

Reactions of Nitrosoarenes with Nitrogen Monoxide (Nitric Oxide) and Nitrogen Dioxide: Formation of Diarylnitroxides

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Dedicated to Professor Paolo Bruni on the occasion of his 70th birthday

Keywords: Nitrosoarenes / Nitrogen oxides / Diazonium salts / Diarylnitroxides

Nitrosoarenes react with nitrogen monoxide (nitric oxide) at room temperature and in aprotic media to afford the corresponding diarylnitroxides by the intermediate formation of *N*-nitrosoarylnitroxides. However, these latter spin adducts, in contrast with literature reports, have never been detected by us. *N*-nitrosophenylnitroxide is obtained only in the oxidation of the ammonium salt of *N*-nitrosophenylhydroxylamine (cupferron) with trace amounts of lead tetraacetate. However, it evolves with time to diphenylnitroxide, as demonstrated by following the reaction course in the ESR cavity. On a macroscale level, the reaction between nitrosobenzene

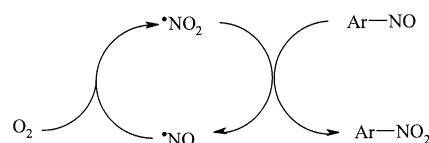
and nitric oxide leads to the formation of *N*-nitrosodiphenylamine, 4-nitro-*N*-nitrosodiphenylamine, 4-nitrodiphenylamine and 4,4'-dinitrodiphenylamine, in addition to diphenylnitroxide. Diarylnitroxides are also obtained when nitrosoarenes react with small amounts of nitrogen dioxide; the mechanism of this reaction is proposed and discussed. The structure of 4-nitro-*N*-nitrosodiphenylamine was determined by X-ray analysis.

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Introduction

The oxidation of aromatic nitroso compounds to the corresponding nitro derivatives by nitrogen dioxide (NO_2) has been considered in several studies,^[1,2] most of which have focused on the kinetic aspects of the reaction. The oxidation of sulfur dioxide (SO_2) to sulfur trioxide (SO_3) by nitric oxide (NO) in the presence of oxygen (and hence NO_2) is also a well-known process.^[3] In this latter case, it is proved that NO_2 works in a catalytic way to transfer an oxygen atom to SO_2 and to release a molecule of NO that then reacts with oxygen thus fuelling another catalytic cycle.

On the basis of this application, in this study we tried to use NO , in the presence of oxygen, as a catalyst for the oxidation of nitrosoarenes to nitroarenes in solution as shown in the cyclic reaction of Scheme 1.



Scheme 1.

Unfortunately, the catalytic action of NO_2 was not observed and the complete consumption of nitrosobenzene was obtained only when NO/O_2 (or NO_2) was added stoichiometrically or in excess. A radical addition mechanism for the oxidation of nitrosoarenes by NO_2 has already been reported and the kinetics of the reaction studied;^[2a] however, some points on the reactivity of nitrosoarenes towards NO_2 or NO still need clarification. For example, on the one hand, the ability of nitroso compounds to act as radical trapping agents is well established,^[4] and on the other hand, the use of these species for trapping NO and related radicals has not been of particular interest likely due to the occurrence of more complex reactions other than simple radical addition. For this reason, the reactions between nitrosoarenes and NO_2 or NO were carried out in the electron spin resonance (ESR) cavity in order to show evidence of the formation of radical intermediates during the oxidation process or the formation of stable spin adducts. The same reactions were also performed on a macroscale level

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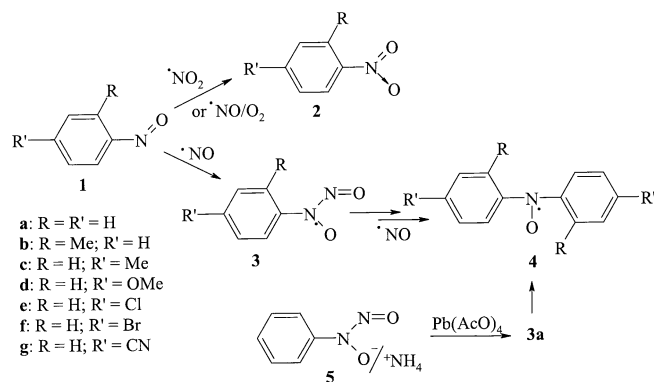
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to identify other products possibly formed, together with the nitroarenes, and to gain further information on the reaction mechanism. In particular, attention was focused on the reaction between nitrosobenzene and $\cdot\text{NO}$, as this latter species is formed during the oxidative process of nitroso compounds by $\cdot\text{NO}_2$ ^[2a] and likely responsible for the failure of the catalytic process.

