$C_2H_8O_2$). Anal. Calcd for $C_{37}H_{74}O_{10}$: C, 65.45; H, 10.98. Found: C, 65.21; H, 10.72.

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Supplementary Material Available: Full experimental details are reported for the preparation of compound **10** (2 pages). Ordering information is given on any current masthead page.

Rearrangement of *N*-(Alkylamino)azoles in Acid Media: A New Entry to *C*-Amino-*N*-substituted Azoles

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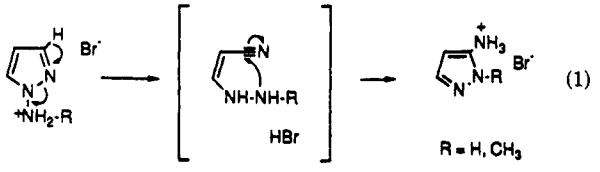
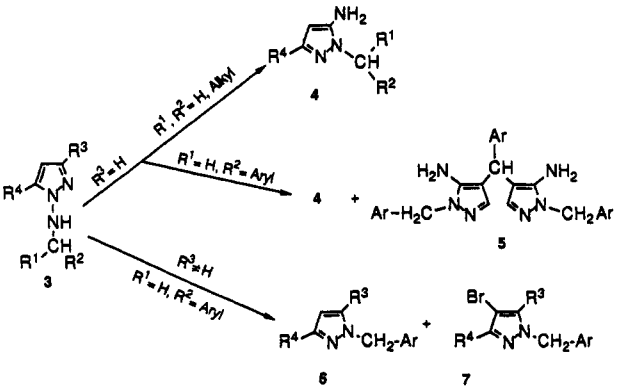
A ring-opening/ring-closure mechanism for the thermal rearrangement of 1-(alkylamino)pyrazoles into 5-amino-1-alkylpyrazoles in acid medium has been established. 1-(Benzylamino)pyrazoles show a different reactivity, affording bis(5-amino-1-benzyl-4-pyrazolyl)phenylmethanes. The reaction was extended to 1-(alkylamino)indazoles but failed in the case of 1-(alkylamino)-1,2,4-triazoles.

Among the several classes of pyrazole rearrangements,[1-3] the best known is the (1,5)-sigmatropic shift of *N*-nitropyrazoles, discovered by Habraken, by which they are transformed into *C*-nitro derivatives.[4,5] Other *N*-nitroazoles such as indazoles[6] and 1,2,4-triazoles[7] behave identically. The related case of *N*-aminoazoles had never been studied until we reported recently that 1-aminopyrazole rearranged to 3(5)-aminopyrazole by heating at 140 °C in 48% hydrobromic acid and, similarly, 1-(methylamino)-pyrazole gave 1-methyl-5-aminopyrazole.[8] This rearrangement was interpreted with the assumption that protonation on the *N*-amino group by hydrobromic acid destabilizes the pyrazole ring, allowing for a ring-opening/ring-closure sequence, which leads to the final product through a β-hydrazinoacrylonitrile intermediate (eq 1). In the present work, we study the scope of this rearrangement and provide experimental evidence for the proposed mechanism.[9]



(1)

Table I. Acid Rearrangement of 1-(Alkylamino)pyrazoles[a]



starting compound		isolated and purified products (% yield)
3a	$R^1 = R^2 = R^3 = R^4 = H$	**4a** (70)
3b	$R^1 = CH_3$, $R^2 = R^3 = R^4 = H$	**4b** (81)
3c	R^1, $R^2 = (CH_2)_5$, $R^3 = R^4 = H$	**4c** (93)
3d	$R^1 = C_6H_5$, $R^2 = R^3 = R^4 = H$	**4d** (58) + **5d** (28)
3e	$R^1 = p\text{-}FC_6H_4$, $R^2 = R^3 = R^4 = H$	**4e** (47) + **5e** (18)
3f	$R^1 = C_6H_5$, $R^2 = R^3 = H$, $R^4 = CH_3$	**4f** (35) + **5f** (39)
3g	$R^1 = C_6H_5$, $R^2 = R^4 = H$, $R^3 = CH_3$	**6g** (39) + **7g** (9)
3h	$R^1 = C_6H_5$, $R^2 = H$, $R^3 = R^4 = CH_3$	**6h** (37) + **7h** (10)

[a] All reactions were performed by heating solutions of **3** in 48% HBr acid, at reflux (external temperature of the bath, 140 °C), 1/1.3 molar equiv for **3a–c** and 1/2.3 for **3d–h** at 140 °C. Analogous results were obtained for **3a** with 99% TFA, 96% H_2SO_4, 35% HCl acids. A typical experiment uses 100 mg of starting material.

Results and Discussion

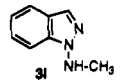
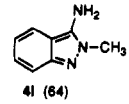
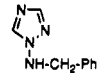
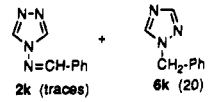
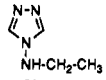
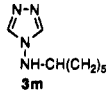
The synthesis of the starting 1-(methylamino)azoles **3a** and **3i** was performed by reduction of the corresponding *N*-formamido derivatives **1**. The remaining 1-(alkylamino)azoles, compounds **3b–h**, Table I, and **3j–m**, Table II, were prepared by reduction of the corresponding imines **2**.

Solutions of 1-(alkylamino)azole hydrobromide salts, prepared by dissolving compounds **3** in 48% hydrobromic

(1) Schiess, P.; Stalder, H. *Tetrahedron* **1980**, *21*, 1417.
(2) Becher, J.; Brondum, K.; Krake, N.; Pluta, K.; Simonsen, O.; Molina, P.; Begtrup, M. *J. Chem. Soc., Chem. Commun.* **1988**, 541.
(3) Takahashi, M.; Mamiya, T.; Hasegawa, H.; Nagai, T.; Wakita, H. *J. Heterocycl. Chem.* **1986**, *23*, 1363.
(4) Schofield, K.; Grimmett, M. R.; Keene, B. R. T. *The Azoles*; Cambridge University Press: Cambridge, 1976; pp 234–235.
(5) Elguero, J. Pyrazoles and their Benzo Derivatives in Comprehensive Heterocyclic Chemistry; Katritzky, A. R., Rees, C. W., Eds.; Pergamon Press: Oxford, 1984.
(6) Zibuck, R.; Stahl, M. A.; Barchiesi, B.; Waalwijk, P. S.; Cohen-Fernandes, P.; Habraken, C. L. *J. Org. Chem.* **1984**, *49*, 3310.
(7) Habraken, C. L.; Cohen-Fernandes, P. *J. Chem. Soc., Chem. Commun.* **1972**, 37.
(8) Sanz, D.; Claramunt, R. M.; Elguero, J.; Salazar, L.; Espada, M. *J. Chem. Soc., Perkin Trans. 1* **1990**, 809.
(9) Abstraction of the proton at position 3 of pyrazoles and indazoles, with concomittant formation of nitriles, is only observed with very strong bases.[4,5,10]
(10) Naumov, Yu. A.; Grandberg, I. I. *Usp. Khim.* **1966**, *35*, 21.

