Novel Rearrangement of *N*-(9*H*-Carbazol-9-yl)arylaminyl Radicals

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The title radicals were generated from 2-(arylazo)-2′-iodobiphenyls using the tin hydride method. When the aryl substituent has an acetyloxy or a benzoyloxy group in the ortho position, besides reduction of the hydrazyl radical, a migration of the acetyl or benzoyl from oxygen to nitrogen atom took place. The mechanism of the rearrangement is discussed, and evidences supporting a radical pathway are reported, including EPR characterization of the intermediates.

The reactions of *N*-(9*H*-carbazol-9-yl)arylaminyl radicals have been studied in our laboratory a few years ago. These radicals, generated by reduction of the diazonium tetrafluoroborates of 2-amino-2′-(arylazo)biphenyls followed by cyclization of the corresponding biphenyl-2-yl radicals, were found to dimerize, via N,N- or C,N-coupling, or to abstract a hydrogen atom.[1,2]

Similar hydrazyl radicals were produced either by intramolecular addition of aryl radicals to the azo group[3] or by oxidation of suitable hydrogenated derivatives,[2,4] and their reactivity was shown to include addition to aromatic rings, with possibility of neophyl-like rearrangements.

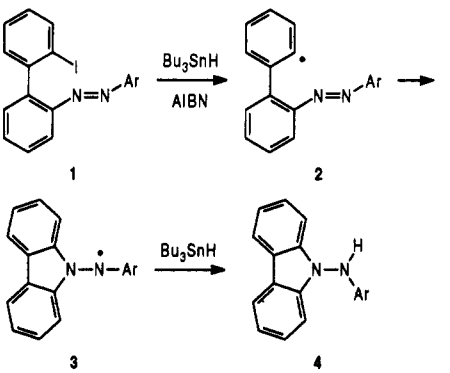
Recently,[5] *N*-(9*H*-carbazol-9-yl)arylaminyl radicals were generated from 2-(arylazo)-2′-iodobiphenyls by iodine atom abstraction with tri-*n*-butyltin hydride and AIBN as a radical initiator: under these conditions they gave only hydrogen abstraction from the stannane to afford *N*-(9*H*-carbazol-9-yl)benzenamines. In this paper we report a new kind of reactivity of the title intermediates, namely the intramolecular addition of these hydrazyl radicals to the carbonyl group of an ester, with concomitant migration of an acyl moiety from the oxygen to the nitrogen atom.

Results and Discussion

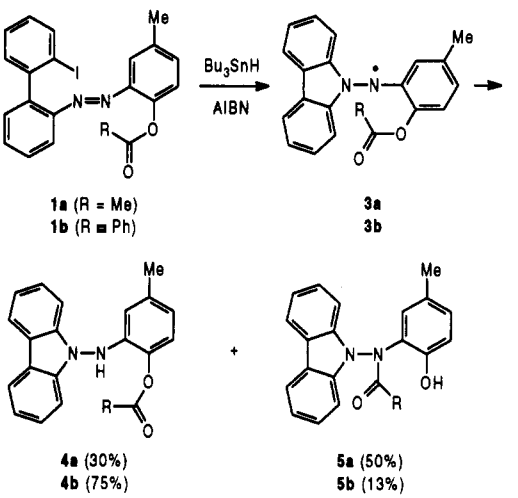
Product Studies. The *N*-(9*H*-carbazol-9-yl)arylaminyl radicals **3** were generated from 2-(arylazo)-2′-iodobiphenyls **1** by iodine atom abstraction with tri-*n*-butyltin radicals[5] and intramolecular ring closure of the intermediate biphenyl-2′-yl radicals **2** (Scheme I). Normally, the aminyl **3** abstracted a hydrogen atom from tin hydride affording the *N*-(carbazol-9-yl)arylamines **4** in high yields.

When the aryl group had an acetyloxy or a benzoyloxy substituent in the ortho position and the concentration of the stannane was kept low, the reaction gave a mixture of

Scheme I. General Reaction of 2-(Arylazo)-2′-iodobiphenyls 1 with Tri-*n*-butyltin Hydride



Scheme II. Reaction of *o*-Acyloxy-Substituted Diazenes 1a,b with Tri-*n*-butyltin Hydride



4 and the rearranged compounds **5** (Scheme II).[6] Compounds **4** and **5** were identified by spectroscopic data and **4a** was also obtained by an independent synthesis (see Experimental Section).

The experimental results can be explained in terms of the mechanism reported in Scheme III.

