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Deoxygenation of Nitro and Nitrosoaromatics by Photolysis with *t*-BuHgI/KI. Regiochemistry of *tert*-Butyl Radical Addition to Nitrosoaromatics [1]

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ABSTRACT

Photolysis of nitroaromatics in the presence of t-BuHgI/KI in Me_2SO or DMF leads to products formed by t-Bu• addition to the nitroso compounds. Similar products are formed in the dark in the presence of $K_2S_2O_8$. Nitroso or nitrobenzene is converted into N,O-di-tert-butylphenylhydroxylamine by a process involving N-tert-butylphenylhydroxylamine as an intermediate. In the presence of PTSA and KI, N-tert-butylphenylhydroxylamine predominates in Me_2SO, but in DMF, the phenylhydroxylamine is reduced to N-tert-butylaniline. In a similar fashion, o-nitrosotoluene is converted into o-MeC_6H_4N(Bu-t)OBu-t, o-MeC_6H_4N(Bu-t)OH, and o-MeC_6H_4NHBu-t. p-Nitroso-N,N-dimethylaniline forms the N,O-di-tert-butylated derivative in the absence of acid but in the presence of PTSA/KI yields p-$Me_2NC_6H_4NHBu$-t. Excellent yields of the N,O-di-tert-butylated arylhydroxylamines are formed in DMF from the nitroaromatics with para Me_2N, OH, I, Br, Cl, and ortho Ph or PhNH substituents. Nitrobenzenes with p-CHO, p-PhCO, or p-CN substituents are deoxygenated to the nitroso compounds which react with t-Bu• to form the tert-butoxyamino radicals (ArNOBu-t). In Me_2SO, the amino radicals react to form ArN(HgI)OBu-t compounds which condense with the nitroso compounds to yield the azoxy compounds. With the p-CN substituent, the azoxy compound is subsequently deoxygenated and tert-butylated to yield p-NCC_6H_4N(Bu-t)NHC_6H_4CN-p. In the presence of PTSA/KI, the amino radicals are reduced to p-Y-ArNHOBu-t (Y = PhCO, CN). The compounds Y-ArN(Bu-t)OBu-t undergo photochemical degradation to yield Y-ArNHBu-t with Y = p-PhCO or p-CN in a reaction that is inhibited by I^-. With PTSA/H_2O/KI in Me_2SO, p-$Me_2NC_6H_4N$(t-Bu)OBu-t is converted into 4-(N-tert-butylimino)-2,5-cyclohexadien-1-one, p-$Me_2NC_6H_4NHBu$-t, and p-tert-butylamino-m-tert-butoxy-N,N-dimethylaniline. o-MeC_6H_4N(Bu-t)OH reacts with PTSA/KI to form o-MeC_6H_4N(Bu-t)H in DMF or a mixture of the aniline and 4-(N-tert-butylimino)-3-methyl-2,5-cyclohexadien-1-one in Me_2SO. In the absence of KI, only the cyclohexadienone is formed in Me_2SO.

INTRODUCTION

Photolysis of nitroaromatics (**1**) in the presence of *t*-BuHgI/KI in Me_2SO or DMF leads to deoxygenation products via electron transfer between $ArNO_2^{\bullet}$ and *t*-$BuHgI_2^-$ or I^- to yield initially the nitroso compounds (**2**) (Scheme 1a) [2].

Deoxygenation will also occur in the dark in the presence of $K_2S_2O_8$, a reagent which readily generates *t*-Bu• by Scheme 1b [3]. Deoxygenation of $ArNO_2$ appears to involve the addition of *t*-Bu• to the nitro group followed by electron transfer with *t*-$BuHgI_2^-$ or I^-. The deoxygenation reactions are not considered to involve coupling of *t*-Bu• with $ArNO_2^{\bullet-}$, since nitro radical anions readily transfer an electron to the more easily reduced alkylmercury halide in a dissociative manner.[4]

Dedicated to Prof. Antonino Fava on the occasion of his seventieth birthday.

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(a) $ArNO_2^* + t\text{-}BuHgI_2^- \longrightarrow ArNO_2^{\bullet -} + t\text{-}Bu^\bullet + HgI_2$

$ArNO_2^{\bullet -} + t\text{-}BuHgI \longrightarrow ArNO_2 + t\text{-}Bu^\bullet + Hg^\circ + I^-$

$ArNO_2 + t\text{-}Bu^\bullet \rightleftharpoons ArN(O^\bullet)OBu\text{-}t$

$ArN(O^\bullet)OBu\text{-}t + t\text{-}BuHgI_2^- \longrightarrow ArN(O^-)OBu\text{-}t + t\text{-}Bu^\bullet + HgI_2$

$ArN(O^-)OBu\text{-}t \longrightarrow ArNO + t\text{-}BuO^-$

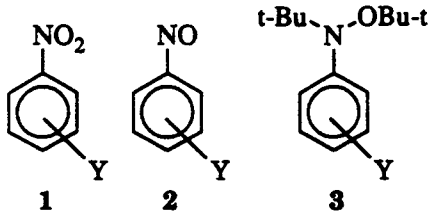
(b) $S_2O_8^{-2} + I^- \longrightarrow I^\bullet + SO_4^{-2} + SO_4^{\bullet -}$

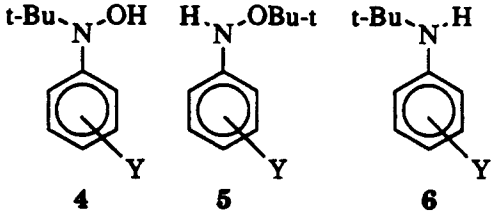
$SO_4^{\bullet -} + I^- \longrightarrow I^\bullet + SO_4^{-2}$

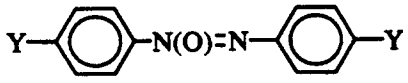
$I^\bullet + t\text{-}BuHgI \longrightarrow HgI_2 + t\text{-}Bu^\bullet$

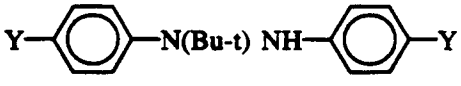
SCHEME 1

The products derived from the intermediate nitroso compounds depend upon the rate of *t*-Bu• generation, the substituents of the nitroso compound, and other reaction variables, such as the presence of bases or acids, e.g., DABCO or PTSA. The major products observed are **3–8**.



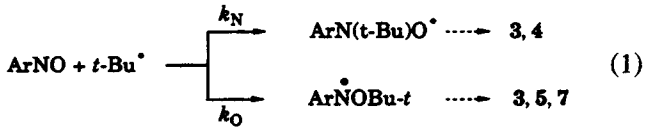




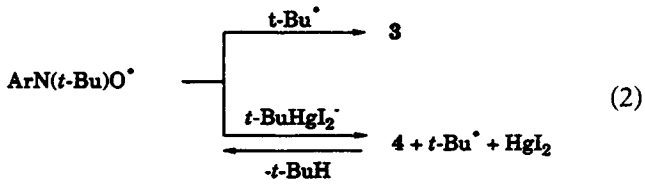


(**a**) Y = H; (**b**) Y = *o*-Me; (**c**) Y = *p*-Me_2N; (**d**) Y = *o*-PhNH; (**e**) Y = *p*-CHO; (**f**) Y = *p*-PhCO; (**g**) Y = *p*-CN; (**h**) *p*-OH; (**i**) Y = *o*-Ph; (**j**) Y = *p*-I; (**k**) Y = *p*-Br; (**l**) Y =*p*-Cl; (**m**) Y = *p*-*t*-Bu; and (**n**) Y = *p*-NO_2

The observed products reflect competitions in the reactions of the nitrosoaromatics with *t*-Bu• (Reaction 1) and in the further reactions of the nitroxyl and aminyl radicals thus formed, e.g., Reaction 2.



(1)



(2)

The competing processes of Reaction 2 and the routes to the completely deoxygenated amines **6** were further studied by the photolysis of the nitroso compounds **2a–c** with *t*-BuHgI/KI.

RESULTS AND DISCUSSION

Reactions of Nitrobenzene

Nitrobenzene (**1a**) gave no significant reaction with excess *t*-BuHgI/KI in the absence of hv or of added $K_2S_2O_8$. Photolysis of mixtures of *t*-BuHgCl and **1a** in the absence of added KI also failed to give significant reaction. Photolysis of nitrobenzene with *t*-BuHgI in the presence of KI yields mainly the di-*tert*-butylated phenylhydroxylamine **3a** which slowly undergoes homolytic aromatic substitution under forcing conditions to form the tri-*tert*-butylated derivative **3m** (Table 1). The reactions are considerably faster in DMF than in Me_2SO, which we ascribe to more rapid electron transfer in Scheme 1a.

The photolysis of **1a** with *t*-BuHgI/KI involves the slow deoxygenation to form **2a** followed by conversion to **3a**. The conversion of **2a** to **3a** involves the initial rapid formation of **4a** which is converted to **3a** slowly by Reaction 3. Because of the

$$\mathbf{4a} \xrightarrow[\text{KI (5 equiv), hv, 8 h}]{\text{t-BuHgI (5 equiv)}} \mathbf{3a}\ (65\%) + \mathbf{4a}\ (10\%) \quad (3)$$

rate of the conversions, **1a** → **2a** → **4a** → **3a**, **4a** is not usually observed as a reaction product even when unreacted **1a** remains. However, in one experiment with DABCO as an additive (Table 1), a mixture of **3a** (58%) and **4a** (39%) was observed.

