Nucleophilic Aromatic Substitution of Hydrogen in the Reaction of *tert*-Alkylamines with Nitrosobenzenes – Synthesis and NMR Study of *N*-(*tert*-Alkyl)-*ortho*-nitrosoanilines

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The reaction of primary amines bearing tertiary alkyl groups (e.g. R–NH_2; R = *t*Bu, 1-adamantyl) with nitrosobenzenes has been found to proceed by oxidative nucleophilic aromatic substitution of hydrogen, thereby affording *N*-(*tert*-alkyl)-*ortho*- and -*para*-nitrosoanilines. The replacement of hydrogen proceeds more rapidly than the replacement of *ortho*- or *para*-nitro or -bromo substituents. With *p*-nitronitrosobenzene, both *ortho*-hydrogen atoms are substituted to afford *N*,*N*′-di(*tert*-alkyl)-4-nitro-2-nitroso-1,3-phenylenediamines **8a**,**b**. The addition of oxidizing agents (e.g. MnO_2) increases the yield of products. ^{1}H-, ^{13}C-, ^{14}N- and ^{15}N-NMR studies have confirmed the structures of the compounds under investigation. In *ortho*-nitrosoanilines, the rotamer with the nitroso group *syn* to the amino group is favored.

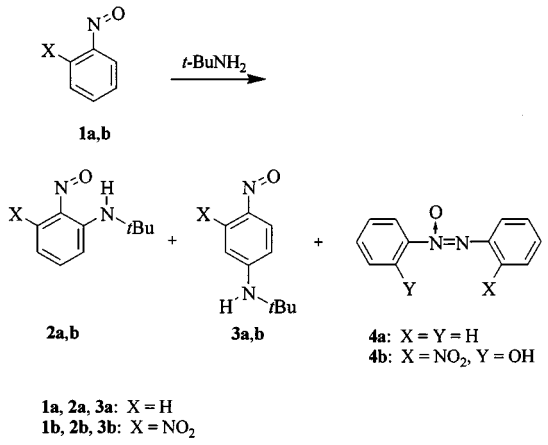
Introduction

As a rule, amines attack nitrosobenzenes at the N atom of the nitroso group[1a]. Thus, reaction of primary amines R−NH_2 (R = Me, Et, CH_2Ph) with nitrosobenzene in $CHCl_3$ as solvent yields alkylphenyldiazenes. *tert*-Butylamine does not react under such conditions.[2] In some cases, amines can displace nucleofugal groups (e.g. OH, OR, NH_2, NHR) in nitrosobenzenes at the position *para* to the nitroso group (S_NAr reactions). Transamination of *para*-nitrosoanilines provides an example of such a reaction.[1b] We have not been able to find any references to reactions of nitrosobenzenes with amines, or with other nucleophiles, which might proceed by nucleophilic aromatic substitution of hydrogen (S_NAr^H reactions).

We wish to report that the reaction of nitrosobenzenes with primary amines bearing a tertiary alkyl group (i.e. R−NH_2; R = *t*Bu, 1-adamantyl) in aprotic dipolar solvents proceeds through nucleophilic aromatic substitution of hydrogen to afford *N*-(*tert*-alkyl)-*ortho*- and -*para*-nitrosoanilines. The aim of the work described herein was to investigate this novel reaction.

Results and Discussion

The reaction of nitrosobenzene (**1a**) with *tert*-butylamine was found to proceed in an unusual manner, compared with the corresponding reactions with other primary amines, e.g. $MeNH_2$ or $EtNH_2$. The nitroso group remained intact and the amine replaced hydrogen at a position *ortho* or *para* to the nitroso group to afford *N*-(*tert*-butyl)-*o*-nitrosoaniline (**2a**) and *N*-(*tert*-butyl)-*p*-nitrosoaniline (**3a**) in a combined yield of ca. 30%.[3] Azoxybenzene (**4a**) was also generated in this reaction in ca. 60% yield (Scheme 1, Table 1).



Scheme 1

Compound **2a** was obtained as a low-melting brown solid, and was found to be rather stable at room temperature. Its structure will be discussed below. In contrast, the yellow *para*-substituted compound **3a** proved to be unstable in the absence of a solvent, although in solution (CH_2Cl_2, benzene) it could be stored for several days with practically no decomposition. The stability of **3a** was enhanced by the presence of a small amount of hydrochloric acid. The ^{1}H- and ^{13}C-NMR spectra of **3a** resemble those of *N*-methyl-*p*-nitrosoaniline.[4] The structure of **3a** was further confirmed by its oxidation to the stable nitro derivative **5**. It is noteworthy that attempts to synthesize **3a** by the Fisher−Hepp reaction were unsuccessful.[5a,5b]

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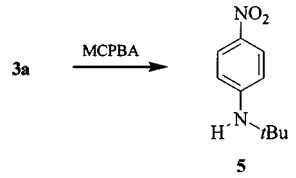
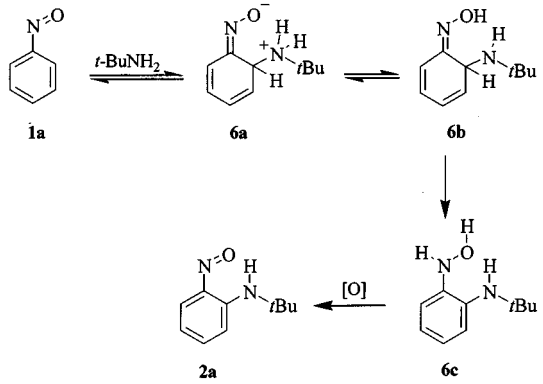


Scheme 2

The reaction of *tert*-butylamine with nitrosobenzene can be considered as an oxidative nucleophilic substitution of hydrogen,[6] involving nucleophilic attack of tBuNH$_2$ at the *ortho* position of nitrosobenzene to give first the σ_H adduct **6a** and then the oxime **6b**. This oxime is subsequently oxidized by a second molecule of nitrosobenzene to yield **2a** and phenylhydroxylamine. The latter, in turn, couples with nitrosobenzene to afford azoxybenzene (**4a**). One can envisage the *para*-substituted compound **3a** being formed in a similar way.



