Heteroatom Chemistry
Volume 3, Number 3, 1992

Reactions of β-Nitrostyrenes with *tert*-Butylmercury Halides in the Presence of Iodide Ion[1]

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Received: 13 December 1991.

ABSTRACT

*Photolysis of t-BuHgCl/KI with $PhC(R^2)=C(R^1)NO_2$ forms $PhC(R^2=C(R^1)Bu\text{-}t$ when $R^1 = R^2 = H$ or in low yield when $R^1 = H$, $R^2 = Ph$. When $R^1 \neq H$, or when $R^2 = Ph$, reactions with t-BuHgI/KI/hv proceed mainly via $PhC(R^2)=C(R^1)NO_2{}^{\bullet -}$, $PhC(R^2)=C(R^1)N(OBu\text{-}t)O^-HgX^+$, $PhC(R^2)=C(R^1)N=O$ and $PhC(R^2)=C(R^1)N(OBu\text{-}t)HgX$ to form a variety of novel products including the dimeric bisnitronic esters (**6**) with R^1 = Me or Ph and $R^2 = H$; $PhCH(R^2)C(R^1) = NOBu\text{-}t$ with R^1 = Me or Ph and $R^2 = H$ or $R^1 = H$ and $R^2 = Ph$; $PhC(R^2)(OBu\text{-}t)C(R^1)=NOH$ with $R^1 = H$ or Me and $R^2 = Ph$; and 3-phenyl-2-R^1-indoles with R^1 = H, Me, Ph, PhS or t-BuS and $R^2 = Ph$. Nitrosoaromatics react with t-BuHgX in the dark to form $ArN(OBu\text{-}t)(OBu\text{-}t)HgX^+$ which condenses with ArNO to form the azoxy compound. tert-Butyl radicals will add to RNO_2 [R = Ph, $Ph_2C=CH$, $Ph_2C=C(Ph)$] in the presence of t-$BuHgI_2^-$ to form products derived from $RN(OBu\text{-}t)O^-HgI^+$.*

INTRODUCTION

The reactions of *t*-BuHgX (X = Cl or I)/KI with β-nitrostyrenes in Me_2SO with sunlamp irradiation yield an interesting series of products which appear to be derived mainly from electron transfer to the photochemically excited nitroalkenes. The system *t*-BuHgX/KI gives rise to ate complexes which can be detected by NMR with the value of *Ke* for *t*-BuHgI + $I^- \rightleftharpoons$ *t*-$BuHgI_2^-$ being ~1 m^{-1} at 25°C in Me_2SO[2]. In free radical processes involving the photochemical or thermal formation of *t*-Bu•, it is observed that the rate of radical production increases from *t*-BuHgCl to *t*-BuHgI to *t*-BuHgI/KI [2]. Chain reactions of the $S_{RN}1$ - type [1] have demonstrated that RHgX is a mild oxidizing agent capable of accepting an electron from the radical anion of a nitro compound or from easily oxidized neutral radicals [3–5]. The reduction potentials of RHgX are in general more positive than −0.6 V (s.c.e.) [6]. The reduction potential of a nitro group is usually −0.7 to −0.8 V, while for the pyridinyl or $(p\text{-}MeOC_6H_4)_2CR^\bullet$ radicals, the reduction potentials of the cations are ~ −1 and −0.6 V, respectively [5, 7]. On the other hand, *t*-$BuHgI_2^-$ is a mild reducing agent capable of reducing enolyl radicals ($E° \sim 0.6$ V) [8] to the anion [2, 9, 10]. With *t*-BuHgCl/KI/hν, chain reactions can be observed involving both types of electron transfer in the same chain sequence [11].

Photochemically excited nitro compounds would be expected to be reduced by *t*-$BuHgI_2^-$ forming $RNO_2{}^{\bullet -}$ and *t*-Bu• in a solvent cage, reaction 1.

$$RNO_2{}^* + t\text{-}BuHgI_2^- \longrightarrow RNO_2{}^{\bullet -}\ t\text{-}Bu^\bullet\ HgI_2 \quad (1)$$

Alternately, reactions 2 and 3 would produce the same products without the involvement of a caged radical pair. It is known that halogen atoms, or other

$$RNO_2{}^* + I^- \rightleftharpoons RNO_2{}^{\bullet -} + I^\bullet \quad (2)$$

$$I^\bullet + t\text{-}BuHgI \longrightarrow HgI_2 + t\text{-}Bu^\bullet \quad (3)$$

electron-accepting radicals, react readily with alkylmercury halides according to reaction 3 [12]. The rapid reaction of I• with RHgI could thus drive reversible reaction 2 to completion.

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[1]This paper is dedicated to Professor Herbert C. Brown on the occasion of his 80th birthday.

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The radical anion $RNO_2^{\bullet -}$ formed in reaction 2, or by cage escape in reaction 1, should readily undergo electron transfer with *t*-BuHgX to generate a second *t*-Bu$^\bullet$ (reaction 4)[3, 4] although in the presence of a high flux of *t*-Bu$^\bullet$, or in the cage resulting from reaction 1, coupling to form RN(OBu-*t*)O$^-$ may occur.

$$RNO_2^* + t\text{-BuHgX} \rightarrow RNO_2 + t\text{-Bu}^{\bullet -} + Hg^\circ + X^- \quad (4)$$

The results to be described implicate RN(OBu-*t*)O$^-$ as a reaction intermediate in the photochemical reactions of several β-nitrostyrene derivatives with *t*-BuHgCl/KI. Furthermore, some of these reactions will occur in the dark, although at a lower rate, suggesting that the *tert*-butyl radical can add to a nitro group. [Electron transfer from I$^-$ or *t*-BuHgI$_2^-$ to the ground state nitro compound, would be prohibitively endergonic.] Electron transfer with I$^-$ or *t*-BuHgI$_2^-$ could then convert this adduct radical into RN(OBu-*t*)O$^-$.

RESULTS AND DISCUSSION

Reactions of *t*-BuHgI/KI/hν with aliphatic 1-nitroalkenes such as 1-nitrocyclohexene give a complex set of reaction products. However, with the β-nitrostyrenes **1** and **2**, fairly clean reactions are observed leading to novel products, particularly for the diphenyl derivatives **1c** and **2**.

