to give a residue, which was purified by flash chromatography on silica gel eluting with $CHCl_3$–CH_3OH (95:5).

The *first fraction* gave compound **14** (yield = 12%) as an amorphous solid: IR (CCl_4) ν_{max} 2860, 2840, and 2760 (Bohlmann–Wenkert bands), 1600 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 0.95 (m, 1 H), 1.0–2.1 (m, 8 H), 2.3 (m, 1 H), 3.3 (m, 2 H), 3.5 (dd, 1 H, J = 6 and 9 Hz), 4.3 (2 H, J_{AB} = 15 Hz, $\Delta\nu$ = 115 Hz), 6.4 (d, 1 H, J = 8 Hz), 6.8 (t, 1 H, J = 8 Hz), 7.1 (t, 1 H, J = 8 Hz), 7.2–7.5 (m, 5 H), 7.8 (d, 1 H, J = 8 Hz); ^{13}C NMR ($CDCl_3$) 150.7, 139.8, 130.9, 127.2, 125.6, 117.8, 107.9, 72.8, 68.5, 54.5, 51.4, 49.2, 37.7, 34.0, 30.4, 29.8, 26.2, 25.9; MS, m/z (relative intensity) 344 (76), 316 (20), 253 (6), 234 (12), 220 (20), 124 (10), 96 (100), 91 (72).

The *second fraction* gave compound **12** (yield = 70%) as an amorphous solid: IR (CCl_4) 2860, 2790, and 2730 (Bohlmann–Wenkert bands), 1605 cm^{-1}; ^1H NMR ($CDCl_3$, 250 MHz) δ 0.9–2.0 (m, 11 H), 2.0–2.35 (m, 2 H), 2.4 (d, 1 H, J = 1.25 Hz), 3.0–3.2 (m, 2 H), 3.35 (dd, 1 H, J = 5 Hz, J' = 10 Hz), 4.25 (2 H, J_{AB} = 15 Hz, $\Delta\nu$ = 68 Hz), 6.35 (d, 1 H, J = 8 Hz), 6.7 (t, 1 H, J = 8 Hz), 6.95 (d and t, 2 H, J = 8 Hz), 7.2–7.5 (m, 5 H); ^{13}C NMR ($CDCl_3$) δ 151.0, 138.8, 135.5, 127.1, 121.9, 117.6, 106.9, 70.0, 68.1, 54.4, 53.9, 52.7, 48.9, 38.4, 32.3, 29.5, 25.4, 22.0, 21.3; MS, m/z (relative intensity) 344 (83), 316 (5), 277 (10), 253 (8), 234 (6), 220 (11), 162 (17), 124 (12), 96 (100), 91 (41), exact mass m/z 344.2269 (calcd for $C_{24}H_{28}N_2$ m/z 344.2259).

The *third fraction* gave compound **13** (yield = 7%) as an amorphous solid: IR (CCl_4) [no Bohlmann–Wenkert bands] 1600 cm^{-1}; ^1H NMR ($CDCl_3$, 250 MHz) δ 0.9–1.9 (m, 9 H), 1.9–2.25 (m, 2 H), 2.28 (d, 1 H, J = 10 Hz), 2.8–3.2 (m, 4 H), 3.45 (dd, 1 H, J = 2 Hz, J' = 4 Hz), 4.20 (2 H, J_{AB} = 16 Hz, $\Delta\nu$ = 70 Hz), 6.35 (d, 1 H, J = 8 Hz), 6.70 (t, 1 H, J = 8 Hz), 6.95 (t, 1 H, J = 8 Hz), 7.2 (d, 1 H, J = 8 Hz), 7.2–7.4 (m, 5 H); ^{13}C NMR ($CDCl_3$) 151.1, 139.8, 126.9, 123.5, 118.5, 107.6, 71.3, 69.5, 52.9, 52.3, 48.1, 46.4, 33.4, 33.3, 31.6, 26.0, 25.2, 21.0; MS, m/z (relative intensity) 344 (34), 316 (4), 220 (4), 162 (3), 124 (4), 96 (100), 91 (22), exact mass m/z 344.2259 (calcd for $C_{24}H_{28}N_2$ m/z 344.2259).

Acknowledgment. We thank Prof. Y. Ban and E. Wenkert for communicating the IR and ^1H NMR spectra of compounds in the series of aspidospermidine and Dr. N. Kunesh for the gift of a sample of 20-deethyl-20-iso-aspidospermidine. The 400-MHz ^1H NMR spectra are due to the courtesy of Dr. S. K. Kan.

