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Oxidative conversion of N-substituted 3-aminopyrazoles to azopyrazoles using electrogenerated NaOCl as the mediator

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Dedicated to Prof. Oleg A. Rakitin on the occasion of his 65th birthday

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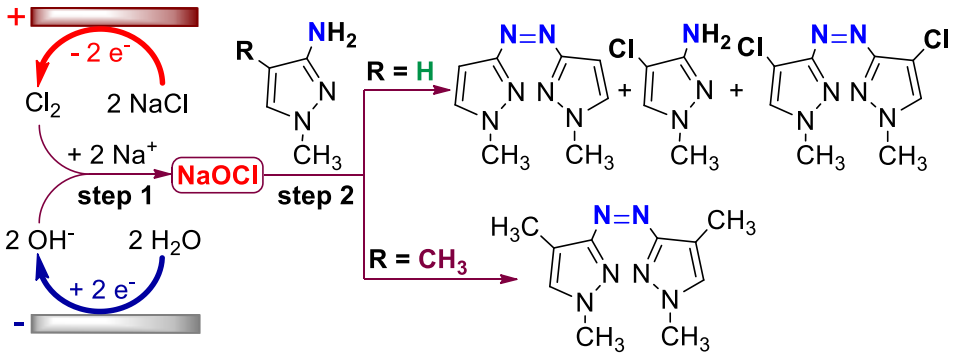
Abstract

The possibility of electrooxidative one-stage (one-pot) and two-stage conversion of *N*-alkylated aminopyrazoles to azopyrazoles involving electrogenerated NaOCl as the mediator has been studied for the first time. It has been found that the process involving NaOCl generation at the 1st stage and its reaction with an aminoazole at the 2nd stage occurs much more efficiently. If the starting aminopyrazole has no substituent at ring position 4 (1-methyl-3-amino-1*H*-pyrazole), the process results in the generation of azo- and 4,4'-dichloroazopyrazoles. It has been shown with 3-amino-1,4-dimethyl-1*H*-pyrazole as an example that under similar conditions, 4-substituted aminopyrazoles selectively give the corresponding azo derivatives.



Keywords: Mediated electrochemical synthesis, NaOCl as mediator, aminoazoles, azo compounds, cyclic voltammetry

Introduction

Processes involving mediators play an important role in today's electroorganic chemistry since they open new prospects for the creation of new organic synthesis methods that are more efficient than traditional ones.[1, 2] The use of catalytic amounts of a mediator that is regenerated during the electrolysis usually allows the process to be carried out under mild conditions and improves its selectivity as well as ecological friendliness. In view of this, mediated synthesis of aromatic azo compounds that has almost not been studied is of undoubted interest.

These compounds have found various practical applications, *e.g.*, in the preparation of organic dyes and pharmaceuticals,[3] in pharmacology due to vasodilatory or cytotoxic activity,[4] in syntheses of polymeric zeolite-like complexes for catalysis or ion exchange,[5] in syntheses of esters,[6] as coreagents in thiocyanation of arenes,[7] and finally as energy-rich compounds.[8, 9]

Recently,[10] we have shown the principal possibility to implement a mediated approach to the synthesis of azopyrazoles by electrooxidation of *N*-alkylaminopyrazoles on a Ni anode in an aqueous NaOH solution using NiO(OH) as the redox mediator. However, the oxidation of methyl 3-amino-1-methyl-*1H*-pyrazole-5-carboxylate under these conditions not gave corresponding azo compound due to alkaline hydrolysis of the starting ester under the conditions of the experiment. It follows that this approach is not suitable for the synthesis of azo compounds from aminoazoles with hydrolytically labile groups. This fact served as an incentive to modification of the suggested method for synthesizing azo compounds by using electrogenerated mediators that do not require alkaline media.

