Reactions of *N*-Alkyl-*N*-phenyl-1*H*-benzotriazole-1-methanamines with *N*-Vinylamides and *N*-Vinylcarbazole. A Convenient Synthesis of 4-(Dialkylamino)tetrahydroquinolines

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Reactions of *N*-alkyl-*N*-phenyl-1*H*-benzotriazole-1-methanamines **1** with *N*-vinyl-2-pyrrolidinone and with *N*-vinyl-*N*-methylacetamide give 4-(2-pyrrolidinon-1-yl)- and 4-(*N*-methylacetamido-*N*-yl)-1,2,3,4-tetrahydroquinolines (**5** and **32**), respectively. In a reaction with *N*-vinyl-2-pyrrolidinone, α-alkyl (**11**) and α-aryl (**18**) derivatives of **1** stereoselectively give *cis*-2,4-disubstituted tetrahydroquinolines **16** and **21**, respectively. The 2-pyrrolidinon-1-yl and acetamido-*N*-yl substituents in the products are reduced with lithium aluminum hydride to the corresponding amino groups. Similar reactions of *N*-phenyl-1*H*-benzotriazole-1-methanamines **1** with 9-vinylcarbazole (**40**) lead to the corresponding 4-(carbazol-9-yl)-1,2,3,4-tetrahydroquinolines (**41** and **42**) and/or analogous 4-(benzotriazol-1-yl) or 4-(benzotriazol-2-yl) derivatives (**37, 38, 43,** and **44**), depending on the nature of the starting material and the reaction conditions. By commencing with aniline derivatives in which the nitrogen atom is built into a heterocyclic system, this method allows for the addition of a another ring to the system, as exemplified by the conversion of phenothiazine into **46** and [3,1]-benzoxazine into **49**, **52**, and **53**.

Introduction

In a preceding paper,[1] we reported on the reaction of *N*-phenyl-1*H*-benzotriazole-1-methanamines **1** with enol ethers giving 4-(benzotriazol-1-yl)- and/or 4-alkoxy-1,2,3,4-tetrahydroquinolines. In the first step, the reaction involves electrophilic attack of the immonium cation **2** on the electron rich β-carbon of the enol ethers. We now report on extensions of this reaction to the N-activated vinyl groups of *N*-vinylamides and *N*-vinyl heterocycles which lead to the corresponding 4-amino-1,2,3,4-tetrahydroquinolines. We have also found that α-alkyl and α-aryl derivatives of **1** can be employed in these reactions, thereby enriching the diversity of the tetrahydroquinolines synthesized; as previously summarized,[1] the present method is a useful alternative to the limited previous routes to these compounds.

Results and Discussion

1,4-Disubstituted 1,2,3,4-Tetrahydroquinolines from the Reaction of *N*-Alkyl-*N*-phenyl-1*H*-benzotriazole-1-methanamines with 1-Vinyl-2-pyrrolidinone. Under acidic catalysis, *N*-alkyl-*N*-phenyl-1*H*-benzotriazole-1-methanamines **1** react with 1-vinyl-2-pyrrolidinone (**4**) to give tetrahydroquinolines **5** in high yield (Scheme 1). The reaction commences with electrophilic attack of the immonium cation **2** on the vinylic β-carbon atom of **4**, producing cation **6**. We assume immonium cation **6** to exist in a dynamic equilibrium with the more stable ammonium cation **7**; formation of azetidinium cations analogous to **7** in reactions of *N,N*-dialkyl-1*H*-benzotriazole-1-methanamines with enol ethers was previously supported by stereochemical analysis of the products obtained.[2] Intramolecular electrophilic attack at the aniline ortho carbon atom of **6** leads to tetrahydroquinolines **5**.

Tetrahydroquinolines **5** appeared to be the only significant products (comprising >90% of the crude material) of these reactions when carried out at 120–150 °C. Analogous reactions at room temperature in organic solvents gave crude products containing 20–30% of adducts **9** and **10** which were separated from the tetrahydroquinolines **5** by column chromatography. Adducts **9** and **10** do not readily revert to species **6** as indicated by their failure to convert to tetrahydroquinolines **5** under these conditions. Reduction with lithium aluminum hydride converted pyrrolidinonyl derivatives **5** quantitatively to 1-alkyl-4-(pyrrolidin-1-yl)tetrahydroquinolines **8**.

1,2,4-Trisubstituted 1,2,3,4-Tetrahydroquinolines. We found that, under mild conditions, acidic catalysis and removal of water by molecular sieves, benzotriazole and *N*-methylaniline undergo condensation with aromatic and secondary aliphatic aldehydes (as well as with formaldehyde) to give mixtures of *N*-[α-(benzotriazol-1-yl)alkyl]anilines **11** and their benzotriazol-2-yl isomers **13** (Scheme 2). In this case, the proportions of the benzotriazol-2-yl isomers are higher than those for the analogous formaldehyde derivatives (e.g. 31% of **13a** vs 17% of **3a**). Products **11** and **13** are also much less stable than **1** and **3**. However, careful workup and recrystallization of crude **11** and **13** from ether containing 5% of the appropriate aldehyde allowed for the preparation of analytically pure samples. Thus, benzaldehyde and isobutyraldehyde gave the expected simple condensation products **11** (and **13**). Due to their increased tendency for self-condensation under acidic catalysis, acetaldehyde and other aliphatic aldehydes containing an α-CH_2 group reacted differently to give more complex products.[3]

Reactions of compounds **11** and **13** with 1-vinyl-2-pyrrolidinone (**4**) to give tetrahydroquinolines **16** proceeded in a manner similar to that of the reactions of

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(1) Katritzky, A. R.; Rachwal, B.; Rachwal, S. *J. Org. Chem.* **1995**, *60*, 2588.

(2) Katritzky, A. R.; Rachwal, S.; Rachwal, B.; Steel, P. J. *J. Org. Chem.* **1992**, *57*, 4932.

(3) Katritzky, A. R.; Rachwal, B.; Rachwal, S. Unpublished results.

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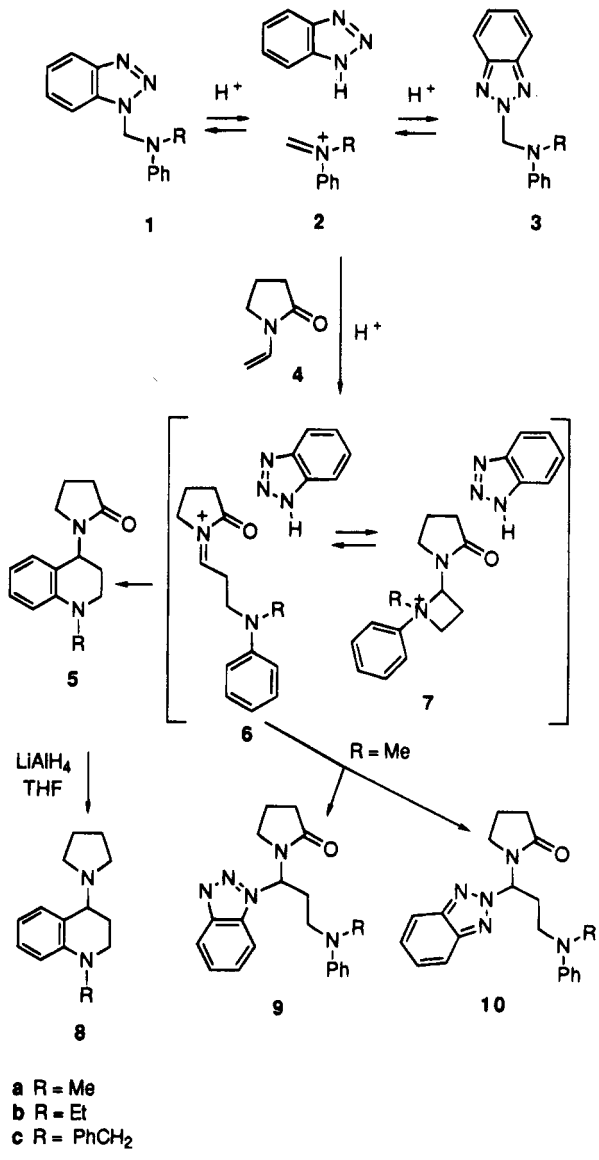
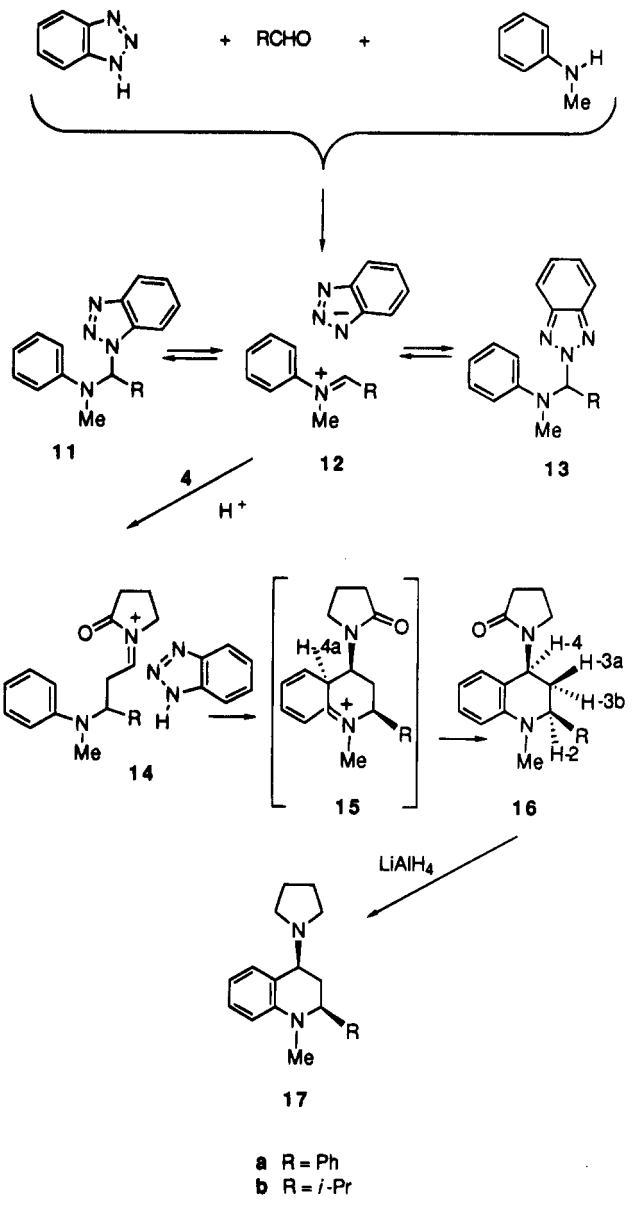
Scheme 1



Scheme 2



the similar formaldehyde derivatives **1**. Ionization of **11** and **13** to immonium cations **12** is more facile than that of **3** due to the additional stabilization of **12** by the R group. Electrophilic attack of cations **12** on the vinyl group of **4** gives cations **14** which then undergo cyclocondensation to produce 1,2,4-trisubstituted 1,2,3,4-tetrahydroquinolines **16**. Reduction with lithium aluminum hydride converted compounds **16** into diamines **17**.