The radical **3** can be reduced by tri-*n*-butyltin hydride to give the *N*-(9*H*-carbazol-9-yl)arylamine **4**, or it can

(1) Benati, L.; Placucci, G.; Spagnolo, P.; Tundo, A.; Zanardi, G. *J. Chem. Soc., Perkin Trans. 1* **1977**, 1684.
(2) Benati, L.; Spagnolo, P.; Tundo, A.; Zanardi, G. *J. Chem. Soc., Perkin Trans.1* **1979**, 1536.
(3) Beckwith, A. L. J.; Wang, S.; Warkentin, J. *J. Am. Chem. Soc.* **1987**, *109*, 5289.
(4) Wang, S. F.; Mathew, L., Warkentin, J. *J. Am. Chem. Soc.* **1988**, *110*, 7235.
(5) Alberti, A.; Bedogni, N.; Benaglia, M.; Leardini, R.; Nanni, D.; Pedulli, G. F.; Tundo, A.; Zanardi, G. *J. Org. Chem.* **1992**, *57*, 607.

(6) If the reactions were performed with 2 mol tri-*n*-butyltin hydride and 0.25 mol AIBN, compounds **4** were only obtained; with 2 mol AIBN products **5** were also formed in small amounts. Finally, with 2 mol AIBN and tri-*n*-butyltin hydride added dropwise to the refluxing reaction mixture, **4** and **5** were obtained in the yields reported in Scheme II.

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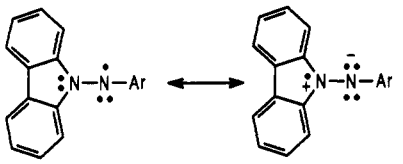
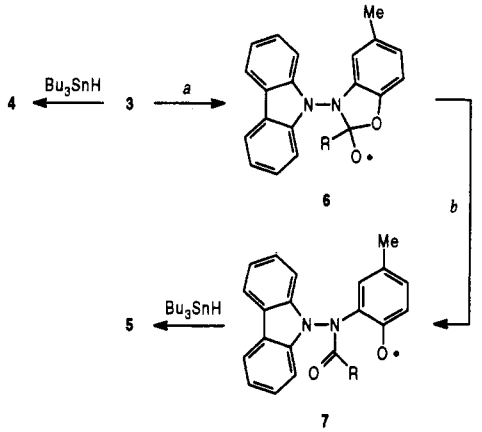


Figure 1. Resonance interaction in radicals 3.

Scheme III. Proposed Mechanism of the Reaction of *o*-Acyloxy-Substituted Diazenes with Tri-*n*-butyltin Hydride



attack the carbonyl moiety, through a 5-exo cyclization, to afford the intermediate **6**, which then leads, by ring opening, to the aryloxy radical **7** and, by subsequent hydrogen abstraction, to the rearranged product **5**. The ring closure step a is probably favored by the presence of the carbazole nitrogen in the position α to the radical center; this increases the nucleophilicity of the hydrazyl radical as exemplified in the resonance structure shown in Figure 1.

The intramolecular radical addition to the carbon atom of a carbonyl group is well known,[7] but apparently there are no examples of this reaction when the carbonyl belongs to an ester, especially if the attacking species is a nitrogen-centered radical.

The mechanism of Scheme III is supported by the following results. In a previous paper[5] we showed that tri-*n*-butyltin hydride can react at the N–N double bond of **1** also by a nonradical mechanism, but we proved that, in the presence of 25% or higher amounts of AIBN, the radical pathway was followed exclusively. Therefore, under the present conditions (Scheme II) iodine atom abstraction and intramolecular ring closure of the resulting radical **2** to give the intermediate **3** is expected. At this point, the fate of the hydrazyl **3**, i.e. reduction or rearrangement, depends on the concentration of stannane. A series of reactions was performed on the substrate **8** (Scheme IV) at different concentrations of tin hydride; compound **8** was used instead of **1a** and **1b** because it was characterized by better workup and chromatography of the reaction mixtures.

As it is shown in Table I, the yield of the hydrazine **10** decreased by reducing the amount of tin hydride present in solution, while, correspondingly, that of the rearranged product **11** increased. This is in agreement with what it is expected on the basis of Scheme III.

Scheme IV. Reaction of Diazene 8 with Tri-*n*-butyltin Hydride

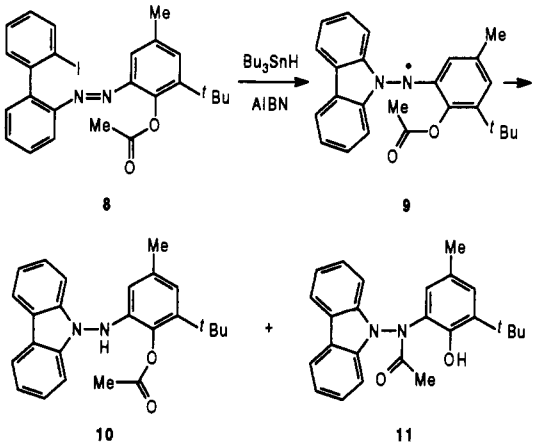
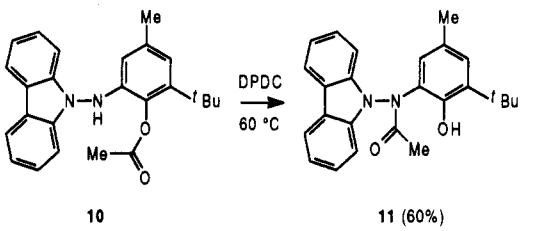