It should be noted that earlier, we successfully used NaOCl, which was generated by electrolysis of an aqueous NaCl solution in an undivided cell, as an electrogenerated mediator in the syntheses of aliphatic *N*-chloroamines,[11] sodium salts of *N*-chloroamides of arylsulfonic acids,[12] and diaziridines.[13]

It is also known that reactions of halogenating agents with aminopyrazoles that occur through generation of *N*-halo derivatives can give azopyrazoles. For example, the conversion of 5-amino-4-cyano-1-phenyl-*1H*-pyrazole to the corresponding azo derivative in the presence of Br_2 occurs by this mechanism.[14]

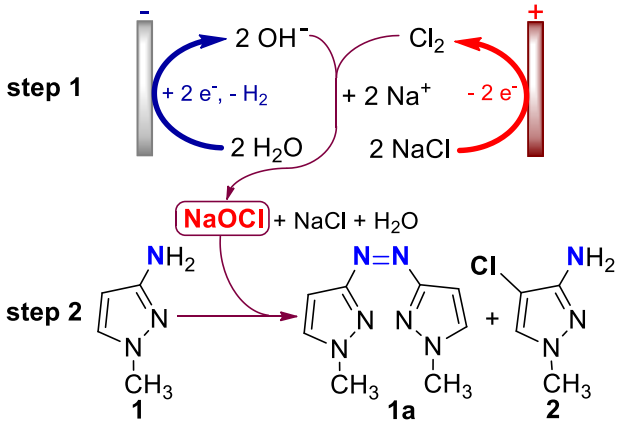
Similar results could be expected from the use of such halogenating agents as hypohalides. For example, the conversion of aminopyrazine to 2,2'-azobispyrazine with participation of NaOCl was reported.[5] This opened prospects for the use of NaOCl as a mediator of electrooxidative conversion of *N*-alkylaminopyrazoles to the corresponding azo derivatives. In this study, we made an attempt to substantiate this possibility in experiments. It should be noted that electrogeneration of NaOCl is an optimal solution for this work's problem since commercially available[15] NaOCl contains NaOH as stabilizer (it is undesirable for azoles with hydrolytically labile groups, see above).

Results and Discussion

To check the possible conversion of *N*-alkylaminopyrazoles to azopyrazoles using electrogenerated NaOCl as the mediator, we chose 3-amino-1-methyl-*1H*-pyrazole (**1**) as the model substrate.

To simplify the implementation of this process, we made an attempt to perform it in one stage (one-pot), so that NaOCl electrogeneration and its subsequent reaction with aminopyrazole **1** would simultaneously occur in the cell as shown in Scheme 1.

However, the one-pot process involving electrogenerated NaOCl implemented as undivided-cell galvanostatic electrolysis of 4M aqueous NaCl solution (a ruthenium-titanium oxide anode – RTOA and a Ti cathode) proved to have poor efficiency (under these conditions, the process was carried out at j_a (anodic current density) 100 $mA \bullet cm^{-2}$, which ensured[16] Cl_2 electrogeneration with nearly quantitative current efficiency).



Scheme 1. NaOCl-mediated electrosynthesis of azopyrazoles (principle scheme).

The reaction mixture after passing 2 F of electricity per mole of aminopyrazole **1**, which is theoretically required for generation of 1 mole NaOCl per mole of aminopyrazole **1**, was found to contain (Scheme 1) 1,2-*bis*(1-methyl-*1H*-pyrazol-3-yl)diazene (**1a**) in only 3% yield and 3-amino-4-chloro-1-methyl-*1H*-pyrazole (**2**), a chlorination product of the starting aminopyrazole **1**, in 5% yield. It should be noted that, though 2 F of electricity was passed, the conversion of aminopyrazole **1** was only 15%. The same results were obtained upon galvanostatic electrolysis of a 4 M aqueous NaCl / aminopyrazole **1** mixture with a Pt anode (similar in properties to RTOA[17]), at j_a = 100 mA·cm^{-2} and Q = 2 F per mole of the starting aminopyrazole **1.**

According to chronopotentiometry data (Figure 1), as early as in the beginning of electrolysis, the anode potential increased abruptly from 1.4 to 2.7 V. This effect is probably due to the passivation of the anode by the readily oxidizable (see Figure 2) aminopyrazole **1** (or its oxidation products) resulting in inhibition of Cl^- anion discharge. As a consequence, water discharge became the main anodic process.

