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N-Dimethoxyphenylation of highly basic pyrazoles during undivided electrolysis

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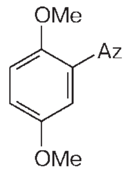
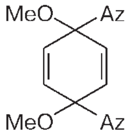
The reactions of pyrazole, 3,5-dimethylpyrazole, and its 4-nitro derivatives with 1,4-dimethoxybenzene during undivided amperostatic electrolysis in MeCN (CH_2Cl_2) were studied. The basicity of the medium, which depends on the solvent nature, the nature and concentration of pyrazole and the acid-base properties of additives, and the amount of electricity passed determine the yield and relative content of the target products, *viz.*, 1,4-dimethoxy-2-(pyrazol-1-yl)benzenes (**1**) and 1,4-dimethoxy-1,4-di(pyrazol-1-yl)cyclohexa-2,5-dienes (**2**). The process occurs mainly through the interaction of the nonionized solvato complex of pyrazole with the 1,4-dimethoxybenzene radical cation and affords radical intermediates structurally similar to compounds **1** and **2**. The key stage of the process determining the **1** : **2** ratio is the rearrangement of the intermediately produced 1,4-dimethoxy-1-(pyrazol-1-yl)arenonium cation to the 1-(pyrazol-1-yl)-2,5-dimethoxyarenonium cation.

Key words: paired electrolysis, *N*-arylation, pyrazoles, pyrazolate anions, 1,4-dimethoxybenzene.

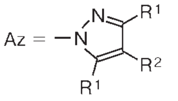
In the previous work we showed[1] that the undivided electrolysis on Pt electrodes of 1,4-dimethoxybenzene (DMB) mixtures with various azoles (pyrazoles, triazoles, and tetrazole) in MeCN using tetraalkylammonium salts of azoles or Bu_4NClO_4 as supporting electrolytes affords the products of *N*-dimethoxyphenylation (hereafter arylation) of azoles. In particular, it was found for pyrazoles that, in addition to the products of *ortho*-substitution **1**, the products of *ipso*-bisaddition **2** are formed.



1a—c



2a—c



a: $R^1 = R^2 = H$
b: $R^1 = Me$, $R^2 = H$
c: $R^1 = Me$, $R^2 = NO_2$

These data partially contradict the results of earlier studies, namely, electrolysis of tetrazole or 5-phenyltetrazole mixtures and their tetrabutylammonium salts with DMB under the conditions close to those used by us in the previous work[1] produces only the corresponding *ortho*-substituted tetrazoles.[2] The single *ortho*-substitution product was found upon electrolysis of a mixture of 3-nitro-1,2,4-triazole tetramethylammonium salt with DMB in the anodic space of a divided cell.[3]

We believed[1] that such a discrepancy between the results of the cited works[2,3] is due to the hydrolytic instability of products **2** and, thus, difficulty of their preparative identification. Therefore, to analyze the composition of the electrolysis products, we widely used[1] NMR spectroscopic monitoring, which allowed us to reliably detect products that are present in minor amounts and labile during isolation. The established formation of several products of electrochemical *N*-arylation[1] was a prerequisite for the refinement of the earlier proposed[2,3] mechanism of this process.

In this work, the problem was solved for the reaction of 3,5-dimethylpyrazole (DMP), pyrazole (P), and 3,5-dimethyl-4-nitropyrazole (DMNP) with DMB during amperostatic undivided electrolysis with Bu_4NClO_4 as a supporting electrolyte. The influence of different factors on the yield and ratio of products **1a—c** and **2a—c** was studied and compared to the data of electrolysis in a divided cell and results of studying the electrochemical behavior of the objects by cyclic voltammetry (CV).

Results and Discussion

Voltammetric measurements. Some information about the regularities of electrochemical *N*-arylation of pyrazoles was obtained from analysis of the voltammetric

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Table 1. Potentials (E, *vs.* Ag/0.1 M Ag^+) of the oxidation (E^{Ox}) and reduction (E^{Red}) peaks in the CV curves ($\nu = 0.2 \text{ V s}^{-1}$) for the reactants studied ($5 \cdot 10^{-3}$ mol L^{-1}) and their pK_a values

