Convenient Synthesis of Julolidines Using Benzotriazole Methodology

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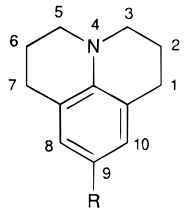
Reaction of *N*,*N*-bis[(benzotriazol-1-yl)methyl]aniline (**2**) with 1-vinylpyrrolidin-2-one gives a mixture of diastereomeric 1,7-bis(2-oxopyrrolidin-1-yl)julolidines **3**. After reduction of **3** with LAH, the predominant *trans* diastereomer of 1,7-di(pyrrolidin-1-yl)julolidine (**4**) is separated. Reaction of **2** with ethyl vinyl ether yields predominantly *trans*-1,7-di(benzotriazol-1-yl)julolidine (**11**). Stepwise synthesis from tetrahydroquinoline **15** gives access to julolidines with two different substituents on C-1 and C-7. Reaction of 1-[(benzotriazol-1-yl)methyl]-1,2,3,4-tetrahydroquinoline (**25**) with enolizable aldehydes gives a mixture of tetrahydroquinolines **26**−**29** which are converted into single julolidine products upon treatment with sodium hydride, LAH, or phenylmagnesium bromide. Reactions of 1,2,3,4-tetrahydroquinolines with benzotriazole and 2 molar equiv of enolizable aldehydes gives 1,2,3-trisubstituted julolidines **38**−**41**, which with lithium aluminum hydride, sodium hydride, or a Grignard reagent produce single diastereomers of products **42**, **43**, and **45**, respectively.

Introduction

Julolidine (**1a**), 2,3,6,7-tetrahydro-1*H*,5*H*-benzo[*ij*]-quinolizine, has been known for over a century (Chart 1).[1] This compound and its derivatives have found recent interest as photoconductive materials,[2] chemiluminescence substances,[3] chromogenic substrates in analytical redox reactions,[4,5] dye intermediates,[6−8] potential antidepressants and tranquilizers,[9] nonlinear optical materials,[10] high sensitivity photopolymerizable materials,[11] and for improving color stability in photography.[12] Superior second-order nonlinear optical properties were shown for julolidine derivative **1b**.[13] The traditional synthetic path for julolidines involves alkylation of a 1,2,3,4-tetrahydroquinoline with 3-chloro-1-bromopropane;[14] a more recent version reacts aniline with an excess of 3-chloro-1-bromopropane.[15] We now present novel syntheses of julolidines based on benzotriazole methodology, which allow the preparation of a variety of substituted derivatives.

Chart 1



1a, R = H

1b, R = $(CH{=}CH)_2CH{=}C(CONEt)_2C{=}S$

Results and Discussion

***N*-Vinyl-2-pyrrolidinone.** In a previous paper, we reported that *N*-alkyl-*N*-[(benzotriazol-1-yl)methyl]anilines react with *N*-vinylamides to give *N*-alkyl-4-amido-1,2,3,4-tetrahydroquinolines.[16] We now find that, under similar conditions, the reaction of *N*,*N*-bis[(benzotriazol-1-yl)methyl]aniline[17] (**2**) with 1-vinyl-2-pyrolidinone yields julolidine **3** in high yield (Scheme 1). According to NMR, the crude product **3** was a mixture of two diastereomers in an approximate ratio of 2:1. Because the asymmetric carbon atoms are relatively distant from each other, the NMR spectral properties of the individual diastereomers were insufficiently different to allow definitive assignment of their geometries. A sample highly enriched in the predominant diastereomer (90%) was characterized by NMR. In a literature example, chemical shifts of the corresponding carbon resonances in diastereomeric *cis*- and *trans*-2,6-dihydroxyjulolidines do not differ more

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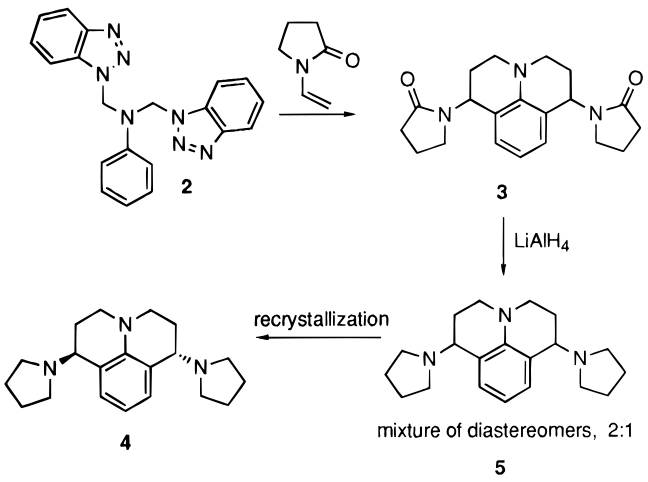
Scheme 1



than 0.5 ppm;[18] however, the diastereomers could be separated by HPLC.[19,20]

Fortunately, reduction of the carbonyl groups of mixed diastereomers **3** gave a mixture of the corresponding amines **5** from which the predominant diastereomer **4** was separated by recrystallization. As the NMR spectra could not determine the molecular geometry of **4**, the *trans* configuration of the substituents was determined by X-ray crystallography (Figure 1).[21] Thus, the predominant diastereomer of **3** must also be *trans*.

The definitive establishment of the structures of compounds **3** and **5**, followed by analysis of their NMR spectra, allowed the formulation of rules which were then used to assign the molecular geometry of similar compounds obtained subsequently. The C-3 and H-3 (cf. structure **1**) resonances are the most sensitive to the molecular geometry and were used diagnostically. Thus, in the case of **4**, the *trans* isomer (δ 44.6) exhibits the C-3 signal at a higher field than the *cis* isomer (δ 45.9) and the individual H-3 resonances of the *cis* isomer (δ 3.05 and 3.64) are more separated than those of the *trans* isomer (δ 3.12 and 3.47).

Ethyl Vinyl Ether. Reaction of **2** with ethyl vinyl ether gave a complex and inseparable mixture of benzotriazolyl derivatives **8** and **10**. Due to two asymmetric centers, and three possible sets of benzotriazol-1-yl and -2-yl substituents,[17] **8** and **10** each exist in several different forms. The composition of the mixture was determined by its treatment with lithium aluminum hydride, eliminating the benzotriazole residues and the asymmetric centers and converting **8** into julolidine (**1**) and **10** into tetrahydroquinoline **12**. This mixture could be easily separated by column chromatography. In another experiment, substitution of the benzotriazolyl by phenyl groups in a reaction with phenylmagnesium bromide eliminated the problem of benzotriazol-1-yl and benzotriazol-2-yl isomerism, reduced dramatically the number of the mixture components, and allowed separation of the main products, **13** and **14**, each, as a mixture of diastereomers (Scheme 2).

Column chromatography allowed separation of a fraction consisting exclusively of isomers and diastereomers

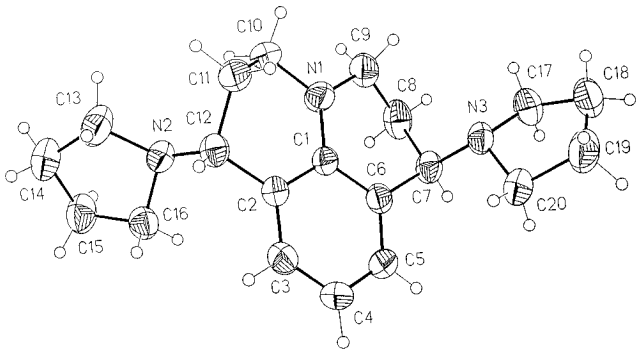


Figure 1.

of **8** which, upon recrystallization from ethanol, gave the predominant isomer **11**. The *trans* configuration of the substituents in **11** was assigned on the basis of its C-3 resonance (δ 46.3) in a higher field than that of the minor diastereomer (δ 46.6), in agreement with the rule deduced from the spectra of compounds **3** and **4**. Phenyl substituents do not cause sufficient differentiation in the physical properties of diastereomers **13** to allow their separation; even the chemical shifts of their aliphatic ^{13}C NMR resonances are almost identical ($\Delta\delta$ < 0.1 ppm). The relatively long distance between the asymmetric carbon atoms in **14** prevented separation of its diastereomers.

We rationalize the formation of two alternative products **8** and **10** by postulating a stepwise reaction of **2** with the two molecules of ethyl vinyl ether giving initially tetrahydroquinoline **6**.[22] Reaction with the second molecule of ethyl vinyl ether proceeds via protonation of the N-3 atom of the benzotriazole ring bound via a methylene bridge to the tetrahydroquinoline nitrogen atom in **6** and subsequent elimination of benzotriazole with formation of the corresponding methyleneimmonium cation. This cation attacks ethyl vinyl ether to produce carboxonium cation **7**, followed by one of two possible conversions: (i) electrophilic attack on the aromatic ring giving **9** or (ii) attack on the benzotriazole system giving **10**. Compound **10** is stable, but under the reaction conditions, the ethoxy group on **9** is substituted by benzotriazole, giving derivative **8**.[22] *N*,*N*-Bis(methoxymethyl)aniline and ethyl vinyl ether are reported to give 1,7-diethoxyjulolidine (45%) in a reaction similar to that depicted in Scheme 2.[23]

Unsymmetrically 1,7-Disubstituted Julolidines. Constructing the saturated rings of julolidines in a stepwise manner enables the introduction of two different substituents in positions 1 and 7 (cf. **1**). Thus, condensation of 4-(2-oxopyrrolidin-1-yl)-1,2,3,4-tetrahydroquinoline[16] (**15**) with 1-(hydroxymethyl)benzotriazole gave derivative **16** which upon reaction with *N*-vinylacetamide was converted to unsymmetrical julolidines **20** and **21** (Scheme 3). The reaction mechanisms involves an electrophilic attack of the methyleneimmonium cation derived from **16** on the vinyl group of *N*-vinylacetamide leading to intermediate **18**, in analogy to the case of the tetrahydroquinolines previously discussed in detail.[16] In the following step, electrophilic attack of **18** on the ortho position of the aromatic ring gives julolidine **20**. Alter-

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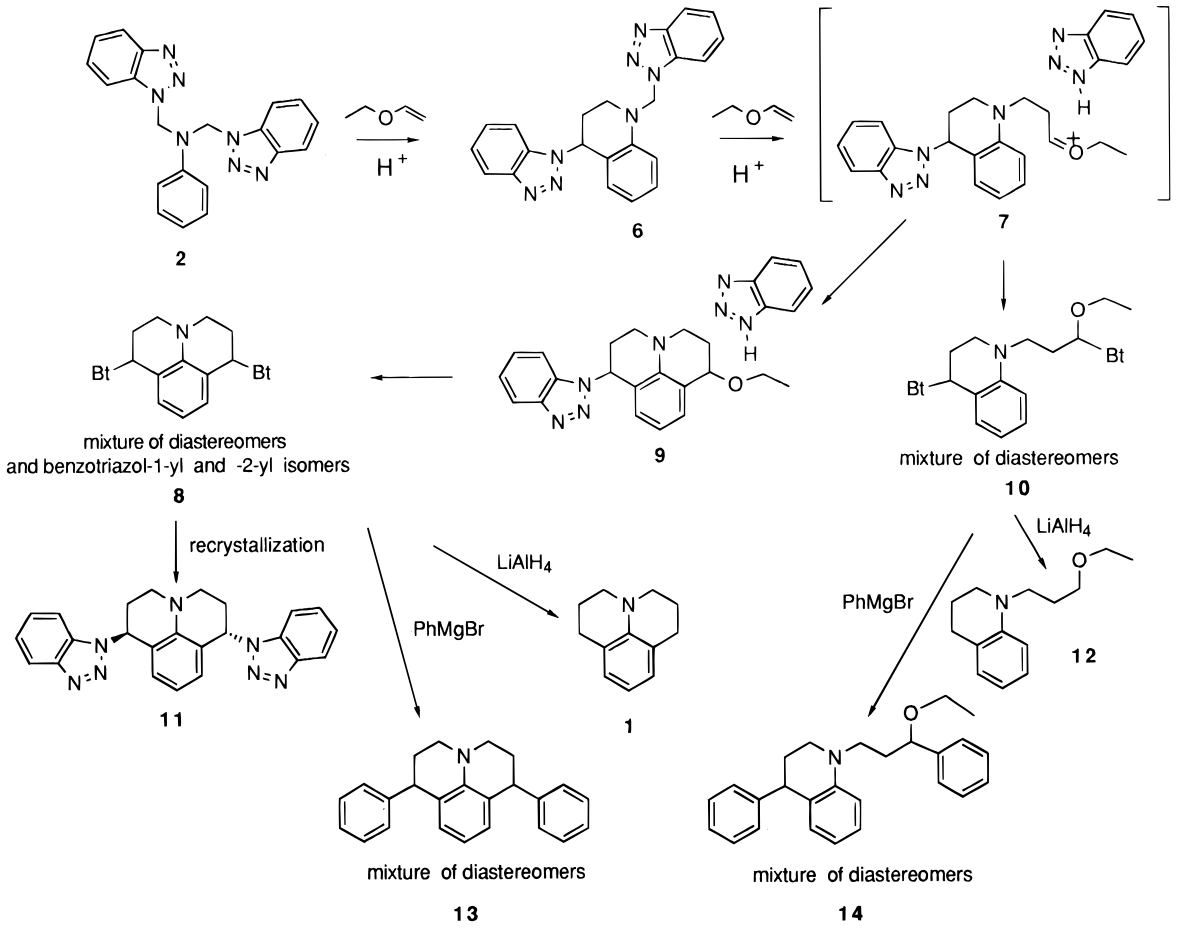
Scheme 2



natively, substitution of the acetamide by benzotriazole *via* intermediate **17** gives cation **19** which leads then to julolidine **21**. The rotational isomerization of **20** caused by the *N*-methylacetamido group hindered interpretation of its NMR. However, **20** was smoothly converted to julolidine **22** by lithium aluminum hydride.