Reactions of Substituted Nitroaromatics

Table 2 summarizes the products observed upon photolysis of **1c–11** with an excess of *t*-BuHgI/KI.

TABLE 1 Reaction of $PhNO_2$ (**1a**) with *t*-BuHgI/KI at 35–40°C[a]

t-BuHgI (equiv)	*KI (equiv)*	*$K_2S_2O_8$ (equiv)*	*Solvent*	*Time (Hours)*	**%3a**	**%3m**	**%1a**
5	5	—	Me_2SO	12	36	5	55
5	5	—	Me_2SO	24	58	9	30
5	5	—	Me_2SO	48	72	21	—
5	5	—	Me_2SO[b]	48	18	tr	80
5	5	—	Me_2SO[c]	25	58	tr	—
5	5	5	Me_2SO[b]	24	35	tr	16
5	10	2	Me_2SO[b]	22	38	tr	30
5	10	5	Me_2SO[b]	22	50	16	—
4	10	—	DMF	6	50	10	27
5	10	—	DMF	10	65	30	—

[a]Reaction of 0.2 mmol of **1a** in 2 mL of solvent. Reactions in the presence of $K_2S_2O_8$ were performed in the dark. In the absence of $K_2S_2O_8$, reactions were irradiated with a 275 W fluorescent sunlamp.
[b]Dark reaction.
[c]In the presence of 5 equiv of DABCO. A 39% yield of **4a** was also formed.

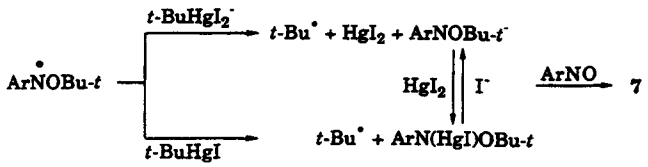
TABLE 2 Photochemical Reactions of Substituted Nitroaromatics with *t*-BuHgI/KI at 35–40°C[a]

	Equivalents				*Time*	*Products (%)*						
Substituent	*t-BuHgI*	*KI*	*Other*	*Solvent*	*(Hours)*	***3***	***4***	***5***	***6***	***7***	***8***	***1***
p-Me_2N (**1c**)	10	20	—	DMSO	20	67	—	—	12	—	—	—
p-Me_2N	10	20	$K_2S_2O_8$(2)	DMSO	20	56	—	—	11	—	—	—
o-PhNH (**1d**)	5	5	—	Me_2SO	22–24	73–90	—	—	—	—	—	—
o-PhNH	5	5	—	Me_2SO	30[b]	30	—	—	—	—	—	+
p-CHO (**1e**)	2	5	—	Me_2SO	48	4	—	—	—	56	—	tr
p-CHO	5	10	—	DMF	10	30	—	—	—	—	—	—
p-PhCO (**1f**)	4	10	—	Me_2SO	48	23	—	—	tr	47	—	—
p-PhCO	5	10	PTSA(5)	Me_2SO	13	31	—	41	—	—	—	—
p-PhCO	5	10	DABCO(5)	Me_2SO	6	27	14	4	3	17	—	—
p-PhCO	5	10	—	DMF	6	80	—	tr	tr	—	—	—
p-PhCO	5	10	PTSA(5)	DMF	2	40	—	42	tr	—	—	—
p-PhCO	5	10	PTSA(5)	DMF	6	30	—	47	13	—	—	—
p-CN (**1g**)	4	10	—	Me_2SO	24	36	—	—	15	—	38	—
p-CN	5	10	PTSA(5)	Me_2SO	5	13	—	30	—	—	tr	—
p-CN	5	10	—	DMF	6	68	—	—	tr	—	13	—
p-CN	5	10	PTSA(5)	DMF	3	14	—	37	tr	—	—	—
p-CN	5	10	PTSA(5)	DMF	8	15	—	36	tr	—	—	—
p-CN	5[c]	10	—	DMF	31	48[c]	—	—	—	—	—	—
p-HO (**1h**)	5	10	DABCO(5)	DMSO	18	72	—	—	—	—	—	26
o-Ph	5	5	DABCO(2)	DMSO	24	90	—	—	—	—	—	—
p-I (**1j**)	5	5	—	Me_2SO	30	16	28	—	6	—	—	10[d]
p-I	5	10	DABCO(5)	DMF	10	75	—	—	—	—	—	—
p-Br (**1k**)	5	10	DABCO(5)	DMF	10	67	—	—	—	—	—	—
p-Cl (**1l**)	5	10	DABCO(5)	DMF	6	52	—	—	—	—	—	—

[a]Reaction of 0.2 mmol of **1** in 2 mL of solvent with irradiation from a 275 W fluorescent sunlamp.
[b]Dark reaction.
[c]*i*-PrHgCl yielding *p*-NCC_6H_4N(*i*-Pr)OPr-*i*.
[d]*p*-$NO_2C_6H_4CMe_3$ (**1m**).

The dimeric products **7** or **8** became the predominant products in Me_2SO for **1e–1g** in sharp contrast to the products observed from **1a** or the other substituted nitroarenes studied. The amines **6** also became important products for several of the nitroaromatics. However, further experiments demonstrated that the amines are formed by secondary reactions of **3** and/or **4**.

The azoxy compounds were formed in Me_2SO from **1e** (*p*-CHO) and **1f** (*p*-PhCO), while **1g** (*p*-CN) yielded the hydrazine **8g** undoubtedly by deoxygenation of the initially formed azoxy compound followed by *tert*-butylation of the azo compound. The azo compound was found to give a high yield of **8g** upon photolysis in the presence of *t*-BuHgCl/KI, while isolated **7e** upon photolysis with *t*-BuHgI/



SCHEME 2

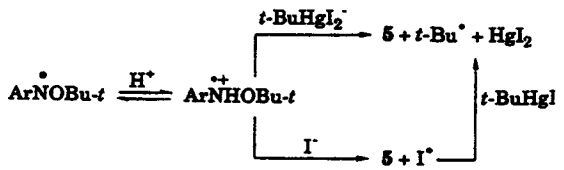
KI formed a mixture of the azo compound and the *tert*-butylated hydrazine (Reaction 4) [5].

$$\mathbf{7e} \xrightarrow[\text{DMF/hv, 10 h}]{t\text{-BuHgI/KI}} \underset{17\%}{p\text{-CHOC}_6\text{H}_4\text{N}=\text{NC}_6\text{H}_4\text{CHO-}p} + \underset{45\%}{\mathbf{8e}} \quad (4)$$

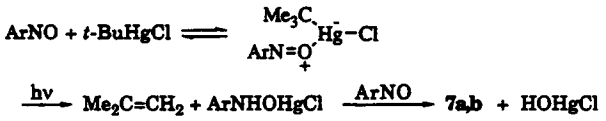
The formation of **7** (or **8**) from **1e–1g** apparently reflects the competition between addition at nitrogen or oxygen in Reaction 1 with k_O predominating with para CHO, PhCO, or CN substituents [6]. The resulting ArNOBu-*t* is most likely converted to ArN(HgI)OBu-*t* which would be expected to undergo rapid condensation with the nitroso compound (Scheme 2). In DMF, the formation of **7** or **8** is no longer important, presumably because of a more rapid generation of *t*-Bu•. The major products are now the di-*tert*-butylated derivatives **3** resulting from trapping of ArNOBu-*t*• by *t*-Bu•.

The presence of PTSA in either Me_2SO or DMF had a dramatic effect on the reaction products of **1e–1g** greatly favoring the O-*tert*-butylphenylhydroxylamine **5** over **3** or **7**. A reasonable interpretation is shown in Scheme 3, where protonation of the aminyl radical leads to a readily reduced amine radical cation. Protonolysis of ArN(HgI)OBu-*t* to yield **5** may also occur. With *i*-PrHgCl/KI in DMF, the reaction with **1g** occurred much slower than with *t*-BuHgI/KI and yielded only the *N,O*-diisopropylphenylhydroxylamine. Since the electron-transfer reactions of $RHgI_2^-$ with ArNOR• are presumably dissociative processes which would occur more rapidly with R = *t*-Bu than with R = *i*-Pr, the absence of **5** and/or **7** seems reasonable. This result also suggests that the reduction of ArNOBu-*t*• to ArNOBu-*t*$^-$ probably involves *t*-$BuHgI_2^-$ rather than I^-, since otherwise, ArNHOR or ArN(O) = NAr would have been expected with R either *i*-Pr or *t*-Bu.

