

PART 1 MONOKETONES

Chapter 2. Compounds derived from halogenoacetic acids

2.1. Compounds derived from bromoacetic acids

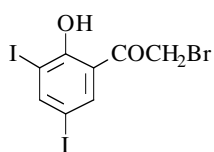
2.1.1. From monobromoacetic acid

2-Bromo-1-(2-hydroxy-3,5-diiodophenyl)ethanone

[32559-04-9]

C₈H₅BrI₂O₂

mol.wt. 466.84



Synthesis

-Preparation by bromination of 2-hydroxy-3,5-diiodoacetophenone in acetic acid at 70-80°, under light irradiation (84%) [332].

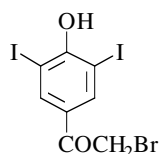
m.p. 150-151° [332].

2-Bromo-1-(4-hydroxy-3,5-diiodophenyl)ethanone

[31827-97-1]

C₈H₅BrI₂O₂

mol.wt. 466.84



Synthesis

-Preparation by reaction of bromine on 4-hydroxy-3,5-diiodoacetophenone in boiling chloroform under light irradiation (81-83%) [330] [331].

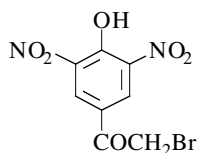
m.p. 171-172° [330] [331]; UV [330].

2-Bromo-1-(4-hydroxy-3,5-dinitrophenyl)ethanone

[120388-18-3]

C₈H₅BrN₂O₆

mol.wt. 305.04



Synthesis

-Preparation by bromination of 4-hydroxy-3,5-dinitroacetophenone with cupric bromide in refluxing ethyl acetate (60%) [210].

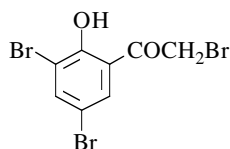
m.p. 92-94° [210]; Crystal Data [210].

2-Bromo-1-(3,5-dibromo-2-hydroxyphenyl)ethanone

[194226-52-3]

C₈H₅Br₃O₂

mol.wt. 372.84



Syntheses

-Preparation by action of bromine with 3,5-dibromo-2-hydroxyacetophenone in refluxing acetic acid for 2.5 h (55%) [490].

-Also obtained by reaction of bromine with 2-hydroxyacetophenone in chloroform in an ice bath for 2 h [1308].

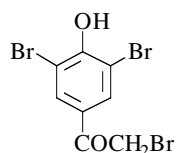
m.p. 107-108° [490]; ¹H NMR [490], IR [490].

2-Bromo-1-(3,5-dibromo-4-hydroxyphenyl)ethanone

[34969-79-4]

C₈H₅Br₃O₂

mol.wt. 372.84

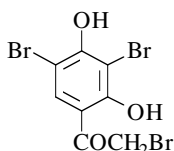
**Synthesis**

-Preparation by bromination of 3,5-dibromo-4-hydroxyacetophenone in chloroform [1108] [1201] [1246], (79%) [1246].

m.p. 137° [1246], 128° [1108] [1201].

2-Bromo-1-(3,5-dibromo-2,4-dihydroxyphenyl)ethanoneC₈H₅Br₃O₃

mol.wt. 388.84

**Synthesis**

-Preparation by bromination of resacetophenone in acetic acid [1303].

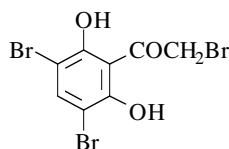
m.p. 112-113° [1303].

2-Bromo-1-(3,5-dibromo-2,6-dihydroxyphenyl)ethanone

[74815-26-2]

C₈H₅Br₃O₃

mol.wt. 388.84

**Synthesis**

-Preparation by bromination of 2,6-dihydroxyacetophenone with cupric bromide in refluxing chloroform-ethyl acetate mixture [109].

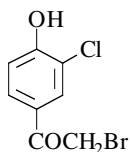
m.p. 150° [109].

2-Bromo-1-(3-chloro-4-hydroxyphenyl)ethanone

[41877-19-4]

C₈H₆BrClO₂

mol.wt. 249.49

**Syntheses**

-Preparation by selective bromination of 3-chloro-4-hydroxyacetophenone with dioxane dibromide in dioxane-ethyl ether mixture at r.t. (85%) [1150].

-Preparation by selective bromination of 3-chloro-4-hydroxyacetophenone with cupric bromide in refluxing chloroform-ethyl acetate mixture [807], (100%) [1340].

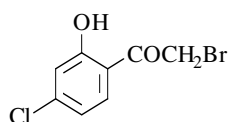
m.p. 128-130° [1150]; ¹H NMR [1150].

2-Bromo-1-(4-chloro-2-hydroxyphenyl)ethanone

[157068-00-3]

C₈H₆BrClO₂

mol.wt. 249.49

**Synthesis**

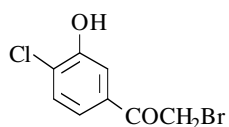
-Obtained by reaction of bromoacetyl bromide on 3-chloroanisole with aluminium chloride in carbon tetrachloride, first at 0°, then at r.t. (16%) [35].

2-Bromo-1-(4-chloro-3-hydroxyphenyl)ethanone

[73898-34-7]

C₈H₆BrClO₂

mol.wt. 249.49

**Synthesis**

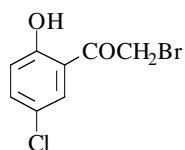
-Preparation by reaction of dioxane dibromide on 4-chloro-3-hydroxyacetophenone in dioxane-ethyl ether mixture at r.t. (84%) [888].

2-Bromo-1-(5-chloro-2-hydroxyphenyl)ethanone

[52727-99-8]

C₈H₆BrClO₂

mol.wt. 249.49

**Syntheses**

-Preparation by bromination of 5-chloro-2-hydroxyacetophenone with cupric bromide in refluxing chloroform-ethyl acetate mixture (73%) [416].
-Also refer to: [1113] (compound 1b).

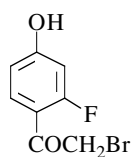
m.p. 64-65° [416]; ¹H NMR [416].

2-Bromo-1-(2-fluoro-4-hydroxyphenyl)ethanone

[220131-30-6]

C₈H₆BrFO₂

mol.wt. 233.04

**Synthesis**

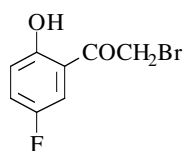
-Refer to: [1436].

2-Bromo-1-(5-fluoro-2-hydroxyphenyl)ethanone

[126581-65-5]

C₈H₆BrFO₂

mol.wt. 233.04

**Synthesis**

-Preparation by reaction of bromine on 5-fluoro-2-hydroxyacetophenone in dioxane-ethyl ether mixture (80%) [556] [557].

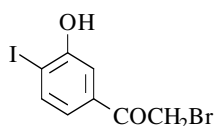
m.p. 86-87° [556] [557]; ¹H NMR [557].

2-Bromo-1-(3-hydroxy-4-iodophenyl)ethanone

[73898-36-9]

C₈H₆BrIO₂

mol.wt. 340.94

**Synthesis**

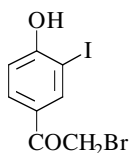
-Preparation by reaction of dioxane dibromide on 3-hydroxy-4-iodoacetophenone in dioxane-ethyl ether mixture at r.t. (75%) [888].

2-Bromo-1-(4-hydroxy-3-iodophenyl)ethanone

[73898-29-0]

C₈H₆BrIO₂

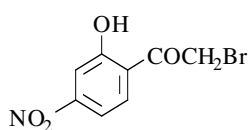
mol.wt. 340.94

**Synthesis**

-Preparation by reaction of dioxane dibromide on 4-hydroxy-3-iodoacetophenone in dioxane-ethyl ether mixture at r.t. (87%) [888].

2-Bromo-1-(2-hydroxy-4-nitrophenyl)ethanoneC₈H₆BrNO₄

mol.wt. 260.04

**Synthesis**

-Preparation by reaction of bromine on 2-hydroxy-4-nitroacetophenone in refluxing acetic acid (63%) [1367].

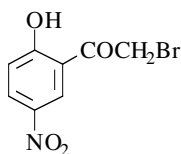
m.p. 112° [1367].

2-Bromo-1-(2-hydroxy-5-nitrophenyl)ethanone

[5037-70-7]

C₈H₆BrNO₄

mol.wt. 260.04

**Synthesis**

-Preparation by bromination of 2-hydroxy-5-nitroacetophenone in acetic acid (60%) [1367].

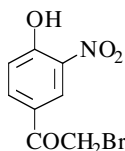
m.p. 127° [1367].

2-Bromo-1-(4-hydroxy-3-nitrophenyl)ethanone

[5029-61-8]

C₈H₆BrNO₄

mol.wt. 260.04

**Syntheses**

-Preparation by bromination of 4-hydroxy-3-nitroacetophenone in chloroform (74%) [537], (71%) [1367] or in acetic acid (58%) [275].

-Preparation by selective bromination of 4-hydroxy-3-nitroacetophenone with dioxane dibromide in dioxane-ethyl ether mixture at r.t. (94%) [1150].

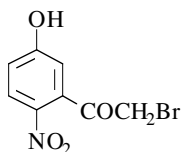
m.p. 93° [275] [1367], 91°5-92° [537], 80-82° [1150]; b.p._{0.2} 150-155° [275].

2-Bromo-1-(5-hydroxy-2-nitrophenyl)ethanone

[50695-17-5]

C₈H₆BrNO₄

mol.wt. 260.04



Synthesis

-Obtained by bromination of 5-hydroxy-2-nitroacetophenone in chloroform-carbon tetrachloride-ethyl acetate mixture at 61° (15%) [537].

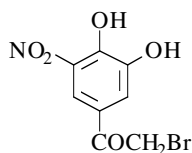
m.p. 112°5-113° [537].

2-Bromo-1-(3,4-dihydroxy-5-nitrophenyl)ethanone

[134610-95-0]

C₈H₆BrNO₅

mol.wt. 276.04



Synthesis

-Preparation by reaction of boron tribromide on 4-hydroxy-3-methoxy-5-nitro- α -bromoacetophenone in methylene chloride [163].

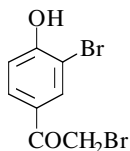
m.p. 138-140° [163].

2-Bromo-1-(3-bromo-4-hydroxyphenyl)ethanone

[41877-18-3]

C₈H₆Br₂O₂

mol.wt. 293.94



Syntheses

-Preparation by reaction of dioxane dibromide on 3-bromo-4-hydroxyacetophenone in dioxane-ethyl ether mixture at r.t. (82-85%) [888] [1150].

-Preparation by reaction of bromine on 4-hydroxyacetophenone in acetic acid at r.t. (37%) [1246].

-Preparation by reaction of phenyltrimethylammonium tribromide on 4-hydroxy- α -bromoacetophenone [977].

-Also refer to: [1202].

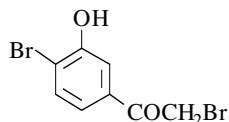
m.p. 143° [1246], 142-144° [1150], 140-142° [1298]; ¹H NMR [1150].

2-Bromo-1-(4-bromo-3-hydroxyphenyl)ethanone

[73898-35-8]

C₈H₆Br₂O₂

mol.wt. 293.94



Synthesis

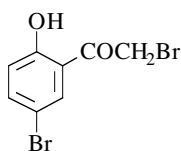
-Preparation by selective bromination of 4-bromo-3-hydroxyacetophenone with dioxane dibromide in dioxane-ethyl ether mixture at r.t. (79%) [888].

2-Bromo-1-(5-bromo-2-hydroxyphenyl)ethanone

[67029-74-7]

C₈H₆Br₂O₂

mol.wt. 293.94

**Syntheses**

-Claimed to be prepared from 2-hydroxyacetophenone or 5-bromo-2-hydroxyacetophenone by reaction of bromine in glacial acetic acid and from 2-hydroxy- α -bromoacetophenone by reaction of bromine in 50% aqueous acetic acid (quantitative yields) (m.p. 107°) [247]. No proof of structure was provided [146]. Actually, it probably concerns

3,5-dibromo-2-hydroxyacetophenone (m.p. 108° [105], 108-109° [1246]), as the use of acetic acid as solvent favours the aromatic ring bromination.

-Preparation by bromination of 5-bromo-2-hydroxyacetophenone with cupric bromide in refluxing chloroform-ethyl acetate mixture [146] [807], (50%) [146].

m.p. 107° [247], 69° [146].

One of the reported melting points is obviously wrong.

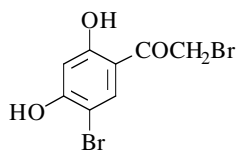
¹H NMR [146], IR [146].

2-Bromo-1-(5-bromo-2,4-dihydroxyphenyl)ethanone

[99657-26-8]

C₈H₆Br₂O₃

mol.wt. 309.94

**Synthesis**

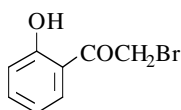
-Preparation by bromination of 5-bromo-2,4-dihydroxyacetophenone with cupric bromide in refluxing chloroform-ethyl acetate mixture [334] [807].

2-Bromo-1-(2-hydroxyphenyl)ethanone

[2491-36-3]

C₈H₇BrO₂

mol.wt. 215.05

**Syntheses**

-Preparation by bromination of 2-hydroxyacetophenone with cupric bromide in refluxing chloroform-ethyl acetate mixture [293] [334] [807] [952] [1049] [1100] [1340], (100%) [293] [807], (56%) [1340], (36%) [952].

-Preparation by reaction of bromine on 2-hydroxyacetophenone in acetic acid at r.t. (47%) [247] or in a mixture of ethyl ether and chloroform [1100] according to [522].

-Preparation by Fries rearrangement of phenyl bromoacetate with aluminium chloride without solvent at 120-140° (45-50%) [1046] [1494].

m.p. 70-71° [1494], 45° [247], 44-45° [1340], 41-43° [1049], 40° [807], 39-41° [952].

One of the reported melting points is obviously wrong.

b.p.₇₋₁₀ 120-125° [1046], b.p.₁₈ 152-158° [247];

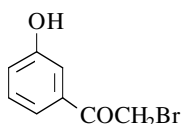
¹H NMR [952], UV [666].

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

[2491-37-4]

C₈H₇BrO₂

mol.wt. 215.05

**Syntheses**

-Preparation by bromination of 3-hydroxyacetophenone,
 *with cupric bromide in refluxing chloroform-ethyl acetate mixture [293] [807] [997] [1049] [1340], (quantitative yield) [293] [807] [1340];

*with dioxane dibromide in dioxane-ethyl ether mixture at r.t. (91%) [1150];

*in using silica gel coated with cupric bromide in refluxing ethyl acetate (94%) [927];

*with bromine in chloroform at 2° (96%) [244].

m.p. 74-75° [1150], 70-72° [244]; amorphous [927];

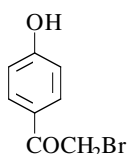
¹H NMR [927] [1150], IR [244] [927], UV [244], MS [927].

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

[2491-38-5]

C₈H₇BrO₂

mol.wt. 215.05

**Syntheses**

-Preparation by bromination of 4-hydroxyacetophenone with cupric bromide in refluxing chloroform-ethyl acetate mixture [293] [807] [952] [997] [1048] [1049] [1100] [1340], (quantitative yield) [293] [807] [1340], (34-38%) [952] [997], (15%) [1048].

-Preparation by reaction of dioxane dibromide on 4-hydroxyacetophenone in dioxane-ethyl ether mixture at r.t. (86%) [1150].

-Preparation by bromination of 4-hydroxyacetophenone in acetic acid (63%) [251] or in a mixture of ethyl ether and chloroform [1100] according to [522].

-Preparation by Fries rearrangement of phenyl bromoacetate with aluminium chloride without solvent between 120-140° (40%) [1046], (30%) [1494].

-Preparation by reaction of tetrabutylammonium tribromide, benzyltrimethylammonium tribromide or phenyltrimethylammonium tribromide on 4-hydroxyacetophenone in tetrahydrofuran [977].

-Preparation by reaction of ammonium tribromide on 4-hydroxyacetophenone in methylene chloride-methanol mixture [977].

-Preparation by reaction of silica gel coated with cupric bromide on 4-hydroxyacetophenone in refluxing ethyl acetate (95%) [927].

-Preparation by sonochemical bromination of 4-hydroxyacetophenone using p-toluenesulfonic acid/N-bromosuccinimide in methanol for 6 h at 35-37° (97%) [8]. **N.B.:** In the absence of ultrasound the reaction takes place at the boiling point of methanol (65°) for 24 h (58%) [8].

-Also refer to: [80] [782] [854] [878] [1434].

m.p. 146° [1494], 132-133° [397], 130-131° [952], 130° [251], 129-131° [997], 128-130° [977], 128-129° [1046], 126-127° [1048], 125-129° [8], 124-126° [807] [1150], 121-122° [927], 105-108° [1414];

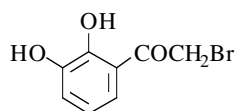
¹H NMR [8] [397] [927] [952] [1048] [1150], IR [8] [927], UV [1048], MS [397] [927].

2-Bromo-1-(2,3-dihydroxyphenyl)ethanone

[19278-79-6]

C₈H₇BrO₃

mol.wt. 231.05

**Synthesis**

-Obtained by reaction of hydrobromic acid on 2,3-diacetoxy- α -bromoacetophenone in refluxing ethanol [1294].

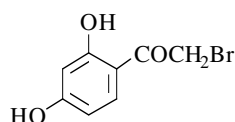
m.p. 75-76° [1294]; UV [666].

2-Bromo-1-(2,4-dihydroxyphenyl)ethanone

[2491-39-6]

C₈H₇BrO₃

mol.wt. 231.05

**Syntheses**

-Preparation by bromination of resacetophenone with cupric bromide in refluxing chloroform-ethyl acetate mixture (quantitative yield) [293] [807], (3%) [952].

-Also obtained by reaction of bromoacetonitrile on resorcinol with zinc chloride and hydrobromic acid in

ethyl ether (Hoesch reaction) [1380] [1382].

-Also obtained by reaction of bromoacetyl chloride on resorcinol with aluminium bromide or aluminium chloride in carbon disulfide [1048] [1062], (80%) [1062], (12%) [1048].

-Also obtained (poor yield) by reaction of bromoacetic acid on resorcinol with zinc chloride or phosphorous oxychloride [436] [516].

m.p. 144-145° [807], 127° [1380] [1382], 126-128° [1048], 118-119° [952].

There is discrepancy between the different melting points.

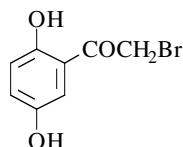
¹H NMR [952] [1048], UV [1048].

2-Bromo-1-(2,5-dihydroxyphenyl)ethanone

[25015-91-2]

C₈H₇BrO₃

mol.wt. 231.05

**Syntheses**

-Preparation by bromination of 2,5-dihydroxyacetophenone, *with cupric bromide in refluxing chloroform-ethyl acetate mixture (74-87%) [293] [807] [1193], (70%) [1277], (37%) [952];

*with bromine in acetic acid at 55-58° (16%) [137].

-Preparation by reaction of hydrobromic acid on 5- α -bromoacetoxy-2-hydroxy- α -bromoacetophenone in methanol at r.t. (87%) [819].

-Preparation by reaction of aluminium bromide on 2-hydroxy-5-methoxy- α -bromo-acetophenone in carbon disulfide at r.t. (87%) [819].

-Also obtained by action of acetic acid saturated with hydrobromic acid (10 min, r.t.) on 2,5-diacetoxy- α -diazoacetophenone, reduced pressure elimination of acetic acid, then action (overnight, r.t.) of a methanolic solution of hydrobromic acid (59%) [819].

-Also obtained by reaction of aluminium bromide on 2,5-dimethoxy- α -chloroacetophenone in refluxing carbon disulfide (28%) [819].

-Also obtained by reaction of bromoacetyl bromide on 1,4-dimethoxybenzene with aluminium bromide at r.t. (11%) [1048], (2%) [819].

-Also obtained by reaction of phenyltrimethylammonium bromide tribromide with 2,5-dihydroxyacetophenone in THF at r.t. overnight (63%) [216], according to [217].

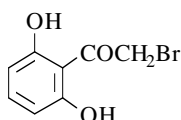
m.p. 120-121° [137], 117°5-119° [819], 117-119° [1048], 114-116° [1277],
113-115° [952] [1193], 112-113° [807];
TLC [216]; flash chromatography [216];
¹H NMR [137] [216] [819] [952] [1048] [1277], IR [216] [1277],
UV [137] [216] [666] [1048], MS [216] [1277].

2-Bromo-1-(2,6-dihydroxyphenyl)ethanone

[2491-40-9]

C₈H₇BrO₃

mol.wt. 231.05

**Syntheses**

-Preparation by bromination of 2,6-dihydroxyacetophenone with cupric bromide in refluxing ethyl acetate (quantitative yield) [1340].
-Preparation by reaction of 40% hydrobromic acid on 2,6-diacetoxy- α -bromoacetophenone in refluxing 60% ethanol (73%) [1356].
-Refer to: [1287] (Japanese patent).

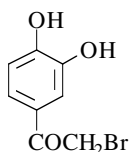
m.p. 143° [1356]; UV [666].

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

[40131-99-5]

C₈H₇BrO₃

mol.wt. 231.05

**Syntheses**

-Preparation by reaction of bromoacetic acid on pyrocatechol with phosphorous oxychloride [437].
-Preparation by reaction of bromoacetyl bromide on pyrocatechol with aluminium bromide in carbon disulfide at r.t. (63%) [827].
-Preparation by reaction of bromine on 3,4-dihydroxyacetophenone in chloroform at r.t. [975] [1054].
-Also refer to: [27] [521] [606] [946] [1181] [1202] and [1064] (Japanese patent).

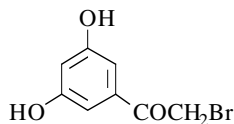
m.p. 167° [437], 61° [827]. One of the reported melting points is obviously wrong.
¹H NMR [827], IR [827], UV [827], MS [827].

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

[62932-92-7]

C₈H₇BrO₃

mol.wt. 231.05

**Syntheses**

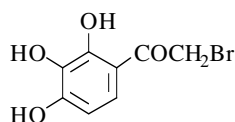
-Preparation by reaction of bromine on 3,5-dihydroxyacetophenone in chloroform at r.t. [975].
-Also refer to: [521] [1202].

2-Bromo-1-(2,3,4-trihydroxyphenyl)ethanone

[105190-52-1]

C₈H₇BrO₄

mol.wt. 247.05

**Syntheses**

-Preparation by reaction of bromoacetyl bromide on pyrogallol with aluminium bromide in carbon disulfide at r.t. (42%) [827].
 -Also obtained by reaction of bromoacetic acid on pyrogallol with phosphorous oxychloride [1083], (poor yield) [436] [516] or with zinc chloride (poor yield) [436] [516].

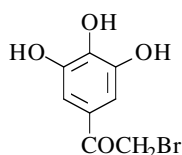
m.p. 159° [1083], 138° [827]. One of the reported melting points is obviously wrong.
¹H NMR [827], IR [827], UV [827], MS [827].

2-Bromo-1-(3,4,5-trihydroxyphenyl)ethanone

[111011-09-7]

C₈H₇BrO₄

mol.wt. 247.05

**Synthesis**

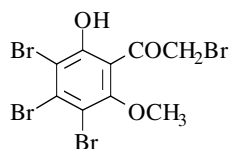
-Refer to: [1566].

2-Bromo-1-(3,4,5-tribromo-2-hydroxy-6-methoxyphenyl)ethanone

[98592-28-0]

C₉H₆Br₄O₃

mol.wt. 481.76

**Synthesis not yet described**

-Only one reference dealing with 2,3',4',5'-tetrabromo-2'-hydroxy-6'-methoxyacetophenone does exist. This reference [Chem. Abstr., Formula Index, page 112F, **52**, 2796h (1958)] is obviously erroneous. The described product is actually 2,2,3',5'-tetrabromo-2'-hydroxy-

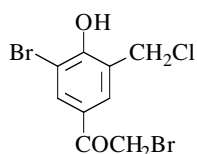
6'-methoxyacetophenone, since in the original paper [358] it is specified that two labile bromine atoms are present in the molecule.

2-Bromo-1-[3-bromo-5-(chloromethyl)-4-hydroxyphenyl]ethanone

[107700-04-9]

C₉H₇Br₂ClO₂

mol.wt. 342.41

**Synthesis**

-Preparation by adding a methylene chloride solution of bromine to a methanol/methylene chloride solution of 3-(chloromethyl)-4-hydroxyacetophenone at r.t. (80%) [214].

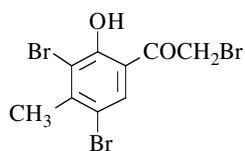
m.p. 95° [214]; ¹H NMR [214], IR [214], MS [214].

2-Bromo-1-(3,5-dibromo-2-hydroxy-4-methylphenyl)ethanone

[260435-53-8]

C₉H₇Br₃O₂

mol.wt. 386.87



Syntheses

-Preparation by reaction of bromine with 2-hydroxy-4-methylacetophenone in chloroform/ethylene dichloride mixture, first in an ice-water bath, then for 2 h at r.t. (50%) [1307].

-Preparation by reaction of bromine with 3,5-dibromo-2-hydroxy-4-methylacetophenone in acetic acid first at r.t., then at reflux to discolouration (72%) [186].

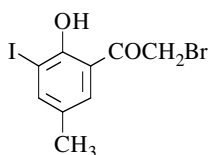
m.p. 139-140° [1307], 136-137° [186];
¹H NMR [186] [1307], IR [186] [1307].

2-Bromo-1-(2-hydroxy-3-iodo-5-methylphenyl)ethanone

[194226-48-7]

C₉H₈BrIO₂

mol.wt. 354.97



Synthesis

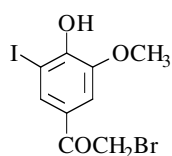
-Preparation [1279] (compound 1a) according to described procedure [270] (Romanian patent).

2-Bromo-1-(4-hydroxy-3-iodo-5-methoxyphenyl)ethanone

[144978-69-8]

C₉H₈BrIO₃

mol.wt. 370.97



Syntheses

-Preparation by reaction of bromine with 5-iodoaceto-vanillone in chloroform (quantitative yield) [892].
 -Preparation from 4-hydroxy-3-methoxy- α -bromoacetophenone by the oxidative procedure using chloramine T and sodium iodide in DMF, DMSO or acetonitrile [826] [892].

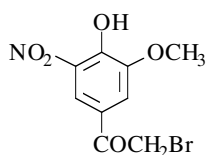
¹H NMR [892], ¹³C NMR [892], MS [892].

2-Bromo-1-(4-hydroxy-3-methoxy-5-nitrophenyl)ethanone

[125629-36-9]

C₉H₈BrNO₅

mol.wt. 290.07



Synthesis

-Preparation by reaction of 96% nitric acid on 4-hydroxy-3-methoxy- α -bromoacetophenone in acetic acid at 20-25° [163] [211], (72%) [211].