Reactant	E^{Ox}	$-E^{Red}$	pK_a [4]	
	V		I[a]	II[b]
1,4-Dimethoxybenzene (DMB)	1.01, 1.16, 1.56	—	—	—
3,5-Dimethylpyrazole (DMP)	1.52	2.32	15.00	4.06
3,5-Dimethylpyrazolate anion	0.20	—	—	—
Pyrazole (P)	1.76	2.15	14.21	2.48
Pyrazolate anion	0.39	—	—	—
3,5-Dimethyl-4-nitropyrazole (DMNP)	2.10	1.67	10.65	−0.45
3,5-Dimethyl-4-nitropyrazolate anion	0.86	—	—	—
2,4,6-Trimethylpyridine (CL)	1.85	—	—	7.43
2-(3,5-Dimethylpyrazol-1-yl)-1,4-dimethoxybenzene	1.06, 1.32, 1.76	—	—	—
1,1,4,4-Tetramethoxycyclohexa-2,5-diene	2.23	—	—	—

[a] Studied azole.

[b] Conjugated acid.

behavior of the initial reactants, their mixtures, and some final products. The results of these studies are collected in Table 1. The CV curves of DMB in a 0.1 M solution of Bu_4NClO_4 in MeCN exhibit two distinct anodic peaks separated by a poorly pronounced peak with $E = 1.16$ V (see Table 1 and Fig. 1, curve *1*). The first of them is reversible and, according to the published data,[5] corresponds to the formation of the corresponding radical cation. We did not specially study the nature of the poorly pronounced second peak and the third peak but one of them corresponds,[5] likely, to the oxidation of the product of the reaction between the radical cation and MeCN.

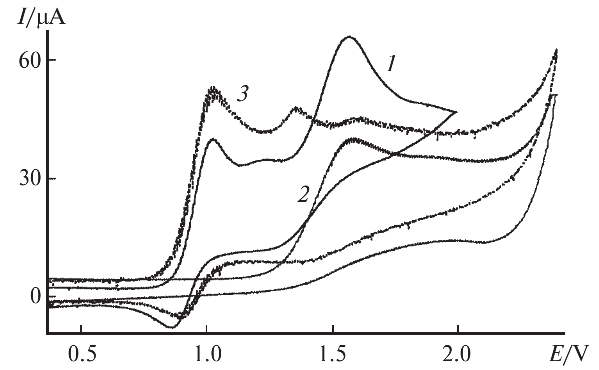

Fig. 1. Cyclic voltammograms of 1,4-dimethoxybenzene (*1*), 3,5-dimethylpyrazole (*2*) ($4 \cdot 10^{-3}$ mol L^{-1}), and their equimolar mixture (*3*) recorded on the Pt electrode in a 0.1 M solution of Bu_4NClO_4 in MeCN; $\nu = 0.5 \text{ V s}^{-1}$.

The redox processes involving DMP, P, and DMNP occur as irreversible one-electron steps. The CV curves usually manifest peaks of both reduction and oxidation of these pyrazoles, and the heights of the peaks depend linearly on the concentrations of pyrazoles in the $2 \cdot 10^{-3}$—$1 \cdot 10^{-2}$ mol L^{-1} interval and the quadratic root of the potential sweep. The data in Table 1 show that DMP is most easily oxidized, and the oxidation of DMNP is most difficult.

The data on the oxidation potentials of the DMP, P, and DMNP anions were also of interest (see Table 1). The oxidation peaks for these anions, which coincide in potential values, were obtained in two independent experiments, *viz.*, by the addition of an equimolar amount of NaOMe to a solution of DMP, P, or DMNP before recording their CV curves and during reductive microelectrolysis (Scheme 1) of solutions of these azoles (~$1 \cdot 10^{-2}$ mol L^{-1}) with the controlled potential chosen in the potential region of the corresponding anodic peaks and by passing 1 F electricity per mole of azole.

Scheme 1

$$\text{AzH} + e^- \longrightarrow \text{Az}^- + 0.5\ H_2$$

Note that this process is in complete accordance with the concept about the direct cathodic deprotonation of organic acids during their reduction in aprotic media on electrodes with a low hydrogen overvoltage.[6] For the pyrazoles under study, the potentials of this process vary from −1.67 V for DMNP to −2.32 V for DMP (see Table 1).

