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Electron-excited dioxygen generated by the tri-*tert*-butoxyaluminum—*tert*-butyl hydroperoxide system as an efficient oxidant of aniline and some *N*-substituted anilines

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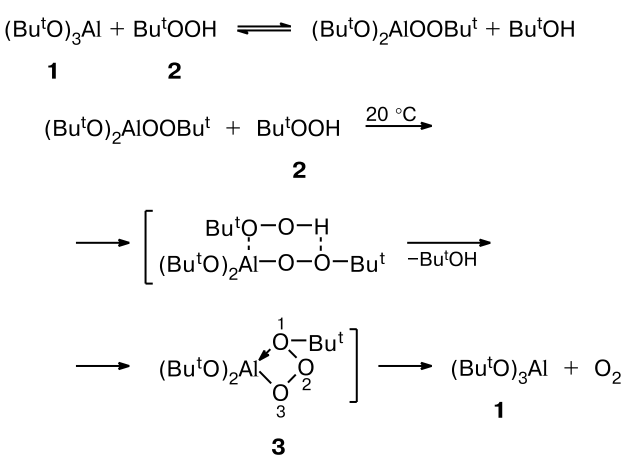
The tri-*tert*-butoxyaluminum—*tert*-butyl hydroperoxide system generates molecular oxygen in the electron-excited singlet state ($^1O_2$), which oxidizes diphenylamine, *N*-ethylaniline, aniline, and 2,6-diisopropylaniline to form nitroxyl radicals. The latters were identified by ESR at 240—293 K. Oxidation proceeds *via* the intermediate formation of nitrogen-containing *N*-peroxide compounds.

Key words: tri-*tert*-butoxyaluminum, *tert*-butyl hydroperoxide, oxidation, aniline, *N*-alkyl(aryl)aniline derivatives, nitroxyl radicals.

The tri-*tert*-butoxyaluminum (**1**)—*tert*-butyl hydroperoxide (**2**) system in CCl_4 and C_6H_6 in a molar ratio of 1 : 2 generates dioxygen in ~80% yield.[1] We have shown[2] that dioxygen is evolved through the intermediate formation of aluminum-containing trioxide (**3**) according to the general Scheme 1. It is known[3] that peroxides (HOOH, Bu^{t}OOH) are stronger nucleophilic reagents in substitution than water or alcohol.

Scheme 1



The evolution of O_2 is catalytic,[1] and the systems **1—2** and di-*tert*-butoxy-*tert*-butylperoxyaluminum—hydroperoxide at room temperature are efficient oxidizing agents of the C—H bonds in methylene fragments to the oxo (ketonation) and hydroxy groups in alkanes and alkylarenes.[2,4—6] Under the same conditions, the oxidation of the C—H methine bonds in alkylarenes forms the corresponding hydroperoxides and the products of their subsequent decomposition.[6]

It should be mentioned that under mild conditions (293 K) this system transforms sulfides into the corresponding sulfones in ~100% yield.[7,8]

As shown in the study[9] of aluminum-containing trioxide (**3**) and the routes of its thermal decomposition using ESR combined with the spin trap technique, trioxide **3** eliminates O_2 and also generates the oxygen-centered radicals Bu^{t}OO$^\bullet$, Bu^{t}O$^\bullet$, (Bu^{t}O)$_2$AlOO$^\bullet$, and (Bu^{t}O)$_2$AlO$^\bullet$. The latters are formed by the homolysis of the O(1)—O(2) and O(2)—O(3) bonds in the molecule of trioxide **3**.

The authors[9] believe that the the main route of thermal decomposition of trioxide **3** produces dioxygen through the transfer of the Bu^{t}O group both with a pair of electron and as a radical to the aluminum atom (S_R2 substitution) to evolve singlet dioxygen according to the spin conservation rule (Scheme 2).

