Reactions of some arenes and pyrazoles in MeCN under conditions of undivided-cell electrolysis

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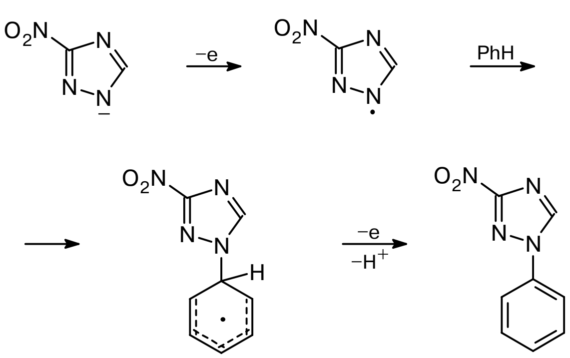
As exemplified for the first time by pyrazole and its 4-nitro and 3,5-dimethyl derivatives, *N*-arylation of pyrazoles can be performed under conditions of undivided-cell amperostatic electrolysis (Pt electrodes, MeCN) of systems containing the pyrazolate anion and (or) pyrazole, arene (benzene, 1,4-dimethoxybenzene, or xylene), and a supporting electrolyte. In the case of electrolysis involving 1,4-dimethoxybenzene as arene, *N*-arylation followed simultaneously three routes to form an *ortho*-substitution product (1,4-dimethoxy-2-(pyrazol-1-yl)benzene), an *ipso*-substitution product (4-methoxy-1-(pyrazol-1-yl)benzene), and an *ipso*-bisaddition product (1,4-dimethoxy-1,4-di(pyrazol-1-yl)cyclohexa-2,5-diene) in a total current yield of up to 50%. The acid-base properties of the pyrazoles under study affect the ratio of the *N*-arylation products and govern the required composition of the starting reaction mixture. In the case of a stronger base, such as 3,5-dimethylpyrazole, *N*-arylation with 1,4-dimethoxybenzene occurred even in the pyrazole—arene—tetraalkylammonium perchlorate system, whereas *N*-arylation of 4-nitropyrazole (a weaker base) proceeded only in the presence of the pyrazolate anion or another base, *viz.*, *sym*-collidine. Oxidation of arene to the radical cation is the key anodic reaction. Not only the pyrazolate anion, but also highly basic pyrazole or a solvate complex of weakly basic pyrazole with collidine can serve as a nucleophilic partner in subsequent transformations of these radical cations.

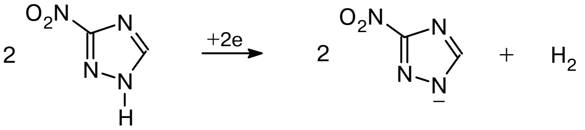
Key words: paired electrosynthesis, *N*-arylation, pyrazoles, azoles, azolate anions.

The data on the possibilities of electrochemical *N*-arylation of azoles are scarce. One of the first publications was devoted to *N*-phenylation of 3-nitro-1,2,4-triazole (hereinafter, nitrotriazole). It was found[1] that electrolysis of a system containing the tetramethylammonium salt (TMA) of nitrotriazole and benzene in MeCN in an undivided cell equipped with Pt electrodes afforded a mixture of isomers of *N*-phenylnitrotriazole (Scheme 1a). The addition of nitrotriazole to the mixture subjected to electrolysis led to an increase in the yield of the target product, which was indicative of reduction of nitrotriazole (Scheme 1b) giving rise to an additional amount of the corresponding N-anions.

