Oxidative *N*—*N* coupling of *N*-alkyl-3-aminopyrazoles to azopyrazoles in aqueous solutions of NaOCl and NaOBr

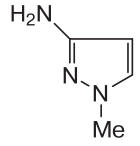
B. V. Lyalin,* V. L. Sigacheva, B. I. Ugrak, and V. A. Petrosyan

N. D. Zelinsky Institute of Organic Chemistry, Russian Academy of Sciences,
47 Leninsky prosp., 119991 Moscow, Russian Federation.
Fax: +7 (499) 135 5328. E-mail: lyalin@ioc.ac.ru

The influence of the structures of *N*-alkyl-3-aminopyrazoles on their transformation into azopyrazoles on treatment with sodium hypohalogenites was studied. The reaction of 3-aminopyrazoles unsubstituted at position 4 containing donor substituents with neutral solutions of sodium hypohalogenites leads to mixtures of 3,3′-azopyrazoles (yields 1—40%) and 4,4′-dihalo-3,3′-azopyrazoles (yields 20—79%). In this case, generation of 3,3′-azopyrazoles is favored by the addition of NaOH to the reaction mixture. The *N*—*N* coupling of aminopyrazoles with acceptor substituents in the aromatic ring results in the selective formation of 3,3′-azopyrazoles even in neutral media. The reactions of 4-substituted 3-aminopyrazoles with NaOBr afford only 3,3′-azopyrazoles. The regularities of occurrence of all the above processes are discussed.

Key words: *N*-alkyl-3-aminopyrazoles, 3,3′-azopyrazoles, 4,4′-dihalo-3,3′-azopyrazoles, oxidative *N*—*N* coupling, sodium hypochlorite (hypobromite).

Oxidation of aromatic amines is one of the demanded methods for synthesis of aromatic azo compounds. At the same time, the use of heavy metal salts as oxidants in these reaction is not environmentally friendly.[1—3] The use of metal hypohalogenites for these purposes seems more attractive. For example, we showed the principal possibility of transformation of 3-aminopyrazoles into azopyrazoles involving electrogenerated NaOCl using 3-amino-1-methyl-1*H*-pyrazole (**1a**) as a model compound and studied a number of regularities of this transformation.[2] In particular, we found that 3-aminopyrazole inhibited the oxidation of Cl^- anions, which dictates the necessity of a two-step process with the isolation of NaOCl electrogeneration in a particular step.



1a

The purpose of the present work is to show that the mentioned above and other regularities of electrosynthesis of azopyrazoles from aminopyrazole **1a** on treatment with electrogenerated NaOCl[2] are valid for rather wide range of aminopyrazoles. In addition, we studied the possibility of using electrogenerated NaOBr in similar processes.

Results and Discussion

The influence of the nature of substituents (donor, acceptor) in the pyrazole cycle on the transformation of 3-aminopyrazoles **1a—d** into azopyrazoles involving electrogenerated sodium hypohalogenites was studied first. As in the previous work,[2] the first step of the process was the preparation of an aqueous solution of NaOCl under the conditions of galvanostatic undivided electrolysis of NaCl, and the second step was the reaction of obtained NaOCl with aminopyrazoles (Scheme 1).

As earlier described[2] aminopyrazole **1a**, aminopyrazoles **1b,c** with the donor substituents in the cycle on treatment with NaOCl give (see Table 1, entries *1* and *3*) the corresponding azopyrazoles **2**, 4-chloro-3-aminopyrazoles **3**, and products of oxidative *N*—*N* coupling of the latter: 4,4′-dichloroazopyrazoles **4**. According to the earlier proposed[2] interpretation of the occurrence of particular steps of the process, hydrolysis of NaOCl affords hypochlorous acid HOCl, which is a very weak acid (pK_a 7.30)[4] but a strong electrophile. For these reasons, HOCl can attack a molecule of aminopyrazole **1a—c** at both the NH_2 group to generate *N*-chloroaminopyrazoles **5a—c** and the N atom of the pyrazole cycle to form 4-chloroaminopyrazoles **3a—c** (see Scheme 1). Chloroaminopyrazoles **5a—c** give azopyrazoles **5** due to the transformations proceeding *via* intermediates **5**, whereas the oxidative transformation of 4-chloroaminopyrazoles **3** leads to 4,4′-dichloroazopyrazoles **4**.