Oxidation of 1-Aminopyrazoles and Synthesis of 1,2,3-Triazines

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Unsubstituted and various substituted monocyclic 1,2,3-triazines were synthesized from 1-aminopyrazoles by oxidation with lead tetraacetate, lead dioxide–CF_3CO_2H, and/or nickel peroxide–AcOH.

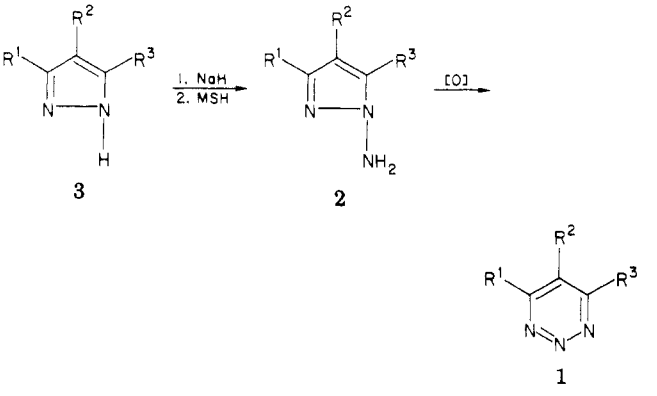
In previous papers,[1,2] we have dealt briefly with the syntheses of unsubstituted[1] and substituted[2] monocyclic 1,2,3-triazines (**1**) by oxidation of *N*-aminopyrazoles (**2**). This paper describes detailed data and additional findings concerning the synthesis of the triazines **1**.

In earlier 1,2,3-triazine synthesis, the substituents on the triazine rings have been mostly limited to be $R^1 = R^2 = R^3$ = alkyl, aryl, or halogen, and this depends on the availability and stability of cyclopropenyl compounds as the synthetic intermediates.[3]

Results and Discussion

We found that alkyl- and/or phenyl-substituted 1,2,3-triazines (**1a–h**) could be synthesized from *N*-aminopyrazoles by oxidation. Unexpectedly, N-amination of pyrazoles **3** did not proceed by Rees and Storr's method[4] using hydroxylamine-*O*-sulfonic acid or chloramine with which N-amination of indazoles has successfully carried out. However, the 1-aminopyrazoles were obtained in medium to high yields from appropriate pyrazoles through a deprotonation by sodium hydride followed by amination using (*O*-mesitylenesulfonyl)hydroxylamine (MSH).[5] The

Scheme I



3 2 1

a, $R^1 = R^2 = R^3 = H$
b, R^1 = Me, $R^2 = R^3 = H$
b', $R^1 = R^2 = H$, R^3 = Me
c, $R^1 = R^3 = H$, R^2 = Me
d, $R^1 = R^3$ = Me, $R^2 = H$
e, $R^1 = R^2 = R^3$ = Me
f, R^1 = Ph, $R^2 = R^3 = H$
f', $R^1 = R^2 = H$, R^3 = Ph
g, R^1 = Ph, $R^2 = H$, R^3 = Me
g', R^1 = Me, $R^2 = H$, R^3 = Ph
h, $R^1 = R^3$ = Ph, $R^2 = H$

yields and some properties of **2** are shown in Table I.

In the N-amination of asymmetrical pyrazoles, a mixture of the isomeric 1-aminopyrazoles due to the positions of the N-amination was obtained. In cases of **2f** and **2f'**, and **2g** and **2g'**, their separations were possible, although their respective distinctions were not accomplished. The ratio **2b**/**2b'** in the product mixture from **3b** was shown to be

(1) Ohsawa, A.; Arai, H.; Ohnishi, H.; Igeta, H. *J. Chem. Soc., Chem. Commun.* **1981**, 1174.
(2) Ohsawa, A.; Arai, H.; Ohnishi, H.; Igeta, H. *J. Chem. Soc., Chem. Commun.* **1980**, 1182.
(3) Kobylecki, R. J.; Mckillop, A. *Adv. Heterocycl. Chem.* **1976**, *19*, 215. Neunhoeffer, H. *Chem. Heterocycl. Compd.* **1978**, *33*, 3 and references cited therein.
(4) Adger, B. M.; Bradbury, S.; Keating, M.; Rees, C. W.; Storr, R. C.; Williams, M. T. *J. Chem. Soc., Perkin Trans. 1* **1975**, 31.
(5) Tamura, Y.; Minamikawa, J.; Sumoto, K.; Fujii, S.; Ikeda, M. *J. Org. Chem.* **1973**, *38*, 1239.

