An Acid Catalyzed Rearrangement of *O*-Aryl-*N*-benzoylhydroxylamines; Synthesis of Catechols from Phenols

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In this communication, we report a new method for preparation of *O*-arylhydroxylamines **1** as well as their use for the conversion of phenols to catechols.

O-Arylhydroxylamines **1** can be prepared in low yields by the reaction of phenoxide ions with hydroxylamine-*O*-sulfonic acid[1] or by hydrogen chloride cleavage of the rather inaccessible aryl benzhydroxamates[2]. Recently, Cadogan and Rowley reported a new route via hydrazinolysis of *N*-phenoxyphthalimide[3]. This compound has already shown promise for the synthesis of benzofuran derivatives[4] and hydroxybiphenyls[5].

The present paper describes a new method for synthesis of *O*-arylhydroxylamines which employs mesitylenesulfonylhydroxylamine as the aminating reagent. Secondly, it describes a method for introduction of a hydroxy group *ortho* to a phenolic hydroxy group by rearrangement of an *N*-acylated *O*-arylhydroxylamine.

Sodium or potassium phenoxides in dimethylformamide, on treatment with 0.75 equivalent mesitylenesulfonylhydroxylamine at 0 °C for 30 min, afford *O*-arylhydroxylamines **1** in yields generally 54–74% (or 77–91% based on

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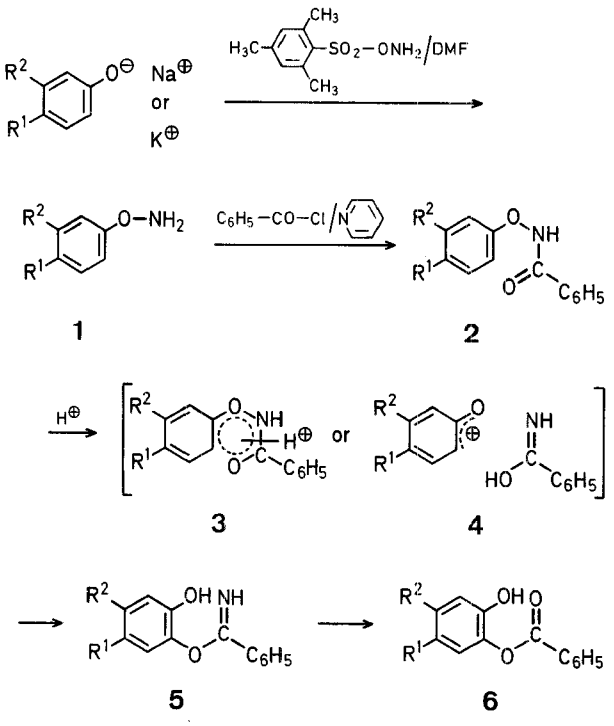
Table 1. *O*-Amination of Phenols

O-Arylhydroxylamine No.	R^1	R^2	Conversion [%]	Yield [%][a]	b.p. [°C]/torr	Molecular formula[b] or Lit. b.p. [°C]/torr	I.R. (neat) ν [cm^{-1}]
1a	H	H	70	54 (77)	67°/6	72°/7[1]	3330, 3260, 1600, 1486, 1253, 1172, 1138, 1076, 1025, 910
1b	CH_3	H	59	48 (81)	80°/8	C_7H_9NO (123.2)	3330, 3260, 1613, 1507, 1251, 1176, 1137, 910, 820
1c	H	CH_3	77	63 (82)	65°/5	C_7H_9NO (123.2)	3330, 3260, 1611, 1596, 1488, 1268, 1192, 1120, 937
1d	—$(CH_2)_4$		66	59 (89)	—[c]	$C_{10}H_{13}NO$ (163.2)	3330, 3260, 2930, 1613, 1597, 1442, 1253, 1180, 1136, 1096, 994, 930, 910, 866, 830
1e	Cl	H	80	73 (91)	66°/2	C_6H_6ClNO (143.6)	3330, 3260, 1600, 1488, 1289, 1251, 1172, 1136, 1092, 1008, 912, 829
1f	H	Cl	83	74 (89)	69°/2	C_6H_6ClNO (143.6)	3330, 3260, 1599, 1477, 1434, 1250, 1164, 1143, 1090, 1068, 998, 917, 863

[a] Yield based on phenol employed, value in brackets is yield based on phenol reacted.
[b] The molecular ion peaks in the M.S. of all compounds were in good agreement with calculated values.
[c] Distillation was accompanied by decomposition.

reacted phenol). *N*-Benzoylation of *O*-arylhydroxylamines **1** with benzoyl chloride in pyridine gave *N*-benzoyl-*O*-arylhydroxylamines **2** in good yields.

Treatment of *N*-benzoates **2** with trifluoroacetic acid and catalytic amount of trifluoromethanesulfonic acid in dichloromethane (or in trifluoroacetic acid as solvent), caused smooth rearrangement to catechol monobenzoates **6**. The yield of product was 48–78%.