At the equimolar ratios of aminopyrazoles **1a—c** and NaOCl (see Scheme 1 and Table 1, entries *1*, *3*, and *5*), the process results in azopyrazoles **2a—c**, 4-chloroaminopyrazoles **3a—c** (chlorination products of the initial aminopyrazoles), and 4,4′-azopyrazoles **4a—c**, which are the products of oxidative transformation of the initial aminopyrazoles.

Note that the total yield of chlorination products **3** and **4** is higher than that of azopyrazoles **2**. This is due, most

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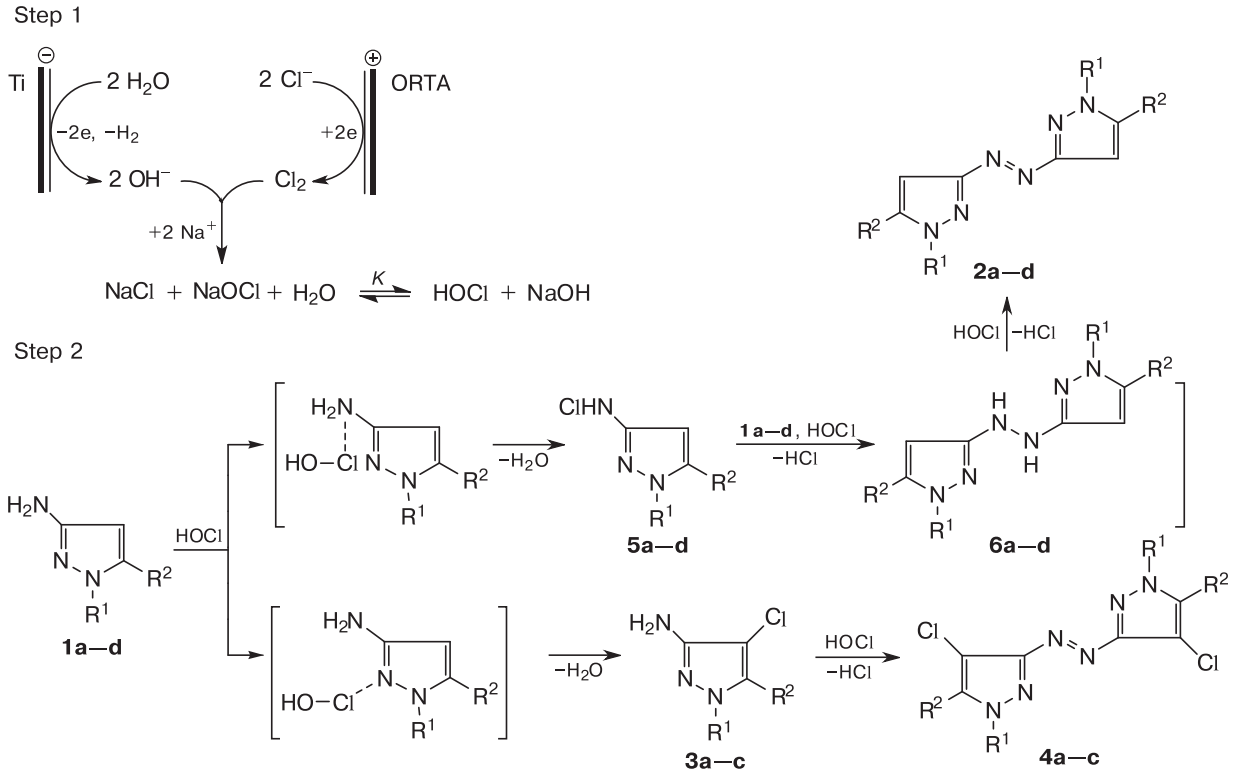
Scheme 1



1—6: R^1 = Me, R^2 = H (**a**); R^1 = Et, R^2 = H (**b**); R^1 = R^2 = Me (**c**); R^1 = Me, R^2 = CF_3 (**d**)

Ti is a Ti cathode, and ORTA is an oxide ruthenium—titanium anode.