NMR spectra showed formation of exclusively one diastereomer for each of **21** and **22**. By analogy to the predominant diastereomer **4**, compounds **21** and **22** were assigned *trans* configurations. Treatment of **21** with lithium aluminum hydride removed the benzotriazolyl substituent and reduced the carbonyl group converting **21** into monosubstituted julolidine **23**. Julolidine **23** was also obtained from 1,2,3,4-tetrahydroquinoline by reacting it with 1-(hydroxymethyl)benzotriazole followed by 1-vinyl-2-pyrrolidinone to give **24** and then reduction of the carbonyl group in **24**.

Enolizable Aldehydes. As recently reported,[24] *N*-[(benzotriazol-1-yl)methyl]anilines react with enolizable aldehydes to provide a convenient synthesis for 3,4-disubstituted 1,2,3,4-tetrahydroquinolines. We now find that this reaction can be effectively applied to the synthesis of unsymmetrically substituted julolidines. Thus, tetrahydroquinoline derivative **25** was reacted with various aldehydes to give julolidines **26**−**29** in quantitative yields, with the *trans* benzotriazol-1-yl isomer (**26**) strongly predominanting (Scheme 4). For example, integration of the C-1 peaks in the ^{13}C NMR spectrum of crude **26a**−**29a** allowed estimation of the relative abundance of the isomers as follows: **26a** (δ 63.2, 60%), **27a** (δ 61.1, 18%), **28a** (δ 69.3, 17%), **29a** (δ 681, 5%). Three major isomers, **26a**−**28a** were separated by column chromatography of the reaction mixture and fully characterized. Column chromatography of a crude mixture of **26b**−**29b** gave a fraction consisting of benzotriazol-1-yl isomers **26b** (H-1, δ 5.94, d, J = 9.4 Hz; CH_3, δ 0.93, d, J = 6.6 Hz) and **27b** (H-1, δ 6.04, d, J = 4.5 Hz; CH_3, δ 0.78, d, J = 6.9 Hz) in the ratio of 3:1. Isomer **26b** was characterized by complete ^{13}C NMR data and **27b** by the ^{13}C NMR of its aliphatic carbon resonances. The *trans* configuration of the substituents in **26b** was confirmed by NOE; thus, irradiation of the methyl group doublet at δ 0.93 produced 13% enhancement of the H-1 doublet at δ 5.94. Mixtures of **26c** and **27c** and **26d** and **27d** were also separated and similarly characterized. In the case of the derivatives of acetaldehyde (R = H), two isomers, **26e** and **28e**, were separated in pure forms.

Treatment with lithium aluminum hydride converted each of the mixtures of four isomers **26**−**29** into the corresponding monosubstituted julolidine **31** in high yields. 2-(Dialkylamino)julolidines (analogs of **31**, R = NR'_2) found recent interest as central nervous system agents; their reported synthesis from 8-(bromomethyl)-quinoline is rather complex,[25,26] but they should be easily prepared from **25** and, e.g., commercially available phthalimidoacetaldehyde diethyl acetal.

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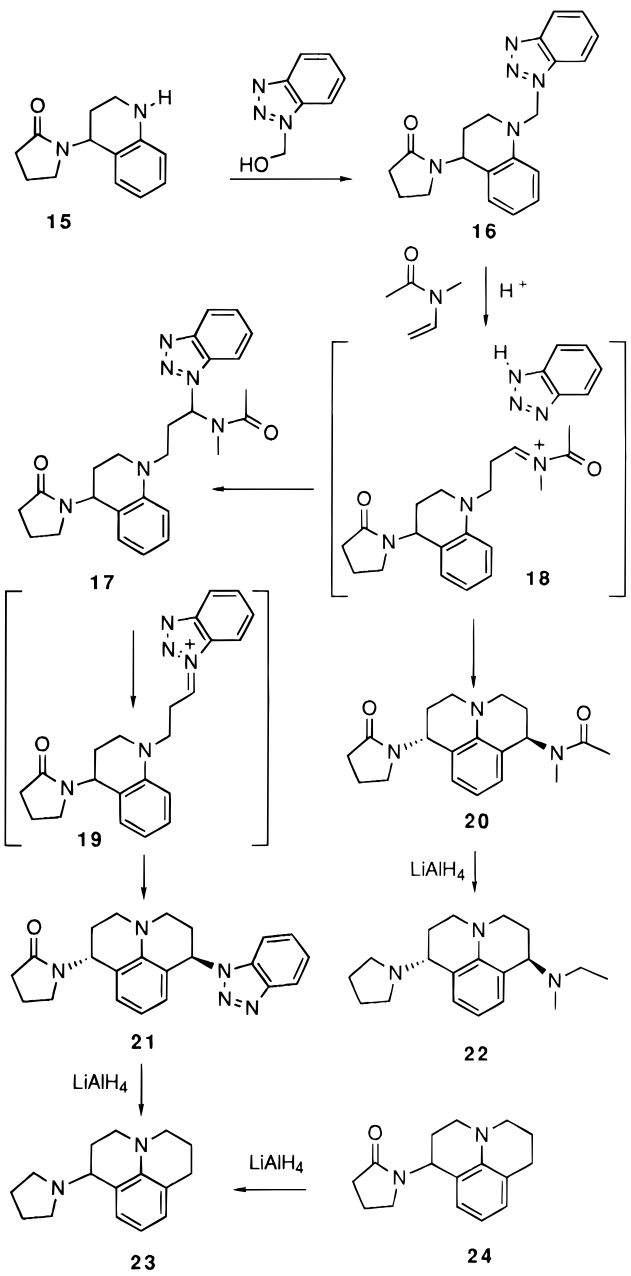
Scheme 3



Reactions of each of the crude mixtures of isomers **26**−**29** with phenylmagnesium bromide produced exclusively *trans* 1,2-disubstituted julolidines **32** in analogy to a similar reaction of 3,4-disubstituted 1,2,3,4-tetrahydroquinolines.[24] As examples of two such products, **32a** (R = Ph) and **32b** (R = Me) were investigated. The *trans* configuration of the substituents in julolidine **32b** was confirmed by NOE; thus, irradiation of the methyl doublet at δ 0.89 produced 12% enhancement of the H-1 doublet at δ 3.60 ($J_{1,2}$ = 9.0 Hz). A similar value of the coupling constant in the case of **32a** ($J_{1,2}$ = 8.4 Hz) suggests that this also has a *trans* configuration of the phenyl substituents. Reaction of a mixture of **26e** and **28e** with the same reagent gave 1-phenyljulolidine (**32e**).

Reactions with sodium hydride[19] also eliminated the asymmetry of julolidines **26**−**29** by conversion into enamino derivatives **30**. Enamine **30a** was stable enough to be separated, purified, and characterized. Upon workup, **30b,c** rearranged into imino derivatives **33b,c** which then were oxidized to alcohols **34b,c** and dehydrated to products **35b,c**. Compound **33e** with R = H did not react with oxygen during workup and was easily separated and characterized. None of the hydroxy derivatives **34a**−**c** could be isolated pure. However, their intermediacy in the reaction sequence is postulated on the basis of previous results with 1,2,3,4-tetrahydroquinolines.[24]

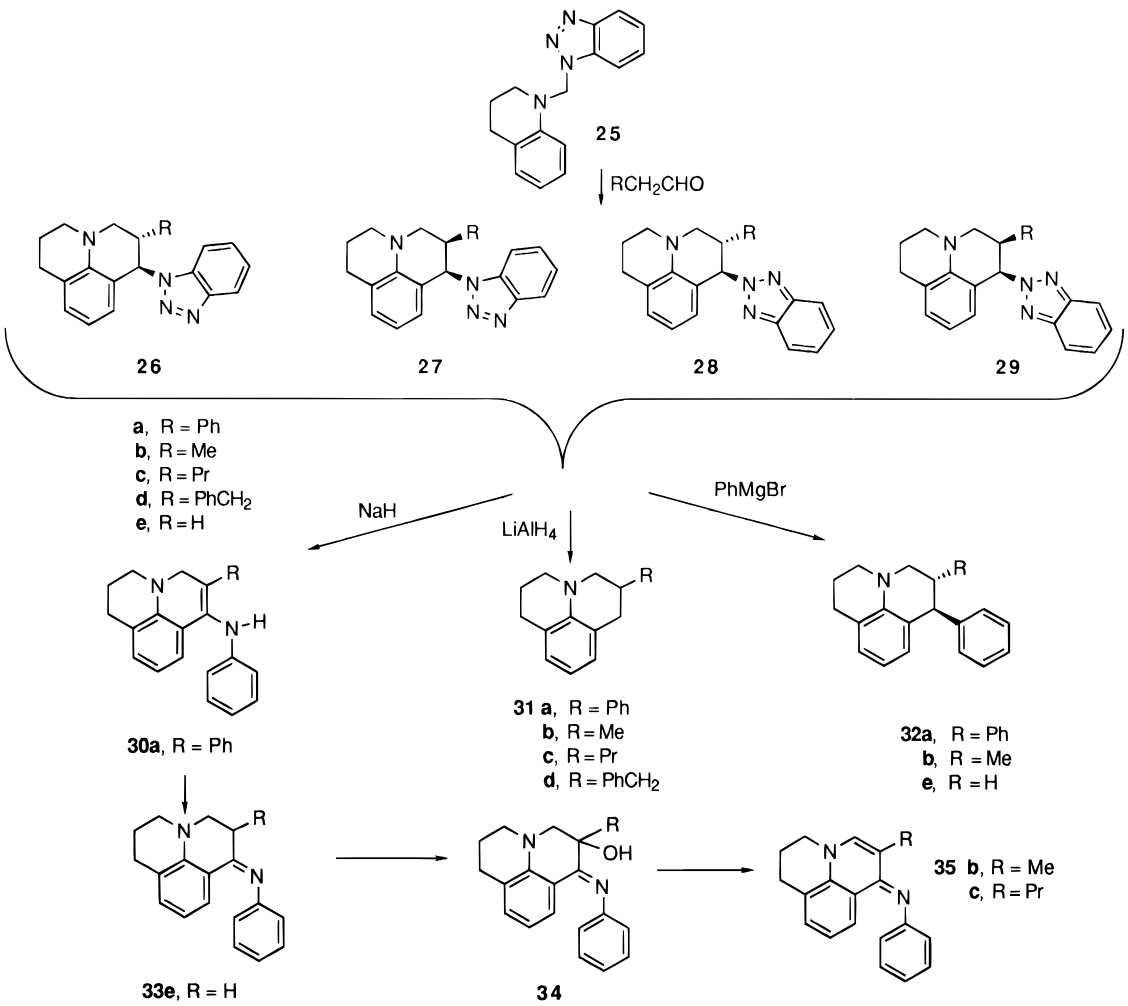
2,3-Disubstituted Julolidines. The new synthetic methods for julolidines discussed so far involve building of the C(1)−C(2)−C(3) bridge from two fragments: (i) the CH_2 group originating from formaldehyde and (ii) a vinyl group from *N*-vinylamide, ethyl vinyl ether, or enolizable aldehyde RCH_2CHO. The use of aldehyde RCH_2CHO enables introduction of a substituent R at C-2. We have also found that the method can be further extended by use of higher aldehydes instead of formaldehyde as fragment i. Thus, condensations of 1,2,3,4-tetrahydroquinolines with two molecules of aldehydes RCH_2CHO produced mixtures of isomeric julolidines **38**−**41**. The reaction is believed to proceed in two steps: (a) condensation of 1,2,3,4-tetrahydroquinoline with an aldehyde and benzotriazole giving **36**, an analog of the formaldehyde derivative **25**; (b) nucleophilic attack of immonium cation **37** on the α carbon atom of an aldehyde in its enol form, followed by cyclocondensation to produce julolidines **38**−**41** (Scheme 5).