Table I. Dependence of the 11/10 Ratio on the Concentration of Tri-*n*-butyltin Hydride

$[Bu_3SnH]$ (mol/L)	10 (%)	11 (%)	11/10
1	59.9	30.1	0.50
0.5	50.6	44.4	0.88
0.2	24.9	67.2	2.70

Scheme V. Reaction of Hydrazine 10 with Diisopropyl Peroxydicarbonate (DPDC)



The observation that the 11/10 ratio was a function of the concentration of the stannane also suggests that steps a and b of Scheme III should not be reversible under our experimental conditions.[8] As far as the driving force of the whole process is concerned, it can be pointed out that the bond dissociation energy (BDE) of the N–H bond in hydrazines and of the O–H bond in phenols are quite close; in fact, the BDE values are 79.6 kcal/mol for DPPH-H and 81.2 kcal/mol for 2,4,6-tri-*tert*-butylphenol.[9] In the present case, the ease by which the rearrangement reaction takes place seems to indicate that the phenoxy radical is more resonance stabilized with respect to the unrearranged hydrazyl by at least few kcal/mol.

The intermediate **9** was also generated by hydrogen atom abstraction from **10** and was seen to be able to rearrange readily to **11**; in fact, **10**, in the presence of diisopropyl peroxydicarbonate (DPDC) in benzene solution at 60 °C, gave good yields of **11** in about 15 min (Scheme V).

It is also worth pointing out that **10**, at room temperature, rearranged slowly to **11** (about 50% in 10 days), probably through an oxidation mechanism leading to the radical **9** similar to that observed by Warkentin and Wang.[4] The same rearrangement occurred into the reaction mixtures by prolonged refluxing after the disappearance of the starting material; since, however, the conversion of **10** to **11** is a slow process (about 2% in 2 h at 80 °C) it does not

(7) Giese, B. *Radicals in Organic Synthesis: Formation of Carbon–Carbon Bonds*; Pergamon Press: Oxford, 1986; p 167. Curran, D. P. *Synthesis* **1988**, 417 and references cited therein. Beckwith, A. L. J.; Hay, B. P. *J. Am. Chem. Soc.* **1989**, *111*, 2674.

(8) Newcomb, M.; Deeb, T. M. *J. Am. Chem. Soc.* **1987**, *109*, 3163.

(9) Mahoney, L. R.; Mendenhall, G. D.; Ingold, K. U. *J. Am. Chem. Soc.* **1973**, *95*, 8610.

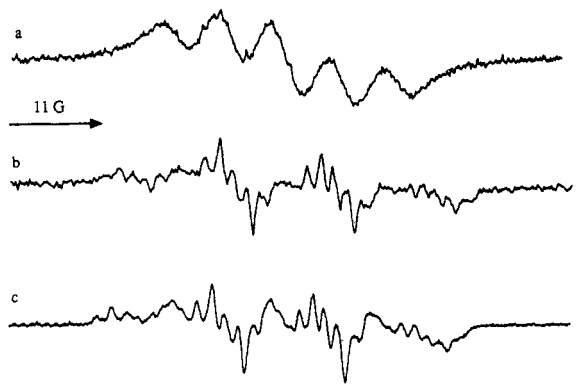


Figure 2. EPR spectra obtained by irradiating benzene solutions of **1d** (Ar = 4-methylphenyl) (a), **8** (b), and **10** (c). In the latter case di-*tert*-butyl peroxide was also present.

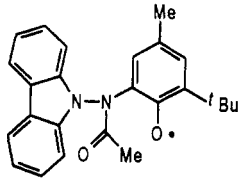


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Figure 3. Radical obtained by photolysis of **8** and by hydrogen abstraction from **10**.

affect significantly the yields reported in Table I. Therefore, although we cannot exclude that **11** might partially derive from **10** by nucleophilic attack of the nitrogen atom to the carbonyl, this kind of mechanism should occur only to a very small extent and its effects are negligible.