Table 1. Influence of the nature of *N*-alkyl-3-aminopyrazoles ($PzNH_2$) and NaOCl : $PzNH_2$ molar ratio on the yields of azopyrazoles under the conditions of *N*—*N* coupling of $PzNH_2$ on treatment with electrogenerated NaOCl[a]

Entry	$PzNH_2$	Molar ratio NaOCl : $PzNH_2$	Conversion $PzNH_2$ (%)	Products	Yield[b] (%)	
					I	II
1[c]	**1a**	1 : 1	71	**2a**	26	37
				3a	30	42
				4a	4	6
2[c]	**1a**	2 : 1	100	**2a**	40	40
				3a	7	7
				4a	40	40
3	**1b**	1 : 1	94	**2b**	37	39
				3b	40	43
				4b	17	18
4	**1b**	3 : 1	100	**2b**	41	41
				4b	46	46
5	**1c**	1 : 1	96	**2c**	1	1
				3c	76	79
6	**1c**	2 : 1	100	**2c**	1	1
				3c	63	63
				4c	32	32
7	**1c**	4 : 1	100	**2c**	2	2
				3c	6	6
				4c	79	79
8	**1d**	2 : 1	100	**2d**	86	86

[a] Reaction conditions: $PzNH_2$ (0.002 mol), 25 °C, 5 h.

[b] The yields of the product based on the initial aminopyrazole (I) and reacted aminopyrazole (II).

[c] Data of Ref. 2.

likely, to a higher reactivity of the N atom of the pyrazole cycle in 3-aminopyrazoles with respect to electrophiles than that of the N atom of the NH_2 group.[5] This agrees with the predominant formation of 4-chloroamine derivative **3c** by the oxidative transformation of 3-amino-1,5-dimethyl-1*H*-pyrazole (**1c**) (see Table 1, entry *5*). Evidently, the additional Me group in pyrazole **1c** makes it more reactive in electrophilic substitution.

As in the case of aminopyrazole **1a**,[2] an excess of NaOCl over aminopyrazoles **1b** and **1c** favor the *N*—*N* coupling of 4-chloroaminopyrazoles **3** to form 4,4′-dichloroazopyrazoles **4**. For example, in entries *2*, *4*, *6*, and *7* (see Table 1), the yields of 4,4′-dichloroazopyrazoles **4a—c** were 40—70%.

It is important that the reaction of electrogenerated NaOCl with aminopyrazole containing an acceptor substituent in the cycle, for example, with 3-amino-1-methyl-5-trifluoromethyl-1*H*-pyrazole (**1d**), is selective and gives 1,2-bis(1-methyl-5-trifluoromethyl-1*H*-pyrazol-3-yl)diazene (**2d**) in a yield of 86% in the complete absence of chlorination products of the initial aminopyrazole (see Scheme 1). This result is consistent with our earlier data[6] on a decrease in the chlorination rate of pyrazoles if the cycle contains acceptor substituents.

N-Bromoamines are known[7] to be more reactive than *N*-chloroamines. Therefore, it could be expected that the replacement of NaOCl by NaOBr would increase the efficiency of azopyrazole synthesis. It turned out that the reactions of *N*-alkyl-3-aminopyrazoles **1a—c** unsubstituted at position 4 with NaOBr* proceeded similarly to the reactions with NaOCl (see Scheme 1) and resulted in a mixture of the corresponding azopyrazoles **2a—c**, 4-bromoaminopyrazoles **7a—c**, and 4,4′-dibromoazopyrazoles **8a—c** (Scheme 2, Table 2). As in the case of NaOCl, the use of NaOBr excess in the reaction favors the formation of 4,4′-dibromoazopyrazoles **8** (see Table 2, entries *2*, *4*, and *6*), and the presence of the acceptor substituent at position 5 of the cycle (compound **1d**) results in the selective formation of azopyrazole **2d** containing no bromine atom in a yield of 93% (see Table 2, entry *7*).

However, contrary to our expectations, the replacement of NaOCl by NaOBr did not increase the efficiency of the process (*cf.* entries *1*, *3*, and *5* in Tables 1 and 2). Probably, this is explained by a higher reactivity of the N atom of the pyrazole cycle (unlike the N atom of the NH_2 group) toward the electrophile. In this case, hypobromous acid HOBr formed by hydrolysis of NaOBr in an aqueous medium acts as an electrophile.