Results

A benzene solution of nitrosobenzene **1a** was treated with a catalytic amount (ca. 10%) of gaseous $\cdot\text{NO}_2$ or $\cdot\text{NO}$ obtained from the decomposition of nitrous acid^[5] (see Experimental Section) in the presence of oxygen; in both cases, only trace amounts of nitrobenzene **2a** were formed with no catalytic action by $\cdot\text{NO}_2$. If the reactions were carried out by using an excess amount of $\cdot\text{NO}_2$ or $\cdot\text{NO}/\text{O}_2$, compound **1a** was oxidized to nitrobenzene **2a**, which was identified by comparison with an authentic sample (Scheme 2).



Scheme 2.

If nitrosoarenes **1a–g** were treated in the ESR cavity with a small amount of nitrogen dioxide, complex signals were recorded due to the overlapping of two different spectra: a larger and unresolved signal disappearing in 15–30 min and a narrower, persistent, and well-resolved signal corresponding to diarylnitroxides **4a–g**. All spectra were computer simulated, and the obtained spectral parameters (hyperfine coupling constants and *g* factors) collected in Table 1 are in agreement with those reported in the literature.^[6] At present, the first radical detected during the reaction remains unidentified. In Figure 1, the experimental and simulated ESR spectra of diphenyl nitroxide **4a** are shown.

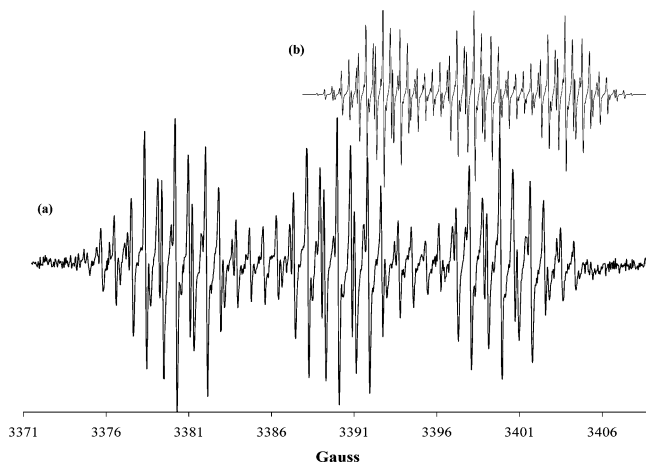


Figure 1. (a) Experimental and (b) computer-simulated spectra of diphenyl nitroxide **4a**.

When $\cdot\text{NO}$ was the reacting species in the absence of oxygen (decomposition of nitrous acid in well-deaerated solution, see Experimental Section), the signals of diarylnitroxides **4a–g** were recorded soon after mixing the reaction solutions.

In all the experiments carried out in the ESR cavity, diphenyl nitroxides **4a–g** were the sole persistent radicals detected: the spectra of nitroso nitroxides **3**, which according to the literature,^[7,8] can be obtained from the trapping of $\cdot\text{NO}$ by nitrosoarenes, were never observed. Nitroso nitroxide **3a** was obtained only by oxidizing a dioxane solution of the ammonium salt of *N*-nitroso-*N*-phenylhydroxylamine (cupferron, **5**) with trace amounts of lead tetraacetate (Figure 2, Table 1). However, even in this case, the recorded signal evolved with time into that of diphenyl nitroxide **4a**.

When the same reaction was carried out with benzene as the solvent, diphenyl nitroxide **4a** was immediately formed. Similarly, **4a** was the sole radical obtained when **5** was oxidized with larger amounts of $\text{Pb}(\text{OAc})_4$, but by following exactly the same experimental conditions described in the literature,^[8a] the expected *N*-nitroso nitroxide was never obtained.

From the macroscale reaction of nitrosobenzene **1a** with sodium nitrite and monochloroacetic acid (nitric oxide was always generated in situ by decomposition of nitrous acid)^[5] in a thoroughly degassed benzene solution, diphenyl nitroxide **4a** was obtained (but not isolated) together with *N*-nitrosodiphenylamine **6** (traces, yields <3%), 4-ni-

Table 1. Hyperfine coupling constants (H.f.c.s in Gauss) and *g*-factors of nitroxide **3a** in dioxane and diarylnitroxides **4a–g** in benzene.