Scheme 3

We suggest that the transformation of oxime **6b** into the nitroso compound **2a** could proceed in two stages, the first being the tautomerization of oxime **6b** to give intermediate hydroxylamine **6c**, and the second being the oxidation of **6c** to nitroso compound **2a**. If this is the case, the rearomatization step should be the result of proton transfer in the **6b** → **6c** tautomerization, in contrast to well-known S_NAr^H reactions in the nitroaromatic series, where the rearomatization step is the result of an oxidation process.[6a,6b]

The reason why tBuNH$_2$ does not attack the nitrogen atom of the nitroso group to give azo compounds is not quite clear. It is noteworthy that the Mg salt of *tert*-butylamine reacts readily with the nitroso group of nitrosobenzene to afford an azo compound.[7]

The rate of the reaction of tBuNH$_2$ with nitrosobenzene depends strongly on the solvent used. The reaction proceeds much faster in DMSO than in CH_3CN. In non-polar solvents (benzene) and in hydroxy solvents (EtOH) it does not take place at all. It should be noted that the reaction only reaches completion when excess tBuNH$_2$ is used. In our experiments we used a threefold excess of tBuNH$_2$. In this connection, it seems plausible that stages of the reaction mechanism **1a** → **6a** → **6b** (Scheme 3) are reversible and that the transformation **6b** → **6c** is a base-catalyzed process.

The reaction also proceeded successfully when tBuNH$_2$ was used as solvent. In this case, *ortho*-substituted **2a** was produced almost exclusively, whereas in CH_3CN or DMSO the predominant product was the *para*-substituted isomer **3a** (see Table 1).

The reaction of substituted nitrosobenzenes was also investigated. *o*-Nitronitrosobenzene (**1b**, Scheme 1) was found to react much faster than nitrosobenzene. In CH_3CN, this reaction reached completion within 2 h at room temperature. The *ortho*-substituted isomer **2b** was the principal product. The product of nitro-group displacement, i.e. **2a**, was not observed.

The introduction of a nitro group on the aromatic ring has contrasting influences on the stabilities of *ortho*- and *para*-nitrosoanilines. Whereas the *ortho* compound **2b** becomes more stable and can be stored at room temperature for a long time, the stability of the *para* product **3b** decreases. It could be separated from the other isomer by chromatography, but partly decomposed to give a tar on concentrating the solution. Its structure was confirmed solely on the basis of mass-spectrometric data.

The azoxy compound **4b** formed in this reaction was found to be 2-hydroxy-2′-nitroazoxybenzene. This compound was shown by Bamberger et al.[8] to be the normal product of condensation of *o*-nitrophenylhydroxylamine with *o*-nitronitrosobenzene. Interpretation of NMR data (see Experimental Section) showed the hydroxy group in **4b** to be located on the ring, and connected with the *N*-oxide nitrogen atom of the azoxy group.

The important aspect of the reaction under investigation is the regioselectivity of the nucleophilic attack at the *ortho* versus the *para* position relative to the nitroso group. The directing effect of the NO_2 group at the *ortho* position is usually accounted for in terms of intramolecular hydrogen bonding in the zwitterionic σ adduct.[6c] The same explanation could be invoked to account for the predominant formation of the *ortho*-substituted compound **2b** from nitronitrosobenzene **1b**. However, in the case of nitrosobenzene **1a**, the *para*-substituted isomer **3a** was predominant when the reaction was carried out in the same solvent. Thus, it is apparent that the problem of regiospecificity in the nitrosobenzene series is rather complicated and a thorough investigation of the reaction mechanism is required.

p-Nitronitrosobenzene (**1c**) underwent coupling with tBuNH$_2$ to afford the *ortho*-substituted compound **2c**. The product of *para* substitution, i.e. **3a**, which might have resulted from a nucleophilic displacement of nitro group, was not detected.

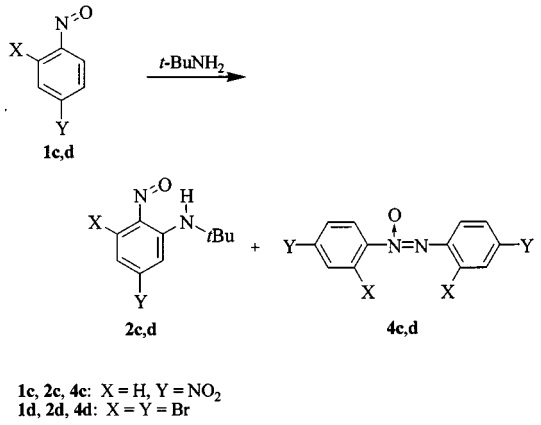
When 2,4-dibromonitrosobenzene (**1d**) was treated with tBuNH$_2$, substitution of hydrogen took place, but not the displacement of a bromine atom. The latter reaction did, however, occur with 2,4,6-tribromonitrosobenzene (**7**), albeit much more slowly (Scheme 5). It is noteworthy that the N=O group also remained intact in this reaction. Both reactions yielded the same *ortho*-substituted compound **2d**.