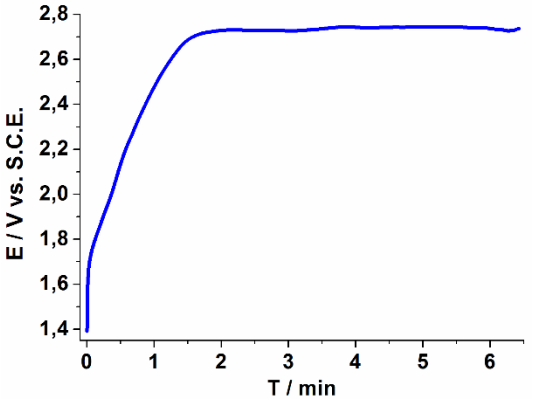


Figure 1. The chronopotentiometric curve of electrolysis of aminopyrazole **1** + NaCl mixture (0.03 and 4 M, respectively) at j_a = 100 mA·cm^{-2}, Q = 2 F / mol of the starting aminopyrazole **1**.

Certain clarity in this issue was obtained from cyclic voltammetry (CV) data. In fact, the CV curve of 0.3M aqueous NaCl solution (Figure 2, curve 1) contains an oxidation peak of chloride anions **a** (E_p^{ox} = 1.4 V) and cathodic peak **b** (E_p^{red} = 0.9 V) that occurs upon potential reversal and corresponds to Cl_2 reduction.

However, on addition of even an insignificant amount of aminopyrazole **1** (C = 2· 10^{-3} M) (Figure 2, curve 2), the oxidation peak **a** decreases ~10-fold in comparison with the original one, whereas peak **b** almost disappears. This agrees with the concept that the oxidation products of aminopyrazole **1** inhibit the Cl_2 electrogeneration stage.

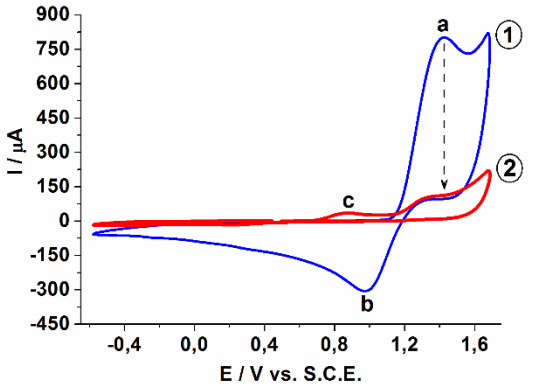


Figure 2. CV-curve of NaCl solution (C = 0.3 M) - **1**; same with addition of aminopyrazole **1** (C = $2\cdot10^{-3}$ M) - **2**. Pt electrode, 1 M $NaNO_3$ solution in H_2O, v = 0.1 V/s.

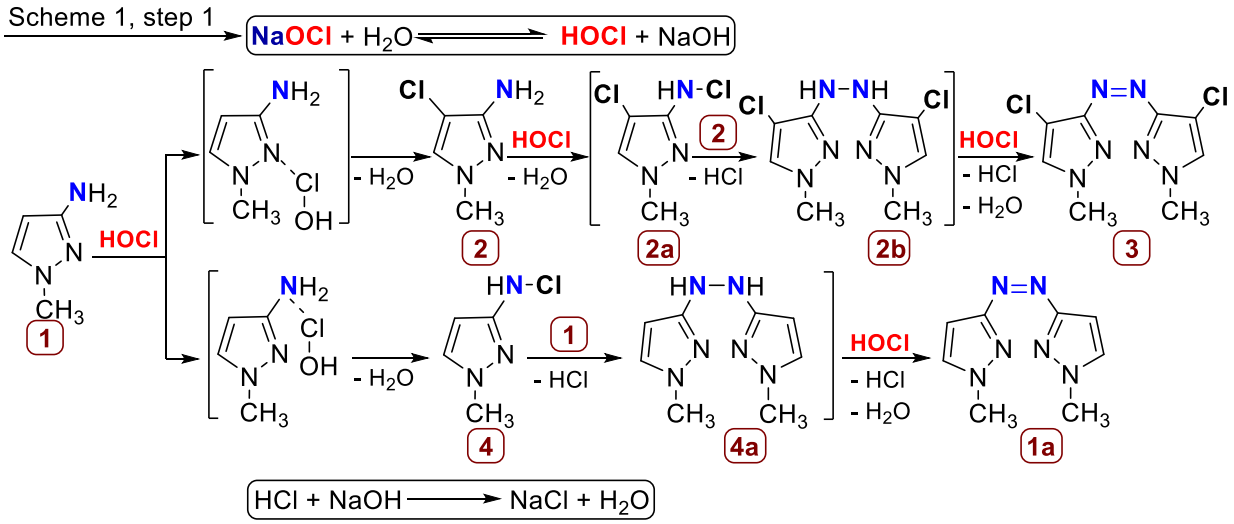
As follows from the above data, efficient implementation of this process is hardly feasible due to the specifics of electrocatalytic one-pot conversion of *N*-alkylaminopyrazoles to azo compounds with NaOCl as the mediator. For this reason, we studied the feasibility of performing the process in question in two stages, so as to completely eliminate the undesirable stage of direct anodic oxidation of aminopyrazole **1**.

