Generation of Biradicals and Subsequent Formation of Quinolines and 5*H*-Benzo[*b*]carbazoles from *N*-[2-(1-Alkynyl)phenyl]ketenimines

Chongsheng Shi and Kung K. Wang*

Department of Chemistry, West Virginia University, Morgantown, West Virginia 26506-6045

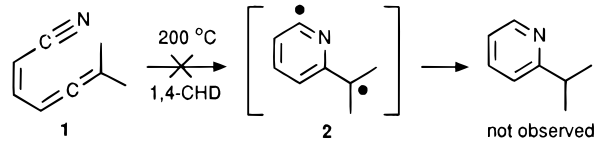
Received March 9, 1998

Introduction

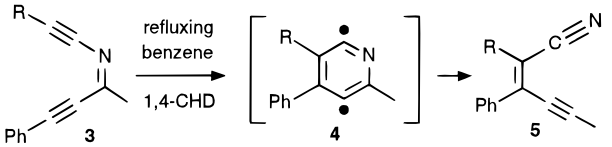
The biradical-forming cycloaromatization reactions have attracted considerable attention in recent years.[1,2] This is due mainly to the discovery of several very potent antitumor antibiotics which cleave DNA via generation of biradicals under mild conditions.[3] Among the thermally induced biradical-forming reactions, the Bergman cyclization of (*Z*)-3-hexene-1,5-diynes (enediynes) to 1,4-didehydrobenzenes and the Myers cyclization of (*Z*)-1,2,4-heptatrien-6-ynes (enyne-allenes) to α,3-didehydrotoluenes have been investigated extensively. The Moore cyclization of enyne-ketenes provides easy access to biradicals having an aryl and a phenoxy radical center.[4]

While several synthetic pathways to enyne-ketenes and their versatility as reactive intermediates have been reported, the biradical-forming reactions involving other heteroatoms in the conjugated system remained virtually unexplored. Attempts to generate biradical **2** and subsequently 2-isopropylpyridine by thermolysis of **1** in C_6D_6 containing an excess of 1,4-cyclohexadiene (1,4-CHD) as a hydrogen-atom donor were unsuccessful (Scheme 1).[5a] A similar attempt to involve the nitrile group in a biradical-forming reaction also failed.[5b] Interestingly, when *C,N*-dialkynyl imines **3** were heated in refluxing benzene, enynyl nitriles **5** were produced in excellent yields presumably through the putative 2,5-didehydropyridines **4**, which could not be captured by 1,4-CHD or, in the case of **4b**, by the carbon−carbon double bond intramolecularly (Scheme 2).[6a] Recently, it was observed that a very small amount of **4a** could be captured to produce 2-methyl-4,5-diphenylpyridine when the reaction was conducted in the presence of moderate amounts of a protic acid.[6b] We now report successful examples of generating and trapping the biradicals produced from cycloaromatization of *N*-[2-(1-alkynyl)phenyl]ketenimines having a nitrogen atom in the conjugated system.

Scheme 1

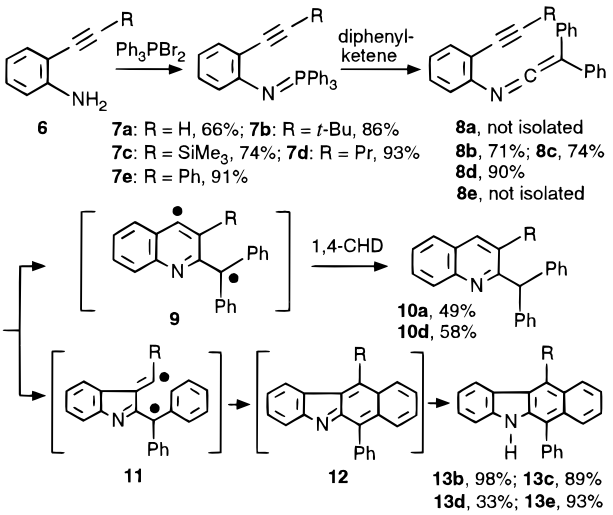


Scheme 2



a: R = Ph; **b**: R = $CH_2CH_2CH{=}CHPh$

Scheme 3



7a: R = H, 66%; **7b**: R = *t*-Bu, 86%
7c: R = $SiMe_3$, 74%; **7d**: R = Pr, 93%
7e: R = Ph, 91%

8a, not isolated
8b, 71%; **8c**, 74%
8d, 90%
8e, not isolated

10a, 49%
10d, 58%

13b, 98%; **13c**, 89%
13d, 33%; **13e**, 93%

titative yields.[7] Treatment of **6** with Ph_3PBr_2 gave the iminophosphoranes **7** (Scheme 3).[8a] The aza-Wittig reaction[8b] between **7a** (R = H) and diphenylketene[9] was carried out in benzene containing a large excess of 1,4-CHD at 0 °C followed by reflux for 2 h to furnish the quinoline **10a** (R = H) in 49% yield. Apparently, the reaction proceeded through an initial formation of the ketenimine **8a** followed by cycloaromatization to produce the biradical **9a** and subsequently **10a**.