EPR Measurements. The radicals formed from the 2-(arylazo)-2′-iodobiphenyls **1** and **8** and from the hydrazine **10** have also been investigated by EPR spectroscopy. Photolysis of deoxygenated benzene solution of **1d** (Ar = 4-methylphenyl) at room temperature, inside the EPR cavity, afforded a radical species whose spectrum, centered at $g = 2.0034$, consists of five broad lines (Figure 2, spectrum a) due to the coupling of the unpaired electron with two almost equivalent nitrogens. This spectrum could be computer simulated by using the following hyperfine splittings: $a(1N) = 6.4$ G, $a(1N) = 7.1$ G. Since these parameters are characteristic of hydrazyl radicals, we can assign the spectrum to radical **3d** (Ar = 4-methylphenyl). By switching off the light, the spectrum persists for several hours. Photolysis of **1d** in the presence of oxygen leads to the formation of a very stable radical which presumably is a nitroxide.

Photolysis of **8** gave rise to a totally different spectrum showing spectral parameters characteristic of a phenoxy radical, where the unpaired electron is coupled with the methyl protons ($a_H = 10.93$ G) in para position with respect to the phenoxylic oxygen, the two meta protons ($a_H = 1.70$ G), and the ortho nitrogen ($a_N = 1.30$ G) (Figure 2, spectrum b). Since these splittings and the *g*-factor (2.0046) are similar to those of the 2,6-di-*tert*-butyl-4-methylphenoxy radical,[10] we can conclude that the spectrum is due to radical **12** (Figure 3). At variance to other phenoxy radicals, this species is transient; in fact, when switching off the light its EPR spectrum quickly disappeared.

Additional support to the conclusion that the radical obtained from **8** has structure **12** was obtained from the observation that the same spectrum could be observed by photolyzing a benzene solution of **10** containing di-*tert*-butyl peroxide (Figure 2, spectrum c); in this case, the formation of **12** should be the result of abstraction of the hydrazylic hydrogen by *tert*-butoxy radicals and subsequent rearrangement.

These spectroscopic data concerning identification of the radical intermediates provide experimental evidence about the rearrangement mechanism exemplified in Scheme III.

Experimental Section

General Procedures. Melting points were determined on an Electrothermal capillary apparatus and are uncorrected. ^{1}H NMR spectra were recorded in deuterochloroform on Varian Gemini 200 (200 MHz) or Varian EM 360L (60 MHz) instruments, using tetramethylsilane as an internal standard. Mass spectra and high resolution mass spectra (HRMS) were performed with a VG 7070E spectrometer by electron impact with a beam energy of 70 eV. IR spectra were recorded in chloroform on a Perkin-Elmer 257 spectrophotometer. Column chromatography was performed on silica gel (ICN Silica 63-200 60A), using light petroleum (40–70 °C) and a light petroleum/diethyl ether gradient (from 0 up to 100% diethyl ether) as eluant. HPLC was performed with a Varian 5000 liquid chromatograph equipped with a C-18 column (Supelcosil LC-18 5μ, 25 cm × 4.6 mm ID) and a Varian 2050 variable λ detector operating at 254 nm, using an acetonitrile/water mixture (93:7 v/v) as eluant.

The assignment of the structures to compounds **4a**, **4b**, **5a**, **5b**, **10**, and **11** was made on the basis of spectroscopic data. The IR spectra of **4a**, **4b**, and **10** were characterized by strong absorptions due to ester carbonyls, whereas **5a**, **5b**, and **11** showed strong bands in the amidic carbonyl region. The ^{1}H NMR spectra of **4a**, **4b**, and **10** had broad signals due to the NH group; on the contrary, products **5a**, **5b**, and **11** showed sharp singlets assignable to the OH substituent. Finally, **4a** was also prepared by an independent synthesis by reacting **4c** (Ar = 2-hydroxy-5-methylphenyl) with 1,1′-carbonyldiimidazole and acetic acid; under these conditions only acetylation of the OH group occurred: in fact, the same reaction performed on the substrate **4d** (Ar = 4-methylphenyl) gave no N-acylated products.

Starting Materials. All reactions were performed in benzene (J. T. Baker). Tri-*n*-butyltin hydride (Aldrich), AIBN (Janssen), 1,1′-carbonyldiimidazole (Aldrich), 4-methylphenol (Aldrich) and 2-*tert*-butyl-4-methylphenol (Aldrich) were commercially available; AIBN was purified by being dissolved in chloroform and reprecipitated with methanol. 2-amino-2′-iodobiphenyl,[11] *N*-(9*H*-carbazol-9-yl)-4-methylbenzenamine (**4d**),[5] and diisopropyl peroxydicarbonate (DPDC)[12] were prepared according to the literature; DPDC was stored at 5 °C as a benzene solution and the peroxide content was determined by iodometric titration.[13]