In conclusion, it can be stated that substitution of the ring hydrogen atom (S_NAr^H reaction) is preferred to the

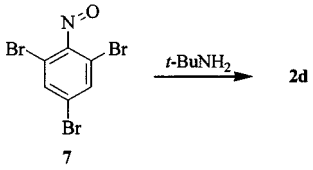
Table 1. Reaction of nitroso compounds **1a**–**d** and **2c** with *tert*-butylamine (CH_3CN as solvent, unless stated otherwise)

No.	Substrate	Temp. [°C]	Time [h]	Oxidant	Products (yield,%)		
1	**1a**	20	144	–	**2a** (6)	**3a** (17)	**4a** (39)
2[a]	**1a**	20	50	–	**2a** (10)	**3a** (22)	**4a** (62)
3[b]	**1a**	20	29	–	**2a** (27)	**3a** (< 1)	**4a** (50)
4	**1b**	20	4	–	**2b** (26)	**3b** (6)[c]	**4b** (60)
5	**1b**	20	0.5	MnO_2	**2b** (55)	**3b** (11)[c]	**4b** (19)
6	**1b**	20	1.7	DMAAD	**2b** (13)	**3b** (5)[c]	**4b** (14)
7	**1c**	40	1.2	–	**2c** (27)	–	**4c** (34)
8	**1c**	20	2.5	MnO_2	**2c** (70)	–	**4c** (< 5)
9	**1c**	20	1.4	DMAAD	**2c** (92)	–	**4c** (< 5)
10	**1c**	40	0.5	NBS	**2c** (74)	–	**4c** (< 5)
11	**1c**	20	72	–	**8a** (10)	–	–
12	**1c**	60	5	MnO_2	**8a** (81)	–	–
13	**1d**	45	1	–	**2d** (29)	–	**4d** (36)
14	**2c**	40	1.3	–	**8a** (23)	–	–
15	**2c**	20	23	DMAAD	**8a** (55)	–	–

[a] DMSO as solvent. – [b] The reaction was carried out without solvent. – [c] A tentative yield of **3b** as it decomposed on concentrating the solution.



Scheme 4

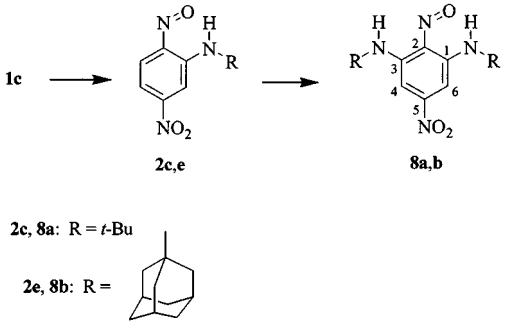


Scheme 5

substitution of nucleofugal groups, e.g. NO_2 and Br (S_NAr reaction), in the nitrosobenzene series. This observation is consistent with Makosza's generalization,[6d] that intermediate σ_H adducts are formed more rapidly than σ_X adducts. It should be noted that nucleophilic substitution in nitronitrosobenzenes **1b**,**c** takes place *ortho* to the nitroso and not *ortho* to the nitro group. This regiospecificity can be attributed to the high stability of intermediate oximes of the type **6b** (see Scheme 3).

To increase the yield of *N*-(*tert*-butyl)nitrosoanilines, the reaction of nitrosobenzenes with *t*$BuNH_2$ was carried out in the presence of an oxidant. The results are summarized in Table 1. The yield of **2b** increased to a maximum (55%) when MnO_2 was employed, while that of azoxy compound **4b** decreased to 19% under these conditions. The yield of **2c** became almost quantitative when the bis(*N*,*N*-dimethylamide) of azodicarboxylic acid (DMAAD) was used (Table 1). It was used in analogy to diethyl azodicarboxylate, which is known to oxidize hydroxylamines to nitroso compounds, but could not be used here as it reacts with *t*$BuNH_2$. The use of MnO_2 or *N*-bromosuccinimide resulted in good yields of **2c**. The bromination of *t*$BuNH_2$ with NBS is very fast, hence the actual oxidant of the intermediate hydroxylamine is likely to be *N*-bromo-*tert*-butylamine.

o-(*tert*-Butylamino)-substituted nitrosobenzene **2c**, bearing the strongly electron-withdrawing nitro group in the *para* position, underwent further displacement of hydrogen with excess *t*$BuNH_2$ to afford the diamine **8a** (Scheme 6). It was obtained in 10% yield directly from *p*-nitronitrosobenzene (**1c**), and in 81% yield using MnO_2 (Table 1).



Scheme 6

We extended this reaction to another primary amine of similar structure, namely 1-adamantylamine. In DMSO as solvent, the reaction of **1c** proceeded in the expected manner, to give *ortho*-substituted compound **2e** in 29% yield. As already mentioned, a high base concentration in the reaction medium is necessary for the reaction to proceed rapidly. As the solubility of 1-adamantylamine is limited, pyridine was added to accelerate the reaction (see Table 2).

The disubstituted compound **8b** was successfully obtained from **2e** when MnO_2 was used as an oxidant. This

Table 2. Reaction of nitroso compounds **1c** and **2e** with 1-adamantylamine (DMSO as solvent)

No.	Substrate	Temp. [°C]	Time [h]	Oxidant	Products (yield, %)	
1	**1c**	40	5.5	–	**2e** (29)	**4c** (54)
2	**1c**	40	2.5	MnO_2	**2e** (65)	**4c** (15)
3[a]	**1c**	40	2	–	**2e** (26)	**4c** (55)
4[a]	**1c**	60	8	MnO_2	**8b** (59)	–
5	**2e**	60	15	MnO_2	**8b** (38)	–

[a] The reaction was carried out in the presence of a 10-mol excess of pyridine.

compound could also be obtained in 59% yield starting from **1c**. Addition of pyridine also accelerated this reaction (see Table 2).