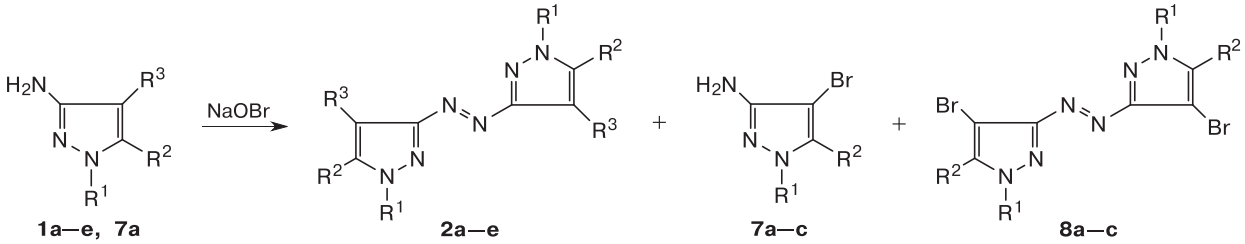
It has previously[2] shown that the reaction of NaOCl with 3-amino-1,4-dimethyl-1*H*-pyrazole (**1e**) is selective and gives the corresponding *N*—*N* coupling product **2e** containing no chlorine atom in the cycle in a yield of 66%. Developing these studies, we found that the reactions of aminopyrazoles **1e** and **7a** substituted at position 4 of the cycle with NaOBr also selectively afford the corresponding azopyrazoles **2e** and **8a** (see Scheme 2 and Table 2, entries *8* and *9*).

The aforementioned formation of 4,4′-dihaloazopyrazoles **4** and **8** by the transformation of aminopyrazoles unsubstituted at position 4 of the cycle into azopyrazoles on treatment with NaOCl or NaOBr (see Tables 1 and 2) is due to the hydrolysis of NaOHal to form hypohaloid acids HOHal (see Scheme 1), which are highly efficient halogenating agents. It could be expected that the suppression of hydrolysis of NaOHal by the addition of NaOH to solutions of sodium hypohalites would allow one to selectively synthesize azopyrazoles containing no halogen atoms in the heterocycle. The results of these studies are presented in Table 3.

It turned out that in the reaction of aminopyrazole **1a** with NaOCl in the presence of NaOH (molar ratio $PzNH_2$: NaOCl : NaOH = 1 : 1 : 1) the yield of azopyr-

* NaOBr was preliminarily synthesized by the undivided galvanostatic electrolysis of an aqueous solution of NaBr (ORTA anode, Ti cathode, j_a = 100 mA cm^{-2}, 20—25 °C).

Scheme 2



Compound **1a—c** and **2a—c**	R^1	R^2	R^3
1a, 2a	Me	H	H
1b, 2b	Et	H	H
1c, 2c	Me	Me	H

Compound **1d,e**, **2d,e**, and **7a**	R^1	R^2	R^3
1d, **2d**	Me	CF_3	H
1e, **2e**	Me	H	Me
7a	Me	H	Br

7, 8: R^1 = Me, R^2 = H (**a**); R^1 = Et, R^2 = H (**b**); R^1 = R^2 = Me (**c**)

Table 2. Influence of the nature of *N*-alkyl-3-aminopyrazoles ($PzNH_2$) and NaOBr : $PzNH_2$ molar ratio on the yields of azopyrazoles under the conditions of *N—N* coupling of $PzNH_2$ on treatment with electrogenerated NaOBr[a]

Entry	$PzNH_2$	Molar ratio NaOCl : $PzNH_2$	Conversion $PzNH_2$ (%)	Products	Yield[b] (%)	
				I	II	
1	**1a**	1 : 1	58	**2a**	20	34
				7a	20	34
				8a	6	10
2	**1a**	2 : 1	100	**2a**	34	34
				7a	22	22
				8a	48	48
3	**1b**	1 : 1	82	**2b**	18	22
				7b	36	43
				8b	12	15
4	**1b**	3 : 1	100	**2b**	23	23
				8b	42	42
5	**1c**	1 : 1	85	**2c**	1	1
				7c	59	69
				8c	24	28
6	**1c**	2 : 1	100	**2c**	1	1
				7c	39	39
				8c	47	47
7	**1d**	2 : 1	100	**2d**	93	93
8	**1e**	1 : 1	84	**2e**	70	70
9	**7a**	1 : 1	89	**8a**	62	62

[a] Reaction conditions: $PzNH_2$ (0.002 mol), 25 °C, 5 h.
[b] The yields of the product based on the initial aminopyrazole (I) and reacted aminopyrazole (II).

