N,N-Bis(*tert*-butyldimethylsilyloxy)aminobenzene as a new synthetic equivalent of nitrosobenzene

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Despite a diverse use of aromatic nitroso compounds in organic synthesis, the main methods for their synthesis are restricted to redox transformations of the corresponding amino or nitro derivatives.[1]

We have previously found that *N,N*-bis(silyloxy)enamines, easily accessible products of the double silylation of aliphatic nitro compounds,[2] are convenient synthetic equivalents of very unstable α-nitrosoalkenes.[3] However, *N,N*-bis(silyloxy)aminobenzenes, which could be used by analogy instead of arylnitroso compounds, have not been known to date.

We synthesized *N,N*-bis(*tert*-butyldimethylsilyloxy)aminobenzene (**1**) by the double silylation of 1-nitro-1,3-cyclohexadiene (**2**)* with dimethyl-*tert*-butylsilyl triflate (Scheme 1). At the same time, when trimethylsilyl triflate was used, we failed to isolate an analog of product **1**, amine $PhN(OSiMe_3)_2$, from the reaction mixture.

Compound **1** containing a structural fragment that has not been described previously (*N,N*-bis(silyloxy)-amino group bound to the aromatic ring) can be considered as a precursor of the new type for nitrosobenzene. This was demonstrated by the successful use of **1** instead of nitrosobenzene in the synthesis of *C,N*-diphenylnitrone by the known reaction[5] (see Scheme 1).

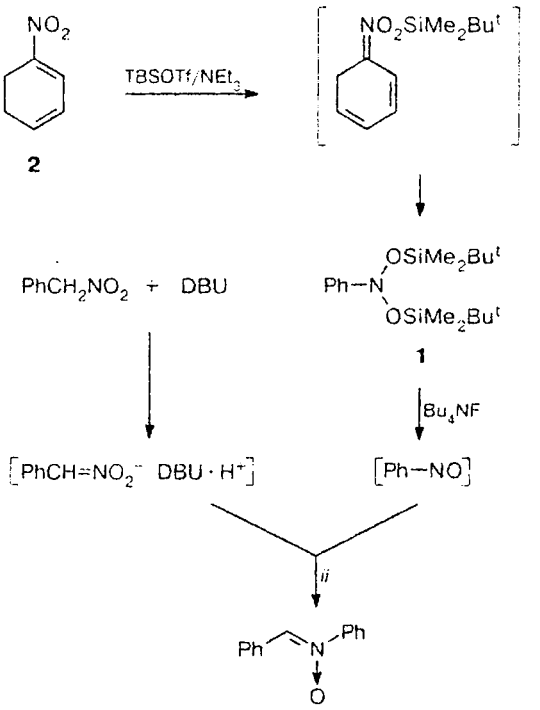
Since some cyclic nitroalkenes can readily be prepared from aromatic nitro compounds,[6] the found silylation reaction could also be used for the preparation of synthetic equivalents of other arylnitroso compounds.

The thermodynamic parameters of nitrogen lone pair inversion in amine **1** ($\Delta H^{\neq}$ = 60±1 kJ mol^{-1}, $\Delta S^{\neq}$ = 36±4 J mol^{-1} K^{-1}; T_c = 242 K, $\Delta G^{\neq}$ = 52±1 kJ mol^{-1}) were determined by mathematical analysis of the temperature dependence of the full shape of the ^{13}C NMR line of the Me groups. Thus, n—π-conjugation somewhat decreases the inversion barrier in product **1** as compared to those in saturated aliphatic *N,N*-dialkoxyamines.[7]

NMR spectra were recorded on Bruker AM-300 and Bruker AC-200 spectrometers using Me_4Si as the internal standard.

* 1-Nitro-1,3-cyclohexadiene (**2**) was synthesized by the nitration of 1,3-cyclohexadiene according to the previously described procedure.[4]

Scheme 1



Reagents and conditions: *i*. Addition of **2** to a mixture of TBSOTf (2.2 equiv.) and NEt_3 (2.5 equiv.) in CH_2Cl_2 at −78 °C, exposure for 2 h to 0 °C;
ii. $PhCH_2NO_2$: DBU = 1 : 1, CH_2Cl_2, 0 °C, successive addition of **1** (1 equiv.) and Bu_4NF (1.1. equiv.) at −78 °C, exposure for 30 min to 0 °C.

***N,N*-Bis(*tert*-butyldimethylsilyloxy)aminobenzene (1).** Yield 77%, b.p. 105—115 °C (0.2 Torr). Found (%): C, 60.54; H, 10.23; N, 3.70; Si, 16.15. $C_{18}H_{35}NO_2Si_2$. Calculated (%): C, 61.13; H, 9.98; N, 3.96; Si, 15.88. ^1H NMR ($CDCl_3$), δ: 0.14 (s, 12 H, 2 $SiMe_2$); 0.87 (s, 18 H, 2 Bu^t); 7.14—7.48 (m, 5 H, Ph). ^{13}C NMR ($CDCl_3$), δ: −4.1 ($SiMe_2$); 17.9 ($\underline{C}Me_3$); 25.9 ($C\underline{Me}_3$); 121.2 and 128.2 (*o*-CH and *m*-CH); 126.7 (*p*-CH); 155.4 (C—N). ^{29}Si NMR {INEPT} ($CDCl_3$), δ: 25.30 (Bu^tMe_2Si); 10.00 (~5% Me_2Bu^tSiOH).

***C,N*-Diphenylnitrone.** Yield 44%, m.p. 114—117 °C (*cf.* Ref. 5: m.p. 112—113 °C).

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