Aromatic homolytic substitution was detected for **1j** (*p*-I) in Me_2SO, but it was a relatively minor process. With **1n** (*p*-NO_2), the major products observed resulted from the homolytic displacement



SCHEME 3



SCHEME 4

of NO_2 by *t*-Bu• (Reaction 5), a process not detected for **1e–1g** [7].

$$\mathbf{1n}\ (p\text{-NO}_2) \xrightarrow[\text{hv, 36 h}]{4\ t\text{-BuHgCl, 10 KI}} \mathbf{1m}\ (25\%) + \mathbf{3m}\ (20\%) + \mathbf{6n}\ (5\%) \quad (5)$$

Photostimulated Reactions of t-BuHgI/KI with the Nitrosoaromatics, 2a–2c

In this section, evidence is presented that the conversion of **2** to **3** (and therefore of **1** to **3**) proceeds mainly by the initial formation of **4**. The conversion of **2** to **4** can be formulated as a chain process (Reactions 6 and 7), while the conversion of **4** to **3**

$$\text{ArNO} + t\text{-Bu}^\bullet \rightarrow \text{ArN(Bu-}t\text{)O}^\bullet \quad (6)$$

$$\text{ArN(Bu-}t\text{)O}^\bullet + t\text{-BuHgI}_2^- \rightarrow \text{ArN(Bu-}t\text{)O}^- + t\text{-Bu}^\bullet + \text{HgI}_2 \quad [7]$$

(Reaction 3) would involve the consumption of two *t*-Bu• in a nonchain fashion. (Reaction 3 occurred only upon the photolysis of **4a** and was more efficient in the absence of PTSA than in its presence.) The addition of PTSA to the reactions of **2a,b** with *t*-BuHgI/KI increases the reaction rate and the probability that the intermediate nitroxide radical is converted to **4** (rather than trapped to form **3**) via the chain sequence involving Reactions 6, 8, and 9. The presence of PTSA can

$$\text{ArN(Bu-}t\text{)O}^\bullet + \text{PTSA} \rightleftharpoons \overset{\bullet+}{\text{ArN}}\text{(Bu-}t\text{)OH} \quad [8]$$

$$\overset{\bullet+}{\text{ArN}}\text{(Bu-}t\text{)OH} + t\text{-BuHgI}_2^- \rightarrow 4 + t\text{-Bu}^\bullet + \text{HgI}_2 \quad [9]$$

also introduce secondary ionic reaction, wherein **4a–c** (or **3c**) are converted to the amines **6a–c**.

The nitrosoaromatics **2a** or **2b** also react with *t*-BuHgCl/Me_2SO in the dark, or more readily upon sunlamp photolysis, to form the corresponding azoxy compounds in high yields [2]. However, upon irradiation with 5 equiv of *t*-BuHgI in the presence of KI, only traces of the azoxy compounds are formed and instead free radical processes leading to **3** and **4** dominate. Azoxybenzene formation with *t*-BuHgCl is accompanied by isobutene formation (from ^{1}H NMR) and apparently proceeds by Scheme 4.

(*a*) *Nitrosobenzene* (**2a**). Table 3 presents yield

TABLE 3 Photostimulated Reactions of PhNO (**2a**) with *t*-BuHgI/KI[a]

Equivalents					% Yield	
t-BuHgI	*KI*	*Other*	*Solvent*	*Time (Hours)*	***3a***	***4a***
5	10	—	Me_2SO-d_6	1	40	37
5	10	—	Me_2SO-d_6	2	58	31
5	10	—	Me_2SO-d_6	4	68	25
5	10	PTSA(5)	Me_2SO-d_6	1	3	68
5	10	PTSA(5)	Me_2SO-d_6	2	4	70
5	10	PTSA(5)	Me_2SO-d_6	4	8	77
5	10	DABCO(5)	Me_2SO-d_6	1	44	25
5	10	DABCO(5)	Me_2SO-d_6	2	50	15
5	10	DABCO(5)	Me_2SO-d_6	4	50	tr
5	10	$K_2S_2O_8$(2)	DMSO[b]	24	58	41
5	10	—	DMF	3	52	—
5	10	DABCO(5)	DMF	3	72	—
5	10	PTSA(5)	DMF	3	16	23[c]

[a]Reaction of 0.2 mmol of **2c** in 2 mL of solvent irradiated by a 275 W fluorescent sunlamp.
[b]Dark reaction.
[c]32% of **6a** formed.

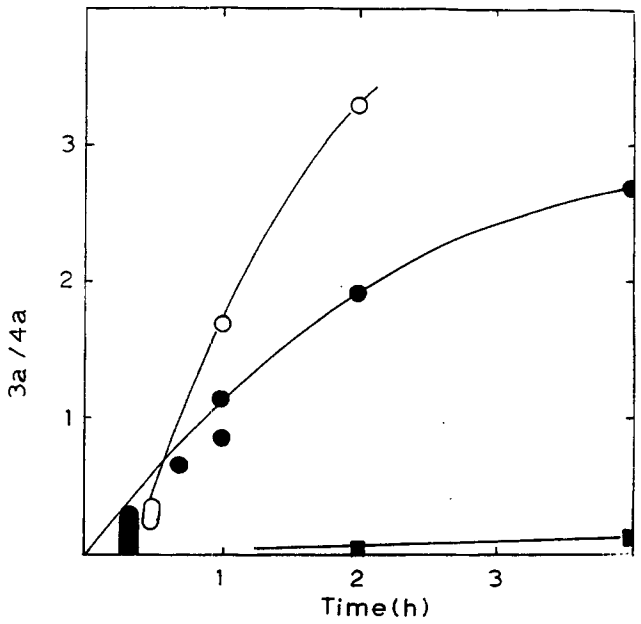


FIGURE 1 Ratio of **3a/4a** (by ^1H NMR) formed in the reactions of 1 M PhNO with 5 equiv of *t*-BuHgI and 10 equiv of KI in the absence (●) and presence of 5 equiv of DABCO (○) or PTSA (■) in Me_2SO-d_6 solution (irradiation by a 275 W fluorescent sunlamp at 35–40°C). Because ^1H NMR line broadening from PhN(*t*-Bu)O• was observed in the initial stages of the reaction, only an approximate ratio of **3a/4a** of <0.3 and of 0.2–0.3 could be obtained for the 20 minute experiment in the absence of additives or the 30 minute experiment in the presence of DABCO.

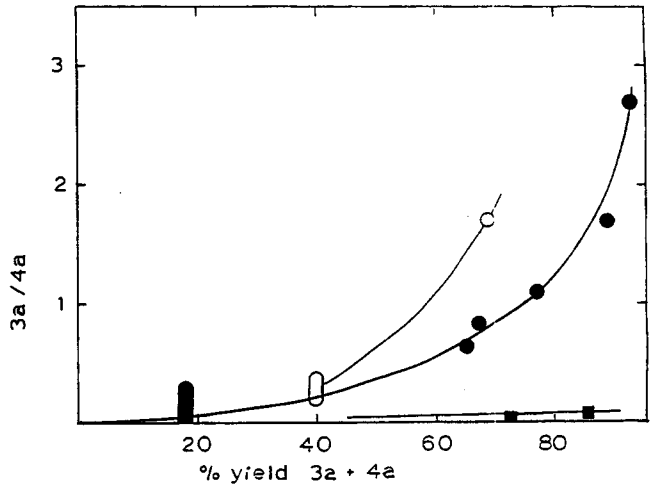


FIGURE 2 Ratio of **3a/4a** formed under the conditions of Figure 1 (●) no additive, 0–4 hours; (○) DABCO, 0–1 hours; and (■) PTSA, 0–4 hours.

data observed mainly in Me_2SO-d_6 by ^1H NMR and confirmed by isolation of the products **3a** and **4a**. The data yield the plot of Figure 1, which clearly shows that the initial reaction product is nearly exclusively **4a** from the competing processes of Reaction 2, the product **3a** being stable under the reaction conditions. At the beginning of the reaction, the steady state concentration of *t*-Bu• will be low because of the facile addition of *t*-Bu• to PhNO. Meanwhile, the concentration of *t*-$BuHgI_2^-$ will be at a maximum. This leads to the nearly exclusive formation of **4a**. Only after an appreciable fraction of the PhNO has been consumed is there an appreciable trapping of the nitroxide radical by *t*-Bu• to yield **3a**. The additions of DABCO or PTSA have appreciable effects upon the rate of the reactions. Experiments performed in the absence and presence of these reagents are plotted in Figure 2 as a function of the degree of the reaction. In the pres-

ence of DABCO, somewhat higher ratios of **3a/4a** are observed at lower conversions of **1a**, but the overall yields of **3a** and **4a** decrease at high conversions from secondary reactions (Table 3). With PTSA in Me_2SO, both **3a** and **4a** are stable and nearly exclusive formation of **4a** is observed. In the presence of PTSA, Reactions 8 and 9 occur so rapidly that there is little chance for the nitroxide radical (formed from either **1a** or **4a**) to be trapped by *t*-Bu•.

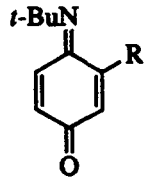
Although both **3a** and **4a** are stable in Me_2SO solution to mixtures of PTSA and KI, in DMF, **4a** but not **3a** was reduced to the amine **6a** (Reaction 10). No

$$\mathbf{4a} \xrightarrow[\text{DMF, Dark}]{\text{PTSA/KI}} \mathbf{6a}\ (100\%) \qquad (10)$$
$$3\ \text{h}$$

reaction was observed for **4a** with PTSA in the absence of KI in DMF. Possibly in DMF in the presence of PTSA, I^- reacts with PhNH(Bu-*t*)OH^+ or PhNH(Bu-*t*)I^+ by nucleophilic displacement to form **6a**.

(*b*) *o-Nitrosotoluene* (**2b**). Reaction of **2b** with *t*-BuHgCl/KI in Me_2SO again demonstrates that the ratio of **3b/4b** increases with the reaction time (Table 4). During the initial stages of the reaction, the intermediate nitroxide radical could be detected by EPR, ^1H NMR line broadening, GCMS, or by isolation via column chromatography. With *t*-BuHgI/KI, more of **4b** was formed, consistent with this reagent being a better reducing agent for the nitroxide radical.

