Reductive *tert*-Butylation of Anils by *tert*-Butylmercury Halides[1]

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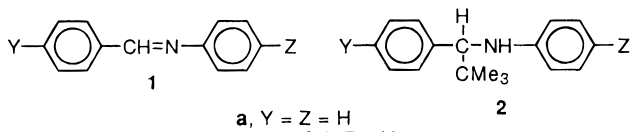
tert-Butyl radicals add to the carbon atom of benzylideneanilines to form anilino radicals, which are protonated in the presence of PTSA or NH_4^+ in Me_2SO. Reduction of the resulting aniline radical cations occurs readily by the ate complex, *t*-$BuHgI_2^-$. In the absence of a proton donor, *t*-BuHgI will also transfer a hydrogen atom to the anilino radical to give the reductive alkylation product. Protonation can promote a free radical chain process involving electron transfer by substrate activation and/or by increasing the electron affinity of the intermediate radicals. Since the adduct radicals formed from benzylideneanilines are more easily protonated than the parent Schiff bases, PTSA but not NH_4^+ demonstrates substrate activation, although both proton donors promote the free radical reaction.

Results and Discussion

Photolysis of an excess of *t*-BuHgCl with benzylideneanilines **1** at 35−40 °C in Me_2SO yields trace amounts of **2** as the major product. The yield of **2** is increased by



a, Y = Z = H
b, Y = CN, Z = H
c, Y = Cl, Z = H
d, Y = Br, Z = H
e, Y = Me, Z = H
f, Y = MeO, Z = H
g, Y = Z = CN

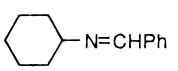
use of *t*-BuHgI, and the reaction is further accelerated by the presence of iodide ion. However, only 0.5 mol of **2** can be formed per mole of *t*-BuHgI, since the formation of **2** is accompanied by $Me_2C{=}CH_2$, Hg^0, and HgI_2 (reaction 1).

$$2t\text{-BuHgI} + \mathbf{1} \xrightarrow[h\nu]{\text{KI}} \mathbf{2} + Me_2C{=}CH_2 + Hg^0 + HgI_2 \quad (1)$$

p-Toluenesulfonic acid (PTSA) dramatically increases the rate of the reaction and yields **2** essentially quantitatively with only 1 equiv of *t*-BuHgI (reaction 2).[2]

$$t\text{-BuHgI} + \mathbf{1} + \text{PTSA} \xrightarrow{\text{KI}} \mathbf{2} + HgI_2 + \text{KOTs} \quad (2)$$

Furthermore, the reaction will now occur slowly in the dark at room temperature by a free radical chain process completely inhibited for days by 10 mol % of $(t\text{-Bu})_2NO^\bullet$. Ammonium iodide also promotes the reaction of *t*-BuHgI with **1** and leads to a reaction approaching a 1:1 stoichiometry. Table 1 presents results obtained for **1a**−**g** as well as for **3** and for the bis-*tert*-butylation of **4**. In all



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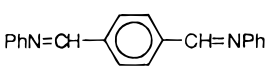

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cases, the *t*-Bu$^\bullet$ added only to the carbon atom of the imine double bond, although from **3**, 10−15% of *c*-C_6H_{11}N(*t*-Bu)CH(*t*-Bu)Ph was also observed. Imines such as $Ph_2C{=}NPh$ and *c*-$C_6H_{10}{=}NPh$ fail to react, even in the presence of PTSA.

Reaction of **1** with *t*-BuHgI in the presence of I^- and PTSA forms only traces of mercury metal and isobutene.