NMR Study of *ortho*-Nitrosoanilines

The structures of the compounds under investigation were confirmed by NMR spectrometry. All resonances in the ^{1}H- and ^{13}C-NMR spectra were unambiguously assigned with the help of special procedures, including NOESY and CH COSY (see notes to Table 3). Some of the nitrosoanilines were also studied by ^{14}N- and ^{15}N-NMR spectroscopy. The ^{14}N-NMR spectrum of **2a** showed a broad signal due to the nitroso group at $\delta = 397$, and an amino group signal at $\delta = -284$, both of which are typical for these groups.[9] The ^{14}N signal of the nitroso group in **2b** was unobservably broad, but was clearly detected in the ^{15}N-NMR spectrum at $\delta = 375.3$. The ^{15}N signal of the NH–*t*Bu group was readily detected by polarization transfer from the N–H proton to the ^{15}N nucleus. The values of the coupling constants $^1J(^1H,^{15}N)$ in **2a**–**d** decreased in the range 90–95 Hz, which is typical for amines.[9] This demonstrates that these compounds are indeed the nitroso compounds, and not the quinone oxime isomers.

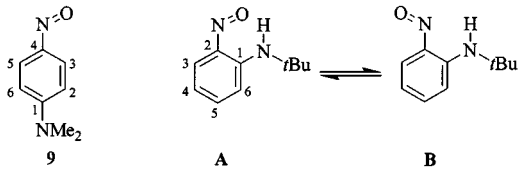
The ^{13}C-NMR data of nitrosoanilines listed in Table 3 merit some comments. It has previously been reported that in nitrosobenzenes bearing an *ortho* substituent (e.g. CH_3[4b] or NO_2[10]), the rotamer having the N=O group *anti* to the substituent is favored because of steric effects. In our case, two rotamers **A** and **B** can a priori be envisaged, in which the N=O group is arranged *syn* to the amino group as in **A**, or *anti* as in **B**. These rotamers would give rise to discrete sets of ^{13}C-NMR signals, where the shifts of carbon atoms C-1 and C-3 *ortho* to the N=O group would differ most markedly because of the large anisotropy of this function. For example, *N*,*N*-dimethyl-*p*-nitrosoaniline (**9**), in which rotation of the N=O group is completely restricted at low temperatures on the NMR timescale, exhibits a chemical-shift difference of ca. 30 ppm between C-3 and C-5.[11]

The ^{1}H- and ^{13}C-NMR spectra of *ortho*-nitrosoanilines lacking a substituent at the 3-position (**2a**,**c**,**e**) are temperature-dependent (see notes to Table 3). At room temperature, the C-1 and C-3 signals, as well as the 3-H signal are broadened, indicating that rotation of the N=O group takes

Table 3. ^{13}C-NMR chemical shifts[a] (δ values, calculated δ in parentheses) of **2a**–**e** and **8a**–**b** in $CDCl_3$ at 297 K (*dynamic broadening is observed)

	2a[b,c]	**2b**	**2c**[d]	**2d**	**2e**[e]	**8a**[f]	**8b**[g]
C-1	135.1 (128.0)	134.5	133.2*	136.0	134.3*	137.4	137.5
C-2	156.7 (158.7)	146.3	154.8	151.0	155.2	146.2	146.1
C-3	141.4 (141.8)	157.4	144.3*	138.8	141.8*	153.1	152.7
C-4	115.7 (114.1)	108.8	109.1	123.4	109.0	91.2	91.6
C-5	137.2 (133.3)	136.7	150.3	132.7	150.7	155.4	155.0
C-6	116.2 (110.6)	120.8	113.5	119.3	114.2	94.4	94.9
Me	29.1	28.4	29.2	29.5		29.49, 29.53	
*C*Me$_3$	51.3	52.4	52.0	52.0		52.0, 52.3	

[a] Assignments were made using the following procedures: 2D CH COSY (for **2a**), proton-coupled spectroscopy (for **2d** and **8a**), selective proton decoupling (for **2a**–**e**), NOESY (for **2a**,**b** and **8a**), selective polarization transfer (for **2b**–**d** and **8a**), APT (for **8a**,**b**) . – [b] The spectra were obtained at 243 K (the signals of C-1 and C-3 are broadened at 297 K). – [c] The calculations were based on the chemical shifts of *N*,*N*-dimethyl-*para*-nitrosoaniline **9**[11] ($CDCl_3$, at 213 K): δ = 110.63 (C-2 and C-6), 109.74 (C-3), 142.06 (C-5), 155.20 (C-1), 162.59 (C-4). – [d] The spectra were obtained at 243 K. – [e] For the adamantyl group of **2e**: δ = 29.35, 35.99, 42.11, 53.14. – [f] At 333 K, signals due to C-1 and C-3 were not observed owing to broadening. – [g] For the adamantyl group of **8b**: δ = 29.40, 29.57, 36.25, 36.12, 42.15, 42.17, 53.11, 53.26.



9 **A** **B**

Scheme 6

place, while at low temperatures all signals are sharp indicating the presence of only one rotamer in the solution. In **2b**,**d**, as well as in **8a**,**b**, all the signals are well-resolved even at room temperature.