In Me_2SO, **4b** was not reduced to **6b** by aqueous $Na_2S_2O_3$ workup. However, with aqueous $Na_2S_2O_4$ workup, **4b** was converted to **6b**. With PTSA/KI in Me_2SO or DMF, the **4b** formed from **2b** was also converted to **6b** (Table 4). At long reaction times in Me_2SO, **4b** was no longer detected and **6b** was accompanied by **9**. However, **9** was only observed in Me_2SO solution. Isolated **3b** was stable to PTSA



9, R=Me
10, R=H

in Me_2SO or DMF in the presence or absence of KI, while isolated **4b** reacted with PTSA/KI in either solvent to form **6b**. In the absence of KI, **4b** was stable to PTSA in DMF but slowly yielded **9** with PTSA in Me_2SO (Reactions 11–13).

$$\mathbf{4b} \xrightarrow[\text{DMF, 2 h}]{\text{PTSA/KI}} \mathbf{6b}\ (83\%) \qquad (11)$$

$$\mathbf{4b} \xrightarrow[\text{Me}_2\text{SO, 14 h}]{\text{PTSA/KI}} \mathbf{6b}\ (41\%) + \mathbf{9}\ (10\%) \qquad (12)$$

$$\mathbf{4b} \xrightarrow[\text{Me}_2\text{SO, 42 h}]{\text{PTSA}} \mathbf{9}\ (95\%) \qquad (13)$$

N-Alkylphenylhydroxylamines, such as PhN(Bu)OH, readily undergo acid-catalyzed rearrangements to form the *N*-alkyl-*p*-hydroxyanilines [8]. However, the *N-tert*-butylarylhydroxyamines **4a,b** were quite unreactive with mineral acids such as 2M H_2SO_4. The formation of **9** apparently involves the formation of the nitrenium ion from **4b** followed by attack of water at the para-position and acid-catalyzed oxidation of the resulting *p*-aminophenol by Me_2SO. (A similar reaction of **4a** to yield **10** was not observed.) Oxidations of 2°-alcohols by species such as Me_2SOX^+ usually require a base to remove a proton [9]. In the present example, **4b** or **9** could serve as the base in this oxidative process.

(*c*) *p-Nitroso-N,N-dimethylaniline* (**2c**). Photolysis of **2c** with *t*-BuHgI/KI in Me_2SO followed by treatment with aq $Na_2S_2O_3$ (to remove mecurials) yielded a mixture of **3c** and **6c** (Table 5). When the workup utilized only aq NaCl, **6c** was not detected upon CH_2Cl_2 extraction and an insoluble tar accompanied **3c**. Possibly, **6c** is formed from the undetected **4c** by reaction with aq $Na_2S_2O_3$. In the presence of PTSA, the photolysis of **2c** with *t*-BuHgI/KI gave an excellent yield of **6c**, presumably via the reduction of **4c** and/or **3c** (aq $Na_2S_2O_3$ workup was not required to form **6c**).

Compound **2c** reacted slowly with *t*-BuHgI/Me_2SO in the dark. After reaction for 1 week, workup with aq $Na_2S_2O_3$ yielded 14% of recovered **2c** and 30% of *N,N*-dimethyl-*p*-phenylenediamine. Apparently, the reactions of Scheme 4 occur thermally to yield *p*-$Me_2NC_6H_4NHOHgI$ which is reduced by $Na_2S_2O_3$ to the diamine upon workup. The azoxy or azo compounds were not formed in significant yields.

Further Reactions of N,O-di-tert-Butylphenylhydroxylamines

We have already described the conversion of the arylhydroxylamines **4a–c** to the anilines **6a–c** by PTSA/KI. When isolated **3c** was reacted with 5 equiv each of *t*-BuHgI, KI, and PTSA in Me_2SO for 3 hours, compound **6c** was cleanly formed in 85% yield in the dark and in 88% yield with sunlamp irradiation. However **3a**, **3b**, or **3i** gave no signifi-

TABLE 4 Photostimulated Reactions of *o*-Nitrosotoluene (**2b**) with *t*-BuHgCl/KI at 35–40°C[a]

Equivalents				Time	% Yield			
t-BuHgCl	KI	Other	Solvent	(Hours)	**3b**	**4b**	**6b**	**9**
5	10	—	Me_2SO-d_6	1.5[b]	47	39	—	—
5	10	—	Me_2SO-d_6	3[b]	57	23	—	—
5	10	—	Me_2SO-d_6	6[b]	69	20	—	—
5	10	—	Me_2SO-d_6	1.5	51	27	tr	—
5	10	—	Me_2SO-d_6	2	64	19	7	—
5	10	—	Me_2SO	2[c]	74	—	14	—
5	10	DABCO(5)	Me_2SO	2	60	7	—	—
5[d]	10	DABCO(5)	Me_2SO	2	53	20	—	—
5	10	PTSA(5)	Me_2SO	2	25	22	8	tr
5	10	PTSA(5)	Me_2SO	2[c]	31	—	17	18
5	10	PTSA(5)	Me_2SO	24	38	—	21	20
5	10	$K_2S_2O_8$(5)	Me_2SO	2	70	15	tr	—
5	10	—	DMF	2	64	—	6	—
5	10	DABCO(5)	DMF	1	89	5	—	—
5	10	PTSA(5)	DMF	2	30	—	16	—

[a]See Table 3. Workup with aq $Na_2S_2O_3$ followed by CH_2Cl_2 extraction.
[b]^1H NMR yield without workup.
[c]Workup with aq $Na_2S_2O_4$.
[d]*t*-BuHgI.

TABLE 5 Photostimulated Reactions of *p*-Nitroso-*N*,*N*-dimethylaniline (**2c**) with *t*-BuHgI/KI at 35–40°C[a]

Equivalents				Time	% Yield	
t-BuHgI	KI	Others	Solvent	(Hours)	**3c**	**6c**
5	5	—	Me_2SO	4	71	28
5	5	—	Me_2SO	4	67	0[b]
5	5	DABCO(5)	Me_2SO	8	72	17
5	10	PTSA(5)	Me_2SO	3	—	80
5	10	$K_2S_2O_8$(2)	Me_2SO[c]	3	80	—
5	5	—	DMF	4	75	—
5	5	PTSA(5)	DMF	3	—	45
5	5	DABCO(5)	DMF	1	95	tr

[a]See Table 3. Workup by aq $Na_2S_2O_3$ and CH_2Cl_2 extraction.
[b]Workup with aq NaCl.
[c]Dark reaction.

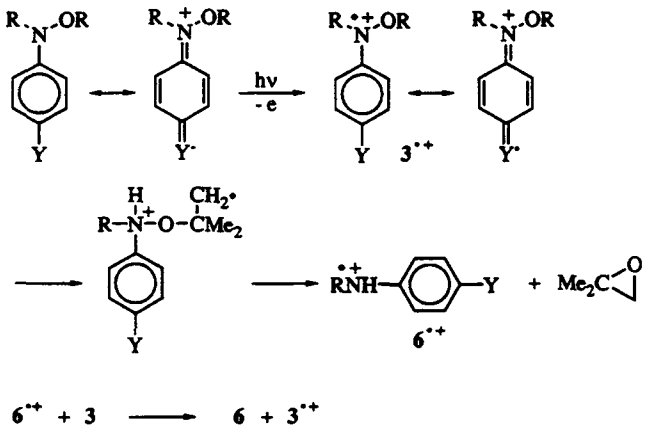
cant reaction upon photolysis in the presence or absence of PTSA or PTSA/KI. In the dark, **3f** and **3g** were also stable, but upon photolysis in the presence or absence of PTSA, the anilines **6f** and **6g** were formed (Reaction 14). Compound **3c** was also photochemically degraded to **6c** in the absence of KI or PTSA.

$$p\text{-Y-C}_6\text{H}_4\text{N(Bu-}t\text{)OBu-}t \xrightarrow[40\text{–}48\ \text{h}]{h\nu,\ Me_2SO} \begin{matrix} \mathbf{e},\ \text{Y} = Me_2N,\ 31\% \\ \mathbf{6f},\ \text{Y} = \text{COPh},\ 47\% \\ \mathbf{g},\ \text{Y} = \text{CN},\ 83\% \end{matrix} \quad (14)$$

The photochemical degradations of **3f** and **3g** are accompanied by the formation of 2,2-dimethyloxirane (from ^1H NMR). These photolyses are also retarded by I^-, which explains the relatively low yields of **6f** or **6g** in Table 2. The photochemical degradations of **3f** or **3g** were cleaner in the presence of $K_2S_2O_8$, but we were unable to achieve degradation with $K_2S_2O_8$ in the dark or degradations of **3a** or **3b** upon photolysis with $K_2S_2O_8$. The reaction products from **3f** or **3g** are well explained by a photostimulated radical cation mechanism (Scheme 5).

A similar process can be formulated for **3c** involving the easily formed *p*-phenylenediamine derivative, *p*-$Me_2NC_6H_4N$(Bu-*t*)OBu-*t*$^{\bullet+}$.

It seems unusual that a radical cation could be formed with Y = CN or PhCO (Scheme 5) but not with Y = H, *o*-Me, or *p*-I. However, as shown in Scheme 5, possibly the radical cation is stabilized by resonance with the electron-withdrawing un-



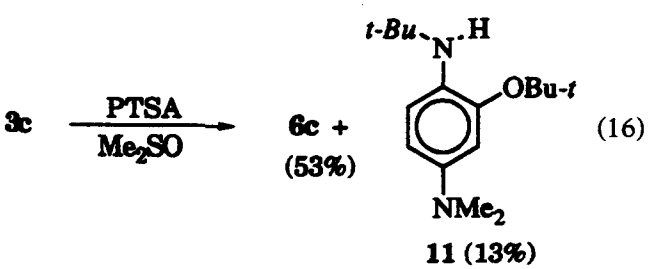
SCHEME 5

saturated substituent Y. The formation of the oxirane in an S_Hi reaction of the distonic radical cation has some precedence, since it is known to occur in the thermolysis of di-*tert*-butyl peroxide (*t*-$BuOOCMe_2CH_2^{\bullet} \rightarrow$ *t*-$BuO^{\bullet}$ + dimethyloxirane) [10].

