Synthesis of salicylaldehydes bearing bulky substituents in the positions 3 and 5*

A. I. Kochnev,[a] I. I. Oleynik,[a] I. V. Oleynik,[a] S. S. Ivanchev,[b] and G. A. Tolstikov[a]*

[a]*N. N. Vorozhtsov Novosibirsk Institute of Organic Chemistry, Siberian Branch of the Russian Academy of Sciences, 9 prosp. Akad. Lavrent´eva, 630090 Novosibirsk, Russian Federation. Fax: +7 (383) 330 9524. E-mail: oleynik@nioch.nsc.ru*

[b]*St. Petersburg Division, G. K. Boreskov Institute of Catalysis, Siberian Branch of the Russian Academy of Sciences, 6 Birzhevoi proezd, 199004 St. Petersburg, Russian Federation*

Reaction of 2,4-disubstituted phenols with paraformaldehyde in the presence of $SnCl_4$ and 2,6-lutidine afforded a number of new salicylaldehydes, containing bulky substituents (*tert*-butyl, 1-phenylethyl, 1-(4-*tert*-butylphenyl)ethyl, α-cumyl, and trityl) in the positions 3 and 5.

Key words: formylation, phenols, salicylaldehydes, styrenes, alkylation, ligands.

The group IV transition metal chelate complexes with salicylaldehyde *N*-arylimines (so called "phenoxyimine" complexes) show a high activity in the polymerization of olefins.[1]

Variation of the ligand structure enables one to regulate sterical hindrance and electron density at an active center of the catalyst and thus affect activity of the catalytic system, which can lead to a change of the mechanism of polymerization.[2] A bulky substituent in the position 3 of the ligand ensures a high activity of the catalyst, since it provides higher distance between a complex cation and a co-catalyst anion and retards an electrophilic attack of a co-catalyst (the Lewis acids) on the phenoxide oxygen. At the same time, a bulky substituent at the imine nitrogen atom, making an access of a monomer to the active center limited, decreases activity of the catalyst.[3] A question about characteristic effects of substituents in the position 5 of the ligand remains open, since the corresponding complexes with various substituents were not widely studied.

In the present work, we obtained of a number of salicylaldehydes with various combinations of bulky substituents (*tert*-butyl, 1-phenylethyl, 1-(4-*tert*-butylphenyl)ethyl, α-cumyl (2-phenylprop-2-yl), and trityl) in the positions 3 and 5 to ensure their availability for the synthesis of the corresponding aryl imine ligands in the group IV transition metal complexes.

A general approach to the synthesis of such salicylaldehydes consists in the formylation of phenols, containing the corresponding substituents in the positions 2 and 4. Classic methods for the synthesis of *o*-hydroxybenzaldehydes comprise the Reimer—Tiemann[4] and the Duff[5] reactions, including a modification of the latter.[6] In the Reimer—Tiemann formylation, *o*-hydroxybenzaldehyde is chemoselectively formed, however, the yield does not exceed 30%. The yields of aldehydes are higher in the Duff formylation (~40—50%), and although the regioselectivity of the process is generally lower, it is reasonable to use this method for the 2,4-disubstituted phenols.[7] The formylation of phenols upon their treatment with paraformaldehyde in the presence of $SnCl_4$ as a catalyst[8] or upon sequential treatment with EtMgBr and paraformaldehyde in the presence of HMPA is also described.[9] The yields of benzaldehydes are close in these cases, being 40—80%; however, the latter method has obvious technological disadvantages.

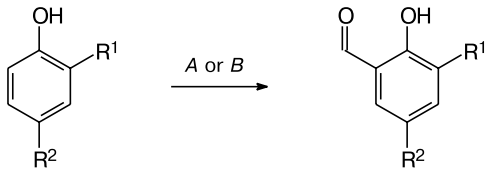
Attempted formylation of 1-(phenyl)ethyl-, 1-(4-*tert*-butylphenyl)ethyl-, and α-cumyl-substituted phenols **1a—k** with the use of $SnCl_4$ (see Ref. 8) showed an imperfection of the described procedure, consisting in a remarkable resinification of the reaction mixture and, as a result, in a complication of the isolation of the target product. We have found that the extent of decomposition can be notably decreased by changing the order of addition of reagents (2,6-lutidine, $SnCl_4$, and, finally, paraformaldehyde should be added to a phenol) and by higher diluting of the reaction mixture. After formylation of substituted phenols **1a—q** under the described conditions, the corresponding aldehydes **2a—k** were isolated in good yields (51—86%); relatively low yields of aldehydes were observed for *p*-tritylphenols **1l—o**; in case of

* Dedicated to the memory of Academician N. N. Vorozhtsov on the 100th anniversary of his birth.

Published in Russian in *Izvestiya Akademii Nauk. Seriya Khimicheskaya,* No. 6, pp. 1084—1088, June, 2007.

o-tritylphenols **1p,q**, we failed to isolate the corresponding aldehydes **2p,q** in pure form (Scheme 1).