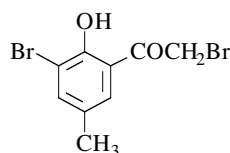
m.p. 147-149° [163] [211]; ¹H NMR [211].

2-Bromo-1-(3-bromo-2-hydroxy-5-methylphenyl)ethanone

[194226-50-1]

C₉H₈Br₂O₂

mol.wt. 307.97



Syntheses

-Preparation by reaction of bromine on 2-hydroxy-5-methyl- α -bromoacetophenone in 50% aqueous acetic acid at 60° (75%) [247].
 -Also obtained by reaction of bromine with 2-hydroxy-5-methylacetophenone in chloroform in an ice bath for 2 h [1308].

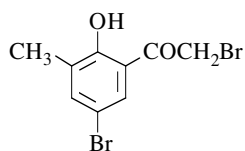
m.p. 106° [247].

2-Bromo-1-(5-bromo-2-hydroxy-3-methylphenyl)ethanone

[194226-51-2]

C₉H₈Br₂O₂

mol.wt. 307.97



Synthesis

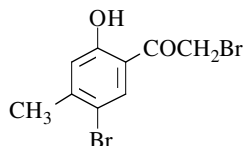
-Preparation by reaction of bromine (1 mol) with 5-bromo-2-hydroxy-3-methylacetophenone (1 mol) in acetic acid on a water bath for 20 min (47%) [185].

m.p. 72-73° [185]; ¹H NMR [185], IR [185].**2-Bromo-1-(5-bromo-2-hydroxy-4-methylphenyl)ethanone**

[194226-49-8]

C₉H₈Br₂O₂

mol.wt. 307.97

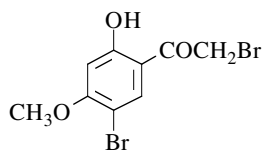


Synthesis

-Obtained by reaction of bromine with 2-hydroxy-4-methylacetophenone in chloroform in an ice bath for 2 h [1308].

2-Bromo-1-(5-bromo-2-hydroxy-4-methoxyphenyl)ethanoneC₉H₈Br₂O₃

mol.wt. 323.97



Syntheses

-Obtained by reaction of bromine with 3,3'-diacetyl-4,4'-di-hydroxy-6,6'-dimethoxydiphenyl ether in acetic acid in the presence of a crystal of iodine, first at 90°, then at r.t. overnight [691].
 -Also obtained (by-product) by reaction of bromine on 5-bromo-2-hydroxy-4-methoxyacetophenone in acetic acid [238].

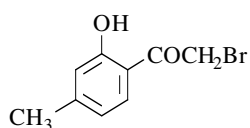
m.p. 178-180° [238], 72-73° [691]. One of the reported melting points is obviously wrong.

2-Bromo-1-(2-hydroxy-4-methylphenyl)ethanone

[144219-74-9]

C₉H₉BrO₂

mol.wt. 229.07

**Synthesis**

-Preparation by reaction of bromine with 2-acetoxy-4-methylacetophenone in refluxing chloroform (44%) [571].

colourless oil [571];

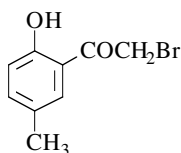
¹H NMR [571], IR [571], MS [571].

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

[51317-87-4]

C₉H₉BrO₂

mol.wt. 229.07

**Syntheses**

-Preparation by reaction of bromoacetic acid on p-cresol with boron trifluoride into an autoclave at 70° (90%) [1111].

-Preparation by Fries rearrangement of p-cresyl bromoacetate with aluminium chloride without solvent at 125° (47%) [1541].

-Preparation by reaction of bromine on 2-hydroxy-5-methylacetophenone in acetic acid at r.t. (39%) [247].

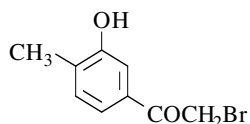
m.p. 45°-46° [1541], 44-45° [1111].

2-Bromo-1-(3-hydroxy-4-methylphenyl)ethanone

[73898-30-3]

C₉H₉BrO₂

mol.wt. 229.07

**Synthesis**

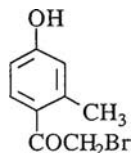
-Preparation by selective bromination of 3-hydroxy-4-methylacetophenone with dioxane dibromide in dioxane-ethyl ether mixture at r.t. (42%) [888].

2-Bromo-1-(4-hydroxy-2-methylphenyl)ethanone

[41877-16-1]

C₉H₉BrO₂

mol.wt. 229.07

**Synthesis**

-Preparation by selective bromination of 4-hydroxy-2-methylacetophenone with dioxane dibromide in dioxane-ethyl ether mixture at r.t. (86%) [1150].

m.p. 122-124° [1150];

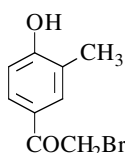
¹H NMR [1150].

2-Bromo-1-(4-hydroxy-3-methylphenyl)ethanone

[41877-17-2]

C₉H₉BrO₂

mol.wt. 229.07

**Syntheses**

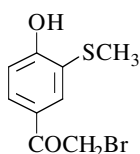
- Preparation by selective bromination of 4-hydroxy-3-methylacetophenone with dioxane dibromide in dioxane-ethyl ether mixture at r.t. (98%) [1150], (78%) [888].
- Preparation by selective bromination of 4-hydroxy-3-methylacetophenone with cupric bromide in refluxing chloroform-ethyl acetate mixture (quantitative yield) [1340].

m.p. 124-125° [1150]; ¹H NMR [1150].**2-Bromo-1-[4-hydroxy-3-(methylthio)phenyl]ethanone**

[66265-63-2]

C₉H₉BrO₂S

mol.wt. 261.14

**Synthesis**

- Preparation by reaction of dioxane dibromide on 4-hydroxy-3-(methylthio)acetophenone in dioxane-ethyl ether mixture (75%) [1177] [1403].

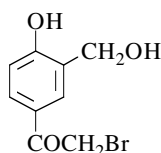
solid [1177].

2-Bromo-1-[4-hydroxy-3-(hydroxymethyl)phenyl]ethanone

[62932-94-9]

C₉H₉BrO₃

mol.wt. 245.07

**Syntheses**

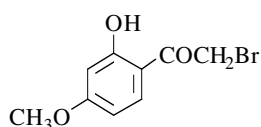
- Refer to: [142] [320] [491] [815] [816] [818] [939] [1203] [1368].

2-Bromo-1-(2-hydroxy-4-methoxyphenyl)ethanone

[60965-24-4]

C₉H₉BrO₃

mol.wt. 245.07

**Syntheses**

- Obtained by reaction of cupric bromide with 2-hydroxy-4-methoxyacetophenone, in refluxing chloroform-ethyl acetate mixture [1100] [1340], (quantitative yield) [1340] according to [807], (62%) [24] or in refluxing dioxane (44%) [405], (10%) [952].
- Preparation by reaction of bromine with 2-hydroxy-4-methoxyacetophenone in a mixture of ethyl ether and chloroform [1100] according to [522].
- Preparation from resorcinol dimethyl ether,
 - *by reaction of bromoacetyl bromide with aluminium bromide at r.t. [1438];
 - *by reaction of bromoacetyl chloride with aluminium chloride in carbon disulfide [96] [405], (23%) [405].
- Preparation by reaction of bromoacetonitrile on resorcinol dimethyl ether with hydrobromic acid gas in ethyl ether [1382].

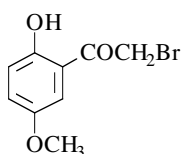
m.p. 161° [405], 92° [1438], 90-92° [952], 70-72° [24].
 There is discrepancy between the different melting points.
¹H NMR [24] [952], IR [24], MS [24].

2-Bromo-1-(2-hydroxy-5-methoxyphenyl)ethanone

[203524-87-2]

C₉H₉BrO₃

mol.wt. 245.07

**Syntheses**

-Preparation by reaction of bromoacetyl bromide on 1,4-dimethoxybenzene with aluminium bromide at r.t. (18%) [819].
 -Also refer to: [1480].

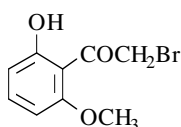
m.p. 65-66° [819].

2-Bromo-1-(2-hydroxy-6-methoxyphenyl)ethanone

[50879-47-5]

C₉H₉BrO₃

mol.wt. 245.07

**Synthesis**

-Claimed to be prepared by bromination of 2-hydroxy-6-methoxyacetophenone in glacial acetic acid [1170].
N.B.: It has been observed that glacial acetic acid promotes side chain bromination of 2-hydroxyacetophenones [251].

However, actually, 3-bromo-2-hydroxy-6-methoxyacetophenone was obtained by bromination of 2-hydroxy-6-methoxyacetophenone in glacial acetic acid, dilute acetic acid (80%) or acetic anhydride [150] [414].

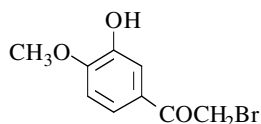
m.p. 106° [414] [1170].

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

[90971-90-7]

C₉H₉BrO₃

mol.wt. 245.07

**Synthesis**

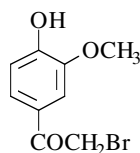
-Preparation by reaction of cupric bromide on 3-hydroxy-4-methoxyacetophenone in refluxing dioxane (80%) [1340].

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

[69638-06-8]

C₉H₉BrO₃

mol.wt. 245.07

**Syntheses**

-Preparation by reaction of cupric bromide on 4-hydroxy-3-methoxyacetophenone in refluxing chloroform-ethyl acetate mixture (quantitative yield) [1340].
 -Preparation by reaction of bromoacetyl bromide on guaiacol with aluminium chloride in carbon disulfide (75%) [1235].

-Preparation by reaction of bromine with 4-hydroxy-3-methoxyacetophenone [397] [399] in ice cooled solution of ethyl ether and dioxane (quantitative yield) [399].

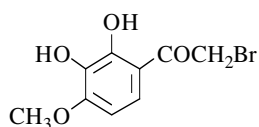
m.p. 78-79° [1235]; ¹H NMR [399], IR [399], MS [399].

2-Bromo-1-(2,3-dihydroxy-4-methoxyphenyl)ethanone

[204648-67-9]

C₉H₉BrO₄

mol.wt. 261.07



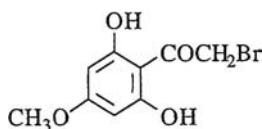
Synthesis

-Refer to: [862] (Japanese patent).

2-Bromo-1-(2,6-dihydroxy-4-methoxyphenyl)ethanone

C₉H₉BrO₄

mol.wt. 261.07



Synthesis

-Preparation by hydrolysis of 2,6-dihydroxy-4-methoxy- α -bromoacetophenone with 16% hydrobromic acid in refluxing ethanol (94%) [426].

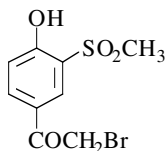
m.p. 139°5-140°5 (d) [426].

2-Bromo-1-[4-hydroxy-3-(methylsulfonyl)phenyl]ethanone

[66264-67-3]

C₉H₉BrO₄S

mol.wt. 293.14



Synthesis

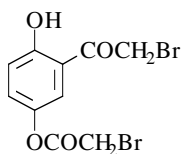
-Preparation by reaction of aluminium chloride on 4-methoxy-3-(methylsulfonyl)- α -bromoacetophenone in refluxing chlorobenzene (70%) [1403].

crystalline solid [1403].

2-Bromo-1-[5-(2-bromoacetyloxy)-2-hydroxyphenyl]ethanone

C₁₀H₈Br₂O₄

mol.wt. 352.00



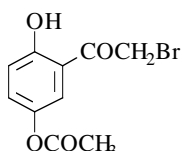
Synthesis

-Preparation by reaction of bromoacetyl bromide on hydroquinone dimethyl ether with aluminium bromide (13-16%) [819] [1048].

m.p. 106-107° [819], 105-107° [1048].

1-[5-(Acetyloxy)-2-hydroxyphenyl]-2-bromoethanoneC₁₀H₉BrO₄

mol.wt. 273.08

**Synthesis**

-Preparation from 2,5-dihydroxy- α -bromoacetophenone on heating with acetyl bromide (62%) [819].

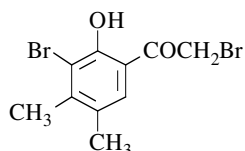
m.p. 143°5-144° [819].

2-Bromo-1-(3-bromo-2-hydroxy-4,5-dimethylphenyl)ethanone

[319923-52-9]

C₁₀H₁₀Br₂O₂

mol.wt. 322.00

**Synthesis**

-Preparation by reaction of bromine with 3-bromo-2-hydroxy-4,5-dimethylacetophenone in acetic acid first at r.t., then at reflux to discolouration (2 min) (80%) [187].

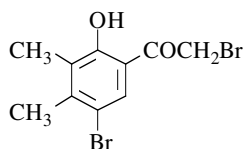
m.p. 109-110° [187]; ¹H NMR [187], IR [187].

2-Bromo-1-(5-bromo-2-hydroxy-3,4-dimethylphenyl)ethanone

[260430-25-9]

C₁₀H₁₀Br₂O₂

mol.wt. 322.00

**Syntheses**

-Preparation by reaction of bromine with 2-hydroxy-3,4-dimethylacetophenone,
 *in chloroform/ethylene dichloride mixture, first in an ice-water bath, then for 1 h at r.t. (68%) [1307];
 *in chloroform in an ice-water bath for 2 h [1308].

-Preparation by reaction of bromine with 5-bromo-2-hydroxy-3,4-dimethylacetophenone in acetic acid first at r.t., then at reflux to discolouration (2 min) (68%) [187].

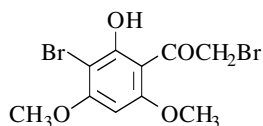
m.p. 97-98° [187] [1307]; ¹H NMR [187] [1307], IR [187] [1307].

2-Bromo-1-(3-bromo-2-hydroxy-4,6-dimethoxyphenyl)ethanone

[29784-35-8]

C₁₀H₁₀Br₂O₄

mol.wt. 354.00

**Synthesis**

-Obtained by reaction of bromine on 2-hydroxy-4,6-dimethoxyacetophenone in chloroform (22%) [150].

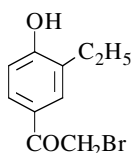
m.p. 194-195° [150]; ¹H NMR [150].

2-Bromo-1-(3-ethyl-4-hydroxyphenyl)ethanone

[73898-24-5]

C₁₀H₁₁BrO₂

mol.wt. 243.10

**Syntheses**

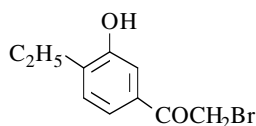
-Preparation by reaction of dioxane dibromide on 3-ethyl-4-hydroxyacetophenone in dioxane-ethyl ether mixture at r.t. (63%) [888].
 -Also refer to: [955].

2-Bromo-1-(4-ethyl-3-hydroxyphenyl)ethanone

[73898-31-4]

C₁₀H₁₁BrO₂

mol.wt. 243.10

**Synthesis**

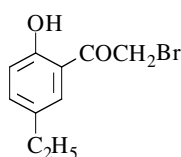
-Preparation by reaction of dioxane dibromide on 4-ethyl-3-hydroxyacetophenone in dioxane-ethyl ether mixture at r.t. (67%) [888].

2-Bromo-1-(5-ethyl-2-hydroxyphenyl)ethanone

[180154-50-1]

C₁₀H₁₁BrO₂

mol.wt. 243.10

**Synthesis**

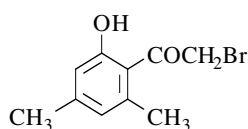
-Refer to: [903].

2-Bromo-1-(2-hydroxy-4,6-dimethylphenyl)ethanone

[67029-80-5]

C₁₀H₁₁BrO₂

mol.wt. 243.10

**Synthesis**

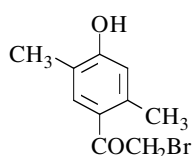
-Preparation by reaction of cupric bromide on 2-hydroxy-4,6-dimethylacetophenone in refluxing chloroform-ethyl acetate mixture [146].

2-Bromo-1-(4-hydroxy-2,5-dimethylphenyl)ethanone

[107584-78-1]

C₁₀H₁₁BrO₂

mol.wt. 243.10

**Synthesis**

-Preparation from 4-hydroxy-2,5-dimethylacetophenone by standard bromination procedure according to [399], (62%) [397].

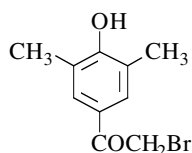
m.p. 129-131° [397]; ¹H NMR [397], MS [397].

2-Bromo-1-(4-hydroxy-3,5-dimethylphenyl)ethanone

[157014-27-2]

C₁₀H₁₁BrO₂

mol.wt. 243.10

**Syntheses**

-Preparation by reaction of 4-hydroxy-3,5-dimethyl- α -chloroacetophenone in boiling methylene chloride with 46-48% aqueous hydrobromic acid in the presence of tetrabutylammonium bromide (0.3 M relative to the ketone) for 24 h, (87% yield) [171].

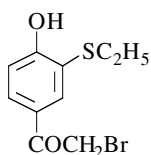
-Also obtained from 4-(benzyloxy)-3,5-dimethyl- α -bromoacetophenone by the former treatment (83%) [170].

-Also refer to: [104].

m.p. 131° [171], 130°6 [170]; ¹H NMR [170] [171], IR [170], MS [170] [171].

2-Bromo-1-[4-hydroxy-3-(ethylthio)phenyl]ethanoneC₁₀H₁₁BrO₂S

mol.wt. 275.17

**Synthesis**

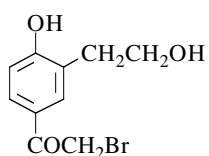
-Preparation by reaction of bromine on 3-(ethylthio)-4-hydroxyacetophenone in chloroform, in the presence of calcium carbonate at 25° [436] [1403].

2-Bromo-1-[4-hydroxy-3-(2-hydroxyethyl)phenyl]ethanone

[101386-50-9]

C₁₀H₁₁BrO₃

mol.wt. 259.10

**Syntheses**

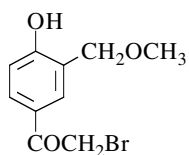
-Refer to: [492] [493].

2-Bromo-1-[4-hydroxy-3-(methoxymethyl)phenyl]ethanone

[91363-39-2]

C₁₀H₁₁BrO₃

mol.wt. 259.10

**Synthesis**

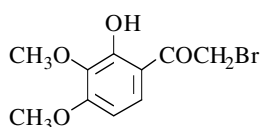
-Refer to: [494].

2-Bromo-1-(2-hydroxy-3,4-dimethoxyphenyl)ethanone

[18064-92-1]

C₁₀H₁₁BrO₄

mol.wt. 275.10

**Syntheses**

-Preparation by reaction of cupric bromide on 2-hydroxy-3,4-dimethoxyacetophenone [353] or 2,3,4-trimethoxyacetophenone [729] in refluxing chloroform-ethyl acetate mixture (47%) [353], (26%) [729].

-Preparation by reaction of bromine on 2-hydroxy-3,4-dimethoxyacetophenone in chloroform-ethyl ether solution (44%) [522].

-Preparation by reaction of bromoacetyl chloride with 1,2,3-trimethoxybenzene in the presence of aluminium chloride in methylene chloride at 20° (42%) [1493].

m.p. 144-145° [522], 142° [1493], 140-142° [729], 140-141° [353];

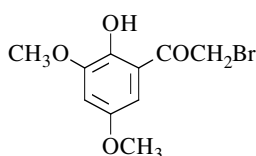
¹H NMR [353] [522] [729], IR [522] [1492] [1493].

2-Bromo-1-(2-hydroxy-3,5-dimethoxyphenyl)ethanone

[204648-51-1]

C₁₀H₁₁BrO₄

mol.wt. 275.10

**Synthesis**

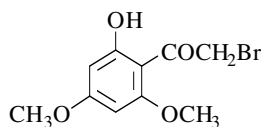
-Refer to: [862] (Japanese patent).

2-Bromo-1-(2-hydroxy-4,6-dimethoxyphenyl)ethanone

[18064-88-5]

C₁₀H₁₁BrO₄

mol.wt. 275.10

**Syntheses**

-Preparation by reaction of aluminium bromide with 2,4,6-trimethoxy- α -bromoacetophenone at 120° [514].

-Preparation by reaction of bromoacetyl bromide with phloroglucinol trimethyl ether according to [425], but using aluminium bromide instead of aluminium chloride in carbon disulfide at r.t. [514].

-Also obtained by reaction of cupric bromide on 2-hydroxy-4,6-dimethoxyacetophenone in refluxing chloroform-ethyl acetate mixture [293] [729], (2%) [729].

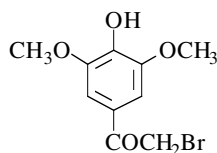
m.p. 130-131° [514], 125-126° [729]; ¹H NMR [293] [729], MS [293].

2-Bromo-1-(4-hydroxy-3,5-dimethoxyphenyl)ethanone

[51149-28-1]

C₁₀H₁₁BrO₄

mol.wt. 275.10

**Syntheses**

-Preparation by bromination of 4-hydroxy-3,5-dimethoxyacetophenone with,

*bromine in chloroform [640] [809] [892] [1005], (90%) [809], (27%) [1005];

*cupric bromide in a refluxing mixture of ethyl acetate and chloroform [1477].

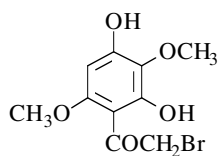
-Also refer to: [377].

m.p. 130° [809], 118-120° [1005]; ¹H NMR [809] [1005], IR [1005], MS [1477].

2-Bromo-1-(2,4-dihydroxy-3,6-dimethoxyphenyl)ethanone

C₁₀H₁₁BrO₅

mol.wt. 291.10



Synthesis

-Preparation by reaction of NBS on 2,4-dihydroxy-3,6-dimethoxyacetophenone in refluxing carbon tetrachloride (64%) [548].

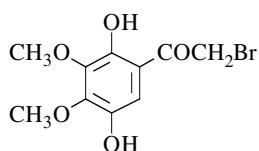
m.p. 159-160° [548].

2-Bromo-1-(2,5-dihydroxy-3,4-dimethoxyphenyl)ethanone

[204648-54-4]

C₁₀H₁₁BrO₅

mol.wt. 291.10



Synthesis

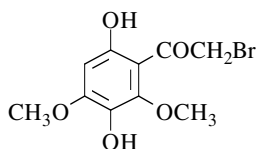
-Refer to: [862] (Japanese paper).

2-Bromo-1-(3,6-dihydroxy-2,4-dimethoxyphenyl)ethanone

[204648-57-7]

C₁₀H₁₁BrO₅

mol.wt. 291.10



Synthesis

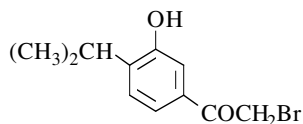
-Refer to: [862] (Japanese paper).

2-Bromo-1-[3-hydroxy-4-(1-methylethyl)phenyl]ethanone

[73898-32-5]

C₁₁H₁₃BrO₂

mol.wt. 257.13



Synthesis

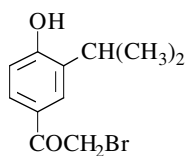
-Preparation by bromination of 3-hydroxy-4-isopropylacetophenone with dioxane dibromide in dioxane-ethyl ether mixture at r.t. (78%) [888].

2-Bromo-1-[4-hydroxy-3-(1-methylethyl)phenyl]ethanone

[73898-25-6]

C₁₁H₁₃BrO₂

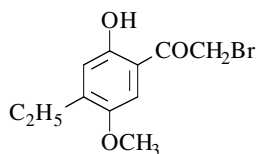
mol.wt. 257.13

**Synthesis**

-Preparation by bromination of 4-hydroxy-3-isopropylacetophenone with dioxane dibromide in dioxane-ethyl ether mixture at r.t. (55%) [888].

2-Bromo-1-(4-ethyl-2-hydroxy-5-methoxyphenyl)ethanoneC₁₁H₁₃BrO₃

mol.wt. 273.13

**Synthesis**

-Preparation by reaction of bromine on 4-ethyl-2-hydroxy-5-methoxyacetophenone in acetic acid at r.t. (59%) [1214].

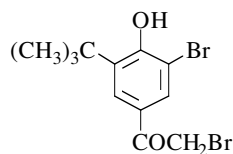
m.p. 75-76° [1214].

2-Bromo-1-[3-bromo-5-(1,1-dimethylethyl)-4-hydroxyphenyl]ethanone

[153355-99-8]

C₁₂H₁₄Br₂O₂

mol.wt. 350.05

**Synthesis**

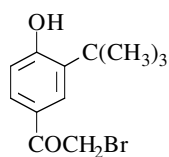
-Refer to: [1562] (Japanese patent).

2-Bromo-1-[3-(1,1-dimethylethyl)-4-hydroxyphenyl]ethanone

[118788-50-4]

C₁₂H₁₅BrO₂

mol.wt. 271.15

**Synthesis**

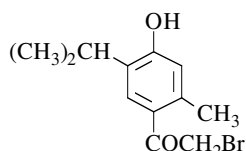
-Refer to: [1457].

2-Bromo-1-[4-hydroxy-2-methyl-5-(1-methylethyl)phenyl]ethanone

[205655-36-3]

C₁₂H₁₅BrO₂

mol.wt. 271.15

**Synthesis**

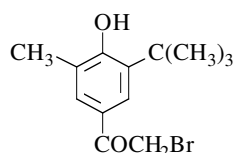
-Refer to: [1395].

N.B.: All reagents and starting materials were from commercial sources. This compound was called 4-hydroxy-3-isopropyl-6-methyl phenacyl bromide (p.185).**2-Bromo-1-[3-(1,1-dimethylethyl)-4-hydroxy-5-methylphenyl]ethanone**

[18611-32-0]

C₁₃H₁₇BrO₂

mol.wt. 285.18

**Syntheses**

-Preparation by bromination of 3-tert-butyl-4-hydroxy-5-methylacetophenone in usual manner in benzene or chloroform [999].

-Preparation by reaction of cupric bromide with 3-tert-butyl-4-hydroxy-5-methylacetophenone in refluxing ethyl acetate (72%) [1457].

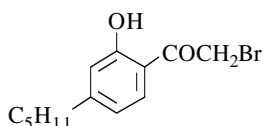
m.p. 95-97° [999], 90-92° [1457].

2-Bromo-1-(2-hydroxy-4-pentylphenyl)ethanone

[133301-45-8]

C₁₃H₁₇BrO₂

mol.wt. 285.18

**Synthesis**

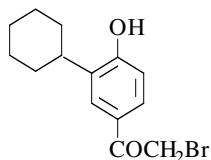
-Obtained by reaction of cupric bromide with 2-hydroxy-4-pentylacetophenone in refluxing ethyl acetate/chloroform mixture (1:1) for 4 h (18%) [1180].