Pyrazole additives to a solution of the supporting electrolyte containing DMB were found to change sharply the shape of the CV curve of this compound. In the presence of DMP, whose oxidation occurs at the same potentials as the potentials of the third peak in the CV curve of DMB, the height of the peak does not increase (see Fig. 1) and, moreover, decreases sharply, while the first peak height of DMB oxidation somewhat increases. The same fact is characteristic of additives of other pyrazoles to a solution of DMB. These results provide a very interesting, although qualitative, observation: the DMB radical cation is capable of interacting directly with the nonionized form of the pyrazoles.

Electrolysis in an undivided cell. Continuing our previous[1] studies, we established that during electrolysis of a DMP—DMB mixture in MeCN (hereafter with Bu_4NClO_4 as supporting electrolyte) the ratio of these substances in the initial solution substantially affects the yield of the final products **1b** and **2b**. An increase in the relative content of DMP increases the yield of **2b**, whereas the yield of **1b** is somewhat decreased (Table 2, entries *1*,

Table 2. Influence of conditions of undivided amperostatic electrolysis of pyrazoles in the presence of DMB on the yield of *N*-dimethoxyphenylation products[a]

Entry	Pyrazole[b]	Pyrazole/DMB[c] (Q^f/F)	Additive[d]	Y^e (%)	
				1	**2**
1	DMP	0.5 (2)	—	35	—
2	DMP	0.5 (1)	—	22	19
3	DMP	1 (2)	—	28	15
4	DMP	1.5 (2)	—	28	30
5	DMP	1.5 (1)	—	24	42
6	DMP	2 (2)	—	20	32
7	DMP	1.5 (2)	CL (0.5)	15	42
8	DMP	1.5 (2)	CL (1.5)	11	43
9	DMP	1.5 (2)	AcOH (1.5)	38	14
10	DMP	1.5 (2)	CAA (1.5)	63	—
11	DMP[g]	1.5 (2)	—	45	—
12	DMP[g]	1.5 (2)	CL (1.5)	14	45
13	DMP[h]	1.5 (2)	—	9[i]	—
14	P	0.5 (2)	—	—	—
15	P	0.5 (1)	—	—	13
16	P	1 (2)	—	—	25
17	P	1.5 (2)	CL (0.5)	—	38
18	P	1.5 (2)	AcOH (1.5)	13	17
19	P[g]	1.5 (2)	—	40	—
20	DMNP	1 (2)	—	9	—
21	DMNP	1.5 (2)	CL (0.5)	—	28

[a] Electrolysis was carried out in MeCN with Bu_4NClO_4 as supporting electrolyte (0.5 mol per mole of DMB).

[b] DMP is 3,5-dimethylpyrazole; P is pyrazole; DMNP is 3,5-dimethyl-4-nitropyrazole; NP is 4-nitropyrazole.

[c] Molar ratio.

[d] CL is collidine; CAA is chloroacetic acid; number of moles per mole of DMB is given in parentheses.

[e] Current yields of products.

[f] Amount of electricity per mole of DMB.

[g] Electrolysis was carried out in CH_2Cl_2.

[h] Electrolysis was carried out in MeOH.

[i] 1,1,4,4-Tetramethoxyhexa-2,5-diene is also formed in 52% current yield.

3, *4*, and *6*). The relatively high (see Table 1) basicity of DMP seems to be manifested in these regularities rather than the influence of the concentration (formation of compound **2**, unlike **1**, needs two pyrazole molecules). For example, an analogous effect (see Table 2, entries *7* and *8*) is observed when rather basic (see Table 1) 2,4,6-trimethylpyridine (*symm*-collidine, CL) is added to the reaction mixture.* At the same time, we have to take into account other factors: formation of the single product **1b** at the DMP : DMB molar ratio equal to 0.5 (see Table 2, entry *1*) cannot be explained only by the change in the DMP concentration. This is indicated by the dependence of the composition of electrolysis products on the amount of electricity passed. It turned out that passing 1 *F* electricity affords products **1b** and **2b** in the reaction mixture, while product **2b** was not found upon the subsequent additional passing 1 *F* electricity (see Table 2, *cf.*, entries *1* and *2*).

A resembling situation, *viz.*, decrease in the yield of product **2b** and predominant formation of compound **1b**, appears during prolonged electrolysis for another ratio of reactants (see Table 2, *cf.* entries *4* and *5*). This effect indicates that the transformation **2b** $\longrightarrow$ **1b** can occur during electrolysis and, thus, directly concerns the *N*-arylation mechanism (see below).