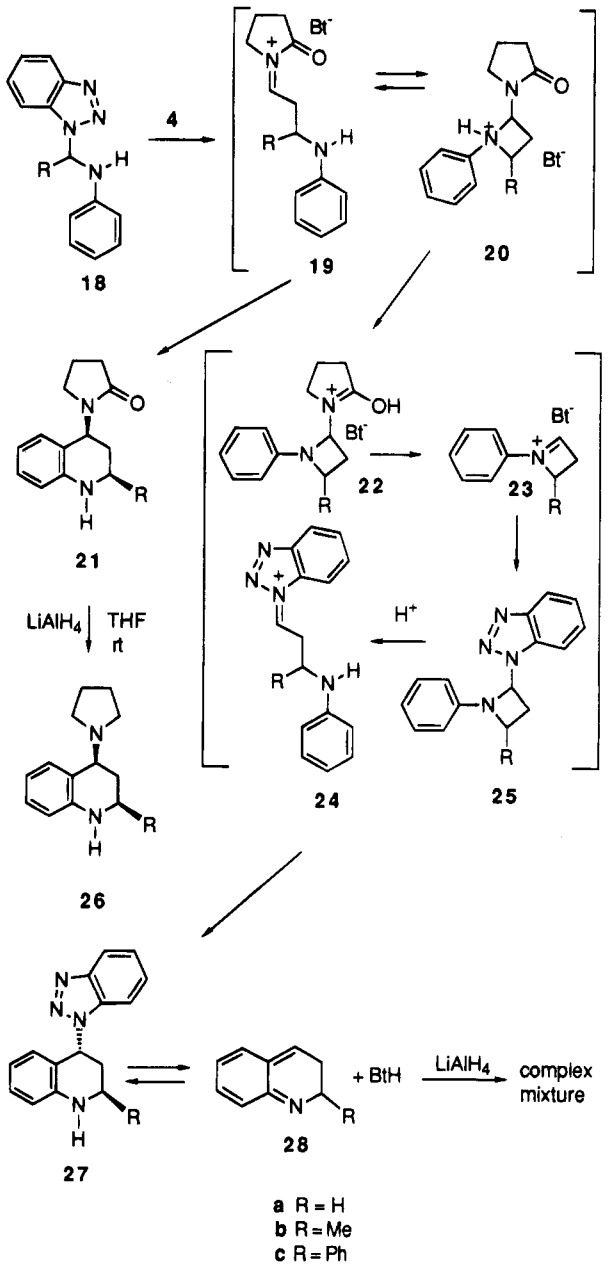
We were initially surprised by the exclusive formation of only one diastereomer of **16**. NOE experiments proved a *cis* configuration of the C-2 and C-4 substituents. Thus, in the case of **16a**, irradiation of H-2 (δ 4.46) produced a strong positive NOE effect (11%) for H-4 (δ 5.62); irradiation of H-4 gave 6% enhancement of the H-2 resonance. The *cis* configuration was additionally supported by the appearance of one of the H-3 resonances in **16b** as a quartet (J = 12.0 Hz). Only a *cis* configuration could give coupling constants of a similar magnitude between the two H-3 hydrogens and H-2 and H-4; for H-3a, the geminal coupling constant coincidentally appeared to be equal to the vicinal coupling constants with H-2 and H-4.

Exclusive formation of *cis*-**16** can be explained by the transition state (σ-complex) **15**. Molecular models indicate that reversing the positions of the pyrrolidin-2-on-1-yl substituent and H-4 would lead to a severe repulsive interaction between the pyrrolidinonyl moiety and one of the protons, H-2 or H-4a, depending on the molecular conformation. Switching the positions of the R group and H-2 would cause a repulsive interaction between R and H-4.

2,4-Disubstituted Tetrahydroquinolines. Reaction of *N*-[(benzotriazol-1-yl)methyl]aniline[4] (**18a**) with 1-vinyl-2-pyrrolidinone gave two products, **21a** and **27a** (Scheme 3). Apparently, in this case, the 2-pyrrolidinon-1-yl moiety can also behave as a leaving group. The difference in reactivity between unsubstituted **18** and the N-substituted products (**11**) probably results from additional stabilization of the four-membered ring in the transition state derived from **18** by proton transfer. Thus, similar to the previous case (Scheme 1), the initially formed immonium cation **19** undergoes cyclization to ammonium cation **20**. Proton transfer from the nitrogen to the oxygen atom in **20** produces the further stable cation **22**. Substitution of the protonated pyrrolidinonyl group by a benzotriazolyl substituent, probably via cation **23**, gives benzotriazole derivative **25**. Upon protonation of the azetidine nitrogen, compound

(4) Licari, J. J.; Hartzel, L. W.; Dougherty, G.; Benson, F. R. *J. Am. Chem. Soc.* **1955**, *77*, 5386.

Scheme 3



25 undergoes successive ring opening to form immonium cation **24** and cyclocondensation to give tetrahydroquinoline **27**.

The reaction of α-methyl-*N*-phenyl-1*H*-benzotriazole-1-methanamine (**18b**) with 1-vinyl-2-pyrrolidinone produced a similar mixture of pyrrolidinonyl- and benzotriazolyl-substituted tetrahydroquinolines **21b** and **27b**, respectively, in an approximate 1:1 ratio. As in the previous case, the products were separated by column chromatography. Rapid decomposition of **21b** under basic conditions facilitated the separation of **27b**; derivative **21b** was readily removed from the solution by washing with 5% sodium hydroxide. Analysis of the crude mixture by NMR indicated that the ratio of **21b**:**27b** was independent of the reaction conditions. The proportions remained the same when the reaction was carried out in solution at room temperature or without solvent at elevated temperature. It seems that the probability of forming tetrahydroquinoline **21b** is equal to that of forming azetidine derivative **20**.

Unexpectedly, the use of α,*N*-diphenyl-1*H*-benzotriazole-1-methanamine (**18c**) in the reaction with *N*-vinyl-2-pyrrolidinone produced almost exclusively the pyrrolidinonyl-substituted tetrahydroquinoline **21c**. Again, the product slate did not depend upon the reaction conditions. Benzotriazole derivative **27c** was isolated in 3% yield by column chromatography

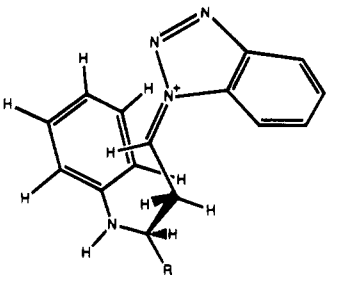
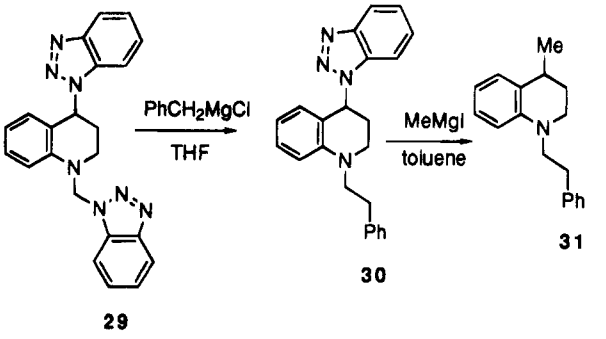


Figure 1. Stereochemical view of cation **24** in a conformation suitable for bond formation with the ortho carbon atom of the aniline ring.

Scheme 4

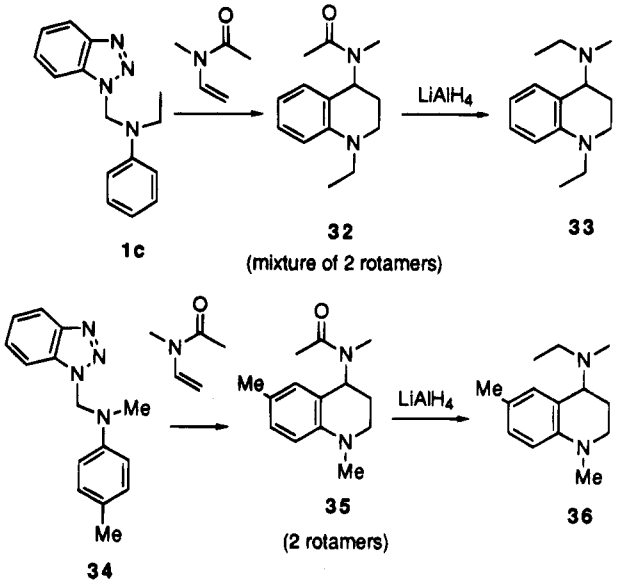


Similar to the case presented in Scheme 2, tetrahydroquinolines **21b,c** and **27b,c** were obtained as single diastereomers. Because the NMR spectral patterns of **21b** and **21c** are similar to those of **16**, compounds **21b** and **21c** were assigned *cis* configurations. As in the previous case, the stereoselectivity of these reactions can be explained by the involvement of transition states analogous to **15**. Quite different ^{1}H NMR spectra were observed for tetrahydroquinolines **27b,c**, suggesting a *trans* relationship between the C-2 and C-4 substituents. Irradiation of the methyl doublet (δ 1.21) of **27b** in an NOE experiment produced enhancement of the H-4 resonance as expected for a *trans* arrangement. It is not clear why the *trans* configuration is preferred in this instance; possibly, the formation of a π-complex (Figure 1) plays a more important role than the stereochemical interactions in the σ-complex.

Treatment with lithium aluminum hydride converted products **21a–c** into 4-(pyrrolidin-1-yl)tetrahydroquinolines **26a–c**. Under the same reaction conditions, products **27a–c** produced complex mixtures. We believe that compounds **27a–c** exist, in solution, in equilibrium with 2,3-dihydroquinolines **28** due to the facile elimination of benzotriazole. Nucleophilic attack of lithium aluminum hydride could occur at several different positions of **28**, including the benzenoid ring.

Substitution of the NH hydrogen atom in **27** stabilized the system, thus allowing for further conversions. Hence, *N*-benzotriazolylmethylation of tetrahydroquinoline **27a** gave bis(benzotriazol-1-yl)derivative **29**. The benzotriazolyl moiety connected by a methylene bridge to the tetrahydroquinoline nitrogen is the more reactive of the two and was selectively replaced by a benzyl group, giving **30** (Scheme 4). The use of less mild conditions in the subsequent step (refluxing in toluene) allowed for

Scheme 5



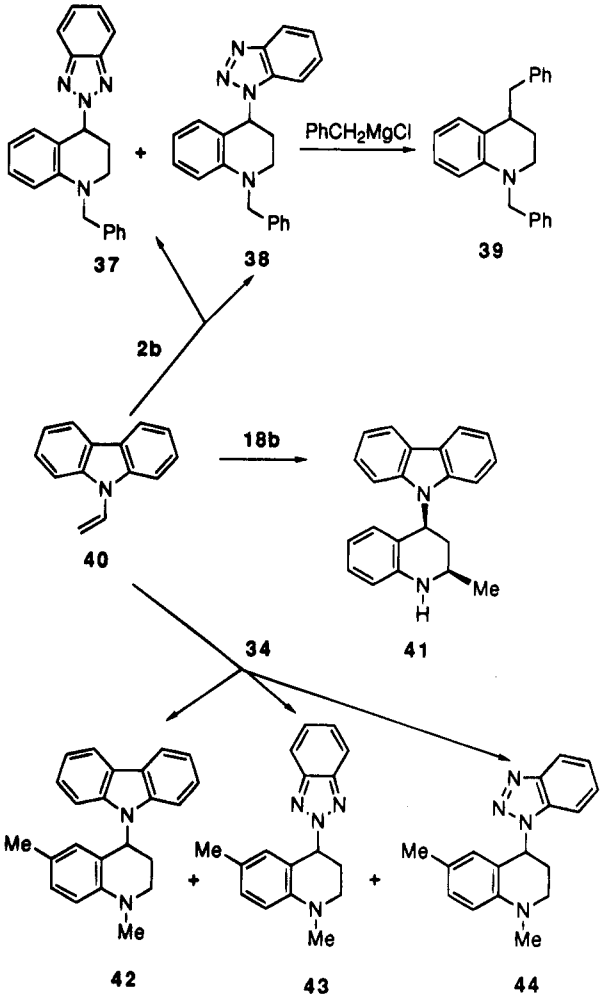
substitution of the 4-benzotriazolyl moiety by a methyl group, leading to tetrahydroquinoline **31**.

***N*-Vinyl-*N*-methylacetamide.** *N*-Vinyl-*N*-methylacetamide appeared to behave in a manner similar to that of *N*-vinyl-2-pyrrolidinone except for the existence of two rotamers exhibiting double sets of NMR resonances. As expected, reduction of such rotamer mixtures with lithium aluminum hydride led to single 1-alkyl-4-(ethylmethylamino)tetrahydroquinolines. Thus, reaction of *N*-ethyl-*N*-phenyl-1*H*-benzotriazole-1-methanamine (**1c**) with *N*-methyl-*N*-vinylacetamide gave, in high yield, derivative **32** (two rotamers in solution by NMR) which was then reduced to 4-aminotetrahydroquinoline **33** (Scheme 5). Similarly, compound **35** was prepared as a mixture of two rotamers from the reaction of *N*-vinyl-*N*-methylacetamide with the *N*-(benzotriazol-1-yl)methyl derivative of *N*-methyl-4-toluidine (**34**). Subsequent reduction provided 4-amino-6-methyltetrahydroquinoline **36**. This last reaction highlights the possibility of synthesizing tetrahydroquinolines substituted in the aromatic ring, starting from appropriately substituted anilines.