PhCH=C(R)NO$_2$
1, **a**, R = H
b, R = Me
c, R = Ph

Ph$_2$C=C(R)NO$_2$
2, **a**, R = H
b, R = Me
c, R = Ph
d, R = SPh
e, R = SCMe$_3$

β-Nitrostyrene, **1a**

No significant reaction was observed with KI or *t*-BuHgCl in Me$_2$SO in the dark at room temperature. With *t*-BuHgI/KI in the dark, or upon irradiation, **1a** was converted into polymeric material. However, in the presence of 2 equiv of *t*-BuHgCl and 5 equiv of KI, **1a** was converted to (*E*)-*t*-BuCH=CHPh in 40% yield by irradiation with a fluorescent sunlamp for 19 hours. Traces of this product were also formed in the dark or by irradiations in the absence of KI. A 24 hour irradiation of **1a** with 4 equiv of *t*-BuHgCl formed t-BuCH=CH-Ph in 2% yield (90% recovered **1a**) while *t*-BuHgI gave 11% of the alkene (33% recovered **1a**).

Substitution of the nitro group by the *tert*-butyl group apparently involves the radical addition/β-elimination sequence of Scheme 1 which has been previously observed to occur in high yields for the β-substituted styrenes PhCH=CHQ with Q=halogen, PhS, PhSO$_2$ or Bu$_3$Sn [13–15].

$$t\text{-BuHgCl/KI} \xrightarrow{h\nu} t\text{-Bu}^\bullet$$
$$t\text{-Bu}^\bullet + \text{PhCH=CHQ} \longrightarrow t\text{-BuCH(Q)}\dot{\text{C}}\text{HPh}$$
$$\longrightarrow t\text{-BuCH=CHPh} + Q^\bullet$$

SCHEME 1

In the presence of *t*-BuHgI$_2^-$ it would be expected that $NO_2^\bullet$ would be reduced to NO_2^- with the generation of *t*-Bu$^\bullet$.

β-Methyl-β-nitrostyrene, **1b**

Reactions of **1b** with *t*-BuHgX (X = Cl or I)/KI in Me$_2$SO in the dark for 24 hours or with sunlamp irradiation for 5 hours gave, after hydrolytic workup, a mixture of **3a** and **4**. Traces of **5a** were also detected by GCMS.

PhCHCOR | PhCHCOR PhCHCOMe | PhCHC(Me)=NOBu-*t* PhCH$_2$C(R)=NOBu-*t*

3, **a**, R = Me **4** **5**, **a**, R = Me
b, R = Ph **b**, R = Ph

The substitution product [*t*-BuC(Me)=CHPh] was not observed presumably because of steric hindrance to the addition of *t*-Bu$^\bullet$ at the β-carbon atoms of **1b**.

Compound **3a** is believed to be formed by the hydrolysis of the bisnitronic ester **6a**, since with **1c** compound **6b** can be isolated, or converted to **3b** when the reaction is performed in the presence of *p*-MeC$_6$H$_4$SO$_3$H(PTSA)·H$_2$0. Addition of PTSA·H$_2$O to the reactions of **1b** did not change the ratio of **3a** to **4** indicating that **4**

PhCH—C(R)=N(O)OBu-*t* | PhCH—C(R)=N(O)OBu-*t* PhCH—C(Me)=N(O)OBu-*t* | PhCH—C(Me)=NOBu-*t*

6, **a**, R = Me **7**
b, R = Ph

is probably not derived from further reaction of **6a**. Compound **7**, formed competitively with **6a**, appears to be a reasonable precursor of **4**. In fact, a compound analogous to **7** (labeled **7a**) was isolated in the reaction of **2a** with *t*-BuHgI/Kl.

Photochemical reactions *t*-BuHgX/KI with **1b** reproducibly demonstrated that the conversion to **3a** and **4** was faster with X = Cl than with X = I. Furthermore, the ratio of **4** to **3a** was significantly greater with X = Cl. A possible explanation for these observations is that the better reducing agent (*t*-BuHgI/KI) prevents the formation of intermediates that are the precursors to **6** and **7**. We believe that the reversible conversion of **8** to **9** may be involved,

$$PhCH{=}C(R)N(OBu\text{-}t)O^{-}HgX^{+} \underset{e^-}{\overset{-HgX^{\bullet}}{\rightleftharpoons}} \underset{\mathbf{8}}{PhCH{=}C(R)N(OBu\text{-}t)O^{\bullet}} \quad (5)$$

$$\updownarrow$$

$$\underset{\mathbf{9}}{PhCH{-}C(R){=}N(O)OBu\text{-}t}$$

reaction 5. With a more powerful reducing agent the probability of **9** being reduced to **8** is enhanced. Radical **9** could decompose to a nitroso compound (reaction 6) which could undergo further reaction with *t*-BuHgX to form **10** (reaction 7). As will be described later, a

$$\mathbf{9} \longrightarrow PhCH{=}C(R)N{=}O + t\text{-}BuO^{\bullet} \quad (6)$$

$$PhCH{=}C(R)N{=}O + t\text{-}BuHgX \longrightarrow \underset{\mathbf{10}}{PhCH{=}C(R)N(OBu\text{-}t)HgX} \quad (7)$$

reaction analogous to **7** occurs readily with PhNO either in the dark or with sunlamp irradiation. Protonolysis upon workup of **10** would lead to the observed *O-tert*-butyl oximes (**5**). Attack of the radical **9** upon **8** or **10** could lead, by an S_H2' process, to the nitronic esters **6** and **7**, Scheme 2, while coupling of **9** would form **6**. Changing from *t*-BuHgCl/KI to *t*-BuHgI/KI retards the reaction by reducing

$$\underset{\mathbf{9}}{PhCHC(R){=}N(O)OBu\text{-}t} + \begin{cases} \mathbf{8} \xrightarrow{-HgX^{\bullet}} \mathbf{6} \xrightarrow{H_2O} \mathbf{3} \\ \mathbf{10} \xrightarrow{-HgX^{\bullet}} \mathbf{7} \xrightarrow{H_2O} \mathbf{4} \end{cases}$$

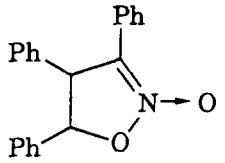
SCHEME 2

the steady state concentrations of **9** (reaction 5) and retarding the formation of **10**. Thus, with *t*-BuHgI/KI and 15 hours of irradiation, **3a** and **4** were formed in yields of 24 and 17%, respectively while with *t*-BuHgCl/KI and 4 hours of irradiation the yields were 7% of **3a** and 22% of **4**. The diketone **3a** was a 90:10 mixture (by GC) of diastereomers with the minor isomer being the high melting isomer previously assigned the meso structure, mp 197–198°C (lit. [16] 201–202°C).

β-Phenyl-β-nitrostyrene, **1c**

The photochemical and dark reactions of *t*-BuHgI/KI led to completely different products. Compound **1c** is very susceptible to Michael-type addition reactions which appear to determine the products observed in the dark. Upon photolysis, electron transfer processes (reactions 1 and 2) become dominant.