Since an increase in the basicity of the medium on going from less to more basic pyrazoles, an increase in the content of the latter, or the addition of CL favor the formation of compound **2**, a decrease in the basicity of the medium, *e.g.*, by the addition of acids to the electrolyte, should favor, from the formal point of view, the predominant formation of product **1**. However, this possibility seemed improbable because the chemical stages resulting in products **1** and **2** assume the nucleophilic attack of the electrophilic intermediate by the azole anion[2,3] or azole.[1] The addition of an acid followed by protonation seemed to impede the formation of the first product and to decrease the nucleophilicity of the second product. Nevertheless, the experiment unambiguously confirmed the uniqueness of the process, namely, addition of AcOH increases the relative content of **1b** in the reaction product with the retention of the overall yield of **1b** and **2b**, and additives of stronger chloroacetic acid result in the formation of product **1b** only (see Table 2, entries *9* and *10*).

The solvent nature also affects the direction and efficiency of *N*-arylation. For example, when MeCN was replaced by less polar CH_2Cl_2, compound **1b** was the single reaction product (see Table 2, entry *11*). However, in the case of CH_2Cl_2, an increase in the medium basicity due to CL additives changes the direction of *N*-arylation toward the predominant formation of product **2b** (see Table 2, *cf.* entries *11* and *12*). In turn, the replacement of MeCN by more basic and nucleophilic MeOH favors a decrease in the yield of **1b** (see Table 2, *cf.* entries *4* and *13*). In this case, product **2b** is not formed at all but its methoxy analog 1,1,4,4-tetramethoxycyclohexa-2,5-diene is formed in considerable amounts, which can be explained (*cf.* literature data[7]) if we take into account a multiply higher concentration of MeOH compared to that of DMP.

A similar influence of the change in the basic properties of the medium and solvent (see Table 2, entries *14*, *16—19*) was observed for electrolysis of a mixture of DMB with P, which is less basic than DMP (see Table 1). In this case, the tendency to a decrease in the yield of

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* Collidine was chosen due to its high redox potentials (see Table 1). At the same time, all pyrazoles studied had relatively low acidity (pK_a = 9.6—15), and their deprotonation by CL to any degree is improbable.

the *ortho*-substitution product is most likely caused by a greater affinity to anodic oxidation of **1a** compared to **1b**. This circumstance and the probable transformation **2a** $\longrightarrow$ **1a** (see above) explain the absence of product **1a** in the case of electrolysis of a mixture with a low content of P (unlike the similar experiment using DMP) and the presence of product **2a** in the reaction mixture only after 1 *F* electricity was passed (see Table 2, entries *14* and *15*).

An increase in the basicity of the medium by the addition of CL has a similar effect on the composition of the final products in the reaction mixtures in the case of DMNP (see Table 2, entries *20* and *21*), which is less basic than P (see Table 1). The experimental data considered above suggest that a combination of such parameters as the concentration and acid-base and solvating properties of pyrazoles, additives, and solvents controls the reactivity of solvato complexes[1] of pyrazoles acting as nucleophilic coreactants toward anodically generated electrophilic polydentate intermediates and thus determines the overall yield and ratio of products **1** and **2**.

Electrolysis in a divided cell. The results of CV studies considered in the previous sections and results of paired electrolysis of pyrazoles with DMB in the presence of acid additives indicated that the DMB radical cations can react directly with the nonionized form of pyrazoles. This conclusion could finally be confirmed by the data of electrolysis of a pyrazole—DMB mixture in the anodic space of a divided cell, *i.e.*, under the conditions where the presence of the pyrazolate anions (Az^-) as nucleophilic coreactant was completely excluded. For comparison, we chose the conditions of entry *4* (see Table 2) but, to prevent the deactivation of the pyrazole component of the reaction mixture (electrolysis in the anodic space of a divided cell is accompanied by proton generation), we used a double amount of DMP. Divided electrolysis produces compound **1b** in the anolite in 47% current yield. This value is comparable with the overall yield of **1b** and **2b** in the experiment in an undivided cell (*cf.* Table 2, entry *4*), and some difference in the composition of the products can be explained by different experimental conditions. Thus, the concept[1] about the possible participation of pyrazole solvato complexes as nucleophilic coreactants in electrochemical *N*-arylation was experimentally substantiated.

