Preparations of Trisubstituted Hydrazines and Pyrazolidines from *N*-(1-Benzotriazolylalkyl)hydrazines

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Received May 22, 1997[⊗]

Reactions of *N*,*N*′-disubstituted hydrazines with benzotriazole and aldehydes give *N*-(α-benzotriazoylalkyl)-*N*,*N*′-disubstituted hydrazines which on treatment with organometallic reagents form *N*-alkyl-*N*,*N*′-disubstituted hydrazines in good yields. *N*-(Benzotriazolylalkyl)-*N*,*N*′-disubstituted hydrazines and electron-rich olefins, in the presence of zinc bromide catalyst, generate *N*,*N*′-disubstituted pyrazolidines in moderate to good yields.

Introduction

Hydrazines are important because of their many applications in organic synthesis and industry. Trisubstituted hydrazines are usually prepared by (i) carbanion addition to the N═N bond of an azo compound using a silyl ester enolate[1] or a lithium amide enolate[2,3] or of an alkyl- or aryllithium,[4] routes which are limited by the type and accessibility of the appropriate nucleophiles; (ii) the alkylation of mono- or disubstituted hydrazines, which rarely gives good yields;[5] (iii) electrophilic aminations of amines;[6,7] and (iv) additions of organometallic reagents to hydrazones.[8]

Pyrazolidines have been widely investigated as fungicides, herbicides, antiinflammatories, antibacterials, anesthetics, and anticonvulsants.[9,10] General methods for the synthesis of pyrazolidines include (i) 1,3-dipole azomethine−imine additions to carbon−carbon double bonds;[11−13] (ii) reductions of pyrazolines, pyrazoles, pyrazolones, and pyrazolium salts;[14,15] and (iii) cyclizations of hydrazines with halogenated compounds.

Benzotriazole has been extensively used as a synthetic auxiliary in organic synthesis.[16−18] *N*-Alkylbenzotriazoles with an electron-donor group at the α-position of the *N*-alkyl group can undergo facile replacement of the benzotriazolyl (Bt) group by nucleophiles such as Grignard reagents or electron-rich alkenes. We now report new preparations of (i) trisubstituted hydrazines in high yields by the reactions of *N*-(1-benzotriazolylalkyl)-*N*,*N*′-disubstituted hydrazines with Grignard reagents or organozinc reagents and (ii) substituted pyrazolidines by the reactions of *N*-(1-benzotriazolylalkyl)-*N*,*N*′-diarylhydrazines with electron-rich alkenes. We recently reported the preparation of trisubstituted and tetrasubstituted hydrazines in yields of 32−57% by additions of α-lithio-1-alkylbenzotriazoles to the N═N bond of azobenzenes, followed by substitution of the benzotriazole residue by Grignard reagents.[19] The present investigations comprise a significant generalization and extension of this methodology.

Results and Discussion

Synthesis of *N*-(1-Benzotriazolylalkyl)-*N*,*N*′-disubstituted Hydrazines. *N*-(1-Benzotriazolylalkyl)-*N*,*N*′-diphenylhydrazines **2a**−**d** were prepared in good yields from *N*,*N*′-diphenylhydrazine (**1a**), benzotriazole, and the appropriate aldehyde in methylene chloride at rt in the presence of molecular sieves as dehydrating agent. These reactions gave mixtures of benzotriazol-1-yl and benzotriazol-2-yl isomers, and these two isomers are in equilibrium in solution.[20] The ratio of Bt-1 and Bt-2 isomers was 8 to 1, according to the integration of the ^{1}H NMR spectrum recorded immediately after dissolving the solid in $CDCl_3$. When the ^{1}H NMR spectrum of the same sample was recorded 30 min later, the ratio had changed to 2 to 1. Considering that both Bt-1 and Bt-2 groups are good leaving groups, the mixture of the two isomers was directly used for further reactions without separation.

1,4-Diphenyl-4-[(benzotriazol-1-yl)methyl]semicarbazide (**2e**) and *N*-phenyl-*N*-[(benzotriazol-1-yl)methyl]-*N*′-propionylhydrazine (**2f**) were prepared from corresponding hydrazines, benzotriazole, and paraformaldehyde under reflux in benzene, with a Dean−Stark trap to remove the water produced, and both of them gave only

[⊗] Abstract published in *Advance ACS Abstracts,* October 1, 1997.

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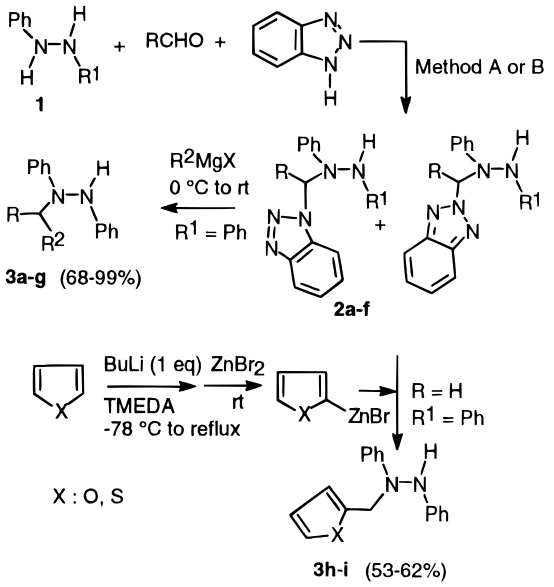
S0022-3263(97)00911-0 CCC: $14.00

Scheme 1



For description of R, R^1, and R^2, see Table 1.

Method A: CH_2Cl_2/rt, 3 Å molecular sieves for **2a-d**.
Method B: benzene/reflux, Dean-Stark trap for **2e-f**.

Table 1. Preparation of *N*-(1-Benzotriazolylalkyl)-*N,N'*-disubstituted Hydrazines 2

compd	R^1	R	time (h)	yield (%)	mp (°C)	Bt-1/ Bt-2[a]
2a	Ph	H	24	88	137−138	97:3
2b	Ph	Et	120	69	127−132	5:2
2b	Ph	*n*-C_3H_7	120	64	122−126	2:1
2d	Ph	Cyclohexyl	120	70	153−156	2:1
2e	PhNHCO	H	48	61[b]	183−184	
2f	C_2H_5CO	H	48	61[b]	157−158	

[a] The ratio of Bt-1/Bt-2 observed just after concentration. [b] In refluxing benzene with Dean−Stark trap.