Despite three asymmetric carbon atoms and benzotriazol-1-yl−benzotriazol-2-yl isomerization giving rise to eight possible isomers, only four structures (**38**−**41**) were detected in the product mixtures by NMR methods. The benzotriazol-1-yl derivative **38** appeared to strongly predominate in all instances. Thus, in the case of R = Me, the crude product mixture consisted of **38b** (70%, δ (H-1) 5.83, $J_{1,2}$ = 7.7 Hz), **39b** (25%, δ (H-1) 6.00, $J_{1,2}$ = 11.9 Hz), **40b** (4%, δ (H-1) 5.74, $J_{1,2}$ = 6.2 Hz), and **41b** (1%, δ (H-1) 5.84, $J_{1,2}$ = 10.8 Hz). *Trans*−*trans* configuration of the substituents in **38b** was assigned by NOE; thus, irradiation of the methyl group at C-2 (δ 0.95) gave 13% enhancement of the H-1 doublet at δ 5.83 and also 13% enhancement of the H-3 multiplet at δ 2.84. In a second experiment, the H-3 (4%) and methyl group signals (1%) were enhanced by irradiation of the H-1 doublet. All other structural assignments in this group of derivatives were made accordingly.

Crude mixtures of **38**−**41** were each reduced with lithium aluminum hydride, giving in each case a single diastereomer **42**. The *trans* configuration of the substituents in **42b** was confirmed by irradiation of the ethyl methylene multiplet at δ 1.35, producing 3% NOE enhancement of the H-2 multiplet at δ 2.00. Single products (**43**) were also obtained from the reactions of **38**−**41** with sodium hydride.

Reaction of **38a** with methylmagnesium iodide produced exclusively the *trans,trans* 1,2,3-trisubstituted julolidine **45a**. This can be explained by steric interaction with the C-2 phenyl group during nucleophilic attack of the Grignard reagent on the ionic intermediate **44**. Reaction of the mixture **38b**−**41b** with phenylmagnesium bromide also gave the single diastereomer, julolidine **45b**, supporting the intermediacy of cation **44**. The *trans,-trans* orientation of the substituents in **45b** was proved by NOE; irradiation of the C-2 methyl group doublet at δ 0.95 gave 10% enhancement of the H-1 resonance at δ 3.67. Formation of diastereomer mixtures on cyclization (**38**−**41**) but only *trans,trans* diastereomers (**45**) after the Grignard addition reflects a general trend in tetrahydroquinoline systems; thus, condensation of *N*-methylaniline with hydroxyethanal gives predominantly

Scheme 4



cis,trans-1-methyl-2-(hydroxymethyl)-3-hydroxy-4-(methylphenylamino)-1,2,3,4-tetrahydroquinoline,[27] whereas a *trans,trans* isomer of 1,2,3,4-tetrakis(trimethylsilyl)-1,2,3,4-tetrahydroquinoline is formed exclusively in a reaction of quinoline with trimethylsilyl chloride and lithium.[28]

Conclusions

The novel julolidine syntheses presented in this paper, based on benzotriazole intermediates of type Ar−N−C−Bt, offer both convenience and versatility. The method is especially useful for the preparation of symmetrically and asymmetrically 1,7-disubstituted julolidines as well as for the introduction of one, two, or three substituents, in any combination, at C-1, C-2, and C-3 in the julolidine system.

Experimental Section

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

1,7-Di(2-oxopyrrolidin-1-yl)julolidine (3). *p*-Toluenesulfonic acid (0.04 g, 0.2 mmol) was added to a mixture of **2** (3.75 g, 10 mmol) and 1-vinyl-2-pyrrolidinone (2.50 g, 22 mmol), preheated to 130 °C (oil bath) and stirred under nitrogen. The stirring at 130 °C was continued for an additional 10 min. After cooling, the reaction mixture was dissolved in chloroform and purified by column chromatography to give a 2:1 mixture of *trans* and *cis* isomers of **3** (3.05 g, 90%). Repeated column chromatography of **3** (hexane/triethylamine) gave a fraction additionally enriched in the *trans* isomer (90%), allowing its full NMR characterization: ^1H NMR δ 1.99 (m, 4 H), 2.11 (m, 4 H), 2.48 (t, J = 8.1 Hz, 4 H), 3.14 (m, 4 H), 3.24 (m, 4 H), 5.35 (t, J = 6.8 Hz, 2 H), 6.60 (t, J = 7.2 Hz, 1 H), 6.79 (d, J = 7.5 Hz, 2 H); ^{13}C NMR δ 18.3 (2 C), 26.9 (2 C), 31.4 (2 C), 44.2 (2 C), 47.4 (2 C), 47.9 (2 C), 116.8, 119.4 (2 C), 127.5 (2 C), 144.5, 175.1(2 C). Anal. Calcd for $C_{20}H_{25}N_3O_2$: C, 70.77; H, 7.42; N, 12.38. Found: C, 70.50; H, 7.42; N, 12.48.

***trans*-1,7-Di(Pyrrolidin-1-yl)julolidine (4).** A solution of crude **3** (3.39 g, 10 mmol) and lithium aluminum hydride (0.76 g, 20 mmol) in THF (20 mL) was stirred at 22 °C under nitrogen for 1 h. The reaction mixture was poured into ice-cold 10% NaOH (100 mL) and extracted with ether (3 × 100 mL). The combined extracts were dried over Na_2CO_3 and evaporated to give a pure mixture of diastereomers **5** (2.20 g, 70%). Recrystallization from hexane/triethylamine (9:1) gave pure *trans* diastereomers **4** as colorless plates: mp 113−114 °C; ^1H NMR δ 1.73 (m, 8 H), 1.84 (tdd, J = 13.2, 5.4, 3.3 Hz, 2 H), 2.10 (dq, J = 13.5, 3.3 Hz, 2 H), 2.40 (m, 4 H), 2.67 (m, 4 H), 3.12 (ddd, J = 11.1, 7.8, 2.7 Hz, 2 H), 3.17 (t, J = 3.3 Hz,

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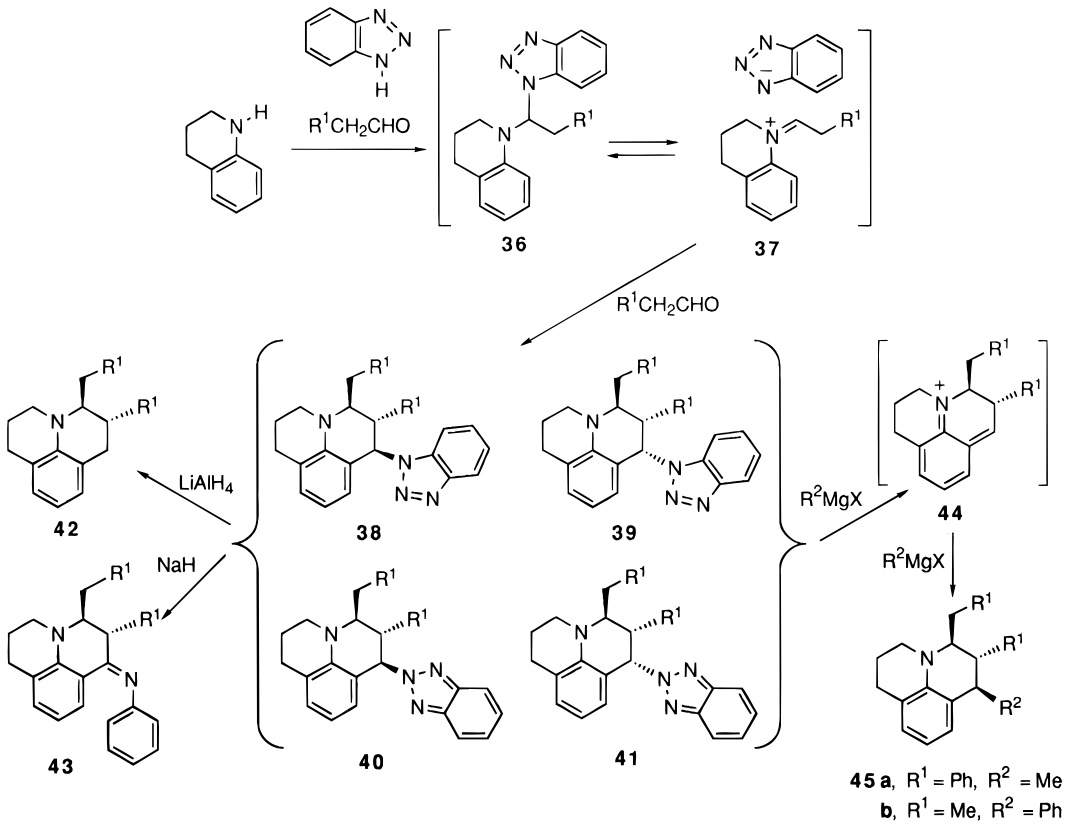
Scheme 5



For **36-43**: **a**, R^1 = Ph; **b**, R^1 = Me; **c**, R^1 = Pr; **d**, R^1 = H

2 H), 3.47 (ddd, J = 12.6, 11.1, 3.9 Hz, 2 H), 6.34 (t, J = 7.2 Hz, 1 H), 6.90 (d, J = 7.5 Hz, 2 H); ^{13}C NMR δ 23.4 (4 C), 25.6 (2 C), 44.6 (2 C), 51.8 (4 C), 61.4 (2 C), 111.6, 121.3 (2 C), 129.7 (2 C), 140.9. Anal. Calcd for $C_{20}H_{29}N_3$: C, 77.12; H, 9.38; N, 13.49. Found: C, 77.25; H, 9.53; N, 13.34.

***trans*-1,7-Di(Benzotriazol-1-yl)julolidine (11).** *p*-Toluenesulfonic acid (0.04 g, 0.2 mmol) was added to a solution of **2** (3.55 g, 10 mmol) and ethyl vinyl ether (2.1 mL, 22 mmol) in THF (40 mL), and the obtained solution was set aside at 22 °C for 18 h. The reaction mixture was poured into ice−water (50 g) and extracted with chloroform (2 × 30 mL). The combined extracts were washed with 10% Na_2CO_3 (50 mL) followed by water and dried over Na_2CO_3. Evaporation of the solvent gave a mixture of **8** and **10** (1:1). The mixture was separated into **10** (first fraction) and **8** (second fraction) using column chromatography with ethyl acetate as eluent. Careful rechromatography of the fraction containing two diastereomers of the di(benzotriazol-1-yl) isomer of **8** and recrystallization of this fraction from ethanol gave pure *trans* isomer **11** (0.57 g, 14%) as fine needles: mp 197−198 °C; ^{1}H NMR δ 2.64 (m, 4 H), 3.37 (m, 4 H), 6.33 (t, J = 6.6 Hz, 2 H), 6.48 (t, J = 7.5 Hz, 2 H), 6.83 (d, J = 7.6 Hz, 2 H), 7.25−7.50 (m, 5 H), 8.08 (d, J = 8.1 Hz, 2 H); ^{13}C NMR δ 28.7 (2 C), 46.3 (2 C), 56.2 (2 C), 110.7 (2 C), 117.0, 117.3 (2 C), 119.8 (2 C), 123.8 (2 C), 127.3 (2 C), 130.4 (2 C), 132.3 (2 C), 144.1, 146.2 (2 C). Anal. Calcd for $C_{24}H_{21}N_7$: C, 70.74; H, 5.19; N, 24.06. Found: C, 70.42; H, 5.22; N, 23.67.