Attempts to isolate **8a** resulted in its decomposition after the solvent was removed. However, the IR spectrum taken immediately after **7a** was treated with diphenylketene in C_6D_6 containing an excess of 1,4-CHD exhibited an intense absorption at 2002 cm^{-1}, attributable to **8a**. The ^1H NMR spectrum of the same solution also showed the disappearance of the acetylenic C−H signal of **7a** at δ 3.26 and the appearance of a new signal at δ 2.86, attributable to the acetylenic C−H of **8a**. The rate of disappearance of **8a** and appearance of **10a** was

(1) (a) Wang, K. K. *Chem. Rev.* **1996**, *96*, 207−222. (b) Grissom, J. W.; Gunawardena, G. U.; Klingberg, D.; Huang, D. *Tetrahedron* **1996**, *52*, 6453−6518. (c) Wang, K. K.; Wang, Z.; Tarli, A.; Gannett, P. *J. Am. Chem. Soc.* **1996**, *118*, 10783−10791.

(2) (a) Wang, Y.; Finn, M. G. *J. Am. Chem. Soc.* **1995**, *117*, 8045−8046. (b) Miyawaki, K.; Suzuki, R.; Kawano, T.; Ueda, I. *Tetrahedron Lett.* **1997**, *38*, 3943−3946.

(3) Maier, M. E. *Synlett* **1995**, 13−26.

(4) (a) Moore, H. W.; Yerxa, B. R. *Chemtracts* **1992**, 273−313. (b) Tarli, A.; Wang, K. K. *J. Org. Chem.* **1997**, *62*, 8841−8847.

(5) (a) Wang, K. K.; Wang, Z.; Sattsangi, P. D. *J. Org. Chem.* **1996**, *61*, 1516−1518. (b) Gillmann, T.; Heckhoff, S. *Tetrahedron Lett.* **1996**, *37*, 839−840.

(6) (a) David, W. M.; Kerwin, S. M. *J. Am. Chem. Soc.* **1997**, *119*, 1464−1465. (b) Hoffner, J.; Schottelius, M. J.; Feichtinger, D.; Chen, P. *J. Am. Chem. Soc.* **1998**, *120*, 376−385.

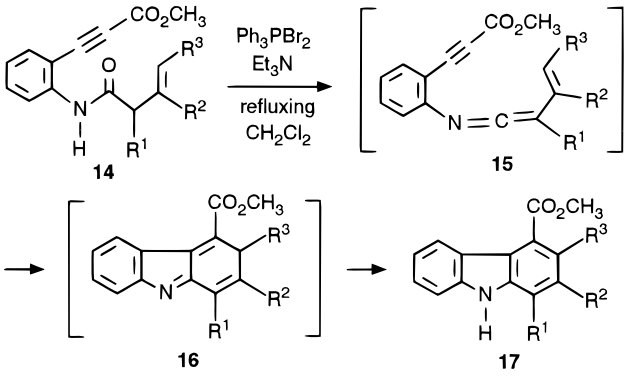
(7) (a) Villemin, D.; Goussu, D. *Heterocycles* **1989**, *29*, 1255−1261. (b) Arcadi, A.; Cacchi, S.; Marinelli, F. *Tetrahedron Lett.* **1989**, *30*, 2581−2584. (c) Iritani, K.; Matsubara, S.; Utimoto. K. *Tetrahedron Lett.* **1988**, *29*, 1799−1802.

(8) (a) Molina, P.; Alajarin, M.; Vidal, A. *J. Chem. Soc., Chem. Commun.* **1990**, 1277−1279. (b) Molina, P.; Alajarin, M.; Vidal, A.; Sanchez-Andrada, P. *J. Org. Chem.* **1992**, *57*, 929−939.

(9) Taylor, E. C.; McKillop, A.; Hawks, G, H. *Org. Synth.* **1972**, *52*, 36−38.