0022-3263/92/1957-1563$03.00/0

Table II. Reactions of *N*-(Alkylamino)indazole and -1,2,4-triazole Derivatives

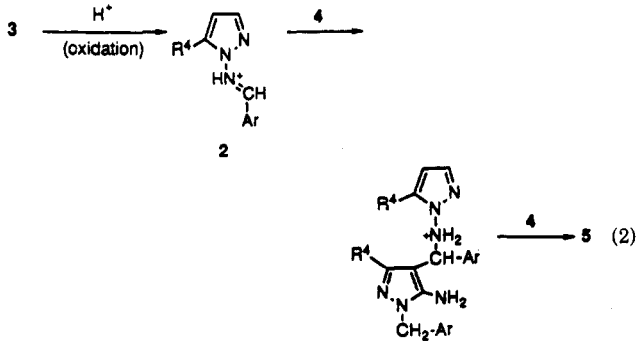
starting compd	reactn conditns (molar equiv, °C)[a]	isolated and purified products (% yield)
 **3i**	48% HBr (1/2.3, 140)	 **4i (64)**
 **3j**	48% HBr (1/2.3, 160)	 **2j (59)**
 **3k**	48% HBr (1/2.3, 160)	 **2k (traces)** **6k (20)**
 **3l**	48% HBr (1/2.3, 180)	4-aminotriazole + *s*-triazole
 **3m**	48% HBr (1/5.9, 160)	4-aminotriazole + *s*-triazole

[a] External temperature of the bath.

acid, afforded the different products by heating between 140 and 160 °C for 5 h. Other acid solutions (see footnote on Table I) gave similar results on heating. All products were isolated and characterized as free bases.

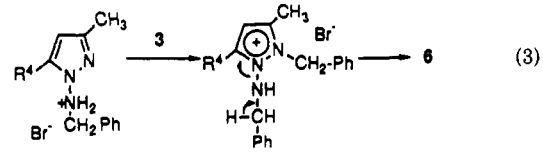
3-Unsubstituted-1-(alkylamino)pyrazoles (compounds **3a–c**) afforded the corresponding 5-amino-1-alkylpyrazoles **4** in high yields. These compounds are not readily obtained by alkylation of 3-aminopyrazole.[11] Therefore, this rearrangement represents a useful alternative to the preparation of the latter compounds through cyclization of (β-cyanoalkyl)hydrazones[12] or *N*-substituted-3-hydrazinopropenonitriles.[13]

The *N*-benzyl derivatives **3d–f** afforded, besides the rearranged 5-amino-1-benzylpyrazoles **4d–f**, compounds **5d–f**, whose structures were established by ^1H and ^{13}C NMR spectroscopy. These compounds can also be obtained by reaction of the corresponding benzaldehydes with 5-amino-1-benzylpyrazoles. Formation of compounds **5** probably implies oxidation of compounds **3** to imines **2** followed by two aromatic electrophilic substitutions on the 4 position of the previously formed 5-amino-1-benzylpyrazoles **4** (eq 2). Isolation of imines **2j** and **2k** (Table II) confirmed their role as intermediates in these reactions.



(2)

According to the mechanism proposed in eq 1, pyrazoles bearing a substituent at position 3 should not give this rearrangement. This assumption was confirmed by studying the behavior of 1-(benzylamino)pyrazoles **3g** and **3h** (Table I). Benzylpyrazoles **6** are formed by intermolecular alkylation reactions (eq 3).[14] The minor amounts of 4-



(3)

bromo derivatives **7** are due to small quantities of bromine formed by oxidation of hydrobromic acid. Thus, the rearrangement cannot take place since the β-hydrazinoacrylonitrile is not formed and, so, transbenzylation occurs instead.

1-(Methylamino)indazole **3i** and 1,2,4-triazole derivatives **3j–m** (Table II) have also been studied. The hydrobromide of **3i** rearranges to **4i**,[15] while those of **3j–m** do not. A transalkylation reaction, similar to that represented in eq 3, explains the transformation **3k** → **6k**, while imines **2j** and **2k** correspond to oxidation reactions. When treating triazoles **3l** and **3m** above 160 °C in hydrobromic acid, only 1,2,4-triazole itself and 4-amino-1,2,4-triazole could be isolated.

NMR spectroscopy has been used as the main tool for establishing the structures of the different compounds, using (^1H–^{13}C) 2D spectroscopy (HETCOR), when necessary (compounds **1i**, **3a**, **5d**). The assignment criteria in the case of pyrazole derivatives has been thoroughly discussed in other publications.[16,17] For instance, rearrangement products **4** are easily identified by the disappearance of proton H-5 and the high shielding and deshielding of the H-4 and *N*-C*H* protons, respectively, in comparison to starting compounds **3**. These compounds also show upper field shifts for C-4 and *N*-C*H* carbons (about 10 and 5 ppm, respectively). The same criteria can be used for the indazole derivative **4i**.

Identification of compounds **5** was a little more complex, but the combined use of mass spectrometry and bidimensional NMR experiments allowed the determination of their structure without ambiguity (the *p*-fluorophenyl derivative **5e** was prepared to identify structures **5** through the ^{13}C–^{19}F couplings of the three aryl substituents). One characteristic of the ^1H NMR spectrum of **5f** is worth mentioning: the protons of the CH_2 groups are diastereotopic (J_{gem} = −16.4 Hz) due to the prochirality of the $CH(pz)_2Ar$ group. The remaining compounds were straighforwardly identified by ^1H and ^{13}C NMR spectroscopy, whereas mass spectrometry was conclusive for the identification of brominated compounds **7**.

Conclusions

A delicate balance of factors is necessary to observe the rearrangement of *N*-aminoazoles into 5-amino derivatives. These conditions are (i) the absence of substituents at position **3** of pyrazoles and indazoles, (ii) the absence of other nitrogen atoms in the ring, (iii) that alkyl groups yield cleaner results than aralkyl groups, since for the latter a mixture of rearrangement and transalkylation reactions

(11) Dorgan, R. J. J.; Parrick, J. *J. Chem. Res.* **1979**, 198.
(12) Höhn, H. *Z. Chem.* **1970**, *10*, 386.
(13) Ege, G.; Franz, H. *J. Heterocycl. Chem.* **1982**, *19*, 1267.
(14) Several cross-experiments with different azoles confirm this mechanism.
(15) In this case, the ring-open intermediate (see eq 1) is an *o*-hydrazinobenzonitrile.
(16) López, C.; Claramunt, R. M.; Sanz, D.; Foces-Foces, C.; Cano, F. H.; Faure, R.; Cayón, E.; Elguero, J. *Inorg. Chim. Acta* **1990**, *176*, 195.
(17) Cabildo, P.; Claramunt, R. M.; Elguero, J. *Org. Magn. Reson.* **1984**, *22*, 603.

are observed, and (iv) that although the rearrangement was observed in all the acids assayed, the best and more reliable results were obtained with 48% hydrobromic acid.