Scheme 1a



Scheme 1b



1,4-Dimethoxybenzene (DMB) was also used as an arylating agent.[2] Electrolysis of a mixture containing the TMA salt of nitrotriazole and DMB in MeCN appeared to generate exclusively the *ortho*-substitution product in the anode compartment of a divided cell. The formation of analogous products was also observed[3] upon electrolysis of a mixture containing tetrazole (or 5-phenyltetrazole), its tetrabutylammonium salt (TBA), and DMB (or 1,3,5-trimethoxybenzene) in an undivided cell. However, only a product of the replacement of the methoxy group by the triazole fragment was identified in the reaction mixture obtained by electrolysis of an equimolar mixture of 1,2,4-triazole (hereinafter, triazole) and DMB. The formation of *N*-arylation products with substantially different structures upon electrolysis of structurally similar azoles is evidence for the ambiguity of the processes and indicates that they can

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simultaneously follow several alternative mechanisms. This fact gave impetus to further studies in this field. Since data on the behavior of genetically related pyrazoles in analogous electrochemical reactions are lacking, we chose these compounds as objects of our investigation, which simultaneously opened up the possibility of extending essentially the experimental basis of these studies.

Results and Discussion

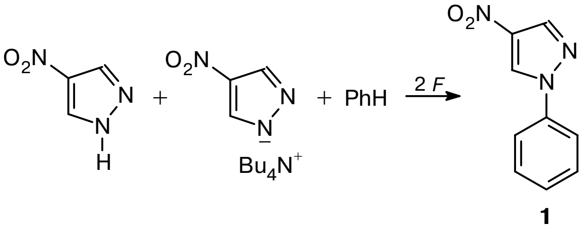
Investigation of electrochemical *N*-arylation of pyrazoles was carried out in the amperostatic mode in an undivided cell with the use of Pt electrodes. These conditions provided paired electrolysis involving the use of the coupled cathodic-anodic processes.

The major aim of the present invstigation was to reveal general regularities of *N*-arylation of azoles and to elucidate the characteristic features of their behavior associated with the structures of particular compounds.* At this stage, a search for preparative procedures was beyond the scope of our study. It should be noted that electrolysis often affords a mixture of *N*-arylation products and, generally, each product is obtained in low yield, some of them being hydrolytically unstable (see below). For these reasons, we analyzed the resulting reaction mixtures using a special procedure based on ^{1}H NMR spectroscopy (see the Experimental section). This approach allowed us not only to reliably establish the formation of minor products labile under the conditions of isolation (including those formed in the intermediate stages of electrolysis), but also to obtain quantitative information on the compositions of the final reaction mixtures which provided the basis for estimation of the current yields of individual products without their isolation.

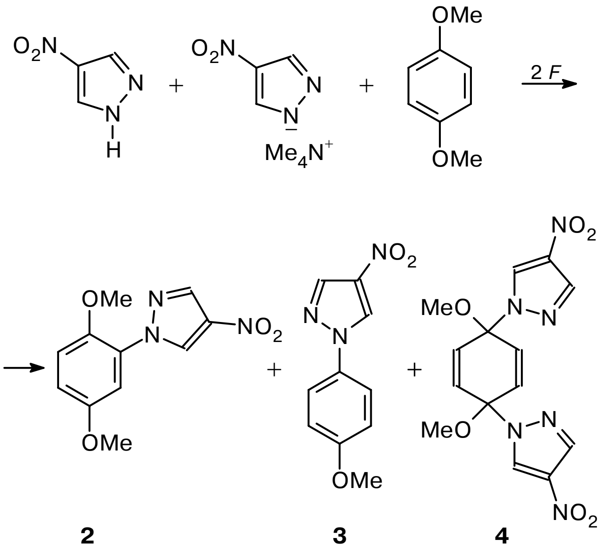
Previously, it has been demonstrated[1,3] that the system containing azole, its tetraalkylammonium salt, and arene is appropriate for use in electrochemical *N*-arylation in an undivided cell. Actually, we found that electrolysis of a solution of 4-nitropyrazole (hereinafter, nitropyrazole), its TBA salt, and benzene taken in a molar ratio of 1 : 0.5 : 10 in MeCN afforded 4-nitro-1-phenylpyrazole (**1**) in 7.5% current yield (Scheme 2).