Table 2. Preparation of Trisustituted Hydrazines 3

compd	R	R^2	yield (%)	mp (°C)
3a	H	Et	79	oil
3b	Et	Et	81	69−70
3c	*n*-C_3H_7	Et	80	59−60
3d	cyclohexyl	Et	70	117−119
3e	*n*-C_3H_7	Ph	68	117−118
3f	H	Allyl	99	oil
3g	*n*-C_3H_7	Allyl	91	oil
3h	H	2-furyl	62	59−60
3i	H	2-thiophenyl	53	60−62

Bt-1 isomers. The results of these reactions are listed in Scheme 1 and Table 1.

Preparation of Trisubstituted Hydrazines 3. *N*-(1-Benzotriazolylalkyl)-*N,N'*-diphenylhydrazines **2a**−**d** reacted with Grignard reagents at 0 °C followed by warming to room temperature to give trisubstituted hydrazines **3a**−**g** in good yields. Treatments of compound **2a** with 2-furyl and 2-thiophenyl organozinc reagents gave **3h** and **3i** in 62% and 53% yields, respectively (Table 2).

Preparation of Substituted Pyrazolidines 4 and 5. We have reported reactions of *N*-(1-benzotriazolylalkyl)aniline both with electron-rich[21] and unactivated alkenes in the presence of Lewis acid[22,23] to give tetrahydroquinolines. In contrast, we now find that treatment

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Scheme 2

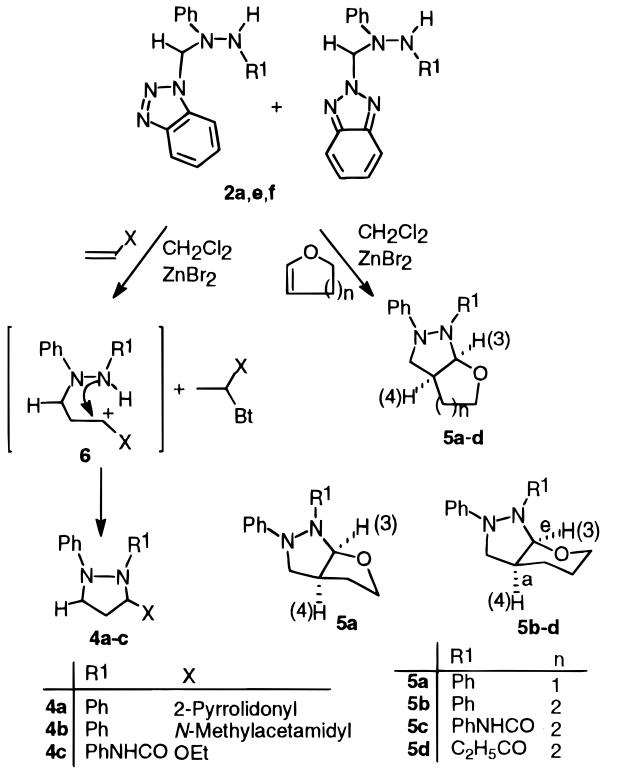

Table 3. Synthesis of Pyrazolidines 4 and 5

compd	R^1	X (for **4**) or *n* (for **5**)	time (h)	yield (%)	mp (°C)
4a	Ph	2-pyrrolidonyl	30	53	107−109
4b	Ph	*N*-methylacetamidyl	24	43	142−143
4c	PhNHCO	OEt	50	60	118−120
5a	Ph	n = 1	24	84	139−142
5b	Ph	n = 2	24	83	168−171
5c	PhNHCO	n = 2	48	60	221−224
5d	C_2H_5CO	n = 2	48	39	124−126

of *N*-(1-benzotriazolylmethyl)-*N,N'*-disubstituted hydrazines **2a** with electron rich alkenes in the presence of Lewis acids gives pyrazolidines **4a**,**b**. Rather than the *ortho*-carbon of the phenyl ring, the nitrogen atom in hydrazines **2** readily attacks the cationic intermediates **6** formed from starting material **2** and the alkene (Scheme 2 and Table 3). In these reactions, **2** → **4**, 2 equiv of alkene was needed because 1 equiv was consumed by the benzotriazolyl anion which is formed simultaneously.

Treatment of **2a** with cyclic vinyl ethers gave *cis*-fused bicyclic compounds **5a** and **5b** exclusively; the *cis* relationship of H-3 and H-4 was determined by NOE experiments and the coupling H-3/H-4 constants in the ^{1}H NMR. These are 6.1 Hz for **5a** and 1.7 Hz for **5b**, consistant with literature reports[24−26] for furan five:five and five:six ring system, respectively. Similarly **2e** was reacted with vinyl ethyl ether and 3,4-dihydropyran under similar conditions to give good yields of the expected cyclic pyrazolines **4c** and **5c**, respectively.

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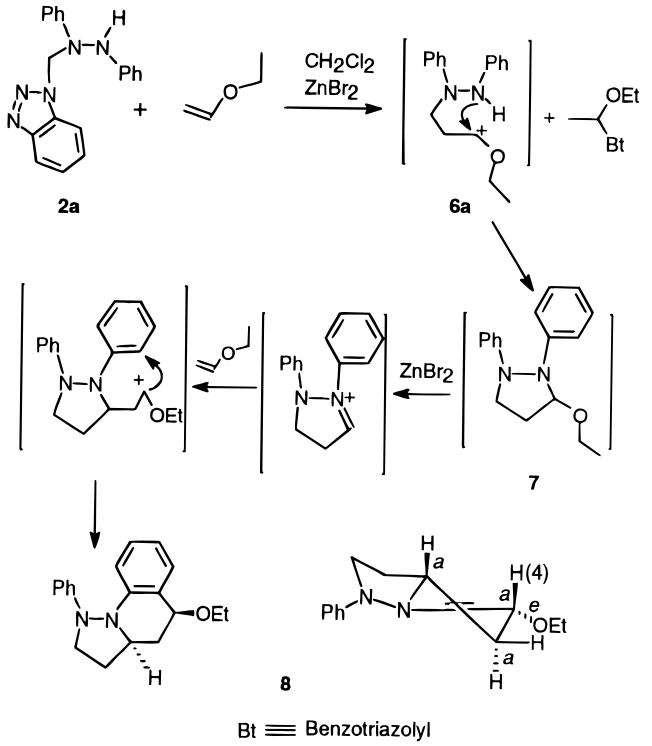
Scheme 3