The ^{13}C-chemical shifts of *ortho*-nitrosoanilines were estimated using additivity rules.[12] The shifts of **9** were taken as a basis for the calculations. As an illustration, the calculated data for **2a** are given in Table 3. Although this method is not particularly precise, we can unambiguously state that in all the *ortho*-nitrosoanilines investigated, the N=O group is *syn* to the amino group, as in rotamer **A**. This rotamer is presumably favored because of intramolecular hydrogen bonding.

The unusually low-field signal in the range $\delta = 11-12$ in the ^{1}H-NMR spectra of **2a**–**e** can be assigned to the NH proton chelated by the N=O group. The disubstituted compounds **8a**,**b** showed two signals due to NH protons at $\delta = 12.8$ and at $\delta = 7.7$. The former signal can be assigned to the chelated NH proton. Selective polarization transfer from these protons allowed the assignment of the C-4 and C-6 signals in **8a**,**b**. The dynamic broadening at elevated temperatures was taken into consideration in assigning the C-1 and C-3 signals.

In conclusion, it should be noted that the synthesis of *N*-substituted *ortho*-nitrosoanilines is rather problematic.[1b,13]

Only a few examples of this class of compounds are known.[14] The described reactions could offer a new access to compounds of this type.

Experimental Section

General: Melting points are uncorrected. *o*-Nitronitrosobenzene,[8] *p*-nitronitrosobenzene,[15] 2,4-dibromonitrosobenzene,[16] 2,4,6-tribromonitrosobenzene,[17] mercury(II) trifluoroacetate,[18] MnO_2,[19] and bis(*N,N*-dimethylamide) of azodicarboxylic acid (DMAAD)[20] were prepared according to published procedures. All other reagents were purchased from commercial sources. − NMR spectra were recorded with a Bruker AM 300 instrument at 298 K unless otherwise stated; chemical shifts are δ values downfield from internal TMS (^{1}H, ^{13}C) or external CH_3NO_2 (^{14}N, ^{15}N). − Mass-spectral data were obtained at 70 eV by electron impact.

Reaction of Nitrosobenzene (1a) with *tert*-Butylamine

(A) In Acetonitrile: *t*$BuNH_2$ (0.2 mL, 9.75 mmol) was added to a stirred solution of **1a** (0.35 g, 3.25 mmol) in CH_3CN (2 mL). After the reaction was complete (Table 1), the solvent was removed in vacuo, the residue was dissolved in diethyl ether (20 mL), and the resulting solution was extracted with 50 mL of 5% aqueous hydrochloric acid. The ethereal extract was dried ($MgSO_4$) and the solvent was removed in vacuo. The residue was crystallized to give azoxybenzene (**4a**) (125 mg), m.p. 35−37°C (benzene), identical with an authentic sample. The aqueous acidic solution was partly neutralized with 5.6 g of Na_2CO_3 and then extracted with diethyl ether. The solvent was removed in vacuo from the organic phase and the residual oil was chromatographed (silica gel, eluent benzene/diethyl ether, 5:1) to yield **2a** (75 mg) and **3a** (5 mg). The remaining aqueous acidic solution was then completely neutralized with Na_2CO_3 and extracted with further diethyl ether to give, after chromatographic separation, additional portions of **2a** (10 mg) and **3a** (30 mg).

***N*-*tert*-Butyl-2-nitrosobenzene (2a):** Brown crystals, m.p. 39−41°C (pentane). − UV (CH_3OH): λ_{max} (lg ε) = 228 nm (4.35), 302 (3.99), 472 (3.79). − ^{1}H NMR ($CDCl_3$, 243 K): δ = 1.46 (s, 9 H, *t*Bu), 6.88 (dd, *J* = 7.5, 7.3 Hz, 1 H, 4-H), 7.05 (d, 1 H, *J* = 8.9 Hz, 6-H), 7.34 (ddd, *J* = 8.9, 7.5, 1.7 Hz, 1 H, 5-H), 8.59 (d, *J* = 7.3 Hz, 1 H, 3-H), 12.05 (s, 1 H, NH); at 298 K the signal of 3-H is broadened. − ^{14}N NMR ($CDCl_3$, 323 K): δ = −284 ($\Delta\nu_{1/2}$ = 750 Hz, NH), 397 ($\Delta\nu_{1/2}$ = 2000 Hz, N=O). − ^{15}N NMR, INEPT ($CDCl_3$): δ = −282.5 (*J* = 94.7 Hz, NH). − MS (70 eV); *m/z*: 178 [M^+]. − $C_{10}H_{14}N_2O$ (178.2): calcd. C 67.38, H 7.92, N 15.72; found C 67.77, H 7.39, N 15.81.

***N*-*tert*-Butyl-4-nitrosoaniline (3a):** Deep-yellow oil. − ^{1}H NMR ([D_6]DMSO, 403 K): δ = 1.40 (s, 9 H), 6.77 (d, 2 H, *J* = 8.2 Hz), 7.59 (d, 2 H, *J* = 8.2 Hz); at 298 K all the signals are broadened. − ^{13}C NMR ([D_6]DMSO, 403 K): δ = 28.4, 50.8, 112.0 (broadened at 298 K), 124.2 (not detected at 298 K due to broadening), 154.1, 162.6. − MS (70 eV); *m/z*: 178 [M^+].

(B) In DMSO: *t*$BuNH_2$ (0.2 mL, 9.75 mmol) was added to a stirred solution of nitrosobenzene (**1a**) (0.35 g, 3.25 mmol) in DMSO (1 mL). After the reaction was complete (see Table 1), the reaction mixture was poured into water (10 mL) and extracted with diethyl ether. The products were separated as described above to give **2a** (58 mg), **3a** (128 mg) and **4a** (200 mg).