However, electrolysis of the system consisting of nitropyrazole, its TBA salt, and DMB taken in a molar ratio 1 : 0.5 : 1 performed under the same conditions gave an unexpected result. It was found that the solution obtained after electrolysis contained (Scheme 3) a mixture of three *N*-arylation products, *viz*., *ortho*- and *ipso*-substitution products and an *ipso*-bisaddition product, namely, 1,4-dimethoxy-2-(4-nitropyrazol-1-yl)benzene (**2**) (7% current yield), 4-methoxy-1-(4-nitropyrazol-1-yl)benzene (**3**) (7%), and 1,4-dimethoxy-1,4-di(4-nitropyrazol-1-yl)cyclohexa-2,5-diene (**4**) (27%), respectively. The last-mentioned compound existed as an approximately equimolar mixture of stereoisomers.

Scheme 2



Scheme 3



The size of the tetraalkylammonium cation exerts only a slight effect on the course of the reaction. Thus, electrolysis with the use of the TMA salt of nitropyrazole instead of TBA afforded products **2**, **3**, and **4** in 10, 8, and 28% yields, respectively. However, a decrease in the content of the nitropyrazole salt in the starting mixture led to a change in the ratio of the final products. For example, when nitropyrazole, its TMA salt, and DMB were taken in a ratio of 1.25 : 0.25 : 1, compounds **2**, **3**, and **4** were obtained in 8, 4, and 43% current yields, respectively. It should be noted that products **2**, **3**, and **4** were not formed in the absence of nitropyrazole or its TMA salt in this system. The reasons for this fact are discussed below.

The reaction with the use of *p*-xylene instead of DMB proceeded differently (according to the data from ^{1}H NMR spectroscopy of the reaction mixture) to give an *N*-benzylation product, *viz*., 1-*p*-methylbenzyl-4-nitropyrazole (**5**), in low yield (the current yield was 3%) along with other compounds (Scheme 4).

Both the published data and the above-considered results of *N*-arylation of azoles assume the necessary

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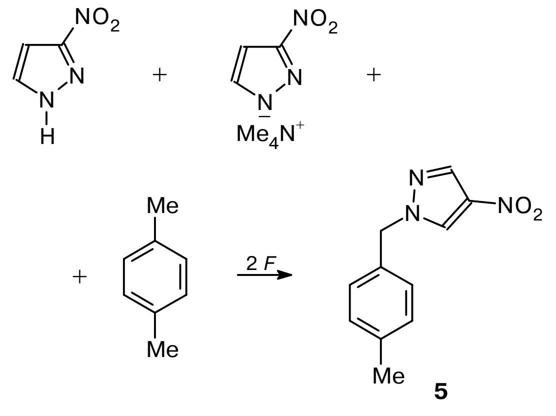
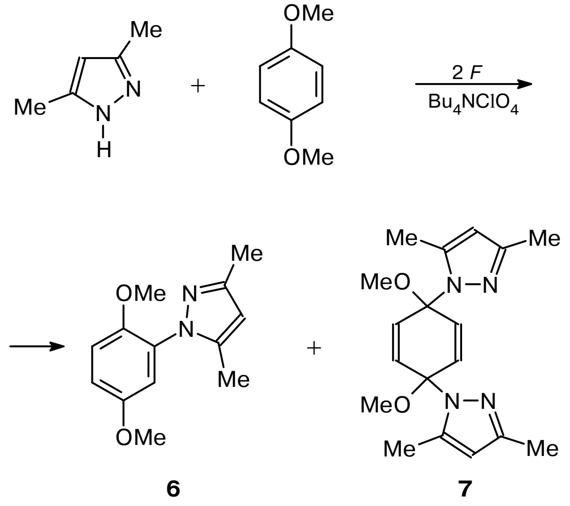
* We believe that the solution of these problems will enable one to found conditions and the scope of azoles promising for preparative electrochemical *N*-arylation.