Experimental Section

General Methods. Melting points were recorded in a Reichert microscope and are uncorrected. Mass spectra were obtained on a Hitachi Perkin-Elmer RMV-6M instrument at 75 eV. Nuclear magnetic resonance spectra were obtained on a Bruker AC-200 spectrophotometer with standard conditions. Chemical shifts (δ) in ppm and coupling constants (J) in hertz were measured in deuteriochloroform or hexadeuteriodimethyl sulfoxide referenced to TMS as internal standard. The ^1H and ^{13}C chemical shifts are accurate to 0.01 and 0.1 ppm, respectively. Coupling constants are accurate to ±0.2 Hz for ^1H NMR and ±0.6 Hz for ^{13}C NMR. The data acquisition parameters for the heteronuclear (^1H–^{13}C) 2D correlation experiments were F_1 domain (SI1, 256 W; SW1, 1099 Hz; relaxation delay D1, 1 s), F_2 domain SI2, 4K; SW2, 10000 Hz), number of transients per FID, NS, 128; number of preparatory dummy transients per FID, DS, O and J values of 166, 10, 7, and 3 Hz. All 2D experiments were processed with a sine bell window (WDW1 = WDW2 = S, SSB1 = 0, SSB2 = 2). Column chromatography was performed on silica gel Merck 60 (70–230-mesh, ASTM) or alumina, with the eluent indicated in each case.

Syntheses. All N-aminoazoles, except 4-amino-1,2,4-triazole (precursor of **3k–m**) which is commercial, were prepared by amination following literature references.[18–20] Formylation of 1-aminopyrazole and 1-aminoindazole was performed following a procedure used for formanilides.[21]

1-Formamidopyrazole (1a): 71% yield; mp 100–102 °C (Et_2O). The compound is a mixture of E/Z isomers.[22] Major isomer: ^1H NMR (DMSO-d_6) δ 11.7 (br s, 1 H, NH), 8.29 (s, 1 H, CHO), 7.72 (dd, 1 H, H-5), 7.49 (dd, 1 H, H-3), 6.34 (dd, 1 H, H-4), J_{34} = 1.7, J_{45} = 2.4, J_{35} = 0.7 Hz; ^{13}C NMR (DMSO-d_6) δ 160.4 (CHO), 137.6 (C-3), 130.8 (C-5), 105.4 (C-4). Minor isomer: ^1H NMR (DMSO-d_6) δ 11.7 (br s, 1 H, NH), 8.32 (s, 1 H, CHO), 7.90 (dd, 1 H, H-5), 7.53 (dd, 1 H, H-3), 6.39 (dd, 1 H, H-4), J_{34} = 1.8, J_{45} = 2.3, J_{35} = 0.7 Hz; ^{13}C NMR (DMSO-d_6) δ 165.2 (CHO), 138.4 (C-3), 131.3 (C-5), 106.2 (C-4).

1-Formamidoindazole (1i): 80% yield (after purification by column chromatography on silica gel, EtOAc/hexane); mp 126–127 °C (Et_2O/EtOAc). The compound is a mixture of E and Z isomers.[22] Major isomer: ^1H NMR (DMSO-d_6) δ 9.0 (br s, 1 H, NH), 8.46 (s, 1 H, CHO), 8.13 (d, 1 H, H-3), 7.80 (dd, 1 H, H-4), 7.50 (m, 1 H, H-6), 7.41 (m, 1 H, H-7), 7.21 (m, 1 H, H-5), J_{37} = 0.8, J_{45} = 7.7, J_{46} = 1.0, J_{65} = 8.0, J_{64} = 6.1, J_{67} = 1.8 Hz; ^{13}C NMR (DMSO-d_6) δ 160.8 (CHO), 138.9 (C-7a), 132.3 (C-3), 127.3 (C-6), 122.4 (C-3a), 121.5 (C-5), 121.2 (C-4), 108.9 (C-7). Minor isomer: ^1H NMR (DMSO-d_6) δ 9.0 (br s, 1 H, NH), 8.45 (s, 1 H, CHO), 8.18 (d, 1 H, H-3), 7.83 (dd, 1 H, H-4), 7.50 (m, 1 H, H-6), 7.41 (m, 1 H, H-7), 7.25 (m, 1 H, H-5); ^{13}C NMR (DMSO-d_6) δ 166.2 (CHO), 139.6 (C-7a), 133.0 (C-3), 127.9 (C-6), 122.6 (C-3a), 122.0 (C-5), 121.3 (C-4), 109.0 (C-7). Anal. Calcd for $C_8H_7N_3O$: C, 59.62; H, 4.38; N, 26.07. Found: C, 59.54; H, 4.12; N, 26.31.

Synthesis of Imines 2. Imines **2** were separated after azeotropic elimination of water from equimolar mixtures of N-aminoazole and the carbonyl compound, using toluene as solvent and p-TsOH as catalyst. The reaction was complete after an 18-h reflux. In the case of acetaldehyde, the condensation was performed without solvent, by 3 h of stirring at rt, using molecular sieves (3 Å) as the dehydrating agent. Imines **2f** and **2g** were prepared from a mixture of the N-amination products of 3(5)-methylpyrazole.

1-(Ethylideneamino)pyrazole (2b): oil, 82% yield (after purification by column chromatography on alumina, EtOAc); ^1H NMR ($CDCl_3$) δ 8.58 (q, 1 H, HC=N), 7.57 (dd, 1 H, H-5), 7.45 (dd, 1 H, H-3), 6.31 (dd, 1 H, H-4), 2.14 (d, 3 H, Me), $J_{H\text{-}Me}$ = 5.6, J_{34} = 1.8, J_{45} = 2.4, J_{35} = 1.0 Hz; ^{13}C NMR ($CDCl_3$) δ 150.4 (HC=N, ^1J = 165.9, ^2J = 7.4 Hz), 136.5 (C-3, ^1J = 186.7, ^2J = 5.3 ^3J = 8.9 Hz), 127.4 (C-5, ^1J = 190.6, ^2J = 9.1, ^3J = 3.9), 105.4 (C-4, ^1J = 177.9, ^2J = 9.6, ^2J = 8.8 Hz), 15.2 (Me).

1-(Cyclohexylideneamino)pyrazole (2c): oil, 67% yield (after purification by column chromatography on alumina, EtOAc); ^1H NMR ($CDCl_3$) δ 7.44 (dd, 1 H, H-3), 7.41 (dd, 1 H, H-5), 6.29 (dd, 1 H, H-4), 2.47 (m, 2 H, cyclohexyl), 1.85 (m, 2 H, cyclohexyl), 1.70 (m, 6 H, cyclohexyl), J_{34} = 2.0, J_{45} = 2.3, J_{35} = 0.8 Hz; ^{13}C NMR ($CDCl_3$) δ 177.1 (C=N), 135.5 (C-3, ^1J = 186.2, ^2J = 5.5, ^3J = 8.8 Hz), 125.8 (C-5, ^1J = 189.3, ^2J = 9.2, ^3J = 4.2 Hz), 104.3 (C-4, ^1J = 177.3, ^2J = ^2J = 9.2 Hz), 35.6, 30.2 (C-2′ and -6′), 27.0, 26.4 (C-3′ and -5′), 25.0 (C-4′) (the minor isomer signals appear at δ 137.3, 131.0, 102.7, 41.5, 30.8, 26.6, 25.2, and 21.6). Anal. Calcd for $C_9H_{13}N_3$: C, 66.23; H, 8.03; N, 25.74. Found: C, 65.88; H, 8.00; N, 25.98.