S0022-3263(98)00428-9 CCC: $15.00
Published on Web 04/23/1998

Scheme 4

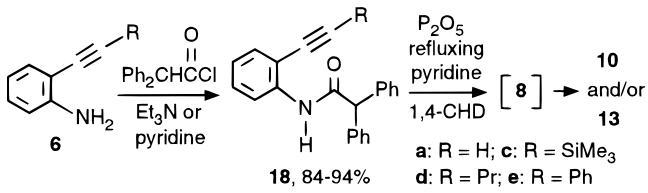


monitored with IR and ^{1}H NMR. The reaction exhibited clean first-order behavior over three half-lives with k = 1.87 ± 0.04 h^{-1} ($t_{1/2}$ = 0.37 h) at 22 °C.

Treatment of **7b** with diphenylketene furnished **8b**, which was isolated in 71% yield. Interestingly, thermolysis of **8b** in refluxing benzene gave the benzocarbazole **13b** in 98% yield. The cascade sequence outlined in Scheme 3 with an initial formation of a five-membered ring to produce biradical **11b** followed by an intramolecular radical−radical combination to form **12b** and a subsequent tautomerization could account for the formation of **13b**. The greater stability of the vinyl radical site in **11b** because of the presence of a *tert*-butyl substituent along with the emergence of severe nonbonded steric interactions between the *tert*-butyl group at the C-3 position and the substituent at the C-2 position of the quinoline biradical **9b** (R = *tert*-butyl) are probably responsible for directing the reaction toward **11b**. Such a preference resembles the formation of the five-membered ring biradicals in several analogous cases of ring closures of enyne-ketenes[10] and enyne-allenes.[11]

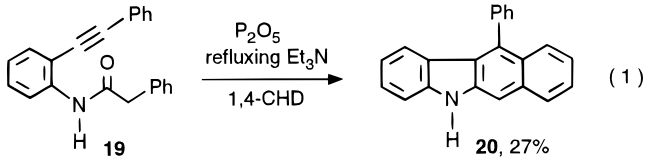
Alternatively, a one-step intramolecular Diels−Alder reaction of **8b** could also produce **12b**[8b,12] as reported previously by Differding and Ghosez in an elegant synthesis of carbazoles **17** by using **14** to generate in situ the acetylenic vinylketenimines **15** (Scheme 4).[12a] However, unlike **15**, a sterically demanding *tert*-butyl group is at the acetylenic terminus of **8b**. Examination of the molecular model for the transformation from **8b** to **12b** via the Diels−Alder mechanism reveals the emergence of severe nonbonded steric interactions in the transition state between the *tert*-butyl group and the phenyl groups at the ketenimine terminus, making the concerted process highly unlikely. On the other hand, the two-step biradical mechanism permits the sterically demanding *tert*-butyl group to bend away in the first step, greatly reducing the steric interactions and allowing the reaction to occur under relatively mild thermal conditions (k = 0.186 ± 0.004 h^{-1}, $t_{1/2}$ = 3.73 h at 72 °C). With the absence of an apparent proton source, it is also unlikely that the reaction could proceed through a cationic reaction mechanism involving an initial protonation of the nitrogen atom in **8b**.

Scheme 5



When **8c** (R = $SiMe_3$) was heated under refluxing benzene, the benzocarbazole **13c** was produced (k = 0.78 ± 0.06 h^{-1}, $t_{1/2}$ = 0.89 h at 72 °C). Again the ability of the trimethylsilyl group in stabilizing the adjacent radical site in **11c**[13] along with the arising of nonbonded interactions in **9c** direct the reaction toward **13c**. Thermolysis of **8d** (R = Pr) in refluxing 1,4-CHD furnished the quinoline **10d** (58%) and the benzocarbazole **13d** (33%) (k of the disappearance of **8d** = 1.01 ± 0.11 h^{-1}, $t_{1/2}$ = 0.69 h at 52 °C). Apparently, the reaction could proceed through biradicals **9d** and **11d** with comparable efficiency. If one compares the rate of formation of **13d** (k = 0.36 h^{-1}, $t_{1/2}$ = 1.93 h at 52 °C) with that of **13b**, the steric factors do not appear to affect the rate of reaction dramatically, again contrary to what would be expected of a concerted Diels−Alder mechanism. When **7e** (R = Ph) was treated with diphenylketene at room temperature for 1 h, the benzocarbazole **13e** (93%) was produced exclusively. Presumably because the phenyl substituent can further stabilize the vinyl radical site in **11e**, the ketenimine **8e** was thermally labile and was readily converted to **13e**.