azole **2a** containing no chlorine atom in the cycle increased from 37 to 49% (based on unreacted aminopyrazole). The total yield of the chlorination products of aminopyrazole **1a**, namely, chloroaminopyrazole **3a** and 4,4′-dichloroazopyrazole **4a**, simultaneously decreases from 48 to 29% (*cf.* entries *1* in Tables 1 and 3), and the conversion of aminopyrazole **1a** is 87% (see Table 3, entry *1*). An increase in the NaOH : NaOCl molar ratio from 1 : 1 to 3 : 1 is accompanied by an increase in the yield of azopyrazole **2a** to 70% and a decrease in the total yield of chlorination products **3a** and **4a** by 14% (*cf.* entries *1* and *2* in Table 3). However, the conversion of aminopyrazole **1a** decreased by 27%. To avoid this decrease, NaOCl excess was used (molar ratio NaOCl : $PzNH_2$ = 3 : 1) with the retention of the molar ratio NaOH : NaOCl = 3 : 1. This resulted in an almost complete conversion of aminopyrazole **1a** (96%) and formation of azopyrazole **2a** in a high yield (75% based on loaded aminopyrazole). In this case, the total yield of chlorination products **3a** and **4a** did not exceed 19% (see Table 3, entry *3*). Thus, a higher selectivity of the process was achieved in the presence of NaOH.

The use of NaOH additives in the transformation of 3-amino-1-ethyl-1*H*-pyrazole (**1b**) into azopyrazole **2b** also favors the yield of the target product (*cf.* entries *4* in Tables 1 and 3). However, the efficiency of NaOH additives in the transformation of 3-amino-1,5-dimethyl-1*H*-pyrazole (**1c**) into azopyrazole **2c** is low. The major reaction product is chloroaminopyrazole **3c**, the yield of which is 67% (based on unreacted aminopyrazole), whereas the yield of azopyrazole **2c** is only 14% (see Table 3, entry *5*). Probably, this is explained by a higher halogenation rate of aminopyrazole **1c** caused by two donor substituents (Me groups) in the cycle along with the NH_2 group. In this case, even the use of a much larger amount of NaOH (molar ratio NaOH : NaOCl = 15 : 1) did not result in the predominant formation of azopyrazole **2c**: the yields of azopyrazole **2c** and chloroaminopyrazole **3c** were 30 and 70%, respectively (see Table 3, entry *6*).

It was mentioned when studying the influence of alkali additives on the transformation of aminopyrazoles in the presence of NaOBr that the yield of azopyrazoles **2** lacking the halogen atom in the cycle was higher than that in the reaction with NaOCl. For example, in the case of aminopyrazole **1a**, the yield of azopyrazole **2a** increased from 70 to 88% with a decrease in the yields of bromination products **7a** and **8a** from 15 to 1% (*cf.* entries *2* and *8* in Table 3). A similar situation is observed for aminopyrazole **1b** (*cf.* entries *4* and *9* in Table 3). An increase in the efficiency of NaOBr in the presence of NaOH additives in the *N—N* coupling of aminopyrazoles can be explained by a higher reactivity in the target process of *N*-bromoamines compared to *N*-chloroamines **5** (see Scheme 1) under the conditions of suppression of aminopyrazole halogenation by alkali additives. At the same time, for the transforma-

Table 3. Influence of the nature of *N*-alkyl-3-aminopyrazoles ($PzNH_2$) and experimental conditions on the yields of azopyrazoles containing no halogen atom in the heterocycle of the *N*–*N* coupling of aminopyrazoles on treatment with sodium hypohalogenites (NaOHal) in the presence of NaOH additives[a]

Entry	$PzNH_2$	NaOHal NaOH : NaOHal	Molar ratio $PzNH_2$ (%)	Conversion I	Products II	Yield[b] (%)	
1	**1a**	NaOCl	1 : 1	87	**2a**	43	49
					3a	21	24
					4a	4	5
2	**1a**	NaOCl	3 : 1	60	**2a**	42	70
					3a	9	15
3[c]	**1a**	NaOCl	3 : 1	96	**2a**	75	78
					3a	5	5
					4a	14	15
4	**1b**	NaOCl	3 : 1	66	**2b**	43	65
					3b	16	24
					4b	6	9
5	**1c**	NaOCl	3 : 1	81	**2c**	14	1
					3c	67	83
6	**1c**	NaOCl	15 : 1	100	**2c**	30	30
					3c	70	70
7	**1a**	NaOBr	1 : 1	90	**2a**	60	6
					7a	10	11
					8a	**7**	8
8	**1a**	NaOBr	3 : 1	82	**2a**	72	88
					7a	1	1
9	**1b**	NaOBr	3 : 1	94	**2b**	73	78
					7b	2	2
					8b	6	6
10	**1c**	NaOBr	3 : 1	73	**2c**	12	16
					7c	48	66
					8c	13	18