A. Dark reaction. In Me_2SO there is no significant reaction between KI and **1c**. However, in the presence of *t*-BuHgI reaction occurs to form PhCHO, PhCOCOPh and compound **11** as a single diastereomer in up to 80% yield (0.4 mol **11**/mol of **1c**) in the presence of DABCO (1,4-*d*iazabicyclo[2.2.2]-octane). The formation of **11** and PhCHO can be rationalized from $PhCH(O^{-})CH(Ph)NO_2$ via



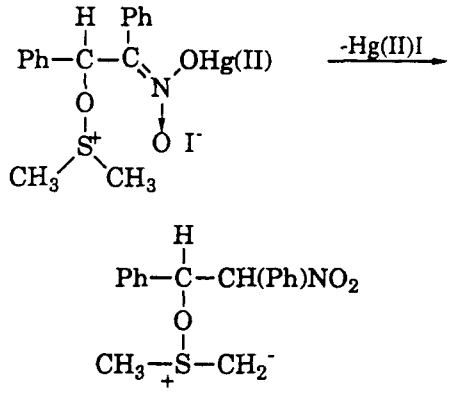
11

elimination of $PhCH = NO_2^{-}$, followed by Michael addition to **1c** and elimination of NO_2^{-} from the adduct (reaction 8).

$$PhCH(NO_2)CH(Ph)C(Ph){=}NO_2^{-} \xrightarrow{-NO_2^{-}}$$

$$PhCH{=}C(Ph)C(Ph){=}NO_2H \longrightarrow \mathbf{11} \quad (8)$$

One possible route to $PhCH(O^{-})CH(Ph)NO_2$ involves the Hg(II)-catalyzed addition of I^{-} to **1c** to form PhCH(I)C(Ph)=N(O)OHg(II). This intermediate might react with Me_2SO to undergo a Pummerer-type process[17] as shown in reaction 9.



$$\longrightarrow PhCH(O^{-})CH(Ph)NO_2 + CH_3S{=}CH_2^{+} \quad (9)$$

B. Photochemical reactions. Photolysis of **1c** with *t*-BuHgI/KI leads to the formation of the stable bisnitronic ester, **6b**. Reaction via Scheme 1 is not observed because of steric hindrance to the addition of *t*-Bu$^{\bullet}$ to this stilbene derivative. The *O-tert*-butyl oxime **5b** was isolated as a minor product, presumably from reactions 5, 6, and 7 followed by protonation of **10** and tautomerization. With 3 equiv of *t*-BuHgI and 6 equiv of KI, typical yields of **6b** and **5b**

after 17 hours of irradiation were 44 and 6%, respectively. The addition of 3 equiv of DABCO increased the yields to 52 and 13%, respectively, while the addition of 3 equiv of PTSA·H_2O gave 6% of **5b**, a trace of **6b** and 48% of **3a** (the hydrolysis product of **5b**) as the thermodynamically more stable [18] lower-melting [18, 19] diastereomer (isobidesyl); mp 158–159°C (lit.[19] mp 160–161°C).

α-Phenyl-β-nitrostyrene, **2a**

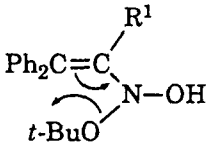
Photolysis of **2a** with 4 equiv of *t*-BuHgI/KI for 43 hours produced minor amounts of *t*-BuCH=CPh_2 (10–14%) via Scheme 1. The major product observed was the dimeric compound **7a** (30%). Also formed was 11% of the *tert*-butoxy oxime (**12a**) and traces of the *O-tert*-butyl oxime **5c** and 3-phenylindole (~ 5%). The yield of **12a** increased to 40% in the presence of 4 equiv of PTSA; also observed were 10% of Ph_2C=CHBu-*t* and 8% of **5c**, isolated as a mixture (~ 9:1 by ^1H NMR or GC) of anti- and syn-isomers. Compound **7a** was not observed in the presence of PTSA although its hydrolysis product may have been formed.

Ph_2C(—CH=N(O)OBu-*t*)$_2$ **7a**

$Ph_2C(OBu\text{-}t)C(R)$=NOH **12**, **a**, R = H; **b**, R = Me

Ph_2CHCH=NOBu-*t* **5c**

Apparently **12** is formed by a novel rearrangement of the initially formed Ph_2C=$C(R^1)$N(OBu-*t*)O^-HgI^+ or from the hydroxylamine itself. The process illustrated in reaction 10 could well proceed via a radical pair intermediate [Me_3CO·$Ph_2\dot{C}C(R^1)$=NOH. Conversion of Ph_2C=CHN(OBu-*t*)O^-HgI^+ to the



12 (10)

nitroso compound and to Ph_2C=CHN(OBu-*t*)HgI (reactions 5–7) explains the formation of **5c**.

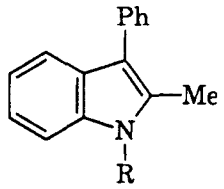
The formation of **7a** also occurred (28%) in the dark upon reaction of **2a** with *t*-BuHgI/KI/$K_2S_2O_8$; Ph_2C=CHBu-*t* was also formed in up to 20% yield. In the presence of $S_2O_8^{-2}/I^-$ there is a rapid formation of *t*-Bu· from *t*-BuHgX by the reactions: $I^- + S_2O_8^{-2} \rightarrow I\cdot + SO_4^{-2} + SO_4\cdot^-$; $SO_4\cdot^- + I^- \rightarrow SO_4^{-2} + I\cdot$; $I\cdot$ + *t*-BuHgI → *t*-Bu· + HgI_2[20]. The formation of **7a** suggests that *t*-Bu· can add to a nitro oxygen atom of **2a** to form $Ph_2\dot{C}CH$=N(O)OBu-*t* which can couple to give **7a**. The high flux of *t*-Bu· also gives rise to an increased yield of the substitution product, Ph_2C=CHBu-*t*.

β-Methyl-β-nitro-α-phenylstyrene, **2b**

Photolysis of **2b** with *t*-BuHgI/KI in Me_2SO gave as a major product compound **13**, the dehydration product of **12b**. Also isolated was the di-*tert*-butylated hydroxylamine derivative **14** and two indoles, **15a** and **15b**. Compound **14** is readily explained by trapping of the nitroso compound formed in reaction 7 by

$[Ph_2C(OBu\text{-}t)C(Me)=N]_2$—O **13**

Ph_2C=C(Me)N(Bu-*t*)OBu-*t* **14**



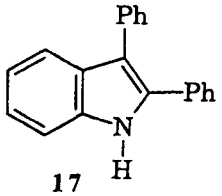
15, **a**, R = H; **b**, R = *t*-BuO

t-Bu·. In a 22 hour photolysis with 4 equiv of *t*-BuHgI and 8 equiv of KI the observed yields were 20% **13**, 10% of **14**, a trace of **15a** and 20% of **15b**. The same reaction in the presence of 4 equiv of DABCO gave 28% of **13**, 12% of **14**, 20% of **15a** and a trace of **15b**. It seems likely that the indoles are formed from further reactions of the nitroso compound generated in reaction 7. Conversion of the nitroso alkene by either a thermal or photochemical reaction with *t*-BuHgI to form **16** could lead to **15a** and **15b** via Scheme 3. The formation of **15a** from **2b** also occurs upon heating in the presence of $(EtO)_3P$ via a process involving deoxygenation to the nitroso compound followed by the formation of Ph_2C=$C(Me)\dot{N}^-OP^+(OEt)_3$ which reacts to give the indole via the 2*H*-azirine and nitrene[21].