1-(Benzylideneamino)pyrazole (2d): oil, 84% yield (after purification by column chromatography on silica gel, hexane/EtOAc 10:1); ^1H NMR ($CDCl_3$) δ 9.18 (s, 1 H, HC=N), 7.84–7.75 (m, 2 H, H-2′ and -6′), 7.71 (dd, 1 H, H-5), 7.56 (dd, 1 H, H-3), 7.52–7.35 (m, 3 H, H-3′, -4′, and -5′), 6.38 (dd, 1 H, H-4), J_{34} = 2.1, J_{45} = 2.4, J_{35} = 0.7 Hz; ^{13}C NMR ($CDCl_3$) δ 149.5 (HC=N, ^1J = 166.7, ^3J = 4.7 Hz), 137.4 (C-3, ^1J = 187.0, ^2J = 5.2, ^3J = 9.0 Hz), 132.9 (C-1′), 130.7 (C-4′), 128.7 (C-5, ^1J = 191.0, ^2J = 8.9, ^3J = 3.8 Hz), 128.5 (C-2′ and 6′), 128.0 (C-3′ and 5′), 105.9 (C-4, ^1J = 178.3, ^2J = 9.6, ^2J = 8.8 Hz). Anal. Calcd for $C_{10}N_9N_3$: C, 70.16; H, 5.29; N, 24.54. Found: C, 69.87; H, 5.27; N, 24.25.

1-[(*p*-Fluorobenzylidene)amino]pyrazole (2e): 71% yield; mp 50–51 °C (pentane); ^1H NMR ($CDCl_3$) δ 9.15 (s, 1 H, HC=N), 7.88–7.80 (m, 2 H, H-2′ and 6′), 7.70 (dd, 1 H, H-5), 7.56 (dd, 1 H, H-3), 7.19–7.10 (m, 2 H, H-3′ and -5′), 6.39 (dd, 1 H, H-4), J_{34} = 2.2, J_{45} = 2.4, J_{35} = 0.8 Hz; ^{13}C NMR ($CDCl_3$) δ 164.3 (C-4′, $^1J_{CF}$ = 252.1, ^2J = 5.4, ^3J = 9.9 Hz), 148.4 (HC=N, ^1J = 166.8, ^3J = 4.5 Hz), 137.6 (C-3, ^1J = 187,2, ^2J = 5.3, ^3J = 9.0 Hz), 130.1 (C-2′ and -6′, $^3J_{CF}$ = 8.6, ^1J = 162.4, ^2J = 8.1, ^3J = 3.8 Hz) 129.3 (C-1′, $^4J_{CF}$ = 3.1, ^2J = 8.1 Hz), 128.9 (C-5, ^1J = 191.4, ^2J = 8.9, ^3J = 3.8 Hz), 116.0 (C-3′ and -5′, $^2J_{CF}$ = 22.0, ^1J = 164.3, ^3J = 4.0 Hz). Anal. Calcd for $C_{10}H_8FN_3$: C, 63.49; H, 4.26; N, 22.21. Found: C, 63.19; H, 4.19; N, 22.33.

1-(Benzylideneamino)-5-methylpyrazole (2f): oil, separated from **2g** by succesive column chromatography on silica gel (hexane/EtOAc, 100:1); 39% yield; ^1H NMR ($CDCl_3$) δ 9.07 (s, 1 H, HC=N), 7.81–7.75 (m, 2 H, H-2′ and -6′), 7.41 (d, 1 H, H-3), 7.38–7.35 (m, 3 H, H-3′, -4′, and -5′), 6.06 (d, 1 H, H-4), 2.40 (s, 3 H, Me), J_{34} = 1.6 Hz; ^{13}C NMR ($CDCl_3$) δ 148.2 (HC=N), 138.3 (C-5), 137.0 (C-3), 133.6 (C-1′), 130.6 (C-4′), 128.6 (C-2′ and -6′), 128.1 (C-3′ and -5′), 105.4 (C-4), 10.4 (Me). Anal. Calcd for $C_{11}H_{11}N_3$: C, 71.33; H, 5.98; N, 22.68. Found: C, 70.96; H, 5.87; N, 22.75.

1-(Benzylideneamino)-3-methylpyrazole (2g): oil, separated from **2f** (see previously); 32% yield; mp 57–59 °C; ^1H NMR ($CDCl_3$) δ 9.07 (s, 1 H, HC=N), 7.82–7.78 (m, 2 H, H-2′ and -6′), 7.57 (d, 1 H, H-5), 7.42–7.37 (m, 3 H, H-3′, -4′, and -5′), 6.13 (d, 1 H, H-4), 2.34 (s, 3 H, Me), J_{45} = 2.4 Hz; ^{13}C NMR ($CDCl_3$) δ 148.3 (HC=N), 147.5 (C-3), 133.5 (C-1′), 130.7 (C-4′), 129.9 (C-5), 128.8 (C-2′ and -6′), 128.0 (C-3′ and -5′), 106.0 (C-4), 14.0 (Me). Anal. Calcd for $C_{11}H_{11}N_3$: C, 71.33; H, 5.98; N, 22.68. Found: C, 71.32; H, 5.93; N, 22.85.

1-(Benzylideneamino)-3,5-dimethylpyrazole (2h): oil; 71% yield (after purification by column chromatography on silica gel, hexane/EtOAc, 10:1); ^1H NMR ($CDCl_3$) δ 8.98 (s, 1 H, HC=N), 7.81–7.79 (m, 2 H, H-2′ and -6′), 7.39–7.37 (m, 3 H, H-3′, -4′, and -5′), 5.88 (s, 1 H, H-4), 2.38 (d, 3 H, Me-5, ^4J = 0.8 Hz), 2.27 (s, 3 H, Me-3); ^{13}C NMR ($CDCl_3$) δ 146.8 (C-3), 146.7 (HC=N), 139.5 (C-5), 134.0 (C-1′), 130.4 (C-4′), 128.7 (C-2′ and -6′), 127.9 (C-3′ and -5′), 105.5 (C-4), 13.9 (Me-3), 10.4 (Me-5). Anal. Calcd for $C_{12}H_{13}N_3$: C, 72.34; H, 6.58; N, 21.09. Found: C, 72.63; H, 6.76; N, 20.96.

1-(Benzylideneamino)-1,2,4-triazole (2j):[23] 59% yield; mp 73–75 °C [mp lit. 79–80 °C].

4-(Benzylideneamino)-1,2,4-triazole (2k):[24] 96% yield; mp 168–170 °C [mp lit. 170–171 °C].

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4-(Ethylideneamino)-1,2,4-triazole (2l):[24] 39% yield; mp 107–110 °C [mp lit. 106–112 °C].