Scheme 4



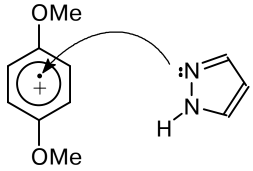
Scheme 5



involvement of tetraalkylammonium salts of azoles, which simultaneously serve as the supporting electrolyte and the donor of N-anions of azoles. Apparently, this fact hinders the involvement of weakly acidic pyrazoles (pK_a > 10)* in *N*-arylation because salts of these pyrazole are readily hydrolyzed and carboxylated in the course of the synthesis, storage, and use. However, we demonstrated that *N*-arylation with the use of rather highly basic pyrazoles proceeded in the absence of the pyrazole salt as well. In these case, tetrabutylammonium perchlorate (TBAP) served as the supporting electrolyte. Thus, electrolysis of a mixture of 3,5-dimethylpyrazole (hereinafter, dimethylpyrazole) (pK_a = 15.0, pK_b = 4.06), TBAP, and DMB (taken in a molar ratio of 1 : 0.5 : 1) in MeCN afforded *ortho*-substitution (**6**) and *ipso*-bisaddition (**7**) products in 28 and 16% current yields, respectively (Scheme 5). It should be noted that *N*-arylation of pyrazole (pK_a = 14.21, pK_b = 2.48) performed under analogous conditions gave rise only to the *ipso*-bisaddition product in 25% current yield.

Moreover, triazole possessing similar acid-base properties (pK_a = 10.04, pK_b = 2.45) in an analogous reaction system produced only the *ipso*-bisaddition product (34% current yield) although, according to the published data,[3] electrolysis under similar conditions resulted only in the *ipso*-replacement of the methoxy group in DMB by the 1-triazole fragment.

Based on the results obtained, some regularities of the processes under study were revealed. Thus, it is evident that oxidation of DMB ($E_{1/2}$ = 1.25 V) rather than of the azole substrate ($E_{1/2}$ > 1.75 V) is the major anodic reaction. Moreover, the adduct of highly basic azoles with the radical cation of DMB is, apparently, the key intermediate involved in subsequent conversions giving rise to the final *N*-arylation products.



Hence, it is not surprising that electrolysis of substantially less basic azoles, such as nitropyrazole (pK_a = 9.64, pK_b = −2.0), nitrotriazole (pK_a = 5.98, pK_b = −3.65), 3,5-dimethyl-4-nitropyrazole (hereinafter, dimethylnitropyrazole, pK_a = 10.65, pK_b = −0.45), and tetrazole (pK_a = 4.9, pK_b = −2.68), in the absence of the corresponding azole salts afforded *N*-arylation products (the reaction mixtures were analyzed by ^{1}H NMR spectroscopy) only in trace amounts. In the case under consideration, the formation of the corresponding N-anions at a cathode (see Scheme 1b) is, apparently, suppressed by anodic generation of protons.

The above-considered conclusions were unexpectedly confirmed by electrolysis of reaction mixtures containing *sym*-collidine as an additive. It appeared that the presence of this base in the electrolyte led to an increase in the relative content of *ipso*-bisaddition products. Moreover, it was demonstrated that the addition of collidine made it possible to exclude the use of the tetraalkylammonium salt of pyrazole (as a necessary component of the reaction mixtures) in the case of weakly basic and relatively acidic pyrazoles. Thus, in the case of nitropyrazole (see above), electrolysis of a mixture of nitropyrazole, TBAP, collidine, and DMB taken in a molar ratio of 1.5 : 0.5 : 0.5 : 1 gave rise to products **2** and **4** in 4 and 52% current yields, respectively, whereas electrolysis involving dimethylnitropyrazole instead of nitropyrazole afforded the *ipso*-bisaddition product in 28% current yield. An analogous effect was also observed in reactions of other azoles. In the case of nitrotriazole, the *ipso*-bisaddition product was obtained in 10% current yield, whereas electrolysis involving tetrazole afforded a mixture of isomeric *ortho*-substitu-

