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Reactions of *N*-Aminopyrazoles with Halogenating Reagents and Synthesis of 1,2,3-Triazines

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Reactions of *N*-aminopyrazoles with halogenating reagents (Cl_2, Br_2, I_2, BrCl, ICl, IBr, *N*-chlorosuccinimide, and *N*-bromosuccinimide) were examined. Some of these reagents preferentially lead to oxidation of the amino group to give the corresponding 1,2,3-triazines as major products, while others mainly gave either or both of 1-amino-4-halopyrazoles and 5-halo-1,2,3-triazines as the result of halogenation of the 4-position of the pyrazole ring prior to the oxidation of the amino group. In some cases, the oxidation of the amino group and the halogenation of the pyrazole ring proceeded concurrently to form not only the unhalogenated triazines but also the 1-amino-4-halopyrazoles and the 5-halotriazines. Various reagents and reaction conditions were explored to utilize the reaction for the synthesis of halogenated and unhalogenated 1,2,3-triazines.

Keywords——1,2,3-triazine; halo-1,2,3-triazine; pyrazole; 1-aminopyrazole; 1-aminohalopyrazole; synthesis; oxidation; halogenation; ring expansion

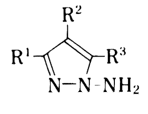
In earlier studies,[1,2] it has been established that the oxidation of *N*-aminopyrazoles with high valency metal salts or their oxides gives 1,2,3-triazines. Another possibility for oxidation of *N*-aminopyrazoles is reaction with halogenating reagents. With the latter, however, electrophilic halogenation of the pyrazole ring may also occur.[3] Consequently, it is of interest to investigate the behavior of *N*-aminopyrazoles with halogenating reagents, as the *N*-aminopyrazoles have sites for halogenation on the pyrazole ring, and also their amino groups are expected to undergo oxidation.

This paper describes the reaction of *N*-aminopyrazoles (**1**—**8**) with halogenating agents and its application to the synthesis of various halogenated[4] and unhalogenated monocyclic 1,2,3-triazines (**9**—**16**, **18**, **20**, **22**, **24**—**29**, **32**, **34**, and **36**).

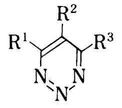
Preparation and Structural Assignment of the *N*-Aminopyrazoles

The starting *N*-aminopyrazoles were prepared by *N*-amination[1,2] of the corresponding pyrazoles. The amination of unsymmetrical pyrazoles *i.e.*, 3-methylpyrazole (**37**), 3-phenylpyrazole (**38**), and 3-methyl-5-phenylpyrazole (**39**) gave mixtures of isomeric 1-aminopyrazoles (**2a**+**2b**, **4a**+**4b**, and **6a**+**6b**, respectively) as described in our previous papers.[1]

The structures of **2a**, **b**, **4a**, **b**, and **6a**, **b** were determined in this work by X-ray analysis and carbon-13 nuclear magnetic resonance (^{13}C-NMR) spectroscopy. Compounds **2a** and **2b** were identified by comparing their ^{13}C-NMR spectra with those of reference compounds (Table I). The ^{13}C-NMR of one isomeric methyl derivative (**2a**) showed signals at δ (ppm) from tetramethylsilane (TMS) 10.8 (methyl carbon), 103.3 (tertiary carbon of pyrazole ring), 135.2 (tertiary carbon of the pyrazole ring), and 137.5 (quaternary carbon of the pyrazole), and the signals are assigned to the methyl carbon at the 5-position, and the 4-, 3-, and 5-carbons of the pyrazole ring, respectively, of 1-amino-5-methylpyrazole. Another isomer (**2b**)



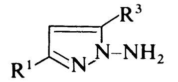
	R1	R2	R3
1	H	H	H
2a	H	H	Me
2b	Me	H	H
3	H	Me	H
4a	Ph	H	H
4b	H	H	Ph
5	Me	H	Me
6a	Ph	H	Me
6b	Me	H	Ph
7	Ph	H	Ph
8	Me	Me	Me



	R1	R2	R3		R1	R2	R3
9	H	H	H	**23**	Ph	Cl	H
10	Me	H	H	**24**	Ph	Br	H
11	H	Me	H	**25**	Me	Cl	Me
12	Ph	H	H	**26**	Me	Br	Me
13	Me	H	Me	**27**	Me	Cl	Ph
14	Me	H	Ph	**28**	Me	Br	Ph
15	Ph	H	Ph	**29**	Ph	Cl	Ph
16	Me	Me	Me	**30**	Ph	Br	Ph
17	H	Cl	H	**31**	Cl	Cl	H
18	H	Br	H	**32**	Br	Br	H
19	Me	Cl	H	**33**	Cl	Cl	Me
20	Me	Br	H	**34**	Br	Br	Me
21	Cl	Me	H	**35**	Cl	Cl	Ph
22	Br	Me	H	**36**	Br	Br	Ph

Chart 1

TABLE I. ^{13}C-NMR of *N*-Aminopyrazoles[a)]



Aminopyrazole	R1	R3	C-3	C-4	C-5	3-$\underline{C}H_3$	5-$\underline{C}H_3$	3-$\underline{C}C_5H_5$	5-$\underline{C}C_5H_5$
1	H	H	136.6	103.8	128.8				
2a	H	Me	135.2	103.3	137.5		10.8		
2b	Me	H	146.0	103.4	129.7	13.8			
4a	Ph	H	148.8	101.2	130.3			132.9	
4b	H	Ph	135.8	104.2	140.9				129.4
5	Me	Me	144.4	102.8	138.5	13.8	10.8		
6a	Ph	Me	147.2	100.6	139.3		11.1	133.2	
6b	Me	Ph	144.8	103.6	141.8	13.8			129.6
7	Ph	Ph	147.4	101.2	142.5			132.8	129.4

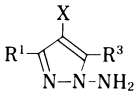
a) The δ values are shown (see the Experimental section).

showed signals at δ 13.8 (methyl carbon), 103.4 (tertiary carbon of pyrazole), 129.7 (tertiary carbon of pyrazole), and 146.0 (quaternary carbon of pyrazole), and the signals are respectively attributable to the methyl carbon at the 3-position, and the 4-, 5-, and 3-carbons of the pyrazole ring of 1-amino-3-methylpyrazole.

The structures of the major isomer from **38** and the major isomer from **39** were respectively confirmed as 1-amino-3-phenylpyrazole (**4a**) and 1-amino-5-methyl-3-phenylpyrazole (**6a**) by X-ray analysis as described in the experimental section; hence, the minor products from **38** and **39** are assigned as the 1-amino-5-phenyl (**4b**) and 1-amino-3-methyl-5-phenyl isomers (**6b**), respectively.