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Table I. Synthesis of 1-Aminopyrazoles (2)

pyrazole	yield[a] of 2, %	mp or bp, °C	isoln and purifn
3a	**2a** 90	bp 80–90 (10–15 mmHg)	D[b]
3b	**2b** + **2b′** (mixture) 85	bp 100–120 (3–5 mmHg)	D
3c	**2c** 77	bp 60–62 (3–4 mmHg)	D
3d	**2d** 91	bp 130–140 (10–15 mmHg) (mp 41–42)	D
3e	**2e** 67	mp 69–70	R[c]
3f	**2f** (or **2f′**) 45	mp 108–109	S[d] and R
	2f′ (or **2f**) 6	mp 79–80	
3g	**2g** (or **2g′**) 52	mp 152–153	A[e] and R
	2g′ (or **2g**) 13	mp 94–95	
3h	**2h** 56	mp 98–99	A and R

[a] Isolation yields are shown. [b] Distillation. [c] Recrystallization. [d] Chromatography using silica gel. [e] Chromatography using alumina.

Table II. Synthesis of 1,2,3-Triazines (1) from 2 by LTA Oxidation

				elemental anal.					
				found			calcd		
triazine	yield[a] %	mp, °C	cryst appearnce[b]	C	H	N	C	H	N
1a	0	70–71	plates (Et_2O)	44.24	3.59	52.00	44.44	3.73	51.83
1b	30[c]	30–31	plates (i-Pr_2O)	50.18	5.54	44.01	50.51	5.30	44.19
1c	14	67–68	needles (i-Pr_2O)	50.37	5.24	44.45	50.51	5.30	44.19
1d	70	87–88	flakes (i-Pr_2O)	55.20	6.45	38.40	55.03	6.47	38.51
1e	68	144–146[d]	plates (i-Pr_2O)	58.83	7.30	33.85	58.51	7.37	34.12
1f	35[c]	110–111	plates (pentane)	69.22	4.20	27.22[e]	68.77	4.49	26.74
1g	57[c]	158–159	needles (benzene-i-Pr_2O)	69.82	5.14	24.50	70.15	5.30	24.55
1h	50	171–172	plates (i-Pr_2O)	77.10	4.67	18.23	77.23	4.75	18.02

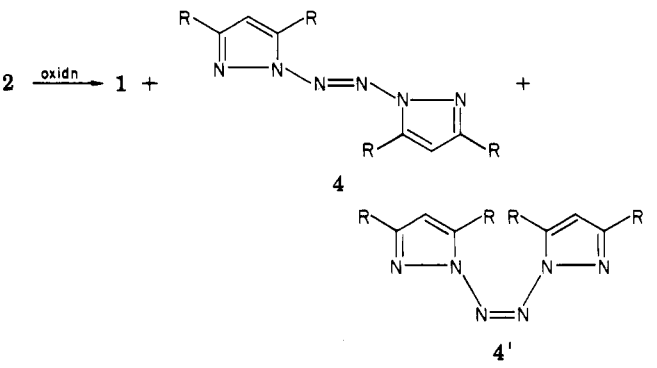
[a] Isolation yields. [b] All colorless. [c] From isomeric mixture. [d] Literature[6] mp 146–147 °C. [e] Although the elemental analysis did not give the satisfactory values, M^+ of MS gave an m/e 157.060 (calcd for M^+, 157.064).

approximately 1/1 by means of nuclear magnetic resonance (NMR) spectrum, although attempts to separate **2b** and **2b′** were unsuccessful.

The oxidation of **2** was carried out by a modification of Rees and Storr's method using lead tetraacetate (LTA) as an oxidizing reagent which was used for the synthesis of 1,2,3-benzotriazines.[4] The oxidation of **2**, with an exception for **2a**, afforded the respective substituted 1,2,3-triazines in 14–70% yields. Both isolated **2f** and **2f′** and **2g** and **2g′** gave the corresponding triazines **1f** and **1g**; and also, these isomeric mixtures, as well as the **2b** + **2b′** mixture, could be employed as the starting materials of the oxidation without the isomeric separations. 4,5,6-Trimethyl-1,2,3-triazine (**1e**) was identical with the alternatively synthesized compound.[3,6] These data are shown in Table II.

Several attempts to obtain unsubstituted 1,2,3-triazine (**1a**) from **2a** by use of LTA under variously modified conditions failed, although formation of a small amount of **1a** was observed by vapor-phase chromatography (VPC) and NMR, together with minor products that could not be isolated. Thus, we investigated other oxidizing reagents. The oxidation of **2a** using freshly prepared nickel peroxide (NPO)[7] with acetic acid afforded the expected 1,2,3-triazine (**1a**).[8] The method of course could also be applied to the synthesis of the other 1,2,3-triazines. By this method, however, the yields varied unpredictably depending on the lot of the NPO. The highest yield of **1a** was 20%, and often the yield was only a trace. The highest yields of **1b** and **1d** according to the method were 10% and 35%, respectively. In the NPO oxidation of **2a** and **2d** in the absence of acetic acid, the major products were azo compounds[8] **4** and **4′** and the best yields of **1a** and **1d** were only 4% and 10%, respectively (Scheme II).