Scheme 1



1a—q **2a—q**

A. CH_2O, $SnCl_4$, 2,6-lutidine. *B*. Hexamethylenetetramine, CF_3COOH.

2	R^1	R^2	Yield (%)
a	Bu^t	$Me_2(Ph)C$	55 (*A*)
b	Me(Ph)CH	H	57 (*A*)
c	Me(Ph)CH	Me	73 (*A*)
d	Me(Ph)CH	Bu^t	86 (*A*), 70 (*B*)
e	Me(4-$Bu^tC_6H_4$)CH	H	61 (*A*)
f	Me(4-$Bu^tC_6H_4$)CH	Me	66 (*A*)
g	Me(4-$Bu^tC_6H_4$)CH	Bu^t	73 (*A*)
h	$Me_2(Ph)C$	H	60 (*A*)
i	$Me_2(Ph)C$	Me	51 (*A*)
j	$Me_2(Ph)C$	Bu^t	60 (*A*)
k	$Me_2(Ph)C$	$Me_2(Ph)C$	66 (*A*)
l	Bu^t	Ph_3C	46 (*A*), 74 (*B*)
m	Me(Ph)CH	Ph_3C	25 (*A*), 77 (*B*)
n	Me(4-$Bu^tC_6H_4$)CH	Ph_3C	32 (*A*), 80 (*B*)
o	$Me_2(Ph)C$	Ph_3C	40 (*A*), 68 (*B*)
p	Ph_3C	Me	52 (*B*)
q	Ph_3C	Bu^t	72 (*B*)

We have found that an aldehyde group can be more easily introduced into trityl-substituted phenols **1l—q** by the Duff method with the use of trifluoroacetic acid (method *B*). Thus after formylation of *o*-tritylphenols **1p,q** by method *B*, pure aldehydes **2p,q** were successfully isolated in 52 and 72% yields, respectively. In case of *p*-tritylphenols **1l—o**, the yields of aldehydes were higher for method *B* than for method *A*. For 2-(1-phenylethyl)-4-*tert*-butylphenol (**1d**) the reverse result was observed (see Scheme 1).

The structure and composition of all the earlier unknown aldehydes **2a,b,d—g,m—p** were established on the bases of analytical and spectral data (high-resolution mass spectra, IR spectra, and ^1H NMR spectra), the structures of known aldehydes **2c,h—l,q** were confirmed by the IR and ^1H NMR spectral data. For the ^1H NMR spectra of substituted salicylaldehydes **2a—q**, a strong downfield shift of a signal for the proton of the OH group (δ 11.12—11.87) in comparison to the starting phenols (δ 4.00—4.50) is observed, which can be explained by the presence of the intramolecular hydrogen bonds in aldehydes **2a—q**. In the IR spectra of the compounds obtained, a strong absorption band, corresponding to the stretching vibrations of the C=O group, is observed in the region 1641—1649 cm^{-1}.

Phenols **1a—k**, used in the synthesis of aldehydes, were obtained by the modification of a known method[10] comprising alkylation of phenols (phenol, *p*-cresol, and *o*- or *p*-*tert*-butylphenol) with styrenes (styrene, 4-*tert*-butylstyrene, and α-methylstyrene) in the presence of aluminum phenoxide. Thus phenol **1a** was obtained from *o*-*tert*-butylphenol and α-methylstyrene in 85% yield (earlier,[11] phenol **1a** was synthesized in the presence of TsOH in 65% yield). Reactions of phenol, *p*-cresol, and *p*-*tert*-butylphenol with styrene, 4-*tert*-butylstyrene, and α-methylstyrene lead to the corresponding 2,4-disubstituted derivatives **1b—k** in 40—90% yields. *p*-Tritylphenols **1l—o** were obtained in good yields by reaction of triphenylmethanol with 2-*tert*-butyl-, 2-(1-phenylethyl)-, 2-[1-(4-*tert*-butylphenyl)ethyl]-, and 2-cumylphenols in the presence of acetic and sulfuric acids.[12]

o-Tritylphenols **1p,q** were synthesized by a known method[13] from *p*-cresol or *p*-*tert*-butylphenol and chlorotriphenylmethane upon treatment with sodium metal in 79 and 35% yields, respectively.

In the conclusion, salicylaldehydes, containing *tert*-butyl, 1-phenylethyl, 1-(4-*tert*-butylphenyl)ethyl, and α-cumyl groups in the positions 3 and 5, can be obtained in good yields by formylation of the corresponding phenols with paraformaldehyde in the presence of $SnCl_4$ and 2,6-lutidine. Trityl-substituted analogs can be synthesized in good yields by treatment of trityl-substituted phenols with hexamethylenetetramine in trifluoroacetic acid.

Experimental

^1H NMR spectra were recorded on a Bruker WP-200 SY spectrometer (200 MHz) for solutions of compounds in CCl_4 or $CDCl_3$. HMDS was used as the internal standard. IR spectra were recorded on a Vector 22 spectrometer for the neat liquid samples or in KBr pellets. The reaction progress and the purity of synthesized compounds were monitored by TLC on Silufol UV-254 plates (eluent, chloroform). Silica gel 5—40 μ was used for flash-chromatography[14] (chloroform—hexane, 1 : 1, as the eluent). Elemental analyses were performed on a Carlo Erba 1106 CHN-analyzer. Molecular formulae of compounds obtained were calculated from the high-resolution mass spectra recorded on a Finnigan MAT 8200 spectrometer. Melting points were determined between glass plates upon heating with the rate of 1 deg min^{-1}.