Reaction of *N*-Aminopyrazoles with Halogenating Reagents

First, the reaction of *N*-aminopyrazoles (**1**—**7**) was carried out using 1 molar eq (with respect to **1**—**7**) of the halogenating reagents, *i.e.*, Cl_2, Br_2, I_2, BrCl, ICl, IBr, *N*-



	R^1	R^3
40	H	H
41a	H	Me
41b	Me	H
42a	Ph	H
42b	H	Ph
43	Me	Me
44a	Ph	Me
44b	Me	Ph
45	Ph	Ph

Chart 2

TABLE II. Reaction of *N*-Aminopyrazoles with Halogenating Reagents[a]

Aminopyrazole	Reagent	Yields (%)[b]				
		Triazine	5-Halotriazine	1-Amino-4-halopyrazole	Other product[c]	Starting material
1	Cl_2	0	0	0	*A*	30[d]
	Br_2	0	**18** tr	**40** X=Br 43		12[e]
	I_2	0	0	0		72
	NCS	0	0	0		84
	NBS[f]	**9** tr	0	0	*A*	tr
2a	Cl_2	0	0	0	*A*	25
	Br_2	**10** tr	**20** 3	**41a** X=Br 53		0
	I_2	**10** 34	0	0		26
	NCS	**10** tr	0	0		56
	NBS	**10** 10[g]	**20** 5[g]	**41a** X=Br 36	*A*	0
2b	Cl_2	0	0	0	*A*, *B*	12
	Br_2	0	0	**41b** X=Br 55		0
	I_2	**10** 48	0	0		16
	NCS	**10** tr	0	0		76
	NBS	**10** tr	**20** tr	**41b** X=Br 19	*A*	0
3	Cl_2	**11** tr	—	—	*A*, *C*	43[d]
	Br_2	**11** 10	—	—	*A*, *C*	20[e]
	I_2	**11** 47	—	—	*C*	11
	NCS	**11** tr	—	—	*A*, *C*	tr
	NBS	**11** 5	—	—	*A*, *C*	7
4a	Cl_2	0	0	0	*A*, *D*	10
	Br_2	0	0	**42a** X=Br 86	*E*	tr
	I_2	**12** 17	0	0	*F*	56
	NCS	**12** tr	0	0	*G*	50
	NBS	0	0	**42a** X=Br 20	*A*, H	19
4b	Cl_2	0	0	0	*A*, *I*	48
	Br_2	0	0	**42b** X=Br 93		4
	I_2	**12** 29	0	0		43
	NCS	**12** tr	0	0		83
	NBS	**12** 5	0	**42b** X=Br 21		8
5	Cl_2	**13** 2	**25** 19	**43** X=Cl tr		40[d]
	Br_2	**13** tr	**26** 2	**43** X=Br 75[e]		5
	I_2	**13** 69	0	**43** X=I tr		18
	BrCl	**13** 2	**25** 14[h]	**43** X=Br 61[d,i]		tr
	ICl	**13** 69	0	**43** X=I 12[i]		tr
	IBr	**13** 70	**26** 7[j]	**43** X=Br tr[k]		tr
	NCS	**13** 14	**25** 7	**43** X=Cl 34		36
	NBS	**13** 3	**26** 23	**43** X=Br 34		16

TABLE II. (continued)

Aminopyrazole	Reagent	Yields (%)[b]				
		Triazine	5-Halo-triazine	1-Amino-4-halopyrazole	Other product[c]	Starting material
6a	Cl_2	0	**27** 4	0		45[d]
	Br_2	0	0	**44a** X = Br quant.		tr
	I_2	**14** 42	0	0	*J*	23
	NCS	0	0	0		Quant.
	NBS	**14** 2	**28** 9[g]	**44a** X = Br 30	*A*, *K*	9[g]
6b	Cl_2	0	**27** 7	**44b** X = Cl tr		62[d]
	Br_2	**14** tr	**28** tr	**44b** X = Br 71		20[g]
	I_2	**14** 59	0	0		22[g]
	NCS	0	0	0		93
	NBS	**14** 11	**28** 10	**44b** X = Br 34	*K*	23
7	Cl_2	0	0	**45** X = Cl 6	*L*	58
	Br_2	0	0	**45** X = Br 82	*M*	0
	I_2	**15** 23[h]	0	0	*N*	69[g]
	NCS	0	0	0		97
	NBS	**15** 11	0	**45** X = Br 21	*O*	32

a) By method A (see the Experimental section; reagent : **1**—**7** = 1 : 1, reaction time 1 h, at room temperature, unless otherwise noted). *b*) Isolation yields (based on 1-aminopyrazoles), unless otherwise noted. *c*) See footnotes *A*—*O*. *d*) Precipitated as the HCl salt. *e*) Precipitated as the HBr salt. *f*) Reaction time 10 min. *g*) Yields were estimated from ^{1}H-NMR integration of the chromatographic fraction containing the compounds. *h*) Bromotriazine (**26**) was formed in a trace amount (by GC-MS). *i*) Compound **43** X = Cl was absent (by MS and GC-MS). *j*) A trace of 5-iodo-4,6-dimethyltriazine was detected (by GC-MS). *k*) Compound **43** X = I was absent (by MS and GC-MS). *A* Unidentified by-products constituted a major part of the reaction mixture. *B* 34% of undefined compound whose composition is $C_8H_{10}ClN_3O$ (mp 168—169 °C, dec.). *C* None of 4-halo-5-methyltriazine, 1-amino-3-halo-4-methylpyrazole, or 1-amino-5-halo-4-methylpyrazole was obtained. *D* **38** (42%), 4-chloro-3-phenylpyrazole [trace; mp 102—104 °C, lit. 102 °C; K. v-. Auwers and T. Breyhan, *J. Pract. Chem.*, **143**, 259 (1935)] and an undefined compound of mp 215—218 °C (11%) whose composition is $C_{18}H_{15}ClN_4$. *E* Undefined compound of mp 199—201 °C (4%) whose composition is $C_{18}H_{14}Br_2N_4$. *F* **38** (6%). *G* **38** (20%). *H* **38** (11%) and the compound of mp 199—201 °C (16%; see footnote *E*). *I* 4-Chloro-3-phenylpyrazole (trace) and an undefined compound of mp 156—158 °C (4%) whose composition is $C_{18}H_{15}ClN_4$. *J* **39** (3%). *K* 4-Bromo-3-methyl-5-phenylpyrazole (trace; see footnote *L* of Table IV). *L* 4-Chloro-3,5-diphenylpyrazole (4%) and an oil of composition $C_{15}H_{11}Cl_2N$ (21%). *M* 4-Bromo-3,5-diphenylpyrazole (3%; see footnote *O* of Table IV). *N* 3,5-Diphenylpyrazole (6%). *O* 3,5-Diphenylpyrazole (8%) and an unidentified compound (9%) of mp 106—110 °C whose composition is $C_{15}H_{11}Br_2N$. tr: trace.

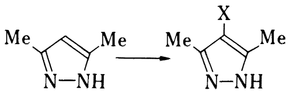
chlorosuccinimide (NCS), and *N*-bromosuccinimide (NBS). The results are summarized in Table II.

