- α -bromoacetophenone and hexamethylenetetramine in ethanol in the presence of Pd/C [67].

2-Amino-1-(2-hydroxy-5-methylphenyl)ethanone (Hydrochloride)C₉H₁₁NO₂, HCl mol.wt. 201.66**Synthesis**

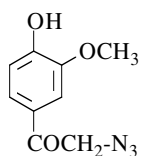
-Obtained by hydrogenolysis of 2-(benzyloxy)-5-methyl- α -aminoacetophenone hydrochloride (m.p. 191-192°) (SM) with hydrogen in the presence of Pd/C in 95% ethanol. SM was prepared by reaction of 2-(benzyloxy)-5-methyl- α -bromoacetophenone with hexamethylene-tetramine, followed by treatment with ethanolic hydrogen chloride [67].

m.p. 222-225° (d) [67].

3.2. Compounds derived from substituted aminoacetic acids**2-Diazo-1-(4-hydroxy-3-methoxyphenyl)ethanone**C₉H₉N₂O₃ mol.wt. 193.28**Synthesis**

-Preparation by reaction of potassium hydroxide with 4-acetoxy-3-methoxy- α -diazoacetophenone (m.p. 92-93°) in methanol at 20° for 15 h (quantitative yield) [454].

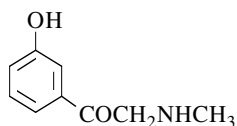
amorphous solid [454].

2-Azido-1-(4-hydroxy-3-methoxyphenyl)ethanoneC₉H₉N₃O₃ mol.wt. 207.19**Synthesis**

-Obtained by reaction of 4-hydroxy-3-methoxy- α -chloroacetophenone with an alkali metal azide in dilute alcohols (C₁-C₅) [1305].

1-(3-Hydroxyphenyl)-2-(methylamino)ethanone (Phenylephrine)

[52093-42-2]

C₉H₁₁NO₂ mol.wt. 165.19**Syntheses**

-Preparation by reductive condensation of m-hydroxyphenyl-glyoxal with methylamine in ethanol under saturated hydrogen atmosphere in the presence of Raney nickel at 45° (55%) [503].

-Also obtained by action of potassium N-methyl-p-toluenesulfonate

sulfonamide with m-acetoxy- α -bromoacetophenone in acetone during some hours. Then, the resulting intermediate compound (m.p. 120-121°) was treated with boiling 55% aqueous hydriodic acid for 1 h [898] [901] [1400].

-Also obtained by reaction of methylamine with α -bromo-m-benzoyloxyacetophenone in isopropanol, and subsequent treatment with aqueous hydrochloric acid [1030].

-Also obtained by reaction of methylamine with α -bromo-m-hydroxyacetophenone in dilute ethanol [900] [897].

-Also refer to: [37] [572] [577] [850].

m.p. 135° [898] [901] [1400], 128° [503].

1-(3-Hydroxyphenyl)-2-(methylamino)ethanone (*Hydrochloride*)

[94240-17-2]

C₉H₁₁NO₂, HCl mol.wt. 201.65



Syntheses

-Preparation by conversion of the base with 35% ethanolic hydrogen chloride [503].

-Also obtained by hydrogenolysis of 2-(benzyl-methylamino)-1-(3-hydroxyphenyl)ethanone hydrochloride with

hydrogen in the presence of Pd-black in ethanol [37].

-Also refer to: [228] [898].

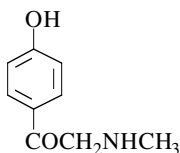
m.p. 238° [897] [900], 234° [503] [898] [901] [1400];

IR [37].

1-(4-Hydroxyphenyl)-2-(methylamino)ethanone

[21213-89-8]

C₉H₁₁NO₂ mol.wt. 165.19



Syntheses

-Preparation by reductive condensation of p-hydroxyphenylglyoxal with methylamine in ethanol under saturated hydrogen atmosphere in the presence of Raney nickel at 45° [503].

-Also obtained by reductive condensation of p-hydroxyphenylglyoxal potassium bisulfite (C₈H₇O₆SK, preparation

given) with methylamine in dilute ethanol under saturated hydrogen atmosphere and cooling with ice (71%) [503].

-Also obtained by reduction of potassium 2-(4-hydroxyphenyl)-2-oxo-1-methylaminoethane sulfonate (C₉H₁₀NO₅SK, preparation given) in dilute ethanol with hydrogen in the presence of Raney nickel (65%) [503].

-Also obtained by reaction of potassium N-methyl-p-toluenesulfonamide with p-acetoxy- α -bromoacetophenone in acetone during some hours. Then, the resulting intermediate compound was treated with boiling 55% aqueous hydriodic acid for 1 h [898].

-Also obtained by degradation of p-toluenesulfonamide (prepared from α -methylamino-p-methoxyacetophenone) on heating with 37% hydrochloric acid for 2 h at 150° under carbon dioxide [797].

-Also obtained by treatment of p-hydroxy- α -bromoacetophenone in ethanol with a 40% methylamine solution, first in an ice bath, then at r.t. overnight [899].

-Also obtained by reaction of methylaminoacetonitrile with phenol (Houben-Hoesch reaction) (75%) [89].

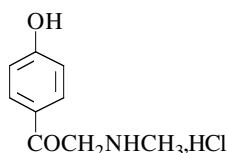
-Also refer to: [228] [327] [572].

m.p. 148° [898], 147-148° [899], 147° [503] [797], 142-144° (d) [89];

pK_B [555].

1-(4-Hydroxyphenyl)-2-(methylamino)ethanone (*Hydrochloride*)

[67828-68-6]

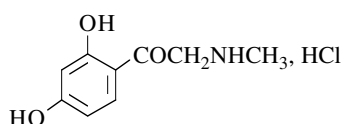
C₉H₁₁NO₂, HCl mol.wt. 201.65

Syntheses

- Obtained by reaction of hydrochloric acid with the corresponding base [797], (83%) [89], (50%) [327].
- Also obtained by treatment of its oxalate (m.p. 166°) with ethanolic hydrogen chloride (72%) [503].
- Also obtained by reaction of methylaminoacetonitrile

hydrochloride with phenol (Hoesch reaction) (88%) [1017].
 -Also refer to: [30] [31] [32] [898].

m.p. 261-263° (d) (pure) [327], 244-246° [1017], 242-244° (d) [89],
 242° (d) [797], 241-243° (d) [327], 239-240° [899], 238-240° [898],
 238-239° [503].

1-(2,4-Dihydroxyphenyl)-2-(methylamino)ethanone (*Hydrochloride*)C₉H₁₁NO₃, HCl mol.wt. 217.65

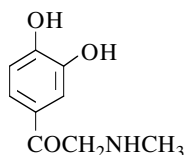
Synthesis

- Preparation by successively adding methylaminoacetonitrile hydrochloride and resorcinol to a solution of aluminium chloride in nitrobenzene, then bubbling hydrogen chloride for 6-8 h through the reaction mixture at 20-30° (73%) [1017].

m.p. 265-267° [1017].