Alternatively, the ketenimines **8** could also be produced in situ by dehydration of **18** with P_2O_5 in refluxing pyridine,[14] leading to **10a** (34%), **10d** (35%), **13d** (31%), and **13e** (70%) (Scheme 5). In the case of **18c** (R = $SiMe_3$), the resulting benzocarbazole **13c** is prone to protodesilylation under the reaction condition, and a significant amount of the desilylated adduct **13a** (R = H) was produced. Treatment of the reaction mixture with 1 N HCl at 40 °C for 1 h completely converted **13c** to **13a**, which was isolated in an overall yield of 81% from **18c**. It is interesting to note that **13a** could not be prepared directly from **18a** or **7a**, which leads to the quinoline **10a**. By starting from **19**, derived from acylation of **6d** with phenylacetyl chloride (97% yield), the benzocarbazole **20** was produced in 27% isolated yield (eq 1).



(1)

Conclusions

In summary, ketenimines **8** having a nitrogen atom in the conjugated system could serve as excellent precur-

(10) Foland, L. D.; Karlsson, J. O.; Perri, S. T.; Schwabe, R.; Xu, S. L.; Patil, S.; Moore, H. W. *J. Am. Chem. Soc.* **1989**, *111*, 975−989.

(11) (a) Schmittel, M.; Strittmatter, M.; Kiau, S. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 1843−1845. (b) Schmittel, M.; Kiau, S.; Siebert, T.; Strittmatter, M. *Tetrahedron Lett.* **1996**, *37*, 7691−7694. (c) Schmittel, M.; Strittmatter, M.; Vollmann, K.; Kiau, S. *Tetrahedron Lett.* **1996**, *37*, 999−1002. (d) Schmittel, M.; Maywald, M.; Strittmatter, M. *Synlett* **1997**, 165−166. (e) Schmittel, M.; Strittmatter, M.; Kiau, S. *Tetrahedron Lett.* **1995**, *36*, 4975−4978. (f) Gillmann, T.; Hulsen, T.; Massa, W.; Wocadlo, S. *Synlett* **1995**, 1257−1259. (g) Garcia, J. G.; Ramos, B.; Pratt, L. M.; Rodriguez, A. *Tetrahedron Lett.* **1995**, *36*, 7391−7394.

(12) (a) Differding, E.; Ghosez, L. *Tetrahedron Lett.* **1985**, *26*, 1647−1650. (b) Molina, P.; Lopez-Leonardo, C.; Alcantara, J. *Tetrahedron* **1994**, *50*, 5027−5036.

(13) Wilt, J. W.; Aznavoorian, P. M. *J. Org. Chem.* **1978**, *43*, 1285−1286.

(14) Stevens, C. L.; Singhal, G. H. *J. Org. Chem.* **1964**, *29*, 34−37.

sors for generation of biradicals. Because of prevalence of the amide functionality in biological systems, structures similar to those of **18** are particularly attractive for the development of new DNA-cleaving agents. The cascade sequences outlined in Schemes 3 and 5 also provide alternative pathways to quinolines and 5*H*-benzo[*b*]carbazoles.[8b,15]

Experimental Section

General. The 2-(1-alkynyl)anilines **6** (83−98% yield) were prepared according to the reported procedures.[7] Diphenylketene was prepared by dehydrochlorination of diphenylacetyl chloride as reported previously.[9] 2-Iodoaniline was purchased from Oakwood Products, Inc. and was used as received. 1-Alkynes were obtained from Farchan Laboratories, Inc. and were used without further purification. Dibromotriphenylphosphorane (Ph_3PBr_2), phenylacetyl chloride, diphenylacetyl chloride, $Pd(PPh_3)_2Cl_2$, 1,4-CHD, and γ-terpinene were purchased from Aldrich. Pyridine and triethylamine were distilled over CaH_2 prior to use. The kinetic studies were carried out in a constant-temperature bath (±0.5 °C). Melting points are uncorrected. ^{1}H (270 MHz) and ^{13}C (67.9 MHz) NMR spectra were recorded in $CDCl_3$ using $CHCl_3$ (^{1}H δ 7.26) or $CDCl_3$ (^{13}C δ 77.00) as the internal standard.