4-(Cyclohexylideneamino)-1,2,4-triazole (2m):[24] 72% yield; mp 98–100 °C [mp lit 96–101 °C].

Reduction of *N*-Formamidoazoles 1. To a 10 M excess suspension of $LiAlH_4$ in Et_2O cooled on an ice bath was added a solution of *N*-formamidoazole dropwise. After stirring at rt for 2 h, the reduced compounds **3a** and **3i** were separated as usual.

1-(Methylamino)pyrazole (3a): oil, purified by distillation (57 °C, 14 mmHg); 67% yield; ^1H NMR ($CDCl_3$) δ 7.38 (dd, 1 H, H-3), 7.34 (dd, 1 H, H-5), 6.09 (dd, 1 H, H-4), 5.2 (br s, 1 H, NH), 2.90 (d, 3 H, Me), J_{34} = 2.1, J_{45} = 2.3, J_{35} = 0.9 J_{NHMe} = 5.9 Hz; ^{13}C NMR ($CDCl_3$) δ 137.2 (C-3, ^1J = 185.9, ^2J = 5.0, ^3J = 8.8 Hz), 127.8 (C-5, ^1J = 187.9, ^2J = 8.2, ^3J = 3.3 Hz), 103.7 (C-4, ^1J = 177.2, ^2J = ^2J = 9.2 Hz), 39.7 (Me, ^1J = 136.7 Hz). Anal. Calcd for $C_4H_7N_3$: C, 49.46; H, 7.26; N, 43.27. Found: C, 50.12; H, 7.09; N, 43.44.

1-(Methylamino)indazole (3i): oil, purified by column chromatography on silica gel (EtOAc/petroleum ether, 1:1); 69% yield; ^1H NMR ($CDCl_3$) δ 7.93 (s, 1 H, H-3), 7.68 (dd, 1 H, H-4), 7.57 (dd, 1 H, H-7), 7.40 (m, 1 H, H-6), 7.15 (ddd, 1 H, H-5), 4.1 (br s, 1 H, NH), 3.03 (s, 3 H, Me), J_{45} = 7.7, J_{46} = 0.9, J_{56} = 7.6, J_{57} = 0.8, J_{67} = 8.0 Hz; ^{13}C NMR ($CDCl_3$) δ 137.9 (C-7a), 130.9 (C-3), 126.4 (C-6), 121.9 (C-3a), 120.7 (C-4), 120.6 (C-5), 109.4 (C-7), 38.7 (Me). Anal. Calcd for $C_8H_9N_3$: C, 65.29; H, 6.16; N, 28.55. Found: C, 64.93; H, 6.23; N, 28.28.

Reduction of Imines 2. This reaction was performed by adding an ethereal solution of the imine to a 2 M excess of a suspension of $LiAlH_4$ in Et_2O and then stirring the solution at rt (**3b** and **3c**) or under reflux (**3d–h**). Reduction of imines **2k–m** was carried out in the same way but in dry THF at rt (**3l** and **3m**) or at reflux (**3k**). Compound **3j** was obtained after a 4-h reflux of a THF solution using $NaBH_4$ as reducing agent.

1-(Ethylamino)pyrazole (3b): oil, 76% yield (after purification by column chromatography on silica gel, Et_2O); ^1H NMR ($CDCl_3$) δ 7.43 (dd, 1 H, H-3), 7.38 (dd, 1 H, H-5), 6.13 (dd, 1 H, H-4), 4.15 (br s, 1 H, NH), 3.26 (q, 2 H, CH_2), 1.10 (t, 3 H, Me), J_{34} = 1.9, J_{45} = 2.2, J_{35} = 0.6, J_{CH_2Me} = 7.2 Hz; ^{13}C NMR ($CDCl_3$) δ 136.6 (C-3, ^1J = 185.6, ^2J = 5.1, ^3J = 8.8 Hz), 128.4 (C-5, ^1J = 189.4, ^2J = 8.8, ^3J = 3.9 Hz), 102.8 (C-4, ^1J – 176.7, ^2J = ^2J = 9.2 Hz), 46.0 (CH_2, ^1J = 136.9, ^2J = 4.4 Hz), 12.0 (Me, ^1J = 126.3, ^2J = 3.2 Hz). Anal. Calcd for $C_5H_9N_3$: C, 54.02; H, 8.16; N, 37.81. Found: C, 53.98; H, 8.22; N, 37.59.

1-(Cyclohexylamino)pyrazole (3c): oil, 84% yield (after purification by column chromatography on alumina, EtOAc); ^1H NMR ($CDCl_3$) δ 7.42 (dd, 1 H, H-3), 7.35 (dd, 1 H, H-5), 6.11 (dd, 1 H, H-4), 4.85 (br s, 1 H, NH), 3.34–3.29 (m, 1 H, cyclohexyl), 1.77–1.60 (m, 5, cyclohexyl), 1.31–1.12 (m, 5 H, cyclohexyl), J_{34} = 1.6, J_{45} = 2.3, J_{35} = 0.7 Hz; ^{13}C NMR ($CDCl_3$) δ 137.0 (C-3, ^1J = 185.6, ^2J = 5.1, ^3J = 8.8 Hz), 129.3 (C-5, ^1J = 189.6, ^2J = 8.7, ^3J = 3.5 Hz), 102.9 (C-4, ^1J = 176.9, ^2J = ^2J = 9.2 Hz), 58.5 (C-1′), 30.5 (C-2′ and -6′), 25.8 (C-4′), 23.7 (C-3′ and -5′). Anal. Calcd for $C_9H_{15}N_3$: C, 65.42; H, 9.15; N, 25.43. Found: C, 65.05; H, 9.11; N, 25.18.

1-(Benzylamino)pyrazole (3d): oil, 82% yield (after purification by column chromatography on silica gel, EtOAc); ^1H NMR ($CDCl_3$) δ 7.43 (dd, 1 H, H-3), 7.29 (m, 5 H, Ph), 7.18 (dd, 1 H, H-5), 6.04 (dd, 1 H, H-4), 5.45 (br s, 1 H, NH), 4.34 (d, 2 H, CH_2), J_{34} = 2.2, J_{45} = 2.3, J_{35} = 0.8, J_{NHCH_2} = 4.9 Hz; ^{13}C NMR ($CDCl_3$) δ 137.2 (C-3, ^1J = 185.9, ^2J = 5.1, ^3J = 8.9 Hz), 136.4 (C-1′), 128.8 (C-5, ^1J = 190.0, ^2J = 8.9, ^3J = 3.8 Hz), 128.8 (C-3′ and -5′), 128.2 (C-2′ and -6′), 127.5 (C-4′), 103.3 (C-4, ^1J = 177.2, ^2J = ^2J = 9.2 Hz), 56.2 (CH_2, ^1J = 138.4 Hz). Anal. Calcd for $C_{10}H_{11}N_3$: C, 69.34; H, 6.40; N, 24.25. Found: C, 69.33; H, 6.71; N, 24.15.