1-(3-Ethoxypropyl)-1,2,3,4-tetrahydroquinoline (12) and Julolidine (1). A crude mixture of **8** and **10**, obtained from the reaction of **2** (3.55 g, 10 mmol) with ethyl vinyl ether, was treated with lithium aluminum hydride (0.76 g, 20 mmol) in refluxing anisole (20 mL) under nitrogen for 5 h. After cooling, the reaction mixture was poured into ice-cold 20% NaOH (100 mL) and extracted with ether (2 × 50 mL). The extract was washed with 10% NaOH, dried over Na_2CO_3, and evaporated under atmospheric pressure to remove ether and then under reduced pressure (1 Torr) to remove anisole. The residue was subjected to column chromatography (hexane) to give julolidine **1** (0.72 g, 41%) as the first fraction: plates, mp 38 °C [lit.[1] mp 40 °C].

After separation of **1**, the column was eluted with chloroform to give **12** (1.16 g, 51%) as a colorless oil: ^{1}H NMR δ 1.22 (t, J = 7.1 Hz, 3 H), 1.85 (q, J = 6.3 Hz, 2 H), 1.93 (m, 2 H), 2.75 (t, J = 6.3 Hz, 2 H), 3.27 (t, J = 5.7 Hz, 2 H), 3.36 (t, J = 7.1 Hz, 2 H), 3.44−3.51 (m, 4 H), 6.54 (td, J = 7.2, 0.9 Hz, 1 H), 6.60 (d, J = 8.2 Hz, 1 H), 6.92 (d, J = 6.8 Hz, 1 H), 7.03 (td, J = 7.2, 1.2 Hz, 1 H); ^{13}C NMR δ 15.2, 22.3, 26.9, 28.2, 48.3, 49.5, 66.2, 68.1, 110.6, 115.3, 122.2, 127.1, 129.1, 145.4. HRMS calcd for $C_{14}H_{21}NO$ (M^+ + 1) 219.1623, found 219.1616.

1,7-Diphenyljulolidine (13) and 1-(3-Ethoxy-3-phenylpropyl)-4-phenyl-1,2,3,4-tetrahydroquinoline (14). An ethereal solution of phenylmagnesium bromide (25 mL, 50 mmol) was added to a crude mixture of **8** and **10** (obtained from 10 mmol of **2** according to the procedure given for **11**) and dissolved in toluene (50 mL). The ether was distilled off, and the remaining toluene solution was heated at reflux under nitrogen for 2 h. The reaction mixture was poured into ice−water (100 g), neutralized with 10% acetic acid, and extracted with ether (2 × 50 mL). The extract was washed with water followed by 10% Na_2CO_3 (50 mL) and dried over anhydrous Na_2CO_3. The solvent was evaporated under reduced pressure, and the residue was subjected to column chromatography (toluene) to give **13** (0.76 g, 23%) as the first fraction: colorless oil; ^{1}H NMR δ 2.12 (m, 2 H), 2.27 (m, 2 H), 3.13 (m, 4 H), 4.16 (m, 2 H), 6.39 (m, 1 H), 6.61 (m, 2 H), 7.16 (m, 5 H), 7.30 (m, 5 H); ^{13}C NMR δ 30.6 (2 C), 43.4 (2 C), 47.2 (2 C), 115.6 (2 C), 123.4, 126.0 (2 C), 128.2 (4 C), 128.5 (2 C), 128.6 (4 C), 143.2, 146.9 (2 C). Anal. Calcd for $C_{24}H_{23}N$: C, 88.57; H, 7.12; N, 4.30. Found: C, 88.40; H, 7.26; N, 4.50.

The second fraction (the same eluent) gave **14** (0.74 g, 20%) as a colorless oil: ^{1}H NMR δ 1.19 (m, 3 H), 1.90−2.10 (m, 3 H), 2.20 (m, 1 H), 3.15−3.55 (m, 6 H), 4.12 (t, J = 5.3 Hz, 1 H), 4.27 (m, 1 H), 6.51 (t, J = 7.3 Hz, 1 H), 6.65 (d, J = 8.3 Hz, 1 H), 6.76 (d, J = 7.1 Hz, 1 H), 7.09 (d, J = 8.1 Hz, 2 H), 7.15−7.35 (m, 9 H); ^{13}C NMR δ 15.3, 30.5, 35.1, 43.3, 45.8, 47.9,

64.1, 79.8, 110.7, 115.4, 123.9, 126.0, 126.4 (2 C), 127.5, 127.6, 128.2 (2 C), 128.4 (2 C), 128.6 (2 C), 130.2, 142.7, 145.4, 146.5. Anal. Calcd for $C_{26}H_{29}NO$: C, 84.06; H, 7.87; N, 3.77. Found: C, 84.11; H, 7.92; N, 4.00.

1-[(Benzotriazol-1-yl)methyl]-4-(2-oxopyrrolidin-1-yl)-1,2,3,4-tetrahydroquinoline (16). A mixture of **15** (2.17 g, 10 mmol) and 1-(hydroxymethyl)benzotriazole (1.49 g, 10 mmol) in toluene (50 mL) was refluxed under a Dean−Stark trap for 1 h. The toluene solution was evaporated to give a crude mixture of **16** and its benzotriazol-2-yl isomer.

Reaction of 16 with *N*-Vinylacetamide. A mixture of crude **16** (3.48 g, 10 mmol) and *N*-vinylacetamide (0.99 g, 10 mmol) was preheated to 120 °C, and then *p*-toluenesulfonic acid monohydrate (0.02 g, 0.1 mmol) was added. The heating at 120 °C was continued for 10 additional minutes, and the mixture was allowed to cool to room temperature. The obtained mass was dissolved in chloroform (50 mL) and washed with 10% Na_2CO_3 (50 mL). The solution was dried (Na_2CO_3) and evaporated under reduced pressure. The residue was subjected to column chromatography (ethyl acetate) to give **21** as the first fraction: glassy material; ^{1}H NMR δ 2.00−2.30 (m, 4 H), 2.55 (m, 4H), 3.10−3.50 (m, 6 H), 5.56 (dd, J = 6.1, 9.5 Hz, 1 H), 6.26 (t, J = 4.9 Hz, 1 H), 6.56 (t, J = 7.6 Hz, 1 H), 6.74−6.82 (m, 2 H), 6.91 (d, J = 7.5 Hz, 1 H), 7.29 (m, 2 H), 8.04 (m, 1 H); ^{13}C NMR δ 18.3, 26.1, 29.7, 31.4, 43.4, 46.3, 47.7, 48.4, 56.6, 110.9, 116.6, 117.1, 119.9, 120.0, 123.6, 127.2, 128.4, 129.6, 132.3, 144.2, 146.2, 175.5. Anal. Calcd for $C_{22}H_{23}N_5O$: C, 70.76; H, 6.21; N, 18.75. Found: C, 71.01; H, 6.26; N, 18.76.

The second fraction from column chromatography (eluted with ethyl acetate/triethylamine, 9:1) gave **20** (1.31 g, 42%) as a mixture of two rotamers: oil. The product was characterized after reduction of its carbonyl groups.

1-(*N*-Ethyl-*N*-methylamino)-7-(pyrrolidin-1-yl)julolidine (22). A solution of **20** (0.95 g, 3 mmol) and $LiAlH_4$ (0.23 g, 6 mmol) in THF (10 mL) was refluxed under nitrogen for 10 min. The reaction mixture was poured into 10% NaOH and extracted with ether (2 × 20 mL). The combined extracts were washed with 10% NaOH (20 mL), dried over Na_2CO_3, and evaporated. The residue was purified by column chromatography (ethyl acetate/triethylamine, 9:1) to give a pure diastereomer **22** (0.30 g, 33%): oil; ^{1}H NMR δ 1.06 (t, J = 7.1 Hz, 3 H), 1.73 (m, 5 H), 1.85 (m, 1 H), 2.00 (m, 1 H), 2.12 (m, 1 H), 2.24 (s, 3 H), 2.44 (m, 3 H), 2.64 (m, 3 H), 3.01 (m, 1 H), 3.18 (t, J = 3.4 Hz, 1 H), 3.23 (ddd, J = 4.5, 6.9, 11.4 Hz, 1 H), 3.31 (ddd, J = 4.2, 7.8, 11.4 Hz, 1 H), 3.47 (ddd, J = 3.5, 11.0, 12.6 Hz, 1 H), 3.72 (dd, J = 4.6, 8.0 Hz, 1 H), 6.46 (t, J = 7.4 Hz, 1 H), 6.91 (dd, J = 1.7, 7.4 Hz, 1 H), 7.20 (ddd, J = 0.9, 1.7, 7.5 Hz, 1 H); ^{13}C NMR δ 12.8, 21.1, 23.3 (2 C), 25.5, 37.9, 45.3, 47.1, 47.5, 51.5 (2 C), 60.0, 60.7, 113.2 (2 C), 128.3 (2 C), 129.5, 142.3. Anal. Calcd for $C_{19}H_{29}N_3$: C, 76.21; H, 9.76; N, 14.03. Found: 76.45; H, 9.83; N, 14.02.

1-(Pyrrolidin-1-yl)julolidine (23). Method A. A solution of **21** (0.37 g, 1 mmol) and $LiAlH_4$ (0.12 g, 3 mmol) in anisole (5 mL) was heated at reflux under nitrogen for 30 min. The reaction mixture was poured into 20% NaOH (10 mL) and extracted with ether (2 × 10 mL). The extract was dried over Na_2CO_3, and the solvents were evaporated using rotavapor and then under 1 Torr (oil vacuum pump) to give **23** (0.21 g, 88%) as a colorless oil: ^{1}H NMR δ 1.68−2.00 (m, 7 H), 2.10 (dq, J = 13.5, 3.9 Hz, 1 H), 2.39−2.47 (m, 2 H), 2.62−2.75 (m, 4 H), 3.00 (dt, J = 8.2, 4.1 Hz, 1 H), 3.11−3.30 (m, 3 H), 3.48 (td, J = 11.6, 3.6 Hz, 1 H), 6.42 (t, J = 7.4 Hz, 1 H), 6.81 (dd, J = 0.8, 7.3 Hz, 1 H), 6.89 (dd, J = 1.2, 7.5 Hz, 1 H); ^{13}C NMR δ 21.7, 23.3 (2 C), 25.0, 27.8, 45.6, 49.6, 51.2 (2 C), 60.5, 113.5, 120.9, 121.3, 127.9, 128.2, 141.8. Anal. Calcd for $C_{16}H_{22}N_2$: C, 79.29; H, 9.15; N, 11.56. Found: C, 79.07; H, 9.08; N, 11.87.

Method B. Lithium aluminum hydride (0.76 g, 20 mmol) was added to a solution of **24** in tetrahydrofuran (20 mL). The obtained mixture was stirred at 22 °C under nitrogen for 2 h and then poured into 20% NaOH (50 mL). The combined extracts were washed with 10% NaOH, dried over Na_2CO_3, and evaporated. The residue was purified by column chromatography (ethyl acetate) to give **23** (1.94 g, 80%) as a colorless oil.