1-(3,4-Dihydroxyphenyl)-2-(methylamino)ethanone (*Adrenalone*)

[99-45-6]

C₉H₁₁NO₃ mol.wt. 181.19

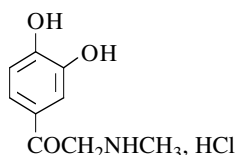
Syntheses

- Preparation by reaction of excess 33% aqueous methylamine with 3,4-dihydroxy- α -chloroacetophenone [356].
- Preparation by adding an aqueous solution of 40% methylamine to an ethanolic solution of 3,4-dihydroxy- α -chloroacetophenone. Then, adding of ammonia to a solution of recrystallized hydrochloride so formed, (71-73%) [1233], (62%) [1404].
- Preparation by reductive condensation of 3,4-dihydroxyphenylglyoxal with methylamine in ethanol under hydrogen atmosphere in the presence of 14% Pd/C [503].
- Also obtained by degradation of p-toluenesulfonamide, prepared from 3,4-dimethoxy- α -methylaminoacetophenone, with refluxing 37% hydrochloric acid (150-160°) for 2 h under carbon dioxide [797].
- Also obtained by treatment of 3,4-diacetoxy- α -chloroacetophenone (m.p. 110°) with 30% methylamine solution (good yield, not specified) [1510].
- Also refer to: [222] [357] [572] [586] [588] [850] [932] [1018] [1207].

m.p. 232° [356], 230° [1404], 229° (d) [797], 215° (d) [139];
 UV [1262] [1454]; pK_B [555] [1226];
 micellar liquid chromatography [1462] [1506] [1508]; electrophoresis [663].

1-(3,4-Dihydroxyphenyl)-2-(methylamino)ethanone (*Hydrochloride*) (*Stryphnon*)

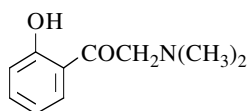
[62-13-5]

C₉H₁₁NO₃, HCl mol.wt. 217.65

Syntheses

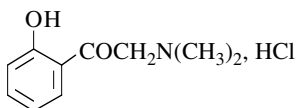
- Obtained by action of hydrochloric acid on 3,4-dihydroxy- α -methylaminoacetophenone (65%) [1233], in methanol [797] [1404].
- Also obtained (poor yield) from the base by saturation of its aqueous solution with hydrogen chloride (7%) [503].
- Also refer to: [31] [32] [228] [356].

m.p. 248° [555], 241° (d) [503] [797], 240° (d) [1404], 237-243° (d) [139];
UV [1018].

2-(Dimethylamino)-1-(2-hydroxyphenyl)ethanoneC₁₀H₁₃NO₂ mol.wt. 179.22

Synthesis

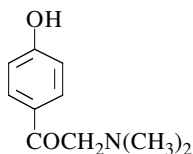
- Obtained by adding a solution of dimethylamine (2 mol) in ethyl ether to a cold solution of o-hydroxy- α -chloroacetophenone (m.p. 71-71.5°) (1 mol) and sodium iodide (1 mol) in acetone. The mixture was then allowed to stand for 14 h at 0° [906].

2-(Dimethylamino)-1-(2-hydroxyphenyl)ethanone (*Hydrochloride*)C₁₀H₁₃NO₂, HCl mol.wt. 215.69

Synthesis

- Obtained by adding of ethanolic hydrochloric acid to a solution of the corresponding base in acetone (61%) [906].

m.p. 105-107° [906].

2-(Dimethylamino)-1-(4-hydroxyphenyl)ethanoneC₁₀H₁₃NO₂ mol.wt. 179.22

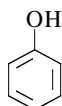
Syntheses

- Obtained by adding a solution of dimethylamine (2 mol) in ethyl ether to a cold solution of p-hydroxy- α -chloroacetophenone (m.p. 151-152°) (1 mol) and sodium iodide (1 mol) in acetone. The mixture was then allowed to stand for 14 h at 0° [906].
- Also obtained by hydrolysis of 1-[4-(benzoyloxy)phenyl]-2-dimethylaminoethanone with aqueous hydrochloric acid [227].
- Also obtained by reaction of dimethylamine with p-(benzoyloxy)- α -bromoacetophenone in isopropanol [327].
- Also refer to: [1482].

m.p. 142° [1482].

2-(Dimethylamino)-1-(4-hydroxyphenyl)ethanone (Hydrochloride)

[2970-79-8]

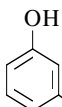
C₁₀H₁₃NO₂, HCl mol.wt. 215.69COCH₂N(CH₃)₂,HCl**Syntheses**

- Obtained by reaction of dimethylamine with p-acetoxy- α -bromoacetophenone in benzene, followed by treatment with dilute hydrochloric acid [512].
- Also obtained by reaction of dimethylamine with p-benzoyloxy- α -bromoacetophenone in isopropanol [327] or in benzene [227] and subsequent treatment with hydrochloric acid (88%) [227], (47%) [327].
- Also obtained by adding ethanolic hydrochloric acid to a solution of the corresponding base in acetone (43%) [906].
- Also refer to: [511].

m.p. 242-243° [906], 235° [512], 234-237° [227], 233-235° [327].

2-(Ethylamino)-1-(3-hydroxyphenyl)ethanone

[22510-12-9]

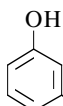
C₁₀H₁₃NO₂ mol.wt. 179.22COCH₂NHC₂H₅**Syntheses**

- Preparation by reductive condensation of 3-hydroxyphenylglyoxal with ethylamine in ethanol under saturated hydrogen atmosphere in the presence of Raney nickel at 45° (49%) [503].
- Also obtained by reaction of ethylamine with 1-(3-acetoxyphenyl)-2-bromoethanone in aqueous isopropanol [578].

m.p. 203-205° [503].

2-(Ethylamino)-1-(3-hydroxyphenyl)ethanone (Hydrochloride)

[22510-04-9]

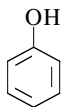
C₁₀H₁₃NO₂, HCl mol.wt. 215.69COCH₂NHC₂H₅,HCl**Syntheses**

- Preparation by crystallization of the base in 2 N hydrochloric acid [503].
- Also obtained by reaction of 40% ethylamine solution with m-acetoxy- α -bromoacetophenone in isopropanol, first at 0°, then at 40° for 10 min, followed by treatment with hydrochloric acid [578].

m.p. 221-222° [503], 212-215° (d) [578].

2-(Ethylamino)-1-(4-hydroxyphenyl)ethanone

[99075-26-0]

C₁₀H₁₃NO₂ mol.wt. 179.22COCH₂NHC₂H₅**Syntheses**

- Preparation by reductive condensation of 4-hydroxyphenylglyoxal with ethylamine in ethanol under saturated hydrogen atmosphere in the presence of Raney nickel at 45° [503].
- Also obtained by reductive condensation of 4-hydroxyphenylglyoxal potassium bisulfite (C₈H₇O₆SK, preparation given) with ethylamine [503].