2-Ethynyl-*N*-(triphenylphosphoranylidene)benzenamine (7a).[8b] Iminophosphorane **7a** was prepared according to the reported procedure.[8a] To 3.798 g of Ph_3PBr_2 (9.00 mmol) was added a mixture of 1.053 g of 2-ethynylaniline (**6a**, 9.00 mmol) and 2.5 mL of anhydrous triethylamine in 100 mL of anhydrous benzene via cannula under a nitrogen atmosphere. The reaction mixture was heated under reflux for 4 h. The white triethylammonium bromide precipitate was removed by filtration, and the filtrate was concentrated in vacuo. The residue was purified through a short column (silica gel/40−60% diethyl ether in hexanes) to furnish 2.239 g (5.94 mmol, 66%) of **7a** as colorless crystals: mp 142−143 °C (lit.[8b] 141 °C); IR (KBr) 3279, 2094, 1584, 1479, 1436, 1368, 1110, 750, 715 cm^{-1}; ^{1}H δ 7.88−7.80 (6 H, m), 7.56−7.39 (10 H, m), 6.87 (1 H, td, J = 7.7 and 1.6 Hz), 6.59 (1 H, t, J = 7.4 Hz), 6.47 (1 H, d, J = 8.1 Hz), 3.34 (1 H, s); ^{13}C δ 153.57, 133.57, 132.61 (d, J = 9.8 Hz), 131.63 (d, J = 2.6 Hz), 130.92 (d, J = 99.7 Hz), 128.82, 128.49 (d, J = 11.9 Hz), 121.19 (d, J = 9.8 Hz), 117.23 (d, J = 23.2 Hz), 116.80, 85.12, 79.22.

Ketenimine 8b. To a solution of 0.433 g of **7b** (1.00 mmol) in 30 mL of anhydrous diethyl ether was introduced 0.194 g of diphenylketene (1.00 mmol) in 5 mL of anhydrous diethyl ether via cannula at 0 °C under a nitrogen atmosphere. The reaction mixture was stirred for 10 min before it was allowed to warm to room temperature. After 1 h, the reaction mixture was concentrated in vacuo. The residue was purified by column chromatography (silica gel/5−10% diethyl ether in hexanes) to furnish 0.248 g (0.71 mmol, 71%) of **8b** as a yellow oil: IR (neat) 2000, 1594, 1491, 758, 693 cm^{-1}; ^{1}H δ 7.49−7.16 (14 H, m), 1.25 (9 H, s); ^{13}C δ 188.80, 141.29, 134.16, 133.73, 128.74, 128.42, 127.89, 126.91, 126.21, 123.43, 119.68, 105.25, 76.47, 75.70, 30.78, 28.19; MS *m*/*z* 349 (M$^+$).

2-(Diphenylmethyl)quinoline (10a). To 0.189 g of **7a** (0.50 mmol) was added a mixture of 0.097 g of diphenylketene (0.50 mmol) and 2.9 mL of 1,4-CHD in 4 mL of anhydrous benzene via cannula at 0 °C under a nitrogen atmosphere. After 10 min, the reaction mixture was allowed to warm to room temperature for 1 h and then was heated under reflux for 2 h. The reaction mixture was concentrated in vacuo, and the residue was purified by column chromatography (silica gel/5−20% of diethyl ether in hexanes). The eluent was allowed to evaporate slowly to furnish 0.072 g of **10a** (0.244 mmol, 49%) as yellow crystals.

The rate of reaction was determined by using a solution obtained from treatment of 0.189 g of **7a** (0.50 mmol) with a solution of 0.097 g of diphenylketene (0.50 mmol) in 2.0 mL of C_6D_6 and 1.5 mL of 1,4-CHD at 22 °C. The rate of disappearance of **8a** and appearance **10a** was monitored with IR (cell thickness = 0.11 mm) and ^{1}H NMR.