The main products were (unhalogenated) triazines, 5-halotriazines, and 1-amino-4-halopyrazoles; and pyrazoles and/or halopyrazoles (*i.e.*, products of deamination)[2a] were frequently obtained as side products. Of these, the triazines are produced through oxidation of the amino group followed by ring expansion, and the halopyrazoles are the products of electrophilic substitution on pyrazoles. As for the formation of the halotriazines, two routes may be considered, one *via* halogenation of the (unhalogenated) triazines and the other through oxidation of the 1-amino-4-halopyrazoles. To clarify this point, the 1-amino-4-halo-3,5-dimethylpyrazoles **43** (X = Cl and X = Br) and 4,6-dimethyl-1,2,3-triazine (**13**) were separately treated with the halogenating reagents under similar conditions. The reaction of **43** with the reagents always afforded the corresponding 5-halotriazines (**25** and **26**, respectively from **43** X = Cl and X = Br) in rather high yields with little or no recovery of **43**. On the other hand, the reaction of **13** with Cl_2 and NCS gave **25** only in low yields, that with ICl gave only **25** in low yield, that with IBr gave only a trace of **26** (5-iodo-4,6-dimethyltriazine was absent in these cases), those with Br_2 and NBS gave moderate yields of **26**, and that with BrCl gave both **25** and **26** in moderate yields (the yield ratio **25**/**26** was approximately 1/2.5).[5] In these runs, the reactions were accompanied with recoveries of **13**, together with formation of appreciable amounts of side products. The reaction of **13** with I_2 resulted in recovery of the

TABLE III. Halogenation of 3,5-Dimethylpyrazole (**46**)[a]

Reagent	Reaction time[b]	Halopyrazole (**47**, yield %)[c]	Recovery of **46** (%)[c]
Cl_2	10 min	77[d]	tr
Br_2	10 min	85[e]	tr
I_2	2 h	33[f]	63[f]
BrCl	1 h	X=Cl 0,[g] X=Br 94[e]	tr
ICl	1 h	X=Cl 0,[g] X=I 81[h]	0
IBr	1 h	X=Br 17,[i] X=I 73[i]	tr
NCS	1 h	94[d]	tr
NBS	1 h	93[e]	tr

a) By method A (see the Experimental section). *b*) At room temperature.[19] *c*) Isolation yields unless otherwise noted. *d*) mp 111—112 °C [lit. 95 °C; G. T. Morgan and I. J. Ackerman, *J. Chem. Soc.*, **123**, 1308 (1923)]. *e*) mp 115—116 °C (lit. 118 °C; see the reference in footnote *d*). *f*) The amounts of **46** and **47** in the resulting mixture were estimated by NMR and GC using the respective standard samples. *g*) By GC-MS. *h*) mp 138—139 °C (lit. 137 °C; see the reference in footnote *d*) *i*) The yields of **47** X=Br and **47** X=I were determined by GC using the respective standard samples.



46 **47** : X=Cl, Br, I

Chart 3

starting triazine **13**, accompanied with small amounts of unidentified by-products. From these observations, it is assumed that the 5-halotriazines **25** and **26** in Table II were mostly formed from **5** *via* **43** (X=Cl and X=Br, respectively), although the route to give **26** through the triazine **13** cannot be ignored in the reactions with Br_2 and with NBS.

Next, the reacting site of the "mixed-halogen molecules" BrCl, ICl, and IBr, in the halogenation of **5** is of interest in connection with the product ratio of **25** and **26** and that of **43** X=Cl, X=Br, and X=I. As a model, 3,5-dimethylpyrazole (**46**) was treated with those reagents under similar conditions, the results being shown in Table III.

The pyrazole **46** reacted with the halogenating reagents to give 4-halo-3,5-dimethylpyrazoles **47**. In this reaction, **46** exclusively attacked the bromine atom of BrCl, and the iodine atom of ICl, and preferentially the iodine atom of IBr. These results are consistent with the polarization of the mixed-halogen molecules due to the electronegativities of the halogen atoms. The halogenation of aminopyrazoles to form 1-amino-4-halopyrazoles as shown in Table II is in agreement with the character of each mixed-halogen. Iodine showed low halogenating ability commonly in the reactions with **1**—**7** and with **46**. In view of the oxidizing character of BrCl towards the aminopyrazole **5** to give **13** and its chlorinating ability towards **13** and brominating (but not chlorinating) ability towards the pyrazoles, the 5-chlorotriazine **25** may be produced *via* chlorination of the triazine **13** but not from **43** X=Cl.

Generally in the described reaction system, Br_2, BrCl, and NBS exhibited not only a strong halogenating ability towards the aminopyrazoles to give 1-amino-4-halopyrazoles, but also a strong oxidizing ability to give halogenated and/or unhalogenated triazines. I_2, ICl, and IBr oxidized the aminopyrazoles to give unhalogenated rather than halogenated triazines as the major products. Although Cl_2 shows high reactivity[6] towards aminopyrazoles, it occasionally tended to cause side-reactions, resulting in a predominant decomposition of the materials in this system. NCS showed moderate to weak oxidizing or chlorinating character, and the reactions were occasionally accompanied with side-reactions.

TABLE IV. Synthesis of Halogenated 1,2,3-Triazines from *N*-Aminopyrazoles

Amino-pyrazole	Reagent	Method[a]	Reaction time[b]	Halotriazines (%)[c]				By-product[d]
1	Cl_2	C[e]	10 min	**17**	0	**31**	0	*A*
	NCS	A	1 h	**17**	0	**31**	0	*B*
	Br_2	C[e]	10 min	**18**	16	**32**	20	
	NBS	A	10 min	**18**	0	**32**	0	*A*
2a + **2b**[f]	Cl_2	C[e]	10 min	**19**	0	**33**	0	*A*
	NCS	A	1 h	**19**	0	**33**	0	*A*
	Br_2	C[e]	5 min	**20**	43	**34**	8	
	NBS	A	1 h	**20**	22	**34**	tr	*A*
3	Cl_2	C[e]	10 min	**21**	0			*A*
	NCS	A	1 h	**21**	0			*A*
	Br_2	C[e]	10 min	**22**	tr			*C*
	NBS	A	15 min	**22**	0			*A*
4a	Cl_2	C[e]	15 min	**23**	0	**35**	0	*A*
	NCS	A	1 h	**23**	0	**35**	0	*A*, *D*
	Br_2	C[e]	1 h[g]	**24**	8	**36**	10	*A*, *E*
	NBS	A	1 h	**24**	0	**36**	tr	*A*, *F*
5[h]	Cl_2	B	10 min	**25**	52			*G*
	NCS	A	3 h	**25**	73			*H*
	Br_2	B	30 min	**26**	62			*I*
	NBS	A	1 h	**26**	92			*G*
6a	Cl_2	B	20 min	**27**	43			*J*
	NCS	A	1 h	**27**	0			*K*
	Br_2	B	5 min	**28**	54			
	NBS	A	30 min	**28**	50			*L*
7	Cl_2	B	15 min	**29**	12			*A*, *M*
	NCS	A	1 h	**29**	0			*N*
	Br_2	B	5 min	**30**	0			*A*, *O*
	NBS	A	30 min	**30**	0			*A*, *P*