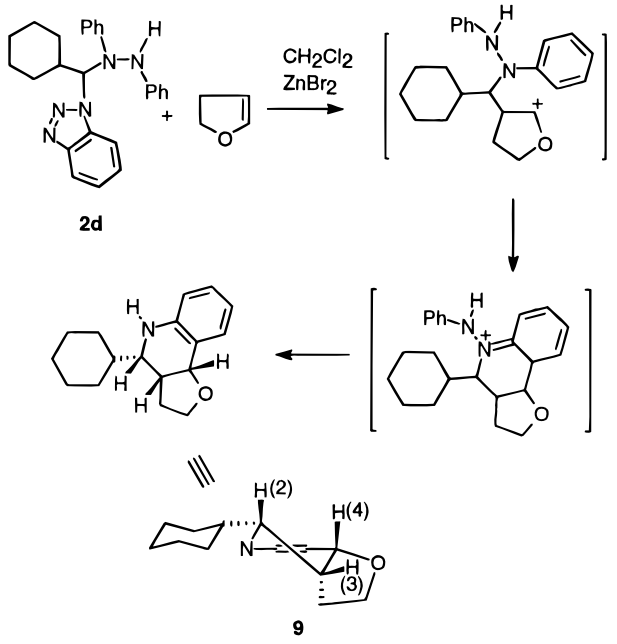
Compound **5c** also has the *cis* configuration, which was confirmed by NOE, and the coupling constant of H-3 and H-4 is 3.8 Hz.

When excess of vinyl ethyl ether was reacted with **2a**, 4-ethoxy-{1-phenyl-[2,3-a]-pyrazolido}tetrahydroquinoline (**8**) was obtained in 31% yield. The formation of **8** can be explained as depicted in Scheme 3: *N*-(1-benzotriazolylmethyl)-*N*,*N*′-diphenylhydrazine and vinyl ethyl ether in the presence of zinc bromide first gave compound **7**, which is unstable under acidic conditions, and then reacted further with a second equivalent of vinyl ethyl ether followed by ring-closure to give compound **8**. From the ^{1}H NMR of **8**, the proton of the ring 4-position CH to which the ethoxy group is attached is assigned to the signal at 4.45 ppm. This signal is a double-doublet with $J = 4.1$ and 10.2 Hz. This means that there is one axial−axial coupling and thus that the ethoxy group is equatorial and *trans* to the proton at the ring junction.

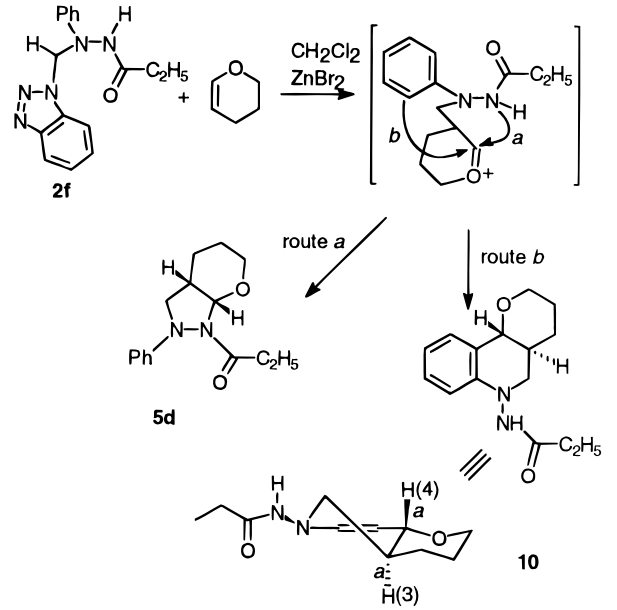
Treatment of *N*-(1-benzotriazolylcyclohexylmethyl)-*N*,*N*′-diphenylhydrazine (**2d**) with 3,4-dihydrofuran in the presence of zinc bromide gave 2-cyclohexyl-2,3,3a,4,5,9b-hexahydrofuro[3,2-*c*]quinoline (**9**) (39%), with cleavage of the N−N bond and the phenylamino group acting as a leaving group (Scheme 4). In the ^{1}H NMR spectrum of **9**, the doublet ($J = 8.0$ Hz) at 5.11 ppm was assigned to the 4-position proton. The coupling indicates[26] that the configuration between the 3- and 4-position protons is *cis*. Furthermore, the 2-position proton was at 3.11 ppm as a doublet ($J = 2.5$ Hz), which showed that the configuration between 2- and 3-position is also *cis*.[26]

Treatment of **2f** with electron-rich alkene under the above conditions gave two products, **5d** and **10**, in 39% and 44%, respectively (Scheme 5). **5d** is also of *cis* configuration, as the coupling constant of H-3 and H-4 is 3.9 Hz. Compound **10** has a *trans* configuration, coupling constant of H-3 and H-4 being 10.2 Hz. In this reaction, the nucleophilicities of the amide nitrogen and *ortho*-carbon at the phenyl ring are comparable.

Scheme 4



Scheme 5



In conclusion, *N*-(1-benzotriazolylalkyl)-*N*,*N*′-disubstituted hydrazines **2** are useful intermediates which provide convenient and novel methods for preparation of trisubstituted hydrazines **3** and substituted pyrazolidines **4** and **5**.

Experimental Section

General Comments. Melting points were determined with a Koefler hot-stage apparatus without correction. The ^{1}H NMR and ^{13}C NMR spectra were recorded on a 300 MHz spectrometer in $CDCl_3$ with tetramethylsilane or the solvent as the internal reference. Tetrahydrofuran (THF) was distilled from sodium/benzophenone prior to use. Grignard reactions were carried out under an atmosphere of dry nitrogen. All glassware was oven-dried. All moisture-sensitive reagents were transferred by means of predried syringes.