Preparation of **10a** by the dehydration method was carried out in a 100-mL flask containing 0.400 g of **18a** (1.29 mmol), 2 g of Florisil, 1.10 g of P_2O_5 (7.72 mmol), 30 mL of pyridine, and 1.66 mL of γ-terpinene (10.3 mmol), and the reaction flask was flushed with nitrogen. The mixture was stirred vigorously and heated under reflux (oil bath temperature 135 °C) for 16 h before it was allowed to cool to room temperature. The liquid phase was filtered through a short Florisil column using dry pyridine as eluent. The residue in the flask was extracted with dry pyridine (3 × 15 mL), and the combined pyridine extracts were passed through the same Florisil column. The combined pyridine solutions were concentrated in vacuo. The residue was purified by column chromatography (silica gel/5−20% of diethyl ether in hexanes). The eluent was allowed to evaporate slowly to furnish 0.128 g of **10a** (0.434 mmol, 34%) as yellow crystals: mp 104−105 °C; IR (KBr) 1594, 1495, 824, 756, 719, 698 cm^{-1}; ^{1}H δ 8.09 (1 H, d, J = 8.3 Hz), 8.07 (1 H, d, J = 8.3 Hz), 7.79 (1 H, dd, J = 8.2 and 1.1 Hz), 7.70 (1 H, tm, J = 7.7 and 1.6 Hz), 7.51 (1 H, tm, J = 7.5 and 1.1 Hz), 7.35−7.20 (11 H, m), 5.94 (1 H, s); ^{13}C δ 163.07, 147.85, 142.59 (2 carbons), 136.29, 129.41, 129.34, 128.40, 127.44, 126.78, 126.55, 126.20, 121.91, 60.08; MS *m*/*z* 295 (M$^+$), 294, 218, 217, 216, 165. Anal. Calcd for $C_{22}H_{17}N$: C, 89.46; H, 5.80; N, 4.74. Found: C, 89.26; H, 5.79; N, 4.73.

6-Phenyl-5*H*-benzo[*b*]carbazole (13a). Preparation of **13a** by the dehydration method was carried out by using the same procedure described for **10a** except that a mixture of 0.766 g of **18c** (2.00 mmol), 4 g of Florisil, 1.70 g of P_2O_5 (12.0 mmol), 50 mL of pyridine, and 0.80 mL of 1,4-CHD (8.5 mmol) was used. A mixture of **13c** and **13a** was isolated by column chromatography (silica gel/5−20% diethyl ether in hexanes). Treatment of the mixture of **13c** and **13a** in 5 mL of dichloromethane with 3.0 mL of 1 N HCl at 40 °C for 1 h converted all of **13c** to the corresponding desilylated adduct **13a**. Purification by column chromatography (silica gel/20% diethyl ether in hexanes) followed by recrystallization from 10% of diethyl ether in hexanes furnished 0.475 g of **13a** (1.62 mmol, 81%) as pale yellow crystals: IR (KBr) 3400, 751, 693 cm^{-1}; ^{1}H δ 8.60 (1 H, s), 8.24 (1 H, d, J = 7.7 Hz), 8.15−8.10 (1 H, m), 7.87−7.84 (1 H, m), 7.82 (1 H, br s, NH), 7.68−7.52 (5 H, m), 7.50−7.41 (3 H, m), 7.34−7.25 (2 H, m); ^{13}C δ 141.84, 137.64, 136.76, 130.74, 130.64, 129.22, 128.75, 128.61, 127.81, 127.34, 125.16, 124.96, 124.44, 123.35, 122.63, 121.15, 119.44, 118.32, 118.10, 110.22; MS *m*/*z* 293 (M$^+$), 146.

11-*tert*-Butyl-6-phenyl-5*H*-benzo[*b*]carbazole (13b). A solution of 0.150 g of **8b** (0.43 mmol) in 3 mL of anhydrous benzene was heated under reflux for 24 h. Benzene was allowed to evaporate slowly to afford 0.147 g of **13b** (0.42 mmol, 98%) as yellow crystals: mp 132−133 °C; IR (KBr) 3410, 1601, 1462, 747, 699 cm^{-1}; ^{1}H δ 8.81 (1 H, dd, J = 8.0 and 2.2 Hz), 8.43 (1 H, d, J = 8.1 Hz), 7.78 (1 H, br, NH), 7.75−7.71 (1 H, m), 7.67−7.54 (5 H, m), 7.44−7.20 (5 H, m), 2.06 (9 H, s); ^{13}C δ 143.17, 141.79, 138.44, 137.08, 131.46, 131.00, 129.27, 128.68, 127.77, 127.32, 127.07, 126.33, 124.60, 124.12, 124.06, 123.66, 120.07, 118.31, 116.93, 109.93, 38.55, 33.63; MS *m*/*z* 349 (M$^+$), 334, 293, 241, 146, 57; HRMS calcd for $C_{26}H_{23}N$ 349.1831, found 349.1827. The rate of reaction was determined by conducting the reaction in C_6D_6 and using ^{1}H NMR to monitor the disappearance of **8b** and the appearance of **13b** at 72 °C.