(C) Without Solvent: Nitrosobenzene (**1a**, 0.3 g, 3.25 mmol) was added to stirred *t*$BuNH_2$ (5 mL). After the reaction was complete (see Table 1), the excess *t*$BuNH_2$ was removed in vacuo and the products were separated as described above to give **2a** (150 mg), **3a** (5 mg) and **4a** (140 mg).

Reaction of *o*-Nitronitrosobenzene (1b) with *tert*-Butylamine: **t**$BuNH_2$ (0.2 mL, 2.75 mmol) was added to a stirred solution of **1b** (0.49 mg, 3.25 mmol) in acetonitrile (2 mL). After the reaction was complete (see Table 1), the solvent was removed in vacuo, and the residue was passed through a short column of silica gel, eluting with benzene. The eluate was concentrated to dryness and the solid residue was extracted with hexane. The residue after extraction was identified as **4b** (280 mg). The solvent was removed from the hexane solution and the residue was chromatographed (silica gel, eluent benzene) to yield **2b** (187 mg) and **3b** (43 mg).

***N*-*tert*-Butyl-3-nitro-2-nitrosoaniline (2b):** Black crystals, m.p. 108−112°C (hexane). − IR (KBr): $\tilde{\nu}$ = 1370 cm^{-1}, 1550 (NO_2). − UV (CH_3OH): λ_{max} (lg ε) = 215 nm (4.55), 228 (4.77), 300 (4.15), 465 (4.24). − ^{1}H NMR ($CDCl_3$): δ = 1.49 (s, 9 H, *t*Bu), 6.98 (d, 1 H, *J* = 7.2 Hz, 6-H), 7.30 (d, 1 H, *J* = 9.2 Hz, 4-H), 7.45 (dd, 1 H, *J* = 9.2, 7.2 Hz, 5-H), 11.9 (s, 1 H, NH). − ^{14}N NMR ($CDCl_3$): δ = −276 ($\Delta\nu_{1/2}$ = 900 Hz, NH), −9 ($\Delta\nu_{1/2}$ = 200 Hz, NO_2). − ^{15}N NMR ($CDCl_3$): δ = −277.4 (NH), −9.2 (NO_2), 375.3 (NO). − ^{15}N NMR, INEPT ($CDCl_3$): δ = −277 (*J* = 91.4 Hz, NH). − MS (70 eV); *m/z*: 223 [M^+]. − $C_{10}H_{13}N_3O_3$ (223.2): calcd. C 53.81, H 5.87, N 18.82; found C 54.04, H 5.44, N 18.92.

***N*-*tert*-Butyl-3-nitro-4-nitrosoaniline (3b):** The eluate from the aforementioned chromatographic separation was concentrated to a small volume at 0°C, CCl_4 was added, and the resulting solution was analyzed by mass spectrometry. − MS (70 eV); *m/z*: 223 [M^+].

1-(2-Hydroxyphenyl)-2-(2′-nitrophenyl)diazene 1-Oxide (4b): Bright-yellow crystals, m.p. 46.5−48.5°C (benzene) (ref.[8] m.p. 48−49°C). − IR (KBr): $\tilde{\nu}$ = 1360 cm^{-1}, 1520 (NO_2). − ^{1}H NMR ($CDCl_3$): δ = 6.93 (dd, 1 H, *J* = 8.5, 7.2 Hz, 5-H), 7.08 (d, 1 H, *J* = 8.4 Hz, 3-H), 7.44 (dd, 1 H, *J* = 8.4, 7.2 Hz, 4-H), 7.46 (dd, 1 H, *J* = 7.3, 8.2 Hz, 4′-H), 7.60 (d, 1 H, *J* = 8.0 Hz, 6′-H), 7.66 (dd, 1 H, *J* = 7.3, 8.0 Hz, 5′-H), 8.05 (d, 1 H, *J* = 8.2 Hz, 3′-H), 8.12 (d, 1 H, *J* = 8.5 Hz, 6-H), 11.22 (s, 1 H, OH). − ^{13}C NMR ($CDCl_3$): δ = 119.5 (C-3), 119.7 (C-5), 123.9 (C-6), 124.99 (C-3′), 125.02 (C-6′), 128.8 (C-4′), 131.6 (C-1), 134.0 (C-5′), 135.0 (C-4), 136.1 (C-1′), 143.0 (C-2′), 153.5 (C-2); the assignment was made with the aid of ^{13}C{^{14}N, ^{1}H} NMR spectra, CH and HH COSY, and the APT procedure. − ^{14}N NMR ($CDCl_3$): δ = −47 [$\Delta\nu_{1/2}$ = 280 Hz, N(O)=], −12 ($\Delta\nu_{1/2}$ = 220 Hz, NO_2). − MS (70 eV); *m/z*: 259 (100) [M^+], 258 (90), 243 (30). − $C_{12}H_9N_3O_4$ (259.1): calcd. C 55.60, H 3.50, N 16.21; found C 55.39, H 3.87, N 16.15.

Reaction of *p*-Nitronitrosobenzene (1c) with *tert*-Butylamine: The coupling of *t*$BuNH_2$ with **1c** was carried out according to the above procedure to afford **2c** (see Table 1) and bis(4-nitrophenyl)diazene *N*-oxide **4c**, m.p. 199−200°C (ref.[8] m.p. 200°C), identical to an authentic sample.