General Procedure for the Synthesis of *N*-(1-Benzotriazolylalkyl)-*N*,*N*′-disubstituted Hydrazines 2. Method A (2a−d). A mixture of benzotriazole (23.8 g, 0.2 mol), aldehyde (0.2 mol), and 1,2-diphenylhydrazine (18.4 g, 0.1 mol)

in methylene chloride (400 mL) was stirred at rt in the presence of molecular sieves (3 Å, 10 g) for an appropriate time until no hydrazine was left. The mixture was washed with aqueous NaOH (2 N, 2 × 100 mL) and water (2 × 100 mL) and the aqueous phase was extracted with ethyl acetate. The combined organic layers were dried over anhydrous sodium sulfate. After the removal of the solvent, the residue was recrystallized from ether to give the expected compounds.

***N*-(Benzotriazol-1-ylmethyl)-*N*,*N*′-diphenylhydrazine (2a)**: ^{1}H NMR ($CDCl_3$) δ 6.13 (s, 1 H), 6.29 (br s, 2 H), 6.87−6.94 (m, 4 H), 7.19−7.30 (m, 6 H), 7.34 (t, 1 H, J = 7.5 Hz), 7.43 (t, 1 H, J = 7.5 Hz), 7.54 (d, 1 H, J = 8.1 Hz), 8.02 (d, 1 H, J = 8.1 Hz); ^{13}C NMR ($CDCl_3$) δ 64.0, 109.8, 112.8, 114.5, 120.0, 120.7, 121.2, 124.1, 127.8, 129.4, 129.6, 133.8, 145.9, 146.2, 146.9. Anal. Calcd for $C_{19}H_{17}N_5$: C, 72.35; H, 5.44; N, 22.22. Found: C, 72.32; H, 5.58; N, 22.45.

***N*-(1-Benzotriazolylpropyl)-*N*,*N*′-diphenylhydrazine (2b)**: ^{1}H NMR ($CDCl_3$) δ (NMR data of Bt-2 isomer are listed in square brackets) 0.94 (t, 3 H, J = 7.4 Hz) [0.90 (t, 3 H, J = 7.4 Hz)], 2.52−2.65 (m, 2 H) [2.34−2.50 (m, 2 H)], 6.33 (br s, 1 H), 6.57 (t, 1 H, J = 7.1 Hz) [6.70 (t, 1 H, J = 7.0 Hz)], 6.80−7.47 (m, 12 H), 7.49 (d, 1 H, J = 8.5 Hz), 8.02 (d, 1 H, J = 8.2 Hz) [7.82−7.86 (m, 2 H)]; ^{13}C NMR ($CDCl_3$) δ 10.6 [10.2], 26.0 [26.9], 78.1 [82.8], 109.9, 112.3 [111.7], 116.3 [115.4], [118.2], [119.2], 119.6, 120.0, 122.0 [121.4], 123.9, [126.3], 127.5, 129.1, 129.3, 133.3, [143.7], 145.5, 147.7, 147.8 [148.2]. Anal. Calcd for $C_{21}H_{21}N_5$: C, 73,43; H, 6.17; N, 20.40. Found: C, 73.31; H, 6.41; N, 20.25.

***N*-(1-Benzotriazolylbutyl)-*N*,*N*′-diphenylhydrazine (2c)**: ^{1}H NMR ($CDCl_3$) δ (NMR data of Bt-1 isomer are listed in square brackets, the ratio of Bt-2 to Bt-1 isomers is 5) 0.89 (t, 3 H, J = 7.5 Hz) [0.87 (t, 3 H, J = 7.3 Hz)], 1.10−1.30 (m, 1 H), 1.32−1.50 (m, 1 H), 2.28−2.41 (m, 1 H), 2.43−2.59 (m, 1 H), 6.27 (br s, 1 H), 6.66 (t, 1 H, J = 7.2 Hz), 6.75−7.47 (m, 12 H), 7.48 (d, 1 H, J = 8.2 Hz), 8.01 (d, 1 H, J = 8.2 Hz) [7.80−7.86 (m, 2 H)]; ^{13}C NMR ($CDCl_3$) δ 13.4, 19.2 [18.8], 34.5 [35.3], 76.4 [81.2], 109.9, 112.3 [111.8], 116.4 [115.5], [118.2], [119.2], 119.7, 120.0, 122.0 [121.5], 123.9 [126.3], 127.5, 129.1, 129.3 [129.4], 133.2, [143.7], 145.6, 147.8 [147.7], 148.3. Anal. Calcd for $C_{22}H_{23}N_5$: C, 73,91; H, 6.49; N, 19.60. Found: C, 73.90; H, 6.53; N, 19.89.

***N*-(1-Benzotriazolyl-1-cyclohexylmethyl)-*N*,*N*′-diphenylhydrazine (2d)**: ^{1}H NMR ($CDCl_3$) δ (NMR data of Bt-2 isomer are listed in square brackets) 0.58−0.70 (m, 1 H), 0.77−1.45 (m, 6 H), 1.48−1.82 (m, 3 H), 2.18−2.30 (m, 1 H) [2.30−2.48 (m, 1 H)], 2.90−3.10 (m, 1 H) [2.69−2.86 (m, 1 H)], 6.41 (d, 1 H, J = 10.0 Hz) [6.41 (d, 1 H, J = 7.5 Hz)], 6.45 (br s, 1 H), 6.70−7.40 (m, 13 H), [7.80−7.85 (m, 2 H)], 7.97 (d, 1 H, J = 8.7 Hz); ^{13}C NMR ($CDCl_3$) δ 25.4 [25.3], 26.1 [26.0], 29.2 [28.8], 30.8 [30.6], 39.2 [39.7], 82.9 [87.7], 109.7, 112.5 [112.3], 112.8, 117.8 [117.7], 118.3 [119.1], [119.4], 119.8, 122.8 [122.1], 123.8, [126.3], 127.5, 129.1 [129.0], 129.2 [129.3], 131.2, [143.5], 145.2, 146.9 [147.4], 147.8 [149.0]. Anal. Calcd for $C_{25}H_{27}N_5$: C, 75.52; H, 6.85; N, 17.63. Found: C, 75.64; H, 6.98; N, 17.63.