Scheme II



	oxidn	% 1	% 4	% 4′
a, R = H	NPO–AcOH/CH_2Cl_2	20	trace	trace
	NPO/CH_2Cl_2	4	25	20
	MnO_2/CH_2Cl_2	0	34	23
d, R = Me	NPO–AcOH/CH_2Cl_2	35	trace	trace
	NPO/CH_2Cl_2	10	27	14
	MnO_2/CH_2Cl_2	10	45	35

Of these azo isomers, **4a′** and **4d′** are rather labile and they changed into the respective isomers **4a** and **4d** in methanol. Thus, the more stable ones might be the trans isomers (**4**).

Next, we examined the oxidation of **2a** using commercial lead dioxide (LDO).[9] Although LDO scarcely reacted with **2a** in methylene chloride only, it oxidized **2a** in the presence of trifluoroacetic acid[10] in methylene chloride to give 23% of **1a**. The yield was not much improved, but the procedure was reasonably simple (see the Experimental Section) and the yield was reproducible; thus, the method has brought about at present the best result regarding the synthesis of unsubstituted 1,2,3-triazine (**1a**). In the above

(6) Closs, G. L.; Harrison, A. M. *J. Org. Chem.* **1972**, *37*, 1051.
(7) Fieser, L. F.; Fieser, M. F. "Reagents for Organic Synthesis"; 1967; p 731 and references cited therein.
(8) The enhancement of formation of **1** by the use of acids may arise from protonation to the nitrene intermediate which retards the dimerization to the azo compounds. However, use of acid in the MnO_2 oxidation of **2** did not give a preferable result.
(9) There was no significant difference in the yields of **1a** from **2a** between the use of a commercial LDO and freshly prepared LDO: Kuhn, R.; Hammer, I. *Ber.* **1950**, *83*, 413.
(10) The use of trifluoroacetic acid led to better yield than the use of acetic acid.

Scheme III

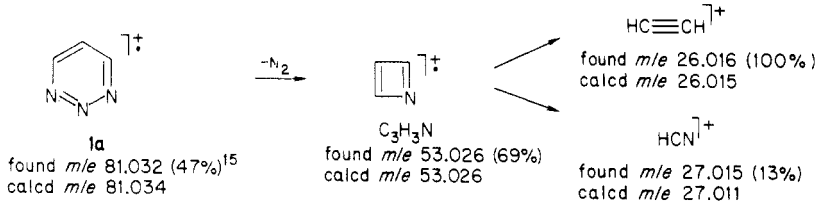
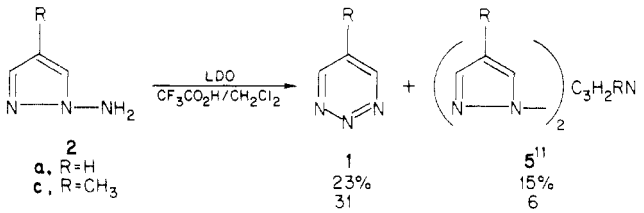


Table III. Physical Data of 1,2,3-Triazines (1)

	IR (KBr): ν_{max}, cm^{-1}	UV (EtOH): λ_{max}, nm (log ϵ)	NMR: δ (J, Hz) 4-posn	5-posn	6-posn
1a	3045 (m), 1550 (s), 1410 (m), 1315 (s)	288 (2.93), 232 (sh)	9.06 (2 H, d, 6.0, 4- and 6-H)	7.45 (1 H, d, 6.0, 5-H)	9.06
1b	3050 (m), 1570 (s), 1400 (m), 1385 (m)	286 (2.71), 228 (sh)	2.70 (1 H, s, CH_3)	7.33 (1 H, d, 6.0, 5-H)	8.92 (1 H, d, 6.0, 6-H)
1c	3030 (m), 1570 (s), 1538 (s), 1345 (s)	288 (2.96), 232 (sh)	8.93 (2 H, s, 4- and 6-H)	2.40 (3 H, s, CH_3)	8.93
1d	3060 (m), 1596 (s), 1405 (m), 1380 (m), 1360 (m)	284 (2.62), 234 (2.77)	2.68 (6 H, s, CH_3)	7.11 (1 H, s, 5-H)	2.68
1e	3010 (w), 1550 (s), 1435 (m), 1390 (s), 1370 (s)	278 (2.67), 240 (sh)	2.62 (6 H, s, 4- and 6-CH_3)	2.28 (3 H, s, 5-CH_3)	2.62
1f	3450 (w), 1562 (s), 1490 (m), 1445 (m), 1372 (m)	267 (4.08)	7.40–7.70 (3 H, m, phenyl-H), 8.17–8.30 (2 H, m, phenyl-H)	7.72 (1 H, d, 6.0, 5-H)	9.05 (1 H, d, 6.0, 6-H)
1g	3060 (w), 1584 (s), 1364 (m)	268 (4.30), 228 (sh)	2.76 (3 H, s, CH_3)	7.46–7.67 (4 H, m, 5-H and phenyl-H), 8.16–8.30 (2 H, m, phenyl-H)	
1h	3070 (m), 1570 (s), 1485 (m), 1375 (s)	269 (4.69), 215 (sh)[a]	7.50–7.70 (6 H, m, phenyl-H), 8.17–8.35 (4 H, m, phenyl-H)	8.01 (1 H, s, 5-H)	7.50–7.70, 8.17–8.35