The authors of the monograph[8] made the general conclusion that arene functionalization (in particular, DMB cyanation) during their electrolysis in the presence of anions proceeds exclusively through the interaction of the nucleophile with the anodically generated arene radical cation, whereas the second mechanism, *viz.*, reaction of the radical (formed by the anodic oxidation of the nucleophile) with arene (Scheme 2), was rejected for several systems. The validity of this conclusion for the electrochemical *N*-arylation of pyrazoles by DMB was of doubtless interest because the majority of Az^- were readily oxidizable (see Table 1).

Scheme 2

$$Az^- - e^- \longrightarrow Az^{\bullet}$$

Using DMP as an example, we showed that the exhaustive amperostatic electrolysis of its solution in the cathodic space of a divided cell after passing ~1 *F* electricity affords a noticeable amount of the corresponding anion (estimation from the height of the characteristic peak $E_p = 0.2$ V in the CV curve). After the polarity of the electrodes was changed and DMB was added (approximately half a concentration of the DMP anion), electrolysis was continued as an oxidative process at the controlled potential $E = 0.2$ V corresponding to the oxidation peak of the DMP anion until this peak completely disappeared (CV monitoring). The reaction mixture after electrolysis was established to contain compound **1b** as the main product. The results obtained suggest that *N*-arylation can proceed *via* both indicated mechanisms during amperostatic electrolysis of a pyrazole—DMB mixture.

Regularities of *N*-arylation of pyrazoles. Based on the above results and data of the previous work,[1] we can conclude that the mechanism of formation of *N*-arylated pyrazoles is not so unambiguous as it has been assumed previously.[2,3] First, it is necessary to correct concepts on the role of the cathodic reaction in the undivided electrolysis of a pyrazole—DMB mixture.

We believe that, in most cases, this process is related to the cathodic deprotonation of onium compounds (BH^+), *viz.*, products of the reaction of the initial pyrazoles or bases of the CL type with protons generated in anodic transformations of the reactants (Scheme 3), rather than to the generation of the Az^- anions (see Scheme 1).

Scheme 3

$$BH^+ + e^- \longrightarrow B + 0.5\ H_2$$

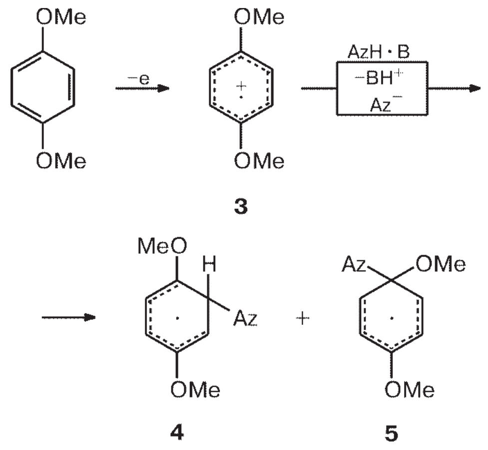
B is pyrazole or CL

This fact is indirectly indicated by very high reduction potentials of the majority of pyrazoles and the formation of products **1b** and **2b** during amperostatic electrolysis of a DMP—DMB mixture in the anodic space of a divided cell (see above). It follows from this that the presence of the pyrazolate anions in the reaction mixture is not necessary for *N*-arylation to occur.

The conclusion experimentally substantiated above is also very important. It states that the ($AzH \cdot B$) complexes of rather basic pyrazoles (of the DMP type) formed by hydrogen bonds between each other or with bases of the CL type act as nucleophilic coreactants in *N*-arylation. When pyrazoles with a comparatively low basicity are used (for example, DMNP), their electrochemical *N*-arylation occurs rather limply.

Considering the mechanism of anodic processes, one should first concentrate attention on the nature of the electrophilic intermediate responsible for subsequent transformations. As already mentioned, the most commonly accepted[8] (see also Refs. 2 and 3) interpretation of the mechanism of electrooxidation of DMB-containing reaction mixtures assumes that radical cation **3** (Scheme 4) formed in the anodic oxidation of DMB participates as such an intermediate. The results of electrolysis in a divided cell suggest that this radical cation is the most probable electrophilic coreactant in *N*-arylation. We believe that the benzene ring of intermediate **3** is subjected to the alternative *ortho*- or *ipso*-attack by the AzH • B complex with proton elimination and affords radical intermediates **4** and **5** as probable precursors of compounds **1** and **2**. This scheme takes place, probably, for electrolysis of the DMB—P (or DMP) system and electrolyses of systems with lowly basic pyrazoles (of the DMNP type) in the presence of the CL additive.