¹H NMR [1180], IR [1180]; TLC [1180].**2-Bromo-1-(3-cyclohexyl-4-hydroxyphenyl)ethanone**

[73898-26-7]

C₁₄H₁₇BrO₂

mol.wt. 297.19

**Synthesis**

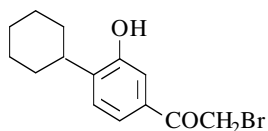
-Preparation by reaction of dioxane dibromide on 3-cyclohexyl-4-hydroxyacetophenone in dioxane and ethyl ether mixture at r.t. (95%) [888].

2-Bromo-1-(4-cyclohexyl-3-hydroxyphenyl)ethanone

[73898-33-6]

C₁₄H₁₇BrO₂

mol.wt. 297.19

**Synthesis**

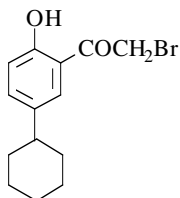
-Preparation by reaction of dioxane dibromide on 4-cyclohexyl-3-hydroxyacetophenone in dioxane and ethyl ether mixture at r.t. (51%) [888].

2-Bromo-1-(5-cyclohexyl-2-hydroxyphenyl)ethanone

[74815-30-8]

C₁₄H₁₇BrO₂

mol.wt. 297.19

**Synthesis**

-Preparation by reaction of cupric bromide on 5-cyclohexyl-2-hydroxyacetophenone in refluxing ethyl acetate [109].

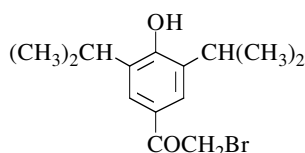
yellow oil [109].

2-Bromo-1-[4-hydroxy-3,5-bis(1-methylethyl)phenyl]ethanone

[157014-26-1]

C₁₄H₁₉BrO₂

mol.wt. 299.21

**Synthesis**

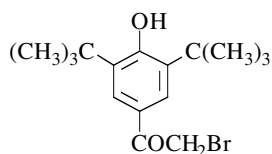
-Preparation by a Friedel-Crafts acylation of propofol (2,6-diisopropylphenol) using aluminium chloride and bromoacetyl bromide in methylene chloride (compound 6) [325].

1-[3,5-Bis(1,1-dimethylethyl)-4-hydroxyphenyl]-2-bromoethanone

[14386-64-2]

C₁₆H₂₃BrO₂

mol.wt. 327.26

**Synthesis**

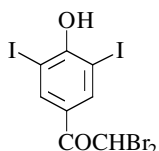
-Preparation by reaction of bromine with 3,5-di-tert-butyl-4-hydroxyacetophenone in ethanol under nitrogen bubbling for 2.5 h (73%) [1577] or in refluxing methylene chloride (67%) [1457].

m.p. 107°5-108°5 [1577], 105-108° [1457]; ¹H NMR [1577].

2.1.2. From dibromoacetic acid

2,2-Dibromo-1-(4-hydroxy-3,5-diiodophenyl)ethanone $C_8H_4Br_2I_2O_2$

mol.wt. 545.74



Synthesis

-Obtained by reaction of bromine on 4-hydroxy-3,5-diiodoacetophenone with sunlight in chloroform at 50-60° (83%) [333].

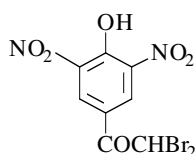
m.p. 132-133° [333].

2,2-Dibromo-1-(4-hydroxy-3,5-dinitrophenyl)ethanone

[120388-19-4]

 $C_8H_4Br_2N_2O_6$

mol.wt. 383.94



Synthesis

-Preparation by bromination of 4-hydroxy-3,5-dinitroacetophenone with excess cupric bromide in refluxing ethyl acetate (66%) [210].

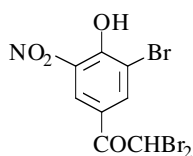
m.p. 93-95° [210].

2,2-Dibromo-1-(3-bromo-4-hydroxy-5-nitrophenyl)ethanone

[35928-54-2]

 $C_8H_4Br_3NO_4$

mol.wt. 417.84



Synthesis

-Preparation by bromination of 3-bromo-4-hydroxy-5-nitroacetophenone in acetic acid-sulfuric acid solution at 25° (78%) [1428].

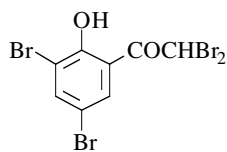
m.p. 121° [1428]; 1H NMR [1428].

2,2-Dibromo-1-(3,5-dibromo-2-hydroxyphenyl)ethanone

[49619-83-2]

 $C_8H_4Br_4O_2$

mol.wt. 451.73



Syntheses

-Preparation by reaction of bromine on 2-hydroxyacetophenone in acetic acid [695] [1246], (62%) [1246].
-Also obtained by reaction of aqueous sodium hypobromite on chromone-3-carboxaldehyde in acetic acid (24-30%) [1096] [1097].

-Also obtained by reaction of sodium sulfite on 3,5-dibromo-2-hydroxy- α,α,α -tribromoacetophenone, in boiling acetic acid [513].

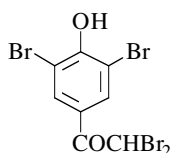
-Also obtained by reaction of bromine on 3,3'-diacetyl-4,4'-dihydroxydiphenyl thioether [692].

m.p. 124-125° [1096], 122-123° [513], 121-122° [1097],
120-121° [692] [695] [1246];

1H NMR [1096] [1097], IR [1096] [1097], UV [1096], MS [1096] [1097].

2,2-Dibromo-1-(3,5-dibromo-4-hydroxyphenyl)ethanoneC₈H₄Br₄O₂

mol.wt. 451.73



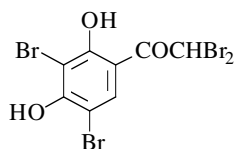
Syntheses

- Preparation by reaction of bromine on 3,5-dibromo-4-hydroxyacetophenone [1201] [1246].
- Preparation by reaction of bromine on 4-hydroxyacetophenone in acetic acid (60%) [1246].

m.p. 105-106° [1246], 105° [1201].

2,2-Dibromo-1-(3,5-dibromo-2,4-dihydroxyphenyl)ethanoneC₈H₄Br₄O₃

mol.wt. 467.73



Synthesis

- Preparation by reaction of bromine on resacetophenone in acetic acid [231].

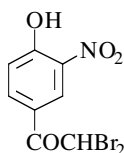
m.p. 110-110°5 [231].

2,2-Dibromo-1-(4-hydroxy-3-nitrophenyl)ethanone

[35928-53-1]

C₈H₅Br₂NO₄

mol.wt. 338.94

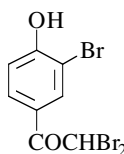


Syntheses

- Preparation by bromination of 4-hydroxy-3-nitroacetophenone with excess cupric bromide in refluxing ethyl acetate (56-82%) [210].
- Preparation by bromination of 4-hydroxy-3-nitroacetophenone in acetic acid-sulfuric acid mixture at 25° (49%) [1428].

m.p. 63° [1428]; ¹H NMR [1428].**2,2-Dibromo-1-(3-bromo-4-hydroxyphenyl)ethanone**C₈H₅Br₃O₂

mol.wt. 372.84



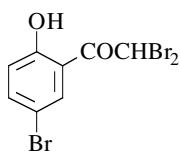
Synthesis

- Preparation by reaction of bromine on 4-hydroxyacetophenone in acetic acid or chloroform (65%) [1246].

m.p. 139° [1246].

2,2-Dibromo-1-(5-bromo-2-hydroxyphenyl)ethanoneC₈H₅Br₃O₂

mol.wt. 372.84

**Synthesis**

-Preparation by reaction of bromine on 2-hydroxyacetophenone in chloroform or acetic acid (quantitative yield) [1246].

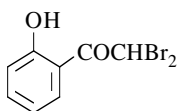
m.p. 103-104° [1246].

2,2-Dibromo-1-(2-hydroxyphenyl)ethanone

[54735-43-2]

C₈H₆Br₂O₂

mol.wt. 293.94

**Syntheses**

-Obtained by transformation of 4-hydroxycoumarin with tetrabutylammonium bromide promoted by hydrogen peroxide and vanadium pentoxide at 5° for 1 h (55%) [209].
-Also refer to: [79].

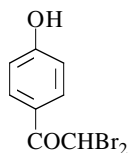
¹H NMR [209], ¹³C NMR [209], UV [79]; TLC [209], GC [209].

2,2-Dibromo-1-(4-hydroxyphenyl)ethanone

[92596-96-8]

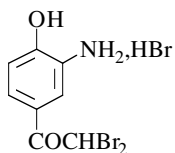
C₈H₆Br₂O₂

mol.wt. 293.94

**Syntheses**

-Preparation by bromination of 4-hydroxyacetophenone with excess cupric bromide in refluxing ethyl acetate (56-82%) [210].
-Also obtained (by-product) by reaction of bromine with p-hydroxyacetophenone in dioxane at r.t. for 40 min (< 6%) [853].

m.p. 121-122° [853]; ¹H NMR [853], IR [853].

1-(3-Amino-4-hydroxyphenyl)-2,2-dibromoethanone (Hydrobromide)C₈H₇Br₂NO₂, HBr mol.wt. 389.87**Synthesis**

-Preparation by reaction of bromine on 3-amino-4-hydroxyacetophenone hydrobromide in acetic acid at 65° (60%) [275].

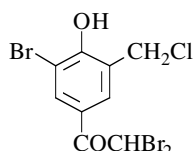
m.p. 215° [275].

2,2-Dibromo-1-[3-bromo-5-(chloromethyl)-4-hydroxyphenyl]ethanone

[107700-05-0]

C₉H₆Br₃ClO₂

mol.wt. 421.31

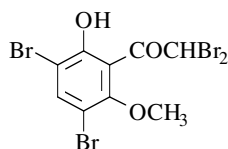
**Synthesis**

-Preparation by adding a methylene chloride solution of bromine to a methanol/methylene chloride solution of 3-(chloromethyl)-4-hydroxyacetophenone at r.t. (82%) [214].

m.p. 140° [214]; ¹H NMR [214], IR [214], MS [214].

2,2-Dibromo-1-(3,5-dibromo-2-hydroxy-6-methoxyphenyl)ethanoneC₉H₆Br₄O₃

mol.wt. 481.76

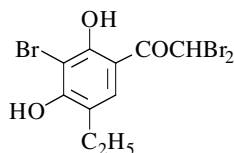
**Synthesis**

-Obtained by reaction of bromine on 3,3'-diacetyl-2,2'-dihydroxy-4,4'-dimethoxydiphenylsulfide in acetic acid, heated in a boiling water bath [358].

m.p. 101-102° [358].

2,2-Dibromo-1-(3-bromo-5-ethyl-2,4-dihydroxyphenyl)ethanoneC₁₀H₉Br₃O₃

mol.wt. 416.89

**Synthesis**

-Preparation by reaction of 5-ethyl-2,4-dihydroxyacetophenone with an excess of bromine in chloroform [1327].

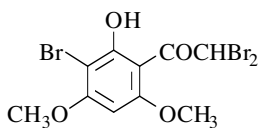
m.p. 144-145° [1327].

2,2-Dibromo-1-(3-bromo-2-hydroxy-4,6-dimethoxyphenyl)ethanone

[88503-19-9]

C₁₀H₉Br₃O₄

mol.wt. 432.89

**Synthesis**

-Preparation by heating for 7 h on a steam bath a mixture of 2-hydroxy-3-iodo-4,6-dimethoxyacetophenone and bromine in acetic acid (67%) [415].

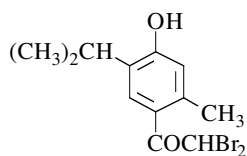
m.p. 167-168° [415].

2,2-Dibromo-1-[4-hydroxy-2-methyl-5-(1-methylethyl)phenyl]ethanone

[72235-94-0]

C₁₂H₁₄Br₂O₂

mol.wt. 350.05

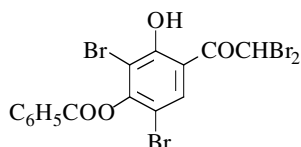
**Synthesis**

-Preparation by reaction of bromine on 4-hydroxy-2-methyl-5-isopropylacetophenone in acetic acid at 18° (45%) [105].

m.p. 111° [105].

1-[4-(Benzoyloxy)-3,5-dibromo-2-hydroxyphenyl]-2,2-dibromoethanoneC₁₅H₈Br₄O₄

mol.wt. 571.84

**Synthesis**

-Preparation by bromination of 4-(benzoyloxy)-2-hydroxyacetophenone at r.t. [694].

m.p. 69-70° [694].

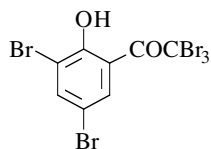
2.1.3. From tribromoacetic acid

2,2,2-Tribromo-1-(3,5-dibromo-2-hydroxyphenyl)ethanone

[98436-51-2]

C₈H₃Br₅O₂

mol.wt. 530.63

**Synthesis**

-Obtained by reaction of bromine on 4-hydroxycoumarin (benzotetronic acid) in methanol or acetic acid at r.t. [513].

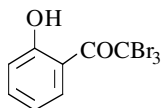
m.p. 125-126° [513].

2,2,2-Tribromo-1-(2-hydroxyphenyl)ethanone

[101495-49-2]

C₈H₅Br₃O₂

mol.wt. 372.84

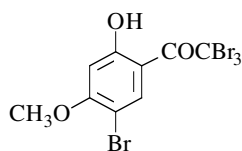
**Synthesis**

-Obtained by reaction of bromine on 4-hydroxycoumarin (benzotetronic acid) in acetic acid-dioxane mixture at r.t. [513].

m.p. 87° [513].

2,2,2-Tribromo-1-(5-bromo-2-hydroxy-4-methoxyphenyl)ethanoneC₉H₆Br₄O₃

mol.wt. 481.76

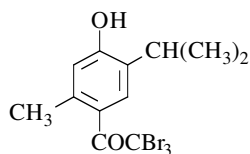
**Synthesis**

-Preparation by reaction of bromine on bromopaeonol (5-bromo-2-hydroxy-4-methoxyacetophenone) in the presence of a crystal of iodine at r.t. [6].

m.p. 123-124° [6].

2,2,2-Tribromo-1-[4-hydroxy-2-methyl-5-(1-methylethyl)phenyl]ethanoneC₁₂H₁₃Br₃O₂

mol.wt. 428.95

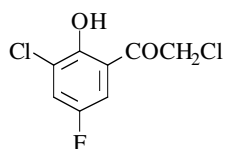
**Synthesis**

-Preparation by reaction of bromine on 4-hydroxy-2-methyl-5-isopropylacetophenone in acetic acid at 18° (90%) [105].

m.p. 69° [105].

2.2. Compounds derived from chloroacetic acids**2.2.1. From monochloroacetic acid****2-Chloro-1-(3-chloro-5-fluoro-2-hydroxyphenyl)ethanone**C₈H₅Cl₂FO₂

mol.wt. 223.03

**Synthesis**

-Preparation by Fries rearrangement of 2-chloro-4-fluorophenyl chloroacetate with aluminium chloride without solvent at 130-140° (63%) [741].

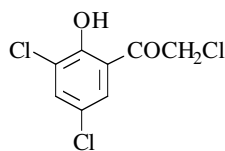
b.p.₂ 116° [741].

2-Chloro-1-(3,5-dichloro-2-hydroxyphenyl)ethanone

[79214-30-5]

C₈H₅Cl₃O₂

mol.wt. 239.48

**Syntheses**

-Preparation by Fries rearrangement of 2,4-dichlorophenyl chloroacetate with aluminium chloride without solvent at 135-145° [1049] [1401], (56%) [1401].

-Preparation by reaction of chloroacetyl chloride on 2,4-dichloroanisole with aluminium chloride in refluxing carbon disulfide (45%) [1298].

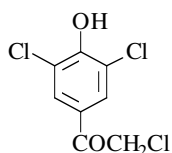
m.p. 136-136°8 [1401], 133° [1298], 132-134° [1049].

2-Chloro-1-(3,5-dichloro-4-hydroxyphenyl)ethanone

[220291-97-4]

C₈H₅Cl₃O₂

mol.wt. 239.48

**Syntheses**

-Preparation by Fries rearrangement of 2,6-dichlorophenyl chloroacetate with aluminium chloride without solvent at 112-114° (77%) [1442].
-Also refer to: [770] (Japanese patent).

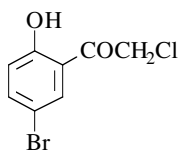
m.p. 120-121° [1442].

1-(5-Bromo-2-hydroxyphenyl)-2-chloroethanone

[100959-21-5]

C₈H₆BrClO₂

mol.wt. 249.49

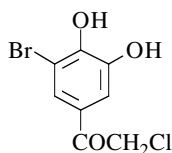
**Synthesis**

-Preparation by reaction of chloroacetyl chloride with 4-bromophenol in the presence of aluminium chloride at 40° (66%) [677].

m.p. 73-74° [677].

1-(3-Bromo-4,5-dihydroxyphenyl)-2-chloroethanoneC₈H₆BrClO₃

mol.wt. 265.50

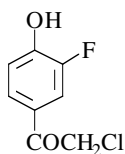
**Synthesis**

-Preparation by bromination of 3,4-dihydroxy- α -chloroacetophenone with bromine in the presence of quinoline sulfate while cooling (60%) [1250] according to the method [1244].

m.p. 137° [1250].

2-Chloro-1-(3-fluoro-4-hydroxyphenyl)ethanoneC₈H₆ClFO₂

mol.wt. 188.59

**Synthesis**

-Preparation by Fries rearrangement of 2-fluorophenyl chloroacetate with aluminium chloride without solvent at 135-140° (27-40%) [612].

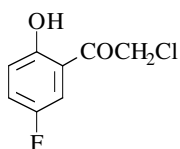
m.p. 101-102° [612].

2-Chloro-1-(5-fluoro-2-hydroxyphenyl)ethanone

[2002-75-7]

C₈H₆ClFO₂

mol.wt. 188.59

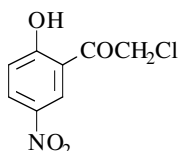
**Synthesis**

-Preparation by Fries rearrangement of 4-fluorophenyl chloroacetate with aluminium chloride without solvent at 130° (50%) [740].

b.p.₁₀ 177° [740].

2-Chloro-1-(2-hydroxy-5-nitrophenyl)ethanoneC₈H₆ClNO₄

mol.wt. 215.59

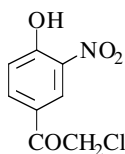
**Synthesis**

-Obtained by nitration of 2-hydroxy- α -chloroacetophenone in acetic acid [101].

m.p. 163-164° [101].

2-Chloro-1-(4-hydroxy-3-nitrophenyl)ethanoneC₈H₆ClNO₄

mol.wt. 215.59

**Syntheses**

-Preparation by reaction of chlorine on 4-hydroxy-3-nitroacetophenone in acetic acid (45%) [275].

-Also obtained by reaction of chloroacetyl chloride on 2-nitrophenol with aluminium chloride in nitrobenzene at 50-60° (19%) [275].

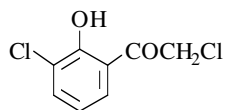
m.p. 88° [275]; b.p._{0.1} 135-140° [275], b.p._{0.4} 140-145° [275].

2-Chloro-1-(3-chloro-2-hydroxyphenyl)ethanone

[75717-49-6]

C₈H₆Cl₂O₂

mol.wt. 205.04

**Synthesis**

-Obtained by reaction of chloroacetonitrile on 2-chlorophenol with aluminium chloride and boron trichloride mixture in ethylene dichloride at r.t. (21%) [1409] [1466].

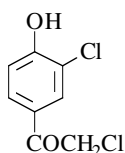
m.p. 72-73° [1409] [1466]; ¹H NMR [1466].

2-Chloro-1-(3-chloro-4-hydroxyphenyl)ethanone

[39066-18-7]

C₈H₆Cl₂O₂

mol.wt. 205.04

**Synthesis**

-Preparation by Fries rearrangement of 2-chlorophenyl chloroacetate with aluminium chloride without solvent at 135-140° (39 to 59%) [164] [507] [612].

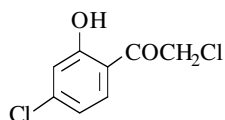
m.p. 141-142° [612].

2-Chloro-1-(4-chloro-2-hydroxyphenyl)ethanone

[75717-50-9]

C₈H₆Cl₂O₂

mol.wt. 205.04

**Synthesis**

-Preparation by reaction of chloroacetonitrile on 3-chlorophenol with aluminium chloride and boron trichloride mixture in refluxing ethylene dichloride (51%) [1409] [1466].

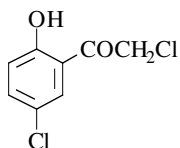
m.p. 75-76° [1409] [1466]; ¹H NMR [1466].

2-Chloro-1-(5-chloro-2-hydroxyphenyl)ethanone

[24483-75-8]

C₈H₆Cl₂O₂

mol.wt. 205.04

**Syntheses**

-Preparation by Fries rearrangement of 4-chlorophenyl chloroacetate with aluminium chloride without solvent at 140-150° [520] [1049] [1219], (30%) [1219].

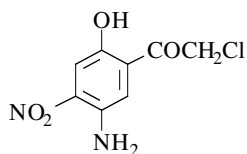
-Also obtained by reaction of chloroacetonitrile on 4-chlorophenol with aluminium chloride and boron

trichloride mixture in ethylene dichloride [1409] [1466], (18%) [1409].

m.p. 107-110° [1049], 65-66° [1409] [1466], 65° [520] [1219]. One of the reported melting points is obviously wrong. ¹H NMR [1466].

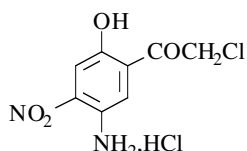
1-(5-Amino-2-hydroxy-4-nitrophenyl)-2-chloroethanoneC₈H₇ClN₂O₄

mol.wt. 230.61

**Synthesis**

-Preparation by treatment of 5-acetamido-2-hydroxy-4-nitro-α-chloroacetophenone with boiling 25% aqueous hydrochloric acid solution [859].

m.p. 145° (d) [859].

1-(5-Amino-2-hydroxy-4-nitrophenyl)-2-chloroethanone (*Hydrochloride*)C₈H₇ClN₂O₄, HCl mol.wt. 267.07

Synthesis

-Preparation from 5-amino-2-hydroxy-4-nitro- α -chloroacetophenone [859] (see above).

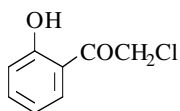
m.p. 210° (d) [859].

2-Chloro-1-(2-hydroxyphenyl)ethanone

[53074-73-0]

C₈H₇ClO₂

mol.wt. 170.60



Syntheses

-Preparation by reaction of acetonitrile on phenol with aluminium chloride and boron trichloride in refluxing ethylene dichloride (78%) [1409] or in methylene chloride at r.t. (85%) [1466].

-Preparation by halogenation of o-hydroxyacetophenone,

*using EGDMA crosslinked polystyrene based benzyltriethylammonium dichloriodate or tetrachloriodate reagents in chloroform for 7-11 h at 30° (80%) [1013];

*using 5% N,N'-MBA crosslinked polyacrylamide-based dichloriodate or tetrachloriodate reagents in chloroform at 30° for 8 h (77-79%) [1012];

*with benzyltrimethylammonium dichloriodate in refluxing methylene chloride/methanol mixture for 10 h (73%) [748].

-Preparation by reaction of hexachloro-2,4-cyclohexadienone on 2-hydroxyacetophenone in refluxing ethanol (66%) [603].

-Preparation by Fries rearrangement of phenyl monochloroacetate,

*with aluminium chloride (50%) [956], without solvent at 120° (50%) [519] or at 140° (by-product) [351];

*with beryllium chloride without solvent at 130-140° (30%) [225].

-Also obtained by reaction of chloroacetyl chloride on bromomagnesium phenolate in toluene at r.t. (17%) [1286].

-Also obtained by reaction of aluminium chloride on 2-chloroacetylanisole in refluxing carbon disulfide [100] [1482].

-Also obtained (by-product) by reaction of chloroacetyl chloride on phenol with aluminium chloride at 140° [351].

-Also obtained (by-product) by treatment of anisole with chloroacetyl chloride in the presence of aluminium chloride in tetrachloroethane in a boiling water bath for 2-3 h [254] [1538].

-Also refer to: [156] [161] [162] [401] [906] [1461] [1478] [1479] [1524].

m.p. 101° [1482], 74-75° [1286], 74° [351] [519] [956] [1012], 73-74° [100], 73° [225] [254] [603] [748] [1482] [1538], 72-73° [1466], 72° [1013], 71-71°5 [906]; One of the reported melting points is obviously wrong.

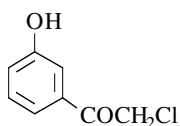
¹H NMR [603] [748] [1286], IR [603] [748].

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

[62932-90-5]

C₈H₇ClO₂

mol.wt. 170.60

**Synthesis**

-Preparation by reaction of hexachloro-2,4-cyclohexadienone on 3-hydroxyacetophenone in refluxing ethanol (50%) [603].

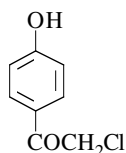
m.p. 93° [603]; ¹H NMR [603], IR [603].

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

[6305-04-0]

C₈H₇ClO₂

mol.wt. 170.60

**Syntheses**

-Preparation by reaction of p-hydroxyacetophenone with benzyltrimethylammonium dichloriodate in refluxing methylene chloride/methanol mixture for 10 h (95%) [748] or for 12 h (92%) [597].

-Preparation by reaction of chloroacetyl chloride,

*with anisole in the presence of aluminium chloride in ligroin (44%) [36], for 1 h in a water bath (50-55°) (32%) [1363], for 4 h (36%) [1263] or for 3 h (41-42%) [515];

*with anisole in the presence of aluminium chloride without solvent [857], in carbon disulfide [1483] or in tetrachloroethane in a boiling water bath for 2-3 h [254], (53%) [1538];

*with phenol in the presence of aluminium chloride without solvent at 140° (71%) [351] or in tetrachloroethane, first at 70° for 5 h, then at r.t. for 10 h [1537].

-Also obtained by Fries rearrangement of phenyl chloroacetate,

*with aluminium chloride without solvent at 120-140° [351] [519], (65%) [351];

*with beryllium chloride without solvent at 130-140° (23%) [225].

-Preparation by reaction of hexachloro-2,4-cyclohexadienone on 4-hydroxyacetophenone in refluxing ethanol (77%) [603].

-Also refer to: [147] [306] [908].

m.p. 151-152° [906], 150-151° [597], 150° [748], 148° [36] [351] [515] [857] [1483], 147-148° (d) [1363], 147° [1263], 147° [254] [1538], 145-146° [225], 142° [603];

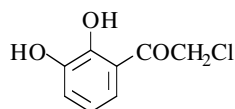
¹H NMR [597] [603] [748], IR [603] [748].

2-Chloro-1-(2,3-dihydroxyphenyl)ethanone

[63704-55-2]

C₈H₇ClO₃

mol.wt. 186.59

**Synthesis**

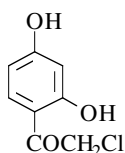
-Refer to: [1412] (Japanese patent).