Compound **3c** is unstable to PTSA/KI in Me_2SO and reacts in the dark to form a mixture of **10** and **6c** (Reaction 15). The ratio of **10**/**6c** in Reaction 15 varies with

$$\mathbf{3c} \xrightarrow[Me_2SO/H_2O]{\text{PTSA/KI}}_{12\text{ h}} \mathbf{10} + \mathbf{6c} \qquad (15)$$

the amount of H_2O present, and with Me_2SO (90%)–H_2O (10%), essentially only **10** is formed. Compound **10** is formed from **3c** only in the presence of KI. This suggests that the *N*-iodo compound [*p*-$Me_2NC_6H_4N$(Bu-*t*)I] may be a precursor to **10** by nucleophilic attack of H_2O at the para position. Reaction of **3c** with PTSA in the dark in Me_2SO or Me_2SO/H_2O failed to form **10** but yielded a mixture of **6c** and **11** (Reaction 16). We interpret this to mean that the nitrenium ion [*p*-$Me_2NC_6H_4N$(Bu-*t*)$^+$] is not the precursor to **10**. In the dark, **6c** and **11** are formed in approximately a 4:1 ratio which is not significantly affected by the presence of water. (Traces of **11** are also formed in Reaction 15) [11]. Apparently, upon protonation, **3c** can rearrange to **11**. Possibly in the absence of KI, the radical chain process of Scheme 5 leading to **6c** can also be initiated.



11 (13%) (16)

EXPERIMENTAL SECTION

General Procedure for the Photochemical Deoxygenation of Nitroso or Nitroarenes

The arene (0.2–1.0 mmol), *t*-BuHgI, or *t*-BuHgCl (1–5 mmol) and KI (2–10 mmol) with or without added DABCO or PTSA were placed in a pyrex test tube and 2–10 mL of deoxygenated Me_2SO or DMF was added under nitrogen. With stirring, the solution was irradiated for 1–48 hours with a 275 W General Electric fluorescent sunlamp ca. 25 cm from the reaction tube. The reaction mixture was poured into 50 mL of saturated aq $Na_2S_2O_3$ solution, neutralized if required, and extracted with CH_2Cl_2. The extract was washed with saturated aq $Na_2S_2O_3$ (3 × 50 mL) and saturated brine (50 mL), dried over anhydrous Na_2SO_4, and concentrated under vacuum. Products were isolated by flash column chromatography using 230–240 mesh, grade 60 Merck silica gel (Aldrich Chemical Co.) with hexane (95%)-ethyl acetate (5%) as the eluent.

Analytical gas chromatography was performed using a Varian 3700 gas chromatograph equipped with a Hewlett-Packard 3390A integrator using $PhCH_3$ and PhPh as internal standards and predetermined response factors. NMR spectra were recorded by a Nicolet NT 300 spectrometer with TMS as the internal standard (300 MHz for ^1H, 75.4 MHz for ^{13}C). Yields were measured by ^1H NMR from integrations with a known amount of $PhCH_3$ as an internal standard. MS spectra were recorded in the GC mode (CI or EI) with a Finnegan 4000 spectrometer. HRMS spectra were recorded with a Kratos MS-50 spectrometer. Infrared spectra were obtained in the FT mode with an IBM IR 98 spectrometer. Melting points were determined with a Thomas-Hoover apparatus and are uncorrected.

Me_2SO was distilled from CaH_2 under vacuum. Me_2SO-d_6 (Cambridge Isotope Laboratories) was dried over 4A molecular series. Compounds **1** and **2** were purchased from Aldrich Chemical Co. and used without further purification. *t*-BuHgCl was prepared from *t*-BuLi and $HgCl_2$ in THF, mp (dec) 110–113°C (Ref. [12] 117–119°C, dec); ^1H NMR ($CDCl_3$) δ 1.51 (s). *t*-BuHgI was prepared from *t*-BuHgCl and 2 equiv of KI in Me_2SO and crystallized from CH_2Cl_2 after an aqueous workup. The material decomposed upon heating; ^1H NMR ($CDCl_3$) δ 1.43 (s).

N-tert-Butoxy-N-tert-butylaniline (**3a**). Compound **3a** was isolated as a liquid; ^1H NMR ($CDCl_3$) δ 7.26–7.16 (m, 3H), 7.08–7.01 (m, 2H), 1.07 (s, 9H), 1.05 (s, 9H); ^{13}C NMR ($CDCl_3$) δ 151.1, 127.1, 126.0, 124.3, 78.0, 59.4, 28.2, 26.8; GC and HRMS, *m/z* (relative intensity) 221.1781 (M^+, 1.0, calcd for $C_{14}H_{23}NO$ 221.1780), 165(25), 148(6), 133(2), 118(9), 109(100), 91(7), 77(16), 57(81).

N-tert-Butylphenylhydroxylamine (**4a**) [13]. Com-

pound **4a** was isolated as a solid, mp 113–114°C (Ref. [12] mp 115–117°C), FTIR at 3219 cm^{-1} (Ref. [12] 3220 cm^{-1}); ^1H NMR ($CDCl_3$) δ 7.23 (d, J = 4.2 Hz, 4H), 7.20 (br·s, 1H), 7.10 (sextet, J = 4.2 Hz, 1H), 1.085 (s, 9H); ^1H NMR (Me_2SO-d_6) δ 8.25 (s, 1H), 7.21–7.16 (m, 4H), 7.04 (tt, J = 6.9, 1.5 Hz, 1H), 1.05 (s, 9H); ^{13}C NMR ($CDCl_3$) δ 149.1, 127.4, 125.1, 124.6, 60.6, 25.9; GCMS, m/z (relative intensity) 165(100), 150(2), 133(4), 118(13), 109(100), 77(21), 57(69).

N-tert-Butylaniline (**6a**) [*13*]. Compound **6a** was isolated as liquid with FTIR ($CDCl_3$) at 3404 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.15 (t, J = 7.8 Hz, 2H), 6.77–6.728 (m, 3H), 3.089 (br·s, 1H), 1.33 (s, 9H); ^{13}C NMR ($CDCl_3$) δ 146.2, 128.3, 117.7, 116.9, 50.9, 29.5; GCMS, m/z (relative intensity) 149(34), 134(100), 118(7), 106(6), 93(75), 77(18), 57(13).

N-tert-Butoxy-N-tert-butyl-o-toluidine (**3b**). Compound **3b** was isolated as a liquid; ^1H NMR ($CDCl_3$) δ 7.56 (d, J = 7.8 Hz, 1H), 7.12–6.98 (m, 4H), 2.38 (s, 3H), 1.09 (s, 9H), 1.02 (s, 9H); ^{13}C NMR ($CDCl_3$) δ 150.6, 134.5, 129.7, 127.2, 124.9, 124.6, 108.9, 60.7, 28.1, 26.2, 19.0; GC and HRMS, m/z (relative intensity) 235.12942 (M^+, 0.7, calcd for $C_{15}H_{25}NO$ 235.1936), 179(24), 164(6), 132(7), 123(100), 106(15), 91(7), 77(4), 57(38).

N-tert-Butyl-N-hydroxytoluidine (**4b**). Compound **4b** was isolated as solid, mp 78–79°C; FTIR at 3229 cm^{-1} ($CDCl_3$); ^1H NMR ($CDCl_3$) δ 7.53–7.03 (m, 4H), 5.56 (br·s, 1H), 2.29 (s, 3H), 1.15 (s, 9H); ^{13}C NMR ($CDCl_3$) δ 147.9, 134.4, 129.7, 125.8, 125.3, 125.1, 61.0, 25.3, 18.6; GC and HRMS, m/z (relative intensity) 179.1311 (M^+, 8, calcd for $C_{11}H_{17}NO$ 179.1310), 123(100), 106(96), 91(4), 77(19), 57(28).

N-tert-Butyl-(2-methylphenyl)nitroxide [*13,14*]. The nitroxide was isolated as a liquid by silica gel chromatography. The resolution of the ^1H NMR spectrum was not very good, but in $CDCl_3$, the chemical shifts were observed to be almost the same as for **4b**; GCMS, m/z (relative intensity) 178 (M^+, 4), 163(7), 148(15), 132(9), 122(37), 106(12), 91(16), 77(18), 57(100); EPR (CCl_4) a^N = 13.5 G (Ref. [14] 13.5).