Table 1. Reaction of Benzylideneamines with *t*-BuHgX

substrate	*t*-BuHgX (X, equiv)	MI (M^+, equiv)	PTSA (equiv)	conditions[a]	% **2**[b]
1a	Cl, 4			*hν*, 30 h	<2
1a	Cl, 4	K, 4		*hν*, 24 h	94
1a	I, 2	K, 2		*hν*, 5 h	53
1a	Cl, 4	K, 4	4	*hν*, 0.5 h	77
1a	Cl, 1.5	K, 2	4	*hν*, 5 h	87
1a	I, 2	K, 2	2	*hν*, 5 h	100
1a	I, 2	NH_4, 2		*hν*, 5 h	81
1a	I, 2	NH_4, 2		dark, 24 h	0[c]
1a	I, 2	K, 2	2	dark, 24 h	95
1a	I, 2	K, 2	2	dark, 24 h	0[c]
1b	I, 2	K, 2		*hν*, 6 h	78[d]
1b	I, 1	K, 1		*hν*, 6−24 h	45
1b	I, 1	NH_4, 1		*hν*, 5 h	68[e]
1b	I, 1	K, 1	1	*hν*, 3 h	91[f]
1c	I, 2	K, 2		*hν*, 5 h	50
1c	I, 2	NH_4, 2		*hν*, 5 h	86
1c	I, 2	K, 2	2	*hν*, 5 h	98
1c	I, 2	K, 2	2	dark, 24 h	95
1d	I, 2	K, 2		*hν*, 5 h	56
1d	I, 2	NH_4, 2		*hν*, 5 h	87
1d	I, 2	K, 2	2	*hν*, 5 h	99
1e	I, 2	K, 2		*hν*, 5 h	53
1e	I, 2	NH_4, 2		*hν*, 5 h	81
1e	I, 2	K, 2	2	*hν*, 5 h	100
1f	I, 2	K, 2	2	*hν*, 5 h	100
1g	I, 2	K, 2		*hν*, 5 h	58
1g	I, 4	K, 4		*hν*, 5 h	92[g]
1g	I, 2	NH_4, 2		*hν*, 5 h	85
1g	I, 2	K, 2	2	*hν*, 1.5 h	98[h]
1g	I, 2	K, 2	2	dark, 24 h	92[i]
3	Cl, 4	K, 4		*hν*, 16 h	62[j]
3	Cl, 4	K, 4	4	*hν*, 1.5 h	88[j]
4	I, 4	K, 4		*hν*, 5 h	50[k]
4	I, 4	NH_4, 4		*hν*, 5 h	81[k]
4	I, 4	K, 4	4	*hν*, 5 h	98[k]

[a] *hν* = photolysis with a 275 W fluorescent sun lamp at 35−40 °C; dark reactions at 25 °C. [b] By ^1H NMR with $PhCH_3$ as an internal standard. [c] In the presence of 10 mol % of $(t\text{-Bu})_2NO^\bullet$. [d] 0.80 equiv of Hg^0 and 0.33 equiv of $Me_2C{=}CH_2$ also observed. [e] 0.11 equiv of $Me_2C{=}CH_2$ observed. [f] Only a trace of Hg^0 and ~0.06 equiv of $Me_2C{=}CH_2$ observed. [g] 1 equiv of Hg^0 and 0.67 equiv of $Me_2C{=}CH_2$ observed. [h] 0.12 equiv of $Me_2C{=}CH_2$ and only a trace of Hg^0 observed. [i] 0.05 equiv of $Me_2C{=}CH_2$. [j] *c*-C_6H_{11}-NHCH(*t*-Bu)Ph. Also detected 10−15% of *c*-C_6H_{11}N(*t*-Bu)CH(*t*-Bu)Ph. [k] To yield PhNHCH(*t*-Bu)C_6H_4CH(*t*-Bu)NHPh.

[⊗] Abstract published in *Advance ACS Abstracts,* November 15, 1996.

(1) Electron Transfer Processes. 61.

(2) Russell, G. A.; Yao, C.-F.; Rajaratnam, R.; Kim, B. H. *J. Am. Chem. Soc.* **1991**, *113*, 373.

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The fast reaction with a long kinetic chain apparently involves the addition of *t*-Bu$^\bullet$ to the iminium ion, followed by an electron transfer step (Scheme 1).[2] Since the ate

Scheme 1

$$\mathbf{1} + \text{PTSA} \rightleftharpoons \text{ArCH=NHAr}^+$$

$$\text{ArCH=NHAr}^+ + t\text{-Bu}^\bullet \rightarrow \text{ArCH}(t\text{-Bu})\text{NHAr}^{\bullet+}$$

$$\text{ArCH}(t\text{-Bu})\text{NHAr}^{\bullet+} + t\text{-BuHgI}_2^- \rightarrow \mathbf{2} + t\text{-Bu}^\bullet + \text{HgI}_2$$

complex (t-BuHgI$_2^-$) has a $\Delta G°$ for complexation of 0 ($K_{eq} \approx 1$ in Me_2SO at 25 °C),[3] and since the reaction of I$^\bullet$ with *t*-BuHgI to form *t*-Bu$^\bullet$ and HgI_2 is exothermic by >25 kcal/mol,[4] the ate complex is expected to be a better reducing agent than I^- itself, provided that the electron transfer from the ate complex is dissociative (t-BuHgI$_2^- \rightarrow t$-Bu$^\bullet$ + HgI_2 + e$^-$).