The first stage of the process corresponding only to generation of NaOCl (see Scheme 1, step 1) was performed under conditions of undivided-cell galvanostatic electrolysis of an aqueous NaCl solution, like in the one-pot process described above. It was expected that addition of a stoichiometric amount of aminopyrazole **1** (with respect to electrogenerated NaOCl) at the second stage would result in azopyrazole **1a** and regeneration of NaCl (compare with the data in[10]).

In reality, the process occurred in a more complex way. In addition to the generation of azopyrazole **1a** (yield 27% with respect to the initial amount of aminopyrazole **1**), it gave chloroaminopyrazole **2** in 27% yield and 1,2-*bis*(4-chloro-1-methyl-*1H*-pyrazol-3-yl)diazene (**3**) in 7% yield, while the conversion of the starting aminopyrazole **1** was 74%. It can be assumed that chloroaminopyrazole **2** is a dichloroazopyrazole **3** precursor whereas azopyrazole **1a** is formed in other way. This prompted us to consider the regularaties of the reaction of electrogenerated NaOCl with aminopyrazole **1** in more detail. Let us note first of all that NaOCl is readily hydrolyzed in aqueous media to give HOCl. The latter is rather a weak acid (pK_a = 7.53[18]) but a strong electrophile than can efficiently react with aminopyrazole **1** at two reaction centers of its molecule. In fact (Scheme 2), the attack of HOCl at the N atom of the pyrazole ring occurs with elimination of an H_2O molecule to give chloroaminopyrazole **2**.[19] On the other hand, the reaction of HOCl with aminopyrazole **1** at the NH_2 group apparently results in the generation of *N*-chloroaminopyrazole **4**. The latter reacts with aminopyrazole **1** to give hydrazopyrazole **4a**, oxidation of which on treatment with HOCl gives the corresponding azopyrazole **1a.**

It may be assumed by analogy that the conversion of chloroaminopyrazole **2** occurs solely through stages **2**→**2a**→**2b**→**3**, since the other possible product resulted of cross-coupling reaction compounds **1** and **2** [4-chloro-1-methyl-3-[(*Z*)-(1-methyl-*1H*-pyrazole-3-yl)diazenyl]-*1H*-pyrazole], was not detected even in trace amounts in the final reaction mixture**.** It should be noted that the alkali generated during NaOCl hydrolysis is consumed (Scheme 2) to bind HCl that is formed in the stages **2**→ →**3** and **4**→ →**1a.**

Quite demonstrative is the fact that in the experiments on implementation of the one-pot process (see above), only two products were detected in minor amounts, namely, chloroaminopyrazole **2** and azopyrazole **1a**. These compounds were also the main products in the two-stage process, but the yield of each of them was noticeably higher.