Nitroxide	a_{N}	$a_{\text{H(o)}}$	$a_{\text{H(p)}}$	$a_{\text{H(m)}}$	$a_{\text{H}(\text{CH}_3)}$	$a_{\text{H}(\text{OCH}_3)}$	$a_{\text{N}(\text{NO})}$	$a_{\text{N}(\text{CN})}$	a_{Cl}	a_{Br}	<i>g</i> factor
3a	10.06	2.51	2.66	0.85	–	–	3.66	–	–	–	2.0059(6)
4a	9.70	1.81	1.88	0.80	–	–	–	–	–	–	2.0058(1)
4b	10.54	1.77	1.30	1.03	0.33	–	–	–	–	–	2.0060(7)
4c	9.97	2.00	–	0.81	1.91	–	–	–	–	–	2.0057(3)
4d	10.19	1.91	–	0.76	–	0.22	–	–	–	–	2.0057(7)
4e	9.51	1.87	–	0.82	–	–	–	–	0.16	–	2.0061(5)
4f	9.48	1.75	–	0.98	–	–	–	–	–	0.18	2.0064(2)
4g	9.44	1.79	–	0.80	–	–	–	0.24	–	–	2.0059(8)

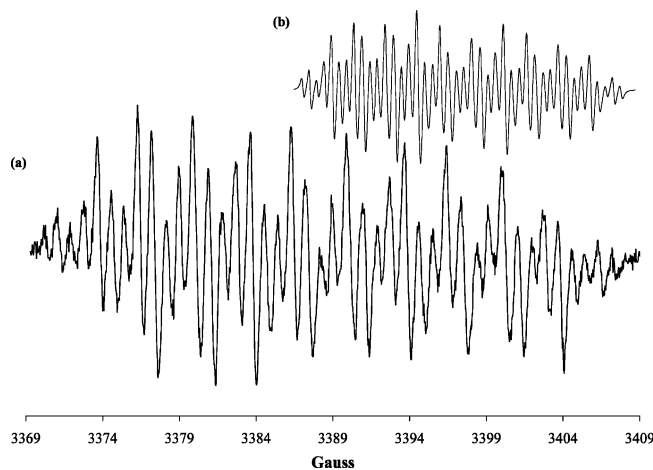


Figure 2. (a) Experimental and (b) computer-simulated spectra of phenyl-*N*-nitrosodiphenylamine **3a**.

tro-*N*-nitrosodiphenylamine **7** (40%), 4-nitrodiphenylamine **8** (21%) and 4,4'-dinitrodiphenylamine **9** (18%). Compound **6** was identified by comparison with an authentic sample; compounds **7**, **8** and **9** were identified by comparing their physical and spectroscopic data with those reported in the literature. Moreover, the structure of diphenylamine **7** was determined by single-crystal X-ray analysis (Figure 3; selected bond parameters are listed in the caption). Bond lengths and angles within the molecule are unexceptional. The dihedral angle formed by the least-squares planes of the aromatic ring is 70.99(9)°. The nitro group is coplanar with the benzene ring [dihedral angle between the least-squares planes is 1.0(2)°], and the N3–C4 bond length of 1.449(4) Å is consistent with a π -electron delocalization between the two groups. In the crystal packing, molecules are linked by intermolecular C–H $\cdots$ N and C–H $\cdots$ O hydrogen-bonding interactions into chains running parallel to the [1 2 0] and [1 $\bar{2}$ 0] directions [C2–H2 0.93 Å, H2 $\cdots$ N2ⁱ 142.2°; C5–H5 0.93 Å, H5 $\cdots$ O2ⁱⁱ 2.42 Å, C5 $\cdots$ O2ⁱⁱ 3.29(5) Å, C5–H5 $\cdots$ O2ⁱⁱ 156.7°. Symmetry codes i: $-x, -y, -z$; ii: $1 - x, -2 - y, -z$].

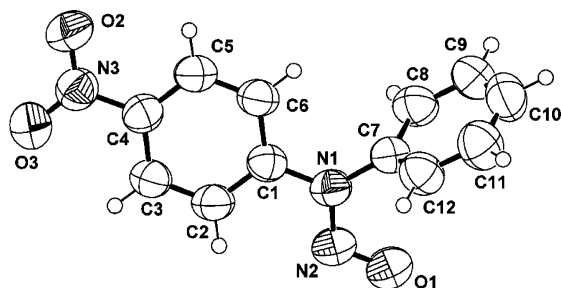
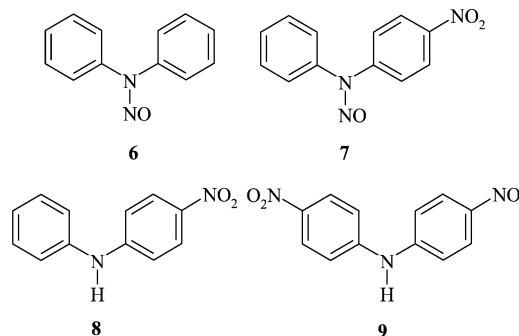


Figure 3. ORTEP drawing of compound **7**; displacement ellipsoids are drawn at the 50% probability level. Selected bond lengths and angles: N1–C1 1.417(4), N1–C7 1.446(4), N1–N2 1.352(3), N2–O1 1.230(3) Å; O1–N2–N1 114.9(3), N2–N1–C1 115.0(3), N2–N1–C7 120.0(3)°.