6-Phenyl-11-(trimethylsilyl)-5*H*-benzo[*b*]carbazole (13c). A mixture of 0.183 g of **8c** (0.50 mmol) in 3 mL of anhydrous benzene was heated under reflux for 24 h. The reaction mixture was then concentrated in vacuo, and the residue was purified by column chromatography (silica gel/5−20% diethyl ether in hexanes). The eluent was allowed to evaporate slowly to afford 0.163 g of **13c** (0.447 mmol, 89%) as pale yellow crystals: mp 153−154 °C; IR (KBr) 3403, 1260, 847, 769, 748, 702 cm^{-1}; ^{1}H δ 8.60−8.53 (1 H, m), 8.33 (1 H, d, J = 7.9 Hz), 7.83 (1 H, br s, NH), 7.82−7.77 (1 H, m), 7.67−7.52 (5 H, m), 7.47−7.36 (3 H, m), 7.32 (1 H, d, J = 7.9 Hz), 7.23 (1 H, tm, J = 7.9 and 1.1 Hz), 0.78 (9 H, s); ^{13}C δ 142.27, 137.01, 136.82, 133.31, 132.29. 131.40, 130.77, 130.20, 129.53, 129.27, 127.92, 126.92, 126.53, 124.89, 124.53, 123.81, 121.67, 119.73, 118.33, 110.06, 3.47; MS *m*/*z* 365

(15) (a) Pindur, U.; Haber, M.; Erfanian-Abdoust, H. *Heterocycles* **1992**, *34*, 781−790. (b) Pindur, U.; Erfanian-Abdoust, H. *Chem. Rev.* **1989**, *89*, 1681−1689. (c) Gribble, G. W.; Saulnier, M. G.; Obaza-Nutaitis, J. A.; Ketcha, D. M. *J. Org. Chem.* **1992**, *57*, 5891−5899. (d) Sha, C.-K.; Chuang, K.-S.; Wey, S.-J. *J. Chem. Soc., Perkin Trans. 1* **1987**, 977−980.

(M^+), 350. Anal. Calcd for $C_{25}H_{23}NSi$: C, 82.14; H, 6.34; N, 3.83. Found: C, 82.26; H, 6.42; N, 3.80. The rate of reaction was determined by conducting the reaction in C_6D_6 and using ^1H NMR to monitor the disappearance of **8c** and the appearance of **13c** at 72 °C.

6,11-Diphenyl-5*H*-benzo[*b*]carbazole (13e). To a solution of 0.453 g of **7e** (1.00 mmol) in 30 mL of anhydrous diethyl ether was introduced 0.194 g of diphenylketene (1.00 mmol) in 5 mL of anhydrous diethyl ether at 0 °C. The reaction mixture was allowed to warm to room temperature and was stirred for 1 h. At this point, the benzocarbazole **13e** had already formed. The reaction mixture was concentrated in vacuo, and the residue was purified by column chromatography (silica gel/5−20% diethyl ether in hexanes). The eluent was allowed to evaporate slowly to afford 0.343 g of **13e** (0.93 mmol, 93%) as pale yellow crystals.

Preparation of **13e** by the dehydration method was carried out by using the same procedure described for **10a** except that a mixture of 0.724 g of **18e** (1.87 mmol), 3 g of Florisil, 1.59 g of P_2O_5 (11.2 mmol), 40 mL of pyridine, and 0.71 mL of 1,4-CHD (7.5 mmol) was used. Purification by column chromatography afforded 0.483 g of **13e** (1.31 mmol, 70%) as pale yellow crystals: mp 241−242 °C; IR (KBr) 3451, 754, 702 cm^{-1}; ^1H δ 7.88 (1 H, d, J = 8.7 Hz), 7.85 (1 H, br s, NH), 7.80 (1 H, d, J = 8.5 Hz), 7.70−7.53 (10 H, m), 7.42 (1 H, tm, J = 7.5 and 1.3 Hz), 7.37−7.27 (3 H, m), 6.92−6.90 (2 H, m); ^{13}C δ 141.99, 139.06, 137.11, 136.83, 133.42, 130.89, 130.53, 130.23, 129.29, 128.95, 127.86, 127.81, 127.65, 126.99, 126.56, 125.01, 124.41, 123.45, 123.20, 122.94, 122.50, 119.14, 117.57, 109.87; MS m/z 369 (M^+), 291, 183, 146. Anal. Calcd for $C_{28}H_{19}N$: C, 91.03; H, 5.18; N, 3.79. Found: C, 90.75; H, 5.27; N, 3.71.