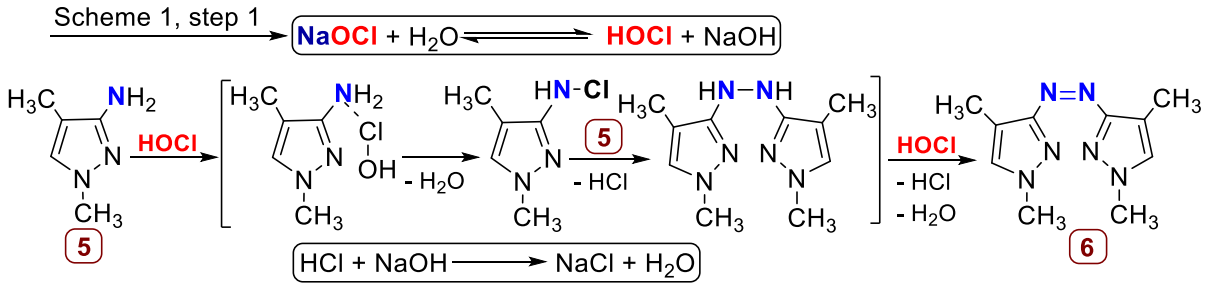


Scheme 2. Proposed mechanism for oxidative conversion of aminopyrazole **1** using electrogenerated NaOCl.

The results that we obtained allow us to conclude that HOCl (see Scheme 2) reacts quite vigorously at both reaction centers of aminopyrazole **1** to give chloroaminopyrazoles **2** and **4**, respectively. However, while the stages **4**→**4a**→**1a** occur with similar efficiency, we can assume that the reactions **2**→**2a**→**2b**→**3** occur much more slowly. That is why the yield of azopyrazole **3** was as low as 7%, whereas aminopyrazole **2** and azopyrazole **1a** were formed in 27% yields each. Rather an important role might belong to the deficiency in electrogenerated NaOCl, since conversion **2**→**2a**→**2b**→**3** involves consumption of additional NaOCl amounts (in comparison with the conversion **4**→**4a**→**1a**) due to the chlorination stage **2**→**2a.** Moreover that it might be the slowest stage since chloroaminopyrazole **2** is less nucleophilic than aminopyrazole **1**.

These factors had to be taken into consideration in order to improve the efficiency of the two-stage process. That is why we optimized it by increasing the molar ratio of electrogenerated NaOCl to aminopyrazole **1** from the previous value, 1:1, to 2:1. As a result, azopyrazoles **1a** and **3** were obtained in 40% yield each (with respect to the loaded aminopyrazole **1**), whereas the yield of aminopyrazole **2** decreased to 7.4%. Since conversion of the starting aminopyrazole **1** reached 100% in this experiment, it may be believed that the conditions suggested for the implementation of the two-stage process are optimal and allow two types of target structures (azopyrazoles **1a** and **3**) to be obtained in a total yield of 80%.

As noted above, the starting aminopyrazole **1** has dual reactivity, which in the process in question is due to the absence of a substituent at position 4 of the heteroring. This suggests that one can affect the selectivity of the process in question by varying the structure of the starting aminopyrazole. With this in mind, we have studied the possibility of two-stage electrocatalytic conversion of 3-amino-1,4-dimethyl-*1H*-pyrazole (**5**) (formation of the 4-chloro derivative of aminopyrazole is impossible in this case) to the corresponding azo derivative with participation of electrogenerated NaOCl as the mediator. As a result, 1,2-*bis*(1,4-dimethyl-1*H*-pyrazol-3-yl)diazene (**6**) was obtained from a stoichiometric amount (with respect to electrogenerated NaOCl) of 3-amino-1,4-dimethyl-*1H*-pyrazole in 66% yield with respect to the loaded aminopyrazole. In this case, conversion of the starting aminopyrazole was 66 % (Scheme 3). We think these results confirmed the reality of transformation **1**→ **4**→**4a**→**1a** (see Scheme 2).



Scheme 3. Proposed mechanism for oxidative conversion of aminopyrazole **5** using electrogenerated NaOCl.

Conclusions

Let us note in conclusion that we were the first to study the possibility of electrooxidative one-stage (one-pot) and two-stage conversion of *N*-alkylated aminopyrazoles to azopyrazoles involving electrogenerated NaOCl as the mediator.