Diphenylnitroxide **4a** (prepared from nitrosobenzene and phenylmagnesium bromide) was also treated with $\cdot$ NO and products **6–9** were again obtained (data not shown). Com-

pound **9** was oxidised with *m*-chloroperbenzoic acid directly in the ESR cavity to afford 4,4'-dinitrodiphenylnitroxide (see Experimental Section).

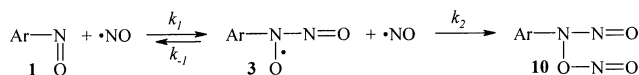


Discussion

In our attempts to use nitrogen dioxide as a catalyst in the oxidation of nitrosobenzene to nitrobenzene we found that the above oxidant cannot be used in a catalytic way and that only when $\cdot$ NO₂ or $\cdot$ NO/O₂ was added in a stoichiometric amount or in excess was nitrosobenzene oxidised to nitrobenzene. This is in agreement with the stoichiometry for reaction (1) established by Bonner and Hancock^[1b] and confirmed by Govenlock et al.^[2a] according to which the ratio ArNO/ $\cdot$ NO₂/ArNO₂ was 1:1:1 [Equation (1)].

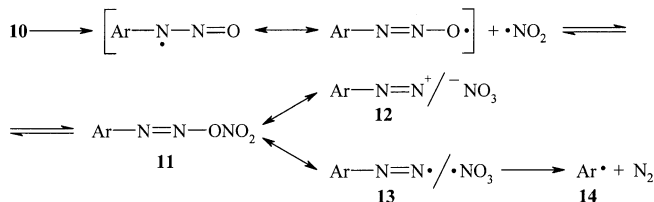


Starting from this point, we decided to take a closer look at the reaction of nitrosobenzene **1a** and other substituted nitrosoarenes **1b–g** with $\cdot$ NO₂ and, above all, with $\cdot$ NO and to follow these reactions by ESR spectroscopy. In fact, very few and also unclear data are reported in the literature concerning the reactivity and the spin-trapping ability^[7] of nitrosoarenes towards nitric oxide and related radicals (nitrosoarenes like other nitroso compounds should behave as good spin-trapping agents). For example, Balaban^[8] described that nitrosobenzene was able to trap $\cdot$ NO to give *N*-nitrosophenylnitroxide when $\cdot$ NO was bubbled into a dilute dioxane solution of nitrosobenzene. We repeated this experiment several times under the same conditions, by changing the solvent (benzene instead of dioxane) and/or nitrosobenzene concentration, but the signal of nitroxide **3a** was never detected. In all of our experiments with **1a** and all other nitrosoarenes **1b–g**, the radicals detected were nitroxides **4a–g**, as already observed by others upon the trapping of $\cdot$ NO by aromatic nitroso compounds.^[4a,4c,4d] On the basis of our knowledge concerning nitric oxide reactivity towards indolinic^[9] and quinolinic^[10] nitroxides, one can explain why $\cdot$ NO cannot be detected by nitroso spin traps and why the reactions of both $\cdot$ NO and $\cdot$ NO₂ give diarylnitroxides. When nitrosoarenes react with $\cdot$ NO, nitroso-nitroxides **3** are indeed formed, but they react further with $\cdot$ NO to give nitrosated adduct **10**, as shown in Scheme 3.



Scheme 3.

Even if the values of the rate constants k_1 and k_2 are not available, it can be assumed that the value of k_2 , which is related to a radical–radical coupling, would be much higher than that of k_1 and, hence, that nitroxides **3** immediately react with $\cdot\text{NO}$, which explains why signals due to radicals **3** (Scheme 3) are never observed. The formation of adduct **10** has already been reported in the literature,^[2b] but without consideration of the fate of this compound. As shown in Scheme 4, adduct **10** may rearrange after cleavage of a nitrogen–oxygen bond in the $>\text{N}-\text{ONO}$ group (computed $\text{BDE}_{\text{N}-\text{ON}} \approx -1.512 \text{ kcal/mol}$),^[11] a deoxygenation also observed in the reaction between $\cdot\text{NO}$ and aromatic nitroxides.^[9,10] The NO_2 group thus released may undergo 1,3-migration to give an arenediazonium nitrate, which can be described by the three canonical structures **11**, **12** and **13**; a similar mechanism was proposed by us to justify the formation of azoindoles in the reaction between nitrosoindoles and nitric oxide in the presence of indole-free base in aprotic solvent.^[12]



Scheme 4.