***N*-*tert*-Butyl-5-nitro-2-nitrosoaniline (2c):** Red crystals, m.p. 69−72°C. − IR (KBr): $\tilde{\nu}$ = 1340 cm^{-1}, 1540 (NO_2). − UV (CH_3OH): λ_{max} (lg ε) = 222 nm (4.23), 247 (4.24), 300 (4.07), 495 (3.84). − ^{1}H NMR ($CDCl_3$): δ = 1.54 (s, 9 H, *t*Bu), 7.61 (dd, 1 H, *J* = 9.1, 2.1 Hz, 4-H), 7.96 (d, 1 H, *J* = 2.1 Hz, 6-H), 8.86 (d, 1 H, *J* = 9.1 Hz, 3-H), 11. 0 (s, 1 H). − ^{14}N NMR ($CDCl_3$): δ = −285 ($\Delta\nu_{1/2}$ = 600 Hz, NH), −14 ($\Delta\nu_{1/2}$ = 160 Hz, NO_2). − ^{15}N NMR, INEPT ($CDCl_3$): δ = −282.6 (*J* = 91.1 Hz, NH). − MS (70 eV); *m/z* 223 [M^+]. − $C_{10}H_{13}N_3O_3$ (223.2): calcd. C 53.81, H 5.87, N 18.82; found C 53.56, H 6.29, N 18.74.

Reaction of 2,4-Dibromonitrosobenzene (1d) with *tert*-Butylamine: Excess *t*$BuNH_2$ was added to a solution of **1d** (0.5 g, 1.8 mmol) in CH_3CN (4 mL). The mixture was heated under reflux until the

reaction was complete (see Table 1). The solvent was then completely evaporated in vacuo and the residue was chromatographed (silica gel, eluent benzene) to yield **2d** (184 mg) and **4d** (175 mg).

3,5-Dibromo-*N*-*tert*-butyl-2-nitrosoaniline (2d): Brown crystals, m.p. 123−125°C. − UV (CH_3OH): λ_{max} (lg ε) = 216 nm (4.31), 237 (4.32), 330 (4.11), 460 (3.84). − ^1H NMR ($CDCl_3$): δ = 1.47 (s, 9 H, *t*Bu), 7.22 (d, 1 H, *J* = 1.7 Hz, 6-H), 7.31 (d, 1 H, *J* = 1.7 Hz, 4-H), 12.23 (s, 1 H, NH). − ^{15}N NMR, INEPT ($CDCl_3$): δ = −281.8 (*J* = 90.0 Hz, NH). − MS (70 eV); *m/z*: 338, 336, 334 (1:2:1) [M^+]. − $C_{10}H_{12}N_2OBr_2$ (336.0): calcd. C 35.74, H 3.60, N 8.34, Br 47.56; found C 35.64, H 3.89, N 8.30, Br 47.72.

Bis(2,4-dibromophenyl)diazene *N*-Oxide (4d): Colorless crystals, m.p. 149−150°C (benzene). − ^1H NMR ([D_6]DMSO): δ = 7.79 (dd, 1 H, *J* = 8.7, 2.1 Hz), 7.89 (AB system, 2 H), 7.93 (d, 1 H, *J* = 8.7 Hz), 8.11 (d, 1 H, *J* = 2.1 Hz), 8.21 (d, 1 H, *J* = 1.7 Hz). − ^{13}C NMR ([D_6]DMSO): δ = 115.3, 119.6, 122.0, 124.30, 124.6, 126.6, 131.2, 132.0, 135.3, 135.9, 140.7, 147.5. − ^{14}N NMR ([D_6]DMSO): δ = −51 [*J* = 270 Hz, N(O)=]. − MS (70 eV); *m/z*: 518, 516, 514, 512, 510 (1:4:6:4:1) [M^+]. − $C_{12}H_6Br_4N_2O$ (513.8): calcd. C 28.05, H 1.18, Br 62.21, N 5.45; found C 28.16, H 1.22, Br 62.45, N 5.47.

2d from 7: *tert*-Butylamine (7.5 mL, 65 mmol) was added to a stirred solution of 2,4,6-tribromonitrosobenzene **7** (1.72 g, 5 mmol) in CH_3CN (65 mL). After 16 h at room temperature, the reaction mixture was heated for an additional 10 min at 70°C. After cooling, the solvent was removed in vacuo, the residue was washed with 15% aqueous hydrochloric acid, and chromatographed (silica gel, eluent benzene) to yield 1.45 g (85%) of **2d**, identical to the sample obtained above.

Reaction of *para*-Nitronitrosobenzene (1c) with 1-Adamantylamine in DMSO: 1-Adamantylamine (210 mg, 1.4 mmol) was added to a stirred solution of **1c** (90 mg, 0.6 mmol) in DMSO (30 mL). After the reaction was complete (see Table 2), the DMSO solution was poured into water (200 mL) and the resulting mixture was extracted with diethyl ether. The combined ethereal extracts were dried ($MgSO_4$) and the solvent was removed in vacuo. The residue was chromatographed (silica gel, eluent benzene) to yield **2e** (52 mg) and **4c** (46 mg).

***N*-(1-Adamantyl)-5-nitro-2-nitrosoaniline (2e):** Bright-red crystals, m.p. 173−175°C (decomp.). − IR (KBr): $\tilde{\nu}$ = 1350 cm^{-1}, 1550 (NO_2). − ^1H NMR ($CDCI_3$): δ = 1.79 (s, 6 H), 2.11 (s, 6 H), 2.23 (s, 3 H), 7.58 (dd, 1 H, *J* = 9.4, 2.0 Hz, 4-H), 8.06 (d, 1 H, *J* = 2.0 Hz, 6-H), 8.82 (d, 1 H, *J* = 9.4 Hz, 3-H), 10.90 (s, 1 H, NH). − ^{14}N NMR ($CDCl_3$): δ = −14 ($\Delta\nu_{1/2}$ = 220 Hz, NO_2). − MS (70 eV); *m/z*: 301 [M^+]. − $C_{16}H_{19}N_3O_3$ (301.3): calcd. C 63.77, H 6.36, N 13.94; found C 63.56, H 6.67, N 13.87.