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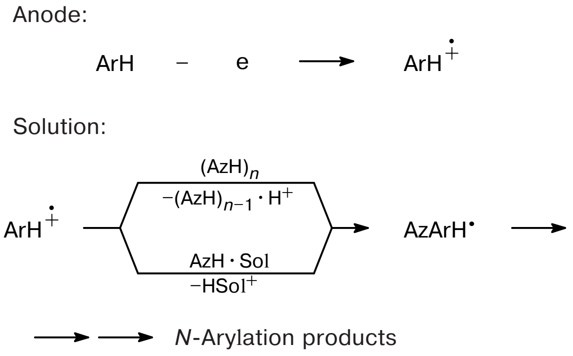
* The pK_a and pK_b values for azoles given below were published in the literature.[4]

tion products similar to that formed in the reaction with the use of the TBA salt of tetrazole instead of collidine.[3]

Therefore, the reactions under consideration involved, apparently, solvate complexes of azoles with collidine or other proton acceptors formed through a hydrogen bond rather than azolate anions (which are virtually absent in the reaction mixture) or azoles, as such, (weakly basic azoles did not form *N*-arylation products; see above) as nucleophiles reacting with radical cations of 1,4-dimethoxybenzene. Based on the data on the regularities of *N*-arylation in the absence of azole salts in the reaction mixture, the following sequence of the key stages of this processes can be suggested (Scheme 6).

Scheme 6



Cathode:

$H^+ + e \rightarrow 0.5\ H_2$

or

$[HSol]^+ + e \rightarrow 0.5\ H_2 + Sol,$

ArH is 1,4-dimethoxybenzene;
AzH is pyrazole, 4-nitropyrazole, 3,5-dimethylpyrazole, 3,5-dimethyl-4-nitropyrazole, 1,2,4-triazole, 3-nitro-1,2,4-triazole, or tetrazole;
Sol is collidine.

From the aforesaid it follows that the reactions presented in Schemes 1a,b reflect only one of the possible routes leading to *N*-arylation products. Thus, electrolysis of a mixture of the readily oxidized TMA salt of nitropyrazole ($E_{1/2}$ = 0.81 V) and DMB ($E_{1/2}$ = 1.25 V), unlike electrolysis of a system consisting of the TMA salt of nitrotriazole and DMB,[2] afforded only resinous products. Therefore, the process depends on the nature of the N anion. The concentration of the readily oxidized nitropyrazolate anion in the reaction mixture needs be only as high as that sufficient for *N*-arylation to proceed through the reaction of this anion with the radical cation of DMB, but it must be lower than that at which electrooxidation of the nitropyrazolate anion becomes the major process. It should be noted that under the conditions of paired electrolysis, the combination of the pyrazolate anion with free pyrazole is, apparently, favorable for maintaining the current concentration of the nitropyrazolate anion at the optimum level due to its generation from nitropyrazole at a cathode.

In conclusion, it should be noted that our studies demonstrated for the first time the possibility of formation of a broad spectrum of products upon electrochemical *N*-arylation of azoles. In our opinion, the fact that the *ipso*- and *ortho*-substitution products and *ipso*-bisaddition products are structurally similar to the products obtained by electrochemical cyanation of DMB[5] is of fundamental importance. We believe that this fact is unambiguous evidence for the generality of the processes under consideration. For this reason, our further efforts will focus on elucidation of conditions and prerequisites for the predominant formation of products with particular structures, which can allow one to refine the mechanisms of these processes and to search for optimum condition of their preparative synthesis.

Experimental

The ^{1}H NMR spectra of solutions of specimens in the DMSO-d_6—CCl_4 mixture (1 : 1 v/v) were recorded on a Bruker AC-300 instrument.

Amperostatic electrolysis of the reagents, supporting salts, and additives dissolved in MeCN was performed in a 45-mL glass undivided temperature-controlled (20—21 °C) cell equipped with a magnetic stirred and axially arranged cylindrical Pt electrodes of sizes 12.3 cm^2 (cathode) and 37.2 cm^2 (anode). In the course of electrolysis, the solution was deaerated with a stream of argon. The required mode of the process was maintained using a B5-50 source of direct current and a coulometer designed at the Special Design Office of the Institute of Organic Chemistry of the Russian Academy of Sciences.