Similarly, it was reported that the reaction between trifluoronitrosomethane and $\cdot\text{NO}$ ^[13] affords a diazonium nitrate through an intermediate (similar to compound **10**) that in some cases has also been isolated.^[14,15] The formation of a phenyldiazonium nitrate from nitrosobenzene and $\cdot\text{NO}$ is a well-known fact, as it was already reported by Bamberger^[16] at the end of the 19th century, but it was explained through a diazoniumdiolate intermediate.^[17] However, on the basis of the spin-trapping ability of nitroso derivatives^[4] and nitroxides towards $\cdot\text{NO}$,^[9,10] intermediates **3** and **10** seem to be more likely than diazoniumdiolates, even if the formation of these latter intermediates cannot be excluded due to the results obtained in the present study. Once formed, aryldiazonium nitrates **11–13** (Scheme 4) decompose at room temperature and in aprotic solvent to give aryldiazanyl and nitrate radicals; the former radical collapses^[18] to dinitrogen and aryl radical **14**, which is trapped by unreacted nitrosoarene to afford diarylnitroxide **4**.

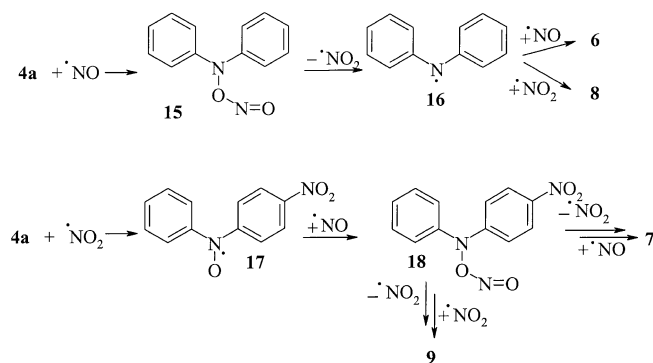
As already mentioned above, the trapping of $\cdot\text{NO}$ (or $\cdot\text{NO}_2$) in the ESR cavity leading to the formation of *N*-nitrosodiphenylamine **3** was never observed. However, to gain information on this radical and on its evolution, the oxidation

(in the ESR cavity) of **5** with lead tetraacetate was attempted as described in the literature.^[19] In actual fact, nitroxide **3a** was obtained but not under the reaction conditions reported in that paper: if the concentrations indicated by Balaban^[19] were used, diphenylnitroxide **4a** was immediately formed (in agreement with the results obtained also by Rassat),^[20] whereas if only trace amounts of $\text{Pb}(\text{OAc})_4$ were added, nitroxide **3a** was obtained. The latter radical was not stable and it rapidly evolved into diphenylnitroxide **4a**, which thus indicates that it represents an intermediate in the formation of **4a**, as shown in Schemes 3 and 4 and that it is in equilibrium with nitrosobenzene and $\cdot\text{NO}$. When the same reaction was carried out in benzene instead of dioxane, diphenylnitroxide was obtained right from the very beginning. This could be due to a solvent effect on the equilibrium of Scheme 3; this aspect has not been studied in detail but it is likely that the dissociation of adduct **3** could be favoured in benzene and hence also the formation of $\cdot\text{NO}$, which drives the reaction towards compound **10** and then to diarylnitroxide.

Nitroxide **4a** was also obtained when nitrosobenzene was treated with trace amounts of $\cdot\text{NO}_2$, although in this case too it derives from the reaction between unreacted nitrosobenzene and $\cdot\text{NO}$ formed during the oxidation of nitrosobenzene by $\cdot\text{NO}_2$ [Equation (1)]^[2] through the same pathways reported in Schemes 3 and 4. Actually, the first spectrum recorded during the reaction was unresolved, because of **4a** and to another nitroxide, which at present remains unidentified, that rapidly disappears. However, it is likely that this signal could be attributed to the $\text{Ar}-\text{N}(\text{O})-\text{O}-\text{N}=\text{O}$ intermediate derived from the trapping of $\cdot\text{NO}_2$, which then evolves into nitrobenzene and $\cdot\text{NO}$.