2-[(2′-Iodo-1,1′-biphenyl-2-yl)azo]-4-methylphenol. 2-Amino-2′-iodobiphenyl (2.95 g, 10 mmol) was diazotized, following the standard procedure, between 0 and 5 °C and added cautiously, at the same temperature, to a stirred solution of 4-methylphenol (1.08 g, 10 mmol) and sodium hydroxide (1.6 g, 40 mmol) in water (50 mL). The mixture was neutralized with hydrochloric acid and filtered and the solid chromatographed on silica gel to give the title product (3.11 g, 75%): mp = 135–136 °C (from ligroin); 60-MHz ^{1}H NMR δ 2.27 (3 H, s, CH_3), 6.45–8.16 (11 H, m, Ar*H* + O*H*); MS *m/e* (rel inten) 414 (M^+, 14), 287 (100), 167 (12), 166 (11), 152 (32), 107 (15), 77 (7); HRMS calcd for $C_{19}H_{15}IN_2O$ 414.02291, found 414.02275. Anal. Calcd for $C_{19}H_{15}IN_2O$: C, 55.09; H, 3.65; I, 30.63; N, 6.76. Found: C, 55.22; H, 3.64; I, 30.55; N, 6.74.

2-[(2′-Iodo-1,1′-biphenyl-2-yl)azo]-4-methylphenyl Acetate (1a). 2-[(2′-Iodo-1,1′-biphenyl-2-yl)azo]-4-methylphenol

(10) Under the same experimental conditions we found $a_m = 1.64$ G, $a_H(CH_3) = 11.05$ G, $g = 2.0045$.

(11) Cade, J. A.; Pilbeam, A. *J. Chem. Soc.* **1964**, 114.
(12) McBay, H. C.; Tucker, O. *J Org. Chem.* **1954**, *19*, 869.
(13) Kokatnur, V. R.; Jelling, M. *J. Am. Chem. Soc.* **1941**, *63*, 1432.

(4.14 g, 10 mmol) was added to a solution of sodium ethoxide (0.68 g, 10 mmol) in absolute ethanol (50 mL); the solvent was evaporated and freshly distilled acetyl chloride (1.57 g, 20 mmol) was added dropwise to a refluxing and stirred suspension of the solid phenolate in anhydrous benzene (100 mL). After a few minutes the reaction mixture was cooled, washed with water, and dried over sodium sulfate; the solvent was removed under reduced pressure and the residue chromatographed to give **1a** (3.42 g, 75%): mp = 106–108 °C (from ethanol); IR ν_{max} 1760 cm^{-1} (C=O stretch); 60-MHz ^1H NMR δ 2.13 (3 H, s, CH_3), 2.27 (3 H, s, CH_3), 6.77–8.00 (11 H, m, Ar*H*); MS *m/e* (rel inten) 329 (M^+ – 127, 100), 287 (62), 167 (13), 166 (15), 152 (38), 43 (20). Anal. Calcd for $C_{21}H_{17}IN_2O_2$: C, 55.28; H, 3.76; I, 27.81; N, 6.14. Found: C, 55.40; H, 3.75; I, 27.71; N, 6.16.

2-[(2′-Iodo-1,1′-biphenyl-2-yl)azo]-4-methylphenyl Benzoate (1b). Following the procedure previously described for **1a**, the sodium salt of 2-[(2′-iodo-1,1′-biphenyl-2-yl)azo]-4-methylphenol (4.14 g, 10 mmol) was treated with freshly distilled benzoyl chloride (1.40 g, 10 mmol) and refluxed for 3 h. After workup and chromatography of the reaction mixture **1b** was obtained (4.04 g, 78%): mp = 121–123 °C (from ethanol); IR ν_{max} 1740 cm^{-1} (C=O stretch); 60-MHz ^1H NMR δ 2.23 (3 H, s, CH_3), 6.78–7.70 (13 H, m, Ar*H*), 7.88 (1 H, d, J = 7.6 Hz, Ar*H*), 8.07–8.43 (2 H, m, Ar*H*); MS *m/e* (rel inten) 391 (M^+ – 127, 100), 285 (9), 167 (5), 166 (6), 152 (19), 105 (66), 77 (25). Anal. Calcd for $C_{26}H_{19}IN_2O_2$: C, 60.25; H, 3.69; I, 24.48; N, 5.40. Found: C, 60.40; H, 3.68; I, 24.43; N, 5.39.