Ph_2C=C(Me)NO + *t*-BuHgI ⟶ Ph_2C=C(Me)N(OBu-*t*)HgI **16**

β-nitro-α,β-diphenylstryrene, **2c**

Reaction of *t*-BuHgX(X = Cl or I)/KI with **2c** produced the indole **17** in the dark or upon irradiation.



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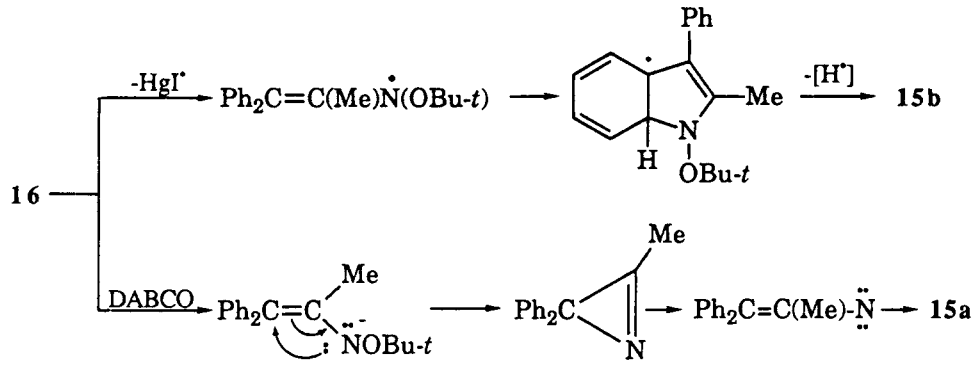


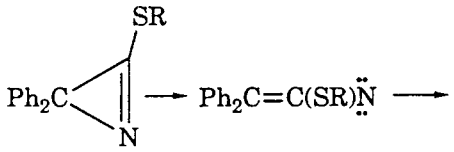
SCHEME 3

The presence of $K_2S_2O_8$ decreased the yield of **17** in the dark reaction possibly suggesting that $Ph_2\dot{C}C(Ph)=N(O)OBu\text{-}t$ or $t\text{-}Bu^{\bullet}$ was an oxidizable intermediate. Table 1 summarizes pertinent results.

If the reaction proceeds via formation of $Ph_2C=C(Ph)N=O$, the subsequent conversion to $Ph_2C=C(Ph)N(OBu\text{-}t)HgX$ and finally to the indole via the azirine must occur quite efficiently. With *t*-BuHgI/KI the best yield of **17** was actually observed in the dark with a long reaction period. The photochemical reactions occurred more readily with *t*-BuHgCl/KI than with *t*-BuHgI/KI suggesting that the better reducing system retarded the conversion of $Ph_2C=C(Ph)N(OBu\text{-}t)O^{\bullet}$ to the nitroso compound, as suggested by reactions 5 and 6.

β-Nitro-α-phenyl-β(phenylthio)styrene, **2d**

The reaction of **2d** with $(EtO)_2PO^-$ in Me_2SO at 25°C or with $(EtO)_3P$ at 150°C has been previously observed to give high yields of the indole, presumably via the 2*H*-azirine **18** and nitrene, reaction 11[21]. With 1.5 equiv of *t*-BuHgCl and 3 equiv of KI photolysis of **2d** for 18 hours gave a 40% yield of **18** (R = Ph) and 30% of unreacted **2d**. With 2 equiv of *t*-BuHgCl and 5 equiv of KI a faster reaction consuming all of the **2d** occurred to yield **19a** in 68% yield. The isolated 2*H*-azirine was observed to be converted to the indole upon heating, or upon photolysis in CH_2Cl_2 solution. Small amounts (9–10%) of the hydroxamic acid derivative **20** were also observed in the reaction of **2d**.



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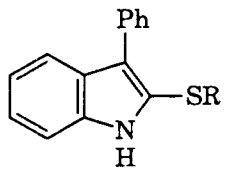


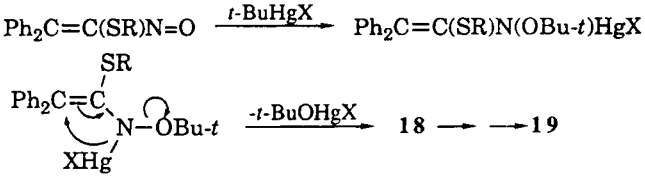
(11)

19, **a**, R = Ph
b, R = *t*-Bu

$$Ph_2CHC(O)NHOBu\text{-}t$$

20

Compound **20** is the expected hydrolysis product of an intermediate such as $Ph_2C=C(SR)N(OBu\text{-}t)HgI$ (Scheme 4).



SCHEME 4

β-(tert-Butylthio)-β-nitro-α-phenylstyrene, **2e**

Compound **2e** reacted with *t*-BuHgX/KI/hν much slower than **2d**. With 3 equiv of *t*-BuHgCl and 6 equiv of KI only a 10% yield of **19b** was observed

TABLE 1. Formation of **17** in the Reactions of *t*-BuHgX/KI with **2c**[a]

t-BuHgX X; equiv.	KI, equiv	conditions	% **17**
Cl, 5	5	dark, 17 h	30
Cl, 5	5	$K_2S_2O_8$, [b] dark, 17 h	17
Cl, 5	5	hν, 8 h	85
Cl, 5	10	hν, 20 h	90
I, 5	10	dark, 47 h	>95
I, 5	10	$K_2S_2O_8$[b], dark, 47 h	68
I, 5	10	hν, 14 h	43

[a] 0.25–0.5 mmol of **2c** in 10 mL of Me_2SO at −35°C; hν, irradiation by a 275 W General Electric fluorescent sunlamp. [b] 2 equiv

after 24 hours and 53% of **2e** was recovered. With the more powerful reducing system *t*-BuHgI/KI, a 53% yield of **19b** was formed in 8 hours accompanied by 9% of **20**. The azirine (**18**, R = *t*-Bu) was not isolated in these reactions although it can be isolated as an intermediate in the conversion of **2e** to **19b** by $(EtO)_2PO^-$ in Me_2SO at 25°C [21]. Presumably it was an intermediate (Scheme IV) but was converted to the indole upon photolysis in the presence of Hg(II) salts.