1-[(Benzotriazol-1-yl)methyl]-1,2,3,4-tetrahydroquinoline (25). A solution of 1-(hydroxymethyl)benzotriazole (14.92 g, 100 mmol) and 1,2,3,4-tetrahydroquinoline (12.6 mL, 100 mmol) in tetrahydrofuran (100 mL) was stored over molecular sieves (4 Å, 40 g) for 20 h. Some crystals of precipitating **25** were manually separated, dried, and submitted for analysis. The remaining crystals were dissolved by addition of chloroform (100 mL), and the obtained solution was evaporated to give **25** (contaminated with its benzotriazol-2-yl isomer)—this mixture was used for further reactions. Pure **25** was obtained as large colorless prisms: mp 139−140 °C; ^{1}H NMR δ 1.86−1.94 (m, 2 H), 2.72 (t, J = 6.3 Hz, 2 H), 3.52 (t, J = 5.5 Hz, 2 H), 6.13 (s, 2 H), 6.75 (td, J = 6.9, 1.6 Hz, 1 H), 7.00 (d, J = 7.3 Hz, 1 H), 7.12−7.21 (m, 2 H), 7.32−7.51 (m, 3 H), 8.06 (dd, J = 0.8, 8.3 Hz, 1 H); ^{13}C NMR δ 21.7, 27.6, 49.3, 65.1, 110.0, 112.6, 118.6, 119.8, 123.8 (2 C), 127.1, 127.4, 129.7, 132.5, 143.0, 146.1. Anal. Calcd for $C_{16}H_{16}N_4$: C, 72.70; H, 6.10; N, 21.20. Found: C, 72.61; H, 6.14; N, 21.26.

1-(2-Oxopyrrolidin-1-yl)julolidine (24). *p*-Toluenesulfonic acid monohydrate (20 mg, 0.1 mmol) was added to a mixture of **25** (2.64 g, 10 mmol) and 1-vinyl-2-pyrrolidinone (1.25 g, 11 mmol) preheated to 120 °C. The mixture was kept at 120 °C for 10 min, cooled, and dissolved in chloroform (50 mL). The solution was washed with 10% Na_2CO_3. The solvent was evaporated, and the residue was subjected to column chromatography (ethyl acetate) to give as the first fraction pure **24** (2.15 g, 84%) as a sticky oil: ^{1}H NMR δ 1.95−2.15 (m, 6 H), 2.50 (t, J = 7.9 Hz, 2 H), 2.70−2.86 (m, 2 H), 3.06−3.28 (m, 6 H), 5.41 (dd, J = 7.2 and 8.3 Hz, 1 H), 6.55 (td, J = 7.4 and 1.1 Hz, 1 H), 6.71 (d, J = 7.6 Hz, 1 H), 6.86 (d, J = 6.6 Hz, 1 H); ^{13}C NMR δ 18.2, 21.9, 26.4, 27.3, 31.4, 43.6, 47.9, 48.2, 50.0, 116.3, 118.7, 122.3, 125.6, 128.3, 143.8, 175.3. Anal. Calcd for $C_{16}H_{20}N_2O$: C, 74.97; H, 7.87; N, 10.93. Found: C, 74.66; H, 8.19; N, 10.79.

1-Benzotriazolyl-2-phenyljulolidines (26a−29a). A solution of **25** (2.64 g, 10 mmol), phenylacetaldehyde (1.2 mL, 10 mmol), and *p*-toluenesulfonic acid monohydrate (20 mg, 0.1 mmol) in THF (20 mL) was stored over molecular sieves (5 g, 4 Å) for 2 h with occasional shaking. The solution was decanted, and the molecular sieves were washed with THF (2 × 10 mL). The solution and the washings were combined and evaporated under reduced pressure to give a crude mixture of **26a**−**29a**. Column chromatography (chloroform) of the mixture gave *trans*-1-(benzotriazol-2-yl)-2-phenyljulolidine (**28a**) (0.51 g, 14%) as cuboids (from ether): mp 141−143 °C; ^{1}H NMR δ 1.95−2.20 (m, 2 H), 2.75−2.87 (m, 2 H), 3.19 (ddd, J = 3.6, 9.3, 11.1 Hz, 1 H), 3.28−3.35 (m, 1 H), 3.45 (dd, J = 4.4, 11.9 Hz, 1 H), 3.54 (dd, J = 10.3, 11.8 Hz, 1 H), 4.22 (td, J = 10.1, 4.4 Hz, 1 H), 6.30 (d, J = 7.7 Hz, 1 H), 6.38 (d, J = 10.1 Hz, 1 H), 6.43 (t, J = 7.7 Hz, 1 H), 6.90 (d, J = 10.1 Hz, 1 H), 7.19 (s, 5 H), 7.31 (m, 2 H), 7.81 (m, 2 H); ^{13}C NMR δ 21.9, 27.5, 44.8, 50.0, 54.5, 69.4, 116.6, 118.3 (2 C), 119.3, 122.4, 125.7, 126.0 (2 C), 127.3, 127.4 (2 C), 128.7 (2 C), 129.2, 139.8, 142.4, 144.1 (2 C). Anal. Calcd for $C_{24}H_{22}N_4$: C, 78.66; H, 6.05; N, 15.29. Found: C, 78.48; H, 6.06; N, 15.05.

The second fraction from column chromatography yielded *trans*-1-(benzotriazol-1-yl)-2-phenyljulolidine (**26a**) (2.23 g, 61%) as cuboids (from ether): mp 133−135 °C; ^{1}H NMR δ 2.01−2.25 (m, 2 H), 2.79−2.98 (m, 2 H), 3.23 (td, J = 7.6, 3.4 Hz, 1 H), 3.30 (t, J = 4.4 Hz, 1 H), 3.37 (dd, J = 3.9, 11.8 Hz, 1 H), 3.62 (dd, J = 10.9, 11.8 Hz, 1 H), 3.96 (td, J = 10.7, 3.8 Hz, 1 H), 6.29 (d, J = 7.6 Hz, 1 H), 6.42 (m, 2 H), 6.93 (d, J = 7.4 Hz, 1 H), 7.00 (m, 2 H), 7.15 (m, 3 H), 7.27 (m, 3 H), 7.99 (m, 1 H); ^{13}C NMR δ 22.0, 27.4, 44.3, 50.1, 55.0, 63.3, 110.7, 117.0, 118.5, 120.1, 122.6, 123.6, 125.9, 127.0, 127.2 (2 C), 127.5, 128.8 (2 C), 129.3, 132.0, 139.3, 143.0, 146.4. Anal. Calcd for $C_{24}H_{22}N_4$: C, 78.66; H, 6.05; N, 15.29. Found: C, 78.73; H, 6.13; N, 15.07.

***cis*-1-(Benzotriazol-1-yl)-2-phenyljulolidine** (**27a**) was obtained as the third fraction from column chromatography (0.58 g, 16%): powder; mp 210−212 °C; ^{1}H NMR δ 2.05−2.20 (m, 2 H), 2.75−3.05 (m, 2 H), 3.26 (ddd, J = 1.5, 3.9, 11.4 Hz, 1 H), 3.32−3.41 (m, 1 H), 3.49 (ddd, J = 4.2, 9.1, 11.4 Hz, 1 H), 3.80 (dt, J = 12.6, 4.2 Hz, 1 H), 4.08 (dd, J = 11.5, 12.6 Hz, 1 H), 6.06 (d, J = 4.5 Hz,1 H), 6.48 (t, J = 7.5 Hz, 1 H), 6.64 (d, J = 8.0 Hz, 2 H), 6.75 (d, J = 7.1 Hz, 1 H), 6.90 (d, J

= 7.3 Hz, 1 H), 6.98 (m, 3 H), 7.15 (m, 3 H), 7.91 (d, J = 7.3 Hz, 1 H); ^{13}C NMR δ 21.9, 27.8, 44.4, 49.2, 50.0, 61.2, 109.5, 116.1, 116.8, 119.6, 122.4, 123.2, 126.6, 127.3, 127.4 (2 C), 128.3, 128.4 (2 C), 129.8, 134.1, 138.3, 143.1, 145.2. Anal. Calcd for $C_{24}H_{22}N_4$: C, 78.66; H, 6.05; N, 15.29. Found: C, 78.48; H, 6.06; N, 15.05.

1-Benzotriazolyl-2-methyljulolidines (26b−29b). A solution of **25** (2.64 g, 10 mmol), propionaldehyde (0.9 mL, 12 mmol), and *p*-toluenesulfonic acid monohydrate (20 mg, 0.1 mmol) in THF (10 mL) was stored over molecular sieves for 2 h with occasional shaking. Workup as above gave a crude mixture of **26b−29b**. Column chromatography (toluene) gave a fraction consisting of **26b** and **27b** (3:1): oil; ^{13}C NMR (**26b**) δ 16.2, 21.7, 27.2, 32.8, 49.9, 54.9, 64.1, 111.0, 116.5, 117.1, 119.8, 122.2, 123.5, 126.0, 126.8, 129.0, 131.6, 142.9, 146.5; ^{13}C NMR (**27b**, aliphatic) 14.7, 21.7, 27.6, 33.0, 49.6, 52.3, 60.7; HRMS calcd for $C_{19}H_{20}N_4$ (M^+) 304.1688, found 304.1676.

1-Benzotriazolyl-2-propyljulolidines (26c−29c). Starting from valeraldehyde (1.1 mL, 10 mmol) and following a procedure analogous to that from **26a−29a**, a crude mixture of **26c−29c** was obtained.

Column chromatography (toluene) gave a fraction consisting of **26c** and **27c** (3:1): oil; ^{13}C NMR (**26c**) δ 13.9, 19.6, 21.8, 27.3, 32.8, 37.6, 50.1, 52.4, 62.8, 111.0, 116.6, 116.9, 119.9, 122.2, 123.5, 126.7, 126.8, 129.1, 131.8, 143.2, 146.5; ^{13}C NMR (**27c**, aliphatic) δ 13.9, 20.0, 21.8, 27.6, 31.3, 37.8, 49.7, 50.4, 59.9. Anal. Calcd for $C_{21}H_{24}N_4$: C, 75.87; H, 7.28; N, 16.80. Found: C, 75.83; H, 7.45; N, 16.76.

1-Benzotriazolyl-2-(phenylmethyl)julolidines (26d−29d). This product was obtained by condensation of **25** (2.64 g, 10 mmol) with hydrocinnamaldehyde (1.3 mL, 10 mmol) according to the procedure for **26a−29a**. Column chromatography of the crude reaction mixture (toluene) gave a fraction consisting of **26d** and **27d** (3:1): oil; ^{13}C NMR (**26d**) δ 21.8, 27.4, 36.9, 39.9, 50.0, 50.8, 61.8, 110.8, 115.9, 116.7, 120.0, 122.3, 123.6, 126.4, 127.0, 127.4, 128.4 (2 C), 129.0 (2 C), 129.5, 132.1, 138.6, 143.1, 146.5; HRMS calcd for $C_{25}H_{24}N_4$ (M^+) 380.2001, found 380.2026.

1-(Benzotriazol-2-yl)julolidine (28e). Starting from **25** (2.64 g, 10 mmol) and acetaldehyde (0.8 mL, 15 mmol), crude product **26e−28e** was obtained according to a procedure analogous to that for **26a−29a**. Column chromatography of this crude product (chloroform) gave as the first fraction analytically pure **28e** (0.35 g, 12%): prisms (ether) mp 122−123 °C; ^{1}H NMR δ 2.03 (m, 2 H), 2.51 (m, 1 H), 2.64 (m, 1 H), 2.81 (m, 2 H), 3.23 (m, 3 H), 3.50 (ddd, J = 3.4, 10.3, 11.6 Hz, 1 H), 6.14 (t, J = 5.3 Hz, 1 H), 6.47 (t, J = 7.5 Hz, 1 H), 6.72 (d, J = 7.6 Hz, 1 H), 6.90 (d, J = 7.2 Hz, 1 H), 7.34 (m, 2 H), 7.86 (m, 2 H); ^{13}C NMR δ 21.9, 27.6, 29.1, 46.1, 50.0, 62.9, 116.1, 118.2 (2 C), 122.5 (2 C), 126.0 (2 C), 127.7, 129.6, 143.2, 144.2 (2 C). Anal. Calcd for $C_{18}H_{18}N_4$: C, 74.46; H, 6.25; N, 19.30. Found: C, 74.67; H, 6.28; N, 19.23.