9-Vinylcarbazole. In this case, depending on the nature of the starting amine and the reaction conditions, either the carbazolyl or benzotriazolyl moiety can act as the leaving group. Thus, reaction of aniline derivative **2b** with 9-vinylcarbazole (**40**) gave a mixture of benzotriazol-1-yl and benzotriazol-2-yl derivatives of tetrahydroquinoline (**38** and **37**, respectively) which was separated by column chromatography (Scheme 6). The mixture of isomers (**37** and **38**) was converted to 1,4-dibenzyltetrahydroquinoline (**39**) upon treatment with benzylmagnesium chloride in refluxing toluene. Reaction of **40** with the unsubstituted aniline derivative **18b** led almost exclusively to 4-(carbazol-1-yl)tetrahydroquinoline **41**. Reaction of 9-vinylcarbazole with toluidine derivative **34** gave 4-(carbazol-9-yl)-1,6-dimethyl-1,2,3,4-tetrahydroquinoline (**42**) as the main product; minor quantities of benzotriazole derivatives **43** and **44** were separated by column chromatography.

Derivatives of Heterocyclic Amines. If one starts from the appropriate heterocyclic amine, application of our method allows for the addition of another ring to the heterocyclic system. Thus, reaction of phenothiazine

Scheme 6



derivative **45**[5] with 1-vinyl-2-pyrrolidinone (**4**) produced amide **46** (Scheme 7). Subsequent reduction of **46** with lithium aluminum hydride gave amine **47**.

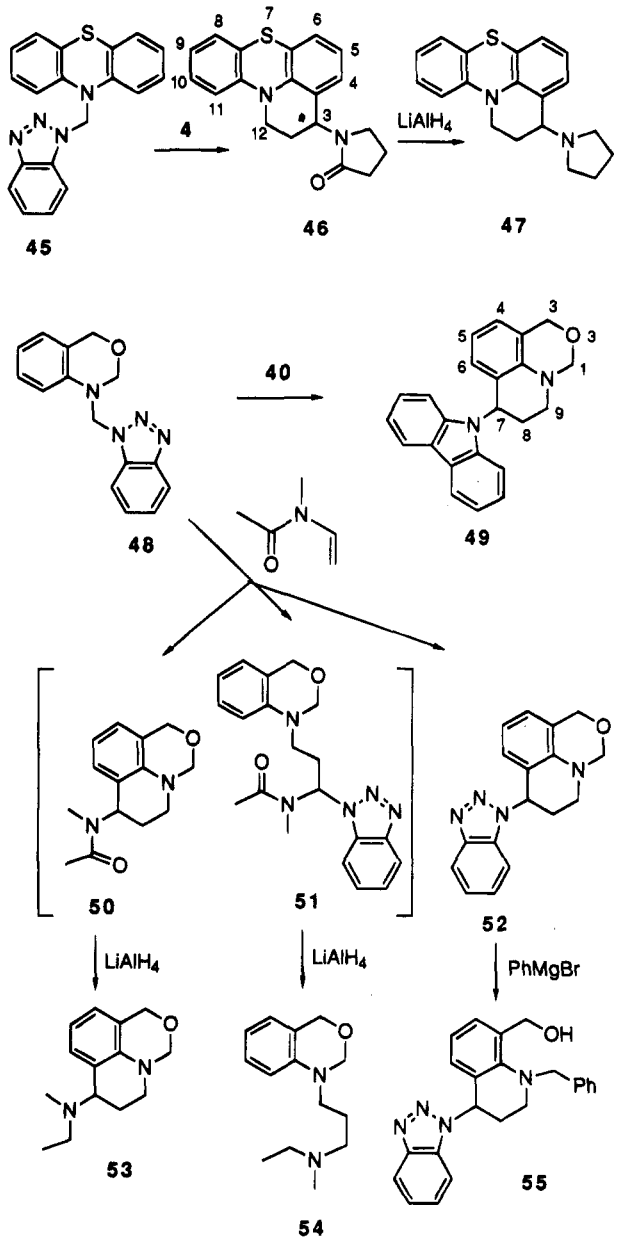
In another experiment, reaction of compound **48** (obtained by condensation of 2-(hydroxymethyl)aniline with formaldehyde and benzotriazole[6]) with 9-vinylcarbazole (**40**) gave tricyclic system **49**. Reaction of **48** with *N*-methyl-*N*-vinylacetamide produced a complex mixture which, upon reduction with lithium aluminum hydride, was converted to a mixture of diamines **53** and **54** and benzotriazole derivative **52**. Obviously, elimination of benzotriazole leading to **50** was competing in this reaction with elimination of acetamide giving derivative **52**. Formation of a noncyclized product analogous to **51** is described above (see Scheme 1). Reaction of **52** (the main product) with phenylmagnesium bromide caused opening of the N–CH_2–O bridge, leading to 1-benzyltetrahydroquinoline **55**.

Conclusions

Reactions of *N*-phenyl-1*H*-benzotriazole-1-methanamines, the condensation products of anilines with formaldehyde and benzotriazole with *N*-vinylamides, provide a simple method for the preparation of 4-(dialkylamino)-1,2,3,4-tetrahydroquinolines. The same reaction performed on products obtained from the condensation of aniline and benzotriazole with higher aldehydes leads

(5) Katritzky, A. R.; Gordeev, M. F. *J. Org. Chem.* **1993**, *58*, 4049.
(6) Katritzky, A. R.; Rachwal, S.; Wu, J. *Can. J. Chem.* **1990**, *68*, 446.

Scheme 7



to *cis* isomers of 2-alkyl- or 2-aryl-4-(dialkylamino)-1,2,3,4-tetrahydroquinolines. 9-Vinylcarbazole behaves in a manner similar to that of *N*-vinylamides, giving 4-(carbazol-9-yl)-1,2,3,4-tetrahydroquinolines. When the aniline nitrogen atom is already built into a heterocyclic system, this method allows for the addition of another ring to the molecule. The results presented here extend our previous work[1,5] on the synthesis of 1,4-dialkyl- or 1,4-(alkylaryl)-1,2,3,4-tetrahydroquinolines to derivatives bearing a dialkylamino group at C-4 and to derivatives bearing an alkyl or aryl substituent at C-2.

Experimental Section

General. Melting points were determined on a capillary melting point apparatus and are uncorrected. NMR spectra were recorded in $CDCl_3$ solution with tetramethylsilane as the internal standard for ^1H (300 MHz) and ^{13}C (75 MHz). Solvents for the Grignard reactions and reductions (ether, THF, and toluene) were dried by refluxing with sodium benzophenone ketyl under nitrogen and distilled immediately before use. Column chromatography was performed with silica gel (60–200 mesh).

***N*-Benzyl-*N*-phenyl-1*H*-benzotriazole-1-methanamine (1c).** A mixture of benzotriazole (2.38 g, 20 mmol), formaldehyde (38% solution, 2 mL), and *N*-benzylaniline (3.66 g, 20 mmol) was dissolved in toluene (100 mL) and refluxed using a Dean–Stark trap for 2 h. Evaporation of the solvent and trituration of the residue with ether gave a crude solid product which was recrystallized from ethanol to give **1c** (5.23 g, 83%) as prisms: mp 112–113 °C; ^1H NMR δ 4.58 (s, 2 H, NCH_2Ph), 6.09 (s, 2 H, CH_2Bt), 6.88 (t, J = 7.2 Hz, 1 H), 7.04 (t, J = 8.0 Hz, 2 H), 7.12 (m, 1 H), 7.29 (m, 9 H), 7.99 (m, 1 H); ^{13}C NMR δ 53.4, 64.8, 109.8, 116.4 (4 C), 119.7, 120.5, 123.7, 127.3 (4 C), 128.5 (2 C), 129.5 (2 C), 132.7, 137.0, 145.9, 147.5. Anal. Calcd for $C_{20}H_{18}N_4$: C, 76.41; H, 5.77; N, 17.82. Found: C, 76.44; H, 5.78; N, 17.66.

1-Methyl-4-(2-oxopyrrolidin-1-yl)-1,2,3,4-tetrahydroquinoline (5a). *p*-Toluenesulfonic acid monohydrate (20 mg, 0.1 mmol) was added to a mixture of **1a**[1] (2.39 g, 10 mmol) and 1-vinyl-2-pyrrolidinone (1.11 g, 10 mmol) preheated to 120 °C to initiate the reaction. The mixture was heated at 130 °C (oil bath) for an additional 10 min and then allowed to cool to room temperature. The crude product was dissolved in $CHCl_3$ and washed with 10% NaOH, followed by water. The chloroform solution was dried ($MgSO_4$) and evaporated. The residue was triturated with ether and separated to give **5a** (2.07 g, 90%) as grains: mp 77–78 °C; ^1H NMR δ 2.00 (m, 2 H), 2.12 (m, 2 H, H-2), 2.49 (t, J = 7.9 Hz, 2 H), 2.88 (s, 3 H, Me), 3.14 (m, 1 H), 3.22 (m, 2 H), 3.33 (m, 1 H), 5.42 (dd, J = 6.1 and 9.0 Hz, 1 H), 6.64 (m, 2 H), 6.87 (d, J = 7.4 Hz, 1 H), 7.14 (t, J = 7.3 Hz, 1 H); ^{13}C NMR δ 18.3, 26.7 (C-2), 31.5, 39.3 (Me), 43.5, 47.9 (C-3), 49.5 (C-1), 111.8, 116.7, 119.8, 127.5, 128.5, 147.5, 175.3. Anal. Calcd for $C_{14}H_{18}N_2O$: C, 73.01; H, 7.88; N, 12.16. Found: C, 72.76; H, 7.91; N, 12.21.

1-Ethyl-4-(2-oxopyrrolidin-1-yl)-1,2,3,4-tetrahydroquinoline (5b). Starting from **1b**[1] (2.52 g, 10 mmol) and **4** (1.11 g, 10 mmol) and following the procedure for **5a**, we obtained crude **5b** (> 90% purity). Column chromatography of the crude material (toluene/AcOEt, 2:1) gave analytically pure **5b** (2.00 g, 82%) as an oil: ^1H NMR δ 1.12 (t, J = 7.0 Hz, 3 H), 2.00 (m, 4 H), 2.12 (m, 2 H), 2.48 (t, J = 7.8 Hz, 2 H), 3.08–3.45 (m, 6 H), 5.36 (dd, J = 5.5 and 8.9 Hz, 1 H), 6.61 (m, 2 H), 6.85 (d, J = 7.5 Hz, 1 H), 7.10 (dt, J = 8.1 and 1.1 Hz, 1 H); ^{13}C NMR δ 10.6, 18.3, 26.6, 31.4, 43.8, 45.3, 46.2, 48.1, 111.4, 115.8, 119.3, 127.8, 128.5, 145.6, 175.3. Anal. Calcd for $C_{15}H_{20}N_2O$: C, 73.74; H, 8.25; N, 11.47. Found: C, 73.43; H, 8.53; N, 11.62.

1-Benzyl-4-(2-oxopyrrolidin-1-yl)-1,2,3,4-tetrahydroquinoline (5c). Starting from **1c** (3.14 g, 10 mmol) and **4** (1.11 g, 10 mmol) and following the procedure given above for **5a**, we obtained compound **5c** (2.80 g, 92%) as an oil after column chromatography (chloroform) of the crude mixture: ^1H NMR δ 2.02 (m, 2 H), 2.10 (m, 2 H, H-2), 2.49 (dt, J = 7.6 and 1.1 Hz, 2 H), 3.24 (m, 2 H, H-1), 3.35 (m, 1 H), 3.49 (m, 1 H), 4.45 (d, J = 17.2 Hz, 1 H), 4.48 (d, J = 17.1 Hz, 1 H), 5.43 (dd, J = 5.3 and 9.0 Hz, 1 H), 6.51 (d, J = 7.8 Hz, 1 H), 6.62 (t, J = 7.4 Hz, 1 H), 6.89 (d, J = 7.3 Hz, 1 H), 7.03 (t, J = 8.2 Hz, 1 H), 7.30 (m, 5 H, Ph); ^{13}C NMR δ 18.2, 26.6, 31.4, 43.7, 47.5, 48.0, 55.1, 111.7, 116.2, 119.2, 126.4 (2 C), 126.8, 127.4, 128.5 (3 C), 138.2, 146.0, 175.3. Anal. Calcd for $C_{20}H_{22}N_2O$: C, 78.40; H, 7.24; N, 9.14. Found: C, 78.04; H, 7.17; N, 9.48.

