# A Facile Synthesis of 2-Phenylimino-3(2*H*)-benzofuranones from the Silyl Enol Ether of 2-Hydroxyacetophenones and Nitrosobenzene

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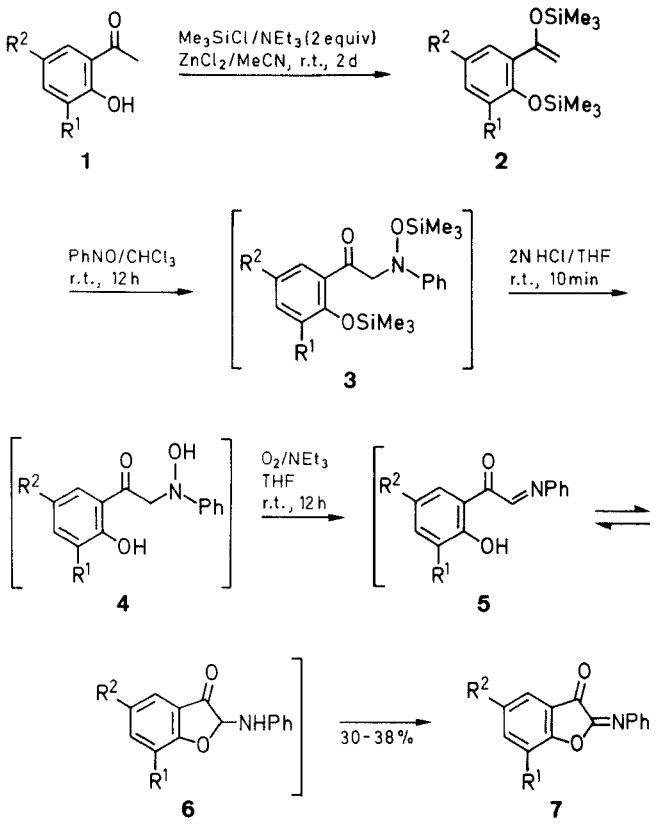
The addition of nitrosobenzene to the silyl enol ether of 2-hydroxyacetophenones followed by desilylation, elimination, cyclization and oxidation afforded 2-phenylimino-3(2*H*)-benzofuranones without isolation of the intermediates.

Aryl silyl enol ethers react readily with nitrosobenzene to give hydroxyaminomethyl aryl ketones.[1] This interesting bifunctional adduct is a promising intermediate for heterocyclic synthesis: elimination followed by cycloaddition with dienes leads to tetrahydropyridine derivatives[2] and cyclocondensation with oxalyl chloride forms a new ring system, 4,5-isoxazolidinedione.[3] Furthermore, 1,2-oxazetidine, resulting from an oxygen anion of the adduct, is a proposed intermediate in a novel fragmentation reaction.[4] We now report the oxidative intramolecular cyclization of (*N*-phenyl)hydroxyaminomethyl aryl ketones **4** to give 2-phenylimino-3(2*H*)-benzofuranones **7**.

The starting materials, 2-siloxyphenyl silyl enol ethers **2**, are prepared by the literature procedure by treatment of **1** with triethylamine/chlorotrimethylsilane/zinc chloride in acetonitrile.[6] Addition of **2** with nitrosobenzene occurs smoothly as a siloxy group is electronically advantageous in the *ortho*-position on the benzene ring.[2] In a typical case the adduct **3a** ($R^1$,$R^2$ = H) is obtained in 85% yield, showing a carbonyl absorption in the IR spectrum 1690 $cm^{-1}$ and in the $^1$H-NMR-spectrum a methylene signal at $\delta = 4.54$. Desilylation of **3a** with 2N hydrochloric acid gives free (*N*-phenyl)hydroxyaminomethyl 2-hydroxyphenyl ketone **(4a)**, which shows in the IR spectrum carbonyl and hydroxyl absorptions at 1660 and 3400 $cm^{-1}$, respectively, and in the $^1$H-NMR spectrum a methylene signal at $\delta = 4.85$. This compound is further treated with base (triethylamine) to give the elimination product **5a** which subsequently undergoes intramolecular cyclization to **6a**. In the presence of oxygen, the cyclization product **6a**, which is in equilibrium with **5a**, is oxidized to 2-phenylimino-3(2*H*)-benzofuranone **(7a)**. The structure is supported by mass spectral data with $m/z$ = 223 (16% to the base peak at $m/z$ = 120). In practice the above three step experiment




| 1–7 | $R^1$ | $R^2$ |
|---|---|---|
| **a** | H | H |
| **b** | H | Me |
| **c** | H | 1-adamantyl |
| **d** | Me | Me |
| **e** | H | Cl |

can be carried out in one pot without vigorous purification of the intermediates. The derivatives **7a–e** are obtained in a moderate overall yield. The elemental and spectral data are in consistant with the structures of **7** (Table). In summary, heterocyclic synthesis utilizing aryl silyl enol ether–nitrosobenzene adducts is extended to