2-*tert*-Butyl-4-(2-phenylprop-2-yl)phenol (1a). A mixture of phenol (1.20 g, 0.0128 mol) and aluminum powder (0.05 g, 0.0018 mol) was heated at 185—190 °C until a melt of aluminum phenoxide was formed, 2-*tert*-butylphenol (62.50 g, 0.416 mol) was added to this. The reaction mixture was cooled down to 130 °C, α-methylstyrene (23.0 g, 0.195 mol) was added and this was stirred for 4 h at 130 °C. After cooling down to ~20 °C, the mixture was treated with 2 *M* aq. HCl (50 mL) and ether (100 mL) was added to this. The etheral layer was separated and the water layer was extracted with ether (3×50 mL). The com-

bined extracts were washed with water (2×50 mL) and brine (30 mL), dried with anhydrous $MgSO_4$ and the solvent was evaporated. The residue was distilled *in vacuo*, a fraction with b.p. 160—162 °C (4—5 Torr) was collected. The yield was 42.30 g (91%). ^{1}H NMR ($CDCl_3$), δ: 1.41 (s, 9 H, 2-Bu^t); 1.71 (s, 6 H, Me); 4.61 (s, 1 H, OH); 6.55 (d, 1 H, H(6), J = 8 Hz); 6.93 (dd, 1 H, H(5), J_1 = 8 Hz, J_2 = 2 Hz); 7.18—7.35 (m, 6 H, H arom.) (*cf.* Ref. 11).

2-(1-Phenylethyl)phenol (1b). A mixture of phenol (68.0 g, 0.723 mol) and aluminum powder (0.3 g, 0.0104 mol) was heated at 180—185 °C until a melt of aluminum phenoxide was formed. The reaction mixture was cooled down to 110 °C, styrene (30.0 g, 0.288 mol) was added and this was stirred for 3 h at 110 °C. Then this was cooled down to ~20 °C, acidified with 2 *M* aq. HCl (50 mL), and ether (100 mL) was added to this. The etheral layer was separated and the water layer was extracted with ether (3×50 mL). The combined extracts were washed with water (2×50 mL) and brine (30 mL) and dried with anhydrous $MgSO_4$ and the solvent was evaporated. The residue was distilled *in vacuo*, a fraction with b.p. 178—180 °C (15—16 Torr) was collected. The yield was 45.5 g (81%). ^{1}H NMR ($CDCl_3$), δ: 1.57 (d, 3 H, Me, J = 7.5 Hz); 4.30 (q, 1 H, CH, J = 7.5 Hz); 4.42 (s, 1 H, OH); 6.55 (d, 1 H, H(6), J = 8 Hz); 6.55 (t, 1 H, H(5), J = 8 Hz); 6.95—7.30 (m, 7 H, H arom.) (*cf.* Ref. 15).

4-Methyl-2-(1-phenylethyl)phenol (1c) was obtained from *p*-cresol and styrene similarly to compound **1b**. The yield was 70%, b.p. 190—195 °C (12—13 Torr). ^{1}H NMR (CCl_4), δ: 1.53 (d, 3 H, Me, J = 7.5 Hz); 2.21 (s, 3 H, 4-Me); 4.22 (q, 1 H, CH, J = 7.5 Hz); 4.44 (s, 1 H, OH); 6.38 (d, 1 H, H(6), J = 8 Hz); 6.73 (d, 1 H, H(5), J = 8 Hz); 6.73 (s, 1 H, H(3)); 6.95—7.30 (m, 5 H, H arom.) (*cf.* Refs 16 and 17).

4-*tert*-Butyl-2-(1-phenylethyl)phenol (1d) was obtained from 4-*tert*-butylphenol and styrene similarly to compound **1b**. The yield was 67%, b.p. 200—205 °C (12—13 Torr). HRMS, found: m/z 254.1671 $[M]^+$. $C_{18}H_{22}O$. Calculated: M = 254.1670. ^{1}H NMR ($CDCl_3$), δ: 1.25 (s, 9 H, 4-Bu^t); 1.56 (d, 3 H, Me, J = 7.5 Hz); 4.25 (q, 1 H, CH, J = 7.5 Hz); 4.45 (s, 1 H, OH); 6.43 (d, 1 H, H(6), J = 8 Hz); 6.95 (d, 1 H, H(5), J = 8 Hz); 6.75—7.50 (m, 6 H, H arom.).

2-[1-(4-*tert*-Butylphenyl)ethyl]phenol (1e) was obtained from phenol and 4-*tert*-butylstyrene similarly to compound **1b**. The yield was 77%, b.p. 165—168 °C (2—3 Torr). HRMS, found: m/z 254.1671 $[M]^+$. $C_{18}H_{22}O$. Calculated: M = 254.1670. ^{1}H NMR ($CDCl_3$), δ: 1.29 (s, 9 H, 4-Bu^t); 1.62 (d, 3 H, Me, J = 7.5 Hz); 4.31 (q, 1 H, CH, J = 7.5 Hz); 4.64 (s, 1 H, OH); 6.70—7.40 (m, 8 H, H arom.).