Method B (for 2e,f). A mixture of benzotriazole (3.57 g, 0.03 mol), paraformaldehyde (0.90 g, 0.03 mol), and the substituted hydrazine (0.02 mol) was heated to reflux in benzene (100 mL) for 24 h with a Dean−Stark trap for removal of the formed water. The reaction mixture was washed with aqueous NaOH (1 N, 2 × 50 mL) and water (2 × 50 mL) and extracted with ethyl acetate. The combined organic layer was dried over anhydrous Na_2SO_4. After removal of the solvent, the residue was recrystallized from ethyl acetate and a white solid was obtained.

1,4-Diphenyl-4-(1-benzotriazol-1-ylmethyl)semicarbazide (2e): ^{1}H NMR ($CDCl_3$) δ 6.21 (s, 1 H), 6.28 (s, 1 H), 6.99−7.07 (m, 2 H), 7.18−7.37 (m, 10 H), 7.47 (t, 1 H, J = 7.5 Hz), 7.58 (d, 1 H, J = 8.40 Hz), 7.81 (s, 1 H), 8.01 (d, 1 H, J = 8.2 Hz); ^{13}C NMR ($CDCl_3$) δ 67.2, 109.3, 115.6, 119.7, 120.3, 123.3, 123.6, 124.5, 128.5, 128.9, 129.8, 133.1, 137.5, 145.9, 146.2, 155.2. Anal. Calcd for $C_{20}H_{18}N_6O$: C, 67.01; H, 5.07; N, 23.46. Found: C, 67.22; H, 5.20; N, 23.23.

***N*-Phenyl-*N*-(benzotriazol-1-ylmethyl)-*N*′-propionylhydrazine (2f)**: ^{1}H NMR ($CDCl_3$) (at 70 °C) δ 1.08 (t, 3 H, J = 7.5 Hz), 2.21 (q, 2 H, J = 7.2 Hz), 6.38 (s, 2 H), 6.86 (t, 1 H, J = 6.9 Hz), 7.12 (d, 2 H, J = 8.1 Hz), 7.27 (t, 2 H, J = 7.5 Hz), 7.41 (t, 1 H, J = 7.5 Hz), 7.55 (t, 1 H, J = 7.5 Hz), 7.78 (d, 1 H, J = 8.4 Hz), 8.04 (d, 1 H, J = 8.1 Hz); ^{13}C NMR ($CDCl_3$) (at 70 °C) δ 9.4, 26.4, 63.8, 111.0, 112.8, 119.1, 119.7, 124.1, 127.4, 129.1, 132.9, 145.3, 146.6, 172.4. Anal. Calcd for $C_{16}H_{17}N_5O$: C, 65.05; H, 5.80; N, 23.72. Found: C, 65.31; H, 5.94; N, 23.93.

General Procedure for Preparation of Trisubstituted Hydrazines 3a−g. To a solution of *N*-(1-benzotriazolylalkyl)-*N*,*N*′-diphenylhydrazine **2a−d** (5 mmol) in THF (50 mL) was added Grignard reagent (10 mmol) dropwise at 0 °C under nitrogen. The mixture was stirred at 0 °C for 1 h and then warmed to rt for 2 h. The reaction mixture was washed with aqueous NaOH solution (2 N, 2 × 25 mL) and water (2 × 25 mL) and extracted with ethyl acetate (2 × 25 mL). The combined organic layers were dried over anhydrous sodium sulfate. After the removal of the solvent under vacuum, the residue was purified by column chromatography on silica gel to give the pure product.

***N*-Propyl-*N*,*N*′-diphenylhydrazine (3a)**: oil; lit.[27] mp 32−34 °C; ^{1}H NMR ($CDCl_3$) δ 0.93 (t, 3 H, J = 7.5 Hz), 1.63−1.71 (m, 2 H), 3.42 (t, 2 H, J = 7.0 Hz), 5.53 (s, 1 H), 6.73−6.80 (m, 4 H), 6.81−6.90 (m, 2 H), 7.15−7.22 (m, 4 H); ^{13}C NMR ($CDCl_3$) δ 11.5, 19.4, 53.9, 112.2, 112.8, 118.4, 119.4, 129.2, 129.3, 147.6, 149.8. Anal. Calcd for $C_{15}H_{18}N_2$: C, 79.59; H, 8.02; N, 12.38. Found: C, 79.49; H, 8.04; N, 12.61.

***N*-3-Pentyl-*N*,*N*′-diphenylhydrazine (3b)**: ^{1}H NMR ($CDCl_3$) δ 0.75−1.14 (m, 6 H), 1.48−1.60 (m, 2 H), 1.62−1.75 (m, 2 H), 3.66 (quintet, 1 H, J = 6.3 Hz), 5.33 (s, 1 H), 6.72−6.83 (m, 4 H), 6.84−6.90 (m, 2 H), 7.12−7.22 (m, 4 H); ^{13}C NMR ($CDCl_3$) δ 12.1, 24.3, 65.5, 112.2, 114.1, 118.8, 119.1, 129.2, 148.7, 150.8. Anal. Calcd for $C_{17}H_{22}N_2$: C, 80.26; H, 8.72; N, 11.02. Found: C, 80.51; H, 8.75; N, 10.92.

***N*-3-Hexyl-*N*,*N*′-diphenylhydrazine (3c)**: ^{1}H NMR ($CDCl_3$) δ 0.78−1.15 (m, 6 H), 1.16−1.80 (m, 6 H), 3.70−3.80 (m, 1 H), 5.31 (s, 1 H), 6.72-6.82 (m, 4 H), 6.84−6.90 (m, 2 H), 7.15−7.25 (m, 4 H); ^{13}C NMR ($CDCl_3$) δ 12.1, 14.2, 20.6, 33.7, 33.8, 63.2, 112.2, 114.1, 118.8, 119.1, 129.2, 148.7, 150.8. Anal. Calcd for $C_{18}H_{24}N_2$: C, 80.54; H, 9.01; N, 10.44. Found: C, 80.55; H, 9.07; N, 10.46.