2-Chloro-1-(2,4-dihydroxyphenyl)ethanone

[25015-92-3]

C₈H₇ClO₃

mol.wt. 186.59

**Syntheses**

-Preparation by reaction of chloroacetonitrile on resorcinol with zinc chloride (Hoesch reaction) (90%) [1381], (82%) [1579] or with triflic acid (trifluoromethanesulfonic acid) (23%) [207].

-Also obtained by reaction of chloroacetic acid on resorcinol with boron trifluoride (30%) [248] or with zinc chloride or phosphorous oxychloride (poor yield) [436] [516].

m.p. 132° [248], 131° [1381], 130-132° [207], 130° [1579];

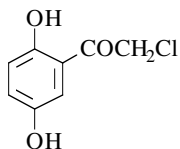
¹H NMR [207], IR [207], UV [666].

2-Chloro-1-(2,5-dihydroxyphenyl)ethanone

[60912-82-5]

C₈H₇ClO₃

mol.wt. 186.59

**Syntheses**

-Obtained by reaction of hydrochloric acid on 2,5-diacetoxy- α -chloroacetophenone in methanol at r.t. (85%) [819].

-Preparation by reaction of aluminium bromide on 2,5-dimethoxy- α -chloroacetophenone in carbon disulfide at r.t. (72%) [819].

-Also obtained by action of acetic acid saturated with hydrochloric acid (10 min, r.t.) on 2,5-diacetoxy- α -chloroacetophenone, reduced pressure elimination of acetic acid, then action (overnight, r.t.) of a methanolic solution of hydrochloric acid (53%) [819].

-Also obtained by reaction of sulfur dioxide on 2-chloroacetyl-1,4-benzoquinone in water [819].

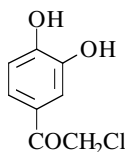
m.p. 132-133° [819].

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

[99-40-1]

C₈H₇ClO₃

mol.wt. 186.59

**Syntheses**

-Preparation by Fries rearrangement of pyrocatechol mono-chloroacetate with aluminium chloride in nitrobenzene at 100° (60%) [1245] or without solvent at 100° (25%) [836].

-Preparation by reaction of chloroacetic acid on pyrocatechol with boron trifluoride in tetrachloroethane or

in carbon tetrachloride at 65-85° (95-98%) [248] or with phosphorous oxychloride [437] [738] [963] [1081] [1365], (80%) [437], (35-58%) [738] [963] [1365].

-Preparation by reaction of chloroacetyl chloride on pyrocatechol [437].

-Preparation by reaction of chloroacetyl chloride on veratrole with aluminium chloride in nitrobenzene at 40° (82%) [1402].

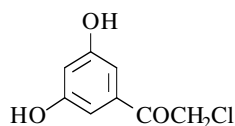
m.p. 173° [248] [437] [738] [963] [1245] [1402], 172° [435] [1365], 171° [836], 169-170° [1193]; b.p.₁₂ 190° [1402].

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

[39878-43-8]

C₈H₇ClO₃

mol.wt. 186.59

**Synthesis**

-Preparation by reaction of hydrochloric acid on 3,5-di-acetoxy- α -diazoacetophenone in aqueous methanol at reflux (97%) [1027].

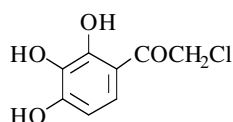
m.p. 117° [1027].

2-Chloro-1-(2,3,4-trihydroxyphenyl)ethanone

[17345-68-5]

C₈H₇ClO₄

mol.wt. 202.59

**Syntheses**

-Preparation by Fries rearrangement of 2,6-dimethoxyphenyl chloroacetate with aluminium chloride without solvent at 100° [980].

-Preparation by reaction of chloroacetyl chloride on pyrogallol [437].

-Preparation by reaction of chloroacetic acid on pyrogallol with phosphorous oxychloride [366] [436] [487] [516] [1081] [1083] [1365] [1381], (55%) [487], (40-41%) [366] [1365], with boron trifluoride [248] [880] or with zinc chloride (poor yield) [436] [516].

-Preparation by reaction of chloroacetic anhydride with pyrogallol in the presence of boron trifluoride in ethyl ether [554].

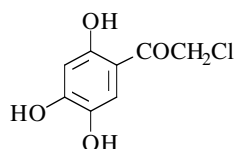
m.p. 169° [366], 167-168° [1083], 167° [248], 166° [1365], 163-165° [1193].

2-Chloro-1-(2,4,5-trihydroxyphenyl)ethanone

[14771-02-9]

C₈H₇ClO₄

mol.wt. 202.59

**Synthesis**

-Preparation by reaction of chloroacetonitrile on 1,2,4-benzenetriol (hydroxyhydroquinone) with zinc chloride in ethyl ether (Hoesch reaction) [553] [1294] [1295].

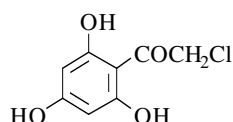
m.p. 182° [1294], 139-140° [1295]. One of the reported melting points is obviously wrong.
¹H NMR [1294], IR [1294] [1295], UV [1294] [1295].

2-Chloro-1-(2,4,6-trihydroxyphenyl)ethanone

[110865-03-7]

C₈H₇ClO₄

mol.wt. 202.59

**Syntheses**

-Preparation by reaction of chloroacetyl chloride on phloroglucinol with aluminium chloride in nitromethane (86%) [880].

-Preparation by reaction of chloroacetonitrile on phloroglucinol (Hoesch reaction) (88%) [1352], (68%) [292].

-Also refer to: [294] (compound **1**).

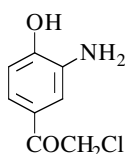
m.p. 190° [880], 188-191° [292] [1352]; ¹H NMR [292], IR [292], MS [292].

1-(3-Amino-4-hydroxyphenyl)-2-chloroethanone

[108708-12-9]

C₈H₈ClNO₂

mol.wt. 185.61



Synthesis

-Preparation by Friedel-Crafts chloroacetylation of N-acetyl-o-anisidine followed by hydrolysis with concentrated hydrochloric acid in ethanol [1153].

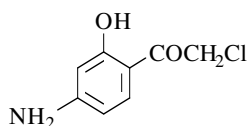
m.p. 113° [1153].

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

[108708-13-0]

C₈H₈ClNO₂

mol.wt. 185.61



Synthesis

-Preparation by Friedel-Crafts chloroacetylation of N-acetyl-m-anisidine followed by hydrolysis with concentrated hydrochloric acid in ethanol [1153].

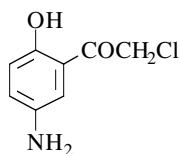
m.p. 214° (d) [1153].

1-(5-Amino-2-hydroxyphenyl)-2-chloroethanone

[108708-11-8]

C₈H₈ClNO₂

mol.wt. 185.61



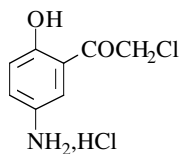
Synthesis

-Preparation by Friedel-Crafts chloroacetylation of N-acetyl-p-anisidine followed by hydrolysis with concentrated hydrochloric acid in ethanol [858] [859] [1153].

m.p. 135° [858] [859], 128° [1153].

1-(5-Amino-2-hydroxyphenyl)-2-chloroethanone (Hydrochloride)

C₈H₈ClNO₂, HCl mol.wt. 222.07



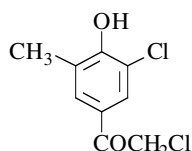
Synthesis

-Obtained by reaction of gaseous hydrochloric acid on 5-amino-2-hydroxy-α-chloroacetophenone in ethyl ether [859].

m.p. 210° (d) [859].

2-Chloro-1-(3-chloro-4-hydroxy-5-methylphenyl)ethanoneC₉H₈Cl₂O₂

mol.wt. 219.07

**Synthesis**

-Preparation by Fries rearrangement of 2-chloro-6-methylphenyl chloroacetate with aluminium chloride at 140° [94].

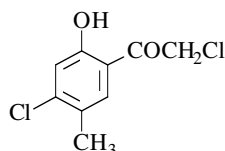
m.p. 98°5-99°5 [94]; b.p.₁₂ 172-180° [94].

2-Chloro-1-(4-chloro-2-hydroxy-5-methylphenyl)ethanone

[22307-95-5]

C₉H₈Cl₂O₂

mol.wt. 219.07

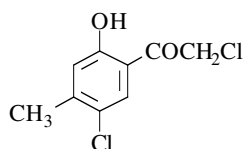
**Synthesis not yet described**

-See [1130]; this reference mentioned in the Chem. Abstr., **70**, 11442s (1969) is erroneous. Actually, the ketone described here as the 2,4'-dichloro-2'-hydroxy-5'-methylacetophenone should be the 2,5'-dichloro-2'-hydroxy-4'-methylacetophenone. In fact, on one hand, it is obtained

by Fries rearrangement of 4-chloro-3-methylphenyl chloroacetate and on the other hand, it provides the 5-chloro-6-methyl-3-[2*H*]-benzofuranone by cyclisation (see below).

2-Chloro-1-(5-chloro-2-hydroxy-4-methylphenyl)ethanoneC₉H₈Cl₂O₂

mol.wt. 219.07

**Synthesis**

-Preparation by Fries rearrangement of 4-chloro-3-methylphenyl chloroacetate with aluminium chloride without solvent at 150° [1130].

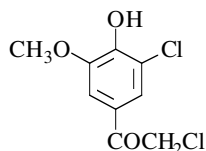
m.p. 111° [1130]; ¹H NMR [1130], IR [1130].

2-Chloro-1-(3-chloro-4-hydroxy-5-methoxyphenyl)ethanone

[160925-81-5]

C₉H₈Cl₂O₃

mol.wt. 235.07

**Syntheses**

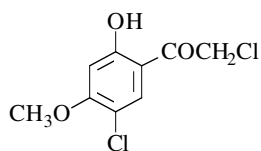
-Preparation by chlorination of acetoguaiacone (4-hydroxy-3-methoxyacetophenone) in dioxane with 2.5 mol. equiv chlorine in acetic acid (67%) [1374].

-Also refer to: [1519].

m.p. 149-150° [1374]; ¹H NMR [1374], ¹³C NMR [1374], MS [1374].

2-Chloro-1-(5-chloro-2-hydroxy-4-methoxyphenyl)ethanoneC₉H₈Cl₂O₃

mol.wt. 235.07

**Syntheses**

- Preparation by reaction of chloroacetyl chloride on 4-chlororesorcinol dimethyl ether with aluminium chloride in carbon disulfide (66%) [96].
- Preparation by reaction of chlorine on 2-hydroxy-4-methoxy- α -chloroacetophenone in chloroform (40-45%) [96].

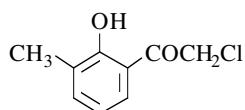
m.p. 178°5-180° [96].

2-Chloro-1-(2-hydroxy-3-methylphenyl)ethanone

[75717-51-0]

C₉H₉ClO₂

mol.wt. 184.62

**Syntheses**

- Preparation by reaction of chloroacetonitrile on o-cresol with aluminium chloride and boron trichloride mixture in ethylene dichloride at r.t. (75%) [1409] [1466] or with only boron trichloride in methylene chloride at r.t. under nitrogen (18%) [183].
- Preparation by Fries rearrangement of 2-methylphenyl chloroacetate with aluminium chloride without solvent at 140° (50%) [679], (20%) [98].

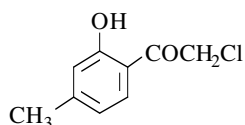
m.p. 67° [98], 66-67° [679], 65-66° [1409] [1466], 63-64° [183];

¹H NMR [183] [1466], IR [183], UV [183], MS [183].**2-Chloro-1-(2-hydroxy-4-methylphenyl)ethanone**

[20834-75-7]

C₉H₉ClO₂

mol.wt. 184.62

**Syntheses**

- Preparation by Fries rearrangement of 3-methylphenyl chloroacetate with aluminium chloride without solvent between 140 to 150° [274] [518] [679] [1130] [1370], (70%) [679], (50%) [518] [1370], (12%) [274].
- Preparation by reaction of chloroacetonitrile on m-cresol with boron trichloride and aluminium chloride in refluxing ethylene dichloride (quantitative yield) [1409].
- Also refer to: [109] [1478].

m.p. 102-102°5 [679], 102° [1130], 101° [518], 100° [274], 95-96° [1409];

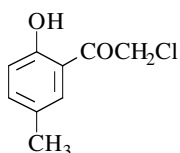
¹H NMR [1130], IR [1130].

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

[22307-94-4]

C₉H₉ClO₂

mol.wt. 184.62

**Syntheses**

- Preparation by Fries rearrangement of p-tolyl chloroacetate with aluminium chloride without solvent at 140° [351] [518] [679] [1049], (90-93%) [518] [679], (37%) [351].
- Preparation by reaction of chloroacetic acid on p-cresol with boron trifluoride etherate (66%) or boron trifluoride (46%) in an autoclave at 70° [1111].
- Preparation by reaction of chloroacetyl chloride on 4-methylanisole with aluminium chloride in refluxing carbon disulfide (50-60%) [95].
- Preparation by reaction of chloroacetyl chloride on p-cresol with aluminium chloride without solvent at 140° (31%) [351].

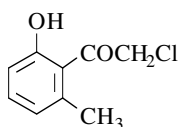
m.p. 65° [351] [518], 63° [95], 62-63° [679] [1049], 62° [1111].

2-Chloro-1-(2-hydroxy-6-methylphenyl)ethanone

[73331-41-6]

C₉H₉ClO₂

mol.wt. 184.62

**Synthesis**

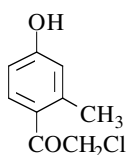
- Refer to: [1020].

2-Chloro-1-(4-hydroxy-2-methylphenyl)ethanone

[37904-71-5]

C₉H₉ClO₂

mol.wt. 184.62

**Synthesis**

- Preparation by Fries rearrangement of 3-methylphenyl chloroacetate with aluminium chloride without solvent at 140° [274] [679], (30%) [679].

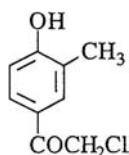
m.p. 148°5-149° [679], 147°5 [274].

2-Chloro-1-(4-hydroxy-3-methylphenyl)ethanone

[40943-24-6]

C₉H₉ClO₂

mol.wt. 184.62

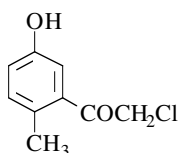
**Synthesis**

- Preparation by Fries rearrangement of 2-methylphenyl chloroacetate with aluminium chloride without solvent at 140° [98] [679], (50%) [679].

m.p. 144-145° [98], 144-144°5 [679].

2-Chloro-1-(5-hydroxy-2-methylphenyl)ethanoneC₉H₉ClO₂

mol.wt. 184.62

**Synthesis**

-Obtained (by-product) by Fries rearrangement of 4-methylphenyl chloroacetate with aluminium chloride without solvent at 140° (7%) [679].

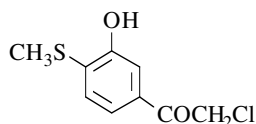
m.p. 155°-156° [679].

2-Chloro-1-[3-hydroxy-4-(methylthio)phenyl]ethanone

[151792-80-2]

C₉H₉ClO₂S

mol.wt. 216.69

**Synthesis**

-Preparation by hydrolysis of 3-hydroxy-4-methylthio- α -chloroacetophenone chloroacetate with 1 N sodium hydroxide in methanol at r.t. (94%) [82].

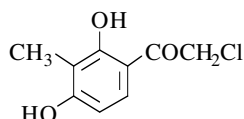
m.p. 140° [82]; ¹H NMR [82], IR [82], MS [82].

2-Chloro-1-(2,4-dihydroxy-3-methylphenyl)ethanone

[21861-21-2]

C₉H₉ClO₃

mol.wt. 200.62

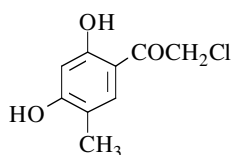
**Synthesis**

-Preparation by reaction of chloroacetonitrile with 2-methyl-resorcinol (72%) (Hoesch reaction) [264].

m.p. 155° [264].

2-Chloro-1-(2,4-dihydroxy-5-methylphenyl)ethanoneC₉H₉ClO₃

mol.wt. 200.62

**Syntheses**

-Preparation by reaction of chloroacetonitrile with 4-methyl-resorcinol (Hoesch reaction) [1053].

-Also obtained by Friedel-Crafts acylation of 4-methyl-resorcinol with chloroacetyl chloride in the presence of aluminium chloride in nitrobenzene [653].

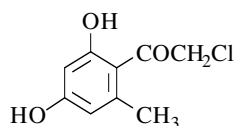
m.p. 157° [653], 156° [1053].

2-Chloro-1-(2,4-dihydroxy-6-methylphenyl)ethanone

[22670-61-7]

C₉H₉ClO₃

mol.wt. 200.62

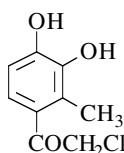
**Synthesis**

-Preparation by reaction of chloroacetonitrile with orcinol (68%) (Hoesch reaction) [264].

m.p. 151° [264].

2-Chloro-1-(3,4-dihydroxy-2-methylphenyl)ethanoneC₉H₉ClO₃

mol.wt. 200.62

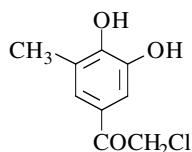
**Synthesis**

-Preparation by reaction of chloroacetyl chloride on 3-methylpyrocatechol with aluminium chloride in refluxing carbon disulfide (59%) [624].

m.p. 178° [624]; ¹H NMR [624], IR [624].

2-Chloro-1-(3,4-dihydroxy-5-methylphenyl)ethanoneC₉H₉ClO₃

mol.wt. 200.62

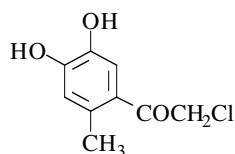
**Synthesis**

-Preparation by reaction of chloroacetic acid on 3-methylpyrocatechol with phosphorous oxychloride in refluxing benzene (28%) [624].

m.p. 180° [624]; ¹H NMR [624], IR [624].

2-Chloro-1-(4,5-dihydroxy-2-methylphenyl)ethanoneC₉H₉ClO₃

mol.wt. 200.62

**Syntheses**

-Preparation by reaction of chloroacetyl chloride on homoveratrole (3,4-dimethoxytoluene) with aluminium chloride in carbon disulfide or nitrobenzene at 40° (82%) [1402].

-Also obtained (very low yield) by Fries rearrangement of creosol chloroacetate with aluminium chloride at 100° [836].

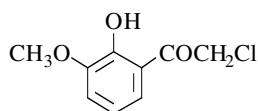
m.p. 130° [836], 128° [1402]; b.p.₁₄ 187° [1402].

2-Chloro-1-(2-hydroxy-3-methoxyphenyl)ethanone

[75717-52-1]

C₉H₉ClO₃

mol.wt. 200.62

**Synthesis**

-Preparation by reaction of chloroacetonitrile on guaiacol with aluminium chloride and boron trichloride in refluxing ethylene dichloride (42%) [1409] [1466].

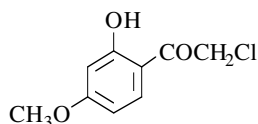
m.p. 113-114° [1409] [1466]; ¹H NMR [1466].

2-Chloro-1-(2-hydroxy-4-methoxyphenyl)ethanone

[60965-23-3]

C₉H₉ClO₃

mol.wt. 200.62

**Syntheses**

-Preparation by reaction of diazomethane on 2,4-dihydroxy- α -chloroacetophenone in ethyl ether (60%) [1381].
 -Preparation by reaction of chloroacetyl chloride on 2,4-dimethoxybenzene with aluminium chloride in refluxing carbon disulfide (86%) [96], (55%) [846] or in ethyl ether at r.t. (57%) [952].
 -Preparation by reaction of chloroacetyl chloride on bromomagnesium 3-methoxyphenolate in toluene at r.t. (84%) [1286].
 -Preparation by reaction of chloroacetonitrile on 3-methoxyphenol with aluminium chloride and boron trichloride in methylene chloride at r.t. (81%) [1409] [1466] or with zinc chloride and hydrochloric acid in ethyl ether (by-product) [1382].
 -Also refer to: [1478].

m.p. 117-118° [1409] [1466], 116° [96] [952], 115-117° [1286], 115-116° [846], 114° [1381];

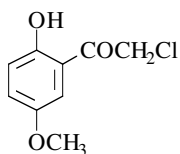
¹H NMR [952] [1286], MS [1286].

2-Chloro-1-(2-hydroxy-5-methoxyphenyl)ethanone

[75717-53-2]

C₉H₉ClO₃

mol.wt. 200.62

**Syntheses**

-Preparation by reaction of chloroacetyl chloride on hydroquinone dimethyl ether with aluminium chloride in refluxing carbon disulfide (65%) [96].
 -Preparation by reaction of chloroacetonitrile on hydroquinone monomethyl ether with boron trichloride and aluminium chloride in ethylene dichloride (67%) [1409] [1466].
 -Also refer to: [1478].

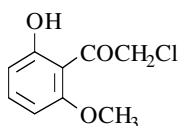
m.p. 83-84° [1409] [1466], 81-81°5 [96]; ¹H NMR [1466].

2-Chloro-1-(2-hydroxy-6-methoxyphenyl)ethanone

[75717-59-8]

C₉H₉ClO₃

mol.wt. 200.62

**Syntheses**

-Obtained (by-product) by reaction of chloroacetyl chloride on bromomagnesium 3-methoxyphenolate in toluene at r.t. (10%) [1286].

-Also obtained (by-product) by reaction of chloroacetonitrile on 3-methoxyphenol with aluminium chloride and boron trichloride mixture in ethylene dichloride at r.t. (5%) [1466].

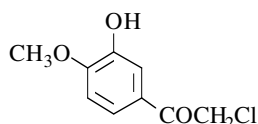
m.p. 105-109° [1286]; ¹H NMR [1286], IR [1286].

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

[55761-46-1]

C₉H₉ClO₃

mol.wt. 200.62

**Syntheses**

-Preparation by Fries rearrangement of guaiacol chloroacetate with aluminium chloride in refluxing carbon disulfide (63%) [1408], (49%) [84] [1094].

-Also obtained by reaction of 5 N sodium hydroxide with 5-chloroacetylguaiacol chloroacetate in dioxane, the mixture being gently warmed [564].

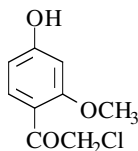
m.p. 122-123° [1094], 121-122° [564], 116-118° [1408].

2-Chloro-1-(4-hydroxy-2-methoxyphenyl)ethanone

[104691-67-0]

C₉H₉ClO₃

mol.wt. 200.62

**Synthesis**

-Preparation by reaction of chloroacetonitrile on resorcinol monomethyl ether (Hoesch reaction) (major product, good yield) [1382].

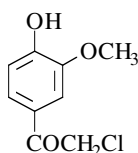
m.p. 173-174° [1382].

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

[6344-28-1]

C₉H₉ClO₃

mol.wt. 200.62

**Syntheses**

-Preparation by reaction of chloroacetyl chloride on veratrole with aluminium chloride in carbon disulfide (72%) [1198].

-Preparation by reaction of chloroacetyl chloride with guaiacol in the presence of aluminium chloride in boiling carbon

disulfide (56%) [478]; the same yield was obtained using tetrachloroethane as solvent [478].

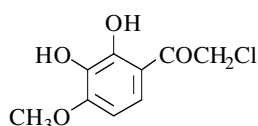
-Preparation by chlorination of the acetate of acetoguaiacone (4-acetoxy-3-methoxyacetophenone) with 1.1 mol. equiv chlorine in chloroform and subsequent hydrolysis (67%) [1374].

m.p. 102-104° [564], 102° [1198], 100-102° [478] [1374];
¹H NMR [1374], ¹³C NMR [1374], MS [210].

2-Chloro-1-(2,3-dihydroxy-4-methoxyphenyl)ethanone

C₉H₉ClO₄

mol.wt. 216.62



Synthesis

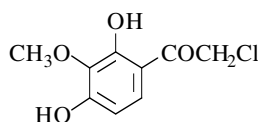
-Preparation from 2,3-dihydroxyanisole by Hoesch acylation by means of chloroacetonitrile (70%) [554].

2-Chloro-1-(2,4-dihydroxy-3-methoxyphenyl)ethanone

[69151-93-5]

C₉H₉ClO₄

mol.wt. 216.62



Synthesis

-Preparation by reaction of chloroacetonitrile with 2,6-dihydroxyanisole (Hoesch reaction) [916].

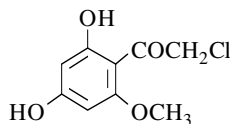
m.p. 71-72° [916].

2-Chloro-1-(2,4-dihydroxy-6-methoxyphenyl)ethanone

[70651-70-6]

C₉H₉ClO₄

mol.wt. 216.62



Syntheses

-Obtained by treatment of 2-hydroxy-4,6-dimethoxy- α -chloroacetophenone with aluminium chloride in refluxing chlorobenzene for 1 h (85%) [592].

-Preparation by reaction of chloroacetonitrile with phloroglucinol monomethyl ether (Hoesch reaction) (41%) [596].
 -Also refer to: [580] [581].

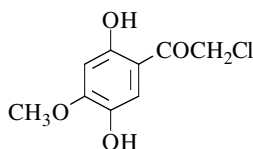
m.p. 184-186° (d) [596], 174-175° [592].
 One of the reported melting points is obviously wrong.

2-Chloro-1-(2,5-dihydroxy-4-methoxyphenyl)ethanone

[163980-43-6]

C₉H₉ClO₄

mol.wt. 216.62



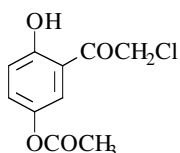
Synthesis

-Preparation by reaction of chloroacetonitrile with methoxyhydroquinone (Hoesch reaction) (84%) [480].

light brown crystals [480]; ¹H NMR [480], MS [480].

1-[5-(Acetyloxy)-2-hydroxyphenyl]-2-chloroethanoneC₁₀H₉ClO₄

mol.wt. 228.63



Syntheses

-Preparation by reaction of acetyl chloride on 2,5-dihydroxy- α -chloroacetophenone at reflux (73%) [819].
 -Also obtained (by-product) by reaction of 2,5-diacetoxy- α -chloroacetophenone with sodium acetate (7%) [819].

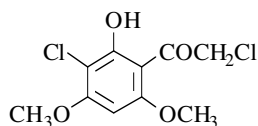
m.p. 151-152° [819].

2-Chloro-1-(3-chloro-2-hydroxy-4,6-dimethoxyphenyl)ethanone

[72565-72-1]

C₁₀H₁₀Cl₂O₄

mol.wt. 265.09

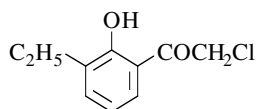


Synthesis

-Preparation by reaction of chloroacetyl chloride with 2-chloro-3,5-dimethoxyphenol in the presence of aluminium chloride in nitrobenzene at r.t. [362] [942] [1558], (88%) [1558], (70%) [942].

m.p. 211° (d) [942]; ¹H NMR [1558], IR [942].**2-Chloro-1-(3-ethyl-2-hydroxyphenyl)ethanone**C₁₀H₁₁ClO₂

mol.wt. 198.65



Synthesis

-Preparation by Fries rearrangement of 2-ethylphenyl chloroacetate with aluminium chloride without solvent at 140° (39%) [290].