It has been found that the process involving the electrogeneration of NaOCl at the 1st stage and the reaction of the latter with an aminoazole at the 2nd stage occurs much more efficiently.

It has been shown using 3-amino-1-methyl-1*H*-pyrazole (**1**) that under these conditions, the aminopyrazoles containing no substituent at ring position 4 can be efficiently converted to the corresponding azo- and 4,4'-dichloroazopyrazoles with complete conversion of the starting aminopyrazole, whereas the reaction of 3-amino-1,4-dimethyl-1*H*-pyrazole (a representative of aminopyrazoles substituted at ring position 4) resulted in the selective formation of the corresponding azopyrazole in quantitative yield with respect to the reacted substrate. The study that we carried out opens up a route to the syntheses of a broad range of aminoazoles with various structures.

Experimental Section

General. ^{1}H and ^{13}C NMR spectra of the products in $CDCl_3$ were obtained on a Bruker Avance 300 instrument (300.13 MHz for ^{1}H and 75.47 MHz for ^{13}C). High resolution mass-spectra (HRMS) were measured on a Bruker micrOTOF II instrument using ESI. Merck plates were used for TLC. Solvents, Silica gel (0.035-0.070 mm, 60 A^{O} for column chromatography) and 3-amino-1-methyl-1*H*-pyrazole are commercial products of Acros Organics. 3-Amino-1,4-dimethyl-1*H*-pyrazole was provided by UAB Crea-Chim (Vilnius, Lithuania). Voltammetric measurements were carried out on a Pt electrode 1 mm in diameter in a Teflon casing, using a P30JM potentiostat from Elins (scan rate 0.1 V/s). Galvanostatic electrolysis was performed in an undivided temperature-controlled (25 °C) glass cell, using a B 5-8 current source or the potentiostat mentioned above (experiment with chronopotentiometry). The electric circuit contained a coulometer devised at the special design bureau of the Institute of Organic Chemistry of the Russian Academy of Sciences. A magnetic stirrer was used to stir the solution during the electrolysis.

One-pot conversion of 3-amino-1-methyl-1*H*-pyrazole (1) to 1,2-*bis*(1-methyl-1*H*-pyrazol-3-yl)diazene (1a) involving electrogenerated NaOCl. Aminopyrazole **1** (3 mmol) and 4 M aqueous NaCl solution (100 ml) were placed in a cell equipped with an ruthenium-titanium oxide anode, RTOA (S = 7.1 cm^2) and a Ti cathode (S = 10 cm^2) and electrolysis was carried out at a current of 710 mA. Once 2 F of electricity per mole of the starting aminopyrazole **1** was passed (Q = 579 C), electrolysis was stopped. The reaction mixture was stirred for 0.5 h and analyzed by TLC with a petroleum ether : ethyl acetate mixture (1 : 1) as the eluent. Concentrated HCl was then added to the mixture to pH~3 and the products were extracted with $CHCl_3$ (3 × 30 ml). The extracts were combined, dried with anhydrous Na_2SO_4, and concentrated in vacuo. Subsequent purification was carried out

by column chromatography using petroleum ether : ethyl acetate as the eluent. Azopyrazole **1a** that was isolated (yield 3%) was identified using the characteristics reported previously[10]. The aqueous solution that remained after the extraction (see above) was concentrated in vacuo and NaOH was added with stirring (to pH~10). After that, the mixture was treated as described above. The hitherto unreported 3-amino-4-chloro-1-methyl-1*H*-pyrazole **2** was isolated (yield 5%) and identified by NMR and HRMS methods. Non-reacted aminopyrazole **1** (85% remained) was identified by TLC and ^{1}H NMR methods.

One-pot conversion of aminopyrazole 1 to azopyrazole 1a involving electrogenerated NaOCl (experiment with chronopotentiometry). Aminopyrazole **1** (1.5 mmol) and 4 M aqueous NaCl solution (50 ml) were placed in a cell equipped with an Pt anode (S = 7.5 cm^2) and a Ti cathode (S = 10 cm^2) and electrolysis was carried out at a current of 750 mA with simultaneous automatic measurement of the anode potential using potentiostat. After electrolysis (Q = 289.5 C), the reaction mixture was stirred 0.5 h, treated, and analyzed as described above. The yield of azopyrazole **1a** was 3% and that of aminopyrazole **2** was 5%. The non-reacted remainder of aminopyrazole **1** was 85%.

