Synthesis of α-Aroyl-*N*-phenylnitrones by Silver Oxide Oxidation of the Adducts of Silyl Enol Ethers to Nitrosobenzene

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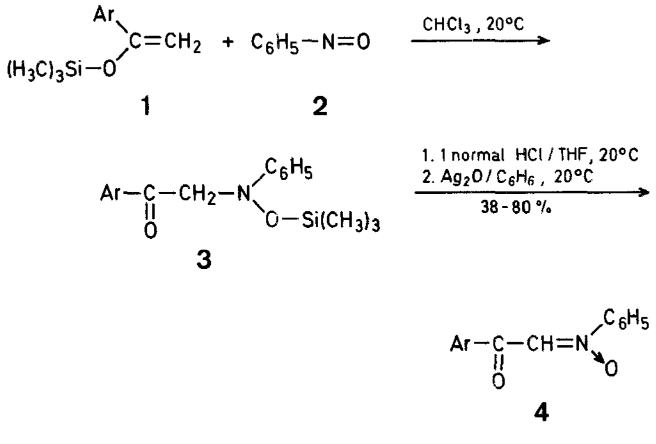
While the reaction of silyl enol ethers with a variety of carbon-electrophiles is well established[1], only a few examples have been reported for the reaction with nitrogen-electrophiles[2]. Recently, we have shown that aryl silyl enol ethers (**1**) react smoothly with nitrosobenzene (**2**) to give the open-chain adducts **3**[3]. The adducts **3** are synthetically useful; e.g. β-elimination yields phenylglyoxal anils, which by further reaction with 2,3-dimethyl-1,3-butadiene give cycloadducts in a one-pot procedure[4]. As an extension of the work utilizing **3**, we describe in this communication the synthesis of aroylnitrones (**4**) by oxidation of the adducts **3** with silver oxide.



The adducts **3** are obtained by the treatment of **1** with **2** at room temperature[3]. After purification by chromatography or recrystallization compounds **3** are desilylated with hydrochloric acid and then oxidized with silver oxide. The reactions are completed within 30 min to give the nitrones **4** in good yields. Although the reaction of silyl dienol ethers may result in the formation of [4 + 2]cycloadducts[3], compound **1i** derived from mesityl oxide affords **3i**, which by subsequent oxidation yields the nitrone **4i**. The structure of compounds **4** has been confirmed by independent synthesis of **4a**[5] and by microanalytical and spectral data; in the ^{1}H-N.M.R. spectra characteristic signals due to the —CH=N proton appear at $\delta = \sim 8$ ppm.

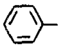
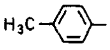
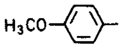
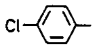
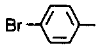
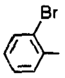
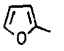
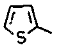
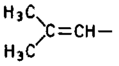
The synthesis of **4** starting with silyl enol ethers provides an alternative to the Kröhnke reaction using halo ketones[5]; in our method, an electron-donating substituent on the aromatic ring is favorable due to resonance-stabilization of the intermediate formed in the reaction of **1** with **2**. In contrast, the Kröhnke reaction is more favored with educts bearing an electron-withdrawing substituent at the aryl group. As a main advantage, our synthesis avoids the use of irritant haloketones as starting materials.

α-Aroyl-*N*-phenylnitrone (4); General Procedure:

The silylated α-hydroxyamino-ketones **3** are obtained by stirring a solution of the corresponding silyl enol ether **1** with an equimolar amount of nitrosobenzene (**2**) in chloroform at room temperature for 5–6 h[3]. Purification is achieved by passing through a short column of silica gel (Florisil) with benzene as eluent except for products **3a, c, g** which are recrystallized from hexane.

A solution of **3** (1 mmol) in tetrahydrofuran (4 ml) is stirred with 1 normal hydrochloric acid (1 ml) at room temperature for 2 min for desilylation. The free hydroxylamine is extracted with benzene (30 ml) and washed with saturated aqueous sodium hydrogen carbonate (20 ml) and water (20 ml) successively, and the solution dried with sodium sulfate. Silver oxide (260 mg, 1.1 mmol) is then added to the solution concentrated to 3–4 ml, and the mixture stirred vigorously at room temperature for 30 min. Precipitates are filtered

Table. α-Aroyl-*N*-phenylnitrones **4** prepared

Product **4** Ar		Yield[a] [%]	m.p. [°C]	Molecular Formula[b] or Lit. m.p. [°C]	I.R. (KBr) ν [cm^{-1}]	^{1}H-N.M.R. (CDCl$_3$) δ [ppm]
a		80	109–110°	109–110°[5]	1650, 1580, 1500, 1490	8.33 (s, 1H); 7.4–8.1 (m, 10H$_{arom}$)
b		78	130–132°	$C_{15}H_{13}NO_2$ (239.3)	1650, 1570, 1505, 1490	8.58 (s, 1H); 7.1–8.0 (m, 9H$_{arom}$); 2.40 (s, 3H)
c		97	150–152°	$C_{15}H_{13}NO_3$ (255.3)	1640, 1575, 1505, 1490	8.20 (s, 1H); 7.3–8.1 (m, 9H$_{arom}$); 3.88 (s, 3H)
d		41	99–101°	$C_{14}H_{10}ClNO_2$ (259.7)	1655, 1585, 1515, 1480	8.23 (s, 1H); 7.3–8.0 (m, 9H$_{arom}$)
e		60	100–102°	–[c]	1655, 1580, 1515, 1480	8.22 (s, 1H); 7.3–8.0 (m, 9H$_{arom}$)
f		38	66–68°	$C_{14}H_{10}BrNO_2$ (304.2)	1650, 1585, 1520, 1485	8.09 (s, 1H); 7.2–7.9 (m, 9H$_{arom}$)
g		80	119–121°	$C_{12}H_9NO_3$ (215.2)	1650, 1605, 1560, 1520, 1490	8.52 (s, 1H); 7.2–7.9 (m, 7H$_{arom}$); 6.57 (dd, 1H, *J* = 3 Hz, 1 Hz)
h		73	149–150°	$C_{12}H_9NO_2S$ (231.3)	1630, 1580, 1520, 1510	8.35 (s, 1H); 7.0–8.0 (m, 8H$_{arom}$)
i		40	69–70°	$C_{12}H_{13}NO_2$ (203.2)	1635, 1580, 1515, 1480	7.55 (s, 1H); 7.3–7.9 (m, 5H$_{arom}$); 7.17 (m, 1H); 2.03 (d, 3H, *J* = 1 Hz); 2.24 (d, 3H, *J* = 1 Hz)

[a] Yield of isolated products based on the purified hydroxyamino ketones **3**.
[b] Satisfactory microanalyses obtained: C ±0.18, H ±0.20, N ±0.23.
[c] No m.p. reported in Ref.[6].

off, and washed several times with ethyl acetate. The combined filtrates are evaporated in vacuo and the residue is recrystallized from ether to give the nitrones **4** as a yellow crystals.

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[2] Ref.[1], p. 213.
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