Summary of β-nitrostyrene Reactions

The substitution patterns for the β-nitrostyrenes derivatives [$PhC(R^2)=C(R^1)NO_2$] have a pronounced effect on the reaction products observed with *t*-BuHgX/KI. With $R^1 = R^2 = H$ the only product observed upon photolysis resulted from *t*-Bu• addition at the β-carbon atom. This reaction pathway was also observed to a minor extent when R^1 = H, R^2 = Ph but was not observed when R^1 = Me, Ph, PhS or *t*-BuS. With R^1 = Me or Ph and R^2 = H or with R^1 = H and R^2 = Ph a major reaction pathway involved a coupling at the α carbon atom by a process postulated to involve $PhC(R^2)$-$C(R^1)N(O)OBu$-*t*. With R^1 = H or Me and R^2 = Ph the rearranged *tert*-butoxy oximes $Ph_2C(OBu\text{-}t)C(R^1)=NOH$ were also formed, presumably by rearrangement of $Ph_2C=C(R^1)N(OBu\text{-}t)O^-HgX^+$ or the hydroxylamine. With R^2 = Ph the 3-phenyl-2-R^1-indoles were formed in a yield which increased from R^1 = H to Me to PhS, *t*-BuS to Ph. The general course of the photochemical reaction appears to involve the formation of $PhC(R^2)=C(R^1)NO_2\bullet^-$, $PhC(R^2)=C(R^1)N(OBu\text{-}t)OHgX$, $PhC(R^2)=C(R^1)N=O$ and $PhC(R^2)=C(R^1)N(OBu\text{-}t)HgX$ with the latter intermediate leading to indoles via the 2*H*-azirine and nitrene when R^2 = Ph.

TABLE 2. Reaction of PhNO with t-BuHgX in Me_2SO at 35°C[a]

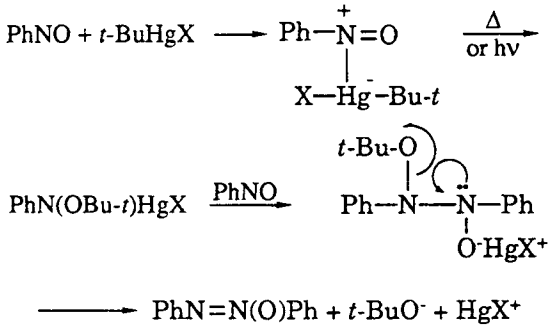
t-BuHgX X; equiv	*conditions*	*% PhN(O)=NPh*
Cl; 5	dark, 24 h	33
Cl; 2	hv, 24 or 44 h	98–100
I; 2	hv, 25 h, CF_3CO_2H[b]	90
I; 2	hv, 24 h, CH_3CO_2H[c]	63
I; 4	dark, 17 h	63
I; 4	hv, 17 h	45[d]
Cl;2	hv, 44h	67[e]

[a]Reactions of 0.1–0.2 mmol of PhNO in 10 mL of Me_2SO; hv, irradiation with a 275 W General Electric fluorescent sunlamp. [b]9 vol % CF_3CO_2H. [c]5O vol % CH_3CO_2H. [d]A 27% yield of PhN(t-Bu)OH was also observed. [e]o-MeC_6H_4NO giving o-$MeC_6H_4N(O)$ = NC_6H_4Me-o.

Reactions of Nitrosoaromatics

The reactions of β-nitrostyrene derivatives implicated the conversion of a nitroso compound to an *O-tert*-butyl hydroxylamine derivative (e.g., reaction 7). This is not the expected product from *t*-Bu• attack upon a nitroso compound and we have investigated this reaction further with nitroso aromatic compounds. The reaction of PhNO with *t*-BuHgCl occurred in the dark, or more rapidly with sunlamp irradiation to give high yields of azoxybenzene, Table 2.

As indicated in Scheme 5, the reaction is pictured to involve the formation of PhN(OBu-*t*)HgX and its condensation with excess PhNO to form azoxybenzene. The reaction occurs readily in the presence of CF_3CO_2H or CH_3CO_2H, presumably because PhNHOBu-*t* also undergoes condensation with PhNO. The reaction of *o*-nitrosotoluene formed the expected azoxy compound thus eliminating a nitrene as an intermediate [22].



SCHEME 5

In the presence of PhCHO, PhCH=NPh was formed presumably by condensation with PhN(OBu-*t*)HgX and deoxygenation of the resulting nitrone. In the dark *t*-BuHgI/Kl converts PhNO to azoxybenzene but in a lower yield since $PhNO_2$ was now observed to be a major (up to 33%) product. Upon photolysis of *t*-BuHgI/KI in the presence of PhNO, PhN(Bu-*t*)OBu-*t* and PhN(Bu-*t*)OH are the major products indicative of *t*-Bu• attack upon PhNO. [Only traces of PhN(O)=NPh or PhN=NPh are observed.] Under these reaction conditions PhN(Bu-*t*)OH is slowly converted to PhN(Bu-*t*)OBu-*t*, particularly in the presence of DABCO. Azoxybenzene is also slowly deoxygenated to azobenzene upon photolysis with *t*-BuHgX/KI. In the reactions of the β-nitrostyrenes with *t*-BuHgX/Kl, azoxy or azo compounds were not observed presumably because the nitroso compounds never achieve high steady state concentration and alternate pathways are available to the intermediate $PhC(R^2)=C(R^1)N(OBu\text{-}t)HgX$ (Schemes 4 and 5).

With $PhNO_2$ there was little reaction upon photolysis with *t*-BuHgX (X = Cl or I) in Me_2SO. In the presence of KI the reactions led mainly to PhN(Bu-*t*)OBu-*t* and PhN(Bu-*t*)OH with only traces of azoxy and azobenzene. In the dark $PhNO_2$ reacted slowly with *t*-BuHgI/KI, or more rapidly with *t*-BuHgI/KI/$K_2S_2O_8$, to produce these same products which are characteristic of *t*-Bu• attack upon PhNO.

CONCLUSIONS

The dark reactions observed between *t*-BuHgX (X = Cl, I) and PhNO implicate the formation of PhN(OBu-*t*)HgX. The regiochemistry of this reaction is opposite to that expected for the addition of radicals or carbanions to a nitroso compound. Even with photolysis it is believed that the formation of PhN(O)=NPh via PhN(OBu-*t*)HgX does not involve reaction of *t*-Bu•.