1-[(*p*-Fluorobenzyl)amino]pyrazole (3e): oil, 71% yield (column chromatography on alumina, petroleum ether/EtOAc, 7:3); ^1H NMR ($CDCl_3$) δ 7.44 (dd, 1 H, H-3), 7.27–7.20 (m, 2 H, H-2′ and -6′), 7.15 (dd, 1 H, H-5), 7.03–6.94 (m, 2 H, H-3′ and -5′), 6.05 (dd, 1 H, H-4), 4.33 (s, 2 H, CH_2), 4.05 (br s, 1 H, NH), J_{34} = 2.1, J_{45} = 2.4, J_{35} = 0.9 Hz; ^{13}C NMR ($CDCl_3$) δ 162.2 (C-4′, $^1J_{CF}$ = 245.8, ^2J = 5.2, ^3J = 10.4 Hz), 137.4 (C-3, ^1J = 186.0, ^2J = 5.1, ^3J = 8.8 Hz), 132.2 (C-1′, $^4J_{CF}$ = 3.3 Hz), 130.6 (C-2′ and -6′, $^3J_{CF}$ = 8.0, ^1J = 161.0, ^3J = 7.9, $^3J_{CH_2}$ = 4.0 Hz), 129.0 (C-5, ^1J = 190.2, ^2J = 8.8, ^3J = 3.7 Hz), 115.1 (C-3′ and -5′, $^2J_{CF}$ = 21.4, ^1J = 164.1, ^2J = 0.8, ^3J = 3.9 Hz), 103.4 (C-4, ^1J = 177.4, ^2J = ^2J = 9.2 Hz), 55.2 (CH_2, ^1J = 137.8 Hz). Anal. Calcd for $C_{10}H_{10}FN_3$: C, 62.82; H, 5.27; N, 21.98. Found: C, 62.79; H, 5.30; N, 21.96.

1-(Benzylamino)-5-methylpyrazole (3f): oil, 72% yield (after purification by column chromatography on silica gel, petroleum ether/EtOAC, 2:1); ^1H NMR ($CDCl_3$) δ 7.33 (d, 1 H, H-3), 7.30–7.20 (m, 5 H, Ph), 5.83 (dd, 1 H, H-4), 4.29 (s, 3 H, N-H and CH_2), 1.97 (s, 3 H, Me), J_{H-Me} = 0.7, J_{34} = 2.0 Hz; ^{13}C NMR ($CDCl_3$) δ 138.0 (C-5), 136.5 (C-1′), 136.1 (C-3, ^1J = 184.6, ^2J = 5.1 Hz), 129.2 (C-3′ and -5′), 128.2 (C-2′ and -6′), 127.6 (C-4′), 102.7 (C-4, ^1J = 175.0, ^2J = 9.4, ^3J = 3.3 Hz), 56.1 (CH_2), 10.1 (Me, ^1J = 129.0 Hz). Anal. Calcd for $C_{11}H_{13}N_3$: C, 70.56; H, 6.99; N, 22.44. Found: C, 70.35; H, 7.05; N, 22.26.

1-(Benzylamino)-3-methylpyrazole (3g): 70% yield (after purification by column chromatography on silica gel, petroleum ether/EtOAc, 2:1); mp 35–37 °C; ^1H NMR ($CDCl_3$) δ 7.33–7.25 (m, 5 H, Ph), 7.10 (d, 1 H, H-5), 5.83 (d, 1 H, H-4), 4.33 (s, 3 H, NH and CH_2), 2.27 (s, 3 H, Me), J_{45} = 2 Hz; ^{13}C NMR ($CDCl_3$) δ 146.5 (C-3), 136.6 (C-1′), 129.7 (C-5, ^1J = 188.7, ^2J = 9.0 Hz), 128.9 (C-3′ and -5′), 128.3 (C-2′ and -6′), 127.5 (C-4′), 102.7 (C-4, ^1J = 175.1, ^2J = 8.3, ^3J = 3.4 Hz), 56.4 (CH_2, ^1J = 137.2 Hz), 13.7 (Me, ^1J = 127.1 Hz). Anal. Calcd for $C_{11}H_{13}N_3$: C, 70.56; H, 6.99; N, 22.44. Found C, 70.27; H, 6.98; N, 22.22.

1-(Benzylamino)-3,5-dimethylpyrazole (3h): oil, 71% yield (after purification by column chromatography on silica gel, petroleum ether/EtOAc, 7:3); ^1H NMR ($CDCl_3$) δ 7.26 (s, 5 H, Ph), 5.60 (s, 1 H, H-4), 5.15 (br s, 1 H, NH), 4.25 (d, 2 H, CH_2), 2.20 (s, 3 H, Me-3), 1.93 (s, 3 H, Me-5); ^{13}C NMR ($CDCl_3$) δ 145.2 (C-3), 138.8 (C-5), 136.7 (C-1′), 129.3 (C-3′ and -5′), 128.2 (C-2′ and -6′), 127.6 (C-4′), 102.4 (C-4), 56.2 (CH_2), 13.6 (Me-3), 10.1 (Me-5). Anal. Calcd for $C_{12}H_{15}N_3$: C, 71.61; H, 7.51; N, 20.88. Found: C, 71.94; H, 7.63; N, 20.48.

1-(Benzylamino)-1,2,4-triazole (3j): 71% yield (after purification by column chromatography on silica gel, EtOAc); mp 66–68 °C; ^1H NMR ($CDCl_3$) δ 7.79 (s, 1 H, H-5), 7.73 (s, 1 H, H-3), 7.29–7.17 (m, 5 H, Ph), 6.16 (t, 1 H, NH), 4.23 (d, 2 H, CH_2), J_{NHCH_2} = 4.1 Hz; ^{13}C NMR ($CDCl_3$) δ 149.7 (C-3, ^1J = 208.7, ^3J = 12.3 Hz), 142.1 (C-5, ^1J = 217.5, ^3J = 6.1, $^3J_{CNNH}$ = 3.0 Hz), 135.3 (C-1′), 128.5 (C-3′ and -5′), 128.1 (C-2′ and -6′), 127.6 (C-4′), 55.5 (CH_2, ^1J = 138.4 Hz). Anal. Calcd for $C_9H_{10}N_4$: C, 62.05; H, 5.78; N, 32.16. Found: C, 62.28; H, 5.70; N, 31.91.

4-(Benzylamino)-1,2,4-triazole (3k):[25] 60% yield; mp 106–107 °C (mp lit. 108 °C).

4-(Ethylamino)-1,2,4-triazole (3l):[25] 88% yield; mp 77–79 °C (mp lit. 80 °C).

4-(Cyclohexylamino)-1,2,4-triazole (3m):[24] 50% yield; mp 167–169 °C (lit. mp 169–171 °C).

Acid Rearrangements (See Tables I and II). The cooled solutions were made basic by addition of an aqueous saturated $NaHCO_3$ solution and extracted with $CHCl_3$. Compounds **4** and **5** were separated by column chromatography on silica gel. In all cases compounds **4** eluted firstly.

5-Amino-1-methylpyrazole (4a):[13] 70% yield; mp 69–70 °C (mp lit. 71–72 °C).