In the absence of a proton donor, addition of *t*-Bu$^\bullet$ to **1** forms an anilino radical, which apparently abstracts a hydrogen atom from *t*-BuHgI (Scheme 2). When the

Scheme 2

$$t\text{-Bu}^\bullet + \mathbf{1} \rightarrow \text{ArCH}(t\text{-Bu})\text{NAr}^\bullet$$

$$\text{ArCH}(t\text{-Bu})\text{NAr}^\bullet + t\text{-BuHgI} \rightarrow \mathbf{2} + \text{MeC=CH}_2 + \text{HgI}^\bullet$$

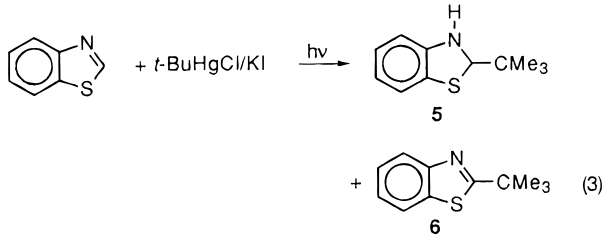
$$\text{HgI}^\bullet \rightarrow \text{Hg}^0 + \text{I}^\bullet \xrightarrow{t\text{-BuHgI}} t\text{-Bu}^\bullet + \text{HgI}_2$$

$$(\text{or } \text{HgI}^\bullet + t\text{-BuHgI} \rightleftharpoons \text{HgI}_2 + t\text{-BuHg}^\bullet \rightarrow \text{Hg}^\bullet + t\text{-Bu}^\bullet)^5$$

reactions are followed by ^{1}H NMR in Me_2SO-d_6, there is no evidence for the formation of intermediates such as PhCH(*t*-Bu)N(HgI)Ph which could yield **2** upon protonolysis. *t*-BuHgI may be more reactive than *t*-BuHgCl in the β-elimination step of Scheme 2 or in the reactions leading to the formation of Hg^0 and HgI_2.[5] However, rate differences for these steps may be less important in determining the overall rate of the reaction than the initiation step involving the photolysis of *t*-BuHgX. *t*-BuHgI is photochemically more labile than the chloride and, in the presence of I^-, forms *t*-Bu$^\bullet$ at a measurable rate at 25 °C in the absence of irradiation, possibly via comproportionation to form the easily homolyzed (t-Bu)$_2$Hg.[3,6]

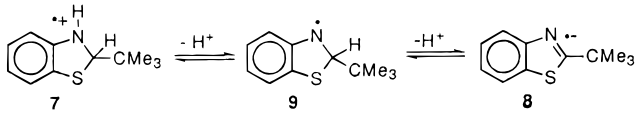
The effect of NH_4^+ on the reaction seems to be connected with proton donation. However, NH_4^+ (pK_a = 9.2 in H_2O) could not appreciably protonate an anil since the pK_a of *p*-ClC$_6$H$_4$CH=NHPh$^+$ is 2.8 (in H_2O).[7] However, NH_4^+ can apparently protonate an anilino radical, since in H_2O the pK_a of PhNH$_2^{\bullet+}$ is 7.0.[8] The aniline radical cations are weaker acids than the anilinium (pK_a of PhNH$_3^+$ = 4.6) or phenyliminium cations (RCH=NHPh$^+$). Thus, promotion by NH_4I appears to be connected with protonation of the adduct anilino radicals to form a radical cation that is readily reduced to **2**. Ammonium ion thus promotes the electron transfer step of the reaction without affecting the reactivity of **1** toward *t*-Bu$^\bullet$, while PTSA additionally provides substrates activation (Scheme 1). Competitive reactions of *t*-BuHgI/I$^-$ with **1a** and (*E*)-PhCH=CHI (to yield (*E*)-PhCH=CHCMe$_3$)[9] support this analysis. Thus, in Me_2SO-d_6, photolysis at 35−40 °C demonstrates that **1a** is 0.84 ± 0.04 as reactive as the β-iodostyrene with added KI (4 equiv) and 1.1 ± 0.1 as reactive with added NH_4I (4 equiv). In the presence of 2 equiv of PTSA, the imine is >4 times as reactive as the styrene with either added KI or NH_4I.[10,11]

With the benzylideneanilines, there is no indication of the formation of ArC(*t*-Bu)=NPh, a possible product of the disproportionation of two ArCH(*t*-Bu)NPh$^\bullet$ radicals or of the coupling of ArCH(*t*-Bu)NPh$^\bullet$ with *t*-Bu$^\bullet$. However, benzothiazole forms both the reductive and oxidative alkylation products, **5** and **6** (reaction 3). By the