N-tert-Butyl-o-toluidine (**6b**). Compound **6b** was isolated as a liquid with FTIR ($CDCl_3$) at 3441 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.10–7.04 (m, 1H), 6.90 (d, J = 7.2 Hz, 1H), 6.64 (t, J = 7.2 Hz, 1H), 2.12 (s, 3H), 1.39 (s, 9H); ^{13}C NMR ($CDCl_3$) 144.9, 130.4, 126.5, 123.6, 117.0, 114.2, 51.2, 30.2, 18.1; GC and HRMS, m/z (relative intensity) 163.1360 (M^+, 38, calcd for $C_{11}H_{17}N$ 163.1361), 148(100), 132(6), 118(3), 107(68), 106(53), 91(10), 77(10), 57(10).

p-Dimethylamino-N-tert-butoxy-N-tert-butylaniline (**3c**). Compound **3c** was isolated as a solid, mp 110–111°C; ^1H NMR ($CDCl_3$) δ 7.13 (br·s, 2H), 6.61 (d, J = 9.0 Hz, 2H), 2.91 (s, 6H), 1.051 (s, 9H), 1.046 (s, 9H); ^{13}C NMR ($CDCl_3$) δ 147.8, 141.8, 126.7, 111.9, 77.4, 59.2, 40.9, 28.2, 26.8; GC and HRMS, m/z (relative intensity) 264.2196 (M^+, 11, calcd for $C_{16}H_{28}N_2O$ 264.2202), 248(0.1), 208(1.3), 166(100), 150(3), 136(19), 119(29), 105(16), 91(11), 77(24), 57(0.4).

p-Dimethylamino-N-tert-butylaniline (**6c**). Compound **6c** was isolated as a liquid with FTIR at 3327 cm^{-1}; ^1H NMR ($CDCl_3$) δ 6.79 (dd, J = 8.7, 2.1 Hz, 2H), 6.65 (dd, J = 9.0, 2.1 Hz, 2H), 2.86 (s, 6H), 1.19 (s, 9H); ^{13}C NMR ($CDCl_3$) δ 146.2, 136.7, 123.8, 113.8, 52.3, 41.4, 30.1; GC and HRMS, m/z (relative intensity) 192.1627 (M^+, 75, calcd for $C_{12}H_{20}N_2$ 192.1627), 177(62), 135(100), 121(38), 88(29), 57(6).

2-(N-tert-Butoxy-N-tert-butylamino)diphenylamine (**3d**). Compound **3d** was isolated as a liquid with FTIR at 3366 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.51–6.76 (m, 9H), 1.13 (s, 9H), 1.09 (s, 9H); ^{13}C NMR ($CDCl_3$) δ 142.7, 139.5, 138.9, 129.3, 127.2, 125.8, 121.0, 118.7, 118.3, 113.8, 77.6, 60.5, 28.0, 26.1; GC and HRMS, m/z (relative intensity) 312.2205 (M^+, 23, calcd for $C_{20}H_{28}N_2O$ 312.2202), 256(40), 239(52), 199(47), 183(100).

2-(N-tert-Butylamino)diphenylamine (**6d**). Compound **6d** was isolated as a liquid with FTIR at 3375 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.22–6.70 (m, 9H), 5.31 (s, 1H), 3.92 (s, 1H), 1.28 (s, 9H); ^{13}C NMR ($CDCl_3$) δ 145.5, 141.5, 131.4, 129.1, 124.7, 124.1, 119.3, 118.4, 117.1, 115.5, 51.3, 29.9; GC and HRMS, m/z (relative intensity) 240.1628 (M^+, 59, calcd for $C_{16}H_{20}N_2$ 240.1626), 225(27), 184(100), 183(63), 182(54), 169(33), 77(21), 57(25).

p-(N-tert-Butoxy-N-tert-butylamino)benzaldehyde (**3e**). Compound **3e** was isolated as a solid, mp 40–45°C; ^1H NMR ($CDCl_3$) δ 9.93 (s, 1H), 7.76 (dd, J = 9.0, 1.5 Hz, 2H), 7.42 (br·s, 2H), 1.12 (s, 9H), 1.07 (s, 9H); GC and HRMS, m/z (relative intensity) 249.1729 (M^+, 0.9, calcd for $C_{15}H_{23}NO_2$ 249.1729), 193(20), 137(100), 91(3), 77(5), 57(69).

4,4'-Azoxybenzaldehyde (**7e**). Compound **7e** was isolated as a solid, mp 190–191°C; ^1H NMR ($CDCl_3$) δ 10.2 (s, 1H), 10.1 (s, 1H), 8.51 (d, J = 8.7 Hz, 2H), 8.28 (d, J = 8.7 Hz, 2H), 8.07 (dd, J = 8.7, 1.5 Hz, 2H), 8.02 (dd, J = 8.4, 1.5 Hz, 2H); GC and HRMS, m/z (relative intensity) 254.0686 (M^+, 19, calcd for $C_{14}H_{10}N_2O_3$ 254.0691), 226(3), 169(3), 133(20), 119(5), 115(3), 105(100), 77(43).

4,4'-Azobenzaldehyde. This compound was isolated as a solid, mp 231–232°C; ^1H NMR ($CDCl_3$) δ 10.13 (s, 2H), 8.08 (td, J = 8.7, 2.4 Hz, 8H); HRMS, m/z (relative intensity) 238.0743 (M^+, 46, calcd for $C_{14}H_{10}N_2O_2$ 238.0742), 207(2), 133(4), 105(100), 77(4).

N-tert-Butyl-4,4'-hydrazobenzaldehyde (**8e**). Compound **8e** was isolated as a solid, mp 142–143°C; ^{1}H NMR ($CDCl_3$) δ 9.88 (s, 1H), 9.74 (s, 1H), 7.77 (d, J = 8.7, 2H), 7.71 (d, J = 8.7, 2H), 7.30 (d, J = 8.7, 2H), 6.91 (d, J = 8.7, 2H), 6.36 (br·s, 1H), 1.38 (s, 9H), HRMS, m/z (relative intensity) 296.1523 (M^+, 6, calcd $C_{18}H_{20}N_2O_2$ 296.1525), 240(100), 211(12), 182(3), 146(6), 133(2), 120(8), 105(13), 77(10), 57(15).

4,4'-Azoxybenzophenone (**7f**). Compound **7f** was isolated as a solid, mp 198.5–199.5°C; ^{1}H NMR ($CDCl_3$) δ 8.16 (dd, J = 9.0, 1.8 Hz, 2H), 8.26 (dd, J = 8.4, 1.8 Hz, 2H), 7.98–7.18 (m, 14H); ^{13}C NMR ($CDCl_3$) δ 217.3, 217.0, 195.5, 195.2, 150.2, 146.5, 140.6, 138.0, 137.2, 136.7, 133.1, 132.6, 130.6, 130.0, 128.5, 128.4, 127.3, 122.5; GC and HRMS, m/z (relative intensity) 406, 1320 (M^+, 65, calcd for $C_{26}H_{18}N_2O_3$ 406.1317), 390(6), 197(10), 181(46), 153(15), 105(100), 77(30).

p-(N-tert-Butoxy-N-tert-butylamino)benzophenone (**3f**). Compound **3f** had ^{1}H NMR ($CDCl_3$) δ 7.81–7.38 (m, 9H), 1.13 (s, 9H), 1.08 (s, 9H); ^{13}C NMR ($CDCl_3$) δ 196.0, 138.1, 133.4, 131.9, 129.8, 129.7, 128.1, 125.3, 78.7, 60.1, 28.1, 26.9; GC and HRMS, m/z (relative intensity) 326.2113 (M + 1$^+$, 2, calcd for $C_{21}H_{28}NO_2$ 326.2120), 325.2052 ($C_{21}H_{27}NO_2^+$, 0.5), 269(15), 252(3), 238(2), 213(100), 182(1), 136(13), 105(24), 77(15), 57(64); GCMS (CI, ammonia) 343 (M + 18$^+$, 19), 326 (M + 1$^+$, 100), 254(22).

p-(N-tert-Butyl-N-hydroxyamino)benzophenone (**4f**). Compound **4f** was isolated as a solid, mp 131–132°C; FTIR ($CDCl_3$) at 3427, 1655 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 7.76–7.70 (m, 4H), 7.57 (t, J = 7.2, 1H), 7.46 (t J = 7.2, 2H), 7.32 (d, J = 8.4, 2H), 6.62 (br·s, 1H), 1.17 (s, 9H); ^{13}C NMR ($CDCl_3$) δ 195.9, 153.5, 137.8, 133.8, 132.0, 129.8, 128.1, 123.7, 61.3, 26.0, HRMS, m/z (relative intensity) 269.1410 (M^+, 5, calcd for $C_{17}H_{19}NO_2$ 269.1416), 253.1470 (M − 16$^+$, 13, calcd for $C_{17}H_{19}NO$ 253.1467), 278(40), 222(12), 213(100), 136(31), 120(30), 105(57), 77(30), 57(57). Anal. calcd for $C_{17}H_{19}NO_2$: C, 75.81; H, 7.11; N, 5.20. Found: C, 75.83; H, 7.28; N, 5.15.

p-(N-tert-Butoxyamino)benzophenone (**5f**). Compound **5f** was isolated as a solid, mp 103.5–104.0°C; FTIR ($CDCl_3$) at 3277, 1645 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 7.80–7.73 (m, 2H), 7.54 (tt, J = 7.2, 1.5 Hz, 1H), 7.46 (tt, J = 7.2, 1.5, 2H), 6.96 (d, J = 8.7, 2H), 6.82 (br·s, 1H), 1.320 (s, 9H); ^{13}C NMR ($CDCl_3$) δ 195.5, 153.9, 138.5, 132.0, 131.6, 130.0, 129.6, 128.1, 112.5, 79.8, 26.5; HRMS, m/z (relative intensity) 269.1413 (M^+, 3, calcd for $C_{17}H_{19}NO_2$ 269.1416), 213(100), 196(8), 168(18), 136(49), 105(21), 77(25), 57(30). Anal. calcd for $C_{17}H_{19}NO_2$: C, 75.81; H, 7.11; N, 5.20. Found: C, 75.37; H, 7.20; N, 5.07.

p-(N-tert-Butylamino)benzophenone (**6f**). Compound **6f** was isolated as a solid, mp 195–197°C; FTIR ($CDCl_3$) at 3362, 1637 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 7.73–7.70 (m, 4H), 7.52 (tt, J = 7.2, 1.2 Hz, 1H), 7.44 (tt, J = 7.2, 1.2 Hz, 2H), 6.66 (d, J = 8.7, 2H), 1.43 (s, 9H); ^{13}C NMR ($CDCl_3$) δ 195.0, 151.0, 139.1, 132.7, 131.1, 129.4, 128.0, 125.5, 113.4, 51.4, 29.7: GC and HRMS, m/z (relative intensity) 253.1463 (M^+, 59, calcd for $C_{17}H_{19}NO_2$ 253.1467), 238(100), 197(24), 120(93), 105(51), 77(43), 57(17); GCMS (CI, ammonia), 507 (2M + 1$^+$, 3), 271 (M + 18$^+$, 0.1), 254 (M + 1$^+$, 100).