2-[1-(4-*tert*-Butylphenyl)ethyl]-4-methylphenol (1f) was obtained from *p*-cresol and 4-*tert*-butylstyrene similarly to compound **1b**. The yield was 75%, b.p. 155—160 °C (0.5 Torr). HRMS, found: m/z 268.1829 $[M]^+$. $C_{19}H_{24}O$. Calculated: M = 268.1827. ^{1}H NMR ($CDCl_3$), δ: 1.30 (s, 9 H, 4-Bu^t); 1.62 (d, 3 H, Me, J = 7.5 Hz); 2.30 (s, 3 H, 4-Me); 4.28 (q, 1 H, CH, J = 7.5 Hz); 4.50 (s, 1 H, OH); 6.60—7.50 (m, 7 H, H arom.).

4-*tert*-Butyl-2-[1-(4-*tert*-butylphenyl)ethyl]phenol (1g) was obtained from 4-*tert*-butylphenol and 4-*tert*-butylstyrene similarly to compound **1b**. The yield was 74%, b.p. 182—187 °C (0.5 Torr). HRMS, found: m/z 310.2298 $[M]^+$. $C_{22}H_{30}O$. Calculated: M = 310.2297. ^{1}H NMR ($CDCl_3$), δ: 1.29, 1.32 (both s, 9 H each, 4-Bu^t); 1.64 (d, 3 H, Me, J = 7.5 Hz); 4.30 (q, 1 H, CH, J = 7.5 Hz); 4.50 (s, 1 H, OH); 6.70 (d, 1 H, H(3), J = 8.5 Hz); 7.10—7.40 (m, 6 H, H arom.).

2-(2-Phenylprop-2-yl)phenol (1h) and **2,4-bis(2-phenylprop-2-yl)phenol (1k)** were obtained from phenol and α-methylstyrene similarly to compound **1b** and were separated by fractional distillation *in vacuo*. Compound **1h**. The yield was 35%, b.p. 170—175 °C (12—13 Torr). ^{1}H NMR (CCl_4), δ: 1.65 (s, 6 H, Me); 4.05 (s, 1 H, OH); 6.60—7.40 (m, 9 H, H arom.). Compound **1k**. The yield was 53%, b.p. 190—196 °C (0.5 Torr). ^{1}H NMR (CCl_4), δ: 1.57, 1.65 (both s, 6 H each, Me); 3.86 (s, 1 H, OH); 6.52 (d, H(6), J = 8 Hz); 6.88—7.30 (m, 12 H, H arom.) (*cf.* Ref. 10).

4-Methyl-2-(2-phenylprop-2-yl)phenol (1i) was obtained from *p*-cresol and α-methylstyrene similarly to compound **1b**. The yield was 90%, b.p. 186—187 °C (12—13 Torr). ^{1}H NMR (CCl_4), δ: 1.62 (s, 6 H, Me); 2.30 (s, 3 H, 4-Me); 3.82 (s, 1 H, OH); 6.51 (d, H(6), J = 8 Hz); 6.74 (dd, H(5), J_1 = 8 Hz, J_2 = 2 Hz); 7.10—7.27 (m, 6 H, H arom.) (*cf.* Ref. 11).

4-*tert*-Butyl-2-(2-phenylprop-2-yl)phenol (1j) was obtained from 4-*tert*-butylphenol and α-methylstyrene similarly to compound **1b**. The yield was 76%, b.p. 196—198 °C (12—13 Torr). ^{1}H NMR (CCl_4), δ: 1.32 (s, 9 H, 4-Bu^t); 1.64 (s, 6 H, Me); 3.90 (s, 1 H, OH); 6.51 (d, 1 H, H(6), J = 8 Hz); 7.05 (dd, 1 H, H(5), J_1 = 8 Hz, J_2 = 2 Hz); 7.10—7.28 (m, 5 H, H arom.); 7.35 (d, 1 H, H(3), J = 8 Hz) (*cf.* Ref. 11).

2-*tert*-Butyl-4-tritylphenol (1l). Triphenylmethanol (10 g, 0.038 mol) and 2-*tert*-butylphenol (15.9 g, 0.106 mol) were dissolved in glacial acetic acid (100 mL) under heating. After the components were dissolved, the reaction mixture was stirred at ~20 °C. When precipitate appeared, conc. H_2SO_4 (10 mL) was added, resulting in turning the color of the solution to black. After 30 min, a precipitate was formed, this was stirred for another 1.5 h. The precipitate was filtered off and washed with acetic acid (20 mL) and methanol (3×20 mL). The yield was 11.4 g (76%). ^{1}H NMR ($(CD_3)_2CO$), δ: 1.24 (s, 9 H, 2-Bu^t); 3.00 (br.s, 1 H, OH); 6.72 (d, 1 H, H(6), J = 8.5 Hz); 6.81 (dd, 1 H, H(5), J_1 = 9 Hz, J_2 = 2.5 Hz); 7.10 (d, 1 H, H(3), J = 2.5 Hz); 7.12—7.33 (m, 15 H, H arom.) (*cf.* Ref. 12).