1-Methyl-4-(pyrrolidin-1-yl)-1,2,3,4-tetrahydroquinoline (8a). Lithium aluminum hydride (0.76 g, 20 mmol) was added portionwise to a solution of **5a** (2.30 g, 10 mmol) in dry THF (50 mL) stirred under nitrogen. After the addition, the reaction mixture was stirred at room temperature for an additional 1 h, then poured into 20% NaOH (100 mL), and extracted with ether (2 × 100 mL). The ethereal solution was dried over Na_2CO_3 and evaporated to give **8a** of high purity (2.05 g, 95%) as an oil: ^1H NMR δ 1.73 (m, 4 H), 1.85 (m, 1 H), 2.12 (m, 1 H), 2.40 (m, 2 H), 2.66 (m, 2 H), 2.90 (s, 3 H), 3.10 (m, 1 H), 3.24 (m, 1 H), 3.58 (m, 1 H), 6.55 (m, 2 H), 7.06 (m, 2 H); ^{13}C NMR δ 23.6 (2 C), 25.7, 38.7, 46.7, 51.4 (2 C), 60.9, 110.5, 114.5, 122.9, 128.6, 130.1, 145.7. Anal. Calcd for $C_{14}H_{20}N_2$: C, 77.73; H, 9.32; N, 12.95. Found: C, 78.01; H, 9.02; N, 13.29.

1-Ethyl-4-(pyrrolidin-1-yl)-1,2,3,4-tetrahydroquinoline (8b). Starting from crude **5b** (obtained from 10 mmol of **1b**) and following the procedure for **8a**, we obtained crude **8b** (purity 90%, according to NMR). Column chromatography of the crude product (toluene/ethyl acetate, 2:1) gave analytically

pure **8b** (1.72 g, 75%) as an oil: ^{1}H NMR δ 1.12 (t, J = 7.0 Hz, 3 H), 1.72 (m, 5 H), 2.10 (m, 1 H), 2.40 (m, 2 H), 2.66 (m, 2 H), 3.14 (m, 1 H), 3.24 (m, 2 H), 3.39 (m, 1 H), 3.54 (m, 1 H), 6.49 (t, J = 7.3 Hz, 1 H), 6.57 (d, J = 8.2 Hz, 1 H), 7.06 (m, 2 H); ^{13}C NMR δ 11.0, 23.4 (2 C), 25.6, 43.5, 44.9, 51.2 (2 C), 60.7, 110.2, 113.7, 122.6, 128.3, 130.3, 144.3. Anal. Calcd for $C_{15}H_{22}N_2$: C, 78.21; H, 9.63; N, 12.16. Found: C, 77.94; H, 9.72; N, 12.49.

1-Benzyl-4-(pyrrolidin-1-yl)-1,2,3,4-tetrahydroquinoline (8c). Using the procedure given for **8a** and starting from **5c** (3.06 g, 10 mmol) and $LiAlH_4$ (0.38 g, 10 mmol), we obtained compound **8c** (2.04 g, 70%) as an oil: ^{1}H NMR δ 1.74 (m, 4 H), 1.89 (m, 1 H), 2.17 (m, 1 H), 2.42 (m, 2 H), 2.68 (m, 2 H), 3.27 (m, 2 H), 3.70 (ddd, J = 3.6, 11.0, and 12.6 Hz, 1 H), 4.45 (d, J = 17.3 Hz, 1 H), 4.59 (d, J = 17.3 Hz, 1 H), 6.51 (m, 2 H), 7.01 (m, 2 H), 7.25 (m, 5 H); ^{13}C NMR δ 23.4 (2 C), 26.0, 44.8, 51.4 (2 C), 54.3, 60.4, 110.8, 114.4, 122.7, 126.4 (2 C), 126.6, 128.4 (2 C), 128.5, 130.2, 138.7, 144.8; HRMS calcd for $C_{20}H_{25}N_2$ 292.194 (M^+), found 292.194.

1-[1-(Benzotriazol-1-yl)-3-(*N*-methyl-*N*-phenylamino)-propyl]-2-pyrrolidinone (9a). *p*-Toluenesulfonic acid monohydrate (20 mg, 0.1 mmol) was added to a solution of **1a** (2.39 g, 10 mmol) and **4** (1.11 g) in dry chloroform (20 mL). After 7 days at 22 °C, the solution was poured into ice–water (50 g) and extracted with chloroform (2 × 50 mL). The extract was washed with 5% NaOH and then water, dried over $MgSO_4$, and evaporated under reduced pressure. The residue was subjected to column chromatography (toluene/ethyl acetate, 9:1) to give **9a** as the first fraction (0.66 g, 19%) as an oil: ^{1}H NMR δ 1.83 (m, 1 H), 1.98 (m, 1 H), 2.26 (ddd, J = 5.3, 9.6, and 17.3 Hz, 1 H), 2.42 (ddd, J = 6.8, 9.6, and 16.8 Hz, 1 H), 2.61 (m, 1 H), 2.91 (s, 3 H), 3.10 (m, 2 H), 3.40 (m, 2 H), 3.56 (m, 1 H), 6.66 (m, 3 H), 6.86 (dd, J = 6.4 and 8.7 Hz, 1 H), 7.18 (t, J = 8.7 Hz, 2 H), 7.38 (t, J = 7.0 Hz, 1 H), 7.48 (m, 1 H), 7.78 (d, J = 8.4 Hz, 1 H), 8.05 (d, J = 8.2 Hz, 1 H); ^{13}C NMR δ 17.6, 27.9, 30.7, 38.6, 42.1, 48.9, 61.3, 110.4, 112.5 (2 C), 116.8, 119.5, 124.4, 127.8, 129.1 (2 C), 132.6, 145.6, 148.7, 175.1; HRMS calcd for $C_{20}H_{23}N_5O$ 349.190 (M^+), found 349.188.

α,*N*-Diphenyl-*N*-methyl-1*H*-benzotriazole-1-methanamine (11a) and Its 2*H*-Benzotriazole Isomer 13a. *p*-Toluenesulfonic acid monohydrate (20 mg, 0.1 mmol) was added to a solution of benzotriazole (2.98 g, 25 mmol), benzaldehyde (2.6 mL, 25 mmol), and *N*-methylaniline (2.7 mL, 25 mmol) in dry ether (20 mL). Molecular sieves (5Å, 5.0 g) were added portionwise to this solution while shaken. Evolution of heat warmed the solution until it was boiling. The mixture was gently shaken every 10 min for 1 h. The solution was separated by decantation, and the molecular sieves were washed with another portion of dry ether (10 mL). The solution and washings were combined and kept at −5 °C for 20 h. The precipitate was separated by filtration under nitrogen, washed with dry ether (10 mL), and dried in a vacuum dessicator over sodium hydroxide to give an analytically pure mixture (7.06 g, 90%) of **11a** (69%) and **13a** (31%) as a white solid: mp 121–125 °C; ^{13}C NMR δ 34.4 (**11a**), 34.9 (**13a**), 77.2 (**11a**), 82.6 (**13a**), 110.1, 114.2, 114.9, 118.5, 119.5, 119.9, 120.1, 124.0, 126.4, 126.8, 127.2, 127.5, 128.6, 128.7, 128.8, 128.9, 129.3, 129.4, 133.0, 136.0, 136.9, 144.1, 145.8, 148.6, 148.9. Anal. Calcd for $C_{20}H_{18}N_4$: C, 76.41; H, 5.77; N, 17.82. Found: C, 76.16; H, 5.83; N, 17.83.

***N*-Methyl-α-(1-methylethyl)-*N*-phenyl-1*H*-benzotriazole-1-methanamine (11b) and Its 2*H*-Benzotriazole Isomer 13b.** Starting from isobutyraldehyde (2.3 mL, 25 mmol) and following the procedure given for **11a**, we obtained a mixture (6.37 g, 91%) of **11b** (65%) and **13b** (35%) as long thin needles: mp 71–74 °C; ^{13}C NMR (mixture) δ 19.1, 19.6, 29.9, 31.4, 32.3, 81.6, 86.4, 109.9, 114.8, 116.2, 118.3, 119.2, 119.6, 120.1, 123.7, 126.1, 127.1, 129.2, 129.3, 133.6, 143.6, 145.4, 149.9. Anal. Calcd for $C_{17}H_{20}N_4$: C, 72.83; H, 7.19; N, 19.98. Found: C, 72.54; H, 7.29; N, 19.88.

***cis*-1-Methyl-4-(2-oxopyrrolidin-1-yl)-2-phenyl-1,2,3,4-tetrahydroquinoline (16a).** Starting from a mixture of **11a** and **13a** (3.14 g, 10 mmol) and following the procedure for **5a**, we obtained crude product **16a** as an oil. Purification by column chromatography (toluene/ethyl acetate, 1:1) gave pure **16a** which was then recrystallized from ether to give colorless needles (2.75 g, 89%): mp 173 °C; ^{1}H NMR δ 2.00 (m, 2 H), 2.18 (m, 2 H), 2.48 (m, 2 H), 2.71 (s, 3 H), 3.14–3.32 (m, 2 H), 4.46 (dd, J = 4.2 and 10.5 Hz, 1 H), 5.62 (dd, J = 5.1 and 11.4 Hz, 1 H), 6.78 (m, 3 H), 7.20 (t, J = 7.2 Hz, 1 H), 7.34 (m, 5 H); ^{13}C NMR δ 18.2, 31.3, 37.1, 37.9, 42.4, 48.0, 63.5, 113.3, 116.9, 121.0, 125.2, 126.7 (2 C), 127.4, 128.4, 128.7 (2 C), 143.3, 148.1, 175.7. Anal. Calcd for $C_{20}H_{22}N_2O$: C, 78.40; H, 7.24; N, 9.14. Found: C, 78.09; H, 7.34; N, 9.05.

***cis*-1-Methyl-2-(1-methylethyl)-4-(2-oxopyrrolidin-1-yl)-1,2,3,4-tetrahydroquinoline (16b).** Starting from a mixture of **11b** and **13b** (2.80 g, 10 mmol) and following the procedure given for **5a**, we obtained crude product **16b** as an oil. Column chromatography, as for **16a**, gave pure **16b** (1.74 g, 64%) as an oil which crystallized after a few days to give white prisms: mp 105 °C; ^{1}H NMR δ 0.79 (d, J = 6.8 Hz, 3 H), 0.95 (d, J = 6.9 Hz, 3 H), 1.80 (q, J = 12.0 Hz, 1 H), 1.90 (m, 1 H), 2.09 (m, 2 H), 2.29 (m, 1 H), 2.54 (m, 2 H), 2.89 (s, 3 H), 3.33 (t, J = 6.6 Hz, 2 H), 5.37 (dd, J = 4.2 and 12.3 Hz, 1 H), 6.63 (m, 2 H), 6.72 (m, 1 H), 7.12 (m, 1 H); ^{13}C NMR δ 14.5, 18.3, 19.4, 26.6, 29.1, 31.4, 36.5, 42.6, 48.0, 62.1, 113.3, 116.2, 122.3, 123.9, 128.1, 148.5, 175.6. Anal. Calcd for $C_{17}H_{24}N_2O$: C, 74.96; H, 8.88; N, 10.28. Found: C, 74.68; H, 8.98; N, 10.50.