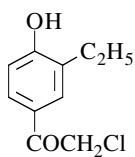
oil [290].

2-Chloro-1-(3-ethyl-4-hydroxyphenyl)ethanone

[145736-97-6]

C₁₀H₁₁ClO₂

mol.wt. 198.65

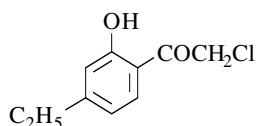


Synthesis

-Refer to: [301].

2-Chloro-1-(4-ethyl-2-hydroxyphenyl)ethanoneC₁₀H₁₁ClO₂

mol.wt. 198.65

**Syntheses**

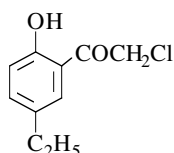
-Preparation by Fries rearrangement of 3-ethylphenyl chloroacetate with aluminium chloride without solvent at 140° (49%) [290].

-Also obtained also by Fries rearrangement of 4-ethylphenyl chloroacetate with aluminium chloride without solvent at 140°, on account of a migration of the ethyl group (46%) [290].

m.p. 69-70° [290].

2-Chloro-1-(5-ethyl-2-hydroxyphenyl)ethanoneC₁₀H₁₁ClO₂

mol.wt. 198.65

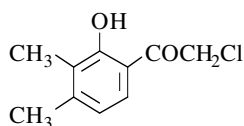
**Synthesis**

-Preparation by reaction of chloroacetyl chloride on 4-ethylanisole with aluminium chloride in carbon disulfide (32%) [290].

m.p. 50-52° [290].

2-Chloro-1-(2-hydroxy-3,4-dimethylphenyl)ethanoneC₁₀H₁₁ClO₂

mol.wt. 198.65

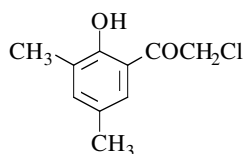
**Synthesis**

-Preparation by reaction of chloroacetonitrile on 2,3-dimethylphenol with aluminium chloride and boron trifluoride in refluxing ethylene dichloride (quantitative yield) [1466].

m.p. 95-96° [1466].

2-Chloro-1-(2-hydroxy-3,5-dimethylphenyl)ethanoneC₁₀H₁₁ClO₂

mol.wt. 198.65

**Synthesis**

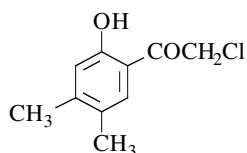
-Preparation by reaction of chloroacetyl chloride on 2,4-dimethylanisole with aluminium chloride in carbon disulfide (20%) [93].

2-Chloro-1-(2-hydroxy-4,5-dimethylphenyl)ethanone

[22307-96-6]

C₁₀H₁₁ClO₂

mol.wt. 198.65

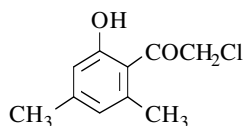
**Synthesis**

-Preparation by Fries rearrangement of 3,4-dimethylphenyl chloroacetate with aluminium chloride without solvent at 150° [1130].

m.p. 101° [1130]; ¹H NMR [1130], IR [1130].

2-Chloro-1-(2-hydroxy-4,6-dimethylphenyl)ethanoneC₁₀H₁₁ClO₂

mol.wt. 198.65

**Synthesis**

-Preparation by Fries rearrangement of 3,5-dimethylphenyl chloroacetate with aluminium chloride without solvent at 135-140° [98] [518], (good yield) [518].

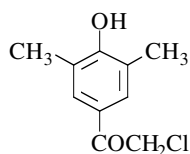
m.p. 92° [518].

2-Chloro-1-(4-hydroxy-3,5-dimethylphenyl)ethanone

[40943-25-7]

C₁₀H₁₁ClO₂

mol.wt. 198.65

**Syntheses**

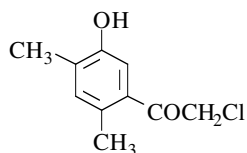
-Preparation by reaction of chloroacetyl chloride with 2,6-dimethylphenol in the presence of aluminium chloride in nitrobenzene at 60° (43%) [171].

-Also obtained (poor yield) by reaction of aluminium chloride on 2,6-dimethyl-4-ethylphenyl chloroacetate without solvent at 150° [94].

m.p. 107° [171]; ¹H NMR [171], IR [171], MS [171].

2-Chloro-1-(5-hydroxy-2,4-dimethylphenyl)ethanoneC₁₀H₁₁ClO₂

mol.wt. 198.65

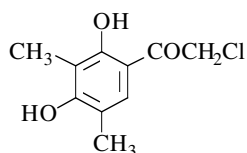
**Synthesis**

-Preparation (by-product) by reaction of chloroacetyl chloride on 2,4-dimethylanisole with aluminium chloride in carbon disulfide (10%) [93].

m.p. 107-107° [93].

2-Chloro-1-(2,4-dihydroxy-3,5-dimethylphenyl)ethanoneC₁₀H₁₁ClO₃

mol.wt. 214.65

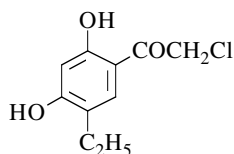
**Synthesis**

-Preparation by reaction of acetonitrile on 2,4-dimethylresorcinol (Hoesch reaction) (93%) [846].

m.p. 126-127° [846].

2-Chloro-1-(5-ethyl-2,4-dihydroxyphenyl)ethanoneC₁₀H₁₁ClO₃

mol.wt. 214.65

**Syntheses**

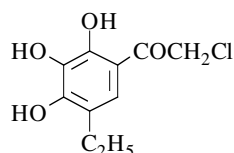
-Preparation by reaction of 4-ethylresorcinol with chloroacetonitrile (Hoesch reaction) [1053], (95%) [367], (88%) [1051].

-Preparation by Friedel-Crafts acylation of 4-ethylresorcinol with chloroacetyl chloride in nitrobenzene in the presence of aluminium chloride for 24 h at r.t. (70%) [653].

m.p. 163-165° [653], 161-161°5 [367], 161° [1051] [1053].

2-Chloro-1-(5-ethyl-2,3,4-trihydroxyphenyl)ethanoneC₁₀H₁₁ClO₄

mol.wt. 230.65

**Synthesis**

-Preparation by reaction of chloroacetonitrile with 4-ethylpyrogallol (m.p. 105-106°) (Hoesch reaction) (60%) [1051].

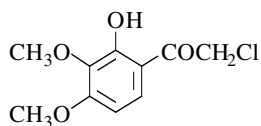
m.p. 131-132°5 [1051].

2-Chloro-1-(2-hydroxy-3,4-dimethoxyphenyl)ethanone

[7507-92-8]

C₁₀H₁₁ClO₄

mol.wt. 230.65

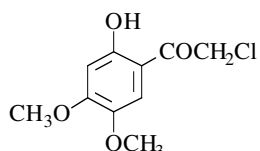
**Synthesis**

-Preparation by reaction of chloroacetyl chloride with 1,2,3-trimethoxybenzene in the presence of aluminium chloride in ethylene dichloride first at 0°, then at r.t. (70%) [1102] or without solvent at 100° (16%) [1199].

m.p. 161°5 [1199], 160-162° [1102]; ¹H NMR [1102], MS [1102].

2-Chloro-1-(2-hydroxy-4,5-dimethoxyphenyl)ethanoneC₁₀H₁₁ClO₄

mol.wt. 230.65

**Synthesis**

-Preparation by reaction of chloroacetonitrile on 3,4-dimethoxyphenol (Hoesch reaction) (47%) [739].

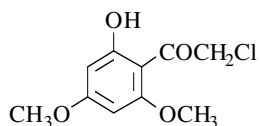
m.p. 154-155° [739].

2-Chloro-1-(2-hydroxy-4,6-dimethoxyphenyl)ethanone

[103040-51-3]

C₁₀H₁₁ClO₄

mol.wt. 230.65

**Syntheses**

-Preparation by reaction of chloroacetonitrile on phloroglucinol dimethyl ether (Hoesch reaction) [292].

-Preparation by reaction of chloroacetyl chloride on phloroglucinol trimethyl ether with aluminium chloride in boiling ligroin [517].

-Preparation by partial demethylation of 2,4,6-trimethoxy- α -chloroacetophenone by heating with aluminium chloride without solvent at 120° (89%) [514].

m.p. 144-146° [514], 142-144° [517], 136-140° [292];

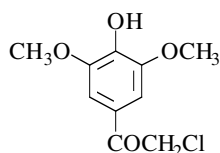
¹H NMR [292], IR [292], MS [292].

2-Chloro-1-(4-hydroxy-3,5-dimethoxyphenyl)ethanone

[59719-58-3]

C₁₀H₁₁ClO₄

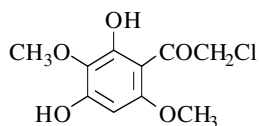
mol.wt. 230.65

**Synthesis**

-Preparation by chlorination of 4-(benzyloxy)-3,5-dimethoxybenzoylacetic acid methyl ester with sulfuryl chloride in acetic acid at r.t., and subsequent hydrolysis of the keto ester so obtained by refluxing in hydrochloric acid (90%) [43].

2-Chloro-1-(2,4-dihydroxy-3,6-dimethoxyphenyl)ethanoneC₁₀H₁₁ClO₅

mol.wt. 246.65

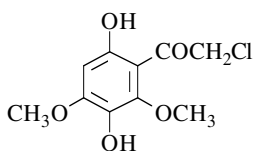
**Synthesis**

-Preparation by reaction of chloroacetonitrile on 2,5-dimethoxyresorcinol (Hoesch reaction) (52%) [548], (25%) [1357].

m.p. 150-151° [1357], 148-149° [548].

2-Chloro-1-(3,6-dihydroxy-2,4-dimethoxyphenyl)ethanoneC₁₀H₁₁ClO₅

mol.wt. 246.65

**Synthesis**

-Obtained by reaction of chloroacetyl chloride with 1,4-dihydroxy-2,6-dimethoxybenzene in ethyl ether in the presence of aluminium chloride, cooling in ice and standing overnight (45%) [124].

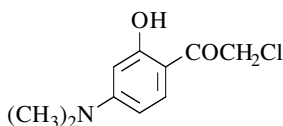
m.p. 154° [124].

2-Chloro-1-[4-(dimethylamino)-2-hydroxyphenyl]ethanone

[127354-36-3]

C₁₀H₁₂ClNO₂

mol.wt. 213.66

**Synthesis**

-Preparation by reaction of chloroacetyl chloride on bromomagnesium 3-(N,N-dimethylamino)phenolate in toluene at r.t. (92%) [1286].

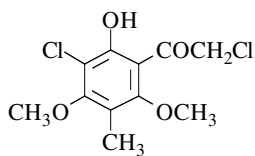
m.p. 96-98° (d) [1286]; ¹H NMR [1286], IR [1286], MS [1286].

2-Chloro-1-(3-chloro-2-hydroxy-4,6-dimethoxy-5-methylphenyl)ethanone

[201288-73-5]

C₁₁H₁₂Cl₂O₄

mol.wt. 279.12

**Synthesis**

-Preparation by reaction of chloroacetyl chloride with 2-chloro-3,5-dimethoxy-4-methylphenol in ethyl ether in the presence of aluminium chloride, first at 0° under an argon atmosphere, then at r.t. for 0.5 h and at reflux for 3 h (90%) [1435].

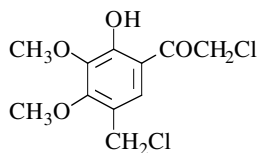
m.p. 144-146° [1435]; ¹H NMR [1435], IR [1435], MS [1435].

2-Chloro-1-[5-(chloromethyl)-2-hydroxy-3,4-dimethoxyphenyl]ethanone

[76439-46-8]

C₁₁H₁₂Cl₂O₄

mol.wt. 279.12

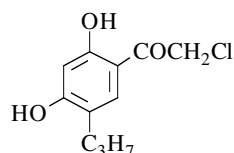
**Synthesis**

-Preparation by reaction of paraformaldehyde with 2-hydroxy-3,4-dimethoxy-α-chloroacetophenone in the presence of hydrochloric acid gas in acetic acid between 60-70° (77%) [1102].

m.p. 130-131° [1102]; ¹H NMR [1102], MS [1102].

2-Chloro-1-(2,4-dihydroxy-5-propylphenyl)ethanoneC₁₁H₁₃ClO₃

mol.wt. 228.68

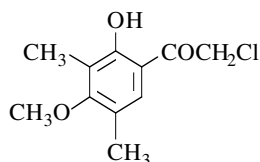
**Synthesis**

-Preparation by reaction of chloroacetonitrile with 4-propyl-resorcinol (Hoesch reaction) [1053].

m.p. 156-157° [1053].

2-Chloro-1-(2-hydroxy-4-methoxy-3,5-dimethylphenyl)ethanoneC₁₁H₁₃ClO₃

mol.wt. 228.68

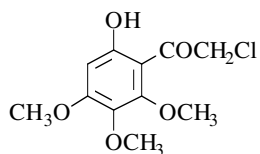
**Synthesis**

-Preparation by reaction of chloroacetyl chloride on 2,4-dimethylresorcinol dimethyl ether with aluminium chloride in refluxing carbon disulfide (42%) [846].

m.p. 158-160° [846].

2-Chloro-1-(6-hydroxy-2,3,4-trimethoxyphenyl)ethanoneC₁₁H₁₃ClO₅

mol.wt. 260.67

**Synthesis**

-Preparation by reaction of chloroacetonitrile on 3,4,5-trimethoxyphenol (antirol) (Hoesch reaction) (42%) [1357].

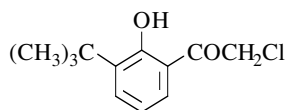
m.p. 107-107°5 [1357].

2-Chloro-1-[3-(1,1-dimethylethyl)-2-hydroxyphenyl]ethanone

[127354-33-0]

C₁₂H₁₅ClO₂

mol.wt. 226.70

**Synthesis**

-Preparation by reaction of chloroacetyl chloride with aluminium or titanium 2-tert-butylphenolate in toluene at r.t. (98% and 70% yields, respectively) [1286].

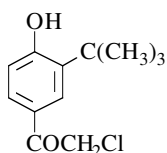
m.p. 52-53° [1286]; ¹H NMR [1286], IR [1286], MS [1286].

2-Chloro-1-[3-(1,1-dimethylethyl)-4-hydroxyphenyl]ethanone

[127354-34-1]

C₁₂H₁₅ClO₂

mol.wt. 226.70

**Synthesis**

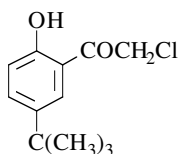
-Obtained by reaction of chloroacetyl chloride with dichloroaluminium 2-tert-butylphenolate or with trichloro (2-tert-butylphenoxy)titanium in toluene at r.t. (50 and 52% yields, respectively) [1286].

2-Chloro-1-[5-(1,1-dimethylethyl)-2-hydroxyphenyl]ethanone

[75060-43-4]

C₁₂H₁₅ClO₂

mol.wt. 226.70

**Synthesis**

-Obtained by reaction of chloroacetyl chloride on 4-tert-butylanisole with aluminium chloride in methylene chloride at r.t. (10%) [685].

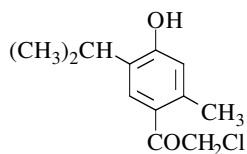
m.p. 51-52° [685]; ¹H NMR [685], IR [685].

2-Chloro-1-[4-hydroxy-2-methyl-5-(1-methylethyl)phenyl]ethanone

[72235-89-3]

C₁₂H₁₅ClO₂

mol.wt. 226.70

**Syntheses**

-Obtained by reaction of chloroacetyl chloride on thymol with aluminium chloride in nitrobenzene at 50° (21%) [737].
-Also obtained by Fries rearrangement of thymyl chloroacetate with aluminium chloride in nitrobenzene at r.t. (15%) [105].

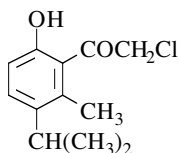
m.p. 133° [737], 132° [105]; b.p._{0.0018} 175-178° [737].

2-Chloro-1-[6-hydroxy-2-methyl-3-(1-methylethyl)phenyl]ethanone

[23053-74-9]

C₁₂H₁₅ClO₂

mol.wt. 226.70

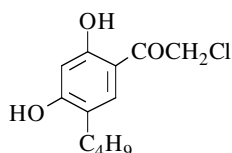
**Synthesis**

-Obtained by reaction of chloroacetyl chloride on 3-methyl-4-isopropylanisole (p-thymol methyl ether) with aluminium chloride in carbon disulfide [1261].

m.p. 68°5 [1261].

1-(5-Butyl-2,4-dihydroxyphenyl)-2-chloroethanoneC₁₂H₁₅ClO₃

mol.wt. 242.70

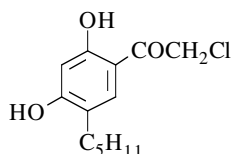
**Synthesis**

-Preparation by reaction of chloroacetonitrile with 4-butyl-resorcinol (Hoesch reaction) [1053].

m.p. 155-156° [1053].

2-Chloro-1-(2,4-dihydroxy-5-pentylphenyl)ethanoneC₁₃H₁₇ClO₃

mol.wt. 256.73

**Synthesis**

-Preparation by reaction of chloroacetonitrile with 4-pentyl-resorcinol (Hoesch reaction) [1053].

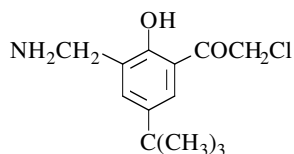
m.p. 148-149° [1053].

1-[3-(Aminomethyl)-5-(1,1-dimethylethyl)-2-hydroxyphenyl]-2-chloroethanone

[75060-96-7]

C₁₃H₁₈ClNO₂

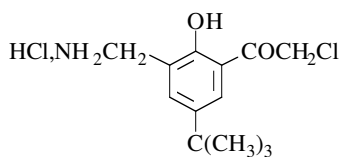
mol.wt. 255.74

**Synthesis**

-From the corresponding hydrochloride (see below) [685].

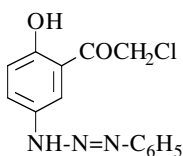
1-[3-(Aminomethyl)-5-(1,1-dimethylethyl)-2-hydroxyphenyl]-2-chloroethanone (Hydrochloride)

[75060-68-3]

C₁₃H₁₈ClNO₂, HCl mol.wt. 292.20**Synthesis**

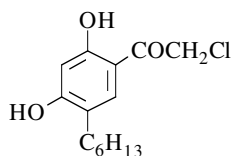
-Preparation by reaction of concentrated hydrochloric acid on 2-chloroacetyl-4-tert-butyl-6-(N-chloroacetylaminomethyl)phenol in refluxing ethanol (64%) [685].

m.p. 160° (d) [685]; ¹H NMR [685], IR [685].

2-Chloro-1-[2-hydroxy-5-(1-triazene-3-phenyl)phenyl]ethanoneC₁₄H₁₂ClN₃O₂ mol.wt. 289.72**Synthesis**

-Obtained by reaction of benzenediazonium chloride on 5-amino-2-hydroxy- α -chloroacetophenone in the presence of an aqueous sodium acetate solution [859].

m.p. 127° [859].

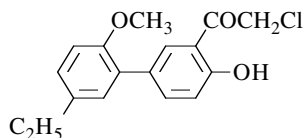
2-Chloro-1-(5-hexyl-2,4-dihydroxyphenyl)ethanoneC₁₄H₁₉ClO₃ mol.wt. 270.76**Synthesis**

-Preparation by reaction of chloroacetonitrile with 4-hexyl-resorcinol (Hoesch reaction) [1053].

m.p. 145° [1053].

2-Chloro-1-(5'-ethyl-4-hydroxy-2'-methoxy[1,1'-biphenyl]-3-yl)ethanone

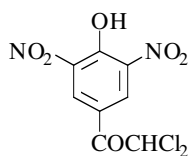
[131845-71-1]

C₁₇H₁₇ClO₃ mol.wt. 304.77**Synthesis**

-Refer to: [1441].

2.2.2. From dichloroacetic acid**2,2-Dichloro-1-(4-hydroxy-3,5-dinitrophenyl)ethanone**

[52129-63-2]

C₈H₄Cl₂N₂O₆ mol.wt. 295.04**Synthesis**

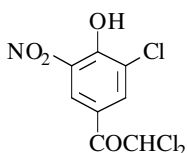
-Preparation by reaction of chlorine on 4-hydroxy-3,5-dinitroacetophenone in methylene chloride-ethanol mixture (93%) [241] [1171].

2,2-Dichloro-1-(3-chloro-4-hydroxy-5-nitrophenyl)ethanone

[52501-35-6]

C₈H₄Cl₃NO₄

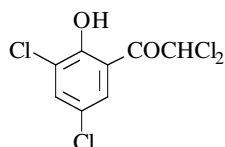
mol.wt. 284.48

**Synthesis**

-Preparation by reaction of chlorine on 4-hydroxy-3-nitroacetophenone with ferric chloride in methylene chloride-ethanol mixture (94%) [241] [1171].

2,2-Dichloro-1-(3,5-dichloro-2-hydroxyphenyl)ethanoneC₈H₄Cl₄O₂

mol.wt. 273.93

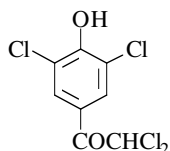
**Syntheses**

-Preparation by Fries rearrangement of 2,4-dichlorophenyl dichloroacetate with aluminium chloride without solvent at 120° (50%) [1311].
 -Also obtained when 4-hydroxycoumarin in acetic acid was treated with an excess of gaseous chlorine at 10-15° and the polychlorinated product so formed hydrolyzed [994] [995].

m.p. 90° [1311], 70° [994] [995].

2,2-Dichloro-1-(3,5-dichloro-4-hydroxyphenyl)ethanoneC₈H₄Cl₄O₂

mol.wt. 273.93

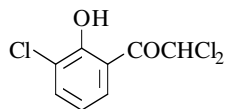
**Synthesis**

-Obtained (by-product) by Fries rearrangement of 2,6-dichlorophenyl dichloroacetate with aluminium chloride without solvent at 135° (9%) [1442].

m.p. 92°5'-94°5' [1442].

2,2-Dichloro-1-(3-chloro-2-hydroxyphenyl)ethanoneC₈H₅Cl₃O₂

mol.wt. 239.48

**Synthesis**

-Preparation by Fries rearrangement of 2-chlorophenyl dichloroacetate with aluminium chloride without solvent at 120° (76%) [1311].

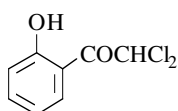
b.p.₈ 173° [1311].

2,2-Dichloro-1-(2-hydroxyphenyl)ethanone

[29003-58-5]

C₈H₆Cl₂O₂

mol.wt. 205.04

**Synthesis**

-Preparation by Fries rearrangement of phenyl dichloroacetate with aluminium chloride without solvent at 120° (50%) [508].

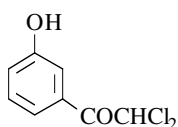
b.p._{0.1} 65-72° [508].

2,2-Dichloro-1-(3-hydroxyphenyl)ethanone

[85299-04-3]

C₈H₆Cl₂O₂

mol.wt. 205.04

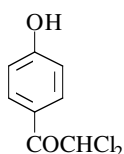
**Synthesis**

-Preparation by reaction of hexachloro-2,4-cyclohexadienone on 3-hydroxyacetophenone in refluxing ethanol (34%) [603].

pale yellow oil [603]; ¹H NMR [603], IR [603].

2,2-Dichloro-1-(4-hydroxyphenyl)ethanoneC₈H₆Cl₂O₂

mol.wt. 205.04

**Synthesis**

-Preparation by reaction of dichloroacetyl chloride on anisole with aluminium chloride in carbon disulfide at 25-30° (34%) [979].

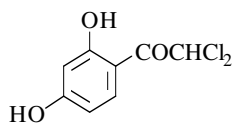
m.p. 98° [979].

2,2-Dichloro-1-(2,4-dihydroxyphenyl)ethanone

[29003-59-6]

C₈H₆Cl₂O₃

mol.wt. 221.04

**Synthesis**

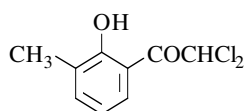
-Refer to: [756].

2,2-Dichloro-1-(2-hydroxy-3-methylphenyl)ethanone

[145818-23-1]

C₉H₈Cl₂O₂

mol.wt. 219.07

**Synthesis**

-Preparation by reaction of dichloroacetonitrile on o-cresol (Hoesch reaction) (25%) [183].

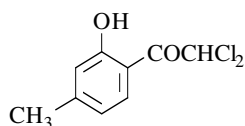
m.p. 33°5 [183]; ¹H NMR [183], IR [183], UV [183], MS [183].

2,2-Dichloro-1-(2-hydroxy-4-methylphenyl)ethanone

[116046-02-7]

C₉H₈Cl₂O₂

mol.wt. 219.07

**Synthesis**

-Preparation by reaction of dichloroacetyl chloride with 3-methylanisole in the presence of aluminium chloride at 80° (30%) [945].

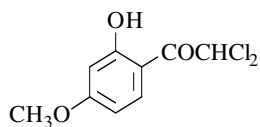
m.p. 125-126° [945]; ¹H NMR [945], IR [945], MS [945].

2,2-Dichloro-1-(2-hydroxy-4-methoxyphenyl)ethanone

[95235-25-9]

C₉H₈Cl₂O₃

mol.wt. 235.07

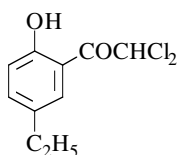
**Syntheses**

-Preparation by Fries rearrangement of 3-methoxyphenyl dichloroacetate with aluminium chloride without solvent at 120° (42%) [1311].
 -Also obtained (by-product) by reaction of dichloroacetyl chloride with resorcinol dimethyl ether in the presence of aluminium chloride at 0-10° (9%) [945].

m.p. 86° [945], 84° [1311].

2,2-Dichloro-1-(5-ethyl-2-hydroxyphenyl)ethanoneC₁₀H₁₀Cl₂O₂

mol.wt. 233.09

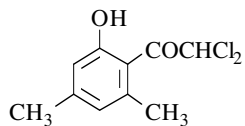
**Synthesis**

-Preparation by Fries rearrangement of 4-ethylphenyl dichloroacetate with aluminium chloride without solvent at 120° (53%) [1311].

b.p.₈ 110° [1311].

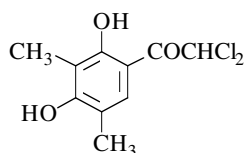
2,2-Dichloro-1-(2-hydroxy-4,6-dimethylphenyl)ethanoneC₁₀H₁₀Cl₂O₂

mol.wt. 233.09

**Synthesis**

-Preparation by Fries rearrangement of 3,5-dimethylphenyl dichloroacetate with aluminium chloride without solvent at 120° (58%) [1311].