2-(1-Phenylethyl)-4-tritylphenol (1m) was obtained from phenol **1b** similarly to compound **1l**. The yield was 55%, m.p. 162—163 °C. HRMS, found: m/z 440.2143 $[M]^+$. $C_{33}H_{28}O$. Calculated: M = 440.2140. ^{1}H NMR ($CDCl_3$), δ: 1.40 (d, 3 H, Me, J = 7.5 Hz); 4.25 (q, 1 H, CH, J = 7.5 Hz); 4.50 (s, 1 H, OH); 7.08—7.33 (m, 23 H, H arom.).

2-[1-(4-*tert*-Butylphenyl)ethyl]-4-tritylphenol (1n) was obtained from phenol **1e** similarly to compound **1l**. The yield was 72%, m.p. 101—103 °C. HRMS, found: m/z 496.2770 $[M]^+$. $C_{37}H_{36}O$. Calculated: M = 496.2766. ^{1}H NMR ($CDCl_3$), δ: 1.30 (s, 9 H, 4-Bu^t); 1.43 (d, 3 H, Me, J = 7.5 Hz); 4.35 (q, 1 H, CH, J = 7.5 Hz); 4.82 (s, 1 H, OH); 6.90—7.30 (m, 23 H, H arom.).

2-(2-Phenylprop-2-yl)-4-tritylphenol (1o) was obtained from phenol **1h** similarly to compound **1l**. The yield was 62%, m.p. 171—173 °C. HRMS, found: m/z 454.2292 $[M]^+$. $C_{34}H_{30}O$. Calculated: M = 454.2297. ^{1}H NMR ($CDCl_3$), δ: 1.45 (s, 6 H, Me); 4.20 (s, 1 H, OH); 6.55 (d, 1 H, H(6), J = 8.5 Hz); 6.91—7.33 (m, 22 H, H arom.).

4-Methyl-2-tritylphenol (1p). Sodium metal (1.1 g, 0.05 mol) was added to *p*-cresol (39.0 g, 0.36 mol) at 100 °C with vigorous stirring. Triphenylchloromethane (10.0 g, 0.036 mol) was added to a formed melt of cresolate and this was heated for 3 h at 135—145 °C with vigorous stirring. After cooling down to ~20 °C, the reaction mixture was treated with 7% aq. NaOH (100 mL)

and ether (100 mL). The etheral layer was separated and washed with 7% aq. NaOH (5×80 mL), water (100 mL), and brine (30 mL). The organic layer was separated, dried with anhydrous Na_2SO_4, the solvent was evaporated, and the residue was recrystallized from ethanol. The yield was 10.00 g (79%), m.p. 184—185 °C. ^{1}H NMR (CCl_4), δ: 2.16 (s, 3 H, 4-Me); 4.02 (s, 1 H, OH); 6.62 (d, 1 H, H(6), J = 8 Hz); 6.68 (dd, 1 H, H(5), J = 8 Hz, J = 2 Hz); 7.08—7.30 (m, 16 H, H arom.) (*cf.* Ref. 13).

4-*tert*-Butyl-2-tritylphenol (1q) was obtained from 4-*tert*-butylphenol similarly to compound **1p**. The yield was 35%. ^{1}H NMR (CCl_4), δ: 1.28 (s, 9 H, 4-Bu^t); 3.93 (s, 1 H, OH); 6.60 (d, 1 H, H(6), J = 8 Hz); 6.68 (dd, 1 H, H(5), J_1 = 8 Hz, J_2 = 2 Hz); 7.05—7.38 (m, 16 H, H arom.) (*cf.* Ref. 12).

Synthesis of salicylaldehydes (general procedure *A*). Tin(IV) chloride (0.59 mL, 0.005 mol) was added under argon to a mixture of the corresponding 2,4-disubstituted phenol **1** (0.05 mol), toluene (50 mL), and 2,6-lutidine (2.14 g, 0.02 mol). The formed yellow suspension was stirred for 1 h at ~20 °C, then paraformaldehyde (3.3 g, 0.110 mol) was added, and this was heated for 8—16 h at 115—125 °C. The reaction mixture was cooled down to ~20 °C, ether (40 mL) was added, and this was acidified with 2 *M* aq. HCl until pH value of 2 was reached. The organic layer was separated and the water layer was extracted with ether (3×20 mL). The combined extracts were washed with water (50 mL) and brine (30 mL), separated, and dried with anhydrous Na_2SO_4. The solvents were evaporated and the residue was subjected to flash-chromatography. Finally the aldehydes were purified by recrystallization from methanol.

General procedure *B*. A mixture of the corresponding trityl-substituted phenol **1l—q** (0.01 mol), hexamethylenetetramine (2.80 g, 0.02 mol), and CF_3COOH (10 mL) was heated for 4 h at 115—125 °C, cooled down to 75—80 °C, 33% aq. H_2SO_4 (15 mL) was added to this, and the resulting mixture was heated for 1—2 h at 125—130 °C. After cooling down to ~20 °C, ethyl acetate (20 mL) and water (30 mL) were added. The organic layer was separated and the water layer was extracted with ethyl acetate (3×10 mL). The combined extracts were washed with water (50 mL) and brine (30 mL), separated, and dried with anhydrous Na_2SO_4. The solvent was evaporated and the residue was subjected to flash-chromatography. Finally the aldehydes were purified by recrystallization from methanol.