a) Reagent : **1**—**7** = 2 : 1 for method A; reagent : Et_3N : **1**—**7** = 2 : 2 : 1 for methods B and C (see the Experimental section). *b*) At room temperature; see footnote 19. *c*) Based on aminopyrazoles. *d*) Identifiable by-products only are noted, the amounts of 1-aminohalopyrazoles (**40**—**45**) and recoveries of the starting materials were trace or undetectable unless otherwise noted. *e*) Halogenation by methods A and B gave a mixture of unisolable products. *f*) A roughly 1 : 1 mixture (see reference 1*c*). *g*) The reaction for 10 min gave **42a** X = Br as the major product; **24** and **36** were trace. *h*) The reaction using ICl or IBr by method B gave neither 5-iodo-4,6-dimethyltriazine nor 1-amino-4-iodo-3,5-dimethylpyrazole (**43** X = I) in isolable yield; see also Table II and related footnotes therein. *A* Unidentified by-products constituted a major part of the reaction mixture. *B* 42% of pyrazole and 31% recovery of **1**. *C* 20% of **11**. *D* 4-Chloro-3-phenylpyrazole (24%; see footnote *D* of Table II). *E* 4-Bromo-3-phenylpyrazole (13%, mp 112—114 °C, lit. 116 °C; J. Elguero and R. Jacquier, *Bull. Soc. Chim. Fr.*, **1966**, 2832) and **42a** X = Br (16%). *F* 4-Bromo-3-phenylpyrazole (trace) and **42a** X = Br (trace). *G* **13** (trace). *H* **13** (16%). *I* **13** (7%). *J* 7% of **14** and 4-chloro-3-methyl-5-phenylpyrazole [9%; mp 111—112 °C, lit. 110—112 °C; J. F. Hansen, Y. I. Kim, and K. A. Merrigan, *J. Org. Chem.*, **44**, 4438 (1979)]; 6% of **6a** was recovered. *K* 88% of **6a** was recovered. *L* **44a** X = Br (25%) and 4-bromo-3-methyl-5-phenylpyrazole (13%; mp 101—102 °C, lit. 98 °C; R. Ketari and A. Foucaud, *Synthesis*, **1982**, 844). *M* **15** (5%) and 4-chloro-3,5-diphenylpyrazole (9%; mp 208—209 °C, lit. 210—211 °C; see the reference in footnote *J*). *N* 85% of **7** was recovered; **45** X = Cl (4%). *O* **15** (6%), 4-bromo-3,5-diphenylpyrazole (6%; mp 193—195 °C, lit. 200 °C; see the reference in footnote *L*), benzonitrile (19%), and an undefined compound of mp 106—110 °C (14%; see footnote *O* of Table II). *P* **15** (9%), 4-bromo-3,5-diphenylpyrazole (13%), benzonitrile (trace), and compound (44%) of mp 106—110 °C (see footnote *O*).

Additionally, the oxidative cyclization of the aminopyrazoles to form triazines was accelerated by the addition of alkali or amine, as observed in proton nuclear magnetic resonance (^{1}H-NMR) examinations.[7]

Application to the Synthesis of Halogenated Triazines

The reaction was employed for the synthesis of halotriazines from *N*-aminopyrazoles.

For this purpose, 2 molar eq (with respect to the aminopyrazoles) of the reagents were used. The reactions with Cl_2 and with Br_2 were carried out in the presence of triethylamine to neutralize hydrogen halide formed in the course of the reaction (methods B and C in the experimental section). The results are shown in Table IV.

In the reactions with Cl_2 and Br_2, the presence of Et_3N promoted the consumption of the starting materials and intermediary 1-amino-4-halopyrazoles, and promotion of halotriazine formation was also observed.[7] The reaction was occasionally accompanied with formation of side products, *e.g.*, pyrazoles (deamination), 4-halopyrazoles (deamination and halogenation), (unhalogenated) triazines, and/or 1-amino-4-halopyrazoles, *etc.*, as shown in the footnotes of Table IV. In the reaction of the aminopyrazoles (**1**—**4**) with an unsubstituted 3- or 5-position, the procedure using Cl_2 and Br_2 (method B) was unsuccessful. However, in the bromination of 4,5- (or 3,4-) unsubstituted 1-aminopyrazoles (**1**, **2**, and **4**), this difficulty was overcome by a modification: 1 molar eq of bromine was added stepwise before and after the addition of 1 molar eq of Et_3N (method C). In these cases, the reaction led to the formation of dibromotriazines (**32**, **34**, and **36**, respectively, from **1**, **2**, and **4**)[8] together with the monobromotriazines. The difficulty in the synthesis of 4-bromo-5-methyltriazine (**22**) from **3**, and of chlorotriazines from the aforementioned aminopyrazoles (**1**—**4**) using Cl_2 could not be overcome even with several modifications (including method C), as well as in the chlorination of **1**—**4** using NCS (shown in the tables). The failure of chlorination is presumably due to side reactions (decomposition of materials). The reason for the failure in the synthesis of **30** is unclear.[9]

Although there have been reports[10] on the synthesis of halotriazines from cyclopropenyl azides, they are limited to the synthesis of 4,5,6-trihalo-1,2,3-triazines. Additionally, although we have reported the halogenation of 1,2,3-triazines,[5] the yields of halotriazines were not always satisfactory. Hence, the one-pot synthesis described here is an efficient synthetic method with respect to both the availabilities and yields of the halotriazines.

Application to the Synthesis of Unhalogenated Triazines

Finally, the reaction of the *N*-aminopyrazoles with iodine was applied to the synthesis of unhalogenated triazines, as iodine showed only oxidative rather than iodinating character. For this purpose, the reaction was carried out with a slight modification, namely in two phases;

TABLE V. Synthesis of 1,2,3-Triazines from *N*-Aminopyrazoles by Iodine Oxidation with Aqueous Alkali[a]

Aminopyrazole	Product (%)[b]		Recovery (%)[b]
1	**9**	15	tr
2a+**2b**[c]	**10**	88	6[d]
3	**11**	50	0
4a	**12**	59	tr
4b	**12**	48	17
5	**13**	84	0
6a	**14**	82	0
6b	**14**	82	4
7	**15**	62	11
8	**16**	71	0
40 X=Br	**18**	28	tr
42a X=Br	**24**	41	tr
42b X=Br	**24**	45	tr

a) Method D (see the Experimental section); reaction time 10—30 min,[19] at room temperature. *b*) Isolation yields. *c*) A roughly 1 : 1 mixture (see ref. 1*c*). *d*) Mixture of **2a** and **2b**.

aqueous alkali/CH_2Cl_2 (method D). The method brought about a reduction in the reaction time compared to the aforementioned reaction system (method A) using iodine. The results are summarized in Table V.