Two-stage conversion of aminopyrazole 1 to azopyrazole 1a and 1,2-bis(4-chloro-1-methyl-1*H*-pyrazol-3-yl)diazene (3) involving electrogenerated NaOCl. *Stage 1. Electrosynthesis of NaOCl.* 100 ml of 4 M aqueous NaCl solution was placed in the cell and electrolysis was carried out as indicated above (Q = 579 C) to give a solution containing 2.3 mmol of NaOCl (according to iodometric analysis). *Stage 2. Reaction of aminopyrazole **1** with NaOCl (ratio 1:1 or ratio 1:2).* Aminopyrazole **1** (2.4 mmol or 1.2 mmol) was added to the NaOCl solution obtained previously. The reaction mixture was stirred for 0.5 h, treated, and analyzed as described above. The yield of azopyrazole **1a** was 27% (or 40%), that of aminopyrazole **2** was 27% (or 7.4%), and that of azopyrazole **3** was 7% (or 40%). The non-reacted remainder of aminopyrazole **1** was 26% (or 0%).

Two-stage conversion of 3-amino-1,4-dimethyl-1*H*-pyrazole (5) to 1,2-bis(1,4-dimethyl-1*H*-pyrazol-3-yl)diazene (6) involving electrogenerated NaOCl. The procedure was carried out as described above using aminopyrazole **5** (2.3 mmol). The yield of azopyrazole **6** was 66%. The non-reacted remainder of aminopyrazole **5** was 34%.

1,2-*Bis*(1-methyl-1*H*-pyrazol-3-yl)diazene (1a). Yellow solid. mp 201 °C. ^{1}H NMR ($CDCl_3$, *δ*) 4.01 (s, 6H), 6.68 (d, *J* 2.2 Hz, 2H), 7.36 (d, *J* 2.2 Hz, 2H) ppm. HRMS (ESI) calcd for $C_8H_{10}N_6$ $[M+H]^+$: 191.1040. Found 191.1043.

3-Amino-4-chloro-1-methyl-1*H*-pyrazole (**2).** White solid. mp 82 °C. ^{1}H NMR ($CDCl_3$, *δ*) 3.55 (br. s, 2H), 3.69 (s, 3H), 7.15 (s, 1H) ppm. ^{13}C NMR ($CDCl_3$, *δ*) 39.0 (CH_3), 95.8 (C), 128.3 (CH), 150.5 (C) ppm. HRMS (ESI) calcd for $C_4H_6ClN_3$ $[M+H]^+$: 132.0323. Found 132.0321.

1,2-Bis(4-chloro-1-methyl-1*H*-pyrazol-3-yl) diazene (3). Yellow solid. mp 215 °C. ^{1}H NMR ($CDCl_3$, *δ*) 4.00 (s, 6H), 7.48 (s, 2H) ppm. ^{13}C NMR ($CDCl_3$, *δ*) 41.0 ($2CH_3$), 106.5 (C), 130.4 (2CH), 156.3 (2C) ppm. HRMS (ESI) calcd for $C_8H_8Cl_2N_6$ [M]: 259.0260. Found 259.0254.

1,2-Bis(1,4-dimethyl-1*H*-pyrazol-3-yl)diazene (6). Yellow solid. mp 190 °C. ^{1}H NMR ($CDCl_3$, *δ*) 2.34 (s, 6H), 3.96 (s, 6H), 7.19 (s, 2H) ppm. ^{13}C NMR ($CDCl_3$, *δ*) 10.4 ($2CH_3$), 39.5 ($2CH_3$), 110.5 (2C), 131.2 (2CH), 150.6 (2C) ppm. HRMS (ESI) calcd for $C_{10}H_{14}N_6$ $[M+H]^+$ 219.1353. Found 219.1352.

Acknowledgements

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Supplementary Material

Additional supporting information may be found in the online version of this article on the publisher's web-site.

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