The macroscale reaction of nitrosobenzene **1a** with in situ generated $\cdot\text{NO}$ showed not only the formation of **4a**, but also that of *C*-nitro- and *N*-nitroso compounds **6–9**. Products **6–9** all derive from diphenylnitroxide through the mechanisms already described in the literature for indolinonic^[9] and quinolinic^[10] nitroxides. In particular, diphenylnitroxide **4a** couples with another $\cdot\text{NO}$ molecule to give adduct **15** (Scheme 5), which is the key product for the formation of **6** and **8** (Scheme 3) through aminyl radical **16**, $\cdot\text{NO}_2$ and $\cdot\text{NO}$. As for intermediate **10**, a low value for the computed BDE of the $>\text{N}-\text{ONO}$ bond in **15** (1.099 kcal/mol)^[11] may justify its cleavage and the formation of aminyl radical **16**. Actually, *N*-nitrodiphenylamine (with or without other nitro groups also on the aromatic rings) could have been obtained together with nitroso analogues **6** and **7**, as obtained, for example, in the reaction of indolinonic nitroxides with $\cdot\text{NO}$;^[9] however, we were unable to observe the formation of such compounds.

To explain the formation of nitroso derivative **7**, nitroxide **17** (Scheme 5) must be considered as an intermediate, and it is likely derived from the trapping of $\cdot\text{NO}_2$ on C-4 of the aromatic ring. Nitroxide **17** can further react with $\cdot\text{NO}$ to give adduct **18**, which then evolves into product **7**. Compound **18** is also involved in the generation of diphenylamine **9**, as cleavage of the $>\text{N}-\text{ONO}$ bond in **18** followed by addition of $\cdot\text{NO}_2$ leads to its formation.



Scheme 5.

Conclusions

Nitric oxide and nitrogen dioxide are two radical species with relevant deleterious effects in biological systems, and they are involved, both directly and indirectly, in oxidative and nitrosating stress.^[21,22] In this regard, the data here described may contribute to a better understanding of the reactivity of these radicals towards nitroso derivatives, which can be formed physiologically by oxidation of biological primary amino groups or as intermediates in the nitration of tyrosine.^[23,24]

Nitrosoarenes cannot be used as spin traps for $\cdot\text{NO}_2$, because the spin adducts potentially formed are unstable and cannot be easily detected. In fact, the expected spin adduct reacts further with another $\cdot\text{NO}$ molecule, which leads to the formation of diphenylnitroxide, likely at a rate higher than that of the initial trapping. Diphenylnitroxide is obtained in the reaction of nitrosobenzene not only with $\cdot\text{NO}$ but also with trace amounts of $\cdot\text{NO}_2$; however, even in this latter case the reaction involved is between nitrosobenzene and $\cdot\text{NO}$ (released during the oxidation of nitrosobenzene).

Diphenylnitroxide, which is also the precursor for all the products isolated from the macroscale reaction between nitrosobenzene and nitric oxide, is obtained from the decomposition of a diarendiazonium nitrate.

Experimental Section

General: Melting points are uncorrected and were measured with an Electrothermal apparatus. ^1H NMR spectra were recorded at room temperature in CDCl_3 solutions with a Varian Gemini 200 spectrometer (TMS was taken as reference peak); J values are given in Hz. IR spectra were recorded in the solid state with a Perkin-Elmer MGX1 Spectrophotometer equipped with Spectra Tech. Mass spectra were recorded with a Carlo Erba QMD 1000 mass spectrometer in the positive EI mode. ESR spectra were run with a Bruker EMX EPR spectrometer equipped with an XL microwave frequency counter, Model 3120 for the determination of g factor and with a Varian E4 spectrometer. The spectra were recorded with the following instrumental settings: modulation frequency 100 kHz, modulation amplitude 0.4, sweep width 40 G, microwave power 5 mW, time constant 1.28 s, receiver gain 5×10^3 . Computer simulation of ESR spectra were calculated by using the WinSim program in the NIEHS public ESR software tools package