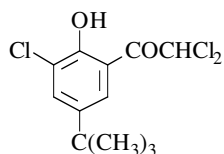
b.p.₄ 150° [1311].

2,2-Dichloro-1-(2,4-dihydroxy-3,5-dimethylphenyl)ethanoneC₁₀H₁₀Cl₂O₃ mol.wt. 249.09

Synthesis

-Preparation by reaction of dichloroacetonitrile on 2,4-dimethylresorcinol (Hoesch reaction) [846].

m.p. 123° [846]; b.p._{0.001} 150° [846].

2,2-Dichloro-1-[3-chloro-5-(1,1-dimethylethyl)-2-hydroxyphenyl]ethanoneC₁₂H₁₃Cl₃O₂ mol.wt. 295.59

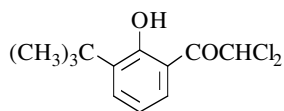
Synthesis

-Preparation by Fries rearrangement of 4-tert-butyl-2-chlorophenyl dichloroacetate with aluminium chloride at 120° (79%) [1311].

b.p.₂₀ 175° [1311].

2,2-Dichloro-1-[3-(1,1-dimethylethyl)-2-hydroxyphenyl]ethanone

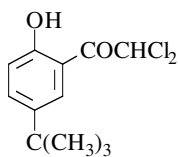
[127354-38-5]

C₁₂H₁₄Cl₂O₂ mol.wt. 261.15

Synthesis

-Preparation by reaction of dichloroacetyl chloride on bromomagnesium 2-tert-butylphenolate in toluene at r.t. (58%) [1286].

yellow oil [1286]; ¹H NMR [1286], IR [1286], MS [1286].

2,2-Dichloro-1-[5-(1,1-dimethylethyl)-2-hydroxyphenyl]ethanoneC₁₂H₁₄Cl₂O₂ mol.wt. 261.15

Synthesis

-Preparation by Fries rearrangement of 4-tert-butylphenyl dichloroacetate with aluminium chloride at 120° (86%) [1311].

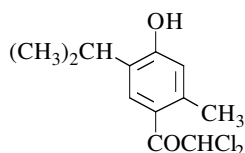
b.p.₁₀ 120° [1311].

2,2-Dichloro-1-[4-hydroxy-2-methyl-5-(1-methylethyl)phenyl]ethanone

[72235-91-7]

C₁₂H₁₄Cl₂O₂

mol.wt. 261.15

**Synthesis**

-Preparation by reaction of dichloroacetyl chloride on thymol with aluminium chloride in nitrobenzene at r.t., *via* a Fries rearrangement (20%) [105].

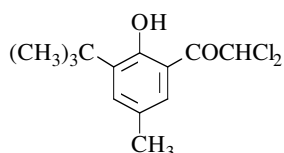
m.p. 110° [105].

2,2-Dichloro-1-[3-(1,1-dimethylethyl)-2-hydroxy-5-methylphenyl]ethanone

[127354-45-4]

C₁₃H₁₆Cl₂O₂

mol.wt. 275.17

**Syntheses**

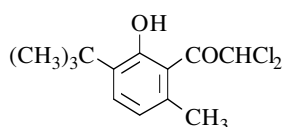
-Preparation by reaction of dichloroacetyl chloride, *on aluminium tri 2-tert-butyl-4-methylphenolate in toluene at r.t. (98%) [1286];

*on bromomagnesium 2-tert-butyl-4-methylphenolate in toluene at r.t. (78%) [1286].

m.p. 55-59° [1286]; ¹H NMR [1286], IR [1286], MS [1286].

2,2-Dichloro-1-[3-(1,1-dimethylethyl)-2-hydroxy-6-methylphenyl]ethanoneC₁₃H₁₆Cl₂O₂

mol.wt. 275.17

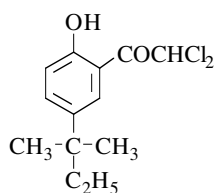
**Synthesis**

-Preparation by Fries rearrangement of 2-tert-butyl-5-methylphenyl dichloroacetate without solvent at 120° (60%) [1311].

b.p.₆ 88° [1311].

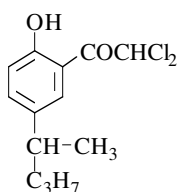
2,2-Dichloro-1-[5-(1,1-dimethylpropyl)-2-hydroxyphenyl]ethanoneC₁₃H₁₆Cl₂O₂

mol.wt. 275.17

**Synthesis**

-Preparation by Fries rearrangement of 4-tert-pentylphenyl dichloroacetate with aluminium chloride without solvent at 120° (54%) [1311].

b.p.₂ 122° [1311].

2,2-Dichloro-1-[2-hydroxy-5-(1-methylbutyl)phenyl]ethanoneC₁₃H₁₆Cl₂O₂ mol.wt. 275.17**Synthesis**

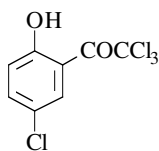
-Preparation by Fries rearrangement of 5-sec-pentylphenyl dichloroacetate with aluminium chloride without solvent at 120° (43%) [1311].

b.p.₁₀ 125° [1311].

2.2.3. From trichloroacetic acid

2,2,2-Trichloro-1-(5-chloro-2-hydroxyphenyl)ethanone

[145818-26-4]

C₈H₄Cl₄O₂ mol.wt. 273.93**Syntheses**

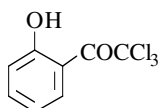
-Preparation by Fries rearrangement of 4-chlorophenyl trichloroacetate with aluminium chloride without solvent at 125-130° (25%) [177] [1310].

-Preparation by reaction of trichloroacetonitrile on 4-chlorophenol (Hoesch reaction) [183].

b.p.₄₄ 129-132° [177] [183] [1310]; ¹H NMR [183], IR [183], UV [183], MS [183].

2,2,2-Trichloro-1-(2-hydroxyphenyl)ethanone

[75717-55-4]

C₈H₅Cl₃O₂ mol.wt. 239.48**Syntheses**

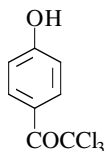
-Preparation by reaction of trichloroacetonitrile on phenol with aluminium chloride and boron trichloride mixture in refluxing methylene chloride (92%) [1409] [1466].

-Preparation by reaction of trichloroacetonitrile on phenol (Hoesch reaction) (64%) [183].

m.p. 53-54° [183]; ¹H NMR [183] [1466], IR [183], UV [183], MS [183].

2,2,2-Trichloro-1-(4-hydroxyphenyl)ethanone

[131170-16-6]

C₈H₅Cl₃O₂ mol.wt. 239.48**Synthesis**

-Preparation by reaction of trichloroacetonitrile on phenol (Hoesch reaction) (95%) [241] [655] [656] [1171], (30%) [183].

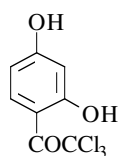
m.p. 99-99°₅ [183] [655] [656]; b.p._{0.5} 170° [655] [656]; ¹H NMR [183], IR [183], UV [183], MS [183].

2,2,2-Trichloro-1-(2,4-dihydroxyphenyl)ethanone

[76569-42-1]

C₈H₅Cl₃O₃

mol.wt. 255.48

**Synthesis**

-Preparation by reaction of trichloroacetonitrile with resorcinol in the presence of triflic acid (52%) [207] or zinc chloride (55%) [439].

m.p. 142°5 [439], 138-141° [207];

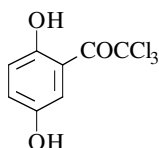
¹H NMR [207], IR [207], UV [207], MS [207].

2,2,2-Trichloro-1-(2,5-dihydroxyphenyl)ethanone

[145818-27-5]

C₈H₅Cl₃O₃

mol.wt. 255.48

**Synthesis**

-Preparation by reaction of trichloroacetonitrile on hydroquinone (Hoesch reaction) (40%) [183].

m.p. 123-124° [183];

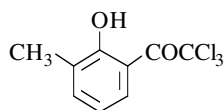
¹H NMR [183], IR [183], UV [183], MS [183].

2,2,2-Trichloro-1-(2-hydroxy-3-methylphenyl)ethanone

[145818-22-0]

C₉H₇Cl₃O₂

mol.wt. 253.51

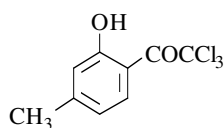
**Synthesis**

-Preparation by reaction of trichloroacetonitrile on o-cresol (Hoesch reaction) (70%) [183].

oil [183]; ¹H NMR [183], IR [183], UV [183], MS [183].

2,2,2-Trichloro-1-(2-hydroxy-4-methylphenyl)ethanoneC₉H₇Cl₃O₂

mol.wt. 253.51

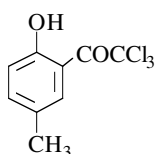
**Synthesis**

-Preparation by reaction of trichloroacetonitrile on m-cresol with aluminium chloride and gaseous hydrochloric acid in chlorobenzene at r.t. (37%) [656].

b.p.₁₇ 162-163° [656].

2,2,2-Trichloro-1-(2-hydroxy-5-methylphenyl)ethanoneC₉H₇Cl₃O₂

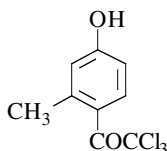
mol.wt. 253.51

**Synthesis**

-Obtained by reaction of trichloroacetonitrile on p-cresol with aluminium chloride and gaseous hydrochloric acid in chlorobenzene at 50-60° (11%) [656].

2,2,2-Trichloro-1-(4-hydroxy-2-methylphenyl)ethanoneC₉H₇Cl₃O₂

mol.wt. 253.51

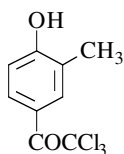
**Synthesis**

-Preparation by reaction of trichloroacetonitrile on m-cresol with aluminium chloride and gaseous hydrochloric acid in chlorobenzene at r.t. (36%) [656].

m.p. 84-87° [656].

2,2,2-Trichloro-1-(4-hydroxy-3-methylphenyl)ethanoneC₉H₇Cl₃O₂

mol.wt. 253.51

**Synthesis**

-Preparation by reaction of trichloroacetonitrile on o-cresol with aluminium chloride and gaseous hydrochloric acid in chlorobenzene at 60° (90%) [656].

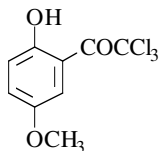
m.p. 90-91° [656].

2,2,2-Trichloro-1-(2-hydroxy-5-methoxyphenyl)ethanone

[145818-25-3]

C₉H₇Cl₃O₃

mol.wt. 269.51

**Synthesis**

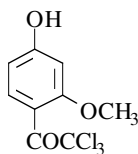
-Preparation by reaction of trichloroacetonitrile on 4-methoxyphenol (Hoesch reaction) (73%) [183].

m.p. 65-66° [183];

¹H NMR [183], IR [183], UV [183], MS [183].

2,2,2-Trichloro-1-(4-hydroxy-2-methoxyphenyl)ethanoneC₉H₇Cl₃O₃

mol.wt. 269.51

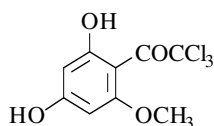
**Synthesis**

-Preparation by reaction of trichloroacetonitrile on 3-methoxyphenol with zinc chloride and gaseous hydrochloric acid in ethyl ether at 0° (Hoesch reaction) (34%) [1533].

m.p. 144° [1533].

2,2,2-Trichloro-1-(2,4-dihydroxy-6-methoxyphenyl)ethanoneC₉H₇Cl₃O₄

mol.wt. 285.51

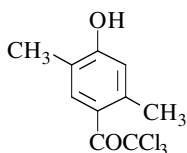
**Synthesis**

-Preparation by reaction of trichloroacetonitrile on phloroglucinol monomethyl ether with zinc chloride and gaseous hydrochloric acid in ethyl ether at 0° (Hoesch reaction) (39 to 49%) [1533].

m.p. 152° [1533].

2,2,2-Trichloro-1-(4-hydroxy-2,5-dimethylphenyl)ethanoneC₁₀H₉Cl₃O₂

mol.wt. 267.54

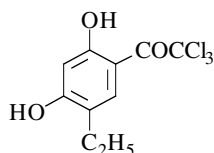
**Synthesis**

-Preparation by reaction of trichloroacetonitrile on 2,5-dimethylphenol with aluminium chloride and gaseous hydrochloric acid in chlorobenzene at r.t. (70%) [655].

m.p. 85-86° [655].

2,2,2-Trichloro-1-(5-ethyl-2,4-dihydroxyphenyl)ethanoneC₁₀H₉Cl₃O₃

mol.wt. 283.54

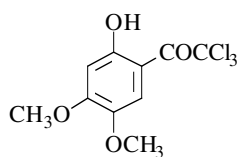
**Synthesis**

-Preparation by reaction of trichloroacetonitrile on 4-ethylresorcinol (Hoesch reaction) (52%) [439].

m.p. 138° [439].

2,2,2-Trichloro-1-(2-hydroxy-4,5-dimethoxyphenyl)ethanoneC₁₀H₉Cl₃O₄

mol.wt. 299.54

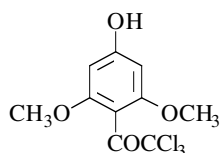
**Synthesis**

-Preparation by reaction of trichloroacetonitrile on 3,4-dimethoxyphenol (Hoesch reaction) (26%) [1533].

m.p. 107° [1533].

2,2,2-Trichloro-1-(4-hydroxy-2,6-dimethoxyphenyl)ethanoneC₁₀H₉Cl₃O₄

mol.wt. 299.54

**Synthesis**

-Preparation by reaction of trichloroacetonitrile on phloroglucinol dimethyl ether (Hoesch reaction) (38%) [1535].

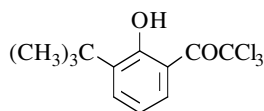
-m.p. 117° [1535].

2,2,2-Trichloro-1-[3-(1,1-dimethylethyl)-2-hydroxyphenyl]ethanone

[111422-36-7]

C₁₂H₁₃Cl₃O₂

mol.wt. 295.59

**Synthesis**

-Preparation by reaction of trichloroacetyl chloride on bromomagnesium 2-tert-butylphenolate in toluene at r.t. (65%) [1286].

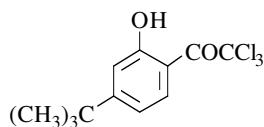
m.p. 54-58° [1286]; ¹H NMR [1286], IR [1286], MS [1286].

2,2,2-Trichloro-1-[4-(1,1-dimethylethyl)-2-hydroxyphenyl]ethanone

[145818-24-2]

C₁₂H₁₃Cl₃O₂

mol.wt. 295.59

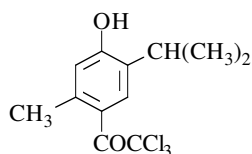
**Synthesis**

-Preparation by reaction of trichloroacetonitrile on 3-tert-butylphenol (Hoesch reaction) (74%) [183].

m.p. 46-47° [183]; ¹H NMR [183], IR [183], UV [183], MS [183].

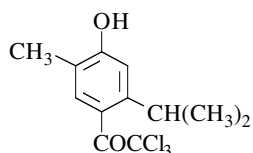
2,2,2-Trichloro-1-[4-hydroxy-2-methyl-5-(1-methylethyl)phenyl]ethanoneC₁₂H₁₃Cl₃O₂

mol.wt. 295.59

**Synthesis**

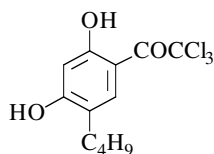
-Preparation by reaction of trichloroacetonitrile on thymol (Hoesch reaction) (73%) [657].

m.p. 99-100° [657].

2,2,2-Trichloro-1-[4-hydroxy-5-methyl-2-(1-methylethyl)phenyl]ethanoneC₁₂H₁₃Cl₃O₂ mol.wt. 295.59**Synthesis**

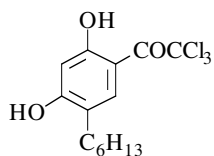
-Preparation by reaction of trichloroacetonitrile on carvacrol (Hoesch reaction) (75%) [657].

oil [657].

1-(5-Butyl-2,4-dihydroxyphenyl)-2,2,2-trichloroethanoneC₁₂H₁₃Cl₃O₃ mol.wt. 311.59**Synthesis**

-Preparation by reaction of trichloroacetonitrile on 4-n-butylresorcinol (Hoesch reaction) (57%) [439].

m.p. 95-98° [439].

2,2,2-Trichloro-1-(5-hexyl-2,4-dihydroxyphenyl)ethanoneC₁₄H₁₇Cl₃O₃ mol.wt. 339.65**Synthesis**

-Preparation by reaction of trichloroacetonitrile on 4-n-hexylresorcinol (Hoesch reaction) (56%) [439].

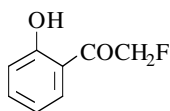
m.p. 71-73° [439].

2.3. Compounds derived from fluoroacetic acids**2.3.1. From monofluoroacetic acid****2-Fluoro-1-(2-hydroxyphenyl)ethanone**

[83505-27-5]

C₈H₇FO₂

mol.wt. 154.14

**Synthesis**

-When refluxed with water, 3-fluoro-4-hydroxycoumarin, undergoes hydrolytic ring opening and decarboxylation to give 2-fluoro-2'-hydroxyacetophenone (32%) [402].

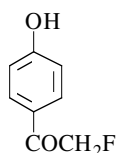
m.p. 67-69° [402]; ¹H NMR [402], ¹⁹F NMR [402], IR [402], MS [402].

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

[295779-85-0]

C₈H₇FO₂

mol.wt. 154.14

**Synthesis**

-Preparation by fluorination of p-hydroxyacetophenone (2 mmol) with 1-fluoro-4-hydroxy-1,4-diazoniabicyclo-[2.2.2]octane bis(tetrafluoroborate) (Accufluor™ NFTh) (2.1 mmol of active compound) in refluxing methanol for 0.5 to 4 h until potassium iodide starch paper showed the consumption of the fluorinating reagent. Then, hydrolysis

of the dimethylketal formed with 10% hydrochloric acid solution in acetonitrile (75-85%) [1399].
N.B.: Accufluor™ NFTh is commercially available as 50% w/w on alumina.

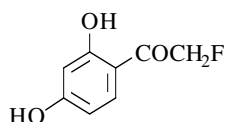
m.p. 180-183° [1397];

¹H NMR [1397], ¹³C NMR [1397], ¹⁹F NMR [1397], IR [1397], MS [1397].**1-(2,4-Dihydroxyphenyl)-2-fluoroethanone**

[147220-82-4]

C₈H₇FO₃

mol.wt. 170.14

**Synthesis**

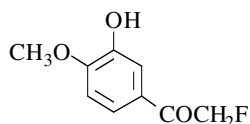
-Refer to: [1182] (compound Io).

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

[85465-61-8]

C₉H₉FO₃

mol.wt. 184.17

**Synthesis**

-Preparation by heating a mixture of 3-acetoxy-4-methoxy- α -bromoacetophenone and potassium hydrogen fluoride in diethylene glycol for 8 h at 100° (61%) [1128] [1129].

m.p. 70-71° [1128] [1129].

2.3.2. From difluoroacetic acid

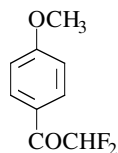
There is no hydroxyketone derived from difluoroacetic acid such as described up to December 2003. Only, a methyl ether, the α,α -difluoro-4-methoxyacetophenone [825] (compound 1G), is mentioned in 1988.

2,2-Difluoro-1-(4-methoxyphenyl)ethanone

[114829-07-1]

C₉H₈F₂O₂

mol.wt. 401.97

**Synthesis**

-Preparation by reaction of difluoroacetyl chloride with anisole in the presence of aluminium chloride in methylene chloride, first at 4°, then at 20° (56%) [825].

m.p. 39-40° [825]; b.p.₂₅ 134-135° [825];¹H NMR [825].

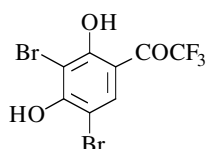
2.3.3. From trifluoroacetic acid

1-(3,5-Dibromo-2,4-dihydroxyphenyl)-2,2,2-trifluoroethanone

[65240-11-1]

C₈H₃Br₂F₃O₃

mol.wt. 363.91



Synthesis

-Preparation by reaction of bromine on 2,4-dihydroxy- α,α,α -trifluoroacetophenone in acetic acid at r.t. (49%) [232].

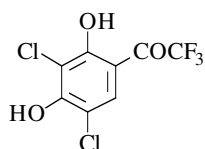
m.p. 81° [232].

1-(3,5-Dichloro-2,4-dihydroxyphenyl)-2,2,2-trifluoroethanone

[65240-09-7]

C₈H₃Cl₂F₃O₃

mol.wt. 275.01



Synthesis

-Preparation by reaction of sulfonyl chloride on 2,4-dihydroxy- α,α,α -trifluoroacetophenone at r. t [232].

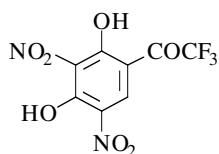
m.p. 101° [232].

1-(2,4-Dihydroxy-3,5-dinitrophenyl)-2,2,2-trifluoroethanone

[65240-17-7]

C₈H₃F₃N₂O₇

mol.wt. 296.12



Synthesis

-Preparation by reaction of 65% nitric acid on 2,4-dihydroxy- α,α,α -trifluoroacetophenone in concentrated sulfuric acid [232].

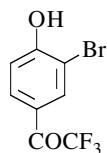
m.p. 68° [232].

1-(3-Bromo-4-hydroxyphenyl)-2,2,2-trifluoroethanone

[303143-05-7]

C₈H₄BrF₃O₂

mol.wt. 269.02



Synthesis

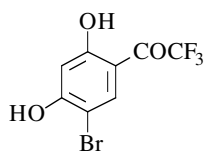
-Obtained by demethylation of 3-bromo-4-methoxy- α,α,α -trifluoroacetophenone with lithium chloride in refluxing DMF for 2 h (93%) [911].

1-(5-Bromo-2,4-dihydroxyphenyl)-2,2,2-trifluoroethanone

[65239-86-3]

C₈H₄BrF₃O₃

mol.wt. 285.02

**Synthesis**

-Preparation by reaction of trifluoroacetic anhydride on 4-bromoresorcinol with aluminium chloride in ethylene dichloride at r.t. (88%) [232].

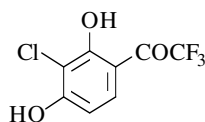
m.p. 81° [232].

1-(3-Chloro-2,4-dihydroxyphenyl)-2,2,2-trifluoroethanone

[65239-93-2]

C₈H₄ClF₃O₃

mol.wt. 240.57

**Synthesis**

-Preparation by reaction of trifluoroacetic anhydride on 2-chlororesorcinol with aluminium chloride in ethylene dichloride at r.t. (83%) [232].

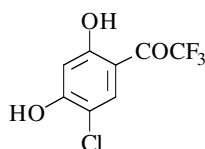
m.p. 113° [232].

1-(5-Chloro-2,4-dihydroxyphenyl)-2,2,2-trifluoroethanone

[65233-63-8]

C₈H₄ClF₃O₃

mol.wt. 240.57

**Synthesis**

-Preparation by reaction of trifluoroacetic anhydride on 4-chlororesorcinol with aluminium chloride in ethylene dichloride at r.t. (90%) [232].

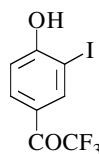
m.p. 110° [232].

2,2,2-Trifluoro-1-(4-hydroxy-3-iodophenyl)ethanone

[303143-06-8]

C₈H₄F₃IO₂

mol.wt. 316.02

**Synthesis**

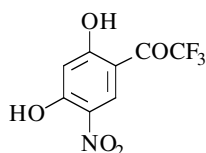
-Obtained by demethylation of 3-iodo-4-methoxy- α,α,α -trifluoroacetophenone with lithium chloride in refluxing DMF for 2 h (87%) [911].

1-(2,4-Dihydroxy-5-nitrophenyl)-2,2,2-trifluoroethanone

[65240-16-6]

C₈H₄F₃NO₅

mol.wt. 251.12

**Synthesis**

-Preparation by reaction of 26% nitric acid on 2,4-dihydroxy- α,α,α -trifluoroacetophenone in acetic acid at 0° [232].

m.p. 81° [232].

2,2,2-Trifluoro-1-(2-hydroxyphenyl)ethanone

[25666-51-7]

C₈H₅F₃O₂

mol.wt. 190.12

Synthesis

-Preparation by Fries rearrangement of phenyl trifluoroacetate with aluminium chloride without solvent at 90° (42%) [976].

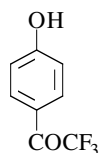
b.p.₅₅ 92° [976]; ¹H NMR [976], IR [976].

2,2,2-Trifluoro-1-(4-hydroxyphenyl)ethanone

[1823-63-8]

C₈H₅F₃O₂

mol.wt. 190.12

**Syntheses**

-Preparation by reaction of trifluoroacetic acid with phenol in hydrofluoric acid at 100° (75%) [1002].

-Obtained in small amount by Fries rearrangement of phenyl trifluoroacetate with aluminium chloride without solvent at 90° [976].

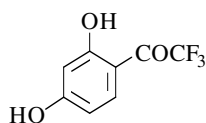
m.p. 105°-106° [976]; ¹H NMR [1002], ¹⁹F NMR [1002], IR [976] [1002].

1-(2,4-Dihydroxyphenyl)-2,2,2-trifluoroethanone

[315-44-6]

C₈H₅F₃O₃

mol.wt. 206.12

**Syntheses**

-Preparation by reaction of trifluoroacetonitrile on resorcinol (Hoesch reaction) (62%) [1511] [1512] [1533].

-Preparation by reaction of trifluoroacetic anhydride on resorcinol with aluminium chloride in ethylene dichloride at r.t. (73-83%) [993].

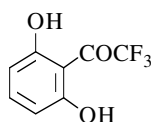
m.p. 106-108° [993], 103° [1511] [1533].

1-(2,6-Dihydroxyphenyl)-2,2,2-trifluoroethanone

[70211-42-6]

C₈H₅F₃O₃

mol.wt. 206.12

**Syntheses**

-Obtained by total demethylation of 2,6-dimethoxy- α,α,α -trifluoroacetophenone with boron tribromide in methylene chloride, first at 0° for 15 min, then at r.t. overnight (22%) [755].

-Also refer to: [891].

N.B.: There is also an erroneous reference. It concerns the 2',6'-dihydroxytrifluoroacetanilide [1346].

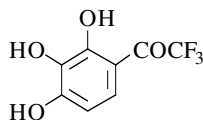
¹H NMR [755], MS [755].

2,2,2-Trifluoro-1-(2,3,4-trihydroxyphenyl)ethanone

[65239-87-4]

C₈H₅F₃O₄

mol.wt. 222.12

**Synthesis**

-Preparation by reaction of trifluoroacetic anhydride on pyrogallol with aluminium chloride in ethylene dichloride at r.t. (75%) [232].

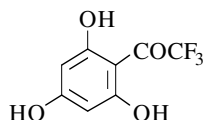
m.p. 134° [232].