(3)

proper choice of conditions, the reaction can be controlled to yield exclusively **5** or **6**. Photolysis of *t*-BuHgI/KI in the presence of PTSA yields only **5** in 70−85% yield, while in the absence of PTSA approximately equal amounts of **5** and **6** are slowly formed. In the presence of PTSA, electron transfer to the radical cation **7** is apparently involved. In the presence of DABCO, only the oxidative *tert*-butylation product **6** is observed, possibly via **8**, but the yield is low. Photolysis of *t*-BuHgCl/KI in the presence of $K_2S_2O_8$ also forms only **6** in yields of ~60%, presumably from hydrogen atom abstraction from **9** by I$^\bullet$, SO$_4^{\bullet-}$ (I$^-$ + S$_2$O$_8^{-2} \rightarrow$ I$^\bullet$ + SO$_4^{2-}$ + SO$_4^{\bullet-}$), or *t*-Bu$^\bullet$.



p-Cyanostyrene failed to yield the reductive alkylation products with *t*-BuHgI under the conditions employed in Table 1; photolysis slowly led to the formation of the *meso* and racemic forms of the dimers obtained from *p*-NCC$_6$H$_4$-CH$^\bullet$CH$_2$CMe$_3$. It is surprising that the sterically hindered anilino radicals can abstract a hydrogen atom from *t*-BuHgI, but the less hindered benzylic radicals do not

(3) Russell, G. A.; Hu, S.; Herron, S.; Baik, W.; Ngoviwatchai, P.; Jiang, W.; Nebgen, M.; Wu, Y.-W. *J. Phys. Org. Chem.* **1988**, *1*, 299.
(4) Cottrell, T. L. *The Strengths of Chemical Bonds*; Academic Press: New York, 1954.
(5) Alkylmercury(I) species have negligible bond dissociation energies: Gowenlock, B. G.; Polanyi, J. C.; Warehurst, E. *Proc. R. Soc. London, Ser. A* **1953**, *219*, 270. The bond dissication energies of HgX$^\bullet$ are 23, 16, and 8 mol for X = Cl, Br, and I, respectively: Gaydon, A. G. *Dissociation Energies and Spectra of Diatomic Molecules*, 3rd ed.; Chapman and Hall: London, 1968.
(6) Blaukat, U.; Newmann, W. P. *J. Organomet. Chem.* **1973**, *49*, 323.
(7) Cordes, E. H.; Jencks, W. P. *J. Am. Chem. Soc.* **1962**, *84*, 832.
(8) Qin, L.; Tripathi, G. N. R.; Schuler, R. H. *Z. Naturforsch. A* **1985**, *40*, 1026.
(9) Russell, G. A.; Ngoviwatchai, P. *J. Org. Chem.***1989**, *45*, 1836.
(10) If the addition of *t*-Bu$^\bullet$ to **1** is reversible, and if a proton donor increases the rate of conversion of the adduct radical to **2**, an apparent increase in substrate reactivity could be observed without substrate protonation. Perhaps the small increase in relative reactivity observed for **1a** in the presence of NH_4I reflects this reversibility.
(11) Russell, G. A.; Shi, B. Z.; Jiang, W.; Hu, S.; Kim, B. H.; Baik, W. *J. Am. Chem. Soc.* **1995**, *117*, 3952.

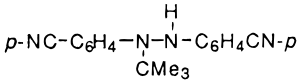
react. Perhaps the hydrogen abstraction is facilitated by the electrophilicity of the attacking radical, as illustrated in transition state **10** (X = NCH(Ar)CMe_3 or $CHCH_2$-CMe_3).

$$ArX:^{-} \quad H^{\bullet} \quad CH_2{=}CMe_2 \quad HgI^{+}$$
10

Azobenzene is converted to the hydrazine **11** by photolysis with *t*-BuHgCl/KI (reaction 4). The reaction does

$$PhN{=}NPh + t\text{-}BuHgI/HI \xrightarrow{h\nu} PhN(t\text{-}Bu)NHPh + Me_2C{=}CH_2 + Hg^0 + HgI_2 \quad (4)$$
11

not appear to be promoted by PTSA, and the best yield of **11** (90%) is achieved by photolysis of a mixture of 4 equiv each of *t*-BuHgI and KI with 2 equiv of $K_2S_2O_8$. *p*,*p*′-Dicyanoazobenzene is more reactive, and good yields of **12** are obtained upon photolysis in Me_2SO with 4 equiv of *t*-BuHgI in the presence of 4 equiv of KI (87% in 19 h), while addition of 2 equiv of $K_2S_2O_8$ gives a 97% yield of **12** in 5 h of photolysis. Di-*tert*-butylated products are