[a] Reaction conditions: $PzNH_2$ (0.002 mol), molar ratio NaOHal : $PzNH_2$ = 1 : 1, 25 °C, 5 h.
[b] The yields of the product based on the initial aminopyrazole (I) and reacted aminopyrazole (II).
[c] Molar ratio NaOCl : $PzNH_2$ = 3 : 1.

tion of aminopyrazole **1c** into azopyrazole **2c**, the use of NaOH additives to a solution of NaOBr also turned out to be inefficient as for the use of NaOCl (*cf.* entries *5* and *10* in Table 3).

To conclude, in this work we studied the regularities of the two-step oxidative transformation of *N*-alkyl-3-aminopyrazoles into azopyrazoles on treatment with electrogenerated sodium hypohalogenites (NaOCl or NaOBr). Under these conditions, aminopyrazoles containing donor substituents bearing the hydrogen atom at position 4 of the cycle were found to give a mixture of the corresponding azopyrazoles and 4,4′-dihaloazopyrazoles in yields of 1—40% and 20—79%, respectively, depending on the aminopyrazole structure. It is shown using 3-amino-1-methyl-5-trifluoromethyl-1*H*-pyrazole as an example that an acceptor substituent in the cycle favors the formation of azopyrazoles in high yields. It is found that the addition of NaOH to the reaction system of aminopyrazoles lacking substituents at position 4 of the cycle interacting with sodium hypohalogenites favors the formation of azopyrazoles. The *N*—*N* coupling of 4-substituted 3-aminopyrazoles involving electrogenerated NaOBr is shown to result in the corresponding azopyrazoles in yields of 62—70%.

Experimental

^1H and ^{13}C NMR spectra were recorded on a Bruker Avance 300 instrument (300.13 (^1H) and 75.47 MHz (^{13}C)) in $CDCl_3$ using Me_4Si as the standard. High-resolution mass spectra (HRMS) were obtained on a Bruker micrOTOF II instrument using electrospray ionization (ESI). Plates purchased from Merck were used for thin-layer chromatography. Melting points were determined on a Koffler heating stage. Petroleum ether, EtOAc, $CHCl_3$, silica gel (0.035—0.070 mm, 60 Å) for column chromatography, and 3-amino-1-methyl-1*H*-pyrazole (**1a**) were commercially available products (Acros Organics). 3-Amino-4-bromo-1-methyl-1*H*-pyrazole (**7a**), 3-amino-1-ethyl-1*H*-pyrazole (**1b**), 3-amino-1,5-dimethyl-1*H*-pyrazole (**1c**), 1-methyl-5-trifluoromethyl-1*H*-pyrazole (**1d**) and 3-amino-1,4-dimethyl-1*H*-pyrazole (**1e**) were provided by UAB Crea-Chim (Lithuania).

Electrochemical preparation of a neutral aqueous solution of NaOCl. A 4 *M* aqueous solution of NaCl (100 mL) was placed in an undivided cell equipped with the oxide ruthenium—titanium anode (ORTA) and (S = 7.8 cm^2) and the Ti cathode (S = 10 cm^2). Electrolysis was carried out at a current of 1260 mA and temperature 20—25 °C passing 588—1764 C electricity. After the end of electrolysis, solutions containing 0.002—006 mol NaOCl, depending on the amount of passed electricity, were obtained. The content of the target product was determined by iodometric analysis.[8]

Electrochemical preparation of a neutral aqueous solution of NaOBr. A 2 *M* aqueous solution of NaBr (100 mL) was placed in a cell, and electrolysis was carried out as described above at a current as 780 mA. After passing 661—1983 C electricity, solutions containing 0.002—0.006 mole of NaOBr, depending on the amount of passed electricity, were obtained (iodometric analysis data).