3-*tert*-Butyl-2-hydroxy-5-(2-phenylprop-2-yl)benzaldehyde (2a). M.p. 82—84 °C. HRMS, found: m/z 296.1772 $[M]^+$. $C_{20}H_{24}O_2$. Calculated: M = 296.1776. IR, ν/cm^{-1}: 1641 (C=O). ^{1}H NMR (CCl_4), δ: 1.32 (s, 9 H, 3-Bu^t); 1.65 (s, 6 H, Me); 7.05—7.28 (m, 7 H, H arom.); 9.76 (s, 1 H, CHO); 11.69 (s, 1 H, OH).

2-Hydroxy-3-(1-phenylethyl)benzaldehyde (2b). M.p. 78—79 °C. HRMS, found: m/z 226.0994 $[M]^+$. $C_{15}H_{14}O_2$. Calculated: M = 226.0993. IR, ν/cm^{-1}: 1645 (C=O). ^{1}H NMR ($CDCl_3$), δ: 1.53 (d, 3 H, Me, J = 7.5 Hz); 4.55 (q, 1 H, CH, J = 7.5 Hz); 6.80—7.40 (m, 8 H, H arom.); 9.78 (s, 1 H, CHO); 11.30 (s, 1 H, OH).

2-Hydroxy-5-methyl-3-(1-phenylethyl)benzaldehyde (2c). M.p. 52—53 °C. IR, ν/cm^{-1}: 1643 (C=O). ^{1}H NMR ($CDCl_3$), δ: 1.60 (d, 3 H, Me, J = 7.5 Hz); 2.29 (s, 3 H, 5-Me); 4.55 (q, 1 H, CH, J = 7.5 Hz); 7.00—7.40 (m, 7 H, H arom.); 9.81 (s, 1 H, CHO); 11.20 (s, 1 H, OH) (*cf.* Ref. 16).

5-*tert*-Butyl-2-hydroxy-3-(1-phenylethyl)benzaldehyde (2d). Oil. HRMS, found: m/z 282.1625 $[M]^+$. $C_{19}H_{22}O_2$. Calculated: M = 282.1620. IR, ν/cm^{-1}: 1642 (C=O). ^{1}H NMR ($CDCl_3$), δ: 1.28 (s, 9 H, 5-Bu^t); 1.62 (d, 3 H, Me, J = 7.5 Hz); 4.60 (q, 1 H, CH, J = 7.5 Hz); 7.10—7.55 (m, 7 H, H arom.); 9.85 (s, 1 H, CHO); 11.25 (s, 1 H, OH).

3-[1-(4-*tert*-Butylphenyl)ethyl]-2-hydroxybenzaldehyde (2e). M.p. 80—81 °C. HRMS, found: m/z 282.1643 $[M]^+$. $C_{19}H_{22}O_2$. Calculated: M = 282.1620. IR, ν/cm^{-1}: 1641 (C=O). ^{1}H NMR ($CDCl_3$), δ: 1.32 (s, 9 H, 4-Bu^t); 1.65 (d, 3 H, Me, J = 7.5 Hz); 4.54 (q, 1 H, CH, J = 7.5 Hz); 6.95 (t, 1 H, H(5), J = 8 Hz); 7.10—7.35 (m, 4 H, H arom.); 7.40 (d, 2 H, H arom., J = 8 Hz); 9.81 (s, 1 H, CHO); 11.45 (s, 1 H, OH).

3-[1-(4-*tert*-Butylphenyl)ethyl]-2-hydroxy-5-methylbenzaldehyde (2f). M.p. 74—76 °C. HRMS, found: m/z 296.1773 $[M]^+$. $C_{20}H_{24}O_2$. Calculated: M = 296.1776. IR, ν/cm^{-1}: 1646 (C=O). ^{1}H NMR ($CDCl_3$), δ: 1.30 (s, 9 H, 4-Bu^t); 1.62 (d, 3 H, Me, J = 7.5 Hz); 2.28 (s, 3 H, 5-Me); 4.50 (q, 1 H, CH, J = 7.5 Hz); 7.00—7.35 (m, 6 H, H arom.); 9.75 (s, 1 H, CHO); 11.51 (s, 1 H, OH).

5-*tert*-Butyl-3-[1-(4-*tert*-butylphenyl)ethyl]-2-hydroxybenzaldehyde (2g). Oil. HRMS, found: m/z 338.2251 $[M]^+$. $C_{23}H_{30}O_2$. Calculated: M = 338.2246. IR, ν/cm^{-1}: 1644 (C=O). ^{1}H NMR ($CDCl_3$), δ: 1.28 (s, 9 H, 4-Bu^t); 1.32 (s, 9 H, 5-Bu^t); 1.62 (d, 3 H, Me, J = 7.5 Hz); 4.50 (q, 1 H, CH, J = 7.5 Hz); 7.00—7.30 (m, 6 H, H arom.); 9.82 (s, 1 H, CHO); 11.54 (s, 1 H, OH).