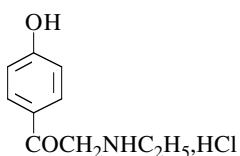
-Also obtained by reaction of ethylamine with 1-[4-(benzoyloxy)phenyl]-2-bromoethanone in isopropanol [327].

$pK_B = 6.23$ [555].

2-(Ethylamino)-1-(4-hydroxyphenyl)ethanone (Hydrochloride)

[74730-79-3]

$C_{10}H_{13}NO_2, HCl$ mol.wt. 215.69



Syntheses

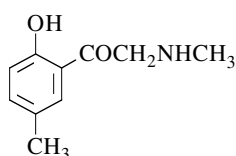
-Preparation by treatment of the oxalate with 28% ethanolic hydrogen chloride (65%) [503].
-Also obtained by reaction of α -bromo-p-benzoyloxy-acetophenone with ethylamine in isopropanol and subsequent treatment with hydrochloric acid (51%) [327].

m.p. 228-231° (d) [327], 221° [503].

1-(2-Hydroxy-5-methylphenyl)-2-(methylamino)ethanone

$C_{10}H_{13}NO_2$

mol.wt. 179.22



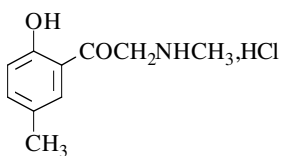
Synthesis

-Preparation by hydrogenolysis of 2-(benzylmethylamino)-1-(2-hydroxy-5-methylphenyl)ethanone with hydrogen in the presence of Pd/C as catalyst [67].

1-(2-Hydroxy-5-methylphenyl)-2-(methylamino)ethanone (Hydrochloride)

$C_{10}H_{13}NO_2, HCl$

mol.wt. 215.69



Synthesis

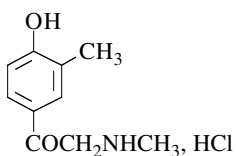
-Obtained by hydrogenolysis of 2-(benzyloxy)-5-methyl-N-benzylmethylaminoacetophenone hydrochloride or of 2-hydroxy-5-methyl-N-benzylmethylaminoacetophenone hydrochloride with hydrogen in the presence of Pd/C in 95% ethanol [67].

m.p. 204-206° [67].

1-(4-Hydroxy-3-methylphenyl)-2-(methylamino)ethanone (Hydrochloride)

$C_{10}H_{13}NO_2, HCl$

mol.wt. 215.69



Synthesis

-Preparation by successively adding methylaminoacetonitrile hydrochloride and o-cresol to a solution of aluminium chloride in nitrobenzene, then bubbling hydrogen chloride for 6-8 h through the reaction mixture at 20-30° (90%) [1017].

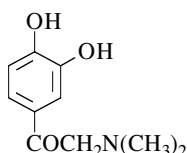
m.p. 237-238° [1017].

1-(3,4-Dihydroxyphenyl)-2-(dimethylamino)ethanone

[150-10-7]

C₁₀H₁₃NO₃

mol.wt. 195.22

**Syntheses**

- Preparation by reaction of 3,4-dihydroxy- α -chloroacetophenone with dimethylamine [1151] [1152], in ethanol at 40° for 75 min [229] [230] or at 60° for 5 h [869].
- Also obtained by action of sodium ethoxide with N-methyl-adrenalone hydrochloride in boiling ethanol (72-74%) [1233].

-Also obtained by demethylation of 2-dimethylamino-1-(3-hydroxy-4-methoxyphenyl)ethanone with concentrated aqueous hydrochloric acid at 130° [1275].

-Also obtained by reaction of dimethylamine with α -chloro-3-acetoxy-4-hydroxyacetophenone in aqueous ethanol [1361].

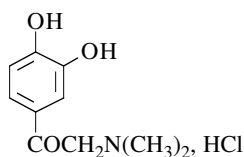
m.p. >130° (d) [1233].

1-(3,4-Dihydroxyphenyl)-2-(dimethylamino)ethanone (Hydrochloride)

[16899-83-5]

C₁₀H₁₃NO₃, HCl

mol.wt. 231.69

**Syntheses**

- Preparation by reaction of the corresponding base (SM) with hydrogen chloride in ethanol, [1151], (66%) [869], (62%) [588], (54%) [1275], (50%) [229] [230]. SM was obtained by reaction of 3,4-dihydroxy- α -chloroacetophenone with concentrated aqueous dimethylamine.

-Direct preparation by reaction of 3,4-dihydroxy- α -chloroacetophenone with dimethylamine in methanol for 20-30 min at < 5° (73-76%) [1233] or in absolute ethanol for 2 h at 60° (45%) [1152].

-Also obtained by treatment of 3,4-dimethoxy- α -dimethylaminoacetophenone (SM) with concentrated hydrochloric acid for 2.5 h at 150-160° in a sealed tube (41%) [1274] or for 2 h at 130° (25%) [1275]. SM was prepared by reaction of 3,4-dimethoxy- α -chloroacetophenone with dimethylamine in benzene at r.t. overnight (91%, b.p. 155-157°) [1274].

-Also obtained by treatment of 3-hydroxy-4-methoxy- α -dimethylaminoacetophenone with concentrated hydrochloric acid for 2 h at 130°, (65%) [1275].

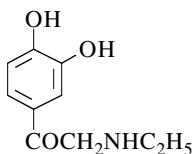
-Also refer to: [228].

m.p. 236-237° (d) [229] [230], 234-236° (d) [588] [1233], 232° (d) [1274], 231-232° (d) [1275], 225-227° (d) [1151] [1152], 213-214° [869].

One note a very large dispersion of the various melting points. ¹H NMR [1152], IR [1152].

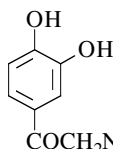
1-(3,4-Dihydroxyphenyl)-2-(ethylamino)ethanoneC₁₀H₁₃NO₃

mol.wt. 195.22

**Syntheses**

- Obtained by adding an aqueous solution of 40% ethylamine to an ethanolic solution of α -chloro-3,4-dihydroxyacetophenone, then adding ammonia in a solution of the recrystallized hydrochloride so formed (50%) [1404].
- Also refer to: [357].

m.p. 185° [1404]; pK_B [555].

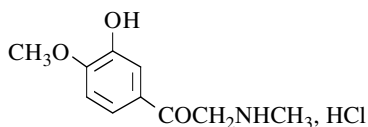
1-(3,4-Dihydroxyphenyl)-2-(ethylamino)ethanone (Hydrochloride)C₁₀H₁₃NO₃, HCl mol.wt. 231.69**Syntheses**

-Obtained by condensation of 3,4-dihydroxy- α -chloroacetophenone with ethylamine in ethanol or isopropanol at 60-80°. The amino ketone base which separated was treated with concentrated hydrochloric acid [328].