The product yields were satisfactory with one exception, *i.e.*, the poor yield of unsubstituted triazine (**9**) from **1**[11]; it seems noteworthy that not only were higher or at least almost equal product yields generally obtained compared to the reported methods,[1,2] but also the required work-up in the present procedure was briefer than that in the earlier triazine syntheses. Additionally, this method was applicable to the synthesis of 5-halotriazines from 1-amino-4-halopyrazoles (*e.g.*, **18** from **40**, and **24** from **42a** X = Br and **42b** X = Br).[12]

Discussion

The mechanism of the triazine formation from *N*-aminopyrazoles by oxidation with the halogenating reagents is not yet clear. Regarding the formation of the triazine **13** from **5** on lead tetraacetate oxidation, Boulton *et al.*[2a] revealed incorporation of the amino nitrogen into the triazine ring as its central nitrogen N-2, probably *via* insertion of the nitrene moiety to the N–N bond of the pyrazole ring. The aminonitrene (1,1-diazene) mechanism may be applicable to the described halogenating oxidation of **1**—**8** because diazene formation has been found in some halogenations of 1,1-disubstituted hydrazines.[13] It should also be noted that Campbell and Rees[14] revealed that oxidation of one molecule of 1-aminobenzotriazole requires two molecules of NBS and they proposed a dibromamine intermediate, which forms a bromine molecule and an *N*-nitrene. However, the participation of a dibromamine intermediate and the formation of a bromine molecule are unclear in the reaction of *N*-aminopyrazoles with NBS, because the bromine itself acted as an oxidant towards the *N*-aminopyrazoles.[15] Considering the fact that the consumptions of **1**—**8** and the formation of triazine occurred preferentially under basic conditions (see runs by methods B, C, and D[7]) we propose a tentative mechanism which includes the intermediary halamine **48** and halamide ion **49**, which is assumed to be inserted into the N–N bond (the mechanism can be regerded as analogous to Hofmann rearrangement: Chart 4).[16]

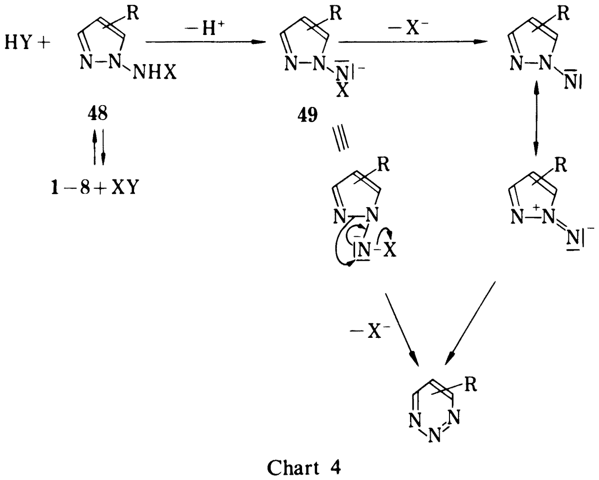


Chart 4

Experimental

Infrared (IR) spectra were recorded on a JASCO A102, ^{1}H-NMR on a JEOL FX-100 (δ *vs.* Me_4Si, in $CDCl_3$), ^{13}C-NMR on the FX-100, or a JEOL GX-400 (δ *vs.* Me_4Si, in $CDCl_3$), gas chromatography (GC) on a Shimadzu

GC-9A (with 1.5% OV-17 and/or 2% SE-30 on Chromosorb W), high performance liquid chromatography (HPLC) on a JASCO TRIROTAR-V (with a Finepac SIL-C_{18} column)-UVIDEC 100V system (solvent: MeCN–H_2O),(16) and mass spectra (MS) and GC-MS on a JEOL JMS-D300 (ionization was carried out with direct electron impact, and CI-MS was run with methane as the reagent gas for ionization).

Halogenating Reagents——Chlorine solution was prepared by introducing Cl_2 gas into carbon tetrachloride chilled in an ice-salt bath; chlorine concentration (1.47 mmol/ml) was measured by iodometry before use. Bromine chloride solution was prepared by combining Cl_2 and Br_2 solutions in carbon tetrachloride as described.(17) Other reagents, Br_2, I_2, ICl, IBr, NCS, and NBS are commercially available, and were used as solutions (1 mmol/l—10 ml, according to the solubility) in methylene chloride.

***N*-Aminopyrazoles (1—8)**——Synthesis, separation, and purification of **1** and **3**—**8** have been reported in our previous papers(1,18) and other reports.(2) The separation of **2a** and **2b** was achieved by a silica gel flash column chromatography (hexane : ether = 2 : 1; the 5-methyl derivative **2a** eluted prior to the 3-methyl derivative **2b**) and structural assignments, as described in the text, were performed in this work. **2a**: Colorless needles of low melting point [picrate mp 116—119 °C (dec.), wet point 101 °C]. ^{1}H-NMR δ: 2.25 (3H, s), 5.30 (2H, br s), 5.88 (1H, d, J = 2 Hz), 7.23 (1H, d, J = 2 Hz). ^{13}C-NMR δ: 10.8, 103.3, 135.2, 137.5. **2b**: Colorless oil [picrate mp 133—136 °C (dec.), wet point 110 °C]. ^{1}H-NMR δ: 2.20 (3H, s), 5.88 (1H, d, J = 2 Hz), 6.00 (2H, br s), 7.27 (2H, d, J = 2 Hz), ^{13}C-NMR δ: 13.8, 103.4, 129.7, 146.0.

X-Ray Analyses of **4a** and **6a**(19); Crystal data for **4a**: $C_9H_9N_3$, monoclinic, $P2_1/n$, $a = 18.728$, $b = 5.751$, $c = 15.814$ Å; $\beta = 104.3°$, $Z = 8$ (including two molecules in an asymmetric unit). **6a**: $C_{10}H_{11}N_3$, orthorhombic, *Pcab*, $a = 10.955$, $b = 21.535$, $c = 7.625$ Å; $Z = 8$. The lattice constants and intensity data for both crystals were obtained with a Rigaku AFC-5 diffractometer using Cu K_α radiation monochromated by a graphite plate. The θ–2θ scan technique was employed for the whole angular range up to $2\theta = 120°$. Measured reflections were 2457 and 1341, respectively for **4a** and **6a**. The crystal structures were determined by the direct method and refined by the full-matrix least-squares method for both compounds. The R values were 0.063 (**4a**) and 0.069 (**6a**), including hydrogen atoms.