2-Hydroxy-3-(2-phenylprop-2-yl)benzaldehyde (2h). M.p. 85—86 °C. IR, ν/cm^{-1}: 1648 (C=O). ^{1}H NMR ($CDCl_3$), δ: 1.72 (s, 6 H, Me); 7.00—7.70 (m, 8 H, H arom.); 9.81 (s, 1 H, CHO); 11.34 (s, 1 H, OH) (*cf.* Ref. 18).

2-Hydroxy-5-methyl-3-(2-phenylprop-2-yl)benzaldehyde (2i). M.p. 69—71 °C. IR, ν/cm^{-1}: 1646 (C=O). ^{1}H NMR (CCl_4), δ: 1.69 (s, 6 H, Me); 2.35 (s, 3 H, 5-Me); 7.00—7.18 (m, 6 H, H arom.); 7.35 (s, 1 H, H(6)); 9.73 (s, 1 H, CHO); 11.12 (s, 1 H, OH) (*cf.* Ref. 19).

5-*tert*-Butyl-2-hydroxy-3-(2-phenylprop-2-yl)benzaldehyde (2j). M.p. 76—78 °C. IR, ν/cm^{-1}: 1649 (C=O). ^{1}H NMR (CCl_4), δ: 1.32 (s, 9 H, 5-Bu^t); 1.71 (s, 6 H, Me); 7.02—7.32 (m, 7 H, H arom.); 9.77 (s, 1 H, CHO); 11.19 (s, 1 H, OH) (*cf.* Ref. 19).

3,5-Bis(2-phenylprop-2-yl)-2-hydroxybenzaldehyde (2k). M.p. 79—80 °C. IR, ν/cm^{-1}: 1643 (C=O). ^{1}H NMR (CCl_4), δ: 1.62, 1.67 (both s, 6 H each, Me); 6.98—7.26 (m, 11 H, H arom.); 7.33 (s, 1 H, H(6)); 9.71 (s, 1 H, CHO); 11.23 (s, 1 H, OH) (*cf.* Ref. 20).

3-*tert*-Butyl-2-hydroxy-5-tritylbenzaldehyde (2l). M.p. 190—192 °C. IR, ν/cm^{-1}: 1647 (C=O). ^{1}H NMR (CCl_4), δ: 1.28 (s, 9 H, 3-Bu^t); 7.00—7.42 (m, 17 H, H arom.); 9.66 (s, 1 H, CHO); 11.81 (s, 1 H, OH) (*cf.* Ref. 19).

2-Hydroxy-3-(1-phenylethyl)-5-tritylbenzaldehyde (2m). M.p. 197—199 °C. HRMS, found: m/z 468.2087 $[M]^+$. $C_{34}H_{28}O_2$. Calculated: M = 468.2089. IR, ν/cm^{-1}: 1644 (C=O). ^{1}H NMR ($CDCl_3$), δ: 1.57 (d, 3 H, Me, J = 7.5 Hz); 4.65 (q, 1 H, CH, J = 7.5 Hz); 6.90—7.50 (m, 22 H, H arom.); 9.75 (s, 1 H, CHO); 11.10 (s, 1 H, OH).

3-[1-(4-*tert*-Butylphenyl)ethyl]-2-hydroxy-5-tritylbenzaldehyde (2n). M.p. 225—226 °C. HRMS, found: m/z 524.2713 $[M]^+$. $C_{38}H_{36}O_2$. Calculated: M = 524.2715. IR, ν/cm^{-1}: 1646 (C=O). ^{1}H NMR ($CDCl_3$), δ: 1.28 (s, 9 H, 4-Bu^t); 1.57 (d, 3 H, Me, J = 7.5 Hz); 4.65 (q, 1 H, CH, J = 7.5 Hz); 6.85—7.50 (m, 21 H, H arom.); 9.85 (s, 1 H, CHO); 11.21 (s, 1 H, OH).

2-Hydroxy-3-(2-phenylprop-2-yl)-5-tritylbenzaldehyde (2o). M.p. 174—176 °C. HRMS, found: m/z 482.2253 $[M]^+$. $C_{35}H_{30}O_2$. Calculated: M = 482.2246. IR, ν/cm^{-1}: 1647 (C=O).

^{1}H NMR (CCl_4), δ: 1.52 (s, 6 H, Me); 6.90—7.40 (m, 22 H, H arom.); 9.61 (s, 1 H, CHO); 11.37 (s, 1 H, OH).

2-Hydroxy-5-methyl-3-tritylbenzaldehyde (2p). M.p. 152—153 °C. HRMS, found: *m/z* 378.1625 $[M]^+$. $C_{27}H_{22}O_2$. Calculated: M = 378.1625. IR, ν/cm^{-1}: 1644 (C=O). ^{1}H NMR ($CDCl_3$), δ: 2.25 (s, 3 H, 5-Me); 7.10—7.35 (m, 17 H, H arom.); 9.77 (s, 1 H, CHO); 11.06 (s, 1 H, OH).

5-*tert*-Butyl-2-hydroxy-3-tritylbenzaldehyde (2q). M.p. 164—166 °C. IR, ν/cm^{-1}: 1647 (C=O). ^{1}H NMR ($CDCl_3$), δ: 1.18 (s, 9 H, 5-Bu^t); 6.95—7.60 (m, 17 H, H arom.); 9.78 (s, 1 H, CHO); 11.08 (s, 1 H, OH) (*cf.* Ref. 21).