2,2,2-Trifluoro-1-(2,4,6-trihydroxyphenyl)ethanone

[13340-79-9]

C₈H₅F₃O₄

mol.wt. 222.12

**Synthesis**

-Preparation by reaction of trifluoroacetic anhydride on phloroglucinol with aluminium chloride in ethylene dichloride at r.t. (40%) [993].

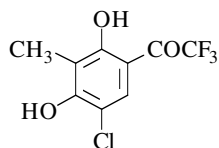
m.p. 174-177° [993]; ¹H NMR [993], ¹⁹F NMR [993], IR [993].

1-(5-Chloro-2,4-dihydroxy-3-methylphenyl)-2,2,2-trifluoroethanone

[65240-08-6]

C₉H₆ClF₃O₃

mol.wt. 254.59

**Synthesis**

-Preparation by reaction of sulfonyl chloride on 2,4-dihydroxy-3-methyl- α,α,α -trifluoroacetophenone in ethylene dichloride at r.t. (76%) [232].

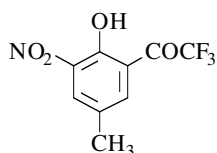
m.p. 96° [232].

2,2,2-Trifluoro-1-(2-hydroxy-5-methyl-3-nitrophenyl)ethanone

[70978-48-2]

C₉H₆F₃NO₄

mol.wt. 249.15

**Synthesis**

-Preparation by reaction of fuming nitric acid ($d = 1.5$) on 2-hydroxy-5-methyl- α,α,α -trifluoroacetophenone in acetic acid-methylene chloride mixture at r.t. [506] [1215], (44%) [506].

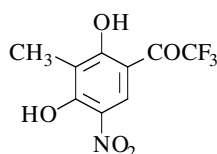
m.p. 94-96° [506], 49-50° [1215]. One of the reported melting points is obviously wrong.

1-(2,4-Dihydroxy-3-methyl-5-nitrophenyl)-2,2,2-trifluoroethanone

[65240-15-5]

C₉H₆F₃NO₅

mol.wt. 265.15

**Synthesis**

-Obtained by reaction of 26% nitric acid on 2,4-dihydroxy-3-methyl- α,α,α -trifluoroacetophenone in acetic acid at 0° (21%) [232].

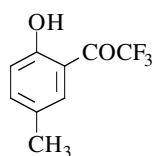
m.p. 104° [232].

2,2,2-Trifluoro-1-(2-hydroxy-5-methylphenyl)ethanone

[70978-57-3]

C₉H₇F₃O₂

mol.wt. 204.15

**Synthesis**

-Preparation by Fries rearrangement of 4-methylphenyl trifluoroacetate with aluminium chloride without solvent at 115° (25%) [1215].

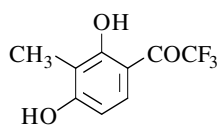
m.p. 40°5-42° [1215].

1-(2,4-Dihydroxy-3-methylphenyl)-2,2,2-trifluoroethanone

[65233-60-5]

C₉H₇F₃O₃

mol.wt. 220.15

**Syntheses**

-Preparation by reaction of trifluoroacetic anhydride on 2-methylresorcinol with aluminium chloride in ethylene dichloride at r.t. (90%) [232].

-Preparation by Fries rearrangement of 2-methylresorcinol monotrifluoroacetate with aluminium chloride in nitrobenzene or without solvent at 120° [232].

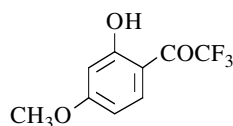
m.p. 101° [232].

2,2,2-Trifluoro-1-(2-hydroxy-4-methoxyphenyl)ethanone

[123716-19-8]

C₉H₇F₃O₃

mol.wt. 220.15

**Synthesis**

-Obtained by refluxing α -(difluoronitromethyl)-2-hydroxy-4-methoxy- α -(trifluoromethyl)benzenemethanol (SM) in hexane for 6 h in the presence of activated charcoal (91%). SM was prepared by reaction of NPFA with resorcinol monomethyl ether in carbon tetrachloride or nitromethane

for 12 h at 20° (99%, m.p. 67-69°) [433].

m.p. 62-64° [433];

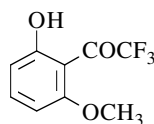
¹H NMR [433], ¹³C NMR [433], ¹⁹F NMR [433]; TLC [433].

2,2,2-Trifluoro-1-(2-hydroxy-6-methoxyphenyl)ethanone

[193738-66-8]

C₉H₇F₃O₃

mol.wt. 220.15

**Synthesis**

-Obtained by partial demethylation of 2,6-dimethoxy- α,α,α -trifluoroacetophenone with boron tribromide in methylene chloride, first at 0° for 15 min, then at r.t. overnight (17%) [755].

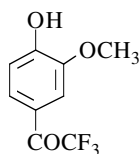
yellow oil [755]; ¹H NMR [755], MS [755].

2,2,2-Trifluoro-1-(4-hydroxy-3-methoxyphenyl)ethanone

[188194-66-3]

C₉H₇F₃O₃

mol.wt. 220.15

**Synthesis**

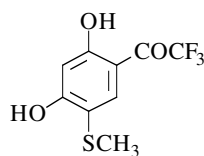
-This compound (**6**) [893] was synthesized according to Dudley [421].

1-[2,4-Dihydroxy-5-(methylthio)phenyl]-2,2,2-trifluoroethanone

[65239-90-9]

C₉H₇F₃O₃S

mol.wt. 252.21

**Synthesis**

-Preparation by reaction of trifluoroacetic anhydride on 4-methylthioresorcinol with aluminium chloride in ethylene dichloride at r.t. (68%) [232].

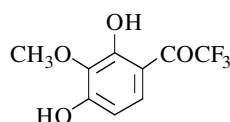
m.p. 57° [232].

1-(2,4-Dihydroxy-3-methoxyphenyl)-2,2,2-trifluoroethanone

[65239-88-5]

C₉H₇F₃O₄

mol.wt. 236.15

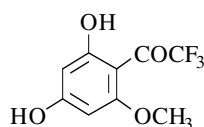
**Synthesis**

-Preparation by reaction of trifluoroacetic anhydride on 2-methoxyresorcinol with aluminium chloride in ethylene dichloride at r.t. (78%) [232].

m.p. 79° [232].

1-(2,4-Dihydroxy-6-methoxyphenyl)-2,2,2-trifluoroethanoneC₉H₇F₃O₄

mol.wt. 236.15

**Synthesis**

-Preparation by reaction of trifluoroacetonitrile on phloroglucinol monomethyl ether with zinc chloride and gaseous hydrochloric acid in ethyl ether at 0° (Hoesch reaction) (33%) [1533].

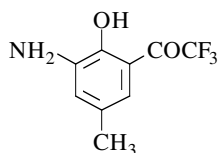
m.p. 154° [1533].

1-(3-Amino-2-hydroxy-5-methylphenyl)-2,2,2-trifluoroethanone

[70977-83-2]

C₉H₈F₃NO₂

mol.wt. 219.16

**Synthesis**

-Preparation by catalytic hydrogenation of 2-hydroxy-5-methyl-3-nitro- α,α,α -trifluoroacetophenone in the presence of 5% Pt/C in ethanol at 25° [506] [1215], (57%) [506].

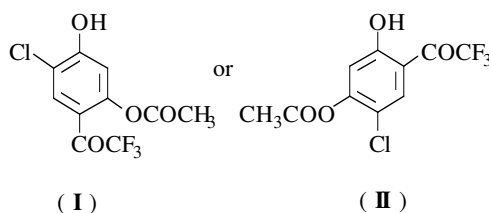
m.p. 87-88° [506] [1215].

1-[2-(Acetyloxy)-5-chloro-4-hydroxyphenyl]-2,2,2-trifluoroethanone
or**1-[4-(Acetyloxy)-5-chloro-2-hydroxyphenyl]-2,2,2-trifluoroethanone**

[65233-64-9]

C₁₀H₆ClF₃O₄

mol.wt. 282.60

**Synthesis**

-Preparation by reaction of acetyl chloride on 5-chloro-2,4-dihydroxy- α,α,α -trifluoroacetophenone with pyridine in benzene at r.t. (72%) [232].

m.p. 80-83° [232].

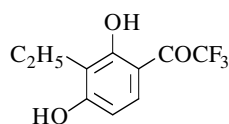
N.B.: The 4-(Acetyloxy)-5-chloro-2-hydroxy- α,α,α -trifluoroacetophenone (**II**) is the most likely formula, for two reasons: On the one hand, there is a strong chelation between hydroxyl and keto groups in the raw material and, on the other hand, the esterification was carried out at r.t.

1-(3-Ethyl-2,4-dihydroxyphenyl)-2,2,2-trifluoroethanone

[577-54-8]

C₁₀H₉F₃O₃

mol.wt. 234.17

**Synthesis**

-Preparation by reaction of trifluoroacetonitrile on 2-ethyl-resorcinol (Hoesch reaction) (74%) [1533].

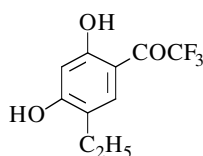
m.p. 139° [1533].

1-(5-Ethyl-2,4-dihydroxyphenyl)-2,2,2-trifluoroethanone

[584-41-8]

C₁₀H₉F₃O₃

mol.wt. 234.17

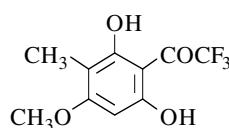
**Synthesis**

-Preparation by reaction of trifluoroacetonitrile on 4-ethyl-resorcinol (Hoesch reaction) (71%) [1533].

m.p. 99° [1533].

1-(2,6-Dihydroxy-4-methoxy-3-methylphenyl)-2,2,2-trifluoroethanoneC₁₀H₉F₃O₄

mol.wt. 250.17

**Synthesis**

-Preparation by reaction of trifluoroacetonitrile on 1,3-dihydroxy-5-methoxy-4-methylbenzene (Hoesch reaction) (22%) [1535].

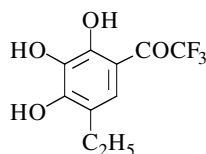
m.p. 145° [1535].

1-(5-Ethyl-2,3,4-trihydroxyphenyl)-2,2,2-trifluoroethanone

[65239-92-1]

C₁₀H₉F₃O₄

mol.wt. 250.17

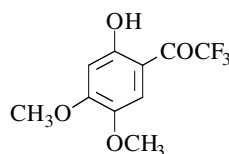
**Synthesis**

-Preparation by reaction of trifluoroacetic anhydride on 4-ethylpyrogallol with aluminium chloride in ethylene dichloride at r.t. (80%) [232].

m.p. 82° [232].

2,2,2-Trifluoro-1-(2-hydroxy-4,5-dimethoxyphenyl)ethanoneC₁₀H₉F₃O₄

mol.wt. 250.17

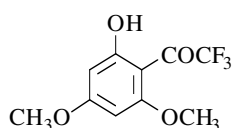
**Synthesis**

-Preparation by reaction of trifluoroacetonitrile on 3,4-dimethoxyphenol (Hoesch reaction) (62%) [1533].

m.p. 82° [1533].

2,2,2-Trifluoro-1-(2-hydroxy-4,6-dimethoxyphenyl)ethanoneC₁₀H₉F₃O₄

mol.wt. 250.17

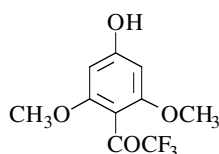
**Synthesis**

-Obtained (by-product) by reaction of trifluoroacetonitrile on phloroglucinol dimethyl ether (Hoesch reaction) (5%) [1535].

m.p. 87° [1535].

2,2,2-Trifluoro-1-(4-hydroxy-2,6-dimethoxyphenyl)ethanoneC₁₀H₉F₃O₄

mol.wt. 250.17

**Synthesis**

-Preparation by reaction of trifluoroacetonitrile on phloroglucinol dimethyl ether (Hoesch reaction) (25%) [1535].

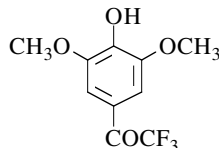
m.p. 155° [1535].

2,2,2-Trifluoro-1-(4-hydroxy-3,5-dimethoxyphenyl)ethanone

[188194-67-4]

C₁₀H₉F₃O₄

mol.wt. 250.17

**Synthesis**

-This compound (7) [893] was synthesized according to Dudley [421].

1-[2-(Acetyloxy)-4-hydroxy-3-methylphenyl]-2,2,2-trifluoroethanone

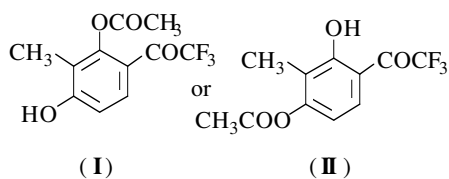
or

1-[4-(Acetyloxy)-2-hydroxy-3-methylphenyl]-2,2,2-trifluoroethanone

[65233-62-7]

C₁₁H₉F₃O₄

mol.wt. 262.19

**Synthesis**

-Preparation by reaction of acetyl chloride on 2,4-dihydroxy-3-methyl- α,α,α -trifluoroacetophenone with pyridine in benzene at r.t. (87%) [232].

m.p. 49-50° [232].

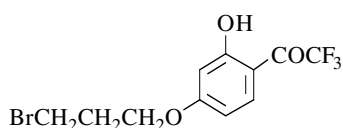
N.B.: The 1-[4-(Acetyloxy)-2-hydroxy-3-methylphenyl]-2,2,2-trifluoroethanone (**II**) is the most likely formula. This hypothesis is supported by the fact that, considering the precursor (2,4-dihydroxy-3-methyl- α,α,α -trifluoroacetophenone), the hydroxy group in the 4-position is less hindered than the hydroxyl substituent in the 2-position which is furthermore chelated with the vicinal carbonyl group. In addition, the reported melting point (49-50°) is in good agreement with those generally measured for o-hydroxyketones (below 80°) compared to those of p-hydroxyketones which are considerably higher (usually 120-200°).

1-[4-(3-Bromopropoxy)-2-hydroxyphenyl]-2,2,2-trifluoroethanone

[125617-37-0]

C₁₁H₁₀BrF₃O₃

mol.wt. 327.10

**Synthesis**

-Preparation by reaction of 1,3-dibromopropane with 2,4-dihydroxy- α,α,α -trifluoroacetophenone in the presence of potassium carbonate and potassium iodide in refluxing methyl ethyl ketone [1388].

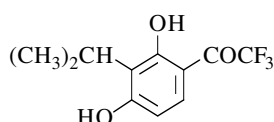
pale yellow oil [1388]; IR [1388].

1-[2,4-Dihydroxy-3-(1-methylethyl)phenyl]-2,2,2-trifluoroethanone

[65239-70-5]

C₁₁H₁₁F₃O₃

mol.wt. 248.20

**Syntheses**

- Preparation by reaction of trifluoroacetic anhydride on 2-isopropylresorcinol with aluminium chloride in ethylene dichloride at r.t. (85%) [232].
- Preparation by reaction of isopropanol on 2,4-dihydroxy- α,α,α -trifluoroacetophenone with polyphosphoric acid at 80° (30%) [232].
- Preparation by reaction of propylene on 2,4-dihydroxy- α,α,α -trifluoroacetophenone with phosphorous oxychloride and phosphoric anhydride at 50° [232].
- Preparation by Fries rearrangement of 2-isopropylresorcinol trifluoroacetate with aluminium chloride without solvent or in nitrobenzene at 120° [232].

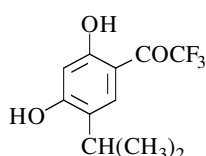
m.p. 145° [232].

1-[2,4-Dihydroxy-5-(1-methylethyl)phenyl]-2,2,2-trifluoroethanone

[65239-68-1]

C₁₁H₁₁F₃O₃

mol.wt. 248.20

**Synthesis**

-Preparation by reaction of trifluoroacetic anhydride on 4-isopropylresorcinol with aluminium chloride in chloroform at r.t. (70%) [232].

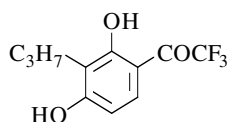
m.p. 97° [232].

1-(2,4-Dihydroxy-3-propylphenyl)-2,2,2-trifluoroethanone

[65239-69-2]

C₁₁H₁₁F₃O₃

mol.wt. 248.20

**Syntheses**

- Preparation by reaction of trifluoroacetic anhydride on 2-propylresorcinol with aluminium chloride in ethylene dichloride at r.t. (88%) [232].
- Preparation by reaction of trifluoroacetonitrile on 2-propylresorcinol (Hoesch reaction) (66%) [237].

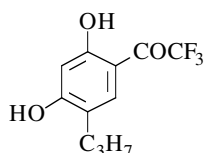
m.p. 114° [232], 110-112° [237]; ¹H NMR [237].

1-(2,4-Dihydroxy-5-propylphenyl)-2,2,2-trifluoroethanone

[65239-67-0]

C₁₁H₁₁F₃O₃

mol.wt. 248.20

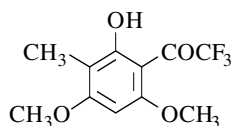
**Synthesis**

-Preparation by reaction of trifluoroacetic anhydride on 4-propylresorcinol with aluminium chloride in ethylene dichloride at r.t. (87%) [232].

m.p. 95° [232].

2,2,2-Trifluoro-1-(2-hydroxy-4,6-dimethoxy-3-methylphenyl)ethanoneC₁₁H₁₁F₃O₄

mol.wt. 264.20

**Synthesis**

-Preparation by reaction of trifluoroacetonitrile on 3,5-dimethoxy-2-methylphenol (Hoesch reaction) (43%) [1535].

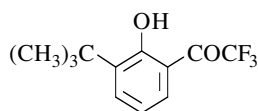
m.p. 100° [1535].

1-[3-(1,1-Dimethylethyl)-2-hydroxyphenyl]-2,2,2-trifluoroethanone

[111422-37-8]

C₁₂H₁₃F₃O₂

mol.wt. 246.23

**Synthesis**

-Preparation by reaction of trifluoroacetyl chloride on bromomagnesium 2-tert-butylphenolate in toluene at r.t. (74%) [1286].

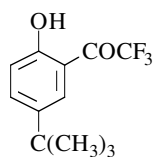
yellow oil [1286]; ¹H NMR [1286], IR [1286], MS [1286].

1-[5-(1,1-Dimethylethyl)-2-hydroxyphenyl]-2,2,2-trifluoroethanone

[75060-56-9]

C₁₂H₁₃F₃O₂

mol.wt. 246.23

**Synthesis**

-Preparation by demethylation of 5-tert-butyl-2-methoxy- α,α,α -trifluoroacetophenone with 47% hydrobromic acid and 57% hydriodic acid in refluxing acetic acid (70%) [685].

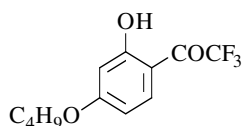
¹H NMR [685], IR [685], MS [685].

1-(4-Butoxy-2-hydroxyphenyl)-2,2,2-trifluoroethanone

[65240-27-9]

C₁₂H₁₃F₃O₃

mol.wt. 262.23

**Synthesis**

-Obtained by reaction of butyl iodide on 2,4-dihydroxy- α,α,α -trifluoroacetophenone with potassium carbonate in refluxing acetone (29%) [232].

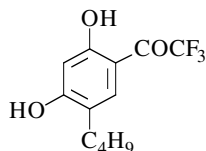
m.p. 66° [232].

1-(5-Butyl-2,4-dihydroxyphenyl)-2,2,2-trifluoroethanone

[65239-71-6]

C₁₂H₁₃F₃O₃

mol.wt. 262.23

**Synthesis**

-Preparation by reaction of trifluoroacetic anhydride on 4-butylresorcinol with aluminium chloride in ethylene dichloride at r.t. (82%) [232].

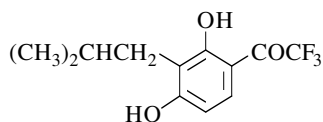
m.p. 96° [232].

1-[2,4-Dihydroxy-3-(2-methylpropyl)phenyl]-2,2,2-trifluoroethanone

[65239-73-8]

C₁₂H₁₃F₃O₃

mol.wt. 262.23

**Syntheses**

-Preparation by reaction of trifluoroacetic anhydride on 2-isobutylresorcinol with aluminium chloride in ethylene dichloride at r.t. (78%) [232].

-Preparation by Fries rearrangement of 2-isobutylresorcinol monotrifluoroacetate with aluminium chloride in nitrobenzene at 120° [232].

-Preparation by reaction of isobutyl alcohol on 2,4-dihydroxy- α,α,α -trifluoroacetophenone with polyphosphoric acid at 80° [232].

-Preparation by reaction of isobutylene on 2,4-dihydroxy- α,α,α -trifluoroacetophenone with phosphorous pentoxide and phosphorous oxychloride at 50° [232].

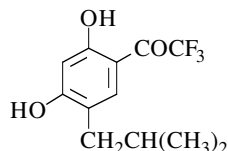
m.p. 114° [232].

1-[2,4-Dihydroxy-5-(2-methylpropyl)phenyl]-2,2,2-trifluoroethanone

[65239-72-7]

C₁₂H₁₃F₃O₃

mol.wt. 262.23

**Syntheses**

-Preparation by reaction of trifluoroacetic anhydride on 4-isobutylresorcinol with aluminium chloride in ethylene dichloride at r.t. (78-84%) [232].

-Preparation by reaction of isobutyl alcohol on 2,4-dihydroxy- α,α,α -trifluoroacetophenone with polyphosphoric acid at 80° [232].

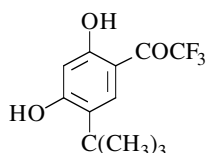
m.p. 90° [232]; b.p._{0.1} 90° [232].

1-[5-(1,1-Dimethylethyl)-2,4-dihydroxyphenyl]-2,2,2-trifluoroethanone

[65239-74-9]

C₁₂H₁₃F₃O₃

mol.wt. 262.23

**Syntheses**

-Preparation by reaction of trifluoroacetic anhydride on 4-tert-butylresorcinol with aluminium chloride in ethylene dichloride at r.t. (80%) [232].

-Preparation by reaction of tert-butyl alcohol on 2,4-dihydroxy- α,α,α -trifluoroacetophenone with polyphosphoric acid at 80° [232].

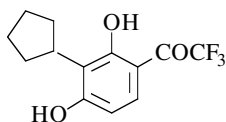
m.p. 159° [232].

1-(3-Cyclopentyl-2,4-dihydroxyphenyl)-2,2,2-trifluoroethanone

[65240-20-2]

C₁₃H₁₃F₃O₃

mol.wt. 274.24

**Synthesis**

-Preparation by reaction of cyclopentene on 2,4-dihydroxy- α,α,α -trifluoroacetophenone with phosphorous oxychloride-phosphorous pentoxide mixture at 50° [232].

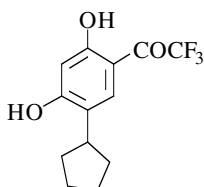
m.p. 166° [232].

1-(5-Cyclopentyl-2,4-dihydroxyphenyl)-2,2,2-trifluoroethanone

[65239-76-1]

C₁₃H₁₃F₃O₃

mol.wt. 274.24

**Synthesis**

-Preparation by reaction of trifluoroacetic anhydride on 4-cyclopentylresorcinol with aluminium chloride in ethylene dichloride at r.t. (75%) [232].

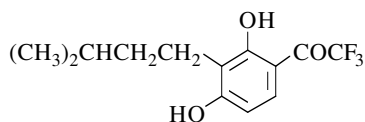
m.p. 94° [232].

1-[2,4-Dihydroxy-3-(3-methylbutyl)phenyl]-2,2,2-trifluoroethanone

[65239-77-2]

C₁₃H₁₅F₃O₃

mol.wt. 276.26

**Synthesis**

-Preparation by reaction of trifluoroacetic anhydride on 2-isopentylresorcinol with aluminium chloride in ethylene dichloride at r.t. (84%) [232].

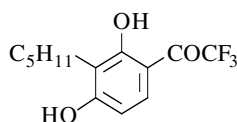
m.p. 101° [232].

1-(2,4-Dihydroxy-3-pentylphenyl)-2,2,2-trifluoroethanone

[65239-78-3]

C₁₃H₁₅F₃O₃

mol.wt. 276.26

**Synthesis**

-Preparation by reaction of trifluoroacetic anhydride on 2-pentylresorcinol with aluminium chloride in ethylene dichloride at r.t. (87%) [232].

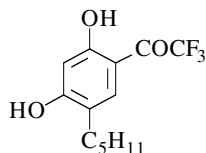
m.p. 105° [232].

1-(2,4-Dihydroxy-5-pentylphenyl)-2,2,2-trifluoroethanone

[65239-75-0]

C₁₃H₁₅F₃O₃

mol.wt. 276.26

**Synthesis**

-Preparation by reaction of trifluoroacetic anhydride on 4-pentylresorcinol with aluminium chloride in ethylene dichloride at r.t. (86%) [232].

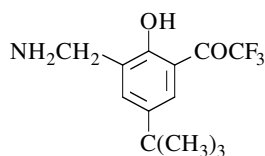
m.p. 97° [232].

1-[3-(Aminomethyl)-5-(1,1-dimethylethyl)-2-hydroxyphenyl]-2,2,2-trifluoroethanone

[75060-97-8]

C₁₃H₁₆F₃NO₂

mol.wt. 275.27

**Synthesis**

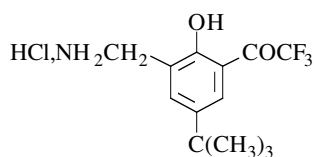
-Preparation from the corresponding hydrochloride (see below) [685].

1-[3-(Aminomethyl)-5-(1,1-dimethylethyl)-2-hydroxyphenyl]-2,2,2-trifluoroethanone (Hydrochloride)

[75060-74-1]

C₁₃H₁₆F₃NO₂·HCl

mol.wt. 311.73

**Synthesis**

-Preparation by reaction of concentrated hydrochloric acid on 4-tert-butyl-6-(N-chloroacetylaminomethyl)-2-(trifluoroacetyl)phenol in refluxing ethanol (83%) [685].

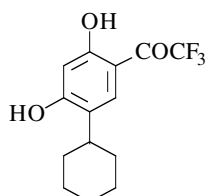
m.p. 180-186° [685]; ¹H NMR [685], IR [685].

1-(5-Cyclohexyl-2,4-dihydroxyphenyl)-2,2,2-trifluoroethanone

[65239-79-4]

C₁₄H₁₅F₃O₃

mol.wt. 288.27

**Synthesis**

-Preparation by reaction of trifluoroacetic anhydride with 4-cyclohexylresorcinol in the presence of aluminium chloride in ethylene dichloride at r.t. (78%) [232].

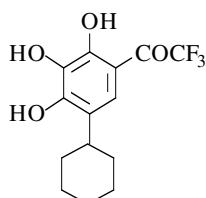
m.p. 80° [232].