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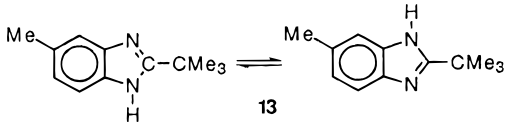
not observed, even under conditions that would favor a high flux of *t*-Bu$^{\bullet}$, i.e., with I^- and $S_2O_8^{2-}$. The reactions of radicals such as ArCH(*t*-Bu)NPh$^{\bullet}$ and ArN(*t*-Bu)NPh$^{\bullet}$ with *t*-Bu$^{\bullet}$ appear to form only the disproportionation products in which the anilino radical has been reduced. On the other hand, 5-methylbenzimidazole gives rise to the oxidative *tert*-butylation product **13** under all conditions employed. Photolysis of the imidazole with *t*-



13

BuHgCl (4 equiv, 7 h) yields only traces of **13**, but with 4 equiv of KI the yield of **13** is 55%. Addition of $K_2S_2O_8$ does not increase the yield of **13**, while the presence of 4 equiv of PTSA decreases the yield of **13** to 35%, possibly because of electrophilic cleavage of *t*-BuHgI. If interaction of the adduct radical with *t*-Bu$^{\bullet}$ is important in the formation of **13**, it must now occur with transfer of the hydrogen atom from the adduct radical to *t*-Bu$^{\bullet}$ with rearomatization of the imidazole ring.

Experimental Section

General Method. NMR spectra were recorded in $CDCl_3$ at 300 MHz for ^{1}H with TMS as an internal standard and at 75.4 MHz for ^{13}C with the central line of $CDCl_3$ the standard (77.00 ppm). GC/MS were recorded with Finnegan 4000 and Magnum spectrometers and HRMS with a Kratos MS-50 spectrometer. Melting points are uncorrected. Elemental analyses were performed by Galbraith Laboratories, Inc.

Reactions were monitored on a 0.05 mmol scale under N_2 in 0.5 mL of Me_2SO-d_6 in Pyrex NMR tubes with irradiation by a 275 W Sylvania sun lamp ca. 25 cm from the reaction tube. Toluene or diiodomethane was added as an internal standard before the yield was measured by NMR integration.

Products were isolated on a 0.2 mmol scale from reactions in 2 mL of deoxygenated Me_2SO under nitrogen by treatment with saturated aqueous $Na_2S_2O_3$, neutralization (if required), and extraction with CH_2Cl_2, followed by washing with brine and drying over $MgSO_4$. After concentration under vacuum, products were isolated by flash column chromatography on silica gel (Merck grade 9385, 230−400 mesh) with hexane−ethyl acetate as the eluent. Solids were recrystallized from the same solvent.

***N*-(2,2-Dimethyl-1-phenylpropyl)benzenamine (2a).** ^{1}H NMR: δ 0.995 (s, 9 H), 4.031 (s, 1 H), 4.245 (s, 1 H), 6.480 (d, J = 7.8 Hz, 2 H), 6.570 (t, J = 7.2 Hz, 1 H), 7.010 (t, J = 8.1 Hz, 2 H), 7.15−7.30 (m, 5 H). GC and HRMS: m/z (relative intensity) 239.1678 (4, calcd for $C_{17}H_{21}N$, 239.1679), 182 (100), 104 (10), 77 (19), 57 (2). Anal. Calcd for $C_{17}H_{21}N$: C, 85.31; H, 8.84; N, 5.85. Found: C, 85.20; H, 8.91; N, 5.83.

4-[2,2-Dimethyl-1-(phenylamino)propyl]benzonitrile (2b). Mp: 159−160 °C. ^{1}H NMR: δ 0.99 (s, 9 H), 4.08 (d, J = 5.4 Hz, 1 H), 4.26 (br d, J = 5.1 Hz, 1 H), 6.43−6.40 (m, 2 H), 6.62 (t, J = 7.2 Hz, 1 H), 7.07−7.02 (m, 2 H), 7.43 (d, J = 8.4 Hz, 2 H), 7.57 (d, J = 8.1 Hz, 2 H). ^{13}C NMR: δ 26.93 (q), 34.93 (s), 67.07 (d), 110.73 (s), 113.08 (d), 117.54 (d), 118.91 (s), 129.10 (d), 129.14 (d), 131.56 (d), 146.89 (s), 147.20 (s). GC and HRMS: m/z (relative intensity) 264.1627 (5, calcd for $C_{18}H_{20}N_2$, 264.1632), 207 (100), 104 (5), 77 (10). Anal. Calcd for $C_{18}H_{20}N_2$: C, 81.78; H, 7.62; N, 10.60. Found: C, 82.12; H, 7.79; N, 10.40.