5-Amino-1-ethylpyrazole (4b):[11] 81% yield (after purification by column chromatography on silica gel, Et_2O/EtOH 95:5); mp 45–47 °C; ^{13}C NMR ($CDCl_3$) δ 144.0 (C-5), 137.8 (C-3, ^1J = 182.6, ^2J = 5.2 Hz), 90.4 (C-4, ^1J = 175.0, ^2J = 10.6 Hz), 41.6 (C-1′, ^1J = 138.2, ^2J = 4.5), 14.2 (C-2′, ^1J = 127.7, ^2J = 3.2).

5-Amino-1-cyclohexylpyrazole (4c):[12] 93% yield (after purification by column chromatography on silica gel, EtOAc/*n*-pentane, 1:1); mp 73–75 °C; ^{13}C NMR ($CDCl_3$) δ 143.3 (C-5, ^2J = 5.6 Hz), 137.5 (C-3, ^1J = 182.3, ^2J = 5.2 Hz), 90.6 (C-4, ^1J = 174.5, ^2J = 10.5 Hz), 55.3 (C-1′, ^1J = 132.0 Hz), 31.9 (C-2′ and -6′, ^1J = 128.7 Hz), 25.2 (C-3′ and -5′, ^1J = 123.4 Hz), 24.8 (C-4′).

5-Amino-1-benzylpyrazole (4d):[13] column chromatography, EtOAc/Et_2O, 1:1; 59% yield; mp 77–78 °C (mp lit. 79 °C); ^{13}C NMR ($CDCl_3$) δ 144.6 (C-5), 138.4 (C-3, ^1J = 183.5, ^2J = 5.0 Hz), 136.5 (C-1′), 91.4 (C4, ^1J = 175.3, ^2J = 10.5 Hz), 128.6 (C-2′ and -6′), 127.5 (C-4′), 126.6 (C-3′ and -5′), 51.2 (CH_2, ^1J = 139.2, ^2J = 4.3 Hz).

5-Amino-1-(*p*-fluorobenzyl)pyrazole (4e): oil; column chromatography, EtOAc; 47% yield; ^1H NMR ($CDCl_3$) δ 7.26 (d, 1 H, H-3), 7.15–6.95 (m, 4 H, Ph), 5.51 (d, 1 H, H-4), 5.08 (s, 2

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H, H-4), 5.08 (s, 2 H, CH_2), 3.61 (br s, 1 H, NH), J_{34} = 2.0 Hz; ^{13}C NMR ($CDCl_3$) δ 162.0 (C-4′, $^1J_{CF}$ = 245.9 Hz), 144.6 (C-5), 138.6 (C-3, ^1J = 183.6, ^2J = 5.0 Hz), 132.3 (C-1′, ^3J = 7.5, $^4J_{CF}$ = 3.0 Hz) 128.3 (C-2′ and -6′, ^1J = 160.5, $^3J_{CF}$ = 8.1, ^3J = 7.6, $^3J_{CH_2}$ = 3.8 Hz), 115.5 (C-3′ and -5′, ^1J = 164.0, $^2J_{CF}$ = 21.5, ^3J = 3.9 Hz), 91.6 (C-4, ^1J = 175.5, ^2J = 10.5 Hz), 50.4 (CH_2, ^1J = 139.2, ^2J = 4.0 Hz). Anal. Calcd for $C_{10}H_{10}FN_3$: C, 62.82; H, 5.27; N, 21.98. Found: C, 62.50; H, 5.36; N, 21.70.

5-Amino-1-benzyl-3-methylpyrazole (4f):[13] column chromatography, Et_2O/EtOAc, 1:1, 35% yield; mp 66–67 °C; ^{13}C NMR ($CDCl_3$) δ 147.2 (C-3), 145.3 (C-5), 136.7 (C-1′), 128.4 (C-2′ and -6′), 127.1 (C-4′), 126.3 (C-3′ and -5′), 90.6 (C-4), 50.5 (CH_2), 13.5 (Me).

3-Amino-2-methylindazole (4i): column chromatography, EtOAc; 64% yield; mp 166–168 °C; ^1H NMR ($CDCl_3$) δ 7.47 (d, 1 H, H-7), 7.42 (d, 1 H, H-4), 7.21 (dd, 1 H, H-6), 6.88 (dd, 1 H, H-5), 3.95 (s, 5 H, NH_2 and Me); ^{13}C NMR ($CDCl_3$) δ 147.3 (C-3), 137.5 (C-7a), 126.6 (C-6), 118.7 (C-5), 118.5 (C-4), 116.3 (C-7), 110.7 (C-3a), 35.2 (Me). Anal. Calcd for $C_8H_9N_3$: C, 65.29; H, 6.16; N, 28.55. Found: C, 64.99; H, 6.06; N, 28.23.

Bis(5-amino-1-benzyl-4-pyrazolyl)phenylmethane (5d): column chromatography, EtOAc/Et_2O, 1:1; 28% yield; mp 140 °C; ^1H NMR ($CDCl_3$) δ 7.28–7.24 (m, 10 H, Ph), 7.14 (m, 5 H, Ph), 7.03 (s, 2 H, H-3), 5.18 (s, 4 H, CH_2), 4.96 (s, 1 H, CH), 3.05 (br s, 4 H, NH_2); ^{13}C NMR ($CDCl_3$) δ 142.2 (C-1″), 141.6 (C-5), 138.4 (C-3, ^1J = 183.0, ^3J = 3.8 Hz), 136.4 (C-1′), 128.8 (C-3′ and -5′), 128.6 (C-3″ and -5″), 128.0 (C-2″ and -6″), 127.7 (C-4′), 126.6 (C-2′, -6′, and -4″), 106.1 (C-4, ^2J = ^2J = 8.6 Hz), 51.7 (CH_2, ^1J = 139.0, ^3J = 3.8 Hz), 36.8 (CH, ^1J = 125.2 Hz). MS *m/z* 435 (M^+) (4.1), 434 (13.3), 357 (5.1), 263 (20.1), 262 (100), 261 (9.5), 260 (39.6), 115 (4.5), 92 (4.6), 91 (57.6), 65 (5.3). Anal. Calcd for $C_{27}H_{26}N_6$: C, 74.63; H, 6.03; N, 19.34. Found: C, 74.25; H, 5.98; N, 19.05.

Bis[5-amino-1-(*p*-fluorobenzyl)-4-pyrazolyl](*p*-fluorophenyl)methane (5e): column chromatography, EtOAc; 18% yield; mp 151–153 °C; ^1H NMR ($CDCl_3$) δ 7.16–6.94 (m, 14 H, H-3 and Ph), 5.12 (s, 4 H, CH_2), 4.93 (s, 1 H, CH), 3.15 (br s, 4 H, NH_2); ^{13}C NMR ($CDCl_3$) δ 162.3 (C-4′, $^1J_{CF}$ = 246.5 Hz), 161.5 (C-4″, $^1J_{CF}$ = 245.9), 141.4 (C-5), 138.7 (C-1″, $^4J_{CF}$ = 3.1 Hz), 138.4 (C-3), 137.8 (C-1″), 132.1 (C-1′, $^4J_{CF}$ = 3.1 Hz), 129.5 (C2″ and -6″, $^3J_{CF}$ = 8.0 Hz), 128.5 (C-2′ and -6′, $^3J_{CF}$ = 8.1 Hz), 115.8 (C-3′ and -5′, $^2J_{CF}$ = 21.6 Hz), 115.5 (C-3″ and -5″, $^2J_{CF}$ = 21.3 Hz), 106.2 (C-4′), 51.0 (CH_2), 36.1 (CH). MS *m/z* 488 (M^+) (8.6), 393 (4.2), 299 (16.2) 298 (85.0), 297 (10.6), 296 (47.9), 191 (6.8), 133 (4.6), 110 (8.3), 109 (100), 83 (8.9). Anal. Calcd for $C_{27}H_{23}F_3N_6$: C, 66.39; H, 4.75; N, 17.20. Found: C, 66.71; H, 4.74; N, 16.83.