The redox characteristics of the specimens were determined by cyclic voltammetry and by the rotating disk electrode method using a PI-50-1.1 potentiostat equipped with a PR-8 programming device. In both cases, 2-mm Pt wire pressed into Teflon was used as the working electrode. An aqueous saturated calomel electrode, which was separated from the solution under examination by a salt bridge filled with a solution of the supporting electrolyte (a 0.1 *M* solution of TBAP in MeCN), was used as the reference electrode.

The specimen of TBAP was prepared by the exchange reaction of the corresponding bromide with $NaClO_4$ followed by recrystallization from ethanol. The TBA and TMA salts of nitropyrazole were synthesized according to a general procedure.[3] 1,4-Dimethoxybenzene, pyrazole, dimethylpyrazole, triazole, and tetrazole (98—99% purity) were purchased from Lancaster. Nitrotriazole,[6] nitropyrazole,[7] and dimethylnitropyrazole[7] were prepared according to procedures reported previously. The solvent MeCN was purified and dried by refluxing and distillation over $KMnO_4$ and double distillation over P_2O_5 followed by distillation over calcined K_2CO_3.

Electrolysis (general procedure). The reaction mixture of the given composition was dissolved in anhydrous MeCN (45 mL) and placed in a cell. Electrolysis was carried out under an atmosphere of argon at a controlled current by passing 2 *F* of electricity per mole of arene. After completion of electrolysis, the solvent and the low-boiling reagents were distilled off on a rotary evaporator at ≤ 100 °C and the residue was analyzed by

^{1}H NMR spectroscopy. The current yields were determined with respect to the two-electron conversion of the arene loaded* by comparing the integral intensities of the signals of the products (the CH protons of the azole and aromatic fragments and the protons of the OCH_3 groups), which were unambiguously identified** and were observed (in most cases) as singlets, and the intensities of the signals of the tetrabutyl- or tetramethylammonium cation of the supporting salt with the known concentration (the protons of the CH_2 and CH_3 groups). It should be noted that analysis of the composition of the reaction mixture thus performed made it possible to found *ipso*-bisaddition products, which have not been detected previously in the case of *N*-arylation of azoles with DMB[2,3] due, apparently, to their tendency to undergo hydrolysis giving rise to hemiketals (and then azole, methanol, and 1,4-benzoquinone) in the course of isolation and purification.

Electrolysis of a mixture of nitropyrazole, the TBA salt of nitropyrazole, and benzene (*p*-xylene). A solution of nitropyrazole (2 mmol), the TBA salt of nitropyrazole (1 mmol), and benzene (*p*-xylene) (20 mmol) in anhydrous MeCN (45 mL) was placed in a cell and electrolysis was carried out at a current of 250 mA. After completion of electrolysis, the reaction mixture was treated according to a standard procedure and analyzed by ^{1}H NMR spectroscopy, which showed that 4-nitro-1-phenylpyrazole[8] (**1**) was obtained as the final product (the current yield was 7.5%). ^{1}H NMR, δ: 7.42 (t, 1 H, CH arom.); 7.53 (t, 2 H, CH arom.); 7.94 (d, 2 H, CH arom.); 8.36 and 9.55 (both s, 1 H each, CH of pyrazole).

Electrolysis with the use of *p*-xylene instead of benzene was carried out analogously. Among the reaction products, 1-(*p*-methylbenzyl)-4-nitropyrazole (**5**) was identified (the current yield was 3%). ^{1}H NMR, δ: 2.55 (s, 3 H, CH_3); 4.69 (s, 2 H, CH_2); 7.10 (dd, 4 H, CH arom.); 8.30 and 9.10 (both s, 1 H each, CH of pyrazole).