***cis*-1-Methyl-2-phenyl-4-(pyrrolidin-1-yl)-1,2,3,4-tetrahydroquinoline (17a).** Lithium aluminum hydride (0.38 g, 10 mmol) was added portionwise to a solution of **16a** (1.53 g, 5 mmol) in dry THF (25 mL) stirred under nitrogen. After the addition, the mixture was heated at reflux for 1 h. After cooling, the reaction mixture was poured into 20% NaOH (25 mL) and extracted with ether (2 × 50 mL). The extracts were dried over Na_2CO_3, the solvent was evaporated, and the residue was purified by column chromatography (toluene/ethyl acetate, 3:1) to give amine **17a** (1.17 g, 80%) as a yellowish oil: ^{1}H NMR δ 1.63 (m, 4 H), 2.05 (dt, J = 12.9 and 9.0 Hz, 1 H), 2.23 (ddd, J = 3.6, 5.1, and 12.9 Hz, 1 H), 2.48 (m, 4 H), 2.72 (s, 3 H), 3.95 (dd, J = 3.6 and 9.3 Hz, 1 H), 4.37 (dd, J = 5.1 and 8.4 Hz, 1 H), 6.69 (m, 3 H), 7.17 (m, 1 H), 7.32 (m, 5 H); ^{13}C NMR δ 23.7 (2 C), 32.7, 37.5, 48.7 (2 C), 57.5, 63.6, 111.6, 116.1, 125.7, 126.8, 127.0 (2 C), 127.1, 127.7, 128.2 (2 C), 144.7, 146.9. Anal. Calcd for $C_{20}H_{24}N_2$: C, 81.15; H, 8.27; N, 9.58. Found: C, 81.75; H, 8.42; N, 9.43.

***cis*-1-Methyl-2-(1-methylethyl)-4-(pyrrolidin-1-yl)-1,2,3,4-tetrahydroquinoline (17b).** Starting from **16b** (1.36 g, 5 mmol) and following a procedure similar to that for **17a**, we obtained amine **17b** (0.97 g, 75%) as a yellowish oil: ^{1}H NMR δ 0.70 (d, J = 6.6 Hz, 3 H), 0.95 (d, J = 7.2 Hz, 3 H), 1.55 (q, J = 12.0 Hz, 1 H), 1.83 (m, 4 H), 2.07 (ddd, J = 3.6, 5.4, and 12.0 Hz, 1 H), 2.29 (m, 1 H), 2.70 (m, 2 H), 2.81 (m, 2 H), 2.90 (s, 3 H), 3.27 (ddd, J = 4.8, 5.4, and 10.2 Hz, 1 H), 3.87 (dd, J = 3.3 and 11.7 Hz, 1 H), 6.57 (d, J = 8.4 Hz, 1 H), 6.67 (t, J = 7.5 Hz, 1 H), 7.10 (m, 1 H), 7.32 (d, J = 7.5 Hz, 1 H); ^{13}C NMR δ 14.8, 19.6, 22.4, 23.9 (2 C), 29.7, 36.6, 48.5 (2 C), 56.2, 63.1, 111.9, 115.9, 124.8, 127.1, 127.8, 147.6. **Picrate**: mp 117 °C. Anal. Calcd for $C_{29}H_{32}N_8O_{14}$: C, 48.61; H, 4.50; N, 15.69. Found: C, 48.68; H, 4.42; N, 15.70.

α-Methyl-*N*-phenyl-1*H*-benzotriazole-1-methanamine (18b) and Its 2*H*-isomer. Acetaldehyde (6.1 mL, 110 mmol) was added portionwise to a mixture of benzotriazole (11.91 g, 100 mmol), aniline (9.1 mL, 100 mmol), and ether (200 mL) stirred and cooled in an ice bath. The obtained solution was set aside at 22 °C until precipitation started. The mixture was kept at −5 °C overnight. The crystals were separated, washed with ether, and dried in a vacuum oven at 50 °C to give **18b** and its Bt-2 isomer in the ratio of 4:1 (19.8 g, 92%) as thick white needles: mp 127–128 °C; ^{1}H NMR δ 1.95 (d, J = 6.6 Hz, 3 H), 6.28 (t, J = 8.2 Hz, 2 H), 6.72 (d, J = 7.8 Hz, 2 H), 6.91 (d, J = 7.8 Hz, 1 H), 7.03 (t, J = 7.4 Hz, 2 H), 7.32 (m, 1 H), 7.41 (m, 1 H), 7.96 (d, J = 8.4 Hz, 2 H), 8.06 (d, J = 8.5 Hz, 2 H); ^{13}C NMR δ 21.6, 67.0, 111.4, 113.1 (2 C), 118.3, 119.5, 123.8, 127.0, 129.1 (2 C), 131.0, 145.4, 146.3. Anal. Calcd for $C_{14}H_{14}N_4$: C, 70.57; H, 5.92; N, 23.51. Found: C, 70.64; H, 5.95; N, 23.79.

α,*N*-Diphenyl-1*H*-benzotriazole-1-methanamine (18c) and Its 2*H*-isomer. Compound **18c** and its Bt-2 isomer (28.50 g, 95%) were obtained by a procedure analogous to that for **18b**, starting from benzotriazole (11.91 g, 100 mmol), aniline (9.1 mL, 100 mmol), and benzaldehyde (10.2 mL, 100 mmol): needles; mp 104–105 °C; ^{1}H NMR (DMSO-d_6) δ 4.80 (m, 3 H),

4.93 (m, 4 H), 5.04 (m, 3 H), 5.46 (m, 4 H), 6.13 (s, 1 H); ^{13}C NMR (DMSO-d_6) δ 114.8 (2 C), 120.9 (2 C), 125.3 (2 C), 125.9, 128.6 (3 C), 128.7 (2 C), 129.1 (2 C), 131.4, 136.0, 151.4, 160.6 (2 C). Anal. Calcd for $C_{19}H_{16}N_4$: C, 75.98; H, 5.37; N, 18.65. Found: C, 75.89; H, 5.30; N, 18.90.

4-(2-Oxopyrrolidin-1-yl)-1,2,3,4-tetrahydroquinoline (21a) and 4-(Benzotriazol-1-yl)-1,2,3,4-tetrahydroquinoline (27a). Starting from **18a**[4] (2.24 g, 10 mmol) and **4** (1.1 g, 10 mmol) and following the procedure given above for compound **5a**, we obtained a mixture of **21a** and **27a** in a molar ratio of 1:1 (by NMR). Column chromatography (ethyl acetate) gave a glassy material (0.56 g, 22%) which NMR showed to be a mixture of **27a** and its benzotriazol-2-yl isomer. Repeated chromatography (toluene/ethyl acetate, 9:1) allowed for separation of the predominant isomer **27a** (0.30 g, 12%) as a glassy material: ^{1}H NMR δ 2.37 (m, 1 H), 2.46 (m, 1 H), 3.24 (ddd, J = 3.6, 8.5, and 12.0 Hz, 1 H), 3.38 (ddd, J = 3.7, 6.9, and 11.3 Hz, 1 H), 4.15 (bs, 1 H), 6.25 (t, J = 6.1 Hz, 1 H), 6.49 (t, J = 7.6 Hz, 1 H), 6.59 (d, J = 8.2 Hz, 1 H), 6.67 (d, J = 7.7 Hz, 1 H), 6.91 (m, 1 H), 7.07 (m, 1 H), 7.20 (m, 2 H), 7.96 (m, 1 H); ^{13}C NMR δ 29.6, 38.9, 56.5, 110.9, 114.8, 116.2, 117.7, 119.9, 123.6, 127.0, 129.5, 129.6, 132.4, 145.3, 146.4; HRMS calcd for $C_{15}H_{14}N_4$ 250.120 (M^+), found 250.122.

The second fraction from the original chromatography (ethyl acetate) appeared to be **21a** (0.97 g, 45%): ^{1}H NMR δ 2.00 (m, 2 H), 2.48 (dd, J = 7.4 and 8.7 Hz, 2 H), 3.10–3.45 (m, 2 H), 3.60 (bs, 1 H), 5.41 (dd, J = 6.1 and 8.6 Hz), 6.52 (d, J = 8.1 Hz, 1 H), 6.64 (t, J = 7.5 Hz, 1 H), 6.85 (d, J = 7.6 Hz, 1 H), 7.01 (t, J = 8.0 Hz, 1 H); ^{13}C NMR δ 18.3, 26.6, 31.5, 40.2, 43.6, 47.4, 114.9, 117.6, 118.8, 127.9, 128.3, 145.5, 175.4. **Picrate**: mp 172 °C. Anal. Calcd for $C_{19}H_{19}N_5O_8$: C, 51.24; H, 4.30; N, 15.72. Found: C, 50.89; H, 4.24; N, 15.76.

***cis*-2-Methyl-4-(2-pyrrolidinon-1-yl)-1,2,3,4-tetrahydroquinoline (21b).** *p*-Toluenesulfonic acid monohydrate (20 mg, 0.1 mmol) was added to a mixture of 1-vinyl-2-pyrrolidinone (1.11 g, 10 mmol) and **18b** (2.31 g, 10 mmol) preheated to 100 °C. The mixture was stirred for 5 min and set aside at 22 °C for 1 h. The crude product was dissolved in ethyl acetate and subjected to column chromatography, using ethyl acetate as the eluent. The first fraction contained mainly **27b**. The second fraction gave **21b** (0.87 g, 38%) as an oil: ^{1}H NMR δ 1.19 (d, J = 6.2 Hz, 3 H), 1.70 (q, J = 11.9 Hz, 1 H), 1.92 (m, 1 H), 2.01 (m, 2 H), 2.48 (m, 2 H), 3.06–3.26 (m, 2 H), 3.51 (m, 1 H), 4.00 (bs, 1 H), 5.54 (dd, J = 6.0 and 12.1 Hz, 1 H), 6.51 (d, J = 8.0 Hz, 1 H), 6.63 (t, J = 7.7 Hz, 1 H), 6.80 (d, J = 7.7 Hz, 1 H), 6.99 (t, J = 8.2 Hz, 1 H); ^{13}C NMR δ 17.8, 21.9, 31.1, 33.7, 41.9, 46.2, 47.7, 114.3, 117.2, 118.4, 126.2, 127.6, 145.6, 175.4. **Picrate**: mp 190 °C. Anal. Calcd for $C_{20}H_{21}N_5O_8$: C, 52.28; H, 4.61; N, 15.24. Found: C, 52.29; H, 4.59; N, 15.23.

***cis*-2-Phenyl-4-(2-pyrrolidinon-1-yl)-1,2,3,4-tetrahydroquinoline (21c) and *trans*-4-(Benzotriazol-1-yl)-2-phenyl-1,2,3,4-tetrahydroquinoline (27c).** According to the procedure for **21b**, starting from **18c** (3.00 g, 10 mmol) and 1-vinyl-2-pyrrolidinone (1.11 g, 10 mmol), we obtained a mixture of **21c** and **27c**. Column chromatography (chloroform) of the crude material gave pure **27c** as the first fraction (0.10 g, 3%): prisms; mp 200 °C; ^{1}H NMR δ 1.80 (bs, 1 H), 2.51 (ddd, J = 4.7, 10.6, and 13.7 Hz, 1 H), 2.64 (dt, J = 3.5 and 13.7 Hz, 1 H), 4.50 (m, 2 H), 6.17 (t, J = 4.4 Hz, 1 H), 6.66 (td, J = 7.5 and 1.1 Hz, 1 H), 6.77 (d, J = 8.2 Hz, 1 H), 6.94 (d, J = 7.4 Hz, 1 H), 7.02 (m, 1 H), 7.20–7.40 (m, 8 H), 8.06 (m, 1 H); ^{13}C NMR δ 38.2, 52.4, 55.7, 110.6, 114.9, 115.1, 117.9, 120.0, 123.7, 126.5 (2 C), 127.2, 128.0, 128.7 (2 C), 130.16, 130.22, 133.0, 142.5, 145.3, 146.2. Anal. Calcd for $C_{21}H_{18}N_4$: C, 77.28; H, 5.56; N, 17.17. Found: C, 77.08; H, 5.64; N, 17.22.

The second fraction gave **21c** (2.22 g, 76%) as a glassy material: ^{1}H NMR δ 1.98 (m, 2 H), 2.07 (m, 2 H), 2.44 (m, 2 H), 3.18 (m, 2 H), 4.05 (bs, 1 H), 4.55 (t, J = 5.0 Hz, 1 H), 5.70 (t, J = 9.5 Hz, 1 H), 6.56 (d, J = 7.5 Hz, 1 H), 6.68 (t, J = 6.6 Hz, 1 H), 6.84 (d, J = 7.4 Hz, 1 H), 7.01 (t, J = 7.1 Hz, 1 H), 7.36 (m, 5 H); ^{13}C NMR δ 18.1, 31.3, 35.1, 42.2, 48.3, 56.2, 114.8, 118.0, 126.3 (2 C), 126.6, 127.6, 127.8, 128.1, 128.6 (2 C), 142.9, 145.8, 175.7. Anal. Calcd for $C_{19}H_{20}N_2O$: C, 77.65; H, 6.98; N, 9.58. Found: C, 77.81; H, 6.82; N, 9.94.