2-*tert*-Butyl-6-[(2′-iodo-1,1′-biphenyl-2-yl)azo]-4-methylphenol. 2-Amino-2′-iodobiphenyl (2.95 g, 10 mmol) was diazotized, following the standard procedure, and added cautiously, between 0 and 5 °C, to a stirred solution of 2-*tert*-butyl-4-methylphenol (1.64 g, 10 mmol) and sodium hydroxide (1.6 g, 40 mmol) in water (50 mL). The mixture was neutralized with hydrochloric acid and the final precipitate chromatographed to give the title compound (3.90 g, 83%): mp = 106–108 °C (from light petroleum/benzene 50:50 v/v); 60-MHz ^1H NMR δ 1.30 (9 H, s, *t*-Bu), 2.30 (3 H, s, CH_3), 6.85–8.03 (11 H, m, Ar*H* + OH); MS *m/e* (rel inten) 470 (M^+, 35), 343 (100), 167 (24), 166 (13), 152 (23); HRMS calcd for $C_{23}H_{23}IN_2O$ 470.08551, found 470.08423. Anal. Calcd for $C_{23}H_{23}IN_2O$: C, 58.73; H, 4.93; I, 26.98; N, 5.96. Found: C, 58.62; H, 4.91; I, 26.92; N, 5.94.

2-*tert*-Butyl-6-[(2′-iodo-1,1′-biphenyl-2-yl)azo]-4-methylphenyl Acetate (8). Following the procedure previously described for **1a**, 2-*tert*-butyl-6-[(2′-iodo-1,1′-biphenyl-2-yl)azo]-4-methylphenol (4.70 g, 10 mmol) afforded **8** (3.84 g, 75%): mp = 102–104 °C (from light petroleum/benzene 50:50 v/v); 60-MHz ^1H NMR δ 1.37 (9 H, s, *t*-Bu), 2.18 (3 H, s, CH_3), 2.38 (3 H, s, CH_3), 6.77–7.70 (9 H, m, Ar*H*), 7.88 (1 H, d, J = 8.0 Hz, Ar*H*); MS *m/e* (rel inten) 385 (M^+ – 127, 81), 343 (43), 167 (18), 166 (15), 152 (44), 91 (10), 77 (8), 57 (9), 43 (100). Anal. Calcd for $C_{25}H_{25}IN_2O_2$: C, 58.60; H, 4.92; I, 24.37; N, 5.47. Found: C, 58.73; H, 4.90; I, 24.71; N, 5.48.

General Procedure for the Reactions of Diazenes 1a, 1b, and 8 with Tri-*n*-butyltin Hydride. A benzene solution of diazene, freshly distilled tri-*n*-butyltin hydride, and AIBN in appropriate ratios was refluxed to complete disappearance of starting material; the solvent was evaporated and the residue chromatographed on silica gel to give the reported products. According to this general procedure the following reactions were performed.

Reaction of 1a with Tri-*n*-butyltin Hydride. **1a** (2.28 g, 5 mmol), tri-*n*-butyltin hydride[14] (2.91 g, 10 mmol), and AIBN (1.64 g, 10 mmol) gave, after a 2-h reflux, 2-[*N*-(9*H*-carbazol-9-yl)amino]-4-methylphenyl acetate (**4a**) (0.50 g, 30%): mp = 172–173 °C (from benzene/ethanol 50:50 v/v) [IR ν_{max} 3360 (NH stretch) and 1765 cm^{-1} (C=O stretch); 200-MHz ^1H NMR δ 2.05 (3 H, s, CH_3), 2.38 (3 H, s, CH_3), 6.14 (1 H, d, J = 1.5 Hz, Ar*H*), 6.65–6.74 (2 H, dd + bs, J = 7.7, 1.5 Hz, Ar*H* + N*H*), 7.02 (1 H, d, J = 7.7 Hz, Ar*H*), 7.24–7.50 (6 H, m, Ar*H*), 8.08–8.14 (2 H, m, Ar*H*); MS *m/e* (rel inten) 330 (M^+, 99), 287 (19), 167 (100), 166 (20), 140 (22), 122 (45); HRMS calcd for $C_{21}H_{18}N_2O_2$ 330.13683, found 330.13598. Anal. Calcd for $C_{21}H_{18}N_2O_2$: C, 76.34; H, 5.49; N, 8.48. Found: C, 76.22; H, 5.47; N, 8.51] and *N*-(9*H*-carbazol-9-yl)-*N*-(2-hydroxy-5-methylphenyl)acetamide (**5a**) (0.83 g, 50%): mp = 188–190 °C (from light petroleum/benzene 50:50 v/v) [IR ν_{max} 3280 (OH stretch) and 1660 cm^{-1} (C=O stretch); 200-MHz ^1H NMR δ 1.95 (3 H, s, CH_3), 2.01 (3 H, s, CH_3), 6.72 (1 H, s, O*H*), 6.84 (1 H, d, J = 1.5 Hz, Ar*H*), 6.97 (1 H, dd, J = 8.1, 1.5 Hz, Ar*H*), 7.06 (1 H, d, J = 8.1 Hz, Ar*H*), 7.30–7.60 (6 H, m, Ar*H*), 8.07–8.15 (2 H, m, Ar*H*); MS *m/e* (rel inten) 330 (M^+, 26), 287 (4), 167 (100), 166 (20), 140 (6), 122 (13); HRMS calcd for $C_{21}H_{18}N_2O_2$ 330.13683, found 330.13612. Anal. Calcd for $C_{21}H_{18}N_2O_2$: C, 76.34; H, 5.49; N, 8.48. Found: C, 76.29; H, 5.48; N, 8.49].