-Also obtained by total demethylation of 1-(3,4-dimethoxyphenyl)-2-(ethylamino)ethanone hydrochloride (m.p. 190-192°), (71%) [1018] according to [1017].

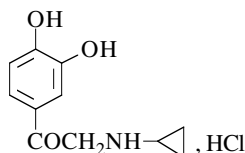
m.p. 260° (d) [1404], 255-257° (d) [1018], 240-242° (d) [328].

One of the reported melting points is obviously wrong.

1-(3-Hydroxy-4-methoxyphenyl)-2-(methylamino)ethanone (Hydrochloride)C₁₀H₁₃NO₃, HCl mol.wt. 231.69**Synthesis**

-Preparation by successively adding methylaminoacetonitrile hydrochloride and guaiacol to a solution of aluminium chloride in nitrobenzene, then bubbling hydrogen chloride for 6-8 h through the reaction mixture at 20-30° (25%) [1017].

m.p. 230-230°5 [1017].

2-(Cyclopropylamino)-1-(3,4-dihydroxyphenyl)ethanone (Hydrochloride)C₁₁H₁₃NO₃, HCl mol.wt. 243.69**Synthesis**

-Obtained (poor yield) by treatment of cyclopropylamine salt of 4-chloroacetylcatechol (m.p. 95-97°) in refluxing isopropanol under nitrogen for 3 h. The formed free base in methanol was treated with ethanolic hydrochloric acid [1446].

m.p. 200-204° [1446].

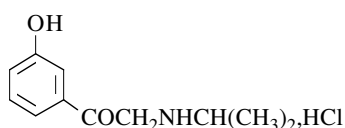
1-(3-Hydroxyphenyl)-2-[(1-methylethyl)amino]ethanoneC₁₁H₁₅NO₂ mol.wt. 193.25**Syntheses**

-Preparation by reductive condensation of 3-hydroxyphenylglyoxal with isopropylamine in ethanol under saturated hydrogen atmosphere in the presence of Raney nickel at 45° [503].

-Also obtained by reaction of isopropylamine with α -bromo-m-hydroxyacetophenone in ethanol [329].

1-(3-Hydroxyphenyl)-2-[(1-methylethyl)amino]ethanone (Hydrochloride)

[101241-90-1]

C₁₁H₁₅NO₂, HCl mol.wt. 229.71

Syntheses

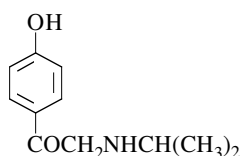
- Preparation by conversion of the oxalate in 28% ethanolic hydrogen chloride (35%) [503].
- Also obtained by [329] according to [327] [328].

m.p. 226-227° [503], 213-216° [329].

One of the reported melting points is obviously wrong.

1-(4-Hydroxyphenyl)-2-[(1-methylethyl)amino]ethanone

[99985-57-6]

C₁₁H₁₅NO₂ mol.wt. 193.25

Syntheses

- Preparation by reductive condensation of 4-hydroxyphenylglyoxal with isopropylamine in ethanol under saturated hydrogen atmosphere in the presence of Raney nickel at 45° (86%) [503].
- Also obtained by reductive condensation of 4-hydroxyphenylglyoxal potassium bisulfite (C₈H₇O₆SK, preparation given) with isopropylamine [503].
- Also obtained by reaction of isopropylaminoacetonitrile with benzyl phenyl ether (m.p. 39-41°) [1017] or with phenol [89] in the presence of aluminium chloride and hydrogen chloride in nitrobenzene.
- Also obtained by reaction of isopropylamine with α-bromo-4-benzoyloxyacetophenone in isopropanol [327].
- Also refer to: [1375].

m.p. 120-121° [503]; pK_B [555] [910].**1-(4-Hydroxyphenyl)-2-[(1-methylethyl)amino]ethanone (Hydrochloride)**

[69716-74-1]

C₁₁H₁₅NO₂, HCl mol.wt. 229.71

Syntheses

- Preparation from the base with aqueous hydrochloric acid (84%) [503].
- Also obtained by reaction of α-bromo-p-benzoyloxyacetophenone with isopropylamine in isopropanol between 20 to 30° for 2 h, then treatment of the formed base with refluxing 15% hydrochloric acid solution (64%) [327].
- Also obtained by reaction of isopropylaminoacetonitrile hydrochloride (m.p. 166-167°),
- *with phenol (Houben-Hoesch reaction) (61%) [89], (42%) [1375];
- *with phenyl benzyl ether in the presence of aluminium chloride in nitrobenzene at 20 to 30°, then bubbling hydrogen chloride for 6 h (39%) [1017].

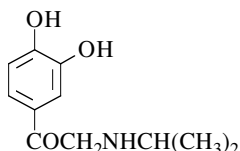
m.p. 272-273° (d) [1017], 263° (d) [1375], 258-260° (d) [89], 250-252° [327], 248-249° [503]. One note a very large dispersion of the various melting points.

1-(3,4-Dihydroxyphenyl)-2-[(1-methylethyl)amino]ethanone (*Isoproterenone*)

[121-28-8]

C₁₁H₁₅NO₃

mol.wt. 209.25



Syntheses

-Obtained by reductive condensation of 3,4-dihydroxy-phenylglyoxal with isopropylamine in ethanol under hydrogen atmosphere in the presence of 14% Pd/C [503].
N.B.: In the same manner, the substance can also be obtained from 3,4-bis(benzyloxy)phenylglyoxal [502].

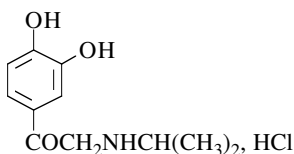
-Also obtained by reaction of 3,4-dihydroxy- α -chloroacetophenone with excess isopropylamine in refluxing ethanol for 2.5 h (76%) [1197].
 -Also obtained from the corresponding sulfate by action of a hot sodium bicarbonate aqueous solution (60°) (80%) [228].
 -Also obtained by treatment of the corresponding hydrochloride in concentrated aqueous solution at 0° with ammonia [153].

m.p. 173° [228], 168-169° [1197], 96° [153]. One of the reported melting points is obviously wrong. pK_B [555];

¹H NMR [1197], IR [1197], UV [1197].

1-(3,4-Dihydroxyphenyl)-2-[(1-methylethyl)amino]ethanone (*Hydrochloride*)

[16899-81-3]

C₁₁H₁₅NO₃, HCl mol.wt. 245.71

Syntheses

-Obtained by condensation of α -chloro-3,4-dihydroxy-acetophenone with isopropylamine [667] in isopropanol at 65-70°. The amino ketone which separated was treated with concentrated hydrochloric acid (54%) [328], (46%) [727].
 -Also obtained by demethylation of 3-methoxy-4-hydroxy-

α -isopropylaminoacetophenone hydrochloride with concentrated hydrochloric acid at 140° for 6 h in a sealed tube (73%) [153].