(www.epr.niehs.nih.gov/).^[25] Gaseous nitrogen dioxide (98.5% purity) was purchased from Fluka. It was used without purification in the volumetric preparation of the solutions: a 20-mL volumetric flask was filled with the indicated volume of the chosen solvent and weighed. $\cdot\text{NO}_2$ was bubbled through for a few seconds and the flask was reweighed: the difference between the two weights gave the amount, and hence the number of mols of $\cdot\text{NO}_2$ dissolved in 20 mL. Solutions of $\cdot\text{NO}_2$ generally contained between 5×10^{-4} and 2×10^{-3} mol in 20 mL. Nitrogen monoxide (nitric oxide, $\cdot\text{NO}$) was obtained from the spontaneous decomposition of nitrous acid generated when monochloroacetic acid is added to sodium nitrite and passed through a deaerated 20% KOH aqueous solution under an atmosphere of argon. Two millimoles of sodium nitrite were used to obtain 1 mmol of $\cdot\text{NO}$. Benzene and dioxane were Carlo Erba or Aldrich RP-ACS grade solvents and were distilled prior to use. *N*-nitrosophenylhydroxylamine ammonium salt (cupferron) and lead tetraacetate were purchased from Sigma-Aldrich and were used as received. Nitrosobenzene and 2-methylnitrosobenzene were purchased from Aldrich, whereas 4-methyl-,^[26] 4-methoxy-,^[27] 4-chloro-,^[28] 4-bromo-,^[28] and 4-cyano-^[29] nitrosobenzenes were prepared according to literature reports. BDE calculations were performed by means of the Gaussian 03 package^[30] on an IBM SP5 supercomputer at Cineca Supercomputing Center (via Magnanelli 6/3, I-40033 Casalecchio di Reno, Bologna, Italy; <http://www.cineca.it/HPSystems>). All calculations were carried out by geometry optimization at the B3LYP/6-311+G(d,p) level followed by single-point frequency calculations at the same level in which imaginary (negative) values were never found, confirming that the computed geometries always refer to a minimum. Unrestricted wave function was used for open-shell species, giving $\langle S^2 \rangle = 0.7501 \pm 0.0001$ for spin contamination (after annihilation).

Macroscale Reactions

A – Reaction of Nitrosobenzene with Nitrogen Dioxide: A nitrogen dioxide benzene solution (0.2 mmol in 5 mL of solvent) was added to a solution of nitrosobenzene in the same solvent (1 mmol in 10 mL of benzene) whilst stirring at room temperature and in the presence of oxygen. After 2 h, most of the starting nitrosobenzene was recovered after evaporation of the solvent. The same reaction was carried out by using an excess amount of nitrogen dioxide (2 mmol of $\cdot\text{NO}_2$ for 1 mmol of nitrosobenzene). After 2 h, nitrosobenzene **2a** was almost quantitatively isolated by evaporation of the solvent, and it was identified by comparison with an authentic sample.

B – Reaction of Nitrosobenzene with Nitric Oxide in the Presence of Oxygen: Nitrosobenzene (1 mmol) was dissolved in benzene (10 mL) and sodium nitrite (3 mmol) was added. Monochloroacetic acid (3 mmol) was added to this suspension, which was stirred at room temperature for 2 h. The reaction mixture was poured into 10% aqueous NaHCO_3 (40 mL); the organic layer was washed with water (2×20 mL) and dried with Na_2SO_4 . Evaporation of the solvent gave nitrosobenzene **2a** in high yield (more than 90%).

C – Reaction of Nitrosobenzene with Nitric Oxide in the Absence of Oxygen: Nitrosobenzene (1 mmol in 5 mL of benzene) was dissolved in one arm of a small Y-reactor together with sodium nitrite (3 mmol), and the other arm contained monochloroacetic acid (3 mmol) suspended in benzene (4 mL). The solutions were accurately degassed by using the freeze–pump–thaw degassing method, and the cycles were repeated at least three times. The two solutions were then mixed and stirred at room temperature for 2 h and worked up as described above in point B. A small portion of the benzene solution (0.3 mL) was taken before complete evaporation, degassed with argon and submitted to ESR spectroscopy: a signal

corresponding to diphenylnitroxide was recorded. A yellowish solid compound precipitated during evaporation of the solvent, which was separated by filtration and identified as 4,4'-dinitrodiphenylamine (**9**; 0.08 mmol, 18%). The filtrate was chromatographed on silica gel (cyclohexane/ethyl acetate, 8:2), and the following products were collected: *N*-nitrosodiphenylamine **6** (trace), 4-nitro-*N*-nitrosodiphenylamine **7** (41%) and 4-nitrodiphenylamine **8** (21%).

Compound 7: Yellow solid, m.p. 129–131 °C (petroleum ether) (ref.^[31] 128–131 °C). IR: $\tilde{\nu}$ = 1599, 1496, 1477, 1341 cm⁻¹.^[31] ¹H NMR (200 MHz, CDCl₃, 25 °C): δ = 8.99 (d, *J* = 9.4 Hz, 2 H, arom.), 7.57 (m, 4 H, arom.), 7.04 (m, 3 H, arom.) ppm.^[32] MS (EI+): *m/z* (%) = 214 (80), 184 (23), 167 (100); the molecular ion peak was not visible in the mass spectrum.