The dark reactions observed with $PhNO_2$ or **2a-c** and *t*-BuHgX/KI, or *t*-BuHgI/KI/$K_2S_2O_8$ suggest that the *tert*-butyl radical can add to the oxygen atom of a nitro group, a group usually considered to be unreactive towards simple alkyl radicals [23]. The equilibrium for radical addition may be unfavorable but in the presence of reducing agent such as *t*-$BuHgI_2^-$, perhaps the reaction can be driven forward by an irreversible electron transfer, Scheme 6.

$$RNO_2 + t\text{-Bu}^\bullet \rightleftharpoons RN(OBu\text{-}t)O^\bullet$$

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

$$RN(OBu\text{-}t)O^- + HgI_2 \rightleftharpoons RN(OBu\text{-}t)O^-HgX^+ + I^-$$

SCHEME 6

The unstable species PhN(OBu-*t*)O• has been previously observed by ESR spectroscopy from the addition of *t*-BuO• to PhNO [24]. The products observed from the reactions of *t*-BuHgX/KI with nitroso or nitro compounds are distinctly different from those recognized to occur with organometallic reagents such as organolithium or Grignard reagents which lead to nitroxides ($R^1R^2NO^\bullet$)[25, 26] or hydroxylamines (R^1R^2NOH) [27, 28]. The reagent *t*-BuHgX/KI is a unique reagent for the deoxygenation/*tert*-butylation of nitroso and nitro compounds.

EXPERIMENTAL

General

All reactions were performed in deoxygenated Me_2SO under a nitrogen atmostphere. Photochemical reactions were performed at ~35°C at a distance of ~25 cm from a 275 watt General Electric sunlamp. Thermal reactions were performed at the same temperature in tubes shielded from light by aluminum foil. The reactions were worked up by treatment with aqueous $Na_2S_2O_3$ to remove mercury salts and organomercurials. The CH_2Cl_2 extracts were dried over Na_2SO_4, concentrated and analyzed by ^1H NMR and/or GC. Products were isolated by flash column chromatography using 230–240 mesh, grade 60 Merck silica gel (Aldrich Chem. 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 $PhCH_3$ or PhPh as an internal standard and predetermined response factors. NMR spectra were recorded by a Nicolet NT 300 spectrometer with TMS as the internal standard. Yields were measured by ^1H NMR from integrations with a known amount of $PhCH_3$. MS were recorded in the GC or solids inlet mode by CI or EI with a Finnegan 4000 spectrometer. HRMS were recorded measured 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.

Reagents and Solvents

Me_2SO was distilled from CaH_2 under vacuum. Me_2SO-d_6 (Cambridge Isotope Laboratories) was dried over 4A molecular series. PhCH=$CHNO_2$, PhNO, *o*-MeC_6H_4NO, PhN(O)=NPh, PhN=NPh, PhN=CHPh, DABCO, and PTSA were purchased from Aldrich Chemical Co. The other β-nitrostyrenes were prepared by literature procedures: **1b** [29], **1c** [30], **2a** [30], **2b** [30], **2c** [31], **2d** [32], and **2e** [32]. *t*-BuHgCl was prepared from *t*-BuLi and $HgCl_2$ in THF, mp (dec.) 110–113°C (lit.[33] 117–119°C, dec.); ^1H NMR (300 MHz, $CDCl_3$) 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 (300 MHz, $CDCl_3$) δ 1.43(s).

O-tert-Butyl 3,4-Diphenyl hexane-2,3-dione Oxime (4)

Compound **4** has mp 117–118°C with FTIR at 1715 and 1641 cm^{-1}; NMR: ^1H (300 MHz $CDCl_3$) δ 1.34(s, 9H), 1.89(s, 3H), 2.18(s, 3H), 4.08(d, *J* = 11.5 Hz, 1H), 4.42(d, *J* = 11.5 Hz, IH), 6.84–7.14(m, 10H); ^{13}C (75.429 MHz, $CDCl_3$) δ 27.77, 29.91, 29.94, 53.56, 61.90, 77.67, 126.56, 126.995, 127.99, 128.31, 128.71, 128.87, 136.405, 138.73, 156.33, 207.25; MS: GC (*m/z*, relative intensity) 337 (1), 294 (5), 281 (15), 264 (11), 238 (11), 220 (4), 204 (8), 180 (50), 148 (80), 134 (21), 91 (33), 77 (9), 57 (49), 43 (100); HR 337.2047 (calcd. for $C_{22}H_{27}NO_2$ 337.2042). Anal. Calcd. for $C_{22}H_{27}NO_2$: C, 78.30; H, 8.06; N, 4.15. Found: C, 78.05; H, 8.10; N, 4.03.

O-tert-Butyl α-Phenylacetophenone Oxime (**5b**)

Compound **5b** was isolated as a solid, mp 114–117°C, with FTIR at 1603 cm^{-1} NMR: 1H (300 MHz, $CDCl_3$) δ 1.31 (s, 9H), 3.86(s, 2H), 7.06–7.41(m, 10H); ^{13}C (75.429 MHz, $CDCl_3$) δ 27.5(q), 41.8(t), 76.4, 126.2, 127.7, 128.3, 128.6, 128.8, 133.9, 137.9, 153.4; GCMS (*m/z*, relative intensity) 267 (M^+, 7.5), 211(53), 193(66), 165(5), 120(5), 103(4), 91(65), 77(12), 57(100); HRMS 267.1623 (calcd. for $C_{18}H_{21}NO$ 264.1624).

O-tert-Butyl Diphenylacetaldehyde Oxime (**5c**)

Compound **5c** was isolated as a mixture of anti- and syn-isomers which gave almost the same GCMS. The ratio of isomers was ~10:1 by GC or ^1H NMR; Major isomer: ^1H NMR (300 MHz, $CDCl_3$) δ 1.28(s, 9H), 4.83(d, J = 8.4 Hz, 1H), 7.74(d, J = 8.4 Hz, 1H), 7.17–7.33 (m); GCMS (*m/z*, relative intensity) 267 (M^+, 0.4), 211(7), 194(58), 167(10), 152(4), 57(100); Minor isomer: ^1H NMR (300 MHZ, $CDCl_3$) δ 1.235(s, 9H), 5.61(d, J = 7.2 Hz), 7.11(d, J = 7.2 Hz, 1H); GCMS (*m/z*, relative intensity) 267 (M^+, 2), 211(24), 194(41), 167(14), 152(6), 57(100); HRMS of mixture 267.1628 (calcd. for $C_{18}H_{21}NO$ 267.1623). Anal. Calcd. for $C_{18}H_{21}NO$: C, 80.86; H, 7.92; N, 5.24. Found: C, 80.86, H, 8.04; N, 5.11.