***N*-(1-Ethyl-1-cyclohexylmethyl)-*N*,*N*′-diphenylhydrazine (3d)**: ^{1}H NMR ($CDCl_3$) δ 0.70−0.93 (m, 2 H), 1.00−1.30 (m, 6 H), 1.35−1.90 (m, 8 H), 3.48−3.58 (m, 1 H), 5.41 (s, 1 H), 6.70−6.90 (m, 6 H), 7.12−7.24 (m, 4 H); ^{13}C NMR ($CDCl_3$) δ 12.7, 22.2, 26.3, 26.5, 32.0, 40.9, 69.2, 112.4, 113.4, 118.2, 119.1, 129.1, 129.2, 148.3, 152.0. Anal. Calcd for $C_{21}H_{28}N_2$: C, 81.77; H, 9.15; N, 9.08. Found: C, 81.70; H, 9.26; N, 9.08.

***N*-(α-Propylbenzyl)-*N*,*N*′-diphenylhydrazine (3e)**: ^{1}H NMR ($CDCl_3$) δ 0.93 (t, 3 H, J = 7.5 Hz), 1.38−1.62 (m, 2 H), 1.88−2.01 (m, 1 H), 2.07−2.19 (m, 1 H), 5.00 (t, 1 H, J = 7.4 Hz), 5.09 (br s, 1 H), 6.71−6.83 (m, 4 H), 6.92−6.96 (m, 2 H), 7.10−7.28 (m, 9 H); ^{13}C NMR ($CDCl_3$) δ 14.1, 20.4, 33.6, 66.0, 112.3, 115.2, 119.1, 119.6, 127.6, 128.3, 129.2, 138.7, 148.5, 150.3. Anal. Calcd for $C_{22}H_{24}N_2$: C, 83.49; H, 7.65; N, 8.86. Found: C, 83.76; H, 7.90; N, 8.98.

***N*-3-Butenyl-*N*,*N*′-diphenylhydrazine (3f)**: ^{1}H NMR ($CDCl_3$) δ 2.43 (q, 2 H, J = 6.9 Hz), 3.59 (t, 2 H, J = 6.9 Hz), 5.06 (d, 1 H, J = 11.4 Hz), 5.11 (d, 1 H, J = 17.1 Hz), 5.63 (s, 1 H), 5.77−5.95 (m, 1 H), 6.72−6.94 (m, 6 H), 7.14−7.27 (m, 4 H); ^{13}C NMR ($CDCl_3$) δ 30.9, 51.3, 112.4, 112.9, 116.9, 118.7, 119.7, 129.4, 129.5, 136.1, 147.6, 149.6. Anal. Calcd for $C_{16}H_{18}N_2$: C, 80.62; H, 7.62; N, 11.76. Found: C, 80.82; H, 7.25; N, 11.89.

***N*-4-(1-Heptenyl)-*N*,*N*′-diphenylhydrazine (3g)**: ^{1}H NMR ($CDCl_3$) δ 0.82−1.00 (m, 3 H), 1.20−1.80 (m, 4 H), 2.22−2.60 (m, 2 H), 3.90−4.03 (m, 1 H), 5.01 (d, 1 H, J = 9.9 Hz), 5.08 (d, 1 H, J = 17.3 Hz), 5.43 (br s, 1 H), 5.76−6.02 (m, 1 H), 6.75−6.92 (m, 6 H), 7.14−7.27 (m, 4 H); ^{13}C NMR ($CDCl_3$) δ 14.1, 20.5, 34.1, 36.2, 61.2, 112.2, 114.0, 116.6, 118.9, 119.2, 129.2, 136.7, 148.6, 150.3. Anal. Calcd for $C_{19}H_{24}N_2$: C, 81.37; H, 8.63; N, 10.00. Found: C, 81.20; H, 8.83; N, 9.98.

General Procedure for Preparation of Trisubstituted Hydrazines 3h,i. To a solution of furan (10 mmol, 0.8 mL) and TMEDA (11 mmol, 1.7 mL) in THF (50 mL) was added *n*-butyllithium (11 mmol, 1.6 M, 6.9 mL) dropwise at −78 °C

(27) Berg-Nielsen, K.; Bernatek, E. *Acta Chem. Scand.* **1972**, *26*, 4130.

under nitrogen. After stirring for 2 h, the reaction mixture was warmed to reflux for 0.5 h. The solution was then cooled to rt for 1 h, and anhydrous zinc bromide (11 mmol, 2.48 g) in THF (10 mL) was added. The mixture was stirred at rt for 1 h, and a solution of *N*-(benzotriazol-1-ylmethyl)-*N*,*N*′-diphenylhydrazine (5 mmol, 1.58 g) in THF (5 mL) was added. The formed mixture was stirred at rt for 16 h. The reaction mixture was washed with aqueous NaOH solution (2 N, 2 × 25 mL) and water (2 × 25 mL) and extracted with ethyl acetate (2 × 25 mL). The combined organic layers were dried over anhydrous sodium sulfate. After the removal of the solvent under vacuum, the residue was purified by column chromatography on silica gel to give the pure product **3h** (0.82 g, yield 62%).

***N*-2-Furyl-*N*,*N*′-diphenylhydrazine (3h)**: ^{1}H NMR ($CDCl_3$) δ 4.67 (s, 2 H), 5.79 (s, 1 H), 6.21 (d, 1 H, J = 3.0 Hz), 6.30 (d, 1 H, J = 2.4 Hz), 6.80−6.85 (m, 2 H), 7.07 (d, 2 H, J = 8.1 Hz), 7.25 (t, 4 H, J = 7.5 Hz), 7.36 (s, 1 H); ^{13}C NMR ($CDCl_3$) δ 47.3, 108.7, 110.2, 112.8, 113.4, 119.2, 120.0, 129.1, 129.4, 142.4, 147.1, 149.4, 150.7. Anal. Calcd for $C_{17}H_{16}N_2O$: C, 77.24; H, 6.11; N, 10.60. Found: C, 77.62; H, 6.33; N, 10.73.