-Also refer to: [224] [1008] [1009] [1017].

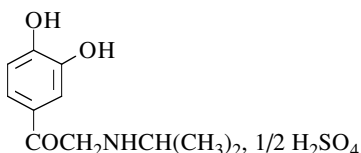
m.p. 257-259° [1017], 255-257° [153], 239-242° (d) [328] [727].

One of the reported melting points is obviously wrong.

¹H NMR [727], ¹³C NMR [727], UV [1018].

1-(3,4-Dihydroxyphenyl)-2-[(1-methylethyl)amino]ethanone (*Sulfate*)

[27693-62-5]

C₁₁H₁₅NO₃, 1/2 H₂SO₄ mol.wt. 258.28

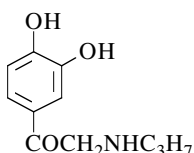
Synthesis

-Preparation by reaction of 5 N ethanolic sulfuric acid with the crude base (58%) [503].

m.p. 243° [503].

1-(3,4-Dihydroxyphenyl)-2-(propylamino)ethanoneC₁₁H₁₅NO₃

mol.wt. 209.25

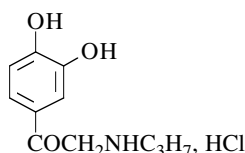
**Syntheses**

- Obtained by condensation of α -chloro-3,4-dihydroxyacetophenone with propylamine in ethanol or isopropanol at 60-80° [328].
- Also obtained by treatment of 1-(3,4-dimethoxyphenyl)-2-(propylamino)ethanone with aqueous hydrobromic acid [1018].

pK = 6.2 [555].

1-(3,4-Dihydroxyphenyl)-2-(propylamino)ethanone (Hydrochloride)C₁₁H₁₅NO₃, HCl

mol.wt. 245.71

**Syntheses**

- Obtained by condensation of α -chloro-3,4-dihydroxyacetophenone with propylamine in ethanol or isopropanol at 60-80°. The amino base which separated was treated with concentrated hydrochloric acid [328].
- Also obtained by total demethylation of 1-(3,4-dimethoxyphenyl)-2-(propylamino)ethanone hydrochloride (m.p. 193-194°), (82%) [1018] according to [1017].

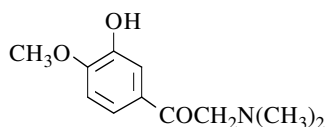
m.p. 240-241° (d) [1018], 234-236° (d) [328].

2-(Dimethylamino)-1-(3-hydroxy-4-methoxyphenyl)ethanone

[55761-48-3]

C₁₁H₁₅NO₃

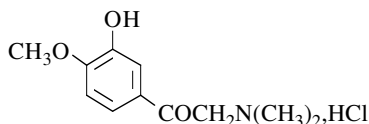
mol.wt. 209.25

**Synthesis**

- Obtained by reaction of dimethylamine with α -chloro-3-hydroxy-4-methoxyacetophenone in benzene [1275].

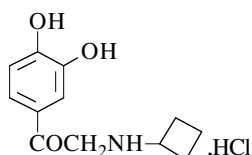
2-(Dimethylamino)-1-(3-hydroxy-4-methoxyphenyl)ethanone (Hydrochloride)C₁₁H₁₅NO₃, HCl

mol.wt. 245.71

**Synthesis**

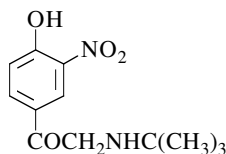
- Obtained by reaction of α -chloro-3-hydroxy-4-methoxyacetophenone with dimethylamine in benzene, first at r.t. overnight, then at 50-60° for 1 h, followed by treatment of the isolated base with hydrochloric acid in ethyl ether (41%) [1275].

m.p. 220-221° (d) [1275].

2-(Cyclobutylamino)-1-(3,4-dihydroxyphenyl)ethanone (Hydrochloride)C₁₂H₁₅NO₃, HCl mol.wt. 257.72**Synthesis**

-Obtained by treatment of 4-chloroacetylcatechol cyclobutylamine salt (m.p. 100-104°) in refluxing isopropanol for 3 h (21%) or in a sealed tube at 100° for 1.5 h (28%) [1446].

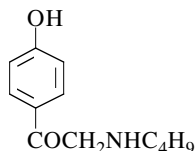
m.p. 225-228° [1446]; IR [1446], UV [1446].

2-[(1,1-Dimethylethyl)amino]-1-(4-hydroxy-3-nitrophenyl)ethanoneC₁₂H₁₆N₂O₄ mol.wt. 252.27**Synthesis**

-Obtained by reaction of aqueous nitric acid with α-tert-butylamino-p-hydroxyacetophenone [1176].

2-(Butylamino)-1-(4-hydroxyphenyl)ethanone

[18986-11-3]

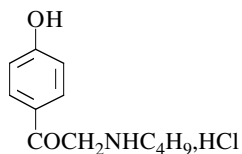
C₁₂H₁₇NO₂ mol.wt. 207.27**Syntheses**

- Preparation by reductive condensation of 4-hydroxyphenylglyoxal with n-butylamine in ethanol under saturated hydrogen chloride atmosphere in the presence of Raney nickel at 45° (75%) [503].
- Also obtained by reductive condensation of 4-hydroxyphenylglyoxal potassium bisulfite (C₈H₇O₆SK, preparation given) with n-butylamine (85%) [503].
- Also obtained by reaction of n-butylamine with α-bromo-p-benzoyloxyacetophenone in isopropanol [327].
- Also obtained by reaction of n-butylaminoacetonitrile with phenol in the presence of aluminium chloride and hydrogen chloride in nitrobenzene [834] [1017].
- Also obtained from the corresponding hydrochloride with ammonia [834].

m.p. 119-120° [503] [834]; pK_B = 5.45 [555].

2-(Butylamino)-1-(4-hydroxyphenyl)ethanone (Hydrochloride)

[28836-20-6]

C₁₂H₁₇NO₂, HCl mol.wt. 243.73**Syntheses**

- Preparation from the base with hydrochloric acid (92%) [503].
- Preparation by reaction of n-butylaminoacetonitrile hydrochloride (m.p. 101-102°5) [1017], (m.p. 95-96°) [834] with phenol in nitrobenzene in the presence of hydrogen chloride and aluminium chloride as catalyst

(Houben-Hoesch reaction), (78%) [1017], (66%) [834].

-Also obtained by reaction of α -bromo-p-benzoyloxyacetophenone with n-butylamine in isopropanol and subsequent treatment with hydrochloric acid (44%) [327].