4-(Pyrrolidin-1-yl)-1,2,3,4-tetrahydroquinoline (26a). To a THF solution of **21a** (2.16 g, 10 mmol) was added portionwise $LiAlH_4$ (0.39 g, 10 mmol), and the reaction mixture was stirred under nitrogen at room temperature for 2 h. The reaction mixture was poured onto ice-cold 20% NaOH, stirred for 20 min, and then extracted with ether (3 × 100 mL). The extracts were combined, washed with 10% NaOH, and dried (NaOH), and the solvent was evaporated under reduced pressure to give analytically pure **26a** (0.85 g, 91%) as a thick oil: ^{1}H NMR δ 1.74 (m, 5 H), 2.11 (m, 1 H), 2.14 (m, 1 H), 2.44 (m, 2 H), 2.67 (m, 2 H), 3.26 (m, 2 H), 3.54 (td, J = 11.6 and 3.4 Hz, 1 H), 3.93 (bs, 1 H), 6.43 (d, J = 8.0 Hz, 1 H), 6.53 (t, J = 7.4 Hz, 1 H), 7.00 (m, 2 H); ^{13}C NMR δ 23.4 (2 C), 25.1, 37.4, 51.3 (2 C), 60.1, 114.0, 115.3, 121.5, 128.2, 130.4, 144.0. **Picrate:** mp 77–79 °C. Anal. Calcd for $C_{25}H_{24}N_8O_{14}$: C, 45.46; H, 3.66; N, 16.96. Found: C, 45.73; H, 3.46; N, 16.77.

***cis*-2-Methyl-4-(pyrrolidin-1-yl)-1,2,3,4-tetrahydroquinoline (26b).** Starting from **21b** (4.60 g, 20 mmol) and following the procedure for **26a**, we obtained product **26b** as an oil (3.97 g, 92%): ^{1}H NMR δ 1.23 (d, J = 6.3 Hz, 3 H), 1.60 (q, J = 11.3 Hz, 1 H), 1.77 (m, 4 H), 1.99 (ddd, J = 2.6, 5.3, and 12.2 Hz, 1 H), 2.59 (m, 2 H), 2.68 (m, 2 H), 3.49 (m, 1 H), 3.61 (bs, 1 H), 4.28 (dd, J = 5.2 and 11.6 Hz, 1 H), 6.46 (d, J = 8.0 Hz, 1 H), 6.68 (td, J = 7.5 and 1.2 Hz, 1 H), 6.98 (m, 1 H), 7.46 (d, J = 7.7 Hz, 1 H); ^{13}C NMR δ 22.9, 23.9 (2 C), 28.0, 47.0, 47.2 (2 C), 55.9, 113.8, 117.2, 123.3, 127.1, 128.0, 145.2. Anal. Calcd for $C_{14}H_{20}N_2$: C, 77.73; H, 9.32; N, 12.95. Found: C, 77.98; H, 9.40; N, 13.24.

***cis*-2-Phenyl-4-(pyrrolidin-1-yl)-1,2,3,4-tetrahydroquinoline (26c).** Following the procedure for **26a,** we obtained compound **26c** as an oil (2.44 g, 88%): ^{1}H NMR δ 1.74 (m, 4 H), 1.98 (q, J = 11.5 Hz, 1 H), 2.15 (m, 1 H), 2.62 (m, 2 H), 2.68 (m, 2 H), 3.88 (s, 1 H), 4.42 (dd, J = 5.2 and 11.3 Hz, 1 H), 4.48 (dd, J = 3.0 and 11.8 Hz, 1 H), 6.48 (d, J = 7.8 Hz, 1 H), 6.72 (t, J = 7.1 Hz, 1 H), 7.00 (t, J = 7.8 Hz, 1 H), 7.32 (m, 3 H), 7.43 (m, 2 H), 7.52 (d, J = 7.8 Hz, 1 H); ^{13} C NMR δ 24.0 (2 C), 29.5, 47.2 (2 C), 56.3, 56.6, 114.0, 117.6, 123.1, 126.4 (2 C), 127.3, 127.5, 127.9, 128.5 (2 C), 144.3, 145.2. **Picrate**: mp 152–153 °C. Anal. Calcd for $C_{25}H_{25}N_5O_7$: C, 59.17; H, 4.96; N, 13.79. Found: C, 58.95; H, 4.87; N, 13.80.

***cis*-4-(Benzotriazol-1-yl)-2-methyl-1,2,3,4-tetrahydroquinoline (27b).** A solution of **18b** (2.31 g, 10 mmol), 1-vinyl-2-pyrrolidinone (1.11 g, 10 mmol), and *p*-toluenesulfonic acid monohydrate (0.10 g, 0.5 mmol) in chloroform (10 mL) was stirred at 22 °C for 3 days. The reaction mixture was diluted with ethyl acetate (100 mL) and washed with 5% NaOH (100 mL), followed by water (2 × 100 mL). The solution was then dried over $MgSO_4$. Evaporation of the solvent gave an oily product which, by trituration with ether, turned into a white solid of pure **27b** (1.95 g, 58%): mp 141 °C; ^{1}H NMR δ 1.21 (d, J = 6.2 Hz, 3 H), 2.13 (ddd, J = 4.8, 11.1, and 13.7 Hz, 1 H), 2.42 (bd, J = 13.7 Hz, 1 H), 3.43 (m, 1 H), 4.23 (bs, 1 H), 6.24 (t, J = 4.5 Hz, 1 H), 6.64 (t, J = 7.3 Hz, 1 H), 6.72 (d, J = 8.1 Hz, 1 H), 6.91 (m, 1 H), 6.99 (d, J = 7.5 Hz, 1 H), 7.19 (t, J = 7.1 Hz, 1 H), 7.26 (m, 2 H), 8.04 (m, 1 H); ^{13}C NMR δ 21.7, 37.8, 43.1, 56.4, 110.8, 114.7, 117.6, 119.8, 123.5, 127.0, 130.1, 130.7, 133.0, 145.6 (2 C), 146.2. Anal. Calcd for $C_{16}H_{16}N_4$: C, 72.70; H, 6.10; N, 21.20. Found: C, 72.59; H, 6.16; N, 21.31.

1-(2-Phenylethyl)-4-(benzotriazol-1-yl)-1,2,3,4-tetrahydroquinoline (30). To a solution of **27a** (1.00 g, 4 mmol) in ethanol was added hydroxymethylbenzotriazole (0.60 g, 4 mmol), and the reaction mixture was stirred at room temperature for 2 h. Evaporation of the ethanol and water with three portions of toluene (each 20 mL) gave crude **29** as a mixture of Bt-1 and Bt-2 derivatives (by NMR). Mixture **29** was dissolved in THF (10 mL). An ethereal solution of benzylmagnesium chloride (10 mmol) was added. The mixture was stirred at 22 °C for 30 min and poured into ice–water (30 g). After neutralization with 10% acetic acid, the organic layer was extracted with ether (2 × 25 mL). The ethereal solution was washed with water, followed by 10% NaOH (20 mL), and then again with water. Drying over Na_2CO_3 and evaporation of the solvent gave an oily product (0.88 g, 62%) which was subjected to column chromatography (chloroform) to give an analytical sample of **30**: ^{1}H NMR δ 1.25 (m, 2 H), 2.34 (m, 1 H), 2.50 (m, 1 H), 2.93 (m, 2 H), 3.16 (m, 1 H), 3.27 (m, 1 H), 3.60 (m, 2 H), 6.24 (t, J = 5.8 Hz, 1 H), 6.54 (t, J = 7.6 Hz, 1 H), 6.76 (d, J = 7.6 Hz, 1 H), 6.84 (d, J = 8.6 Hz, 1 H), 6.90 (m, 1 H), 7.27 (m, 8 H), 8.03 (m, 1 H); ^{13}C NMR δ 29.2, 32.6,

46.2, 53.4, 57.2, 111.0, 111.3, 116.2, 116.8, 119.9, 123.6, 126.3, 126.9, 128.5 (2 C), 128.7 (2 C), 129.8, 130.1, 132.5, 139.3, 145.2, 146.4; HRMS calcd for $C_{23}H_{22}N_4$ 354.184 (M^+), found 354.181.

4-Methyl-1-(2-phenylethyl)-1,2,3,4-tetrahydroquinoline (31). To a solution of **30** (0.35 g, 1 mmol) in dry toluene (5 mL) stirred at reflux was added portionwise MeMgI (3 mmol) in ether (2 mL). The reaction mixture was then stirred at reflux for 20 min and worked up as described above to give a crude product which was purified by column chromatography (hexanes/toluene, 3:1) to give pure **31** (0.16 g, 63%): ^{1}H NMR δ 1.23 (d, J = 7.0 Hz, 3 H), 1.30 (m, 1 H), 1.63 (dtd, J = 13.0, 6.2, and 3.8 Hz, 1 H), 1.93 (m, 1 H), 2.88 (t, J = 7.7 Hz, 2 H), 3.14 (m, 1 H), 3.26 (m, 1 H), 3.48 (q, J = 7.5 Hz, 2 H), 6.60 (td, J = 7.3 and 1.1 Hz, 1 H), 6.65 (d, J = 7.8 Hz, 1 H), 7.07 (m, 2 H), 7.27 (m, 5 H); ^{13}C NMR δ 22.5, 29.4, 31.0, 32.4, 46.3, 53.4, 110.4, 115.5, 126.1, 127.1, 128.2, 128.4 (2 C), 128.8 (2 C), 140.0, 144.2. **Picrate**: mp 136 °C. Anal. Calcd for $C_{24}H_{24}N_4O_7$: C, 60.00; H, 5.03; N, 11.66. Found: C, 60.25; H, 5.17; N, 11.52.

***N*-(1-Ethyl-1,2,3,4-tetrahydroquinolin-4-yl)-*N*-methylacetamide (32).** A mixture of **1c** (2.66 g, 10 mmol) and *N*-methyl-*N*-vinylacetamide (1.11 g, 11 mmol) was preheated to 140–150 °C for 5 min, and *p*-toluenesulfonic acid monohydrate (20 mg, 0.1 mmol) was added in one portion. Heating was continued for an additional 30 min, and then the solution was cooled, dissolved in chloroform, and washed with 10% Na_2CO_3 (3 × 20 mL). The chloroform solution was dried over Na_2SO_4 and the solvent evaporated under vacuum to give **32** (1.95 g, 84%) as a yellowish oil. By NMR, the product appeared to be a mixture of two rotamers in a molar ratio of 3:5. An analytical sample was prepared by column chromatography (ethyl acetate). Anal. Calcd for $C_{14}H_{20}N_2O$: C, 72.38; H, 8.68; N, 12.06. Found: C, 72.26; H, 8.79; N, 12.12.

1-Ethyl-4-(*N*-ethyl-*N*-methylamino)-1,2,3,4-tetrahydroquinoline (33). Starting from **32** (4.60 g, 20 mmol) and following the procedure given for **8**, we obtained pure **33** as an oil (2.86, 66%). An analytical sample was prepared by column chromatography (ethyl acetate): ^{1}H NMR δ 1.06 (t, J = 7.2 Hz, 3 H), 1.09 (t, J = 7.2 Hz, 3 H), 1.90 (m, 2 H), 2.23 (s, 3 H), 2.41 (dq, J = 12.3 and 6.9 Hz, 1 H), 2.57 (dq, J = 12.3 and 7.2 Hz, 1 H), 3.16–3.42 (m, 4 H), 3.76 (dd, J = 5.4 and 8.4 Hz, 1 H), 6.58 (m, 2 H), 7.05 (td, J = 8.1 and 2.1 Hz, 1 H), 7.38 (m, 1 H); ^{13}C NMR δ 10.5, 13.2, 20.9, 37.4, 45.1, 46.3, 46.8, 59.8, 110.5, 115.0, 123.5, 127.5, 128.5, 145.3. Anal. Calcd for $C_{14}H_{22}N_2$: C, 77.02; H, 10.16; N, 12.83. Found: C, 77.36; H, 9.86; N, 12.78.