Reaction of 3-amino-1-ethyl-1*H*-pyrazole (1b) with a neutral solution of NaOCl (see Table 1, entry *3*). Aminopyrazole **1b** (0.22 g, 0.002 mol) was added to a neutral solution of NaOCl (0.002 mol) preliminarily prepared as described previously. The reaction mixture was stirred for 5 h and analyzed by TLC using a petroleum ether—ethyl acetate (1 : 1) mixture as an eluent. Then concentrated HCl were added (to pH ≈ 3), and the products were extracted with $CHCl_3$ (3×30 mL). The extracts were combined, dried over anhydrous $MgSO_4$, and evaporated *in vacuo*. Column chromatography on silica gel (petroleum ether—ethyl acetate (1 : 2) mixture as eluent) gave 1,2-bis(1-ethyl-1*H*-pyrazol-3-yl)diazene (**2b**) (0.081 g, 37% yield, identified by m.p. 180—181 °C (*cf.* Ref. 3: m.p. 180 °C)) and previously described[3] ^{1}H NMR spectra) and 1,2-bis(4-chloro-1-ethyl-1*H*-pyrazol-3-yl)diazene) (**4b**) (0.049 g, 17% yield, identified by NMR spectroscopy and HRMS). The aqueous solution remained after extraction was concentrated *in vacuo*, NaOH was added (to pH ≈ 10) with stirring, and the mixture was worked up as described above. 3-Amino-4-chloro-1-ethyl-1*H*-pyrazole (**3b**) (0.012 g, 40% yield, identified using NMR spectroscopy and HRMS) and unreacted aminopyrazole **1b** (0.013 g, 94% conversion, identified using TLC and NMR spectroscopy) were isolated.

3-Amino-4-chloro-1-ethyl-1*H*-pyrazole (3b). Oil. R_f 0.80 (petroleum ether—ethyl acetate (1 : 2) as eluent). ^{1}H NMR, δ: 1.41 (t, 3 H, Me, J = 7.1 Hz); 3.53 (br.s, 2 H, NH_2); 3.94 (q, 2 H, CH_2, J = 7.1 Hz); 7.18 (s, 1 H, CH). ^{13}C NMR, δ: 14.9 (Me), 46.7 (CH_2), 95.0 (CCl), 126.4 (CH), 150.2 (CNH_2). MS, found: m/z 146.0480 $[M]^+$. Calculated for $C_5H_8ClN_3$: 146.0480.

1,2-Bis(4-chloro-1-ethyl-1*H*-pyrazol-3-yl)diazene (4b). Yellow crystals. M.p. 163—164 °C. R_f 0.23 (petroleum ether—ethyl acetate (1 : 2) as eluent). ^{1}H NMR, δ: 1.54 (t, 6 H, Me, J = 7.1 Hz); 4.24 (q, 4 H, CH_2, J = 7.1 Hz); 7.50 (s, 2 H, CH). ^{13}C NMR, δ: 15.2 (2 Me), 48.7 (2 CH_2), 105.62 (2 CCl), 128.9 (2 CH), 156.3 (2 CN). MS, found: m/z 146.0771 $[M]^+$. Calculated for $C_{10}H_{12}Cl_2N_6$: 146.0480.

Reactions of aminopyrazoles 1c and 1d with a neutral solution of NaOCl (general procedure) (see Table 1, entries *6* and *8*). Aminopyrazole **1c** or **1d** (0.002 mol) was added to the preliminarily prepared as described above neutral solution of NaOCl (0.004 mol). The reaction mixture was stirred, worked up, and analyzed as described above for the reaction of compound **1b** with NaOCl.

1,2-Bis(1,5-dimethyl-1*H*-pyrazol-3-yl)diazene (2c) was identified by m.p. 252—253 °C (*cf.* Ref. 3: m.p. 252 °C) and previously described[3] ^{1}H NMR spectra.

3-Amino-4-chloro-1,5-dimethyl-1*H*-pyrazole (3c). White crystals. M.p. 108 °C. R_f 0.23 (petroleum ether—ethyl acetate (1 : 2) as eluent). ^{1}H NMR, δ: 2.15 (s, 3 H, Me); 3.51—3.58 (m, 5 H, Me + NH_2). ^{13}C NMR, δ: 11.2 (C<u>Me</u>), 37.8 (NMe), 94.4 (CCl), 135.8 (<u>C</u>Me), 149.3 (CNH_2). MS, found: m/z 146.0477 $[M]^+$. Calculated for $C_5H_8ClN_3$: 146.0480.