Reaction of Pyrazole Derivatives with Halogenating Reagents and Work-up——Method A (without Base): A solution of the halogenating reagent (5 mmol) was added dropwise to a solution of an aminopyrazole or 3,5-dimethylpyrazole **46** (5 mmol) in methylene chloride with stirring and ice bath cooling. Precipitation occasionally occurred in the reaction mixture. The mixture was stirred for the period(20) shown in Tables II—IV at room temperature and then an aqueous solution of potassium bicarbonate (approx. 10%)–sodium sulfite (approx. 10%) was added as a quencher, with stirring. The layers were separated and the aqueous layer was extracted with CH_2Cl_2. The organic layers were combined, washed with water, and dried over magnesium sulfate, then the solvent was evaporated off under reduced pressure. In the runs using NCS or NBS as the reagent, the residue contained succinimide which could be mostly removed by filtration using hexane–ether, as the imide is only slightly soluble in the solvent. In some cases, the mixture was darkly colored and a treatment with active charcoal in hexane–ether was applied before the recrystallization. The residue was recrystallized from the appropriate solvent and the mother liquid was concentrated and submitted to alumina or silica gel thick layer chromatography or silica gel flash column chromatography(21) to give further product and the by-products. When the mixture of the products was complex, the crude residue was directly chromatographed to give the products. For some minor compounds, their amounts were only estimated by ^{1}H-NMR, GC and/or HPLC,(16) after their identification by ^{1}H-NMR, GC, GC-MS, HPLC, and/or TLC, *etc.*

Method B (with Triethylamine): A solution of the reagent (2 molar eq) in CH_2Cl_2 was added to a solution of aminopyrazole and Et_3N (2 molar eq with respect to the aminopyrazole) in CH_2Cl_2, under the described conditions. The mixture was treated as above.

Method C (Modified Procedure of Method B): A CH_2Cl_2 solution containing an aminopyrazole was treated with a solution of the halogenating reagent (1 molar eq with respect to the aminopyrazole), followed by addition of a solution of Et_3N (1 molar eq) in CH_2Cl_2, with stirring and cooling. Again a solution of the halogenating reagent (1 molar eq) was added to the reaction mixture with stirring and cooling, then the mixture was stirred for the period(20) shown in Table IV at room temperature. The work-up described above was applied to the reaction mixture.

Method D (Oxidation with Aqueous Alkali): A solution of the reagent (1.5 molar eq to aminopyrazole) was added dropwise to a two-phase mixture of aminopyrazole in CH_2Cl_2 and $KHCO_3$ (approx. 20%) in water with stirring and cooling. The mixture was stirred during the period(20) shown in Table V at room temperature and quenched by adding aqueous Na_2SO_3, then the mixture was separated. The aqueous layer was extracted with CH_2Cl_2 and the organic layers were combined. The organic solution was washed with water, dried, and worked-up as above.

Oxidation of **8** with NCS (^{1}H-NMR Observation): A solution of **8** in $CDCl_3$ containing benzene as an internal standard for ^{1}H-NMR quantitative analysis was put in an NMR sample tube. NCS (approx. 1.1 molar eq with respect to **8**) was added, followed immediately by 1 drop (approx. 1.7 molar eq to **8**) of Et_3N, and the sample was immediately submitted to ^{1}H-NMR measurement. Less than 10 min was required to consume about half of **8**, forming **16** in about corresponding yield, although it took about 60 min to consume about half of **8** in the absence of Et_3N. On addition of K_2CO_3/D_2O (1 drop) to the **8**/$CDCl_3$ + NCS, followed by vigorous shaking of the sample mixture, similar acceleration was observed in the ^{1}H-NMR experiment.

Oxidation of **42b** X = Br with I_2 (^{1}H-NMR Observation): On ^{1}H-NMR observation of a reaction system of I_2/(**42b** X = Br) = 1.1/1 in $CDCl_3$ ($CHCl_3$ was used as a standard for ^{1}H-NMR integration), similar acceleration was observed. The major product was **24**.

1,2,3-Triazines (10—16)——The compounds were identified by comparison with the reported data.[1c)]

Halogenated 1,2,3-Triazines——**18**: Needles from hexane, mp 125—126 °C (dec.). ^{1}H-NMR δ: 9.22 (s). MS *m/z*: 159 (M^+), 131 ($C_3H_2BrN^+$), 104 (C_2HBr^+). These data support the view that the compound is not 4-bromo-, but is 5-bromotriazine. *Anal.* Calcd for $C_3H_2BrN_3$: C, 22.52; H, 1.26; N, 26.27. Found: C, 22.79; H, 1.24; N, 26.10. **20**[22)]: Needles from hexane, mp 73—74 °C. ^{1}H-NMR δ: 2.82 (3H, s), 9.07 (1H, s). MS *m/z*: 173 (M^+), 145 ($C_4H_4BrN^+$), 118 ($C_3H_3Br^+$), 104 (C_2HBr^+). These data support the view that the compound is not 4-bromo-6-methyl-, but is 5-bromo-4-methyltriazine. *Anal.* Calcd for $C_4H_4BrN_3$: C, 27.61; H, 2.32; N, 24.15. Found: C, 27.87; H, 2.37; N, 23.94. **22**: Needles from hexane (highly sublimable), mp 36—38 °C. ^{1}H-NMR δ: 2.46 (3H, d, $J \leqq 1.0$ Hz), 8.79 (1H, br s). MS *m/z*: 172.957 (M^+, Calcd for $C_4H_4{}^{79}BrN_3$: 172.959), 144.956 ($M-N_2^+$, Calcd for $C_4H_4{}^{79}BrN$: 144.953), 130 ($C_4H_3Br^+$ or C_3HBrN^+, weak), 118 ($C_3H_3Br^+$), 94 ($C_4H_4N_3^+$). **24**: Flakes from hexane–ether, mp 125—126 °C (dec.). ^{1}H-NMR δ: 7.54—7.61 (3H, m), 7.91—8.01 (2H, m), 9.23 (1H, s). MS *m/z*: 235 (M^+, weak), 207 ($C_9H_6BrN^+$, weak), 180 ($C_8H_5Br^+$), 128 ($C_9H_6N^+$); $C_8H_6^+$ absent. CI-MS *m/z*: 236 ($M+H^+$). The data indicate that the compound is not the 4-bromo-, but is the 5-bromotriazine derivative. *Anal.* Calcd for $C_9H_6BrN_3$: C, 45.79; H, 2.56; N, 17.80. Found: C, 45.57; H, 2.48; N, 17.69. **25**: Needles from hexane, mp 89—90 °C. ^{1}H-NMR δ: 2.76 (s). MS *m/z*: 143 (M^+), 115 ($C_5H_6ClN^+$, weak), 80 ($C_5H_6N^+$), 74 ($C_3H_3Cl^+$). *Anal.* Calcd for $C_5H_6ClN_3$: C, 41.82; H, 4.21; N, 29.27. Found: C, 42.10; H, 4.16; N, 29.32. **26**: Needles from hexane, mp 104—105 °C. ^{1}H-NMR δ: 2.79 (s). MS *m/z*: 187 (M^+), 159 ($C_5H_6BrN^+$), 118 ($C_3H_3Br^+$), 80 ($C_5H_6N^+$). *Anal.* Calcd for $C_5H_6BrN_3$: C, 31.93; H, 3.22; N, 22.35. Found: C, 31.99; H, 3.17; N, 22.49. **27**: Needles from hexane, mp 112—113 °C. ^{1}H-NMR δ: 2.87 (3H, s), 7.53—7.63 (3H, m), 7.88—7.98 (2H, m). MS *m/z*: 205 (M^+, weak), 177 ($C_{10}H_8ClN^+$), 142 ($C_{10}H_8N^+$), 136 ($C_8H_5Cl^+$), 103 ($C_7H_5N^+$), 74 ($C_3H_3Cl^+$). CI-MS *m/z*: 206 ($M+H^+$). *Anal.* Calcd for $C_{10}H_8ClN_3$: C, 58.40; H, 3.92; N, 20.44. Found: C, 58.54; H, 3.73; N, 20.70. **28**: Needles from hexane, mp 138—140 °C. ^{1}H-NMR δ: 2.89 (3H, s), 7.52—7.58 (3H, m), 7.80—7.90 (2H, m). MS *m/z*: 249 (M^+), 221 ($C_{10}H_8BrN^+$), 180 ($C_8H_5Br^+$), 142 ($C_{10}H_8N^+$), 118 ($C_3H_3Br^+$), 103 ($C_7H_5N^+$). *Anal.* Calcd for $C_{10}H_8BrN_3$: C, 48.02; H, 3.22; N, 16.80. Found: C, 48.18; H, 3.21; N, 16.82. **29**: Needles from hexane–ether, mp 159—160 °C. ^{1}H-NMR δ: 7.55—7.62 (6H, m), 7.92—8.02 (4H, m). MS *m/z*: 267 (M^+, absent), 239 ($C_{15}H_{10}ClN^+$), 204 ($C_{15}H_{10}N^+$), 136 ($C_8H_5Cl^+$), 103 ($C_7H_5N^+$). CI-MS *m/z*: 268 ($M+H^+$). *Anal.* Calcd for $C_{15}H_{10}ClN_3$: C, 67.29; H, 3.77; N, 15.70. Found: C, 67.58; H, 3.53; N, 15.77. **32**: Needles from hexane–ether, mp 138—139 °C (dec.). ^{1}H-NMR δ: 9.11 (s). MS *m/z*: 237 (M^+, weak), 209 ($C_3HBr_2N^+$), 182 ($C_2Br_2^+$), 158 ($C_3HBrN_3^+$), 130 (C_3HBrN^+), 104 (C_2HBr^+). CI-MS *m/z*: 238 ($M+H^+$). These data indicate that the compound is not 4,6-dibromo-, but is 4,5-dibromotriazine. *Anal.* Calcd for $C_3HBr_2N_3$: C, 17.59; H, 0.42; N, 15.08. Found: C, 17.83; H, 0.38; N, 15.35. **34**: Granules from hexane–ether, mp 130—132 °C (dec.). ^{1}H-NMR δ: 2.87 (s). MS *m/z*: 251 (M^+, weak), 182 ($C_2Br_2^+$), 144 ($C_4H_3BrN^+$), 129 (C_3BrN^+), 118 ($C_3H_3Br^+$). CI-MS *m/z*: 252 ($M+H^+$). *Anal.* Calcd for $C_4H_3Br_2N_3$: C, 18.99; H, 1.20; N, 16.62. Found: C, 19.01; H, 1.10; N, 17.01. **36**: Needles from hexane–ether, mp 110—112 °C (dec.). ^{1}H-NMR δ: 7.54—7.61 (3H, m), 7.82—7.92 (2H, m). MS *m/z*: 313 (M^+, absent), 285 ($C_9H_5Br_2N^+$), 206 ($C_9H_5BrN^+$), 127 ($C_9H_5N^+$), 103 ($C_7H_5N^+$). CI-MS *m/z*: 314 ($M+H^+$). *Anal.* Calcd for $C_9H_5Br_2N_3$: C, 34.32; H, 1.60; N, 13.34. Found: C, 34.57; H, 1.57; N, 13.05.