Electrolysis of a mixture of nitropyrazole, the TMA salt of nitropyrazole, and DMB. A solution of nitropyrazole (2 mmol), the TMA salt of nitropyrazole (1 mmol), and DMB (2 mmol) in MeCN (45 mL) was placed in a cell and electrolysis was carried out at a current of 50 mA. After completion of electrolysis, the reaction mixture was treated as described above and analyzed by ^{1}H NMR spectroscopy, which showed that the reaction afforded 1,4-dimethoxy-2-(4-nitropyrazol-1-yl)benzene (**2**) (the current yield was 10%), 4-methoxy-1-(4-nitropyrazol-1-yl)benzene (**3**) (8%), and a mixture (~1 : 1) of stereoisomers of 1,4-dimethoxy-1,4-di(4-nitropyrazol-1-yl)cyclohexa-2,5-diene (**4a,b**) (28%). ^{1}H NMR of compound **2**, δ: 3.79 and 3.91 (both s, 6 H, 2 CH_3O); 7.04—7.20 (m, 2 H, CH arom.); 7.31 (m, 1 H, CH arom.); 8.30 and 9.02 (both s, 1 H each, CH of pyrazole). ^{1}H NMR of compound **3**, δ: 3.85 (s, 3 H, CH_3O); 7.05 and 7.85 (both d, 4 H, C_6H_4); 8.33 and 9.39 (both s, 1 H each, CH of pyrazole). ^{1}H NMR of compound **4a**, δ: 3.28 (s, 6 H, CH_3O); 6.60 (s, 4 H, C_6H_4); 8.17 and 9.00 (both s, 1 H each, CH of pyrazole). ^{1}H NMR of compound **4b**, δ: 3.33 (s, 6 H, CH_3O); 6.73 (s, 4 H, C_6H_4); 8.11 and 8.94 (both s, 1 H each, CH of pyrazole).

Electrolysis of a mixture of dimethylpyrazole, TBAP, and DMB. A solution of dimethylpyrazole (2 mmol), TBAP (1 mmol), and DMB (2 mmol) in MeCN (45 mL) was placed in a cell and electrolysis was carried out at a current of 50 mA. The reaction mixture was treated as described above and analyzed by ^{1}H NMR spectroscopy, which showed that the reaction afforded 1,4-dimethoxy-2-(3,5-dimethylpyrazol-1-yl)benzene (**6**) (the current yield was 28%) and a mixture (~1 : 1) of stereoisomers of 1,4-dimethoxy-1,4-di(3,5-dimethylpyrazol-1-yl)cyclohexa-2,5-diene (**7a,b**) (16%). ^{1}H NMR of compound **6**, δ: 2.14 and 2.20 (both s, 6 H, 2 CH_3); 3.70 and 3.78 (both s, 6 H, 2 CH_3O); 5.90 (s, 1 H, CH of pyrazole); 6.81 (m, 1 H, CH arom.); 6.97—7.07 (m, 2 H, CH arom.). ^{1}H NMR of compound **7a**, δ: 2.08 and 2.10 (both s, 6 H, 2 CH_3); 3.13 (s, 6 H, CH_3O); 5.85 (s, 1 H, CH of pyrazole); 6.40 (s, 4 H, C_6H_4). ^{1}H NMR of compound **7b**, δ: 2.44 and 2.45 (both s, 6 H, 2 CH_3); 3.19 (s, 6 H, CH_3O); 5.88 (s, 1 H, CH of pyrazole); 6.50 (s, 4 H, C_6H_4).

In the case of electrolysis of **a mixture of pyrazole, TBAP, and DMB** performed under analogous conditions, a mixture (~1 : 1) of stereoisomers of 1,4-dimethoxy-1,4-di(pyrazol-1-yl)cyclohexa-2,5-diene (**8a,b**) was detected (the current yield was 25%). ^{1}H NMR of compound **8a**, δ: 3.13 (s, 6 H, CH_3O); 6.33 (t, 1 H, CH of pyrazole); 6.53 (s, 4 H, C_6H_4); 7.47 and 7.93 (both d, 1 H each, CH of pyrazole). ^{1}H NMR of compound **8b**, δ: 3.2 (s, 6 H, CH_3O); 6.27 (t, 1 H, CH of pyrazole); 6.64 (s, 4 H, C_6H_4); 7.44 and 7.85 (both d, 1 H each, CH of pyrazole).