[a] Equivocal shoulder.

described LDO/H^+ oxidation, neither **4a** nor **4a′** was found in the reactin mixture, and, instead, the isolable byproduct was a compound of the composition $C_9H_9N_5$ (**5a**) whose structure has not been fully confirmed.[11]



Additionally, the yields of **1b–d** were 35%, 31%, and 56%, respectively, from a **2b** + **2b′** mixture, **2c**, and **2d**. Moreover, the reaction of **2** with MnO_2[8,12] afforded again the described azo compounds as major products (Scheme II).

All the triazines were appreciably stable at room temperature, and their physical data are listed in Table III.

Infrared spectra (IR) of the triazines showed strong absorptions in 1550–1600 cm^{-1} region, owing to the double-bond stretchings in the triazine molecules. Unsubstituted and methyl triazines showed the ultraviolet (UV) absorptions of medium intensities in the 278–288-nm region. These may be due to n–π^*, and the π–π^* absorptions seem to appear as shoulders in short region near 230 nm or to be indistinguishable from strong end absorptions in shorter wavelength. However, our present examination on the UV spectra is insufficient to discuss the electronic structure of the triazines.

In NMR spectra, the absorption signals of 4-H adjacent to the nitrogen atom appeared near δ 9, and those of 5-H appeared in the region δ 7–8. These δ values suggest that the triazine ring has roughly equal deshielding effect with pyridazine and pyrimidine rings.[13] In ^{13}C NMR of **1a**, the signals due to 4-C and 5-C appeared at δ 149.7 and 117.9, respectively. The chemical shifts again suggest that the deshielding effect of 1,2,3-triazine ring is not so different from those of pyridazine and pyrimidine rings.[14]

The mass spectrum (MS) of **1a** showed a strong peak attributed to N_2 elimination from the parent ion and characteristic fragmentation peaks as shown in Scheme III.

Finally, the triazine **1a** was appreciably stable although it decomposed in strongly acidic solution or in alkaline solution, and the crystallographic study has been already reported.[16]

Experimental Section

MS and VPC–MS were recorded on a JEOL JMS-D300 instrument, IR on a Jasco A102, UV on a Hitachi EPS340, and NMR on a JEOL FX-100 (δ vs. Me_4Si, in $CDCl_3$).

Synthesis of 1-Aminopyrazoles (2). General Procedure. To a suspension of sodium hydride (60% in paraffin; 1.5 g, 37.5 mmol) in 50 mL of dry tetrahydrofuran (THF) was added a

(11) In the mass spectrum of **5a**, peaks at m/e 107.084 ($M^+ - C_4H_4N_2$) and 80.038 ($C_4H_4N_2$) suggest the presence of the (pyrazole + CH) moiety in the molecule. Presence of the (pyrazole + N) moiety in **5a** is expected from the starting material (**2a**), and it was supported by the mass peak at m/e 106.053 ($M^+ - C_3H_3N_3$). In the NMR spectrum, **5a** showed signals at δ 6.25 (triplet of J = 3 Hz, 3-H of pyrazole ring), 6.35 (t, J = 3 Hz, 3′-H of pyrazole ring), and 7.35–7.65 (2-, 2′-, 4-, and 4′-H of pyrazole rings plus an olefinic proton), suggesting the presence of two (nonequivalent) pyrazole rings in the molecule. The spectral data of **5c** also revealed the analogous features (see the Experimental Section).

(12) Goldman, I. M. *J. Org. Chem.* **1969**, *34*, 1979.