Bis-tert-Butyl Nitronic Ester of 1,4-Dinitro-1,2,
MHz, $CDCl_3$) δ 1.01(br. s, 18H), 5.20 (br. s, 2H), 6.23

Compound **6b** had mp 185–186°C; NMR: ^1H (300 MHz, $CDCl_3$) δ 1.01(br. s, 18H), 5.20 (br. s, 2H), 6.23 (d, J = 6.9 Hz, 4H), 7.04–7.51 (m, 16H); ^{13}C (75.429 MHz, $CDCl_3$ δ 27.6, 46.6, 84.2, 127.3, 127.9, 128.3, 128.6, 129.4, 130.9, 132.7, 138.1; MS(CI, methane, *m/z*, relative intensity) 565(M+ 1^+, 1.5), 406(7), 391(16), 339(7), 316(14), 298(10), 283(10), 282(6), 266(9), 238(8), 226(12), 210(33), 179(19), 105(100). Anal. Calcd. for $C_{36}H_{40}N_2O_4$: C, 76.57; H, 7.14; N, 4.96. Found: C, 76.39; H, 7.22; N, 4.89.

tert-Butyl Nitronic Ester of O-tert-Butyl-γ-nitro-α, α, β, β-tetraphenylbutyraldehyde Oxime (**7a**)

The sharp ^1H and ^{13}C NMR spectra of **7a** indicate a symmetrical structure possibly from a rapid oxygen atom transfer between the nitronic ester and imino ether groups. Compound **7a** had mp 146–147°C with FTIR at 1599 cm^{-1}; NMR: ^1H (300 MHz, $CDCl_3$) δ 1.11 (s, 18H), 7.61(s, 2H), 7.19–7.46(m, 20H); ^{13}C (75.429 MHz, $CDCl_3$) α 27.6(q), 78.8(s), 8.32(s), 126.8(d), 127.5(d), 127.8(d), 144.9(s), 151.0(d); MS: EI (solids probe *m/z*, relative intensity) 548(M^+, 0.8), 310(8), 266(14), 237(9), 226(4), 210(86), 195(13), 183(24), 165(18), 132(24), 105(56), 77(27), 57(100); CI (solids probe, NH_3, *m/z*, relative intensity) 549 (M+ 1^+, 14), 463(10), 428(13), 284(50), 266(100), 200(32). Anal. Calcd. for $C_{36}H_{40}N_2O_3$: C, 78.80; H, 7.35; N, 5.11. Found: C, 78.83; H, 7.53; N, 5.04.

3,4,5-Triphenyl-2-isoxazoline-2-oxide (**11**)

Compound **11** was a solid, mp 157–159°C, with strong FTIR at 1612 cm^{-1}; NMR: ^1H (300 MHz, $CDCl_3$) δ 4.42(d, J = 4.5 Hz, 1H), 4.82(d, J = 4.5 Hz, 1H), 7.28–7.44(m, 10H), 7.82–7.87(m, 2H); ^{13}C (75.429 MHz, $CDCl_3$) δ 59.7, 83.7, 115.4, 125.1, 126.1, 126.7, 127.3, 128.3, 128.5, 128.8, 129.0, 129.2, 129.5, 138.9, 139.0; GCMS: EI (*m/z*, relative intensity) 297 (M^+ −18, 14), 180(22), 165(17), 105(100), 89(15), 77(50); CI(NH_3, *m/z*, relative intensity) 648 (2M + 18 $^+$, 1.0), 631 (2M+ 1^+, 1.5), 333 (M + 18 $^+$, 79) 316 (M + 1 $^+$, 26), 298(100); CI(isobutane, m/z, relative intensity) 316 (M+ 1^+, 100). Anal. Calcd for $C_{21}H_{17}NO_2$: C, 79.98; H, 5.43; N, 4.44. Found: C, 80.31; H, 5.53; N, 4.39.

α-tert-Butyldiphenylacetaldehyde Oxime (**12a**)

The compound was isolated as a solid, mp 94.0–94.5°C, with FTIR at 3487 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 1.30(s, 9H), 4.38(s, 1H), 7.20–7.38(m, 10H), 7.97(s, 1H); GCMS: EI (*m/z*, relative intensity) 284 (M + 1^+, 0.2), 266(0.2), 227(1.8), 209(30), 192(9), 183(40), 178(82), 165(10), 152(6), 122(87), 105(64), 77(50), 57(100); CI (NH_3, *m/z*, relative intensity) 301(M + 18$^+$, 0.4), 284(M + 1^+, 86), 266(11), 217(7), 200(100); HRMS 284.1648 (calcd. for $C_{18}H_{22}NO_2$ 284.1651), 266.1540 (calcd. for $C_{18}H_{20}NO$ 266.1545). Anal. Calcd. for $C_{18}H_{21}NO_2$: C, 76.30; H, 7.47; N, 4.94. Found: C, 75.87; H, 7.43; N, 4.94.

Bis(1-tert-butoxy-1,1-diphenyl-2-propyliden-imino) Ether (**13**)

The anhydride of **12b** was isolated as a solid, mp 169.0–169.5°C with FTIR at 1599 cm^{-1}; NMR: ^1H (300 MHz, $CDCl_3$) δ 1.19(s, 18H), 1.51(s, 6H), 7.11–7.45(m, 20H); ^{13}C (75.429 MHz, $CDCl_3$) δ 13.7, 28.0, 77.8, 86.8, 126.77, 126.79, 130.3, 143.1, 157.2; MS: CI (methane, *m/z*, relative intensity) 617(M + $C_3H_5^+$, 0.2), 605(M + $C_2H_5^+$, 0.4), 577(M + 1^+, 8), 521(0.4), 394(0.9), 280(100); HR (*m/z*, relative intensity) 296.1651 (5.6, calcd. for $C_{19}H_{22}NO_2$ 296.1651), 280.1699 (21, Calcd. for $C_{19}H_{22}NO$ 280.1701), 224.1071 (100, calcd. for $C_{15}H_{14}NO$ 224.1075). Anal. Calcd for $C_{38}H_{44}N_2O_3$ C, 79.13, H, 7.69; N, 4.86. Found: C, 78.99; H, 7.68; N, 4.81.

2-(N-tert-Butoxy-N-tert-butylamino)-1, 1-diphenylpropropene (**14**)

The compound was isolated as a liquid; NMR: ^1H (300 MHz, $CDCl_3$) δ 1.04(s, 9H), 1.34(s, 9H), 1.83(s, 3H), 7.04–7.62(m, 10H); ^{13}C (75.429 MHz, $CDCl_3$) δ 17.6, 28.0, 30.9, 62.6, 77.8, 125.3, 126.1, 127.1, 128.4, 129.8, 130.2, 131.6, 142.4, 144.3, 145.0; MS: GC (*m/z*, relative intensity) 337(M^+, 0.2), 321(0.2), 281(22), 266(3), 234(0.9), 225(37), 208(33), 193(9), 178(7),

165(22), 105(46), 91(20), 77(17), 57(100); HR 337.2401 (calcd. for $C_{23}H_{31}NO$ 337.2406).