The catechol monobenzoate isolated from *O*-4-tolyl-*N*-benzoylhydroxylamine **(2b)** was the more stable 2-hydroxy-4-methylphenyl benzoate **(6c)**, as shown by its identity with an authentic sample of the methylcatechol benzoate synthesized unambiguously[6,7]. Similarly, *O*-4-chlorophenyl- **(2e)** and *O*-3-chlorophenyl-*N*-benzoylhydroxylamine **(2f)** gave the same product **6f**. The structure of **6f** was confirmed by comparison of its methyl ether with authentic 2-methoxy-4-chlorophenyl benzoate prepared independently from 2-methoxy-4-chlorophenol[8]. *O*-(5,6,7,8-Tetrahydronaphthyl)-*N*-benzoylhydroxylamine **(2d)** gave only one isomer **6d**. All the hydroxyphenyl esters isolated, represent rearrangement to the *ortho* position and one of the hydroxy groups of the resulting catechols is protected. Thus, it is possible to differentiate the two hydroxy groups.

The mechanism of rearrangement may be interpreted similar to the rearrangement of *N*,*N*-dimethylaniline *N*-oxide[9]

Table 2. *O*-Aryl-*N*-benzoylhydroxylamines **2a–f**

Product	Yield [%]	m.p. [°C] (solvent)	Molecular formula[a] or Lit. m.p. [°C]
2a	82	137–138° (ethanol)	137.5–139°[2]
2b	78	137–138° (benzene)	$C_{14}H_{13}NO_2$ (227.3)
2c	81	107–109° (benzene)	$C_{14}H_{13}NO_2$ (227.3)
2d	79	148.5–150° (CH_2Cl_2/hexane)	$C_{17}H_{17}NO_2$ (267.3)
2e	92	117–118° (CH_2Cl_2/hexane)	$C_{13}H_{10}ClNO_2$ (247.7)
2f	86	102–103° (CH_2Cl_2/hexane)	$C_{13}H_{10}ClNO_2$ (247.7)

[a] The microanalyses for all products were in satisfactory agreement with the calculated values (C ±0.27, H ±0.11, N ±0.22).

Table 3. 2-Hydroxyaryl Benzoates **6**

Product	Yield [%]	m.p. [°C] (C_6H_6/C_6H_{14})	Molecular formula[a] or Lit. m.p. [°C]
6a	78	135–136°	134°[7]
6c	70 (77)[b]	161–162°	163–164°[6]
6d	49	143–145°	$C_{17}H_{16}O$ (268.3)
6f	70 (52)[c]	148–149°	$C_{13}H_{10}ClO$ (248.7)

[a] The microanalyses of all products were in satisfactory agreement with the calculated values (C ±0.30, H ±0.10).
[b] Yield from **2b**.
[c] Yield from **2e**.

or *N*-acyl-*N*-arylhydroxylamine with acetic anhydride[10], that is via a transition state similar to that of the Claisen rearrangement **(3)** or via an ion pair **(4)**. The iminoester **5** is apparently hydrolyzed to the benzoate ester during the work-up procedure. The general procedure is described below and results are summarized in the Tables.

***O*-Arylhydroxylamines 1a–f; General Procedure:**
To a solution of the phenol (3 mmol) in methanol (6 ml) is added powdered potassium *t*-butoxide (364 mg, 3 mmol, purity 95%). The methanol is removed by evaporation, and the residue is dissolved in dimethylformamide (4 ml). To the solution is added all at once a solution of freshly prepared mesitylenesulfonylhydroxylamine (2.25 mmol) in dimethylformamide (2 ml) at 0 °C. The solution is stirred for an additional 0.5 h at 0 °C, the reaction mixture is then diluted with water (100 ml), and extracted with dichloromethane (3 × 50 ml). The extract is dried and evaporated, and a brownish oily substance remained. Purification of the product by silica gel chromatography using dichloromethane as eluent gives the *O*-arylhydroxylamine **1** as a pale yellow viscous liquid, in 54–74% yields, as well as 20–41% of unreacted phenol. The product is sufficiently pure for the subsequent reaction, further purification is possible by distillation under reduced pressure.

***O*-Aryl-*N*-benzoylhydroxylamines 2a–f; General Procedure:**
N-Benzoylation of **1a–f** (1 mmol) with benzoyl chloride (1.25 mmol) in pyridine (2 ml) at room temperature gives **2a–f** in good yields.

2-Hydroxyaryl Benzoates (Catechol Monobenzoates 6a, c, d, f); General Procedure:
The *O*-aryl-*N*-benzoylhydroxylamine **2** (1 mmol) is dissolved in trifluoroacetic acid (3.8 ml, 50 mmol) and trifluoromethanesulfonic acid (0.05 ml, 0.5 mmol) is added at 0 °C. After standing for 1 h at room temperature, the mixture is diluted with water (50 ml) and extracted with dichloromethane (3 × 30 ml). The organic layer is dried and evaporated; the residue is the 2-hydroxyaryl benzoate (**6**; catechol monobenzoate). The crude product is purified by column chromatography on silica gel using dichloromethane/ethyl acetate (20:1) as eluent.

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