1-Amino-4-halopyrazoles——**40** X = Br: Needles from hexane, mp 59—60 °C. ^{1}H-NMR δ: 5.31 (2H, s), 7.33 (1H, s), 7.42 (1H, s). *Anal.* Calcd for $C_3H_4BrN_3$: C, 22.24; H, 2.49; N, 25.94. Found: C, 22.51; H, 2.31; N, 25.68. **41a** X = Br: flakes from hexane–ether, mp 103—103.5 °C. ^{1}H-NMR δ: 2.24 (3H, s), 4.90—5.10 (2H, br s), 7.20 (1H, s). *Anal.* Calcd for $C_4H_6BrN_3$: C, 27.29; H, 3.44; N, 23.87. Found: C, 27.55; H, 3.43; N, 23.89. **41b** X = Br: Needles from hexane–ether, mp 94—94.5 °C. ^{1}H-NMR δ: 2.16 (3H, s), 4.80—5.20 (2H, br s), 7.30 (1H, s). *Anal.* Calcd for $C_4H_6BrN_3$: C, 27.29; H, 3.44; N, 23.87. Found: C, 27.44; H, 3.41; N, 23.82. **42a** X = Br: Needles from hexane, mp 81—82 °C. ^{1}H-NMR δ: 5.15 (2H, s), 7.30—7.44 (3H, m), 7.45 (1H, s), 7.70—7.89 (2H, m). *Anal.* Calcd for $C_9H_8BrN_3$: C, 45.40; H, 3.39; N, 17.65. Found: C, 45.71; H, 3.40; N, 17.77. **42b** X = Br: Needles from hexane, mp 69—69.5 °C. ^{1}H-NMR δ: 5.27 (2H, s), 7.41 (1H, s), 7.42—7.62 (5H, m). *Anal.* Calcd for $C_9H_8BrN_3$: C, 45.40; H, 3.39; N, 17.65. Found: C, 45.41; H, 3.36; N, 17.94. **43** X = Cl: Needles from hexane, mp 81—82 °C. ^{1}H-NMR δ: 2.18 (3H, s), 2.22 (3H, s), 4.90 (2H, br s). *Anal.* Calcd for $C_5H_8ClN_3$: C, 41.24; H, 5.54; N, 28.86. Found: C, 41.53; H, 5.58; N, 29.05. **43** X = Br: Needles from hexane–ether, mp 101—102 °C. ^{1}H-NMR δ: 2.18 (3H, s), 2.24 (3H, s), 4.85 (2H, br s). *Anal.* Calcd for $C_5H_8BrN_3$: C, 31.60; H, 4.24; N, 22.11. Found: C, 31.86; H, 4.21; N, 21.84. **43** X = I: Needles from hexane, mp 104—105 °C. ^{1}H-NMR δ: 2.17 (3H, s), 2.30 (3H, s), 5.05 (2H, br s). *Anal.* Calcd for $C_5H_8IN_3$: C, 25.33; H, 3.40; N, 17.73. Found: C, 25.61; H, 3.39; N, 17.68. **44a** X = Br: Needles from hexane, mp 88—89 °C. ^{1}H-NMR δ: 2.36 (3H, s), 5.10 (2H, br s), 7.30—7.50 (3H, m), 7.75—7.90 (2H, m). *Anal.* Calcd for $C_{10}H_{10}BrN_3$: C, 47.64; H, 4.00; N, 16.67. Found: C, 47.88; H, 4.00; N, 16.81. **44b** X = Cl: Needles from hexane, mp 92—94 °C. ^{1}H-NMR δ: 2.26 (3H, s), 5.09 (2H, s), 7.33—7.67 (5H, m). MS *m/z*: 207.056 (M^+, Calcd for $C_{10}H_{10}{}^{35}ClN_3$: 207.056), 209.050 ($M+2^+$, Calcd for $C_{10}H_{10}{}^{37}ClN_3$: 209.053). **44b** X = Br: Needles from hexane, mp 60.5—61 °C. ^{1}H-NMR δ: 2.26 (3H, s), 5.13 (2H, s), 7.40—7.60 (5H, m). *Anal.* Calcd for $C_{10}H_{10}BrN_3$: C, 47.64; H, 4.00; N, 16.67. Found: C, 47.86; H, 4.01; N, 16.77. **45** X = Cl: Needles from hexane, mp 110—112 °C. ^{1}H-NMR δ: 5.24 (2H, br s), 7.36—7.70 (8H, m), 7.85—8.00 (2H, m). MS *m/z*: 269.072 (M^+, Calcd for $C_{15}H_{12}{}^{35}ClN_3$: 269.072), 271.071 ($M+2^+$, Calcd for $C_{15}H_{12}{}^{37}ClN_3$:

271.073). **45** X = Br: Needles from hexane–ether, mp 138—139.5 °C. ^{1}H-NMR δ: 5.24 (2H, s), 7.30—7.68 (8H, m), 7.80—7.95 (2H, m). *Anal.* Calcd for $C_{15}H_{12}BrN_3$: C, 57.34; H, 3.85; N, 13.38. Found: C, 57.62; H, 3.72; N, 13.35.

References and Notes

1) *a*) A. Ohsawa, H. Arai, H. Ohnishi, and H. Igeta, *J. Chem. Soc., Chem. Commun.*, **1980**, 1182; *b*) *Idem, ibid.*, **1981**, 1174; *c*) A. Ohsawa, H. Arai, H. Ohnishi, T. Itoh, T. Kaihoh, M. Okada, and H. Igeta, *J. Org. Chem.*, **50**, 5520 (1985) and references cited therein.

2) *a*) A. J. Boulton, R. Fruttero, J. D. K. Saka, and M. T. Williams, *J. Chem. Soc., Perkin Trans. 1*, **1986**, 1249; *b*) H. Neunhoeffer, M. Clausen, H.-D. Vötter, H. Ohl, C. Krüger, and K. Angermund, *Justus Liebigs Ann. Chem.*, **1985**, 1732.

3) For example, A. N. Kost and I. I. Grandberg, *Adv. Heterocycl. Chem.*, **6**, 347 (1963) and references cited therein.

4) A brief outline was given in a previous communication: T. Kaihoh, T. Itoh, A. Ohsawa, M. Okada, C. Kawabata, and H. Igeta, *Chem. Pharm. Bull.*, **35**, 3952 (1987).

5) The reaction under similar conditions was mentioned in our previous communication: T. Kaihoh, A. Ohsawa, T. Itoh, H. Arai, and H. Igeta, *Chem. Pharm. Bull.*, **34**, 4432 (1986).

6) The reaction with Cl_2 frequently resulted in recoveries of appreciable amounts of the starting aminopyrazoles; this is probably mainly due to precipitation of the aminopyrazoles as insoluble salts with hydrogen chloride formed in the course of the reaction.

7) The details are described in the experimental section.

8) Dibromotriazines probably arose through intermediary 1-amino-4,5-dibromopyrazoles; bromination of **40** X = Br afforded **32** but the monobromotriazines (**18**, **20**, **24**) did not give the corresponding dibromides (**32**, **34**, **36**).

9) See footnotes *A* and *O* in Table II and *A*, *O*, and *P* in Table IV; see also note 12.

10) R. Gompper and K. Schönafinger, *Chem. Ber.*, **112**, 1529 (1979) and references cited therein.

11) The unsuccessful results were most likely due to the instability of **9** under the acidic and/or basic reaction conditions.

12) Synthesis of 5-bromo-4,6-diphenyl-1,2,3-triazine (**30**) from 1-amino-4-bromo-3,5-diphenylpyrazole (**45** X = Br) by this method was unsuccessful, although **45** was completely consumed and two major products were obtained (mp 151—152 °C and mp 106—110 °C); the structures remain undetermined (see footnote *O* of Table II).

13) For example, C. Wentrup, *Adv. Heterocycl. Chem.*, **28**, 231 (1981) and references cited therein.

14) C. D. Campbell and C. W. Rees, *J. Chem. Soc.* (*C*), **1969**, 752.

15) The fact that the reaction of NBS with hydrogen bromide (which would be formed from bromamine) generates Br_2 (which can react with **1**—**8**) would further increase the mechanistic complexity; *e.g.*, see J. S. Pizey, "Synthetic Reagents," Vol. 2, J. Wiley & Sons Inc., New York, 1974, p. 1; H. O. House, "Modern Synthetic Reactions," W. A. Benjamin Inc., California, 1972, p. 422, and references cited therein.

16) On GC and/or HPLC, some triazines underwent decomposition to some extent, depending on the chromatographic conditions.

17) G. Bellucci, G. Ingrosso, F. Marioni, E. Mastrorilli, and I. Morelli, *J. Org. Chem.*, **39**, 2562 (1974) and refs. cited therein.

18) The ^{1}H-NMR data for compounds **4a**, **4b**, **6a** and **6b** were incorrectly stated in our previous paper.$^{1c)}$ The corrections are as follows: the ^{1}H-NMR data δ 5.34 (2H), 6.45 (1H), 7.28—7.45 (4H), and 7.71—7.80 (2H) are those for the major product (**4a**, mp 108—109 °C) from the amination of **38**, and the signals at δ 5.23 (2H), 6.33 (1H), 7.37—7.53 (4H), and 7.63—7.76 (2H) are due to the minor product (**4b**, mp 79—80 °C); similarly, the signals at δ 2.34 (3H), 5.08 (2H), 6.27 (1H), 7.29—7.54 (3H), 7.67—7.85 (2H), and those at δ 2.27 (3H), 5.15 (2H), 6.13 (1H), 7.38—7.55 (3H), 7.65—7.80 (2H) are those of the major product (**6a**, mp 152—153 °C) and the minor product (**6b**, mp 94—95 °C), respectively, from **39**.

19) Details of the X-ray crystallographic analysis of **4a** and **6a** are obtainable from K.Y.

20) The reaction times shown in the tables are not necessarily the optimum ones.

21) Some triazines (*e.g.*, **9**) suffered entire or partial decomposition on column chromatography, especially with active aluminum oxide, although silica gel seemed to be innocuous.

22) 5-Bromo-4-methyltriazine (**20**) was also obtained in the iodine oxidation (method D) in 37% yield from a roughly 1 : 1 mixture of **41a** X = Br and **41b** X = Br, which was obtained from the bromination of the mixture **2a** + **2b** using Br_2.