***N*-(1,6-Dimethyl-1,2,3,4-tetrahydroquinolin-4-yl)-*N*-methylacetamide (35).** Starting from **34**[1] (2.52 g, 10 mmol) and *N*-vinyl-*N*-methylacetamide (1.1 g, 11 mmol) and following the procedure given for **32**, we obtained **35** (2.10 g, 86%) as an oil, as a mixture of two rotamers in a molar ratio of 3:5 (by NMR). An analytical sample was prepared by column chromatography (ethyl acetate). Anal. Calcd for $C_{14}H_{20}N_2O$: C, 72.38; H, 8.68; N, 12.06. Found: C, 72.22; H, 8.78; N, 12.16.

1,6-Dimethyl-4-(*N*-methyl-*N*-ethylamino)-1,2,3,4-tetrahydroquinoline (36). $LiAlH_4$ (0.40 g, 10 mmol) was added portionwise to a stirred solution of **35** (1.70 g, 7.3 mmol) in dry THF (20 mL). The reaction mixture was stirred at room temperature for 30 min. Workup as for compound **8** gave 95% pure **36** (1.20 g, 75%). An analytical sample was prepared by column chromatography (ethyl acetate): ^{1}H NMR δ 1.08 (t, J = 6.9 Hz, 3 H), 1.96 (m, 2 H), 2.39 (s, 3 H), 2.40 (dq, J = 12.3 and 6.9 Hz, 1 H), 2.57 (dq, J = 12.3 and 7.2 Hz, 1 H), 2.80 (s, 3 H), 3.18 (m, 2 H), 3.84 (dd, J = 5.7 and 9.0 Hz, 1 H), 6.49 (d, J = 8.0 Hz, 1 H), 6.90 (m, 1 H), 7.26 (m, 1 H); ^{13}C NMR δ 13.4, 20.4, 20.8, 37.4, 39.5, 46.7, 50.0, 59.5, 111.4, 124.3, 125.4, 128.0, 128.7, 145.3. Anal. Calcd for $C_{14}H_{22}N_2$: C, 77.02; H, 10.16; N, 12.83. Found: C, 77.12; H, 9.93; N, 12.77.

1-Benzyl-4-(benzotriazol-2-yl)-1,2,3,4-tetrahydroquinoline (37) and 1-Benzyl- 4-(benzotriazol-1-yl)-1,2,3,4-tetrahydroquinoline (38). A mixture of **2b** (3.14 g, 10 mmol) and **40** (1.93 g, 10 mmol) was heated under nitrogen at 120–130 °C (oil bath) until homogeneity was achieved. *p*-Toluenesulfonic acid monohydrate (20 mg, 0.1 mmol) was added, and heating at 130 °C was continued for 20 min. After cooling, the crude product was dissolved in chloroform. The solution was washed with 10% NaOH, followed by water, and then dried over Na_2CO_3. The solvent was evaporated to give a glassy material (according to NMR, a 1:1 mixture of **37** and **38**). The whole sample was subjected to column chromatography (toluene) to give a mixture of carbazole and 9-vinylcarbazole as the first fraction and pure **37** as the second fraction (1.45 g, 45%): mp 127-128 °C; ^{1}H NMR δ 2.41–2.52 (m, 1 H), 2.62–2.72 (m, 1 H), 3.32 (dt, J = 11.9 and 4.9 Hz, 1 H), 3.65 (ddd, J = 3.6, 10.7, and 12.0 Hz, 1 H), 4.54 (s, 2 H), 6.15 (t, J = 4.9 Hz, 1 H), 6.55 (td, J = 8.9 and 1.1 Hz, 1 H), 6.63 (d, J = 8.5 Hz, 1 H), 6.93 (dd, J = 7.6 and 1.7 Hz, 1 H), 7.04–7.20 (m, 4 H), 7.32 (m, 4 H), 7.85 (m, 2 H); ^{13}C NMR δ 28.9, 45.5, 55.1, 63.0, 112.0, 116.2, 117.5, 118.2, 126.1, 126.6, 126.9, 128.7, 129.9, 130.1, 138.2, 144.2, 145.6. Anal. Calcd for $C_{22}H_{20}N_4$: C, 77.62; H, 5.92; N, 16.46. Found: C, 77.63; H, 5.97; N, 16.36.

The eluent was then changed to chloroform, and **38** was obtained as the third fraction (1.52 g, 46%): mp 105–106 °C; ^{1}H NMR δ 2.43 (m, 1 H), 2.59 (m, 1 H), 4.53 (s, 2 H), 6.26 (dd, J = 5.6 and 11.2 Hz, 1 H), 6.49 (t, J = 7.3 Hz, 1 H), 6.73 (dd, J = 8.5 and 12.9 Hz, 2 H), 6.97 (m, 1 H), 7.01 (dd, J = 7.3 and 8.3 Hz, 1 H), 7.28 (m, 7 H), 8.02 (m, 1 H); ^{13}C NMR δ 29.1, 46.0, 54.9, 56.8, 110.6, 111.8, 116.3, 116.6, 119.6 (2 C), 123.4, 126.4 (2 C), 126.8, 128.4 (2 C), 129.3, 129.8, 132.4, 137.8, 145.6, 146.0. Anal. Calcd for $C_{22}H_{20}N_4$: C, 77.62; H, 5.92; N, 16.46. Found: C, 77.62; H, 6.01; N, 16.27.

1,4-Dibenzyl-1,2,3,4-tetrahydroquinoline (39). Benzylmagnesium chloride (ethereal solution, 20 mL, 20 mmol) was added to a mixture of **37** and **38** (3.40 g, 10 mmol) and dry toluene (50 mL) and stirred at reflux. The ether was allowed to distill off, and the toluene solution was stirred and heated at reflux for 1 h. After workup with ice-cold water, acidification with CH_3COOH, extraction with ether (3 × 50 mL), drying (Na_2CO_3), and evaporation of the solvent, the crude oily product was subjected to column chromatography (toluene) to give a solid (2.72 g, 87%): mp 94–95 °C; ^{1}H NMR δ 1.75 (m, 1 H), 1.90 (m, 1 H), 2.75 (dd, J = 11.9 and 16.2 Hz, 1 H), 3.09 (m, 3 H), 3.24 (dt, J = 11.8 and 4.4 Hz, 1 H), 3.51 (td, J = 11.2 and 3.8 Hz, 1 H), 4.51 (s, 2 H), 6.55 (m, 2 H), 7.08 (m, 2 H), 7.24 (m, 10 H); ^{13}C NMR δ 25.0, 38.4, 42.7, 45.8, 55.0, 111.1, 115.7, 125.4, 126.0, 126.5 (2 C), 126.8, 127.4, 128.3 (2 C), 128.6 (2 C), 128.8, 129.3 (2 C), 138.7, 140.3, 144.9. Anal. Calcd for $C_{23}H_{23}N$: C, 88.14; H, 7.40; N, 4.47. Found: C, 88.46; H, 7.46; N, 4.49.

***cis*-4-(Carbazol-9-yl)-2-methyl-1,2,3,4-tetrahydroquinoline (41).** A suspension of **18b** (2.31 g, 10 mmol), 9-vinylcarbazole (1.93 g, 10 mmol), and *p*-toluenesulfonic acid monohydrate (20 mg, 0.1 mmol) in chloroform (10 mL) was stirred at 22 °C for 2 h. The reaction mixture was poured into water (50 mL) and extracted with chloroform (50 mL). The extract was washed with 10% Na_2CO_3 (50 mL), followed by water, and then dried over $MgSO_4$. Evaporation of the solvent under reduced pressure and column chromatography of the residue (toluene) gave **41** as the main fraction (1.93 g, 62%): prisms (from chloroform); mp 210 °C; ^{1}H NMR δ 1.27 (d, J = 6.3 Hz, 3 H), 2.15 (ddd, J = 1.9, 6.3, and 12.7 Hz, 1 H), 2.48 (q, J = 12.0 Hz, 1 H), 3.80 (m, 1 H), 3.91 (s, 1 H), 6.15 (dd, J = 6.3 and 11.8 Hz, 1 H), 6.50 (t, J = 7.6 Hz, 1 H), 6.66 (m, 2 H), 6.91 (d, J = 8.0 Hz, 1 H), 7.07 (t, J = 7.2 Hz, 1 H), 7.21 (td, J = 8.0 and 1.9 Hz, 2 H), 7.29 (m, 1 H), 7.52 (m, 2 H), 8.14 (m, 2 H); ^{13}C NMR δ 22.2, 34.7, 47.6, 51.7, 108.0, 112.5, 114.6, 118.2, 118.8, 119.0, 119.6, 120.2, 120.4, 123.1, 123.8, 125.2, 125.7, 127.7, 128.4, 138.2, 141.3, 145.3. Anal. Calcd for $C_{22}H_{20}N_2$: C, 84.58; H, 6.45; N, 8.97. Found: C, 84.70; H, 6.50; N, 8.95.

Reaction of 34 with 9-Vinylcarbazole, products 42–44. A mixture of **34** (2.52 g, 10 mmol) and **40** (1.93 g, 10 mmol) was heated under nitrogen at 120 °C. *p*-Toluenesulfonic acid monohydrate (20 mg, 0.1 mmol) was added, and heating was continued for an additional 20 min. Workup as described above for **41** and evaporation of the solvent gave a crude oily product. Trituration with ethyl ether gave a solid material, which was separated and recrystallized from EtOH to give pure 4-(carbazol-9-yl)-1,6-dimethyl-1,2,3,4-tetrahydroquinoline (**42**) (1.63 g, 50%): mp 163–165 °C; ^{1}H NMR δ 1.95 (s, 3 H, Me), 2.17 (m, 1 H), 2.77 (m, 1 H), 2.95 (s, 3 H, Me), 3.26 (dt, J = 11.6 and 4.2 Hz, 1 H), 3.41 (td, J = 11.4 and 3.0 Hz, 1 H), 6.00 (dd, J = 6.8 and 10.2 Hz, 1 H), 6.55 (s, 1 H), 6.68 (d, J = 8.3 Hz, 1 H), 6.97 (d, J = 8.4 Hz, 1 H), 7.21 (m, 3 H), 7.35 (m, 3 H), 8.05 (d, J = 8.1 Hz, 1 H), 8.11 (d, J = 7.9 Hz, 1 H); ^{13}C NMR δ 20.2, 27.3, 39.9, 50.6, 51.7, 110.5, 112.3, 118.8 (2 C),

119.3, 120.19, 120.24 (2 C), 120.7, 123.2, 125.4, 125.7, 126.6, 128.4, 129.3, 139.4, 145.3 (2 C). Anal. Calcd for $C_{23}H_{22}N_2$: C, 84.63; H, 6.79; N, 8.58. Found: C, 84.44; H, 6.58; N, 8.43.