(13) The signals of 3-H and 4-H of pyrazidine appear at δ 9.17 and 7.68, respectively; 2-H, 4-H, and 5-H of pyrimidine absorb at δ 9.15, 8.60, and 7.09, respectively: Newkome, G. R.; Paudler, W. W. "Contemporary Heterocyclic Chemistry"; Wiley: New York, 1982.

(14) 3-C and 4-C of pyridazine resonate at δ 153 and 128, respectively, and 2-C, 4-C, and 5-C at δ 159, 157, and 122, respectively. See ref 13.

(15) The relative intensities of the ion peaks were obtained from the ionization at 70 eV.

(16) Yamaguchi, K.; Ohsawa, A.; Arai, H.; Ohnishi, H.; Igeta, H.; Iitaka, Y. *Chem. Pharm. Bull.* **1983**, *31*, 3762.

solution of a pyrazole (30 mmol) in 50 mL of THF dropwise during 10 min at 0 °C, under stirring. The precipitation of NaH disappeared along with an evolution of hydrogen gas during the addition. The solution was again cooled on an ice bath and added with a benzene solution of (*O*-mesitylenesulfonyl)hydroxylamine (MSH), which was prepared as follows: MSH (58%, freezed with water;[5] 14 g, 38 mmol) was suspended in 140 mL of benzene. The benzene layer was separated, and the aqueous layer was extracted with additional benzene (40 mL). The benzene layers were combined to be dried over $MgSO_4$. The $MgSO_4$ was filtered off prior to the addition.

The reaction mixture formed a milky precipitate when it was stirred for 30 min at room temperature. After filtration of the precipitate the solution was evaporated to dryness under a reduced pressure. The residue was subjected to distillation or alumina or silica gel column chromatography and recrystallization. The results are shown in Table I.

Amination of pyrazole **3a** gave an oily product **2a**: NMR δ 5.55 (2 H, br s), 5.99 (1 H, t, J = 3 Hz), 7.25 (2 H, t, J = 3 Hz); acetamide mp 124–126 °C (colorless needles from benzene); *p*-methoxybenzamide, mp 164–165 °C (colorless needles from chloroform); picrate mp 147–148 °C.

Amination of 3-methylpyrazole (**3b**) gave an oil whose NMR showed that it was a mixture of about the equal amounts of the isomers **2b** and **2b′**: NMR δ 2.20 (3 H, s), 2.25 (3 H, s), 5.18 (2 H, br s), 5.37 (2 H, br s), 5.88 (2 H, br s, 4-H of **2b** and 4-H of **2b′**), 7.18 (2 H, br s, 5-H of **2b** and 3-H of **2b′**).

Amination of 4-methylpyrazole (**3c**) gave **2c**: colorless oil; NMR δ 2.03 (3 H, s), 5.22 (2 H, s), 7.15 (2 H, s).

Amination of 3,5-dimethylpyrazole (**3d**) afforded **2d**: colorless needles from pentane–hexane; NMR δ 2.13 (3 H, s), 2.19 (3 H, s), 5.10 (2 H, br s), 5.66 (1 H, s). Anal. Calcd for $C_5H_9N_3$: C, 54.03; H, 8.16; N, 37.81. Found C, 53.95; H, 8.22; N, 37.55. Picrate mp 120–122 °C.

Amination of 3,4,5-trimethylpyrazole (**3e**) afforded colorless needles (pentane) of **2e**: NMR δ 1.86 (3 H, s), 2.10 (3 H, s), 2.15 (3 H, s), 4.89 (2 H, br s). Anal. Calcd for $C_6H_{11}N_3$: C, 57.57; H, 8.86; N, 33.57. Found: C, 57.22; H, 9.08; N, 33.66.

Amination of 3-phenylpyrazole (**3f**) gave a mixture of **2f** and **2f′**. The major product was colorless needles (hexane): mp 108–109 °C; NMR δ 5.23 (2 H, br s), 6.33 (1 H, d, J = 2 Hz), 7.37–7.53 (4 H, m), 7.63–7.76 (2 H, m). Anal. Calcd for $C_9H_9N_3$: C, 67.90; H, 5.70; N, 26.40. Found: C, 68.01; H, 5.85; N, 26.05. The minor was colorless flakes (hexane): mp 79–80 °C; NMR δ 5.34 (2 H, br s), 6.45 (1 H, d, J = 2 Hz), 7.28–7.45 (4 H, m), 7.71–7.80 (2 H, m). Anal. Found: C, 68.02; H, 5.51; N, 26.00.