***N*-[1-(4-Chlorophenyl)-2,2-dimethylpropyl]benzenamine (2c).** Mp: 95−96 °C. ^{1}H NMR: δ 0.96 (s, 9 H), 4.00 (s, 1 H), 4.20 (s, 1 H), 6.45 (d, J = 8.1 Hz, 2 H), 6.60 (t, J = 8.1 Hz, 1 H), 7.04 (t, J = 8.1 Hz, 2 H), 7.23 (br s, 4 H). ^{13}C NMR: δ 26.97 (q), 34.82 (s), 66.62 (d), 113.13 (d), 117.15 (d), 127.87 (d), 129.01 (d), 129.71 (d), 132.39 (s), 169.69 (s), 147.32 (s). GC and HRMS: m/z (relative intensity) 273.1291 (2, calcd for $C_{17}H_{20}ClN$, 273.1284), 216 (100), 104 (10), 77 (18). Anal. Calcd for $C_{17}H_{20}ClN$: C, 74.57; H, 7.36; N, 5.12. Found: C, 73.45; H, 7.14; N, 4.90.

***N*-[1-(4-Bromophenyl)-2,2-dimethylpropyl]benzenamine (2d).** Mp: 91−92 °C. ^{1}H NMR: δ 0.96 (s, 9 H), 3.98 (s, 1 H), 4.20 (s, 1 H), 6.42−6.45 (m, 2 H), 6.60 (t, J = 7.2 Hz, 1 H), 7.04 (dd, J = 8.4, 7.5 Hz, 2 H), 7.17 (d, J = 8.4 Hz, 2 H), 7.39 (d, J = 8.4 Hz, 2 H). GC and HRMS: m/z (relative intensity) 317.0780 (7, calcd for $C_{17}H_{20}BrN$, 317.0779), 260 (100), 180 (15), 104 (46). Anal. Calcd for $C_{17}H_{20}BrN$: C, 64.16; H, 6.33; N, 4.40. Found: C, 63.78; H, 6.05; N, 4.27.

***N*-[2,2-Dimethyl-1-(4-methylphenyl)propyl]benzenamine (2e).** Mp: 67−68 °C. ^{1}H NMR: δ 0.95 (s, 9 H), 2.29 (s, 3 H), 4.00 (d, J = 6.3 Hz, 1 H), 4.22 (d, J = 6.0 Hz, 1 H), 6.47 (dd, J = 8.4, 0.9 Hz, 2 H), 6.56 (tt, J = 7.5, 0.9 Hz, 1 H), 7.04 (m, 4 H), 7.17 (d, J = 8.1 Hz, 2 H). ^{13}C NMR: δ 21.05 (q), 27.04 (q), 34.84 (s), 66.81 (d), 113.09 (d), 116.74 (d), 128.30 (d), 128.33 (d), 128.93 (d), 136.11 (s), 137.94 (s), 147.73 (s). HRMS: m/z 253.1834 (calcd for $C_{18}H_{23}N$, 253.1830). Anal. Calcd for $C_{18}H_{23}N$: C, 85.32; H, 9.15; N, 5.53. Found: C, 84.06; H, 9.07; N, 5.32.

***N*-[1-(4-Methoxyphenyl)-2,2-dimethylpropyl]benzenamine (2f).** Mp: 102−103 °C. ^{1}H NMR: δ 0.92 (s, 9 H), 3.79 (s, 3 H), 3.98 (d, J = 5.1 Hz, 1 H), 4.21 (d, J = 5.1 Hz, 1 H), 6.47 (dd, J = 8.7, 0.9 Hz, 2 H), 6.58 (tt, J = 7.5, 0.9 Hz, 1 H), 6.81 (d, J = 8.7 Hz, 2 H), 7.04 (dd, J = 8.7, 7.5 Hz, 2 H), 7.20 (d, J = 8.7 Hz, 2 H). ^{13}C NMR: δ 26.98 (q), 34.91 (s), 55.03 (q), 66.49 (d), 113.01 (d), 113.11 (d), 116.73 (d), 128.90 (d), 129.27 (d), 132.99 (s), 147.70 (s), 158.30 (s). GC and HRMS: m/z (relative intensity) 269.1787 (3, calcd for $C_{18}H_{23}NO$, 269.1780), 212 (100), 197 (2), 168 (4), 104 (17). Anal. Calcd for $C_{18}H_{23}NO$: C, 80.25; H, 8.61; N, 5.20. Found: C, 80.09; H, 8.98; N, 5.11.