Compound 8: Orange solid, m.p. 138–140 °C (acetone/petroleum ether 60–80 °C) (ref.^[31] 132–135 °C). IR: $\tilde{\nu}$ = 3330, 1591, 1512, 1341 cm⁻¹.^[31] ¹H NMR (200 MHz, CDCl₃, 25 °C): δ = 8.12 (d, *J* = 9.16 Hz, 2 H, arom.), 7.39 (pseudo t, 2 H, arom.), 7.23 (m, 3 H, arom.), 6.94 (d, *J* = 9.16 Hz, 2 H, arom.), 6.26 (br. s, 1 H, NH) ppm.^[33,34] MS (EI+): *m/z* (%) = 214 (89) [M]⁺, 167 (100).

Compound 9: Yellow solid, m.p. 210–212 °C (acetone/petroleum ether 60–80 °C) (ref.^[31] 132–135 °C). IR: $\tilde{\nu}$ = 3340, 1614, 1585, 1504, 1323, 1304 cm⁻¹. ¹H NMR (200 MHz, CDCl₃, 25 °C): δ = 7.21 (d, *J* = 9.16 Hz, 4 H, arom.), 8.24 (d, *J* = 9.16 Hz, 4 H, arom.), 6.68 (br. s, 1 H, NH) ppm.^[35] MS (EI+): *m/z* (%) = 259 (100) [M]⁺, 229, (24), 183 (23), 167 (64).

In order to exclude the presence of [•]NO₂ that could be formed during the decomposition of nitrous acid, the reaction between nitrosobenzene and [•]NO was repeated by passing the gas evolved in the decomposition of nitrous acid through a well-degassed 20% KOH aqueous solution. No differences were found with the results obtained in the reaction described above with those obtained from in situ generated nitric oxide.

Reactions Carried Out in the ESR Cavity

A – Reaction of Nitrosoarenes with Nitrogen Dioxide: Nitrosoarenes (0.5 mmol in 1 mL of benzene) were introduced into one arm of an inverted U cell and carefully degassed with argon; a solution of [•]NO₂ (0.5 M in benzene, 0.25 mL) was introduced into the other arm. The two solutions were mixed, and the cell was placed in the ESR cavity. A composite signal was recorded due to two different radicals: an unidentified one, which disappeared in 15–30 min, and the diarylnitroxide.

B – Reaction of Nitrosoarenes with Nitric Oxide: Nitrosoarenes (0.5 mmol) were introduced into one arm of an inverted U cell and dissolved in a solution of monochloroacetic acid (0.5 M, 1 mL). In the other arm, sodium nitrite (4 mg) was suspended in benzene (1 mL). The two solutions were carefully degassed with argon and then mixed, and the cell was placed in the ESR cavity; a well-resolved ESR signal of the corresponding diarylnitroxide was recorded soon after.

C – Oxidation of Cupferron: Cupferron (**5**; 2 mg) was suspended in dioxane (0.5 mL) in an ESR tube and degassed with argon for 5 min. A trace amount of lead tetraacetate was added to the solution, and the sample was then placed in the ESR cavity: the signal of *N*-nitrosophenylnitroxide **3a** was immediately recorded, but it evolved into that of diphenylnitroxide **4a** in 4–6 h.

Crystal Data for Compound 7: C₁₂H₉N₃O₃, *M* = 243.22, monoclinic, space group *P*2₁/*c*, *a* = 8.125(2) Å, *b* = 6.0212(9) Å, *c* = 23.490(15) Å, β = 95.93(3)°, *V* = 1143.0(8) Å³, *Z* = 4, *D*_{calcd.} = 1.413 mg m⁻³, *F*(000) = 504, λ = 1.54178 Å, μ (Cu-K α) = 0.880 mm⁻¹, *T* = 295(2) K, total/unique reflections = 2221/2173 [*R*(int) = 0.058],

θ range = 3.78–70.42°, final *R* [*I* > 2 σ (*I*)]: *R*₁ = 0.065, *wR*₂ = 0.182, *R*(all data): *R*₁ = 0.106, *wR*₂ = 0.207.

CCDC-677132 (for **7**) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Supporting Information (see footnote on the first page of this article): Bond dissociation energies and geometry optimizations of [•]NO₂, PhN–N=O[•], **10**, **16** and **18**.

Acknowledgments

The authors would like to thank MIUR (Ministero dell'Università e della Ricerca Scientifica e Tecnologica) and Università Politecnica delle Marche for financial support.

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Received: February 25, 2008
Published Online: May 9, 2008