Amination of 3-methyl-5-phenylpyrazole (**3g**) produced a mixture of isomers **2g** and **2g′**. The major product was colorless plates (benzene): mp 152–153 °C; NMR δ 2.27 (3 H, s), 5.15 (2 H, br s), 6.13 (1 H, s), 7.38–7.55 (3 H, m), 7.65–7.80 (2 H, m). Anal. Calcd for $C_{10}H_{11}N_3$: C, 69.34; H, 6.40; N, 24.26. Found: C, 69.32; H, 6.28; N, 24.23. Minor product was obtained as colorless needles (hexane): mp 94–95 °C; NMR δ 2.34 (3 H, s), 5.08 (2 H, br s), 6.27 (1 H, s), 7.29–7.54 (3 H, m), 7.67–7.85 (2 H, m). Anal. Found: C, 69.60; H, 6.22; N, 24.00.

N-aminated product from 3,5-diphenylpyrazole **3h** was colorless needles (*i*-Pr_2O) **2h**: NMR δ 5.83 (2 H, br s), 6.64 (1 H, s), 7.33–7.55 (6 H, m), 7.68–7.87 (4 H, m). Anal. Calcd for $C_{15}H_{13}N_3$: C, 76.57; H, 5.57; N, 17.86. Found: C, 76.25; H, 5.60; N, 18.06.

Oxidation of 1-Aminopyrazoles (2) with Lead Tetraacetate (LTA). General Procedure. To a cold (−30 °C) solution of LTA (11 g, 25 mmol) in dry CH_2Cl_2 (150 mL) was added a solution of a 1-aminopyrazole (21 mmol) in CH_2Cl_2 (50 mL) dropwise under stirring. The mixture was stirred for 10 min at room temperature and then neutralized with saturated aqueous $KHCO_3$. The mixture was filtered through a layer of Celite. The filtrate was evaporated, and organic layer was dried over $MgSO_4$ and filtered. The solution was evaporated, the residue was subjected to a silica gel column chromatography (benzene–CH_2Cl_2), and the material was purified by recrystallization. The synthetic data are summarized in Table II.

Oxidation of **2a** with LTA according to above procedure or some modified procedure gave a mixture of complicated composition in which small amount of the expected product **1a** was found by VPC and NMR. The attempts to isolate **1a** from the mixture was unsuccessful.

Oxidation of 2a with Nickel Peroxide (NPO).[7] A solution of **2a** (0.5 g) in dry CH_2Cl_2 (50 mL) was added dropwise to a stirred suspension containing 2.3 g of NPO (activity 2.7 mmol of oxygen/g) in CH_2Cl_2 (50 mL) at 0 °C. The mixture was stirred until most **2a** was consumed (it usually took 2–3 h; check by alumina TLC, CH_2Cl_2), and inorganic precipitate was filtered off. The solvent was evaporated off under reduced pressure, and the residue was chromatographed over silica gel (Et_2O–CH_2Cl_2) to give an approximately 5/4 (by NMR see below) mixture of **4a** and **4a′** (total 0.22 g; 45%), 4% of **1a**, and 10% of **3a**. **4a** + **4a′** mixture: NMR δ 6.34 (0.8 × 1 H, br m, 4- and 4′-H of **4a′**), 6.49 (1 H, br m, 4- and 4′-H of **4a**), 7.50 (0.8 × 1 H, br d, 5- and 5′-H of **4a′**), 7.60 (0.8 × 1 H, d, J = 5 Hz, 3- and 3′-H of **4a′**), 7.70 (1 H, br d, 5- and 5′-H of **4a**), 8.10 (1 H, d, J = 5 Hz, 3- and 3′-H of **4a**).

Oxidation of 2d with NPO. Similar oxidation of **2d** with NPO gave 27% of **4d** and 14% of **4d′**, which could be separated from each other by alumina chromatography (benzene–CH_2Cl_2), 10% of **1d** and 16% of **3d**. **4d**: colorless needles from Et_2O; mp 154–155 °C; NMR δ 2.30 (6 H, s, CH_3 × 2), 2.50 (6 H, s, CH_3 × 2), 5.96 (2 H, s, 4-H); MS, m/e 218.128 (calcd for M^+, 218.128), 123.071 (calcd for M^+–$C_5H_7N_2$, 123.067), 95.061 (calcd for $C_5H_7N_2$, 95.061). Anal. Calcd for $C_{10}H_{14}N_6$: C, 55.03; H, 6.47; N, 38.51. Found: C, 55.43; H, 6.40; N, 38.30. **4d′**: yellow needles from pentane; mp 93–94 °C; NMR δ 2.10 (6 H, s), 2.36 (6 H, s) 5.82 (2 H, s); MS m/e 218.126, 123.071, 95.059. Anal. Found: C, 55.40; H, 6.33; N, 38.22.