***N*-(2-Ethynylphenyl)diphenylacetamide (18a).** To 0.351 g of 2-ethynylaniline (**6a**, 3.00 mmol) in a 50-mL flask were added 0.762 g of diphenylacetyl chloride (3.30 mmol), 5 mL of anhydrous diethyl ether, and 0.8 mL of anhydrous triethylamine under a nitrogen atmosphere. The reaction mixture was heated under reflux for 2 h and then was concentrated in vacuo. The residue was purified by column chromatography (silica gel/10−20% diethyl ether in hexanes) to furnish 0.803 g (2.58 mmol, 86%) of **18a** as yellow crystalline needles: IR (KBr) 3290, 3219, 2107, 1665, 755, 701, 656 cm^{-1}; ^1H δ 8.55 (1 H, d, J = 8.1 Hz), 8.24 (1 H, br s), 7.43−7.29 (12 H, m), 7.03 (1 H, td, J = 7.6 and 1.1 Hz), 5.21 (1 H, s), 3.01 (1 H, s); ^{13}C δ 170.25, 139.45, 138.83, 131.81, 130.13, 129.19, 128.96, 127.45, 123.48, 118.98, 110.84, 84.18, 78.25, 60.63; MS m/z 311 (M^+), 194, 168, 167, 165, 152, 116.

***N*-[2-(Phenylethynyl)phenyl]phenylacetamide (19).** The same procedure was repeated as described for **18a** except that a mixture of 0.965 g of 2-(phenylethynyl)aniline (**6e**, 5.00 mmol), 0.70 mL of phenylacetyl chloride (0.82 g, 5.3 mmol), and 1.4 mL of triethylamine in 20 mL of diethyl ether was stirred at room temperature for 3 h to afford 1.512 g (4.86 mmol, 97%) of **19** as colorless crystals: IR (KBr) 3300, 1664, 756, 688 cm^{-1}; ^1H δ 8.45 (1 H, d, J = 8.3 Hz), 7.96 (1 H, br s), 7.44−7.29 (9 H, m), 7.15 (2 H, tm, J = 7.2 and 1.0 Hz), 7.09−7.01 (2 H, m), 3.80 (2 H, s); ^{13}C δ 169.21, 138.67, 133.86, 131.87, 131.79, 129.64, 129.50, 129.18, 128.85, 128.28, 127.65, 123.52, 122.19, 119.29, 112.00, 95.92, 83.60, 45.39; MS m/z 311 (M^+), 220, 193, 165, 91.

11-Phenyl-5*H*-benzo[*b*]carbazole (20). The same dehydration procedure was repeated as described for **10a** except that a mixture of 0.622 g of **19** (2.00 mmol), 3 g of Florisil, 1.42 g of P_2O_5 (10.0 mmol), 30 mL of triethylamine, and 0.57 mL of 1,4-CHD (6.0 mmol) was used. The reaction mixture was heated under reflux for 40 h. Purification by column chromatography followed by recrystallization afforded 0.157 g of **20** (0.54 mmol, 27%) as pale yellow crystals: IR (KBr) 3408, 748, 704 cm^{-1}; ^1H δ 8.00 (1 H, br s, NH), 7.97 (1 H, d, J = 8.3 Hz), 7.79 (1 H, s), 7.73 (1 H, d, J = 8.5 Hz), 7.68−7.60 (3 H, m), 7.55−7.45 (3 H, m), 7.39−7.36 (2 H, m), 7.31 (1 H, tm, J = 7.6 and 1.2 Hz), 6.96−6.87 (2 H, m); ^{13}C δ 142.15, 138.92 (2 carbons), 133.87, 132.55, 130.13, 128.90, 127.78, 127.51, 126.97, 126.90, 126.34, 125.00, 123.60, 123.29, 123.11, 122.68, 119.15, 109.87, 104.73; MS m/z 293 (M^+), 146.

Acknowledgment. We thank the National Science Foundation (CHE-9618676) for financial support.

Supporting Information Available: Experimental procedures, spectroscopic and analytical data for **7b**−**e**, **8c**,**d**, **10d**, **13d**, and **18c**−**e**, and ^1H and ^{13}C NMR spectra for compounds **7b**−**e**, **8b**−**d**, **10a**, **10d**, **13a**−**e**, **18a**, **18c**−**e**, **19**, and **20** (46 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

JO9804285