The second fraction gave **1-(benzotriazol-1-yl)-julolidine (26e)**: 2.20 g, 76%; prisms (EtOH/Et_2O, 1:1); mp 103−104 °C; ^{1}H NMR δ 2.07 (m, 2 H), 2.47 (m, 1 H), 2.60 (m, 1 H), 2.86 (t, J = 6.3 Hz, 2 H), 3.14−3.35 (m, 4 H), 6.31 (t, J = 7.1 Hz, 1 H), 6.46 (m, 1 H), 6.56 (d, J = 7.5 Hz, 1 H), 6.95 (d, J = 7.4 Hz, 1 H), 7.03 (m, 1 H), 7.28 (m, 2 H), 8.06 (m, 1 H); ^{13}C NMR δ 21.8, 27.4, 29.3, 46.9, 49.9, 57.0, 110.9, 116.3, 119.8, 122.4 (2 C). 123.5, 126.8, 127.1, 129.5, 132.3, 143.4, 146.3. Anal. Calcd for $C_{18}H_{18}N_4$: C, 74.46; H, 6.25; N, 19.30. Found: C, 74.49; H, 6.34; N, 19.27.

1-(Phenylimino)-2,3,6,7-tetrahydro-1*H*,5*H*-benzo[*ij*]-quinolizine (30a). Sodium hydride (0.34 g, 10 mmol) was added to a solution of crude **26a−29a** (3.66 g, 10 mmol) in dioxane (20 mL), and the obtained mixture was heated at reflux under nitrogen for 14 h. The reaction mixture was poured into ice−water (50 g), acidified with acetic acid to pH 5, and extracted with toluene (2 × 30 mL). The combined extracts were washed with water (50 mL), dried over $MgSO_4$, and evaporated. The residue was subjected to column chromatography (toluene). Finally, the product was recrystallied from toluene to give pure compound **30a** (2.75 g, 81%) as cuboids: mp 146−147 °C; ^{1}H NMR δ 2.12 (quintet, J = 6.3 Hz, 2 H), 2.81 (t, J = 6.3 Hz, 2 H), 3.12 (t, J = 5.2 Hz, 2 H), 4.11 (s, 2 H), 5.26 (s, 1 H), 6.51 (t, J = 7.5 Hz, 1 H), 6.62 (d, J = 7.7 Hz, 2 H), 6.79 (t, J = 7.3 Hz, 1 H), 6.87 (d, J = 7.4 Hz, 1 H), 7.06 (d, J = 7.8 Hz, 1 H), 7.15 (t, J = 7.7 Hz, 2 H), 7.20−7.31 (m, 5 H); ^{13}C NMR δ 21.6, 27.0, 49.9, 55.0, 115.9 (2 C), 117.3, 119.0, 120.3, 122.3 (2 C), 123.3, 126.6 (2 C), 127.2, 128.5 (2 C), 129.0 (3 C), 131.5, 138.3, 143.1, 146.4. Anal. Calcd for $C_{24}H_{22}N_2$: C, 85.17; H, 6.25; N, 8.28. Found: C, 85.14, H, 5.95; N, 8.17.

2-Phenyljulolidine (31a). A solution of crude **26a−29a** (10 mmol) and lithium aluminum hydride (0.34 g, 10 mmol) in anisole (20 mL) was heated at reflux under nitrogen for 1 h. After cooling, methanol (10 mL) was added dropwise, and the flask contents were poured into 10% NaOH (50 mL). The mixture was extracted with ether (2 × 50 mL). The combined extracts were dried over Na_2CO_3, and the solvent was evaporated (first ether under atmospheric pressure and then anisole under high vacuum). Column chromatography of the residue (hexane/ether, 4:1) gave pure julolidine **31a** (2.25 g, 90%) as a yellowish oil: ^{1}H NMR δ 1.93−2.05 (m, 3 H), 2.69−2.82 (m, 3 H), 2.98 (m, 2 H), 3.16 (m, 1 H), 3.22 (bs, 2 H), 6.53 (t, J = 7.4 Hz, 1 H), 6.82 (d, J = 7.4 Hz, 2 H), 7.20−7.35 (m, 5 H); ^{13}C NMR δ 22.1, 27.6, 35.3, 38.6, 50.0, 56.3, 115.9, 121.4, 121.5, 126.6, 127.0, 127.1 (3 C), 128.5 (2 C), 142.2, 143.9. Anal. Calcd for $C_{18}H_{19}N$: C, 86.70; H, 7.68; N, 5.62. Found: C, 87.08; H, 7.63; N, 5.55.

2-Methyljulolidine (31b). Starting from crude **26b−29b** and following a procedure as above, julolidine **31b** (1.48 g, 79%) was obtained as colorless oil: ^{1}H NMR δ 1.00 (d, J = 6.6 Hz, 3 H), 1.82−2.00 (m, 2 H), 2.00−2.15 (m, 1 H), 2.38 (dd, J = 10.5, 15.9 Hz, 1 H), 2.65−2.80 (m, 4 H), 3.00 (ddd, J = 2.3, 3.8, 11.0 Hz, 1 H), 3.05−3.10 (m, 2 H), 6.46 (t, J = 7.4 Hz, 1 H), 6.74 (d, J = 7.4 Hz, 2 H); ^{13}C NMR δ 19.1, 22.0, 26.9, 27.6, 36.1, 49.8, 57.0, 115.6, 121.1 (2 C), 126.7, 126.8, 142.2. Anal. Calcd for $C_{13}H_{17}N$: C, 83.37; H, 9.15; N, 7.48. Found; C, 83.06; H, 8.95; N, 7.84.

2-Propyljulolidine (31c). Starting from crude **26c−29c** and following a procedure as above, julolidine **31c** (1.75 g, 81%) was obtained as a colorless oil: ^{1}H NMR δ 0.93 (t, J = 7.4 Hz, 3 H), 1.25−1.50 (m, 4 H), 1.85−2.05 (m, 3 H), 2.39 (dd, J = 10.7, 15.9 Hz, 1 H), 2.65−2.85 (m, 4 H), 3.02−3.20 (m, 3 H), 6.47 (t, J = 7.3 Hz, 1 H), 6.75 (d, J = 7.2 Hz, 2 H); ^{13}C NMR δ 14.2, 19.9, 22.1, 27.6, 31.8, 34.3, 36.3, 50.0, 55.6, 115.7, 121.2 (2 C), 126.8, 126.9, 142.6. Anal. Calcd for $C_{15}H_{21}N$: C, 83.67; H, 9.83; N, 6.50. Found: C, 83.99; H, 9.80; N, 6.61.

2-(Phenylmethyl)julolidine (31d). A crude mixture of **26d−29d** (10 mmol) was converted to julolidine **31d** (2.28 g, 87%) according to a procedure analogous to that above: yellowish oil; ^{1}H NMR δ 1.82−2.00 (m, 2 H), 2.22−2.35 (m, 1 H), 2.48 (dd, J = 8.8, 15.7 Hz, 1 H), 2.61 (d, J = 7.4 Hz, 2 H), 2.65−2.85 (m, 5 H), 3.03 (m, 2 H), 6.47 (t, J = 7.5 Hz, 1 H), 6.75 (t, J = 7.1 Hz, 2 H), 7.10−7.38 (m, 5 H); ^{13}C NMR δ 22.0, 27.6, 33.9 (2 C), 40.1, 49.9, 54.4, 115.8, 120.6, 121.3, 125.9, 126.9, 127.1, 128.2 (2 C), 129.0 (2 C), 140.2, 142.5. Anal. Calcd for $C_{19}H_{21}N$: C, 86.65; H, 8.04; N, 5.32. Found: C, 86.39; H, 8.15; N, 5.51.

***trans*-1,2-Diphenyljulolidine (32a).** An ethereal solution of phenylmagnesium bromide (10 mL, 20 mmol) was added to a solution of crude **26a−29a** (3.66 g, 10 mmol) in toluene (50 mL). The ether was distilled off, and the residue was heated at reflux under nitrogen for 1 h. After cooling, the reaction mixture was poured into ice−water (100 g), acidified with 5% acetic acid to pH 6, and extracted with ether (2 × 50 mL). The ethereal solution was washed with water followed by 10% Na_2CO_3 and dried over Na_2CO_3. Column chromatography of the residue (hexane/ether, 4:1) gave julolidine **32a** (2.95 g, 91%) as a greenish oil: ^{1}H NMR δ 1.98−2.20 (m, 2 H), 2.75−2.95 (m, 2 H), 3.10−3.40 (m, 5 H), 4.22 (d, J = 8.4 Hz, 1 H), 6.49 (m, 2 H), 6.85 (d, J = 7.3 Hz, 1 H), 6.95−7.25 (m, 10 H); ^{13}C NMR δ 22.1, 27.7, 47.4, 50.3, 51.2, 55.4, 116.3, 121.7, 125.3, 126.0, 126.4, 127.3, 127.8 (2 C), 128.0 (2 C), 128.3 (2 C), 128.4, 129.2 (2 C), 142.8, 143.2, 145.2. Anal. Calcd for $C_{24}H_{23}N$: C, 88.57; H, 7.12; N, 4.30. Found: C, 88.18; H, 7.09; N, 4.07.

***trans*-2-Methyl-1-phenyljulolidine (32b).** Reaction of crude **26b−29b** (3.04 g, 10 mmol) with phenylmagnesium bromide (15 mL, 30 mmol) according to the above procedure gave julolidine **32b** (2.27, 86%) as a colorless oil: ^{1}H NMR δ 0.89 (d, J = 6.9 Hz, 3 H), 1.92−2.08 (m, 2 H), 2.15−2.26 (m, 1

H), 2.75−2.82 (m, 2 H), 2.87 (dd, J = 9.0, 11.1 Hz, 1 H), 3.05−3.14 (m, 2 H), 3.15−3.24 (m, 1 H), 3.60 (d, J = 9.0 Hz, 1 H), 6.41 (m, 2 H), 6.78 (m, 1 H), 7.10−7.30 (m, 5 H); ^{13}C NMR δ 18.2, 22.0, 27.7, 34.7, 50.2, 52.0, 55.7, 115.9, 121.2, 124.5, 126.1, 127.1, 128.2 (2 C), 128.3, 129.2 (2 C), 142.9, 145.9. Anal. Calcd for $C_{19}H_{21}N$: C, 86.65; H, 8.04; N, 5.32. Found: C, 86.32; H, 7.93; N, 5.28.

1-Phenyljulolidine (32e). Reaction of a crude mixture of **26e** and **28e** (2.90 g, 1 0 mmol) with phenylmagnesium bromide (15 mL, 30 mmol) according to the above procedure gave julolidine **32e** (2.15 g, 86%) as a colorless oil: ^{1}H NMR δ 2.00 (m, 2 H), 2.05 (m, 1 H), 2.20 (m, 1 H), 2.80 (t, J = 6.5 Hz, 2 H), 3.09 (m, 2 H), 3.16 (t, J = 5.4 Hz, 2 H), 4.10 (t, J = 5.6 Hz, 1 H), 6.43 (t, J = 7.4 Hz, 1 H), 6.54 (d, J = 7.4 Hz, 1 H), 6.81 (d, J = 7.2 Hz, 1 H), 7.10−7.30 (m, 5 H); ^{13}C NMR δ 22.1, 27.8, 30.9, 43.5, 47.4, 50.2, 115.6, 121.5, 123.6, 126.0, 127.4, 128.0, 128.2 (2 C), 128.6 (2 C), 143.1, 146.9. Anal. Calcd for $C_{18}H_{19}N$: C, 86.70; H, 7.68; N, 5.62. Found: C, 86.66; H, 7.86; N, 5.56.

1-(Phenylimino)julolidine (33e). Sodium hydride (0.48 g, 20 mmol) was added to a solution of **26e** (2.90 g, 10 mmol) in dioxane (20 mL), and the obtained mixture was stirred and heated to reflux under nitrogen for 2 h. After cooling, the reaction mixture was poured into ice−water (100 g), acidified with acetic acid to pH 5, and extracted with chloroform (2 × 20 mL). The combined extracts were washed with water (50 mL), dried over $MgSO_4$, and evaporated. Column chromatography of the residue (toluene) gave pure **33e** (2.12 g, 81%) as yellow prisms (from toluene/ether): mp 103−104 °C; ^{1}H NMR δ 2.04 (quintet, J = 6.3 Hz, 2 H), 2.61 (t, J = 6.1 Hz, 2 H), 2.79 (t, J = 6.6 Hz, 2 H), 3.13 (m, 4 H), 6.68 (t, J = 7.9 Hz, 1 H), 6.80 (d, J = 8.4 Hz, 2 H), 7.05 (m, 2 H), 7.32 (m, 2 H), 8.03 (d, J = 7.9 Hz, 1 H); ^{13}C NMR δ 21.8, 27.0, 28.8, 49.6, 50.3, 117.1, 120.1 (2 C), 120.2, 122.9, 123.2, 124.8, 128.8 (2 C), 132.1, 146.8, 151.4, 162.5. Anal. Calcd for $C_{18}H_{18}N_2$: C, 82.41; H, 6.92; N, 10.68. Found: C, 82.06; H, 6.93; N, 10.44.