Oxidation of 2a with NPO–Acetic Acid. The aminopyrazole (3 g) in 220 mL of CH_2Cl_2 was added to a mixture of NPO (17 g) and 2.2 g of acetic acid in CH_2Cl_2 under the similar conditions as above. The suspension was stirred for 2–3 h until most the **2a** was consumed. After filtration, the solution was neutralized with saturated aqueous $KHCO_3$ and the organic layer was dried over $MgSO_4$ and evaporated to dryness. The residue was chromatographed over silica gel. The major fraction was purified by sublimation under reduced pressure and by a recrystallization from Et_2O to give 0.59 g (20%) of pure **1a**.

Oxidation of 2 with Manganese Dioxide. The aminopyrazoles were treated with MnO_2[12] in CH_2Cl_2 at room temperature. The workup was carried out similarly as above.

Oxidation of 2 with Lead Dioxide (LDO)–Trifluoroacetic Acid (TFA). To a suspension containing 30 g of commercial LDO and 5 mL of TFA in 200 mL of CH_2Cl_2 was added a solution of **2a** (4 g) in 100 mL of CH_2Cl_2 during 30 min at room temperature with vigorous stirring. After all of the solution was added, every 10 g of LDO was added three times at 20-min intervals to complete the reaction. After filtration, the solution was evaporated (without neutralization) and the oily residue was subjected to a silica gel column chromatography to give 0.90 g (23%) of **1a** and 0.45 g (15%) of **5a**: colorless prisms from hexane–chloroform; mp 132–134 °C; IR (KBr) 1640 cm^{-1}; NMR δ 6.25 (1 H, t, J = 3 Hz), 6.35 (1 H, t, J = 3 Hz), 6.80 (1 H, dd, J = 9.5 and 13 Hz), 7.35–7.65 (5 H, m), 8.80 (1 H, d, J = 9.5 Hz); MS m/e 187.085 (calcd for M^+, 187.086), 120.055 (calcd for $M^+ - C_3H_3N_2$, 120.056), 107.084 (calcd for $M^+ - C_4H_4N_2$, 107.084), 106.053 (calcd for $M^+ - C_3H_3N_3$, 106.053), 80.038 (calcd for $C_4H_4N_2$, 80.038), 68.038 (calcd for $C_3H_4N_2$, 68.038). Anal. Calcd for $C_9H_9N_5$: C, 57.74; H, 4.85; N, 37.41. Found: C, 57.62; H, 4.51; N, 37.61.

Similar treatment of **2c** afforded 31% of **1c** and 6% of **5c**: colorless needles from hexane–chloroform; mp 138–140 °C; IR (KBr) 1635 cm^{-1}; NMR δ 2.10 (3 H, s), 2.15 (3 H, s), 2.35 (3 H, s), 7.15 (1 H, s), 7.19 (1 H, s), 7.30 (1 H, s), 7.40 (1 H, s), 7.42 (1 H, s), 8.65 (1 H, s); MS, m/e 229.132 (calcd for M^+, 229.133), 148.089 (calcd for $M^+ - C_4H_5N_2$, 148.088), 134.085 (calcd for $M^+ - C_4H_5N_3$, 134.085), 95.045 (calcd for $C_4H_5N_3$, 95.048). Anal. Calcd for $C_{12}H_{15}N_5$: C, 62.86; H, 6.60; N, 30.55. Found: C, 62.59; H, 6.38; N, 30.29.

Registry No. **1a**, 289-96-3; **1b**, 77202-08-5; **1c**, 86402-30-4; **1d**, 77202-09-6; **1e**, 33209-85-7; **1f**, 99214-46-7; **1g**, 77202-10-9; **1h**, 99214-47-8; **2a**, 3994-46-5; **2a**·picrate, 99214-44-5; **2b**, 77202-04-1; **2b′**, 77202-03-0; **2c**, 99232-51-6; **2d**, 77202-06-3; **2d**·2picrate, 99214-45-6; **2e**, 77202-07-4; **2f**, 99214-40-1; **2f′**, 99214-41-2; **2g**, 77202-05-2; **2g′**, 99214-42-3; **2h**, 99214-43-4; **3a**, 288-13-1; **3b**, 1453-58-3; **3c**, 7554-65-6; **3d**, 67-51-6; **3e**, 5519-42-6; **3f**, 2458-26-6; **3g**, 56426-41-6; **3h**, 1145-01-3; **4a**, 99214-48-9; **4a′**, 99214-49-0; **4d**, 99214-50-3; **4d′**, 99214-51-4.