The reactions in Scheme 2 can be considered as a route of catalytic generation of singlet dioxygen. The yield of the latter determined from its interaction with such typical $^1O_2$ acceptors as anthracene and 9,10-dimethylanthracene is 40% in C_6H_6 and 50% in CCl_4, depending on the solvent.[9]

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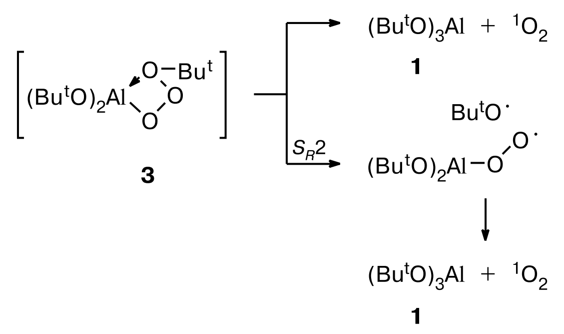
Scheme 2



It is noteworthy that since organic dialkyl trioxides are decomposed homolytically to form alkoxy- and alkylperoxy radicals and singlet dioxygen, the yield of the latter depends substantially on the experimental conditions, especially on the solvent nature.[10,11]

The purpose of this work is to study the low-temperature oxidation of the N—H bonds in aniline and some its *N*-alkyl(aryl) derivatives by the **1**—**2** system.

Experimental

Benzene (analytical grade), which was purified by distillation over P_2O_5 and stored above metallic sodium, was used as solvent. Chlorobenzene (reagent grade, for chromatography) was distilled and stored above Na_2SO_4. Aniline and *N*-ethylaniline (both pure grade) were distilled and stored above NaOH. Tri-*tert*-butoxyaluminum (**1**) was synthesized by the reaction of *tert*-butanol and aluminum followed by sublimation[12] (b.p. 160—170 °C (1 Torr)). Found (%): Al, 11.12. $C_{12}H_{27}AlO_3$. Calculated (%): Al, 10.96. All procedures with tri-*tert*-butoxyaluminum (**1**) were carried out under dry oxygen-free argon. The concentration of *tert*-butyl hydroperoxide **2** was ≥99.5—99.8%. 2,2´-Dipyridylamine (99%, Aldrich) was used. Diphenylamine (analytical grade) was purified by recrystallization from a benzene—hexane mixture. Tetraphenylhydrazine was synthesized using a known procedure[13] by oxidation with potassium permanganate in acetone. Melting points of the synthesized compounds coincide with the published values.

ESR spectra were detected on a Bruker ER200D-SRC spectrometer equipped with an ER 4105 DR double resonator (working frequency ~9.5 GHz) and an ER 4111 VT temperature-controlling unit. Diphenylpicrylhydrazyl (DPPH) was used as standard in determination of the *g* factor.

GLC analysis of the volatile products was carried out on an LKhM-80 chromatograph (flame-ionization detector, column 120 cm, 30% dinonyl phthalate on Chromaton N-AW-DMCS). The temperature was varied within 30—120 °C. GLC analysis of the high-boiling products was carried out on a Tsvet-2-65 chromatograph (flame-ionization detector, helium as carrier gas, column 120 cm, 15% Reoplex-400 on Chromaton N-AW-DMCS, 120—190 °C).

Reaction of aniline with the tri-*tert*-butoxyaluminum (1)—*tert*-butyl hydroperoxide (2) (1 : 1 : 2) system. To Bu^tOOH (0.72 g) was added a mixture of $(Bu^tO)_3Al$ (0.98 g) and $PhNH_2$ (0.37 g) in benzene (20 mL) and was left for 1 day at ~20 °C. Then the solvent and volatile components were condensed off in a trap cooled with liquid nitrogen. The volatile fraction contained $PhNO_2$ (0.04 g) and Bu^tOH (0.91 g). The residue, a dry yellow powder, was hydrolyzed with 10% H_2SO_4, extracted with diethyl ether, and dried with Na_2SO_4. GLC analysis of the ether hydrolyzate detected $PhNO_2$ (0.04 g), Bu^tOH (0.33 g), Bu^tOOH (0.09 g), PhN=NPh (0.01 g), and PhN(O)=NPh (0.29 g).

ESR analysis was carried out in a tube of the ESR spectrometer. Reaction solutions were degassed to improve the resolution of ESR spectral lines and to remove oxygen, which evolved in the interaction of components **1**—**2**.

The reactions in the system **1**—**2** with other amines were carried out analogously.

Results and Discussion

Diphenylamine, *N*-ethylaniline, 2,2´-dipyridylamine, aniline, and 2,6-diisopropylaniline were chosen as oxidized substrates to study the reactivity of trioxide **3** as an $^1O_2$ source and an efficient low-temperature oxidizing agent. The reactions were carried out in benzene at room temperature and the ratio amine : **1** : **2** = 1 : 1 : 2.