1-(Phenylimino)-2-methyl-6,7-dihydro-1*H*,5*H*-benzo[*ij*]-quinoline(35b). Sodium hydride (0.48 g, 20 mmol) was added to a solution of **26b**−**29b** (3.04 g, 10 mmol) in dioxane (50 mL). The obtained mixture was stirred and heated at reflux under nitrogen for 2 h. After cooling, the mixture was poured into ice−water (100 g), acidified with 10% acetic acid to pH 5, and extracted with chloroform (2 × 50 mL). The extract was washed with water (2 × 50 mL), dried over $MgSO_4$, and evaporated under reduced pressure. The residue was subjected to column chromatography (toluene) to give pure **35** (2.26 g, 82%) as yellow prisms: mp 150−152 °C; ^{1}H NMR δ 1.72 (s, 3 H), 2.12 (m, 2 H), 2.97 (t, J = 6.1 Hz, 2 H), 3.90 (t, J = 5.7 Hz, 2 H), 6.82−6.94 (m, 4 H), 7.00 (dd, J = 7.2, 8.2 Hz, 1 H), 7.19−7.27 (m, 3 H), 8.12 (d, J = 8.5 Hz, 1 H); ^{13}C NMR δ 18.8, 21.3, 27.4, 50.9, 111.2, 120.4 (2 C), 120.6, 121.8, 123.3, 124.8 (2 C), 125.8, 128.2 (2 C), 129.3, 137.8, 152.9, 153.9. Anal. Calcd for $C_{19}H_{18}N_2$: C, 83.18; H, 6.61; N, 10.21. Found: C, 83.50; H, 6.73; N, 10.03.

1-(Phenylimino)-2-propyl-6,7-dihydro-1*H*,5*H*-benzo[*ij*]-quinoline (35c). By a procedure analogous to **35b**, compound **35c** (2.53 g, 84%) was prepared from a crude mixture of **26c**−**29c** (3.32 g, 10 mmol) as yellow grains: mp 146 °C; ^{1}H NMR δ 0.71 (m, 3 H), 1.38 (m, 2 H), 2.13 (m, 4 H), 2.94 (m, 2 H), 3.90 (m, 2 H), 6.78−6.96 (m, 5 H), 7.12−7.28 (m, 3 H), 7.96 (d, J = 6.8 Hz, 1 H); ^{13}C NMR δ 13.7, 21.2, 22.3, 27.4, 32.8, 50.8, 117.5, 119.6 (2 C), 120.2, 121.1, 123.0, 124.8, 126.0, 128.5 (2 C), 129.1, 136.6 (2 C), 152.2, 154.2. Anal. Calcd for $C_{21}H_{22}N_2$: C, 83.40; H, 7.33; N, 9.26. Found: C, 83.26; H, 7.42; N, 9.16.

***trans,trans*-1-(Benzotriazol-1-yl)-2-phenyl-3-(phenylmethyl)julolidine (38a).** A solution of 1,2,3,4-tetrahydroquinoline (1.3 mL, 10 mmol), benzotriazole (1.19 g, 10 mmol), phenylacetaldehyde (2.4 mL, 20 mmol), and *p*-toluenesulfonic acid monohydrate (20 mg, 0.1 mmol) in THF was shaken for 2 h with molecular sieves (4 Å, 5 g), filtered, and evaporated to give crude product (a mixture of **38a**−**41a**). Trituration of the crude product with ether (20 mL) produced crystals of pure isomer **38a** (1.92 g, 42%): tiny needles (toluene); mp 187−188 °C; ^{1}H NMR δ 1.90−2.15 (m, 2 H), 2.59 (dd, J = 7.7, 16.4 Hz, 1 H), 2.81 (dd, J = 5.0, 14.3 Hz, 1 H), 2.88 (m, 2 H), 3.15 (dt, J = 11.8, 9.3 Hz, 1 H), 3.44−3.58 (m, 1 H), 3.72 (m, 1 H), 3.78 (q, J = 4.5 Hz, 1 H), 6.14 (d, J = 5.0 Hz, 1 H), 6.53 (m, 2 H), 6.65 (m, 2 H), 6.82 (m, 1 H), 6.99−7.15 (m, 9 H), 7.27 (m, 2 H), 8.05 (m, 1 H); ^{13}C NMR δ 22.1, 28.2, 36.7, 47.1, 48.7, 61.6, 63.9, 110.8, 115.1, 116.1, 120.0, 123.1, 123.6, 126.2, 127.1 (2 C), 127.5 (2 C), 127.9, 128.3 (2 C), 128.7 (2 C), 128.9 (2 C), 129.6, 132.8, 138.0, 141.9, 142.1, 146.2. Anal. Calcd for $C_{31}H_{28}N_4$: C, 81.55; H, 6.18; N, 12.27. Found: C, 81.95; H, 6.32; N, 11.92.

***trans,trans*-1-(Benzotriazol-1-yl)-2-methyl-3-ethyljulolidine (38b) and Its Isomers 39b−41b.** Using a procedure as above, condensation of 1,2,3,4-tetrahydroquinoline (1.3 mL, 10 mmol) with propionaldehyde (1.8 mL, 25 mmol) and benzotriazole (1.19 g, 10 mmol) produced a crude mixture of **38b**−**41b**. Column chromatography of the mixture gave a fraction (0.35 g) containing 60% of **40b** in a mixture with other isomers: ^{13}C NMR (aliphatic) δ 8.3, 17.9, 22.2, 28.1, 34.9, 47.8, 50.2, 53.5, 69.2.

The second fraction gave a mixture of **38b** and **39b** (1.91 g). Trituration of the mixture with ether (10 mL) caused precipitation of **38b** (0.95 g, 29%) as colorless prisms: mp 114 °C; ^{1}H NMR δ 0.64 (t, J = 7.4 Hz, 3 H), 0.95 (d, J = 6.8 Hz, 3 H), 1.45 (m, 1 H), 1.58 (m, 1 H), 1.95 (m, 1 H), 2.07 (m, 1 H), 2.70−2.94 (m, 3 H), 3.20 (m, 2 H), 3.45 (m, 1 H), 5.83 (d, J = 4.3 Hz, 1 H), 6.33−6.46 (m, 2 H), 6.88 (m, 1 H), 6.94 (d, J = 6.1 Hz, 1 H), 7.29 (m, 2 H), 8.06 (m, 1 H); ^{13}C NMR δ 7.7, 17.4, 22.1, 22.3, 28.0, 34.4, 47.2, 63.2, 63.3, 111.3, 115.7, 120.0, 123.0 (2 C), 123.6, 126.8, 126.9, 129.2, 132.3, 142.6, 146.4. Anal. Calcd for $C_{21}H_{24}N_4$: C, 75.87; H, 7.28; N, 16.85. Found: C, 76.25; H, 7.49; N, 16.83.

Evaporation of the filtrate from **38b** gave a mixture of **39b** and **38b** (0.96 g, ratio 2:1): ^{13}C NMR δ of **39b** 13.1, 15.4, 21.1, 22.3, 27.9, 35.8, 50.2, 62.1, 64.6, 111.2, 115.3, 116.6, 120.0, 122.3, 123.6, 125.8, 126.8, 128.9, 131.6, 141.1, 146.8.

***trans,trans*-1-(Benzotriazol-1-yl)-3-butyl-2-propyljulolidine (38c).** Using the procedure above, condensation of 1,2,3,4-tetrahydroquinoline (1.3 mL, 10 mmol) with valeraldehyde (2.2 mL, 20 mmol) and benzotriazole (1.19 g, 10 mmol) gave a crude mixture of **38c**−**41c**. Column chromatography (toluene) of the mixture gave a fraction containing 70% of **38c** allowing its characterization: ^{13}C NMR δ 13.3, 14.1, 20.2, 21.8, 22.2, 27.3, 28.3, 29.9, 34.9, 39.3, 48.9, 60.7, 61.2, 111.7, 115.1, 119.7, 122.0 (2 C), 123.2, 126.7, 129.9 (2 C), 132.8, 141.7, 146.1. Anal. Calcd for $C_{25}H_{32}N_4$: C, 77.28; H, 8.30; N, 14.42. Found: C, 77.46; H, 8.69; N, 14.28.

1-(Benzotriazol-1-yl)-3-methyljulolidines (38d and 39d). Using the procedure above, condensation of 1,2,3,4-tetrahydroquinoline (1.3 mL, 10 mmol) with acetaldehyde (1.7 mL, 30 mmol) and benzotriazole (1.19 g, 10 mmol) gave a crude mixture of **38d**−**41d**. Column chromatography of the mixture gave the main fraction consisting of **38d** and **39d** (approximately 1:1): ^{13}C NMR δ (16.5), 20.0, (21.9), 22.2, (27.7), 27.7, (34.6), 37.4, 45.8, (47.5), (52.0), 52.1, (55.0), 57.2, (111.1), 111.2, (115.6), 116.5, 118.0, 119.8, (119.8), 122.4, 123.5, (123.5), (125.1), 125.5, (125.7), 126.7, (128.0), (128.8), 129.1, (129.3), 131.6, (131.6), (141.5), 143.3, 146.5 (146.5); HRMS calcd for $C_{19}H_{20}N_4$ (M^+) 304.1688, found 304.1690.

***trans*-2-Phenyl-3-(phenylmethyl)julolidine (42a).** Reduction of a crude mixture of **38a**−**41a** (4.56 g, 10 mmol) with lithium aluminum hydride (0.76 g, 20 mmol) according to the procedure for **31a** and recrystallization of the crude product from ethanol gave pure **42a** (2.95 g, 87%) as fine colorless needles: mp 98−100 °C; ^{1}H NMR δ 1.70−1.90 (m, 2 H), 2.64−2.86 (m, 4 H), 2.91−3.04 (m, 2 H), 3.13 (dd, J = 5.7, 13.5 Hz, 1 H), 3.23 (ddd, J = 3.6, 9.6, 11.1 Hz, 1 H), 3.33−3.44 (m, 2 H), 6.53 (t, J = 7.5 Hz, 1 H), 6.81−6.97 (m, 3 H), 7.00 (m, 2 H), 7.08−7.19 (m, 3 H), 7.20−7.40 (m, 4 H); ^{13}C NMR δ 21.9, 28.2, 28.5, 37.4, 38.4, 49.3, 65.3, 115.1, 118.6, 121.4, 125.9, 126.2, 126.8, 127.4 (3 C), 128.1 (2 C), 128.5 (2 C), 129.2 (2 C), 139.3, 141.1, 145.6. Anal. Calcd for $C_{25}H_{25}N$: C, 88.45; H, 7.42; N, 4.13. Found: C, 88.44; H, 7.60; N, 4.27.

***trans*-2-Methyl-3-ethyljulolidine (42b).** Reduction of a crude mixture of **38b**−**41b** (3.32 g, 10 mmol) with lithium aluminum hydride (0.76 g, 20 mmol) according to the procedure for **31a** and column chromatography of the crude product (hexane) gave pure **42b** (1.85 g, 86%) as an oil: ^{1}H NMR δ

0.90 m, 6 H), 1.36 (m, 1 H), 1.64 (m, 1 H), 1.90 (m, 2 H), 2.00 (m, 1 H), 2.28 (d, J = 16.2 Hz, 1 H), 2.66 (m, 1 H), 2.73 (m, 2 H), 2.89 (dd, J = 5.3, 16.2 Hz, 1 H), 3.13 (dt, J = 11.5, 4.7 Hz, 1 H), 3.41 (ddd, J = 7.4 Hz, 1 H), 6.41 (t, J = 7.3 Hz, 1 H), 6.76 (d, J = 7.3 Hz, 2 H); ^{13}C NMR δ 10.5, 19.3, 22.1, 25.2, 26.3, 28.3, 30.1, 49.6, 65.7, 114.2, 118.1, 120.4, 126.7, 127.8, 140.6. Anal. Calcd for: $C_{15}H_{21}N$: C, 83.67; H, 9.83; N, 6.50. Found: C, 83.30; H, 9.91; N, 6.65.