**Table.** 2-Phenylimino-3(2*H*)-benzofuranones **7** Prepared

| Product | Yield (%) | mp (°C) | Molecular Formula[a] or Lit. mp (°C) | IR (KBr) $\nu$ ($cm^{-1}$) | $^1$H-NMR (200 MHz, $CDCl_3$/TMS) $\delta$ |
|---|---|---|---|---|---|
| **7a** | 30 | 99–100 | 102.5[5] | 1730, 1690, 1615, 1090 | 7.2–7.9 (m, 9H) |
| **7b** | 35 | 136–137 | $C_{15}H_{11}NO_2$ (237.3) | 1740, 1720, 1690, 1615, 1090 | 2.41 (s, 3H), 7.1–7.7 (m, 8H) |
| **7c** | 30 | 212–214 | $C_{24}H_{23}NO_2$ (357.4) | 2920, 1720, 1680, 1610, 1095 | 1.7–2.2 (m, 15H), 7.2–7.8 (m, 8H) |
| **7d** | 38 | 155–156 | $C_{16}H_{13}NO_2$ (251.3) | 1720, 1680, 1615, 1000 | 2.35 and 2.37 (s, each 3H), 7.3–7.7 (m, 7H) |
| **7e** | 36 | 154–155 | $C_{14}H_8NO_2Cl$ (257.7) | 1730, 1680, 1610, 1000 | 7.3–7.8 (m, 8H) |

[a] Satisfactory microanalyses obtained: C ±0.24, H ±0.10, N ±0.29.

the essentially one-pot conversion to 2-phenylimino-3(2*H*)-benzofuranones via an oxidative intramolecular cyclization.[5]

The silyl enol ethers **2** are prepared from **1** according to the literature procedure[6] followed by distillation *in vacuo*.

**2-Phenylimino-3(2*H*)-benzofuranones 7; General Procedure:**
A solution of **2** (1 mmol) and nitrosobenzene (1 mmol) in dry $CHCl_3$ (3 mL) is stirred at r.t. (12 h) during which the blue color fades to light yellow. After evaporation of the solvent, the residue is dissolved in THF (8 mL) and treated with 2N HCl (1 mL) for 10 min. Then, the solution is saturated with $O_2$ by bubbling, $NEt_3$ (404 mg, 4 mmol) is added, and stirring is continued at r.t. (12 h), under an atmosphere of $O_2$. The reaction mixture is diluted with $Et_2O$, washed with $H_2O$, and dried ($Na_2SO_4$). Evaporation of the solvent leaves an oil, which is chromatographed on a silica gel column (Fuji-Davison BW-300) using hexane/EtOAc (20:1) as eluent to give a yellow-colored product **7**. Analytical samples are obtained by recrystallization from $Et_2O$/hexane.

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(1) Sasaki, T.; Ishibashi, Y.; Ohno, M. *J. Chem. Res. (M)* **1984**, 1972.
(2) Sasaki, T.; Ishibashi, Y.; Ohno, M. *Chem. Lett.* **1983**, 863.
(3) Ohno, M.; Ido, M.; Eguchi, S. *Synthesis* **1986**, 666.
(4) Ohno, M.; Ido, M.; Eguchi, S. *J. Chem. Soc., Chem. Commun.* **1988**, 1530.
(5) This type of compound is obtained only from condensation reaction of 3(2*H*)-benzofuranones and nitrosobenzene: Tomchin, A.B.; Ioffe, I.S.; Rusakov, E.A. *Zh. Org. Khim.* **1972**, *8*, 1533; *C.A.* **1972**, *77*, 139993.
(6) Brownbridge, P.; Chan, T.H. *Tetrahedron Lett.* **1980**, *21*, 3423.