It is known[14] that $^1O_2$ generated in a benzene—ethanol mixture (Bengal Rose as sensitizer, $\lambda = 5.46 \cdot 10^3$ Å) oxidizes the secondary and tertiary amines to free nitroxyl radicals.

Our experiments showed that trioxide **3** oxidizes diphenylamine at room temperature only at the N—H bond of the amine to form the diphenylnitroxyl radical[15] (Fig. 1) ($a_N = 0.985$ mT, $a_{6H}{}^{O,P} = 0.188$ mT, $a_{4H}{}^{M} = 0.082$ mT, $g = 2.0058$) according to Scheme 3.

Scheme 3

$$\mathbf{3} + H{-}NPh_2 \xrightarrow[\substack{-(Bu^tO)_3Al\\(\mathbf{1})}]{} [HOO^{\cdot}\,{}^{\cdot}NPh_2] \longrightarrow$$

$$\longrightarrow [Ph_2NOOH] \longrightarrow Ph_2N\overset{\cdot}{-}O + {}^{\cdot}OH$$

The intermediate formation of the diphenylnitrogen-centered radicals is indicated by the formation of tetraphenylhydrazine, which is the dimerization product of this radical (the yield was 0.12 moles per mole of diphenylamine).

We failed to oxidize 2,2´-dipyridylamine under similar conditions to the corresponding nitroxyl radical. This is probably reasoned by the association of alkoxide **1** with this amine, resulting in the strong shielding of the N—H bond.

It was of interest to study the transformations of *N*-ethylaniline in the **1**—**2** system. This amine contains the C—H bonds of the methylene group, which are readily oxidized to the oxo and hydroxy functional groups,[2,4—6]

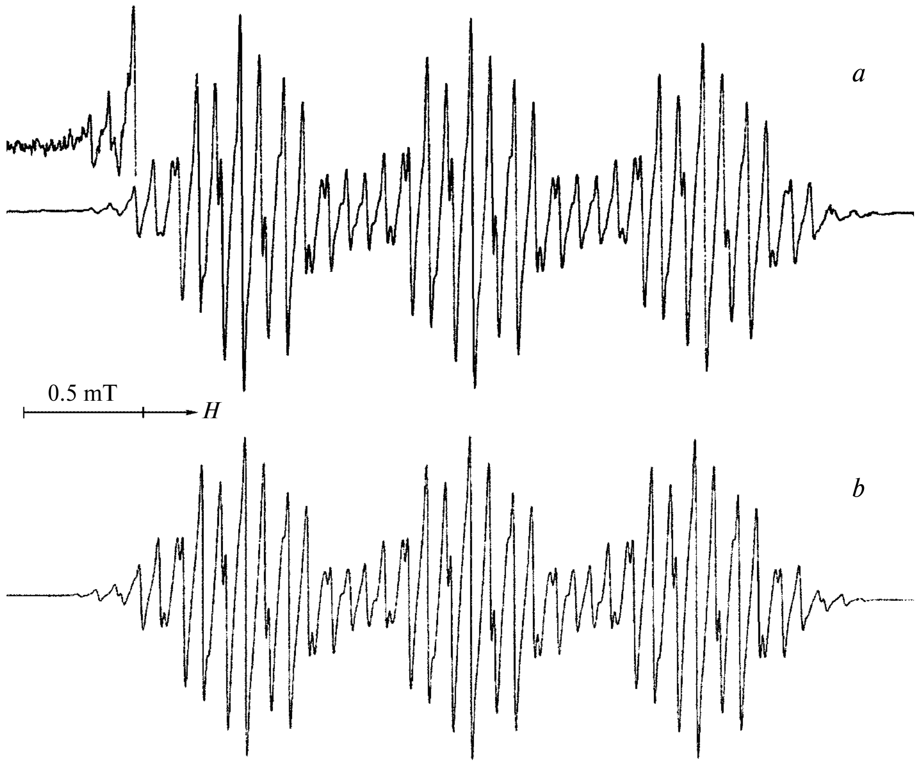
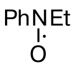
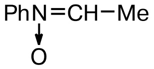
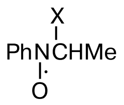
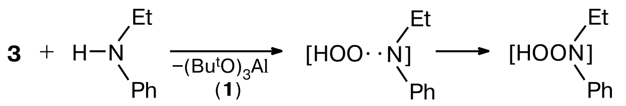