N-tert-Butyl-4,4'-dicyanohydrazobenzene (**8g**). Compound **8g** was isolated as a solid, mp 62–65°C with FTIR at 3312, 2250, 2214 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 7.52 (d, J = 8.7 Hz, 2H), 7.41 (d, J = 8.7 Hz, 2H), 7.27 (d, J = 8.7 Hz, 2H), 6.89 (d, J = 8.7 Hz, 2H), 6.68 (s, 1H), 1.32 (s, 9H); ^{13}C NMR ($CDCl_3$) δ 152.0, 151.7, 133.6, 132.4, 132.2, 120.2, 119.0, 111.5, 106.0, 100.1, 60.6, 27.3; GC and HRMS, m/z (relative intensity) 290.1530 (M^+, 13, calcd for $C_{18}H_{18}N_4$ 190.1532), 234(100), 207(2), 143(5), 117(8), 102(21), 57(60).

4,4'-Azoxybenzonitrile (**7g**). Traces of **7g** were isolated from the reaction of **7g** with *t*-BuHgI/KI in Me_2SO. The compound had mp 214–216°C; ^{1}H NMR ($CDCl_3$) δ 8.46 (dt, J = 9.0, 1.2 Hz, 2H), 8.23 (dt, J = 8.7, 1.2 Hz, 2H), 7.87 (dt, J = 8.7, 1.2 Hz, 2H), 7.79 (dt, J = 8.7, 1.2 Hz, 2H); HRMS, m/z (relative intensity) 248.0699 (M^+, 18, calcd for $C_{14}H_8N_4O$ 248.0698), 232(6), 220(7), 130(28), 116(22), 102(100).

p-(N-tert-Butoxy-N-tert-butylamino)benzonitrile (**3g**). Compound **3g** was isolated as a liquid with FTIR at 2226 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 7.52 (d, J = 8.7 Hz, 2H), 7.38 (br, 2H), 1.09 (s, 9H), 1.05 (s, 9H); ^{13}C NMR ($CDCl_3$) δ 156.9, 131.4, 126.2, 119.2, 107.6, 79.0, 60.3, 28.0, 26.8; GC and HRMS, m/z (relative intensity) 246.1732 (M^+, 0.3, calcd for $C_{15}H_{25}N_2O$ 246.1732), 190(22), 173(10), 143(9), 134(77), 102(8), 75(2), 57(100); GCMS (CI, ammonia) 510 (2M + 18$^+$, 2), 493 (2M + 1$^+$, 0.4), 281 (M + 35$^+$, 67), 264 (M + 18$^+$, 100), 247(M + 1, 18).

p-(N-tert-Butoxyamino)benzonitrile (**5g**). Compound **5g** was isolated as a solid, mp 80–81°C; FTIR ($CDCl_3$) at 3281, 2220 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 7.51 (dd, J = 8.7, 1.5), 6.94 (dt, J = 8.7, 1.5), 6.78 (br·s, 1H), 1.30 (s, 9H); ^{13}C NMR ($CDCl_3$) δ 153.6, 133.0, 119.7, 113.2, 102.7, 79.8, 26.3; GC and HRMS, m/z (relative intensity) 190.1106 (M^+, 10, calcd for $C_{11}H_{14}N_2O$ 190.1106), 174(2), 159(6), 134(100), 117(40), 90(6), 57(90); GCMS (CI, ammonia) 398 (2M + 18$^+$, 4), 225 (M + 35$^+$, 100), 208 (M + 18$^+$, 86), 191 (M + 1$^+$, 1.4); Anal. calcd for $C_{11}H_{14}N_2O$: C, 69.45; H, 7.42; N, 14.72. Found: C, 69.15; H, 7.47; N, 14.47.

p-(N-tert-Butylamino)benzonitrile (**6g**). Compound **6g** was isolated as liquid with FTIR ($CDCl_3$)

at 3381, 2212 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.38 (dt, J = 8.7, 1.8), 6.62 (dt, J = 8.7, 1.8), 4.20 (br·s, 1H), 1.40 (s, 9H); ^{13}C NMR ($CDCl_3$) δ 150.2, 133.3, 120.5, 114.1, 98.0, 51.3, 29.5; GC and HRMS, m/z (relative intensity) 174.1158 (M^+, 19, calcd for $C_{11}H_{14}N_2$ 174.1157), 159(63), 143(4), 131(2), 118(100), 102(8), 84(0.2), 57(51); GCMS (CI, ammonia) 366 ($2M + 18^+$, 0.9), 349 ($2M + 1^+$, 1.5), 209 ($M + 35^+$, 38), 192 ($M + 18^+$, 100), 175 ($M + 1^+$, 79).

N-tert-Butoxy-N-tert-butyl-p-hydroxyaniline (**3h**). Compound **3h** was isolated as a solid, mp 111–112°C; ^1H NMR ($CDCl_3$) δ 7.13 (br·s, 2H), 6.70 (d, J = 9.0 Hz, 2H), 4.86 (br·s, 1H), 1.05 (s, 9H), 1.04 (s, 9H); GC and HRMS, m/z (relative intensity) 237.1725 (M^+, 3.4, calcd for $C_{14}H_{23}N_2$ 237.1729), 181(29), 125(100), 108(35), 57(35).

N-tert-Butoxy-N-tert-butyl-o-phenylaniline (**3i**). Compound **3i** was isolated as a solid, mp 93–94°C; ^1H NMR ($CDCl_3$) δ 7.81 (dd, J = 8.1, 1.2 Hz, 1H), 7.70 (dd, J = 8.4, 1.2, 2H), 7.28–7.12 (m, 6H), 1.209 (s, 9H), 0.821 (s, 9H); ^{13}C NMR ($CDCl_3$) δ 149.7, 142.6, 136.8, 130.7, 129.9, 127.6, 126.9, 126.6, 126.2, 125.0, 77.8, 62.0, 28.4, 26.4; GCMS, m/z (relative intensity) 297 (M^+, 17), 281(45), 266(72), 250(12), 241(53), 210(60), 185(70), 167(29), 57(45); Anal. calcd for $C_{20}H_{27}NO$: C, 80.76; H, 9.15; N, 4.71. Found: C, 80.70; H, 9.21; N, 4.41.

p-Iodo-N-tert-butoxy-N-tert-butylaniline (**3j**). Compound **3j** was isolated as a solid, mp 75–78°C; ^1H NMR ($CDCl_3$) δ 7.52 (d, J = 8.7 Hz, 2H), 7.02 (br·s, 2H), 1.06 (s, 9H), 1.04 (s, 9H); GC and HRMS, m/z (relative intensity) 347.0741 (M^+, 0.6, calcd for $C_{14}H_{22}INO$ 347.0746), 291(16), 235(17), 218(5), 127(0.1), 108(4), 91(2), 77(2), 76(7), 57(100).

N-tert-Butyl-p-iodophenylhydroxylamine (**4j**). Compound **4j** was isolated as a solid, mp, 119–120°C with FTIR at 3381 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.53 (d, J = 8.4 Hz, 2H), 6.95 (d, J = 8.7 Hz, 2H), 1.08 (s, 9H); GC and HRMS, m/z (relative intensity) 291.0114 (M^+, 17, calcd for $C_{10}H_{14}INO$ 291.0120), 275(49), 260(100), 235(95), 218(30), 127(8), 57(90); CI (ammonia), m/z (relative intensity) 309 ($M + 18^+$, 27), 292 ($M + 1^+$), 276(100), 166(14), 150(14).

p-Iodo-N-tert-butylaniline (**6j**). Compound **6j** was isolated as a liquid with FTIR at 3410 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.38 (d, J = 8.4 Hz, 2H), 6.50 (d, J = 8.7 Hz, 2H), 3.29 (br·s, 1H), 1.32 (s, 9H); GC and HRMS, m/z (relative intensity) 275.0167 (M^+, 54, calcd for $C_{10}H_{14}IN$ 275.0171), 260(94), 244(3), 219(100), 148(4), 77(5), 57(49).

p-Bromo-N-tert-butoxy-N-tert-butylaniline (**3k**). Compound **3k** was isolated as a solid, mp 38–39°C; ^1H NMR ($CDCl_3$) δ 7.3 (dd, J = 9.0, 1.2 Hz, 2H), 7.15 (br·s, 2H), 1.06 (s, 9H), 1.04 (s,9H); GC and HRMS, m/z (relative intensity) 299.0881 (M^+, 0.6, calcd for $C_{14}H_{22}BrNO$ 299.0885), 245(8), 243(10), 228(3), 226(2), 189(41), 187(39), 108(2), 91(2), 77(1), 57(100).

p-Chloro-N-tert-butoxy-N-tert-butylaniline (**3l**). Compound **3l** was isolated as a liquid; ^1H NMR ($CDCl_3$) δ 7.18 (m, 4H), 1.06 (s, 9H), 1.05 (s, 9H); GC and HRMS, m/z (relative intensity) 257(1), 255.1386 (M^+, 3, calcd for $C_{14}H_{22}ClNO$ 255.1390), 201(7), 199(18), 184(3), 182(5), 145(25), 143(86), 128(2), 126(5), 113(2), 111(5), 57(100).