2-[*N*-(9*H*-Carbazol-9-yl)amino]-4-methylphenol (4c). Following the procedure reported for *N*-(9*H*-carbazol-9-yl)-4-methylbenzenamine (**4d**),[5] the title product was obtained after a 15-h reflux and a very fast column chromatography (0.29 g, 20%): mp = 153–155 °C (from ethanol); 60-MHz ^1H NMR δ 2.00 (3 H, s, CH_3), 4.92 (1 H, bs, N*H*), 6.08 (1 H, d, J = 1.2 Hz, Ar*H*), 6.57 (1 H, dd, J = 7.9, 1.2 Hz, Ar*H*), 6.77 (1 H, d, J = 7.9 Hz, Ar*H*), 7.00 (1 H, s, O*H*), 7.25–7.50 (6 H, m, Ar*H*), 8.10–8.17 (2 H, m, Ar*H*); MS *m/e* (rel inten) 288 (M^+, 1), 167 (100), 166 (15), 140 (8), 139 (7), 123 (13), 122 (7); HRMS calcd for $C_{19}H_{16}N_2O$ 288.12626, found 288.12585. Anal. Calcd for $C_{19}H_{16}N_2O$: C, 79.14; H, 5.59; N, 9.71. Found: C, 79.32; H, 5.57; N, 9.68.

2-[*N*-(9*H*-Carbazol-9-yl)amino]-4-methylphenyl Acetate (4a). A solution of 1,1′-carbonyldiimidazole (0.81 g, 5 mmol) and acetic acid (0.32 mL, 5 mmol) in THF (50 mL) was kept at room temperature under magnetic stirring until complete liberation of CO_2[15] **4c** (1.44 g, 5 mmol) was added and the mixture warmed at 60 °C for 1 h. Imidazole was filtered off, the solvent evaporated, and the residue recrystallized to give **4a** (1.57 g, 95%): mp = 172–173 °C (from benzene/ethanol 50:50 v/v); spectroscopic data are identical to those reported for compound **4a** obtained in the above reaction of **1a** with tri-*n*-butyltin hydride. The same synthesis, carried out on **4d**, afforded only unreacted starting material.

Reaction of 1b with Tri-*n*-butyltin Hydride. **1b** (2.59 g, 5 mmol), tri-*n*-butyltin hydride[14] (2.91 g, 10 mmol), and AIBN (1.64 g, 10 mmol) yielded, after a 2-h reflux, 2-[*N*-(9*H*-carbazol-9-yl)amino]-4-methylphenyl benzoate (**4b**) (1.47 g, 75%): mp = 184–186 °C (from ligroin/benzene 70:30 v/v) [IR ν_{max} 3360 (NH stretch) and 1740 cm^{-1} (C=O stretch); 200-MHz ^1H NMR δ 2.05 (3 H, s, CH_3), 6.17 (1 H, d, J = 1.6 Hz, Ar*H*), 6.70–6.80 (2 H, dd + bs, J = 8.0, 1.6 Hz, Ar*H* + NH), 7.14 (1 H, d, J = 8.0 Hz, Ar*H*), 7.22–7.70 (9 H, m, Ar*H*), 8.04–8.12 (2 H, m, Ar*H*), 8.26–8.35 (2 H, m, Ar*H*); MS *m/e* (rel inten) 392 (M^+, 22), 287 (4), 167 (82), 166 (28), 140 (14), 120 (14), 105 (100), 78 (30), 77 (32); HRMS calcd for $C_{26}H_{20}N_2O_2$ 392.15248, found 392.15179. Anal. Calcd for $C_{26}H_{20}N_2O_2$: C, 79.57; H, 5.14; N, 7.14. Found: C, 79.35; H, 5.13; N, 7.16] and *N*-(9*H*-carbazol-9-yl)-*N*-(2-hydroxy-5-methylphenyl)benzamide (**5b**) (0.26 g, 13%): mp = 164–166 °C (from light petroleum/benzene 50:50 v/v) [IR ν_{max} 3280 (OH stretch) and 1645 cm^{-1} (C=O stretch); 200-MHz ^1H NMR δ 1.98 (3 H, s, CH_3), 6.35 (1 H, s, O*H*), 6.55–7.55 (14 H, m, Ar*H*), 7.94–8.05 (2 H, m, Ar*H*); MS *m/e* (rel inten) 392 (M^+, 31), 287 (5), 167 (89), 166 (22), 140 (5), 120 (8), 105 (100), 77 (23); HRMS calcd for $C_{26}H_{20}N_2O_2$ 392.15248, found 392.15212. Anal. Calcd for $C_{26}H_{20}N_2O_2$: C, 79.57; H, 5.14; N, 7.14. Found: C, 79.32; H, 5.13; N, 7.15].