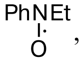
Fig. 1. ESR spectrum detected in the $(Bu^tO)_3Al$—Bu^tOOH—Ph_2NH (1 : 2 : 1) system without spin traps in benzene at 293 K (degassed sample) (*a*) and the model spectrum simulated by the WINEPR SimFonia Version 1.25 program (*b*).

and also the N—H bonds of the amino group. The latters, as established by ESR, undergo predominant oxidation to form radicals of two types:  $\mathrm{Ph\underset{\underset{O}{|\cdot}}{N}Et}$ (in benzene, 293 K) with the constants a_N = 1.078 mT, $a_{3H}^{O,P}$ = 0.290 mT, a_{2H}^{M} = 0.102 mT, a_{2H}^{α} = 0.786 mT, and g = 2.0059 [16] (Fig. 2) and the spin-adduct of nitron  $\mathrm{Ph\underset{\underset{O}{\downarrow}}{N}{=}CH{-}Me}$ (**4**) (in chlorobenzene, 286 K) with the X radical, which is present in the system (X is the oxygen-centered radical),  $\mathrm{Ph\underset{\underset{O}{|\cdot}}{N}\overset{\overset{X}{|}}{C}HMe}$ with the constants a_N = 1.038 mT, $a_{3H}^{M\alpha}$ = 0.108 mT, $a_{3H}^{O,P}$ = 0.256 mT, and g = 2.0059 (Fig. 3).

The formation of these nitroxyl radicals indicates that trioxide **3** oxidizes the N—H bonds of the initial amine through intermediate *N*-hydroperoxide *via* Scheme 4.

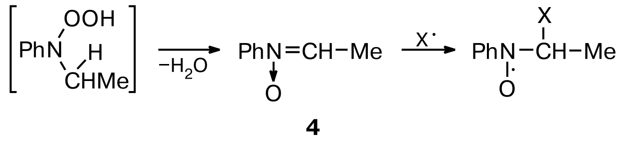
Scheme 4



Unstable nitrogen-containing hydroperoxide decomposes to the nitroxyl radical  $\mathrm{Ph\underset{\underset{O}{|\cdot}}{N}Et}$, which was detected by ESR (see Fig. 2).

In addition, this *N*-hydroperoxide also decomposes to form nitron **4**. The latter, as known, can serve as a good spin trap (Scheme 5).

Scheme 5



Nitron **4** also could be formed through the oxidation of the nitroxyl radical. The adduct of nitron **4** with the $X^{\cdot}$ radical was also found by ESR (see Fig. 3). The $X^{\cdot}$ radical is, most likely, the $Bu^tO^{\cdot}$ radical.

N-Ethylaniline is partially oxidized at the CH_2 group of the Et fragment, which is indicated by the presence of acetic acid (~7%) and azoxybenzene (to 10%) in the reaction products. These products are formed due to the cleavage of the N—C bond of the substrate. However, their