***N*-2-Thiophenyl-*N*,*N*′-diphenylhydrazine (3i)**: ^{1}H NMR ($CDCl_3$) δ 4.87 (s, 2 H), 5.64 (s, 1 H), 6.82−6.92 (m, 4 H), 6.93−6.98 (m, 2 H), 7.08 (d, 2 H, J = 6.3 Hz), 7.18−7.31 (m, 5 H); ^{13}C NMR ($CDCl_3$) δ 49.3, 113.0, 113.8, 119.5, 120.1, 125.4, 126.8, 127.0, 129.3, 129.5, 138.1, 147.0, 149.2. Anal. Calcd for $C_{17}H_{16}N_2S$: C, 72.83; H, 5.76; N, 10.00. Found: C, 72.71; H, 5.89; N, 10.01.

General Procedure for the Preparation of Pyrazolidine Derivatives 4 and 5 and Compounds 8−10. A mixture of *N*-(1-benzotriazolylalkyl)-*N*,*N*′-disubstituted hydrazine **2** (2 mmol), alkene (4 mmol), and anhydrous zinc bromide (20 mg) in dry methylene chloride (30 mL) was stirred at rt for an appropriate time. After the reaction was completed, the mixture was washed with aqueous NaOH (2 N, 2 × 15 mL) and water (2 × 15 mL) and extracted with ethyl acetate. The combined organic layers were dried over anhydrous sodium sulfate. After the removal of the solvent under vacuum, the residue was purified by column chromatography on silica gel to give the pure products.

3-Pyrrolidonyl-1,2-diphenylpyrazolidine (4a): ^{1}H NMR ($CDCl_3$) δ 1.85−1.98 (m, 2 H), 2.17−2.26 (m, 1 H), 2.36−2.48 (m, 3 H), 3.06−3.16 (m, 1 H), 3.22−3.32 (m, 1 H), 3.56−3.68 (m, 1 H), 3.89−3.98 (m, 1 H), 6.11 (t, 1 H, J = 6.5 Hz), 6.84−6.96 (m, 4 H), 7.06 (d, 2 H, J = 8.1 Hz), 7.23−7.32 (m, 4 H); ^{13}C NMR ($CDCl_3$) δ 18.1, 30.4, 31.6, 43.7, 49.1, 72.9, 113.8, 114.5, 119.7, 120.9, 129.1, 149.8, 150.0, 174.9. Anal. Calcd for $C_{19}H_{21}N_3O$: C, 74.23; H, 6.89; N, 13.68. Found: C, 74.50; H, 7.02; N, 13.77.

1,2-Diphenyl-3-(*N*-methylacetamidyl)pyrazolidine (4b): ^{1}H NMR ($CDCl_3$) δ 2.01−2.08 (m, 1 H), 2.15 (s, 3 H), 2.39−2.46 (m, 1 H), 2.76 (s, 3 H), 3.46−3.54 (m, 1 H), 3.96−4.08 (m, 1 H), 6.54 (t, 1 H, J = 4.5 Hz), 6.84−6.98 (m, 6 H), 7.22−7.28 (m, 4 H); ^{13}C NMR ($CDCl_3$) δ 22.7, 30.8, 31.0, 48.8, 75.2, 113.9, 114.1, 119.5, 120.6, 129.1, 149.9 (overlapped), 170.8. Anal. Calcd for $C_{18}H_{21}N_3O$: C, 73.18; H, 7.17; N, 14.23. Found: C, 73.48; H, 7.35; N, 14.37.

1-Phenyl-2-(phenylcarbamoyl)-3-ethoxypyrazolidine (4c): ^{1}H NMR ($CDCl_3$) δ 1.16 (t, 3 H, J = 6.9 Hz), 2.12−2.26 (m, 1 H), 2.29−2.40 (m, 1 H), 3.52−3.68 (m, 1 H), 3.70−3.85 (m, 2 H), 3.86−4.00 (m, 1 H), 5.81−5.87 (m, 1 H), 6.88−7.10 (m, 2 H), 7.15 (d, 2 H, J = 8.2 Hz), 7.22−7.36 (m, 4 H), 7.45 (d, 2 H, J = 8.0 Hz), 8.14 (br s, 1 H); ^{13}C NMR ($CDCl_3$) δ 14.8, 33.6, 53.2, 63.9, 88.4, 115.5, 119.2, 122.0, 123.3, 128.8, 129.0, 138.0, 150.9, 156.6. Anal. Calcd for $C_{18}H_{21}N_3O_2$: C, 69.42; H, 6.80; N, 13.50. Found: C, 69.40; H, 7.15; N, 13.53.

***N*,*N*′-Diphenyl-2,3,3a,4,5,6a-hexahydrofuro[2,3-*c*]pyrazole (5a)**: ^{1}H NMR ($CDCl_3$) δ 1.58−1.69 (m, 1 H), 1.97−2.22 (m, 1 H), 3.07−3.17 (m, 1 H), 3.69−3.91 (m, 4 H), 5.83 (d, 1 H, J = 6.1 Hz), 6.80−6.92 (m, 2 H), 6.92−7.00 (m, 2 H), 7.00−7.10 (m, 2 H), 7.18−7.30 (m, 4 H); ^{13}C NMR ($CDCl_3$) δ 31.2, 46.0, 56.7, 67.5, 100.0, 113.4, 114.0, 119.5, 120.1, 128.9, 129.1, 147.8, 150.6. Anal. Calcd for $C_{17}H_{18}N_2O$: C, 76.65; H, 6.82; N, 10.52. Found: C, 76.93; H, 7.13; N, 10.57.

***N*,*N*′-Diphenyl-1,2,3,3a,4,5,6,7a-octahydropyrano[2,3-*c*]pyrazole (5b)**: ^{1}H NMR ($CDCl_3$) δ 1.38−1.48 (m, 1 H), 1.65−1.88 (m, 3 H), 2.46−2.58 (m, 1 H), 3.48−3.61 (m, 2 H), 3.82−3.99 (m, 2 H), 5.12 (d, 1 H, J = 2.3 Hz), 6.80−6.98 (m, 4 H), 7.10−7.32 (m, 6 H); ^{13}C NMR ($CDCl_3$) δ 20.9, 22.0, 36.8, 52.5, 64.8, 94.3, 113.6, 115.9, 119.0, 121.3, 128.9, 149.2, 151.5. Anal. Calcd for $C_{18}H_{20}N_2O$: C, 77.10; H, 7.19; N, 10.00. Found: C, 77.27; H, 7.50; N, 10.02.