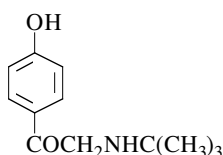
m.p. 231° [503] [834], 228-230° [1017], 228-229° [327].

2-[(1,1-Dimethylethyl)amino]-1-(4-hydroxyphenyl)ethanone

[60853-18-1]

C₁₂H₁₇NO₂

mol.wt. 207.27



Syntheses

-Obtained by reaction of tert-butylamine with α -bromo-p-benzoyloxyacetophenone in isopropanol [327].
-Also obtained by reaction of tert-butylaminoacetonitrile hydrochloride with phenol in the presence of aluminium chloride and hydrogen chloride in nitrobenzene (modified Hoesch reaction) [1017] [1375].

-Also refer to: [835].

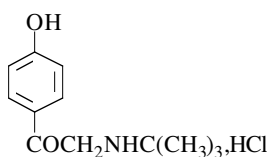
pK_B = 6.1 [555].

2-[(1,1-Dimethylethyl)amino]-1-(4-hydroxyphenyl)ethanone (Hydrochloride)

[41489-87-6]

C₁₂H₁₇NO₂, HCl

mol.wt. 243.73



Syntheses

-Preparation by successively adding tert-butylaminoacetonitrile hydrochloride and phenol to a solution of aluminium chloride in nitrobenzene, then bubbling hydrogen chloride for 6-8 h through the reaction mixture at 20-30° (75%) [1017], (63%) [1375].

-Also obtained by reaction of α -bromo-p-benzoyloxyacetophenone with tert-butylamine in isopropanol and subsequent treatment with hydrochloric acid to complete hydrolysis (25%) [327].
-Also refer to: [835].

m.p. 268-270° (d) [835] [1017], 254-257° (d) [327], 253-255° [1375].

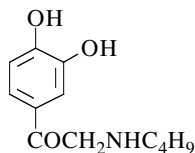
One of the reported melting points is obviously wrong.

2-(Butylamino)-1-(3,4-dihydroxyphenyl)ethanone

[33406-44-9]

C₁₂H₁₇NO₃

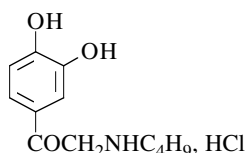
mol.wt. 223.27



Synthesis

-Obtained by condensation of α -chloro-3,4-dihydroxyacetophenone with butylamine in ethanol or isopropanol at 60-80° [328].

pK_B [555].

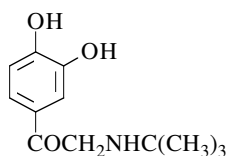
2-(Butylamino)-1-(3,4-dihydroxyphenyl)ethanone (Hydrochloride)C₁₂H₁₇NO₃, HCl mol.wt. 259.73**Synthesis**

-Obtained by condensation of α -chloro-3,4-dihydroxyacetophenone with butylamine in ethanol or isopropanol at 60-80°. The amino base which separated was treated with concentrated hydrochloric acid [328].

m.p. 206-208° (d) [328].

1-(3,4-Dihydroxyphenyl)-2-[(1,1-dimethylethyl)amino]ethanone

[105644-17-5]

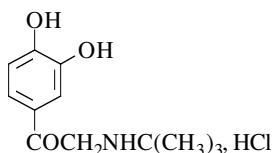
C₁₂H₁₇NO₃ mol.wt. 223.27**Syntheses**

-Preparation by demethylation of 2-tert-butylamino-1-(3,4-dimethoxyphenyl)ethanone hydrochloride with aqueous hydrobromic acid [1017].
 -Also obtained by reaction of tert-butylamine with 2-chloro-1-(3,4-dihydroxyphenyl)ethanone in dioxane [328].
 -Also refer to: [643] [1006].

m.p. 199-201° [643]; pK_B [555].

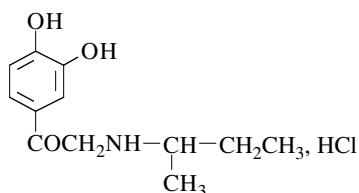
1-(3,4-Dihydroxyphenyl)-2-[(1,1-dimethylethyl)amino]ethanone (Hydrochloride)

[34715-64-5]

C₁₂H₁₇NO₃, HCl mol.wt. 259.73**Syntheses**

-Obtained by condensation of α -chloro-3,4-dihydroxyacetophenone with tert-butylamine in dioxane at 60-80°. The amino ketone base which separated was treated with concentrated hydrochloric acid [328].
 -Also refer to: [1007] [1008] [1009].

m.p. 233-235° (d) [328].

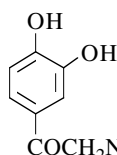
1-(3,4-Dihydroxyphenyl)-2-[(1-methylpropyl)amino]ethanone (Hydrochloride)C₁₂H₁₇NO₃, HCl mol.wt. 259.73**Synthesis**

-Obtained by condensation of α -chloro-3,4-dihydroxyacetophenone with sec-butylamine in ethanol or isopropanol at 60-80°. The amino base which separated was treated with concentrated hydrochloric acid [328].

m.p. 226-227° [328].

1-(3,4-Dihydroxyphenyl)-2-[(2-methylpropyl)amino]ethanoneC₁₂H₁₇NO₃

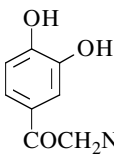
mol.wt. 223.27

**Synthesis**

-Obtained by condensation of α -chloro-3,4-dihydroxyacetophenone with isobutylamine in ethanol or isopropanol at 60-80° [328].

pK_B = 6.52 [555].**1-(3,4-Dihydroxyphenyl)-2-[(2-methylpropyl)amino]ethanone (Hydrochloride)**C₁₂H₁₇NO₃, HCl

mol.wt. 259.73

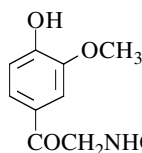
**Synthesis**

-Obtained by condensation of α -chloro-3,4-dihydroxyacetophenone with isobutylamine in ethanol or isopropanol at 60-80°. The amino ketone base which separated was treated with concentrated hydrochloric acid [328].

m.p. 214-216° [328].

1-(4-Hydroxy-3-methoxyphenyl)-2-[(1-methylethyl)amino]ethanone (Hydrochloride)C₁₂H₁₇NO₃, HCl

mol.wt. 259.73

**Synthesis**

-Preparation by treatment of the corresponding oxalate (SM) with 26% ethanolic hydrogen chloride (61% yield). SM was obtained in two steps. First, gradual addition of a 3-methoxy-4-hydroxyphenylglyoxal potassium bisulfite and isopropylamine solution in dilute ethanol to a suspension of Raney nickel in 84% ethanol maintained

at 45° under excess hydrogen. Then, after catalyst elimination, addition of oxalic acid to the obtained solution [153].

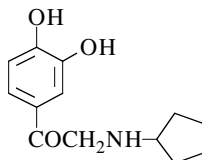
m.p. 236° (d) [153].