***N*-[1-(4-Cyanophenyl)-2,2-dimethylpropyl]-4-cyanobenzenamine (2g).** Mp: 178−179 °C. ^{1}H NMR: δ 1.01 (s, 9 H), 4.13 (d, J = 6.3 Hz, 1 H), 4.78 (d, J = 6.0 Hz, 1 H), 6.41 (d, J = 9.0 Hz, 2 H), 7.31 (d, J = 8.7 Hz, 2 H), 7.40 (d, J = 8.4 Hz, 2 H), 7.61 (d, J = 8.4 Hz, 2 H). ^{13}C NMR: δ 26.68 (q), 34.81 (s), 66.30 (d), 98.68 (s), 110.94 (s), 112.69 (d), 118.61 (s), 120.22 (s), 128.94 (d), 131.65 (d), 123.34 (d), 145.65 (s), 150.12 (s). HRMS: m/z 289.1575 (calcd for $C_{19}H_{19}N_3$, 289.1579). Anal. Calcd for $C_{19}H_{19}N_3$: C, 78.86; H, 6.62; N, 14.52. Found: C, 78.58; H, 6.68; N, 14.25.

***N*-Cyclohexyl-*N*-(2,2-dimethyl-1-phenylpropyl)-amine.** Photolysis of **3** with *t*-BuHgCl/KI yielded a mixture of the mono- and di-*tert*-butylation products. The product of reductive *tert*-butylation had the following characteristics. ^{1}H NMR: δ 0.865 (s, 9 H), 1.03−1.69 (m, 10 H), 1.907 (t, 1 H), 2.03−2.17 (m, 1 H), 3.43 (s, 1 H), 7.18−7.29 (m, 5 H). ^{13}C NMR: δ 24.67 (t), 25.11 (t), 26.30 (t), 27.18 (q), 32.63 (t), 34.62 (s), 35.04 (t), 53.71 (d), 68.95 (d), 126.29 (d), 127.19 (d), 128.87 (d), 142.76 (s). GC and HRMS: *m*/*z* (relative intensity) 244.2061 (0.02, calcd for $C_{17}H_{26}N$, 244.2065), 188 (100), 144 (2), 132 (2), 106 (88). CIMS (NH_3): *m*/*z* 246 (M + 1, 100), 188 (7). Anal. Calcd for $C_{17}H_{26}N$: C, 82.87; H, 10.64; N, 6.49. Found: C, 82.70; H, 11.10; N, 6.35. The di-*tert*-butylated products, *N*-cyclohexyl-*N*-(1,1-dimethylethyl)-*N*-(2,2-dimethyl-1-phenylpropyl)amine was identified by GC/MS and ^{1}H NMR. GC/MS: *m*/*z* (relative intensity) 302 (M + 1, 0.1), 245 (18), 244 (100), 162 (51), 147 (13), 57 (17). ^{1}H NMR: δ 0.856 (s, 9 H), 1.03−1.69 (m, 10 H), 1.313 (s, 9 H), 2.071−2.155 (m, 1 H), 2.388 (s, 1 H), 7.150−7.300 (m, 5 H).

1,4-Bis[2,2-dimethyl-1-(phenylamino)propyl]benzene. Photolysis of **4** with excess *t*-BuHgI/KI produced the di-*tert*-butylated product. Mp: 131−132 °C. ^{1}H NMR: δ 0.94 (s, 18 H), 3.96 (d, J = 3.0 Hz, 2 H), 4.21 (br s, 2 H), 6.42−6.46 (m, 4 H), 6.53−6.60 (m, 2 H), 7.00−7.04 (m, 4 H), 7.19 (s, 4 H). ^{13}C NMR: δ 27.06 (q), 34.92 (s), 66.98 (d), 113.06 (d), 116.70 (d), 127.68 (d), 128.87 (d). GC and HRMS: *m*/*z* (relative intensity) 400.2869 (4, calcd for $C_{28}H_{36}N_2$, 400.2878), 343 (100), 286 (78), 236 (5), 209 (10), 143 (6), 104 (13), 77 (9). Anal. Calcd for $C_{28}H_{36}N_2$: C, 83.93; H, 9.06; N, 6.99. Found: C, 83.42; H, 9.15; N, 6.73.