***trans*-2-Propyl-3-butyljulolidine (42c).** Reduction of a crude mixture of **38c**−**41c** (3.89 g, 10 mmol) with lithium aluminum hydride (0.76 g, 20 mmol) according to the procedure for **31a** and column chromatography of the crude product (hexane) gave pure **42c** (2.45 g, 90%): oil; ^{1}H NMR δ 0.88 (m, 6 H), 1.20−1.45 (m, 9 H), 1.65 (m, 1 H), 1.80 (m, 1 H), 1.93 (m, 2 H), 2.40 (d, J = 16.3 Hz, 1 H), 2.74 (m, 2 H), 2.80−2.94 (m, 2 H), 3.14 (m, 1 H), 3.42 (m, 1 H), 6.43 (t, J = 7.4 Hz, 1 H), 6.77 (m, 2 H); ^{13}C NMR δ 14.1, 14.2, 20.5, 22.1, 22.9, 28.1, 28.3, 28.5, 32.0, 32.2, 34.9, 49.5, 62.3, 114.2, 118.2, 120.3, 126.7, 127.7, 140.7. Anal. Calcd for $C_{19}H_{29}N$: C, 84.07; H, 10.77; N, 5.16. Found: C, 83.72; H, 10.94; N, 5.08.

3-Methyljulolidine (42d). Reduction of a crude mixture of **38d**−**41d** (3.04 g, 10 mmol) with lithium aluminum hydride (0.76 g, 20 mmol), according to the procedure for **31a**, and column chromatography of the crude product (hexane/ether, 9:1) gave pure **42d** (1.74 g, 93%): colorless oil; ^{1}H NMR δ 1.11 (d, J = 6.4 Hz, 3 H), 1.71 (qt, J = 6.4, 3.7 Hz, 1 H), 1.92 (m, 3 H), 2.57−2.86 (m, 4 H), 3.04 (dt, J = 11.3, 5.0 Hz, 1 H), 3.25−3.38 (m, 2 H), 6.44 (t, J = 7.4 Hz, 1 H), 6.76 (m, 2 H); ^{13}C NMR δ 17.3, 22.1, 23.7, 27.8, 28.1, 47.8, 52.7, 114.8, 120.8, 121.2, 126.8, 127.0, 141.6. Anal. Calcd for $C_{13}H_{17}N$: C, 83.37; H, 9.15; N, 7.48. Found: C, 83.38; H, 9.31; N, 7.44.

***trans*-2-Phenyl-3-(phenylmethyl)-1-(phenylimino)julolidine (43a).** Reaction of a crude mixture of **38a**−**41a** (4.56 g, 10 mmol) with sodium hydride (0.48 g, 20 mmol), according to a procedure analogous to that for **35b**, gave crude **43a** which was purified by recrystallization from toluene to give pure **43a** (3.95 g, 92%) as yellow prisms: mp 128 °C; ^{1}H NMR δ 1.60−1.80 (m, 2 H), 2.66 (m, 2 H), 2.74 (dd, J = 8.0, 13.5 Hz, 1 H), 2.80−2.93 (m, 2 H), 3.09 (dd, J = 6.9, 13.2 Hz, 1 H), 3.40 (m, 1 H), 3.71 (s, 1 H), 6.54 (d, J = 7.7 Hz, 2 H), 6.68 (t, J = 7.4 Hz, 1 H), 6.88 (m, 2 H), 6.94 (t, J = 6.8 Hz, 1 H), 7.05−7.30 (m, 11 H), 8.11 (d, J = 7.9 Hz, 1 H); ^{13}C NMR δ 21.5, 27.5, 36.7, 45.2, 49.8, 67.9, 115.7, 118.5, 120.4 (2 C), 122.8, 123.0, 125.3, 126.4, 126.5, 127.6 (2 C), 128.2 (2 C), 128.37 (2 C), 128.43 (2 C), 129.3 (2 C), 132.0, 138.3, 141.0, 143.2, 150.5, 161.9. Anal. Calcd for $C_{31}H_{28}N_2$: C, 86.88; H, 6.59; N, 6.54. Found: C, 86.58; H, 6.62; N, 6.37.

***trans*-3-Ethyl-2-methyl-1-(phenylimino)julolidine (43b).** Reaction of a crude mixture of **38b**−**41b** (3.32 g, 10 mmol) with sodium hydride (0.48 g, 20 mmol) according to a procedure analogous to that for **35b** gave a crude **43b** which was recrystallized from toluene to give pure **43b** (2.53 g, 83%) as yellow prisms: mp 126−127 °C; ^{1}H NMR δ 0.80 (t, J = 7.5 Hz, 3 H), 1.10 (d, J = 6.9 Hz, 3 H), 1.41 (m, 1 H), 1.66 (m, 1 H), 1.99 (m, 2 H), 2.65−2.77 (m, 4 H), 3.25 (dt, J = 11.6, 4.6 Hz, 1 H), 3.43 (dt, J = 11.2, 6.1 Hz, 1 H), 6.56 (t, J = 7.5 Hz, 1 H), 6.78 (dd, J = 1.2, 8.4 Hz, 2 H), 7.00−7.07 (m, 2 H), 7.31 (t, J = 7.8 Hz, 2 H), 7.86 (dd, J = 1.6, 7.9 Hz, 1 H); ^{13}C NMR δ 10.7, 17.8, 21.7, 22.7, 27.6, 33.0, 49.6, 67.0, 115.0, 116.5, 119.8 (2 C), 121.9, 122.6, 125.4, 128.7 (2 C), 131.8, 142.6, 151.6, 166.2. Anal. Calcd for $C_{21}H_{24}N_2$: C, 82.85; H, 7.95; N, 9.20. Found: C, 82.62; H, 8.09; N, 9.24.

***trans*-3-Butyl-2-propyl-1-(phenylimino)julolidine (43c).** Starting from a crude mixture of **38c**−**41c** (3.89 g, 10 mmol) and sodium hydride (0.48 g, 20 mmol) and following a procedure analogous to that for **35b** produced crude **43c**. Column chromatography of the crude product (toluene) gave pure **42c** (3.15 g, 87%) as a yellow powder: mp 90−92 °C; ^{1}H NMR δ 0.71 (t, J = 7.2 Hz, 3 H), 0.88 (t, J = 7.5 Hz, 3 H), 1.04−1.68 (m, 10 H), 1.98 (m, 2 H), 2.57 (m, 1 H), 2.74 (m, 2 H), 2.95 (m, 1 H), 3.22 (m, 1 H), 3.42 (m, 1 H), 6.55 (t, J = 6.9 Hz, 1 H), 6.76 (d, J = 7.8 Hz, 2 H), 7.01 (m, 2 H), 7.29 (m, 2 H), 7.83 (d, J = 7.8 Hz, 1 H); ^{13}C NMR δ 13.9, 14.0, 20.1, 21.7, 22.8, 27.5, 28.4, 29.7, 32.9, 38.4, 49.4, 61.8, 115.0, 117.0, 119.9 (2 C), 121.8, 122.5, 125.3, 128.5 (2 C), 131.7, 142.7, 151.5, 165.9. Anal. Calcd for $C_{25}H_{32}N_2$: C, 83.28; H, 8.95; N, 7.77. Found: C, 883.32; H, 9.07; N, 7.75.

3-Methyl-1-(phenylimino)julolidine (43d). Reaction of a crude mixture of **38d**−**41d** (3.04 g, 10 mmol) with sodium hydride (0.48 g, 20 mmol), according to a procedure analogous to that for **35b**, gave a crude product which was purified by column chromatography (toluene) to give pure **43d** (2.42 g, 87%) as fine yellow needles: mp 118−119 °C; ^{1}H NMR δ 1.08 (d, J = 6.3 Hz, 3 H), 2.02 (m, 2 H), 2.52 (dd, J = 3.3, 15.0 Hz, 1 H), 2.63 (dd, J = 5.1, 15.3 Hz, 1 H), 2.77 (m, 2 H), 3.15 (m, 1 H), 3.25−3.50 (m, 2 H), 6.62 (t, J = 7.5 Hz, 1 H), 6.78 (d, J = 7.5 Hz, 2 H), 7.04 (m, 2 H), 7.32 (t, J = 7.7 Hz, 2 H), 7.95 (d, J = 7.5 Hz, 1 H); ^{13}C NMR δ 14.6, 21.8, 27.4, 34.5, 47.8, 53.8, 115.9, 119.1, 120.1 (2 C), 122.7, 122.9, 124.6, 128.7 (2 C), 132.2, 144.0, 151.6, 161.6. Anal. Calcd for $C_{19}H_{20}N_2$: C, 82.57; H, 7.29; N, 10.14. Found: C, 82.37; H, 7.64; N, 10.02.

***trans,trans*-1-Methyl-3-phenyl-2-(phenylmethyl)julolidine (45a).** Reaction of pure **38a** (1.85 g, 4 mmol) with methylmagnesium iodide (10 mL of an ethereal solution, 20 mmol), according to the procedure for **32a**, gave **45a** (0.95 g, 67%) as tiny needles: mp 109 °C; ^{1}H NMR δ 1.34 (d, J = 7.2 Hz, 3 H), 1.83 (m, 1 H), 1.95 (m, 1 H), 2.74 (t, J = 5.6 Hz, 2 H), 2.81 (t, J = 5.0 Hz, 1 H), 2.88−3.03 (m, 4 H), 3.31 (ddd, J = 4.2, 9.7, 11.0 Hz, 1 H), 3.55 (q, J = 6.3 Hz, 1 H), 6.61 (t, J = 7.4 Hz, 1 H), 6.88 (d, J = 7.3 Hz, 1 H), 7.00 (dd, J = 1.6, 8.1 Hz, 2 H), 7.10−7.30 (m, 9 H); ^{13}C NMR δ 22.1, 22.5, 28.3, 36.0, 37.6, 48.8, 50.0, 65.5, 115.7, 122.8, 125.5, 126.0, 126.1, 126.5, 126.6, 127.7 (2 C), 128.3 (4 C), 129.3 (2 C), 139.6, 141.3, 146.3. Anal. Calcd for: $C_{26}H_{27}N$: C, 88.34; H, 7.70; N, 3.96. Found: C, 88.18; H, 7.86; N, 3.95.

***trans,trans*-3-Ethyl-2-methyl-1-phenyljulolidine (45b).** An ethereal solution of phenylmagnesium bromide (15 mL, 30 mmol) was added to a solution of crude **38a**−**41a** (3.32 g, 10 mmol) in toluene (40 mL), stirred under nitrogen, and heated to reflux. The ether was distilled off, and the residue was additionally heated at reflux for 30 min. After being cooled to room temperature, the reaction mixture was poured into ice−water (100 g), neutralized with 10% acetic acid, and extracted with ether, followed by 10% Na_2CO_3, and dried over anhydrous Na_2CO_3. The solvent was evaporated, and the residue was purified by column chromatography (hexane/ether, 5:1) to give pure **45a** (2.46 g, 84%) as a colorless powder: mp 70−76 °C; ^{1}H NMR δ 0.67 (t, J = 7.4 Hz, 3 H), 0.95 (d, J = 6.7 Hz, 3 H), 1.40−1.65 (m, 3 H), 1.80−2.15 (m, 2 H), 2.31 (m, 1 H), 2.77 (m, 1 H), 2.90 (m, 1 H), 3.05 (m, 1 H), 3.42 (ddd, J = 4.0, 8.7, 11.0 Hz, 1 H), 3.67 (d, J = 6.9 Hz, 1 H), 6.45 (m, 2 H), 6.84 (m, 1 H), 7.10−7.40 (m, 5 H); ^{13}C NMR δ 8.3, 20.3, 22.6, 22.8, 28.3, 35.9, 47.7, 49.6, 65.1, 114.9, 122.0, 123.1, 125.9, 127.0, 128.1 (2 C), 128.2, 129.2 (2 C), 142.4, 145.3. Anal. Calcd for $C_{21}H_{25}N$: C, 86.55; H, 8.65; N, 4.81. Found: C, 86.71; H, 8.79; N, 4.76.

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