N-tert-Butoxy-2-methyl-3-phenylindole (**15b**)

Compound **15b** was isolated as a liquid; NMR: ^1H (300 MHz, $CDCl_3$) δ 1.51(s, 9H), 2.47(s, 3H), 7.04–7.64(m, 9H); ^{13}C (75.429 MHz, $CDCl_3$) δ 11.8, 28.3, 86.0, 111.3, 118.4, 120.1, 121.3, 123.6, 125.8, 128.4, 129.5, 134.0, 135.2, 136.1; MS: GC (*m/z*, relative intensity) 279 (M^+, 26), 223(1.2), 206(73), 194(4), 178(7), 165(9), 91(1), 77(2), 57(100); HR 279.16229 (calcd. for $C_{19}H_{21}NO$ 279.16231).

2,2-Diphenyl-3-(phenylthio)-2-H-azirine (**18**)

The compound was isolated as a solid with FTIR at 1600 cm^{-1}. Upon heating it rearranged to 3-phenyl-2-(phenylthio)indole, mp 199–203°C (lit.[21] 199–203°C). The GC retention time and GCMS were the same as the indole but the NMR was different; NMR: ^1H (300 MHz, $CDCl_3$) δ 6.99–7.32(m); ^{13}C (75.429 MHz, $CDCl_3$) δ 50.6, 125.9, 126.5, 126.7, 126.8, 126.9 127.2, 128.3, 128.9, 129.1, 129.4, 134.3, 138.6; MS: GC (*m/z*, relative intensity) 300(100), 267(12), 233(32), 178(1), 165(9), 134(10), 77(4); HR 301.0924 (calc. for $C_{20}H_{15}NS$ 301.0926).

3-Phenyl-2-substituted Indoles (**15, 17, 19**)

The isolated indoles had spectra consistent with previous reports, [21, 34] and mp in agreement with literature values: 3-phenylindole, mp 85.5–86.0°C (lit.[35] mp 86–87°C); 2-methyl-3-phenylindole (**15**), mp 57–59°C (lit. [36] mp 58–60°C); 2,3-diphenylindole (**17**), mp 113–114°C from hexane and CH_2Cl_2 (lit. 113–114°C from ligroin [37], 114–116°C from heptane [38]); 3-phenyl-2-(phenylthio) indole (**19a**) m.p. 199–203°C(lit. [21] mp 199–203°C); 2-(*tert*-butylthio)-3-phenylindole (**19b**), mp 137–139°C (lit. [21] 137–139°C).

2,3-Diphenylindole (**17**) had FTIR at 3412 cm^{-1}; NMR: ^1H (300 MHz, $CDCl_3$) δ 7.11–7.67(m, 14H), 8.11(br. s, 1H); ^{13}C (75.429 MHz, $CDCl_3$) δ 110.0, 114.9, 119.6, 120.4, 122.6, 126.2, 127.6, 128.1, 128.5, 128.6, 128.65, 130.1, 132.6, 134.0, 135.0, 135.8; MS: GC (*m/z*, relative intensity) 269 (M^+, 100), 165(16), 134(25), 127(16), 77(12); HR 269.1200 (calcd. for $C_{20}H_{15}N$ 269.1204).

N-tert-Butoxydiphenylacetamide (**20**)

This substance was isolated as a solid, mp 194–197°C, with FTIR at 1643 and 3294 cm^{-1}; NMR: ^1H (300 MHz, $CDCl_3$) δ 1.32(s, 9H), 4.81(s, 1H), 5.42 (br. s, 1H), 7.24–7.34(m, 10H); ^{13}C (75.429 MHz, $CDCl_3$) δ 28.7(q), 51.5(s), 59.8(d), 127.0, 128.6, 128.8, 139.9, 170.9; MS: GC (*m/z*, relative intensity) 283 (M^+, 3), 183(19), 167(100); HR 283.1572 (calcd. for $C_{18}H_{21}NO_2$ 283.1566). Anal. Calcd. for $C_{18}H_{21}NO_2$: C, 76.30; H, 7.47; N, 4.94. Found: C, 76.90; H, 7.54; N, 4.89.

N-tert-Butylphenylhydroxylamine [25]

The compound had mp 113–114°C (lit.[25] 115–117°C); ^1H NMR: (300 MHz): $CDCl_3$ δ 1.085(s, 9H), 7.09(septet, J = 4.5 Hz, 1H), 7.20(br. s, 1H), 7.22–7.23 (m, 5H); Me_2SO-d_6, δ 1.05(s, 9H), 7.04(tt, J = 6.9, 1.5 Hz, 1H), 7.16–7.26(m, 4H), 8.25(s, 1H); GCMS (*m/z*, relative intensity) 165(M^+, 9) 150(2), 133(4), 118(10), 109(100).

N-tert-Butyl-N-tert-butoxyaniline [25]

Material isolated as an oil was >95% pure by GC and ^1H NMR; NMR: ^1H (300 MHz, $CDCl_3$) 1.05(s, 9H), 1.07(s, 9H), 7.01–7.08(m, 2H), 7.16–7.26(m, 3H); ^{13}C (75.429 MHz, $CDCl_3$) 26.8, 28.2, 59.4, 78.0, 124.3, 126.0, 127.1, 151.1; GCMS: EI (*m/z*, relative intensity) 221(M^+, 1) 165(18), 109(100), 57(48); CI (NH_3) 222 ($M + 1^+$); HRMS 221.1781 (calcd. for $C_{14}H_{23}NO$ 221.1780).

o,o'-Dimethylazoxybenzene [39]

The isolated material had ^1H NMR (300 MHz, $CDCl_3$) 2.37(s, 3H), 2.51(s, 3H), 7.26–7.37(m, 6H), 7.665(d, J = 7.5 Hz, 1H), 8.035 (d, J = 7.5 Hz, 1H); GCMS (*m/z*, relative intensity) 226 (M^+, 24), 225(28), 211(60), 210(7), 183(5), 168(6), 119(6), 104(28), 91(100).

Other Products

(*E*)-*t*-BuCH=CHPh,[40] *t*-BuCH=Ph_2,[40] PhCH=NPh, PhN(O)=NPh, and PhN=NPh had GC retention times, GCMS and ^1H NMR identical with authentic samples. $PhCH_2C(CH_3)$=NOBu-t hydrolyzed upon chromatography and was identified by GCMS in the crude reaction mixture; GCMS (*m/z*, relative intensity) 205(M^+, 4), 149(57), 131(19), 116(14), 91(49), 65(10), 57(100).

ACKNOWLEDGMENT

Work was supported by Grant CHE-8717871 from the National Science Foundation and by the donors of the Petroleum Research Fund, administered by the American Chemical Society.

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