2,3-Dihydro-2-(1,1-dimethylethyl)benzothiazole (5). ^{1}H NMR: δ 0.965 (s, 9 H), 4.191 (br s, 1 H), 5.145 (d, J = 2.7 Hz, 1 H), 6.530 (dd, J = 7.8, 0.6 Hz), 6.630 (td, J = 7.5, 1.2 Hz, 1 H), 6.836 (td, J = 7.8, 1.2 Hz, 1 H), 6.989 (dd, J = 7.5, 1.2 Hz). GC and HRMS: *m*/*z* (relative intensity) 193.0924 (9, calcd for $C_{11}H_{15}NS$, 193.0925), 176 (2), 136 (100). Anal. Calcd for $C_{11}H_{15}NS$: C, 68.37; H, 7.82; N, 7.25. Found: C, 68.34; H, 7.86; N, 7.21.

2-(1,1-Dimethylethyl)benzothiazole (6).[12] The ^{1}H NMR: and FTIR agreed with previously reported values.[13] ^{1}H NMR: δ 1.521 (s, 9 H), 7.320 (td, J = 7.8, 0.9 Hz, 1 H), 7.422 (td, J = 8.1, 0.9 Hz, 1 H), 7.831 (d, J = 7.8 Hz, 1 H), 7.989 (d, J = 8.1 Hz, 1 H). GC and HRMS: *m*/*z* (relative intensity) 191.0767 (28, calcd for $C_{11}H_{13}NS$, 191.0769), 176 (100), 149 (16).

***N*-(2,2-Dimethylpropyl)-*N*,*N*′-diphenylhydrazine (11).**[14] This compound had been previously prepared in low yield by the reaction of the disodium adduct of azobenzene with *t*-BuCl.[14] Mp: 53−56 °C (lit.[14] mp 57.0−57.6 °C). ^{1}H NMR: δ 1.199 (s, 9 H), 5.650 (s, 1 H), 6.671 (t, J = 7.5 Hz, 1 H), 6.913 (d, J = 7.8 Hz, 2 H), 7.045−7.160 (m, 3 H), 7.204−7.238 (m, 4 H). ^{13}C NMR: δ 26.96 (q), 58.75 (s), 112.72 (d), 118.45 (d), 124.96 (d), 126.63 (d), 128.18 (d), 128.82 (d), 148.36 (s), 149.27 (s). GC and HRMS: *m*/*z* (relative intensity) 240.1622 (28, calcd for $C_{16}H_{20}N_2$, 240.1626), 185 (9), 184 (74), 183 (100).

***N*-(2,2-Dimethylpropyl)-*N*,*N*′-bis(4-cyanophenyl)hydrazine (12).** The compound was isolated as an oil by column chromatography. ^{1}H NMR: δ 1.32 (s, 9 H), 6.68 (s, 1 H), 6.88 (d, J = 8.7 Hz, 2 H), 7.27 (d,J = 8.7 Hz, 2 H), 7.41 (d, J = 8.7 Hz, 2 H), 7.52 (d, J = 8.7 Hz, 2 H). ^{13}C NMR: δ 27.33 (q), 60.58 (s), 100.17 (s), 106.00 (s), 111.49 (d), 119.04 (s), 120.17 (s), 123.22 (d), 132.44 (d), 133.61 (d), 151.74 (s), 152.01 (s). HRMS: 290.1533 (calcd for $C_{18}H_{18}N_4$, 290.1532). Anal. Calcd for $C_{18}H_{18}N_4$: C, 74.46; H, 6.25; N, 19.29. Found: C, 74.30; H, 6.31; N, 19.20.

2-(1,1-Dimethylethyl)-5-methyl-1(3)*H*-benzimidazole (13). The compound was isolated as a solid. Mp: 205−208 °C. ^{1}H NMR: (Me_2SO-d_6): δ 1.385 (s, 9 H), 2.385 (d, J = 5.4 Hz, 3 H), 6.85−6.95 (m, 1 H), 7.10−7.40 (m, 2 H). ^{1}H NMR: ($CDCl_3$): δ 9.25 (br s). GC and HRMS: *m*/*z* (relative intensity) 188.1311 (5, calcd for $C_{12}H_{16}N_2$ 188.1314), 173 (100), 157 (3), 131 (8). Anal. Calcd for $C_{12}H_{16}N_2$: C, 76.56; H, 8.57; N, 14.88. Found: C, 76.23; H, 8.61; N, 14.72.

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(12) Metgerand, T.; Plank, H. *Bull. Soc. Chim. Fr.* **1956**, 1692.

(13) Katritzky, A. R.; Kuzmierkiewicz, W.; Aurrecoechea, J. M. *J. Org. Chem.* **1987**, *52*, 844.

(14) Reesor, J. W. B.; Wright, G. F. *J. Org. Chem.* **1957**, *22*, 375.