Bis(5-amino-1-benzyl-3-methyl-4-pyrazolyl)phenylmethane (5f): column chromatography, EtOAc/Et_2O, 1:1; 39% yield; mp 153–5 °C; ^1H NMR ($CDCl_3$) δ 7.30–7.20 (m, 10 H, Ph), 7.08–7.05 (m, 5 H, Ph), 5.15 (s, 1 H, CH), 5.12 and 5.07 (dd, J_{AB} = 16.4 Hz, 4 H, CH_2), 2.86 (br s, 4 H, NH_2), 2.04 (s, 6 H, Me), J_{AB} = −16.4 Hz; ^{13}C NMR ($CDCl_3$) δ 146.1 (C-3), 142.6 (C-1′), 141.3 (C-5), 136.8 (C-1′), 128.8 (C-2′ and -6′), 128.7 (C-2″ and -6″), 128.1 (C-3″ and -5″), 127.6 (C-4′), 126.6 (C-4″), 126.4 (C-3′ and -5′), 102.3 (C-4), 51.3 (CH_2, ^1J = 138.8 Hz), 36.1 (CH, ^1J = 124.8 Hz), 12.3 (Me, ^1J = 127.0 Hz). Anal. Calcd for $C_{29}H_{30}N_6$: C, 75.30; H, 6.54; N, 18.17. Found: C, 75.61; H, 6.56; N, 17.82.

1-Benzyl-5-methylpyrazole (6g):[26] column chromatography, $CHCl_3$; ^{13}C NMR ($CDCl_3$) δ 138.3 (C-3), 138.1 (C-5), 136.9 (C-1′), 128.5 (C2′ and -6′), 127.3 (C-4′), 126.5 (C-3′ and -5′), 105.6 (C-4), 52.7 (CH_2), 10.9 (Me).

1-Benzyl-3,5-dimethylpyrazole (6h):[27] column chromatography $CHCl_3$; ^{13}C NMR ($CDCl_3$) δ 146.5 (C-3), 138.3 (C-5), 136.7 (C-1′), 127.9 (C-2′ and -6′), 126.6 (C-4′), 125.8 (C-3′ and -5′), 104.8 (C-4), 51.7 (CH_2), 12.8 (Me-3), 10.2 (Me-5).

1-Benzyl-4-bromo-5-methylpyrazole (7g): column chromatography, $CHCl_3$; 9% yield; mp 49–51 °C; ^1H NMR ($CDCl_3$) δ 7.44 (s, 1 H, H-3), 7.34–7.20 (m, 3 H, Ph), 7.09–7.06 (m, 2 H, Ph), 5.26 (s, 2 H, CH_2), 2.14 (s, 3 H, Me-5); ^{13}C NMR ($CDCl_3$) δ 138.7 (C-3, ^1J = 191.4 Hz), 136.9 (C-5), 136.1 (C-1′), 128.7 (C-2′ and -6′, ^1J = 161.7, ^3J = 7.2 Hz), 127.8 (C-4′, ^1J = 160.9, ^3J = 7.4 Hz), 126.7 (C-3′ and -5′, ^1J = 162.2 Hz), 93.7 (C-4), 54.3 (CH_2, ^1J = 139.3, ^2J = 4.4 Hz), 9.8 (Me, ^1J = 129.4 Hz); MS *m/z* (M^+ + 2) (11.4), 251 (M^+ + 1) (9.1), 250 (M^+) (12.1), 149 (33.3), 111 (25.8), 109 (20.5), 97 (31.8), 95 (25.8), 91 (76.5), 85 (54.5), 83 (62.1), 81 (51.5), 73 (39.4), 71 (55.3), 69 (100), 57 (78.8), 55 (55.3). Anal. Calcd for $C_{11}BrH_{11}N_2$: C, 52.61; H, 4.41; N, 11.15. Found: C, 52.88; H, 4.56; N, 10.80.

1-Benzyl-4-bromo-3,5-dimethylpyrazole (7h): column chromatography, $CHCl_3$; 9% yield; mp 49–51 °C; ^1H NMR ($CDCl_3$) δ 7.31–7.25 (m, 3 H, Ph), 7.10–7.06 (m, 2 H, Ph), 5.23 (s, 2 H, CH_2), 2.24 (s, 3 H, Me-3), 2.14 (s, 3 H, Me-5); ^{13}C NMR ($CDCl_3$) δ 146.1 (C-3), 137.3 (C-5), 136.5 (C-1′), 128.8 (C2′ and -6′), 127.7 (C-4′), 126.7 (C-3′ and -5′), 94.5 (C-4), 53.9 (CH_2), 12.3 (Me-3), 10.4 (Me-5). Anal. Calcd for $C_{12}BrH_{13}N_2$: C, 54.36; H, 4.94; N, 10.56. Found: C, 54.15; H, 5.13; N, 10.48.

Registry No. 1a, 137968-10-6; **1i**, 137968-11-7; **2b**, 137968-12-8; **2c**, 137968-13-9; **2d**, 137968-14-0; **2e**, 137968-15-1; **2f**, 137968-16-2; **2g**, 137968-17-3; **2h**, 137968-18-4; **2j**, 122583-48-6; **2h**, 18998-48-6; **2l**, 33761-49-8; **2m**, 114274-07-6; **3a**, 128315-64-0; **3b**, 137968-19-5; **3c**, 137968-20-8; **3d**, 137968-21-9; **3e**, 137968-22-0; **3f**, 137968-23-1; **3g**, 137968-24-2; **3h**, 137968-25-3; **3i**, 137968-26-4; **3j**, 137968-27-5; **3k**, 6111-75-7; **3l**, 21614-54-0; **3m**, 114274-09-8; **4a**, 1192-21-8; **4b**, 3528-58-3; **4c**, 3528-50-5; **4d**, 3528-51-6; **4e**, 137968-28-6; **4f**, 1134-82-3; **4i**, 97990-19-7; **5d**, 137968-29-7; **5e**, 137968-30-0; **5f**, 137968-31-1; **6g**, 86327-93-7; **6h**, 1134-81-2; **7g**, 137968-32-2; **7h**, 51108-53-3.

Supplementary Material Available: ^1H and ^{13}C NMR spectra of **3a**, **3b**, and **2b** (6 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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