In the case of electrolysis of **a mixture of triazole, TBAP, and DMB** performed under analogous conditions, a mixture (~1 : 1) of stereoisomers of 1,4-dimethoxy-1,4-di(1,2,4-triazol-1-yl)cyclohexa-2,5-diene (**9a,b**) was detected (the current yield was 34%). ^{1}H NMR of compound **9a**, δ: 3.20 (s, 6 H, CH_3O); 6.59 (s, 4 H, C_6H_4); 7.92 and 8.72 (both s, 1 H each, CH of triazole). ^{1}H NMR of compound **9b**, δ: 3.30 (s, 6 H, CH_3O); 6.70 (s, 4 H, C_6H_4); 7.88 and 8.61 (both s, 1 H each, CH of triazole).

Electrolysis of a mixture of nitropyrazole, TBAP, *sym*-collidine, and DMB. A solution of nitropyrazole (3 mmol), TBAP (1 mmol), collidine (1 mmol), and DMB (2 mmol) in MeCN (45 mL) was placed in a cell and electrolysis was carried out at a current of 50 mA. After completion of electrolysis, the reaction mixture was treated as described above and analyzed by ^{1}H NMR spectroscopy, which showed that the reaction afforded compound **2** (the current yield was 4%) and a mixture (~1 : 4) of stereoisomers **4a,b** (52%).

In the case of electrolysis of **a mixture of dimethylnitropyrazole, TBAP, *sym*-collidine, and DMB** performed under analogous conditions, a mixture (~1 : 3) of stereoisomers of 1,4-dimethoxy-1,4-di(3,5-dimethyl-4-nitropyrazol-1-yl)cyclohexa-2,5-diene (**10a,b**) was detected (the current yield was 28%). ^{1}H NMR of compound **10a**, δ: 2.39 and 2.45 (both s, 6 H, 2 CH_3); 3.25 (s, 6 H, CH_3O); 6.52 (s, 4 H, C_6H_4). ^{1}H NMR of compound **10b**, δ: 2.32 and 2.45 (both s, 6 H, 2 CH_3); 3.31 (s, 6 H, CH_3O); 6.62 (s, 4 H, C_6H_4).

In the case of electrolysis of **a mixture of nitrotriazole, TBAP, *sym*-collidine, and DMB** performed under analogous conditions, a mixture of stereoisomers (or isomers with respect to the N atom) of 1,4-dimethoxy-1,4-di(3-nitro-1,2,4-triazolyl)cyclohexa-2,5-diene (**11**) was detected (the current

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* In the case of electrolysis of nitropyrazole performed in the presence of excess benzene and *p*-xylene, the current yield was determined with respect to azole.

** The spectral characteristics of compounds **2—7** used for identification are lacking in the literature and were determined based on the results of analysis of the ^{1}H NMR spectra of the following structurally similar compounds using the ACD/labs program: 3-nitro-1-phenyl-1,2,4-triazole,[1] 1,4-dimethoxy-2-(3-nitro-1,2,4-triazol-1-yl)benzene,[2] 1,4-dimethoxy-2-(*N*-tetrazolyl)benzene and 4-methoxy-1-(triazol-1-yl)benzene,[3] 1,1,4,4-tetramethoxycyclohexa-2,5-diene and 1,4-dicyano-1,4-dimethoxycyclohexa-2,5-diene,[5] and 4-nitro-1-phenyl- and 1-benzyl-4-nitropyrazoles.[8]

yield was 10%). ^{1}H NMR, δ: 3.36 and 3.41 (both s, 6 H, CH_3O); 6.72 and 6.84 (both s, 4 H, C_6H_4); 9.04 and 9.14 (both s, 1 H, CH of nitrotriazole).

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