Reaction of 1c in the Presence of MnO_2: This reaction of **1c** with 1-adamantylamine was carried out as described above, but in the presence of MnO_2 (100 mg, 1.2 mmol, prepared from $KMnO_4$ and $MnSO_4$ in H_2SO_4 and dried at 120°C,[19] see Table 2).

Reaction of 1c in the Presence of MnO_2 and Pyridine: This reaction of **1c** with 1-adamantylamine was carried out as described above, but in the presence of pyridine (0.45 mL, 4.65 mmol, see Table 2).

Reaction of 1a−c and 2c with *tert*-Butylamine in the Presence of an Oxidant

General Procedure: *tert*-Butylamine (0.2 mL, 9.75 mmol) and the oxidizing agent (5 mmol) were added to a stirred solution of the nitroso compound (3.25 mmol) in CH_3CN (2 mL). After the reaction was complete (see Table 1), the inorganic by-products were filtered off, the filtrate was concentrated in vacuo, and the residue was chromatographed on silica gel (see Table 1).

***N*-*tert*-Butyl-4-nitroaniline (5):** A 0.5 M solution of *m*CPBA in CH_2Cl_2 (1 mL) was added dropwise to a stirred solution of **3a** (89 mg, 0.5 mmol) in CH_2Cl_2 (2 mL). After 2 min, the reaction mixture was carefully shaken with concentrated Na_2CO_3 solution until the evolution of CO_2 subsided. The organic layer was then separated and dried ($MgSO_4$). The solvent was evaporated to leave **5** as a yellow solid (93 mg, 95%), m.p. 70−72°C (hexane, ref.[21] m.p. 71.1−71.6°C). − ^1H NMR ($CDCl_3$): δ = 1.42 (s, 9 H), 6.62 (d, 2 H), 8.02 (d, 2 H).

***N,N′*-Di-*tert*-butyl-4-nitro-2-nitroso-1,3-phenylenediamine (8a):** The reaction of **2c** with *t*BuNH$_2$ in CH_3CN was carried out as described for the reaction of **1b**. After the reaction was complete (see Table 1), the solvent was removed in vacuo, and the residue was passed through a short column of silica gel, eluting with benzene. Diamine **8a** was obtained as deep-blue crystals, m.p. 141−144°C (hexane). − IR (KBr): $\tilde{\nu}$ = 1320 cm^{-1}, 1540 (NO_2). − UV (CH_3OH): λ_{max} (lg ε) = 214 nm (4.59), 244 (4.52), 275 (3.79), 410 (3.81), 600 (3.86). − UV (pentane): λ_{max} = 276 nm, 400, 560. − ^1H NMR ($CDCl_3$): δ = 1.46 [s, 9 H, *t*Bu (C-1)], 1.52 [s, 9 H, *t*Bu (C-3)], 6.75 (s, 2 H, Ar), 7.77 [s, 1 H, NH (C-3)], 12.79 [s, NH (C-1)]. − ^{14}N NMR ($CDCl_3$): δ = −285 ($\Delta\nu_{1/2}$ = 950 Hz, NH), −12 ($\Delta\nu_{1/2}$ = 200 Hz, NO_2). − MS (70 eV); *m/z*: 294 [M^+]. − $C_{14}H_{22}N_4O_3$ (294.6): calcd. C 57.13, H 7.53, N 19.03; found C 57.32, H 7.22, N 19.10.

***N,N′*-Bis(1-adamantyl)-4-nitro-2-nitroso-1,3-phenylenediamine (8b):** 1-Adamantylamine (60 mg, 0.4 mmol) and pyridine (0.2 mL, 2.68 mmol) were added to a stirred solution of **1c** (20 mg, 0.134 mmol) in DMSO (7 mL) in the presence of MnO_2 (40 mg, 0.268 mmol). After the reaction was complete (see Table 2), the DMSO solution was poured into water (50 mL) and the resulting mixture was extracted with diethyl ether. The combined ethereal extracts were dried ($MgSO_4$) and the solvent was removed in vacuo. The residue was chromatographed (silica gel, eluent benzene) to yield **8b** (35 mg, 59%) as deep-blue crystals, m.p. 215−217°C (decomp.). − IR (KBr): $\tilde{\nu}$ = 1330 cm^{-1}, 1540 (NO_2). − ^1H NMR ($CDCl_3$): δ = 1.75 (s, 6 H), 1.77 (s, 6 H), 2.09 (s, 6 H), 2.15 (s, 6 H), 2.20 (br. s, 6 H), 6.82 (s, 2 H), 7.67 (s, 1 H, NH), 12.75 (s, 1 H, NH). − ^{14}N NMR ($CDCl_3$): δ = −17.30 ($\Delta\nu_{1/2}$ = 200 Hz). − MS (70 eV); *m/z*: 450 [M^+]. − $C_{26}H_{34}N_4O_3$ (450.3): calcd. C 69.31, H 7.61, N 12.43; found C 69.46, H 7.51, N 12.36.

8b from 2e: 1-Adamantylamine (100 mg, 0.5 mmol) and MnO_2 (30 mg, 0.34 mmol) were added to a stirred solution of **2e** (50 mg, 0.17 mmol) in DMSO (17 mL). After the reaction was complete (see Table 2), work-up was carried out as described above to give **8b** (29 mg).

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