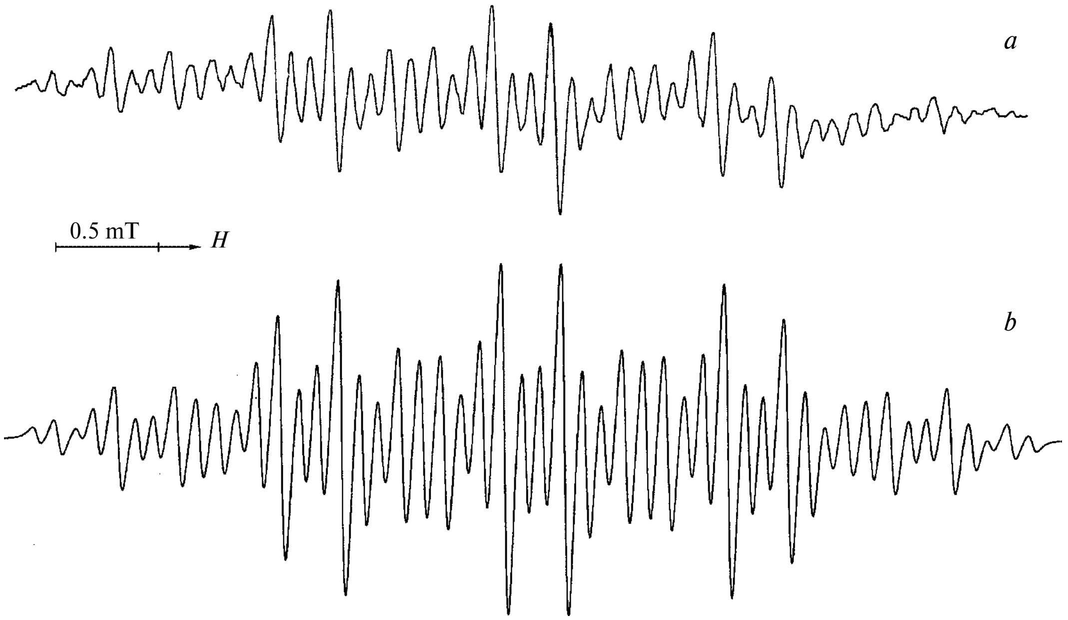


Fig. 2. ESR spectrum detected in the $(Bu^tO)_3Al$—Bu^tOOH—PhNHEt (1 : 2 : 1) system without spin traps in benzene at 293 K (degassed samples) (*a*) and the model spectrum simulated by the WINEPR SimFonia Version 1.25 program (*b*).

minor yield indicates that the attack of the oxidant is predominantly directed to the amino group of the initial compound.

The following compounds were identified as the main products of aniline oxidation (mole per mole of amine): nitrobenzene (0.12—0.14), azoxybenzene (0.28—0.36), and azobenzene (0.02).

After mixing of compounds **1** and **2** in benzene or CCl_4, in the absence of spin traps, we could not detect by ESR the unresolved singlet with ΔH = 2.5 mT and g = 2.014—2.015 belonging to the aluminum-containing peroxy radical $(Bu^tO)_2AlOO^•$.[9] No oxygen evolution was detected, which is caused by its reaction with the initial substrate.

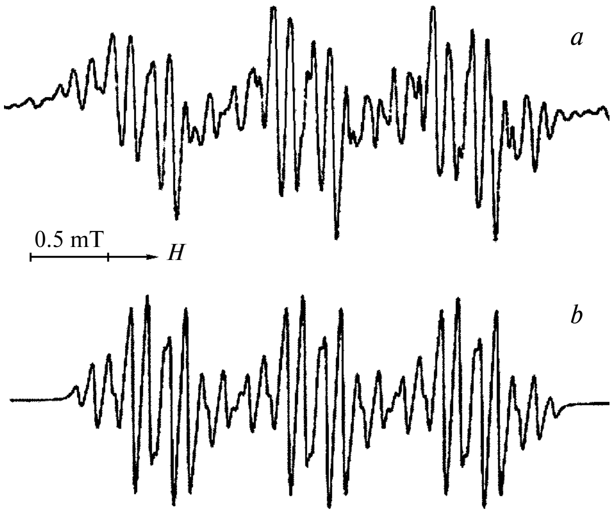


Fig. 3. ESR spectrum detected in the $(Bu^tO)_3Al$—Bu^tOOH—PhNHEt (1 : 2 : 1) system without spin traps in chlorobenzene at 286 K (degassed sample) (*a*) and the model spectrum simulated by the WINEPR SimFonia Version 1.25 program (*b*).

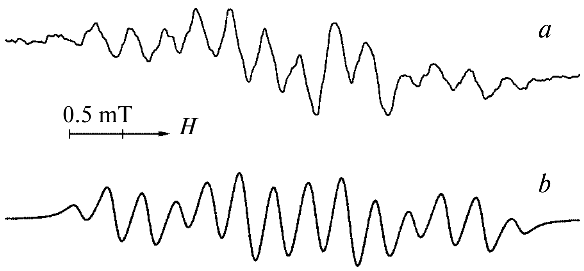


Fig. 4. ESR spectrum detected in the $(Bu^tO)_3Al$—Bu^tOOH—$PhNH_2$ (1 : 2 : 1) system in the presence of phenyl-*tert*-butylnitron in chlorobenzene at 251 K (degassed sample) (*a*) and the model spectrum simulated by the WINEPR SimFonia Version 1.25 program (*b*).