1-(5-Cyclohexyl-2,3,4-trihydroxyphenyl)-2,2,2-trifluoroethanone

[65239-91-0]

C₁₄H₁₅F₃O₄

mol.wt. 304.27

**Synthesis**

-Preparation by reaction of trifluoroacetic anhydride with 4-cyclohexylpyrogallol in the presence of aluminium chloride in ethylene dichloride at r.t. (78%) [232].

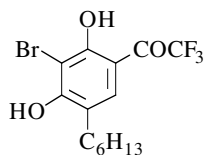
m.p. 128° [232].

1-(3-Bromo-5-hexyl-2,4-dihydroxyphenyl)-2,2,2-trifluoroethanone

[65240-12-2]

C₁₄H₁₆BrF₃O₃

mol.wt. 369.18

**Synthesis**

-Preparation by reaction of bromine on 5-n-hexyl-2,4-dihydroxy- α,α,α -trifluoroacetophenone in acetic acid at r.t. (43%) [232].

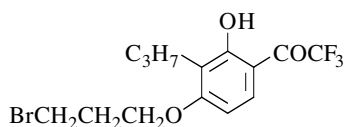
m.p. 39° [232].

1-[4-(3-Bromopropoxy)-2-hydroxy-3-propylphenyl]-2,2,2-trifluoroethanone

[125617-40-5]

C₁₄H₁₆BrF₃O₃

mol.wt. 369.18

**Synthesis**

-Preparation by reaction of 1,3-dibromopropane with 2,4-dihydroxy-3-propyl- α,α,α -trifluoroacetophenone in the presence of potassium carbonate and potassium iodide in refluxing methyl ethyl ketone [1388].

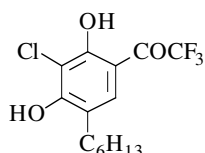
yellow oil [1388]; IR [1388].

1-(3-Chloro-5-hexyl-2,4-dihydroxyphenyl)-2,2,2-trifluoroethanone

[65240-10-0]

C₁₄H₁₆ClF₃O₃

mol.wt. 324.73

**Synthesis**

-Preparation by reaction of sulfonyl chloride on 5-n-hexyl-2,4-dihydroxy- α,α,α -trifluoroacetophenone at r.t. [232].

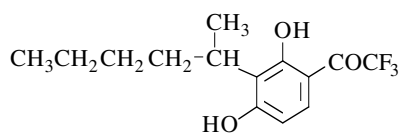
m.p. 40° [232].

1-[2,4-Dihydroxy-3-(1-methylpentyl)phenyl]-2,2,2-trifluoroethanone

[65240-18-8]

C₁₄H₁₇F₃O₃

mol.wt. 290.28

**Synthesis**

-Preparation by reaction of 1-hexene on 2,4-dihydroxy- α,α,α -trifluoroacetophenone with phosphorous oxychloride and phosphorous pentoxide at 50° (30%) [232].

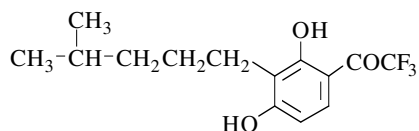
m.p. 97° [232].

1-[2,4-Dihydroxy-3-(4-methylpentyl)phenyl]-2,2,2-trifluoroethanone

[65240-07-5]

C₁₄H₁₇F₃O₃

mol.wt. 290.28

**Synthesis**

-Preparation by Fries rearrangement of 2-iso-hexyl-3-hydroxyphenyl trifluoroacetate with aluminium chloride in nitrobenzene or without solvent at 120° [232].

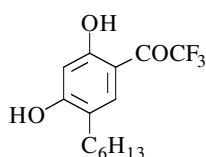
m.p. 97° [232].

2,2,2-Trifluoro-1-(5-hexyl-2,4-dihydroxyphenyl)ethanone

[65233-68-3]

C₁₄H₁₇F₃O₃

mol.wt. 290.28

**Syntheses**

-Preparation by Fries rearrangement of 4-hexyl-3-hydroxyphenyl trifluoroacetate with aluminium chloride at 120°, in nitrobenzene (47%) or without solvent (38%) [232].

-Preparation by reaction of trifluoroacetamide on 4-hexyl-resorcinol at reflux, with boron trifluoride etherate (55%)

or with p-toluenesulfonic acid (20%) [232].

-Preparation by reaction of trifluoroacetonitrile on 4-hexylresorcinol, in the presence of hydrochloric acid,

*with zinc chloride in ethyl ether at 0° (Hoesch reaction) (69%) [232];

*with aluminium chloride (Houben reaction), in ethylene dichloride (60%), in phosphorous oxychloride (55%), in toluene (20%) or in nitrobenzene (15%) [232].

-Preparation by reaction of trifluoroacetyl chloride on 4-hexylresorcinol at r.t. [232],
 *with aluminium chloride in ethylene dichloride (92%) or in phosphorous oxychloride (20%);
 *with boron trifluoride etherate in ethylene dichloride (40%);
 *with zinc chloride in ethylene dichloride (30%).
 -Preparation by reaction of trifluoroacetic acid on 4-hexylresorcinol in ethylene dichloride [232],
 *with phosphorous pentachloride (54%) or p-toluenesulfonic acid (30%) at r.t.;
 *with boron trifluoride etherate at reflux (40%).
 -Also obtained by reaction of ethyl trifluoroacetate on 4-hexylresorcinol with p-toluenesulfonic acid at reflux (25%) [232].
 -Preparation by reaction of trifluoroacetic anhydride on 4-hexylresorcinol at r.t. (see table below) [232].

Catalyst	Solvent	Yield (%)
AlCl ₃	POCl ₃	80
"	C ₆ H ₅ CH ₃	10
"	C ₆ H ₅ NO ₂	75
"	CH ₂ Cl-CH ₂ Cl	85
ZnCl ₂	POCl ₃	60
"	C ₆ H ₅ CH ₃	65
"	C ₆ H ₅ NO ₂	83
"	CH ₂ Cl-CH ₂ Cl	87
"	(C ₂ H ₅) ₂ O	15
FeCl ₃	POCl ₃	30
"	C ₆ H ₅ CH ₃	30
"	C ₆ H ₅ NO ₂	45
"	CH ₂ Cl-CH ₂ Cl	68
PCl ₅	POCl ₃	60 (at 100°)
"	C ₆ H ₅ CH ₃	20
"	C ₆ H ₅ NO ₂	20
4-CH ₃ C ₆ H ₄ SO ₃ H	C ₆ H ₅ CH ₃	25
"	C ₆ H ₅ NO ₂	25
"	CH ₂ Cl-CH ₂ Cl	22
BF ₃ -Et ₂ O	C ₆ H ₅ CH ₃	35
"	CH ₂ Cl-CH ₂ Cl	60
"	(C ₂ H ₅) ₂ O	70

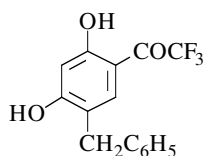
m.p. 90° [232].

1-[2,4-Dihydroxy-5-(phenylmethyl)phenyl]-2,2,2-trifluoroethanone

[65239-81-8]

C₁₅H₁₁F₃O₃

mol.wt. 296.25



Synthesis

-Preparation by reaction of trifluoroacetic anhydride on 4-benzylresorcinol with aluminium chloride in ethylene dichloride at r.t. (80%) [232].

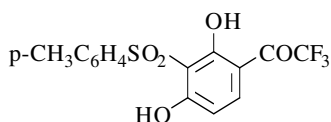
m.p. 114° [232].

1-[2,4-Dihydroxy-3-[(4-methylphenyl)sulfonyl]phenyl]-2,2,2-trifluoroethanone

[65240-14-4]

C₁₅H₁₁F₃O₅S

mol.wt. 360.31

**Synthesis**

-Obtained by reaction of p-toluenesulfonyl chloride on 2,4-dihydroxy- α,α,α -trifluoroacetophenone with aluminium chloride in phosphorous oxychloride (22%) [232].

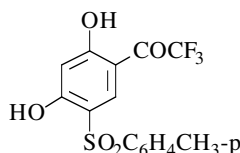
m.p. 127° [232].

1-[2,4-Dihydroxy-5-[(4-methylphenyl)sulfonyl]phenyl]-2,2,2-trifluoroethanone

[65240-13-3]

C₁₅H₁₁F₃O₅S

mol.wt. 360.31

**Synthesis**

-Preparation by reaction of p-toluenesulfonyl chloride on 2,4-dihydroxy- α,α,α -trifluoroacetophenone with ferric chloride in phosphorous oxychloride at 120° (40%) [232].

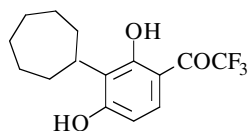
m.p. 145° [232].

1-(3-Cycloheptyl-2,4-dihydroxyphenyl)-2,2,2-trifluoroethanone

[65240-21-3]

C₁₅H₁₇F₃O₃

mol.wt. 302.29

**Synthesis**

-Preparation by reaction of cycloheptene on 2,4-dihydroxy- α,α,α -trifluoroacetophenone with phosphorous trichloride and phosphorous pentoxide at 50° [232].

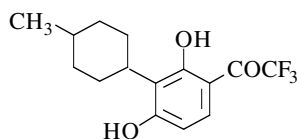
m.p. 174° [232].

1-[2,4-Dihydroxy-3-(4-methylcyclohexyl)phenyl]-2,2,2-trifluoroethanone

[65239-82-9]

C₁₅H₁₇F₃O₃

mol.wt. 302.29

**Syntheses**

-Preparation by reaction of trifluoroacetic anhydride on 2-(4-methylcyclohexyl)resorcinol with aluminium chloride in ethylene dichloride at r.t. (76%) [232].

-Preparation by Fries rearrangement of 3-hydroxy-

2-(4-methylcyclohexyl)phenyl trifluoroacetate with aluminium chloride in nitrobenzene or without solvent at 120° [232].

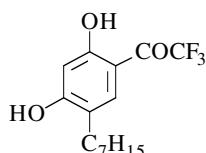
m.p. 143° [232].

2,2,2-Trifluoro-1-(5-heptyl-2,4-dihydroxyphenyl)ethanone

[65239-80-7]

C₁₅H₁₉F₃O₃

mol.wt. 304.31

**Syntheses**

- Preparation by reaction of trifluoroacetic anhydride on 4-heptylresorcinol with aluminium chloride in ethylene dichloride at r.t. (79%) [232].
- Preparation by Fries rearrangement of 4-heptyl-3-hydroxy-phenyl- α,α,α -trifluoroacetate with aluminium chloride

in nitrobenzene or without solvent at 120° [232].

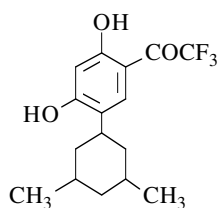
m.p. 85° [232].

1-[5-(3,5-Dimethylcyclohexyl)-2,4-dihydroxyphenyl]-2,2,2-trifluoroethanone

[65239-83-0]

C₁₆H₁₉F₃O₃

mol.wt. 304.31

**Synthesis**

- Preparation by acylation of 4-(3,5-dimethylcyclohexyl)-resorcinol (1 mol) with trifluoroacetic anhydride (1.2 mol) in the presence of aluminium chloride (2 mol) in ethylene dichloride at r.t. (79%) [232].

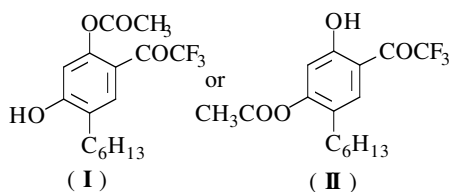
m.p. 126° [232].

1-[2 (or 4)-(Acetyloxy)-5-hexyl-4 (or 2)-hydroxyphenyl]-2,2,2-trifluoroethanone

[65233-69-4]

C₁₆H₁₉F₃O₄

mol.wt. 332.32

**Synthesis**

- Preparation by reaction of acetyl chloride on 5-hexyl-2,4-dihydroxy- α,α,α -trifluoroacetophenone with pyridine in benzene at r.t. (83%) [232].

m.p. 30° [232].

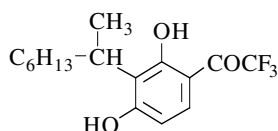
N.B.: The 1-[4-(acetyloxy)-5-hexyl-2-hydroxyphenyl]-2,2,2-trifluoroethanone (**II**) is the most likely formula. This hypothesis is supported by the fact that, considering the precursor (5-hexyl-2,4-dihydroxy- α,α,α -trifluoroacetophenone), the hydroxy group in the 2-position is chelated with the carbonyl group. In addition, the reported melting point (30°) is in good agreement with those generally measured for o-hydroxyketones (below 80°) compared to those of p-hydroxyketones which are considerably higher (usually 120-200°).

1-[2,4-Dihydroxy-3-(1-methylheptyl)phenyl]-2,2,2-trifluoroethanone

[65240-22-4]

C₁₆H₂₁F₃O₃

mol.wt. 318.34



Synthesis

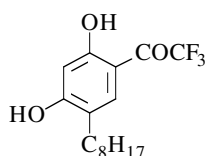
-Refer to: [232].

1-(2,4-Dihydroxy-5-octylphenyl)-2,2,2-trifluoroethanone

[65239-94-3]

C₁₆H₂₁F₃O₃

mol.wt. 318.34



Synthesis

-Preparation by reaction of trifluoroacetic anhydride on 4-octylresorcinol with aluminium chloride in ethylene dichloride at r.t. (74%) [232].

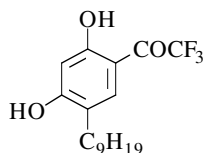
m.p. 87° [232].

1-(2,4-Dihydroxy-5-nonylphenyl)-2,2,2-trifluoroethanone

[65239-84-1]

C₁₇H₂₃F₃O₃

mol.wt. 332.36



Synthesis

-Preparation by reaction of trifluoroacetic anhydride with 4-nonylresorcinol in the presence of aluminium chloride in ethylene dichloride at r.t. (85%) [232].

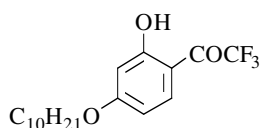
m.p. 87° [232].

1-[4-(Decyloxy)-2-hydroxyphenyl]-2,2,2-trifluoroethanone

[65240-25-7]

C₁₈H₂₅F₃O₃

mol.wt. 346.39



Synthesis

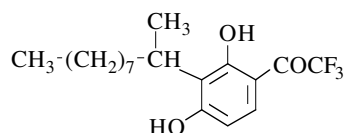
-Preparation by reaction of decyl iodide on 2,4-dihydroxy- α,α,α -trifluoroacetophenone with potassium carbonate in refluxing acetone (53%) [232].m.p. 27-28° [232]; b.p._{0.1} 150° [232].

1-[2,4-Dihydroxy-3-(1-methylnonyl)phenyl]-2,2,2-trifluoroethanone

[65134-36-3]

C₁₈H₂₅F₃O₃

mol.wt. 346.39

**Synthesis**

-Preparation by reaction of 1-decene on 2,4-dihydroxy- α,α,α -trifluoroacetophenone with phosphorous oxychloride and phosphorous pentoxide at 50° [232].

m.p. 98° [232].

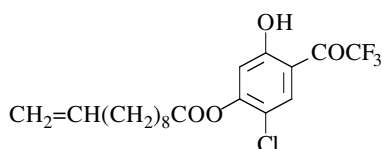
1-[5-Chloro-2-hydroxy-4-(10-undecenoyloxy)phenyl]-2,2,2-trifluoroethanone

10-Undecenoic acid, 2 (or 4)-Chloro-5-hydroxy-4 (or 2)-(trifluoroacetyl)phenyl ester

[65233-67-2]

C₁₉H₂₂ClF₃O₄

mol.wt. 406.83

**Synthesis**

-Preparation by reaction of 10-undecenoyl chloride on 5-chloro-2,4-dihydroxy- α,α,α -trifluoroacetophenone with pyridine in benzene at r.t. (65%) [232].

b.p._{0.07} 168° [232].

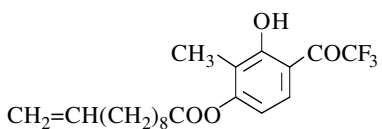
1-[2-Hydroxy-3-methyl-4-(10-undecenoyloxy)phenyl]-2,2,2-trifluoroethanone

10-Undecenoic acid, 3-Hydroxy-2-methyl-4 (or 6)-(trifluoroacetyl)phenyl ester

[65233-66-1]

C₂₀H₂₅F₃O₄

mol.wt. 386.41

**Synthesis**

-Preparation by reaction of 10-undecenoyl chloride on 2,4-dihydroxy-3-methyl- α,α,α -trifluoroacetophenone with pyridine in benzene at r.t. (64%) [232].

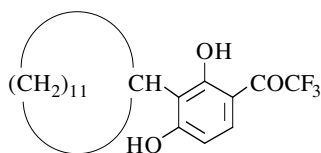
b.p._{0.07} 165° [232].

1-(3-Cyclododecyl-2,4-dihydroxyphenyl)-2,2,2-trifluoroethanone

[65240-19-9]

C₂₀H₂₇F₃O₃

mol.wt. 372.43

**Synthesis**

-Preparation by reaction of cyclododecene on 2,4-dihydroxy- α,α,α -trifluoroacetophenone with phosphorous oxychloride and phosphorous pentoxide at 50° [232].

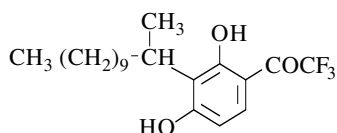
m.p. 166° [232].

1-[2,4-Dihydroxy-3-(1-methylundecyl)phenyl]-2,2,2-trifluoroethanone

[65134-37-4]

 $C_{20}H_{29}F_3O_3$

mol.wt. 374.44

**Synthesis**

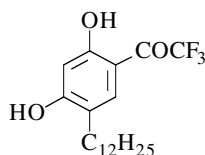
-Preparation by reaction of 1-dodecene on 2,4-dihydroxy- α,α,α -trifluoroacetophenone with phosphorous oxychloride and phosphorous pentoxide at 50° [232].

m.p. 96° [232].**1-(5-Dodecyl-2,4-dihydroxyphenyl)-2,2,2-trifluoroethanone**

[65239-85-2]

 $C_{20}H_{29}F_3O_3$

mol.wt. 374.44

**Synthesis**

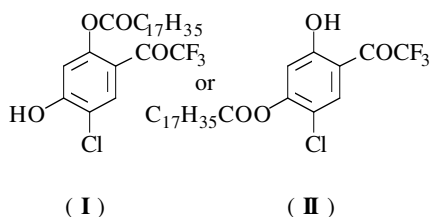
-Preparation by reaction of trifluoroacetic anhydride on 4-dodecylresorcinol with aluminium chloride in ethylene dichloride at r.t. (84%) [232].

m.p. 92° [232].**1-[5-Chloro-2 (or 4)-hydroxy-4 (or 2)-(octadecanoyloxy)phenyl]-2,2,2-trifluoroethanone**

[65233-65-0]

 $C_{26}H_{38}ClF_3O_4$

mol.wt. 507.03

**Synthesis**

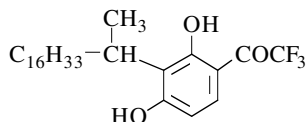
-Preparation by reaction of stearoyl chloride on 5-chloro-2,4-dihydroxy- α,α,α -trifluoroacetophenone with pyridine in benzene at r.t. (40%) [232].

m.p. 51° [232].

N.B.: The 1-[5-Chloro-2-hydroxy-4-(octadecanoyloxy)phenyl]-2,2,2-trifluoroethanone (**II**) is the most likely formula.

1-[2,4-Dihydroxy-3-(1-methylheptadecyl)phenyl]-2,2,2-trifluoroethanone $C_{26}H_{41}F_3O_3$

mol.wt. 458.60

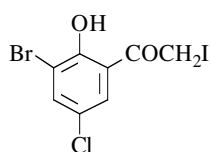
**Synthesis**

-Preparation by reaction of 1-octadecene on 2,4-dihydroxy- α,α,α -trifluoroacetophenone with phosphorous oxychloride and phosphorous pentoxide at 50° [232].

m.p. 98° [232].

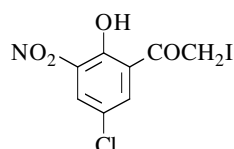
2.4. *Compounds derived from iodoacetic acids*

2.4.1. From monoiodoacetic acid

1-(3-Bromo-5-chloro-2-hydroxyphenyl)-2-iodoethanoneC₈H₅BrClIO₂ mol.wt. 375.39

Synthesis

-Obtained by reaction of iodine monochloride with 3-bromo-5-chloro-2-hydroxyacetophenone in boiling acetic acid [172].

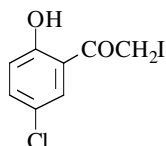
1-(5-Chloro-2-hydroxy-3-nitrophenyl)-2-iodoethanoneC₈H₅ClINO₄ mol.wt. 309.49

Synthesis

-Obtained by reaction of iodine monochloride with 5-chloro-2-hydroxy-3-nitroacetophenone in boiling acetic acid [172].

1-(5-Chloro-2-hydroxyphenyl)-2-iodoethanone

[438625-16-2]

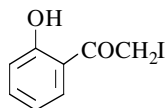
C₈H₆ClIO₂ mol.wt. 296.49

Synthesis

-Obtained by reaction of iodine monochloride with 5-chloro-2-hydroxyacetophenone in boiling acetic acid [172].

1-(2-Hydroxyphenyl)-2-iodoethanone

[99233-30-4]

C₈H₇IO₂ mol.wt. 262.05

Syntheses

-Refer to: [254] [255] [1398] [1538] [1539].

N.B.: The iodination kinetics of o-hydroxy-acetophenone have been investigated at 25° in aqueous buffer solutions.

The foregoing analysis assumes that only one mol of iodine reacts with each mol of o-hydroxyacetophenone, which may be incorrect. The title substance does not appear to have been isolated [156].

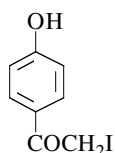
m.p. 65° [254] [1538].

1-(4-Hydroxyphenyl)-2-iodoethanone

[99233-31-5]

C₈H₇IO₂

mol.wt. 262.05

**Syntheses**

-Obtained by reaction of iodine with p-hydroxyacetophenone in the presence of 1-fluoro-4-chloromethyl-1,4-diazonia-bicyclo[2.2.2]octane bis(tetrafluoroborate)* in methanol for 19 h at r.t. (64%) [1398].

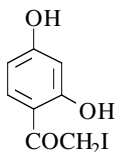
*This reagent is known under the commercial name of Selectfluor™ F-TEDA-BF₄.

-Also refer to: [254] [255] [1468] [1538].

m.p. 130° [254] [1538]; 126-128° [1398]; TLC [1398]; Crystal data [254] [1538];
¹H NMR [1398], IR [1398], MS [1398].

1-(2,4-Dihydroxyphenyl)-2-iodoethanoneC₈H₇IO₃

mol.wt. 278.05

**Synthesis**

-Preparation by reaction of sodium iodide on 2,4-dihydroxy-α-chloroacetophenone in acetone at r.t. (70%) [1380].

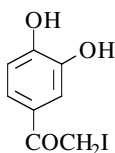
m.p. 141° [1380].

1-(3,4-Dihydroxyphenyl)-2-iodoethanone

[105174-59-2]

C₈H₇IO₃

mol.wt. 278.05

**Syntheses**

-Preparation by reaction of sodium iodide on 3,4-dihydroxy-α-chloroacetophenone in acetone at r.t. (34%) [827].

-Also refer to: [1350].

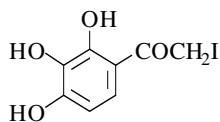
no m.p.: This compound progressively decomposed from 140° and gave a black residue at 162-163° [827]; ¹H NMR [827], IR [827], UV [827], MS [827].

2-Iodo-1-(2,3,4-trihydroxyphenyl)ethanone

[105174-62-7]

C₈H₇IO₄

mol.wt. 294.05

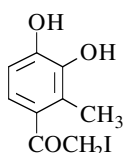
**Synthesis**

-Preparation by reaction of sodium iodide on 2,3,4-trihydroxy-α-chloroacetophenone in acetone at r.t. (63%) [827].

m.p. 144-145° [827]; ¹H NMR [827], IR [827], UV [827], MS [827].

1-(3,4-Dihydroxy-2-methylphenyl)-2-iodoethanoneC₉H₉IO₃

mol.wt. 292.07

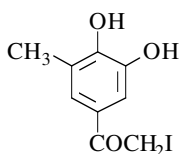
**Synthesis**

-Preparation by reaction of sodium iodide on 3,4-dihydroxy-2-methyl- α -chloroacetophenone in acetone at r.t. (62%) [624].

m.p. 171-172° [624].

1-(3,4-Dihydroxy-5-methylphenyl)-2-iodoethanoneC₉H₉IO₃

mol.wt. 292.07

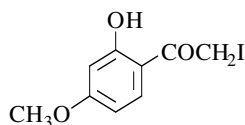
**Synthesis**

-Preparation by reaction of sodium iodide on 2,4-dihydroxy-5-methyl- α -chloroacetophenone in acetone [624].

m.p. 177° [624].

1-(2-Hydroxy-4-methoxyphenyl)-2-iodoethanoneC₉H₉IO₃

mol.wt. 292.07

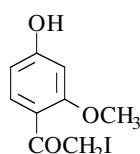
**Synthesis**

-Preparation by heating 2-hydroxy-4-methoxy- α -bromoacetophenone with concentrated aqueous potassium iodide solution [1438].

m.p. 102° [1438].

1-(4-Hydroxy-2-methoxyphenyl)-2-iodoethanoneC₉H₉IO₃

mol.wt. 292.07

**Synthesis**

-Preparation by reaction of sodium iodide on 4-hydroxy-2-methoxy- α -chloroacetophenone in acetone at r.t. [1380].

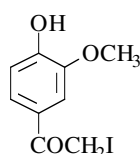
m.p. 128° [1380].

1-(4-Hydroxy-3-methoxyphenyl)-2-iodoethanone

[105174-52-5]

C₉H₉IO₃

mol.wt. 292.07

**Synthesis**

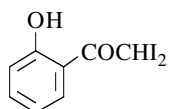
-Preparation by reaction of sodium iodide on 4-hydroxy-3-methoxy- α -bromoacetophenone in acetone at r.t. (52%) [827].

m.p. 103° [827]; ¹H NMR [827], IR [827], UV [827], MS [827].

2.4.2. From diiodoacetic acid

2,2-Diiodo-1-(2-hydroxyphenyl)ethanone $C_8H_6I_2O_2$

mol.wt. 387.94



Synthesis not yet described

N.B.: Not obtained.

-The iodination kinetics of o-hydroxyacetophenone have been investigated at 25° in aqueous buffer solutions. The foregoing analysis assumes that only one mol of iodine reacts with each mol of o-hydroxyacetophenone, which may be incorrect. Cyclisation probably predominates over the introduction of a second iodine atom into o-hydroxyacetophenone, at least in the early stages of the reaction. There is formation of 3-coumaranone [156].

2.4.3. From triiodoacetic acid

There is no hydroxyketone derived from triiodoacetic acid such as described up to December 2003.