The mother liquor was evaporated and the residue subjected to column chromatography (chloroform) to give compound **42** (0.26 g, 8%) as the first fraction. The second fraction was found to be 1,6-dimethyl-4-(benzotriazol-2-yl)-1,2,3,4-tetrahydroquinoline (**43**) (0.28 g, 10%) as an oil: ^{1}H NMR δ 2.10 (s, 3 H), 2.49 (m, 1 H), 2.95 (s, 3 H), 3.21 (m, 1 H), 3.54 (ddd, J = 3.3, 10.2, and 11.6 Hz, 1 H), 6.13 (t, J = 5.2 Hz, 1 H), 6.66 (d, J = 8.5 Hz, 1 H), 6.74 (s, 1 H), 6.99 (m, 1 H), 7.34 (m, 2 H), 7.86 (m, 2 H); ^{13}C NMR δ 20.1, 29.6, 39.4, 47.4, 62.4, 62.8, 112.3, 118.3 (2 C), 120.4, 120.7, 126.0 (2 C), 126.4, 130.0, 130.6, 144.2 (2 C). Anal. Calcd for $C_{17}H_{18}N_4$: C, 73.35; H, 6.52; N, 20.12. Found: C, 73.25; H, 6.56; N, 20.22.[1]

The third fraction gave 1,6-dimethyl-4-(benzotriazol-1-yl)-1,2,3,4-tetrahydroquinoline (**44**) (0.69 g, 25%) as a glassy solid: ^{1}H NMR δ 2.03 (s, 3 H), 2.24 (m, 1 H), 2.55 (m, 1 H), 2.94 (s, 3 H), 3.18 (ddd, J = 3.6, 7.8, and 11.7 Hz, 1 H), 3.28 (ddd, J = 2.4, 7.2, and 11.4 Hz, 1 H), 6.27 (t, J = 6.3 Hz, 1 H), 6.56 (s, 1 H), 6.69 (d, J = 8.4 Hz, 1 H), 6.97 (m, 1 H), 7.03 (d, J = 8.7 Hz, 1 H), 7.26 (m, 2 H), 8.02 (m, 1 H); ^{13}C NMR δ 20.1, 29.9, 39.5, 48.3, 57.0, 111.0, 112.2, 117.5, 119.9, 123.6, 126.2, 126.9, 129.6, 130.6, 132.3, 145.1, 146.4. Anal. Calcd for $C_{17}H_{18}N_4$: C, 73.35; H, 6.52; N, 20.12. Found: C, 73.78; H, 6.55; N, 19.68.[1]

3-(2-Pyrrolidinon-1-yl)-1,2,3,11b-tetrahydrobenzo[1,10]phenothiazine (46). A mixture of **45**[5] (3.30 g, 10 mmol) and N-vinyl-2-pyrrolidinone (1.1 g, 10 mmol) was heated under nitrogen at 140–150 °C for 15 min. p-Toluenesulfonic acid monohydrate (20 mg, 0.1 mmol) was added, and heating was continued for an additional 1 h. After cooling, the crude reaction mixture was dissolved in chloroform, washed with 10% NaOH and then water, and dried over Na_2CO_3. Evaporation of the solvent and trituration of the glassy residue with ether gave pure **46** (2.85 g, 88%): mp 149–152 °C; ^{1}H NMR δ 2.01 (m, 2 H), 2.12–2.36 (m, 2 H), 2.51 (t, J = 7.8 Hz, 2 H), 3.08 (m, 1 H), 3.19 (m, 1 H), 3.73 (m, 1 H), 3.79 (m, 1 H), 5.39 (dd, J = 4.8 and 9.4 Hz, 1 H), 6.76 (d, J = 7.6 Hz, 1 H), 6.85 (t, J = 7.5 Hz, 2 H), 6.92 (d, J = 7.5 Hz, 1 H), 6.98 (t, J = 7.3 Hz, 1 H), 7.1–7.2 (m, 2 H); ^{13}C NMR δ 18.2, 25.7, 31.3, 43.6, 44.2, 48.0, 112.8, 120.6, 122.1, 122.2, 122.7, 125.6, 126.6, 127.2, 127.6, 142.2, 144.1, 175.6. Anal. Calcd for $C_{19}H_{18}N_2OS$: C, 70.78; H, 5.63; N, 8.69. Found: C, 70.64; H, 5.67; N, 8.72.

3-(2-Pyrrolidin-1-yl)-1,2,3,11b-tetrahydrobenzo[1,10]phenothiazine (47). $LiAlH_4$ (0.16 g, 4 mmol) was added portionwise to a solution of pyrrolidinone derivative **46** (1.25 g, 4 mmol) in dry THF under nitrogen. After the addition was accomplished, the reaction mixture was stirred for an additional 1 h. Workup with ice-cold 20% NaOH, extraction with ether (3 × 50 mL), drying over Na_2CO_3, and evaporation of the solvent afforded **47** (0.92 g, 75%) as an oil. An analytical sample was prepared by column chromatography (ethyl acetate): ^{1}H NMR δ 1.69 (m, 4 H), 1.98 (tt, J = 3.6 and 12.9 Hz, 1 H), 2.33 (m, 4 H), 2.66 (m, 2 H), 3.18 (t, J = 3.0 Hz, 1 H), 3.40 (dt, J = 10.5 and 3.6 Hz, 1 H), 3.88 (ddd, J = 3.3, 10.8, and 12.9 Hz, 1 H), 6.71 (t, J = 7.5 Hz, 1 H), 6.80–7.22 (m, 6 H); ^{13}C NMR δ 23.5 (2 C), 25.8, 41.5, 51.5 (2 C), 60.2, 113.1, 119.8, 120.8, 121.2, 122.4, 125.7, 126.4, 126.6, 127.3, 129.1, 140.7, 147.4. Anal. Calcd for $C_{19}H_{20}N_2S$: C, 73.99; H, 6.54; N, 9.08. Found: C, 73.66; H, 6.42; N, 9.14.

1*H*,3*H*,9*H*-7-(Carbazol-9-yl)-7,8-dihydrobenzo[1,8][3,1]benzoxazine (49). p-Toluenesulfonic acid monohydrate (20 mg, 0.1 mmol) was added to a suspension of **48**[6] (2.66 g, 10 mmol) and **40** (1.93 g, 10 mmol) in chloroform (10 mL). The mixture was stirred at 22 °C for 1 h to give a transparent solution. The obtained solution was poured into 10% Na_2CO_3 (50 mL) and extracted with chloroform (2 × 50 mL). The combined extracts were washed with water, dried over Na_2CO_3, and evaporated under reduced pressure. Trituration of the mixture with ether (50 mL) gave analytically pure **49** (2.56 g, 75%) as a white powder: mp 209 °C; ^{1}H NMR (DMSO-d_6) δ 2.23 (m, 1 H), 2.63 (qd, J = 11.2 and 3.8 Hz, 1 H), 3.30 (m, 2 H), 4.56 (d, J = 7.7 Hz, 1 H), 4.77 (d, J = 7.7 Hz, 1 H), 4.86 (d, J = 15.1 Hz, 1 H), 4.93 (d, J = 15.1 Hz, 1 H), 6.29 (m, 2 H), 6.43 (t, J = 7.6 Hz, 1 H), 6.81 (d, J = 7.4 Hz, 1 H), 7.10–7.60 (m, 6 H), 8.17 (d, J = 7.9 Hz, 2 H); ^{13}C NMR (DMSO-d_6) δ 25.9, 43.5, 50.2, 67.0, 79.8, 110.0 (2 C), 117.4, 118.8 (2 C), 120.3 (2 C), 120.4, 120.7, 122.7 (2 C), 123.7, 125.2, 125.5 (2 C), 138.0 (2 C), 141.4. Anal. Calcd for $C_{23}H_{20}N_2O$: C, 81.15; H, 5.92; N, 8.23. Found: C, 81.09; H, 5.92; N, 8.27.

1*H*,3*H*,9*H*-7-(Benzotriazol-1-yl)-7,8-dihydrobenzo[1,8][3,1]benzoxazine (52), 1*H*,3*H*,9*H*-7-(*N*-Ethyl-*N*-methylamino)-7,8-dihydrobenzo[1,8][3,1]benzoxazine (53), and 1-[3-(*N*-Ethyl-*N*-methylamino)propyl]-1,2-dihydro-4*H*-[3,1]benzoxazine (54). A solution of N-methyl-N-vinylacetamide (1.0 mL, 10 mmol), **48**[6] (2.66 g, 10 mmol), and p-toluenesulfonic acid monohydrate (20 mg, 0.1 mmol) in chloroform (10 mL) was kept at 22 °C for 22 h. Toluene (20 mL) was added and the solvent evaporated under reduced pressure. $LiAlH_4$ (0.76 g, 20 mmol) was added to the residue dissolved in THF (20 mL). The mixture was then stirred and heated at reflux under nitrogen for 1 h. The reaction mixture was poured into ice-cold 10% NaOH (50 mL) and extracted with ether (2 × 50 mL). The combined extracts were dried over Na_2CO_3 and evaporated. The residue was subjected to column chromatography (ethyl acetate) to give **52** (1.00 g, 34%) as a glassy material. After trituration with ether, a white solid was afforded: mp 144–146 °C; ^{1}H NMR δ 2.56 (m, 1 H), 2.63 (m, 1 H), 3.22 (m, 2 H), 4.66 (d, J = 7.7 Hz, 1 H), 4.74 (d, J = 7.7 Hz, 1 H), 4.98 (s, 2 H), 6.33 (t, J = 6.8 Hz, 1 H), 6.59 (m, 2 H), 6.88 (m, 1 H), 7.08 (m, 1 H), 7.32 (m, 2 H), 8.06 (m, 1 H); ^{13}C NMR δ 28.9, 42.3, 56.0, 67.9, 80.2, 110.7, 117.6, 118.0, 120.0, 120.8, 123.7, 124.9, 127.0, 127.2, 131.9, 141.2, 146.4. Anal. Calcd for $C_{17}H_{16}N_4O$: C, 69.85; H, 5.52; N, 19.16. Found: C, 70.00; H, 5.62; N, 19.09.

The second fraction gave **53** (0.35 g, 15%) as an oil: ^{1}H NMR δ 1.10 (t, J = 7.1 Hz, 3 H), 2.03 (m, 2 H), 2.26 (s, 3 H), 2.45 (m, 1 H), 2.58 (m, 1 H), 3.03 (m, 1 H), 3.16 (m, 1 H), 3.91 (dd, J = 6.0 and 9.1 Hz, 1 H), 4.50 (d, J = 7.6 Hz, 1 H), 4.61 (d, J = 7.5 Hz, 1 H), 4.85 (d, J = 14.5 Hz, 1 H), 4.89 (d, J = 14.3 Hz, 1 H), 6.72 (m, 2 H), 7.35 (d, J = 7.3 Hz, 1 H); ^{13}C NMR δ 13.6, 19.9, 37.2, 43.9, 46.9, 59.2, 67.9, 80.5, 117.5, 120.0, 122.8, 124.4, 126.7, 141.4; HRMS calcd for $C_{14}H_{20}N_2O$ 232.158 (M^+), found 232.160.

The third fraction eluted with ethyl acetate/triethylamine (98:2) gave **54** (0.49 g, 21%) as an oil: ^{1}H NMR δ 1.01 (t, J = 7.1 Hz, 3 H), 1.70 (quintet, J = 6.9 Hz, 2 H), 2.15 (s, 3 H), 2.34 (m, 4 H), 3.26 (t, J = 6.8 Hz, 2 H), 4.62 (s, 2 H), 4.78 (s, 2 H), 6.71 (t, J = 7.3 Hz, 1 H), 6.80 (d, J = 7.6 Hz, 2 H), 7.07 (t, J = 6.6 Hz, 1 H); ^{13}C NMR δ 11.9, 25.8, 41.0, 49.4, 51.1, 54.2, 67.5, 80.2, 115.4, 118.3, 122.8, 124.4, 126.9, 143.8. Anal. Calcd for $C_{14}H_{22}N_2O$: C, 71.76; H, 9.46; N, 11.95. Found: C, 71.59; H, 9.39; N, 11.99.

1-Benzyl-4-(benzotriazol-1-yl)-8-(hydroxymethyl)-1,2,3,4-tetrahydroquinoline (55). An ethereal solution of phenylmagnesium bromide (3 mmol) was added to a solution of **52** (0.29 g, 1 mmol) in toluene (5 mL). The obtained mixture was heated at reflux under nitrogen for 30 min. The reaction mixture was poured into ice–water (20 g), neutralized with acetic acid, and extracted with ether (20 mL). The extract was washed with water, dried over Na_2CO_3, and evaporated. The crude product was purified by column chromatography (toluene/ethyl acetate, 4:1) to give **55** (0.19 g, 52%) as an oil: ^{1}H NMR δ 2.37 (m, 1 H), 2.51 (m, 1 H), 3.25 (m, 2 H), 3.61 (bs, 1 H), 4.34 (s, 2 H), 4.88 (d, J = 12.9 Hz, 1 H), 4.98 (d, J = 12.9 Hz, 1 H), 6.35 (t, J = 7.1 Hz, 1 H), 6.74 (d, J = 7.6 Hz, 1 H), 6.94 (t, J = 7.7 Hz, 1 H), 6.98 (m, 1 H), 7.32–7.50 (m, 8 H), 8.08 (m, 1 H); ^{13}C NMR δ 24.0, 44.2, 56.8, 58.5, 62.8, 110.4, 120.2, 123.6, 123.9, 126.1, 127.3, 127.7, 128.0 (2 C), 128.3, 128.9 (2 C), 129.8, 132.1, 135.0, 137.7, 146.5, 147.3; HRMS calcd for $C_{23}H_{23}N_4O$ 371.187(M^+ + 1), found 371.184.

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