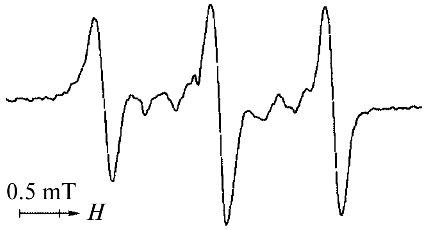
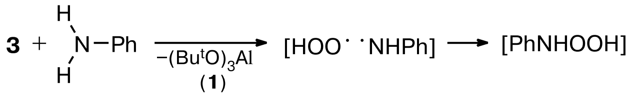
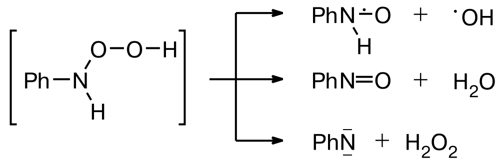


Fig. 5. ESR spectrum detected in the $(Bu^tO)_3Al$—Bu^tOOH—$Pr^i_2C_6H_3NH_2$ (1 : 2 : 1) system without spin traps in chlorobenzene at 240 K (degassed sample).

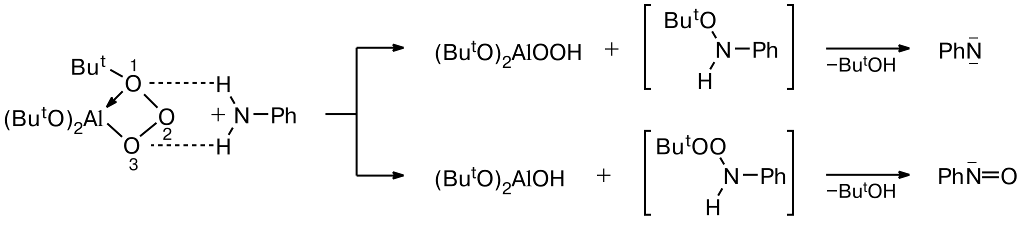
Scheme 6

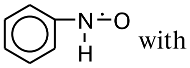


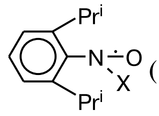
Scheme 7



Scheme 8



The expected phenylnitroxyl radical  with the constants a_N = 0.95 mT, $a_{3H}{}^{O,P}$ = 0.32 mT, and $a_H{}^N$ = 1.21 mT[17] was observed only in the presence of phenyl-*tert*-butylnitron in chlorobenzene at 251 K (Fig. 4). Probably, under the reaction conditions, this radical enters rapidly into further transformations.

In order to prove the formation of similar primary radicals, which was expected for the oxidation of the amino group, we used 2,6-diisopropylaniline. In this compound, the amino group is strongly shielded. Therefore, the reactivity of this group and intermediate radical species should differ substantially from that of the unsubstituted aniline. In fact, the oxidation of 2,6-diisopropylaniline by the **1**—**2** system in chlorobenzene at 240 K afforded the radical  (Fig. 5) with the constant a_N = 1.44 mT, which is the adduct of the X$^\bullet$ radicals, which are present in the system, with the corresponding nitrosoarene. Based on a comparison of these results with the published data,[18] we believe that X is most likely the Bu^{t}O group.

The presence of the earlier identified stable products of aniline oxidation and the ESR data suggest that hydroperoxyphenylamine is the primary oxidation product (Scheme 6).

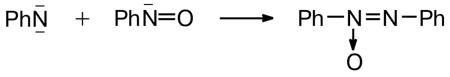
The product of this reaction, *viz.*, nitrogen-containing hydroperoxide, can undergo both homolytic and intramolecular transformations according to the general Scheme 7.

We also cannot exclude the molecular route of formation of these compounds through the activation of the O(1) or O(3) atoms by one of the H atoms *via* Scheme 8.

The dissociation energy of the O—O bond determined for organic alkyl hydrotrioxides[10] is 21—23.3 kcal mol^{-1}.

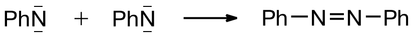
Azoxybenzene, being the main product of aniline oxidation, is formed due to the fast reaction of nitrosobenzene with phenylnitrene[17,19] (Scheme 9).

Scheme 9



The dimerization of nitrene affords azobenzene[20] (Scheme 10).

Scheme 10



It was shown in a particular experiment that azobenzene is not oxidized to azoxybenzene by the **1**—**2** system. The sole products of the oxidation of nitrosobenzene and 2-methyl-2-nitrosopropane by this system are the corresponding nitro derivatives formed in 80—90% yield at room temperature for 1 h.

The efficient reaction of phenylnitrene with nitrosobenzene (see Scheme 9) and the complete absence of spin-adducts of the latter indicate that the escape of the oxygen-centered radicals into the bulk is insignificant in this reaction and singlet dioxygen is a predominant oxidizing agent.

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