This work was financially supported by the Siberian Branch of the Russian Academy of Sciences (Integrational Project No. 4.6).

References

1. S. Matsui, Y. Tohi, M. Mitani, J. Saito, H. Makio, H. Tanaka, M. Nitabaru, T. Nakano, and T. Fujita, *Chem. Lett.*, 1999, **28**, 1065.
2. J. Saito, M. Mitani, J. Mohri, Y. Yoshida, S. Matsui, S. Ishii, S. Kojoh, N. Kashiwa, and T. Fujita, *Angew. Chem., Int. Ed.*, 2001, **40**, 2918; M. Mitani, J. Mohri, Y. Yoshida, J. Saito, S. Ishii, K. Tsuru, S. Matsui, R. Furuyama, T. Nakano, H. Tanaka, S. Kojoh, T. Matsugi, N. Kashiwa, and T. Fujita, *J. Am. Chem. Soc.*, 2002, **124**, 3327; H. Makio, N. Kashiwa, and T. Fujita, *Adv. Synth. Catal.*, 2002, 344; M. Mitani, J. Saito, S. Ishii, Y. Nakayama, H. Makio, N. Matsukawa, S. Matsui, J. Mohri, R. Furuyama, H. Terao, H. Bando, H. Tanaka, and T. Fujita, *Chem. Rec.*, 2004, **4**, 137.
3. S. Matsui, M. Mitani, J. Saito, Y. Tohi, H. Makio, H. Tanaka, and T. Fujita, *Chem. Lett.*, 1999, **28**, 1263; S. Matsui, M. Mitani, J. Saito, N. Matsukawa, H. Tanaka, T. Nakano, and T. Fujita, *Chem. Lett.*, 2000, **29**, 554; S. Reinartz, A. F. Mason, E. B. Lobkovsky, and G. W. Coates, *Organometallics*, 2003, **22**, 2542; A. Pärssinen, T. Luhtanen, M. Klinga, T. Pakkanen, M. Leskelä, and T. Repo, *Eur. J. Inorg. Chem.*, 2005, 2100.
4. H. Wynberg, *Chem. Rev.*, 1960, **60**, 169; H. Wynberg and E. W. Meijer, *Org. React.*, 1982, **28**, 1.
5. L. N. Ferguson, *Chem. Rev.*, 1946, **38**, 230.
6. J. F. Larrow, E. N. Jacobsen, Y. Gao, Y. Hong, X. Nie, and C. M. Zepp, *J. Org. Chem.*, 1994, **59**, 1939.
7. J. F. Larrow and E. N. Jacobsen, *Org. Synth.*, 1998, **75**, 1.
8. G. Casiraghi, G. Casnati, G. Puglia, G. Sartori, and G. Terenghi, *J. Chem. Soc., Perkin Trans. 1*, 1980, 1862.
9. G. Casiraghi, G. Casnati, M. Cornia, A. Pochini, G. Puglia, G. Sartori, and R. Ungaro, *J. Chem. Soc., Perkin Trans. 1*, 1978, 318.
10. T. G. Veretyakhina, M. V. Kurashev, G. M. Mamedaliev, N. V. Kolesnichenko, and A. Yu. Koshevnik, *Zh. Org. Khim.*, 1974, **10**, 359 [*J. Org. Chem. USSR*, 1974, **10** (Engl. Transl.)].
11. J. Rosevear and J. F. K. Wilshire, *Aust. J. Chem.*, 1985, **38**, 1163.
12. A. T. Shulgin, *J. Org. Chem.*, 1962, **27**, 3868.
13. P. Schorigin, *Ber. Deutsch. Chem. Ges.*, 1927, **60**, 2378.
14. W. C. Still, M. Kahn, and A. Mitra, *J. Org. Chem.*, 1978, **43**, 2923.
15. US Pat. 3075832; *Chem. Abstrs*, 1963, **59**, 12706h.
16. A. Berkessel, M. R. Vennemann, and J. Lex, *Eur. J. Org. Chem.*, 2002, 2800.
17. Ya. B. Kozlikovsky, B. V. Chernyaev, A. L. Litvin, and A. V. Kofanova, *Zh. Org. Khim.*, 1986, **22**, 1469 [*J. Org. Chem. USSR*, 1986, **22** (Engl. Transl.)].
18. T. Yamada, K. Imagawa, T. Nagata, and T. Mukaiyama, *Bull. Chem. Soc. Jpn*, 1994, **67**, 2248.
19. P. Pietikainen, *Tetrahedron*, 2000, **56**, 417.
20. S. Matsui, M. Mitani, J. Saito, Y. Tohi, H. Makio, N. Matsukawa, Y. Takagi, K. Tsuru, M. Nitabaru, T. Nakano, H. Tanaka, N. Kashiwa, and T. Fujita, *J. Am. Chem. Soc.*, 2001, **123**, 6847.
21. S.-H. Zhao, P. R. Ortiz, B. A. Keys, and K. G. Davenport, *Tetrahedron Lett.*, 1996, **37**, 2725.

Received March 14, 2007;
in revised form May 25, 2007