2-(Cyclopentylamino)-1-(3,4-dihydroxyphenyl)ethanone

[16149-16-9]

C₁₃H₁₇NO₃

mol.wt. 235.28

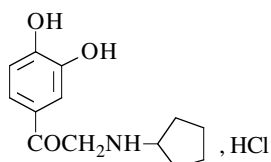
**Synthesis**

-Obtained by condensation of α -chloro-3,4-dihydroxyacetophenone with cyclopentylamine in ethanol or isopropanol at 60-80° [328] or in boiling isopropanol for 30 min (98%) [1446].

hemihydrate: m.p. 182° [1446]; UV [1446].

2-(Cyclopentylamino)-1-(3,4-dihydroxyphenyl)ethanone (Hydrochloride)

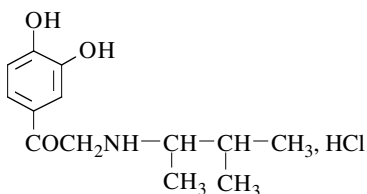
[16149-17-0]

C₁₃H₁₇NO₃, HCl mol.wt. 271.74**Syntheses**

-Obtained by condensation of α -chloro-3,4-dihydroxyacetophenone with cyclopentylamine in ethanol or isopropanol at 60-80°. The amino ketone base which separated was treated with concentrated hydrochloric acid [328].

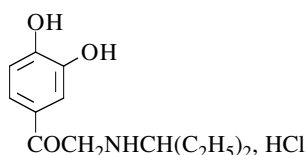
-Obtained by reaction of N-cyclopentylnoradrenalone with hydrochloric acid (44%) [1446].

m.p. 213-214° (d) [328], 205-207° [1446].

1-(3,4-Dihydroxyphenyl)-2-(1,2-dimethylpropylamino)ethanone (Hydrochloride)C₁₃H₁₉NO₃, HCl mol.wt. 273.76**Synthesis**

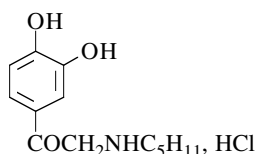
-Obtained by condensation of α -chloro-3,4-dihydroxyacetophenone with 1,2-dimethylpropylamine in ethanol or isopropanol at 60-80°. The amino ketone base which separated was treated with concentrated hydrochloric acid [328].

m.p. 231-233° [328].

1-(3,4-Dihydroxyphenyl)-2-(1-ethylpropylamino)ethanone (Hydrochloride)C₁₃H₁₉NO₃, HCl mol.wt. 273.76**Synthesis**

-Obtained by condensation of α -chloro-3,4-dihydroxyacetophenone with 1-ethylpropylamine in methanol or isopropanol at 60-80°. The amino ketone base which separated was treated with concentrated hydrochloric acid [328].

m.p. 198-201° [328].

1-(3,4-Dihydroxyphenyl)-2-(pentylamino)ethanone (Hydrochloride)C₁₃H₁₉NO₃, HCl mol.wt. 273.76**Synthesis**

-Obtained by condensation of α -chloro-3,4-dihydroxyacetophenone with pentylamine in ethanol or isopropanol at 60-80°. The amino ketone base which separated was treated with concentrated hydrochloric acid [328].

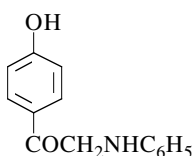
m.p. 201-202° (d) [328].

1-(4-Hydroxyphenyl)-2-(phenylamino)ethanone

[100866-41-9]

C₁₄H₁₃NO₂

mol.wt. 227.26

**Syntheses**

-Preparation by adding aniline (0.1 ml) and rhodium (II) acetate dimer (2 mg) to a suspension of resin **6** (52 mg) in benzene and the mixture stirred at 85° for 2 h. The compound was isolated and purified by preparative TLC (51%) [682].

N.B.: Resin **6** (resin-bound α -TMS diazoketone **6**) (preparation given).
-Also refer to: [1349].

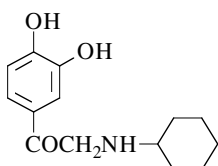
¹H NMR [682], ¹³C NMR [682], IR [682], MS [682].

2-(Cyclohexylamino)-1-(3,4-dihydroxyphenyl)ethanone

[16149-18-1]

C₁₄H₁₉NO₃

mol.wt. 249.31

**Syntheses**

-Obtained by condensation of α -chloro-3,4-dihydroxyacetophenone with cyclohexylamine in ethanol or isopropanol at 60-80° [328] or in boiling isopropanol for 30 min [1446].

-Also obtained by reaction of 3,4-diacetoxy- α -iodoacetophenone with cyclohexylamine in the presence of

potassium carbonate in boiling acetone for 4 h (24%) [1446].

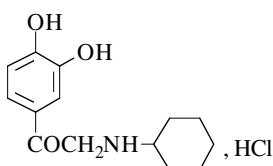
hemihydrate [1446]; m.p. 187-188° [1446]; IR [1446], UV [1446].

2-(Cyclohexylamino)-1-(3,4-dihydroxyphenyl)ethanone (Hydrochloride)

[16149-19-2]

C₁₄H₁₉NO₃, HCl

mol.wt. 285.77

**Synthesis**

-Obtained by condensation of α -chloro-3,4-dihydroxyacetophenone with cyclohexylamine in ethanol or isopropanol at 60-80°. The amino ketone base which separated was treated with concentrated hydrochloric acid [328] [1446].

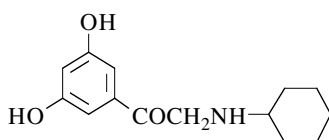
m.p. 256-258° (d) [328], 242-245° [1446].

2-(Cyclohexylamino)-1-(3,5-dihydroxyphenyl)ethanone

[161040-30-8]

C₁₄H₁₉NO₃

mol.wt. 249.31

**Synthesis**

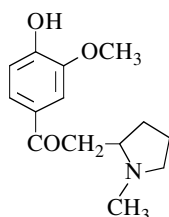
-Obtained by treatment of 3,5-diacetoxy- α -bromoacetophenone with cyclohexylamine in ethyl acetate and then refluxing with hydrochloric acid [240].

1-(4-Hydroxy-3-methoxyphenyl)-2-(1-methyl-2-pyrrolidinyl)ethanone (-) (*Phyllostone*)

[126262-24-6]

C₁₄H₁₉NO₃

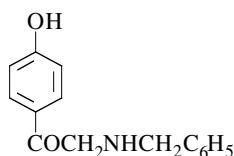
mol.wt. 249.31



Isolation from natural sources

-From the New Caledonian lauraceous plant *Cryptocarya phyllostemon* [276].Gum [276]; (α)_D = -5° (ethanol);¹H NMR [276], IR [276], UV [276], MS [276].**1-(4-Hydroxyphenyl)-2-[(phenylmethyl)amino]ethanone**C₁₅H₁₅NO₂

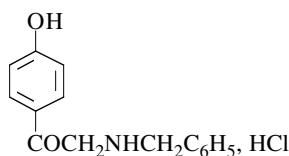
mol.wt. 241.29



Synthesis

-Obtained by adding ammonia to an aqueous solution of its hydrochloride [504].

m.p. 132-133° [504].