1,2-Bis(4-chloro-1,5-dimethyl-1*H*-pyrazol-3-yl)diazene (4c). Yellow crystals. M.p. 248—249 °C. R_f 0.71 (chloroform—methanol (10 : 1) as eluent). ^{1}H NMR, δ: 2.34 (s, 6 H, CH_3); 3.90 (s, 6 H, CH_3). ^{13}C NMR, δ: 10.0 (2 C<u>Me</u>), 38.5 (2 NMe), 95.2 (2 CCl), 138.6 (2 <u>C</u>Me), 156.3 (2 CN). MS, found: m/z 287.0572 $[M]^+$. Calculated for $C_{10}H_{12}Cl_2N_6$: 287.0573.

1,2-Bis(1-methyl-5-trifluoromethyl-1*H*-pyrazol-3-yl)diazene (2d). Yellow crystals. M.p. 145—147 °C. R_f 0.83 (petroleum ether—ethyl acetate (1 : 2) as eluent). ^{1}H NMR, δ: 4.14 (s, 6 H, CH_3); 7.06 (s, 2 H, CH). ^{13}C NMR, δ: 38.9 (2 NMe), 97.2 (2 CH), 119.5 (q, 2 CF_3, $^1J_{CF}$ = 269.4 Hz); 133.9 (q, 2 <u>C</u>CF_3, $^2J_{CF}$ = 39.2 Hz), 161.7 (2 CN). MS, found: m/z 327.0786 $[M + H]^+$. Calculated for $C_{10}H_8F_6N_6$: 327.0787.

Reactions of aminopyrazoles 1a—e and 7a with a neutral solution of NaOBr (general procedure) (see Table 2, entries *1*, *3*, *5*, and *7—9*). Aminopyrazole **1a—c,e** or **7a** (0.002 mol) was added to the preliminarily prepared as described above neutral solution of NaOBr (0.002 mol). In entry *7*, 0.004 mole of NaOBr and 0.002 mole of aminopyrazole **1d** were used. The reaction mixture was stirred, worked up, and analyzed as described above for the reaction of compound **1b** with NaOCl.

3-Amino-4-bromo-1-methyl-1*H*-pyrazole (7a) was identified by m.p. 97 °C (*cf.* Ref. 9: m.p. 97—98 °C) and previously described[9] ^{1}H NMR spectra.

1,2-Bis(4-bromo-1-methyl-1*H*-pyrazol-3-yl)diazene (8a) was identified by m.p. 212 °C (*cf.* Ref. 9: m.p. 211—213 °C) and previously described[9] ^{1}H NMR spectra.

3-Amino-4-bromo-1-ethyl-1*H*-pyrazole (7b). Oil. The product was identified by previously described[9] ^{1}H and ^{13}C NMR spectra.

1,2-Bis(4-bromo-1-ethyl-1*H*-pyrazol-3-yl)diazene (8b) was identified by m.p. 156 °C (*cf.* Ref. 9: m.p. 154—156 °C) and previously described[9] ^{1}H NMR spectra.

3-Amino-4-bromo-1,5-dimethyl-1*H*-pyrazole (7c) was identified by m.p. 111 °C (*cf.* Ref. 9: m.p. 111—113 °C) and previously described[9] ^{1}H NMR spectra.

1,2-Bis(4-bromo-1,5-dimethyl-1*H*-pyrazol-3-yl)diazene (8c) was identified by m.p. 248 °C (*cf.* Ref. 9: m.p. 247—249 °C) and previously described[9] ^{1}H NMR spectra.

1,2-Bis(1,4-dimethyl-1*H*-pyrazol-3-yl)diazene (2e) was identified by m.p. 190 °C (*cf.* Ref. 2: m.p. 190 °C) and previously described[2] ^{1}H NMR spectra.

Reactions of aminopyrazoles 1a—c with an aqueous solution of NaOCl containing NaOH (general procedure) (see Table 3, entries *2*, *4*, and *5*). Aminopyrazole **1a—c** (0.002 mol) and NaOH (0.006 mol) were added to the preliminarily prepared as described above neutral solution of NaOCl (0.002 mol). The reaction mixture was stirred, worked up, and analyzed as described above for the reaction of compound **1b** with NaOCl.

Reactions of aminopyrazoles 1a—c with an aqueous solution of NaOBr containing NaOH (general procedure) (see Table 3,

entries *8—10*). Aminopyrazole **1a—e** (0.002 mol) and NaOH (0.006 mol) were added to the preliminarily prepared as described above neutral solution of NaOBr (0.002 mol). The reaction mixture was stirred, worked up, and analyzed as described above for the reaction of compound **1b** with NaOCl.

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