N-tert-Butoxy-p,N-di-tert-butylaniline (**3m**). Compound **3m** was isolated as a liquid; ^1H NMR ($CDCl_3$) δ 7.20–7.13 (m, 4H), 1.29 (s, 9H), 1.07 (s, 9H), 1.04 (s, 9H); GC and HRMS, m/z (relative intensity) 277.2401 (M^+, 1.1, calcd for $C_{18}H_{31}NO$ 277.2406), 221(22), 165(100), 150(71), 91(3), 77(2), 57(39).

p-Nitro-N-tert-butylaniline (**6n**). Compound **6n** was isolated as a liquid; ^1H NMR ($CDCl_3$) δ 8.04 (ddd, J = 9.0, 3.6, 1.5 Hz, 2H), 6.60 (ddd, J = 9.3, 3.3, 1.5 Hz, 2H), 4.57 (br·s, 1H), 1.44 (s, 9H); GC and HRMS, m/z (relative intensity) 194.1055 (M^+, 27, calcd for $C_{10}H_{14}N_2O_2$ 194.1055), 179(100), 138(38), 108(19), 92(17), 91(6), 77(4), 57(72).

Reaction of 3b with PTSA. The reaction of compound **3b** (0.2 mmol) and PTSA·H_2O (0.2 mmol) in 1 mL of Me_2SO-d_6 was followed by ^1H NMR. After 42 hours, compound **3b** was no longer detected. Workup yielded **9** in 95% yield. Reaction of **3b** (0.2 mmol) with PTSA·H_2O (0.4 mmol) and KI (0.7 mmol) in 1 mL of Me_2SO-d_6 for 14 hours gave upon workup 41% of **6b** and 10% of **9**. Reaction of **3b** (0.2 mmol) with PTSA·H_2O (1.4 mmol) and KI (1.4 mmol) in 2 mL of DMF for 2 hours gave **6b** in 83% yield. There was no reaction observed between **3b** and PTSA in DMF in the absence of KI.

4-tert-Butylimino-3-methyl-2,5-cyclohexadien-1-one (**9**). Compound **9** was isolated as a liquid with FTIR ($CDCl_3$) at 1653 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.3 (d, J = 11.1 Hz, 1H), 6.46–6.44 (m, 1H), 6.41 (dd, J = 11.2, 2.4 Hz, 1H), 2.1 (d, J = 1.2 Hz, 3H), 1.451 (s, 9H); ^{13}C NMR ($CDCl_3$) δ 187.6(s), 155.6(s), 152.2(s), 130.8(d), 129.2(d), 128.4(d), 57.9(s), 32.0(q), 18.8(q). The compound slowly dimerized after isolation and before the HRMS was obtained, m/z (relative intensity) 354.2301 ($2M^+$ calcd for $C_{22}H_{30}N_2O_2$ 354.2307). The GCMS of freshly isolated material was 177 (M^+, 25), 162(68), 121(36), 93(7), 78(7), 57(100).

4-N-tert-Butylimino-2,5-cyclohexadien-1-one (**10**). Compound **3c** (0.2 mmol), KI (1 mmol), and PTSA·H_2O (1 mmol) were dissolved in 5 mL of Me_2SO and stirred for 12 hours. The solution was added to water and neutralized with aq NaOH. Extraction by CH_2Cl_2 followed by drying and solvent evaporation gave an oily mixture which by ^1H NMR with toluene as an internal standard con-

tained 12% of **3c**, 7% of **6c**, 7% of **11**, and 72% of **10**. Compound **10** decomposed when chromatography was attempted with silica gel or alumina. The crude mixture had FTIR absorptions at 1657 and 1618 cm^{-1}, which are assigned to the C = O and C = N of **10**. The GCMS of **10** gave *m/z* (relative intensity) 163 (M^+, 7), 148(98), 133(12), 120(2), 107(14), 77(3), 57(100); ^1H NMR ($CDCl_3$) δ 7.39 (dd, J = 10.5, 2.7 Hz, 1H), 7.01 (dd, J = 10.2, 2.7 Hz, 1H), 6.54 (dd, J = 10.8, 2.4 Hz, 1H), 6.51 (dd, J = 10.8, 2.4 Hz, 1H), 1.47 (s, 9H); ^{13}C NMR ($CDCl_3$) 187.2(s), 156.1(s), 145.7(d), 131.8(d), 131.1(d), 128.1(d), 58.5(s), 32.0(q).

m-tert-Butoxy-p-(tert-butylamino)-N,N-dimethylaniline (**11**). Reaction of **3c** with excess PTSA · H_2O in Me_2SO for 3 hours formed 53% of **6c** and 13% of **11**. Compound **11** was isolated as a yellow liquid; ^1H NMR ($CDCl_3$) δ 6.90 (d, J = 8.7, 1H), 6.53 (d, J = 2.7, 1H), 6.43 (dd, J = 8.7, 2.7 Hz, 1H), 3.77 (br · s, 1H), 2.83 (s, 6H), 1.39 (s, 9H), 1.25 (s, 9H); ^{13}C NMR ($CDCl_3$) δ 146.8(s), 144.6(s), 132.6(s), 119.6(d), 109.3(d), 108.8(d), 79.4(s), 52.1(s), 41.8(q), 30.2(q), 29.2(q); HMRS, *m/z* (relative intensity) 264.2211 (M^+, 46, calcd for $C_{16}H_{28}N_2O$ 264.2196), 208(100), 193(56), 177(15), 137(25), 123(99), 57(10). Anal. calcd for $C_{16}H_{28}N_2O$: C, 72.68; H, 10.67; N, 10.60. Found: C, 72.69; H, 10.63; N, 10.35.

Photodegradation of **3**. Compounds **3f** and **3g** were photolyzed in Me_2SO-d_6 by a 275 W sunlamp. The only aromatic products observed were **6f** (47% in 40 hours) and **6g** (83% in 42 hours). Also observed were two ^1H NMR signals at δ 2.066 and 1.095 in the ratio of 1:3. These two peaks are believed to belong to 1.1-dimethyloxirane. The yield of **6f** increased to 60% upon photolysis for 40 hours in the presence of 30 mol% of $K_2S_2O_8$.

Photolysis of **3c** and **3d** in Me_2SO in the presence of $K_2S_2O_8$ for 14 hours produced the amines **6c** and **6d** in yields of 31 and 50%, respectively.

Thermal Reaction of **2c** *with t-BuHgI*. Reaction of 0.2 mmol of **2c** and 1.0 mmol of *t*-BuHgI in 2 mL of Me_2SO for 1 week gave by ^1H NMR analysis 14% of unreacted **2c** and 30% of *N,N*-dimethyl-*p*-phenylenediamine. Column chromatography with basic alumina using hexane (90%)-ethyl acetate (10%) as eluent gave the pure diamine whose IR and ^1H NMR spectra were identical with material obtained from Aldrich Chemical Company.

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[5] The isolated azoxy compound **7f** was also destroyed by further photolysis with *t*-BuHgI/KI in Me_2SO. However, in this case, the azo or hydrazo compounds were not formed in significant yields. Among the products observed was the *N-tert*-butylarylhydroxylamine **4f**. The **4f** reported in Table 2 in only one experiment may well have been formed by further reaction of the initially formed **7f**. The addition of *t*-Bu$^\bullet$ to **2f** may occur only at oxygen. Alternately, if all the **3f** observed (Table 2) comes from *p*-$PhCOC_6H_4N(Bu\text{-}t)O^\bullet$ (and none from *p*-$PhCOC_6H_4NOBu\text{-}t^\bullet$), the value of k_O/k_N for **2f** may be as low as one.
[6] A number of β-nitrostyrene derivatives react with *t*-BuHgI/KI/hv to yield products derived from $PhC(R^1)=C(R^2)N(HgI)OBu\text{-}t$ [2] (with R^1=Ph the major product observed on the 2,2-diphenyl-3-R^2-2*H*-azirines or the 3-phenyl-2-R^2-indoles). Apparently, nitrosoalkenes also are attacked by *t*-Bu$^\bullet$ to yield mainly the resonance-stabilized amino radical, $PhC(R^1)=C(R^2)\dot{N}OBu\text{-}t$.
[7] The 1-adamantyl radical attacks **1e–1g** as well as **1n** to displace a nitro group; L. Testaferri, M. Tiecco, M. Tingoli, M. Fiorentino, L. Troisi, *J. Chem. Soc., Chem. Commun.*, 1978, 93. The absence of denitration with *t*-Bu$^\bullet$ for **1e–1g** is rather surprising but may be a result of the rapid formation of **2** in Scheme 1a followed by the efficient trapping of *t*-Bu$^\bullet$ by **2** and/or $Ar\dot{N}OBu\text{-}t$.
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[11] Since neither **3c**, **10** or **11** is observed in the reaction of **2c** with *t*-BuHgI/KI/PTSA in Me_2SO or DMF, it appears that the **6c** observed (Table 5) is formed by the rapid reduction of undetected **4c**.
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