1-(4-Hydroxyphenyl)-2-[(phenylmethyl)amino]ethanone (*Hydrochloride*)C₁₅H₁₅NO₂, HCl mol.wt. 277.75

Synthesis

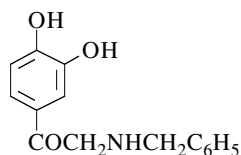
-Obtained by reductive condensation of p-hydroxyphenylglyoxal hydrate and benzylamine under hydrogen in the presence of Raney nickel in ethanol at 40°. Then, treatment of the mixture with 6 N ethanolic hydrogen chloride (82%) [504].

N.B.: The same reaction from p-hydroxyphenylglyoxal-potassium bisulfite at 45° gave a 79% yield [504].

m.p. 240° [504].

1-(3,4-Dihydroxyphenyl)-2-[(phenylmethyl)amino]ethanoneC₁₅H₁₅NO₃

mol.wt. 257.29

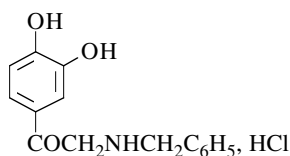


Syntheses

-Obtained by reaction of α -chloro-3,4-dihydroxyacetophenone with benzylamine [357].

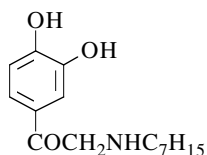
-Also obtained by adding ammonia to an aqueous solution of its hydrochloride [504].

m.p. 147-148° [504].

1-(3,4-Dihydroxyphenyl)-2-[(phenylmethyl)amino]ethanone (Hydrochloride)C₁₅H₁₅NO₃, HCl mol.wt. 293.75**Synthesis**

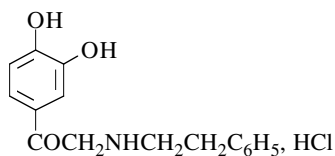
-Obtained by reductive condensation of 3,4-dihydroxyphenylglyoxal and benzylamine under hydrogen in the presence of Raney nickel in ethanol at 45°. Then, treatment of the mixture with ethanolic hydrogen chloride (73%) [504].

m.p. 220-221° [504].

1-(3,4-Dihydroxyphenyl)-2-(heptylamino)ethanoneC₁₅H₂₃NO₃ mol.wt. 265.35**Synthesis**

-Preparation by reaction of excess heptylamine with α-chloro-3,4-diacetoxyacetophenone [357].

m.p. 125° [357].

1-(3,4-Dihydroxyphenyl)-2-[2-(phenylethyl)amino]ethanone (Hydrochloride)C₁₆H₁₇NO₃, HCl mol.wt. 307.78**Synthesis**

-Obtained by total demethylation of 1-(3,4-dimethoxyphenyl)-2-[(phenylethyl)amino]ethanone hydrochloride (m.p. 219-222°), (79%) [1018] according to [1017].

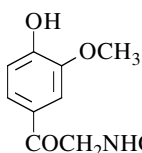
monohydrate [1018]; m.p. 220-222° (d) [1018].

1-(3-Hydroxy-4-methoxyphenyl)-2-[(phenylmethyl)amino]ethanone (Hydrochloride)C₁₆H₁₇NO₃, HCl mol.wt. 307.78**Synthesis**

-Obtained by reductive condensation of 3-hydroxy-4-methoxyphenylglyoxal and benzylamine under hydrogen in the presence of Raney nickel in ethanol at 45° for 45 min. Then, elimination of the catalyst and

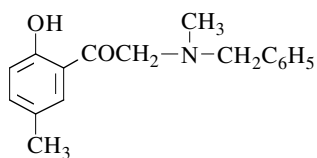
acidification of the mixture with hydrochloric acid (54%) [504].

m.p. 226° [504].

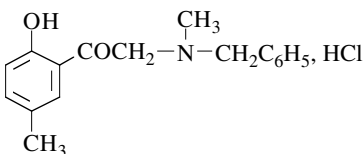
1-(4-Hydroxy-3-methoxyphenyl)-2-[(phenylmethyl)amino]ethanone (Hydrochloride)C₁₆H₁₇NO₃, HCl mol.wt. 307.78COCH₂NHCH₂C₆H₅, HCl**Synthesis**

-Preparation by reductive condensation of 4-hydroxy-3-methoxyphenylglyoxal-potassium-bisulfite and benzylamine under hydrogen in the presence of Raney nickel in dilute ethanol at 45° for 1.75 h. Then, elimination of the catalyst and acidification of the mixture with hydrochloric acid (76%) [504].

m.p. 230° [504].

2-(Benzyl-methyl-amino)-1-(2-hydroxy-5-methylphenyl)ethanoneC₁₇H₁₉NO₂ mol.wt. 269.34**Synthesis**

-Obtained by condensation of 2-hydroxy-5-methyl-α-bromoacetophenone with benzyl methyl amine in ethyl ether at r.t. for 24 to 72 h [67].

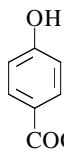
2-(Benzyl-methyl-amino)-1-(2-hydroxy-5-methylphenyl)ethanone (Hydrochloride)C₁₇H₁₉NO₂, HCl mol.wt. 305.80**Synthesis**

-Obtained by reaction of 2-hydroxy-5-methyl-α-bromoacetophenone with N-benzylmethylamine in ethyl ether at r.t. for 24 to 72 h, followed by treatment with hydrochloric acid [67].

m.p. 186°5-187° [67].

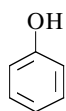
2-[Bis(phenylmethyl)amino]-1-(4-hydroxyphenyl)ethanone

[88693-95-2]

C₂₂H₂₁NO₂ mol.wt. 331.41COCH₂N(CH₂C₆H₅)₂**Synthesis**

-Preparation by reaction of p-hydroxyphenacyl chloride (1 mol) with dibenzylamine (2 mol) in refluxing ethanol for 4 h [1363].

uncrystallizable oil [1363].

2-[Bis(phenylmethyl)amino]-1-(4-hydroxyphenyl)ethanone (*Hydrochloride*) $\text{C}_{22}\text{H}_{21}\text{NO}_2, \text{HCl}$ mol.wt. 367.87 $\text{COCH}_2\text{N}(\text{CH}_2\text{C}_6\text{H}_5)_2, \text{HCl}$

Synthesis

-Preparation by adding a solution of ethanolic hydrogen chloride to a solution of α -dibenzylamino-p-hydroxyacetophenone in chloroform (77%) [1363].

m.p. 239-241° (d) [1363].