Reactions of 8 with Tri-*n*-butyltin Hydride. **8** (2.56 g, 5 mmol), tri-*n*-butyltin hydride (2.91 g, 10 mmol), and AIBN (1.64 g, 10 mmol) afforded, after a 1-h reflux, *N*-(9*H*-carbazol-9-yl)-*N*-(3-*tert*-butyl-2-hydroxy-5-methylphenyl)acetamide (**11**) (1.33 g, 69%): mp = 163–164 °C (from ethanol) [IR ν_{max} 3220 (NH stretch) and 1670 cm^{-1} (C=O stretch); 200-MHz ^1H NMR δ 1.49 (9 H, s, *t*-Bu), 1.95 (3 H, s, CH_3), 2.00 (3 H, s, CH_3), 6.60 (1 H, s, O*H*), 6.78 (1 H, d, J = 1.6 Hz, Ar*H*), 7.01 (1 H, d, J = 1.6 Hz, Ar*H*), 7.30–7.40 (2 H, m, Ar*H*), 7.48–7.58 (4 H, m, Ar*H*), 8.06–8.14 (2 H, m, Ar*H*); MS *m/e* (rel inten) 386 (M^+, 9), 178 (15), 167 (100), 166 (16), 43 (8); HRMS calcd for $C_{25}H_{26}N_2O_2$ 386.19943, found 386.19865. Anal. Calcd for $C_{25}H_{26}N_2O_2$: C, 77.69; H, 6.78; N, 7.25. Found: C, 77.42; H, 6.76; N, 7.27] and 2-[*N*-(9*H*-carbazol-9-yl)amino]-6-*tert*-butyl-4-methylphenyl acetate (**10**) (0.50 g,

(14) This reaction was carried out by adding dropwise a solution of tri-*n*-butyltin hydride in benzene (10 mL) to the refluxing mixture of diazene and AIBN (rate = 0.2 mL/min).

(15) Staab, H. A. *Angew. Chem. Int. Ed. Engl.* **1962**, *1*, 351.

26%): mp = 128–129 °C (from ethanol) [IR ν_{max} 3370 (NH stretch) and 1760 cm^{-1} (C=O stretch); 200-MHz ^1H NMR δ 1.40 (9 H, s, t-Bu), 2.01 (3 H, s, CH_3), 2.44 (3 H, s, CH_3), 5.97 (1 H, d, J = 1.6 Hz, Ar*H*), 6.43 (1 H, bs, NH), 6.76 (1 H, d, J = 1.6 Hz, Ar*H*), 7.25–7.34 (2 H, m, Ar*H*), 7.40–7.47 (4 H, m, Ar*H*), 8.07–8.15 (2 H, m, Ar*H*); MS *m/e* (rel inten) 386 (M^+, 11), 178 (11), 167 (100), 166 (16), 43 (7); HRMS calcd for $C_{25}H_{26}N_2O_2$ 386.19943, found 386.19884. Anal. Calcd for $C_{25}H_{26}N_2O_2$: C, 77.69; H, 6.78; N, 7.25. Found: C, 77.37; H, 6.77; N, 7.27]. The same reaction was repeated with 1 mmol of **8** in benzene (10 mL) and the products ratio (**11**/**10**) carefully determined by HPLC analysis, using calibration plots based on pure previously isolated **11** and **10**; the resulting values were in the linearity range of the calibration. Both **11** and **10** were stable under HPLC conditions, i.e., there was no appreciable conversion of a pure isomer into the other one. **8** (1 mmol) was also reacted with tri-*n*-butyltin hydride (5 and 10 mmol) in the presence of AIBN (4 mmol) in benzene (10 mL) to give, by HPLC analysis, variable products yields: Table I reports the tin hydride concentrations and the **11**/**10** ratios obtained. The overall yields of the reactions are in the range 90–95%.

Reaction of 10 with DPDC. A solution of **10** (0.39 g, 1 mmol) and DPPC (1 mmol) in benzene (20 mL) was kept at 60 °C for 15 min. The solvent was removed under reduced pressure and the residue chromatographed to give **11** (0.23 g, 60%): mp = 163–164 °C (from ethanol).

EPR Measurements. EPR spectra were recorded on a Bruker ESP300 instrument equipped with a Hewlett-Packard 5350B frequency counter for the determination of the *g* factors, which were corrected with respect to that of the perylene radical cation (2.00258). Photolysis was carried out with the light from a 500-W high pressure mercury lamp.

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