2-Phenyl-1-(phenylcarbamoyl)-1,2,3,3a,4,5,6,7a-octahydropyrano[2,3-*c*]pyrazole (5c): ^{1}H NMR ($CDCl_3$) δ 1.29−1.40 (m, 1 H), 1.53−1.68 (m, 1 H), 1.77−1.96 (m, 2 H), 2.44−2.58 (m, 1 H), 3.45 (q, 2 H, J = 9.90 Hz), 3.80−4.00 (m, 2 H), 5.74 (d, 1 H, J = 3.8 Hz), 6.95−7.12 (m, 4 H), 7.20−7.33 (m, 4 H), 7.34−7.43 (m, 2 H), 7.97 (br s, 1 H); ^{13}C NMR ($CDCl_3$) δ 19.9, 21.5, 38.3, 55.3, 65.6, 85.8, 115.0, 119.3, 121.6, 123.3, 128.7, 129.0, 137.9, 152.1, 155.6. Anal. Calcd for $C_{19}H_{21}N_3O_2$: C, 70.55; H, 6.55; N, 13.00. Found: C, 70.75; H, 6.74; N, 13.04.

2-Phenyl-1-propionyl-1,2,3,3a,4,5,6,7a-octahydropyrano[2,3-*c*]pyrazole (5d): ^{1}H NMR ($CDCl_3$) δ 0.97 (t, 3 H, J = 7.5 Hz), 1.26−1.38 (m, 1 H), 1.47−1.58 (m, 1 H), 1.62−1.72 (m, 1 H), 2.14−2.28 (m, 1 H), 2.32−2.50 (m, 1 H), 3.32−3.50 (m, 2 H), 3.66−3.84 (m, 2 H) H), 5.58 (d, 1 H, J = 3.9 Hz), 6.82−6.90 (m, 3 H), 7.20 (t, 2 H, J = 8.1 Hz); ^{13}C NMR ($CDCl_3$) δ 7.9, 19.2, 20.4, 25.2, 36.8, 55.2, 63.7, 83.2, 114.9, 120.0, 127.8, 151.8, 173.6. Anal. Calcd for $C_{15}H_{20}N_2O_2$: C, 69.19; H, 7.75; N, 10.77. Found: C, 69.21; H, 8.02; N, 10.75.

4-Ethoxy-(1,2,3,3a,4,5-hexahydro-1-phenylpyrazolo[1,5-*a*]quinoline (8): mp 113−115 °C; ^{1}H NMR ($CDCl_3$) δ 1.35 (t, 3 H, J = 6.9 Hz), 1.54−1.69 (m, 1 H), 1.88−1.98 (m, 1 H), 2.28−2.38 (m, 1 H), 2.52−2.60 (m, 1 H), 3.49−3.88 (m, 5 H), 4.45 (dd, 1 H, J = 4.1, 10.2 Hz), 6.82−6.97 (m, 5 H), 7.10 (t, 1 H, J = 7.5 Hz), 7.24 (t, 2 H, J = 7.8 Hz), 7.37 (d, 1 H, J = 7.5 Hz); ^{13}C NMR ($CDCl_3$) δ 15.6, 32.6, 34.0, 51.1, 55.0, 65.0, 72.9, 113.7, 114.0, 119.0, 119.7, 123.8, 126.2, 127.9, 128.9, 144.7, 151.5. Anal. Calcd for $C_{19}H_{22}N_2O$: C, 77.51; H, 7.54; N, 9.52. Found: C, 77.36; H, 7.72; N, 9.53.

2-Cyclohexyl-2,3,3a,4,5,9b-hexahydrofuro[3,2-*c*]quinoline (9): mp 148−151 °C; ^{1}H NMR ($CDCl_3$) δ 0.94−1.08 (m, 2 H), 1.15−1.49 (m, 4 H), 1.60−2.10 (m, 7 H), 2.74 (q, 1 H, J = 8.1 Hz), 3.11 (dd, 1 H, J = 2.5, 9.1 Hz), 3.70−3.82 (m, 3 H), 5.11 (d, 1 H, J = 8.0 Hz), 6.52 (d, 1 H, J = 7.8 Hz), 6.74 (t, 1 H, J = 7.5 Hz), 7.04 (t, 1 H, J = 8.2 Hz), 7.29 (d, 1 H, J = 7.5 Hz); ^{13}C NMR ($CDCl_3$) δ 23.9, 25.9, 26.0, 26.3, 28.9, 30.1, 40.3, 40.4, 57.7, 66.5, 76.0, 114.4, 118.6, 122.8, 128.1, 130.0, 145.1. Anal. Calcd for $C_{17}H_{23}N_1O$: C, 79.32; H, 9.01; N, 5.44. Found: C, 79.13; H, 9.14; N, 5.44.

***N*-(Propionylamino)-3,4,4a,5,6,10b-hexahydropyrano[3,2-*c*]quinoline (10)**: yield 44%, mp 166−168 °C; ^{1}H NMR ($CDCl_3$) δ 1.12 (t, 3 H, J = 7.2 Hz), 1.42−1.54 (m, 1 H), 1.62−1.84 (m, 2 H), 1.84−1.98 (m, 2 H), 2.17−2.29(m, 2 H), 2.49−2.54 (m, 1 H), 3.19 (d, 1 H, J = 10.2 Hz), 3.58−3.72 (m, 2 H), 3.81 (d, 1 H, J = 10.2 Hz), 4.44 (s, 1 H), 6.65−6.75 (m, 2 H), 7.07−7.19 (m, 2 H), 9.09 (s, 1 H); ^{13}C NMR ($CDCl_3$) δ 8.8, 21.8, 24.4, 26.2, 31.7, 50.0, 65.7, 72.5, 111.3, 117.1, 120.9, 128.0, 129.6, 145.3, 171.4. Anal. Calcd for $C_{17}H_{23}N_1O$: C, 69.19; H, 7.75; N, 10.77. Found: C, 69.23; H, 8.12; N, 10.22.

JO9709110