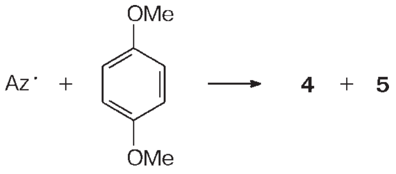
Scheme 4



B is pyrazole or CL

As mentioned above, the anodic stage of the process under consideration can be associated not only with the generation of radical cation **3** but also (or) with the oxidation of the Az^- anions to the $Az^{\bullet}$ radicals (see Scheme 2) as key intermediates, the more so, such anions are more easily oxidized than DMB (see Table 1). This variant of the mechanism is very close to the previously[9] described *N*-phenylation of 3-nitro-1,2,4-triazole in the nitrotriazole—benzene system and, which is substantial for further discussion, also produces radicals **4** and **5** formed due to the alternative *ortho*- or *ipso*-attacks of DMB by the $Az^{\bullet}$ radical (Scheme 5).

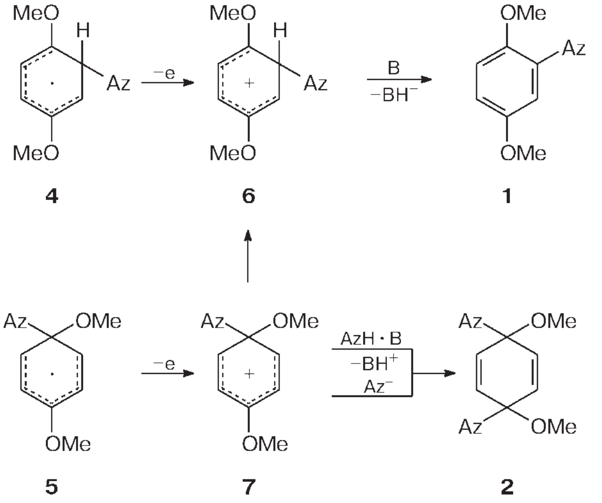
Scheme 5



The special experiments (see above) confirmed that this process is real. Its partial occurrence involving the $Az^{\bullet}$ radicals should be taken into account because the cathodic generation of Az^- (along with the deprotonation of onium compounds) during amperostatic electrolysis of the pyrazole—DMB systems in a divided cell cannot be neglected *a priori*.

It follows from the aforesaid that radicals **4** and **5** are precursors of compounds **1** and **2** regardless of the nature of the pyrazole used and electrolysis conditions. The electrooxidation of radicals **4** and **5** produces arenonium cations **6** and **7**, respectively (Scheme 6). Then the deprotonation of **6** gives compound **1**, and the *ipso*-interaction of compound **7** with the Az^- anion or AzH • B complex affords compound **2**.

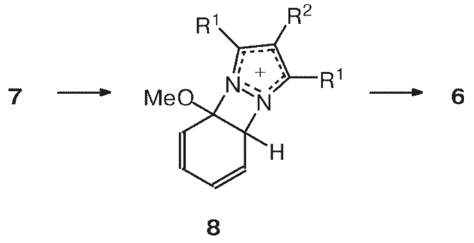
Scheme 6



B is pyrazole or CL

At the same time, to describe all available experimental facts, Schemes 4—6 should be supplemented by the concept about the rearrangement of cation **7** to cation **6**. Rearrangements of this type are well known for aromatic electrophilic substitution.[10] In our case, the transformation **7** ⟶ **6** can proceed especially readily through the intermediate formation of the relatively stable (compared to the classical transition state) four-membered onium intermediate **8** (Scheme 7). This explains the preferential migration of precisely the pyrazole group instead of the methoxy group and indicates that such a rearrangement is most real for pyrazoles capable of efficient delocalization of the positive charge, namely, P, DMP (but is unlikely for DMNP).

Scheme 7

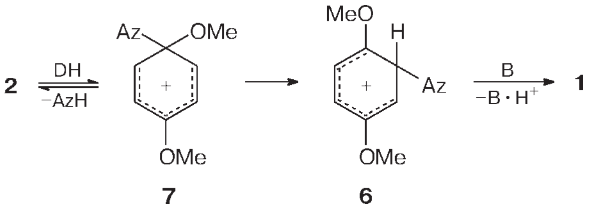


R^1, R^2 = H, Me

The rearrangement **7** ⟶ **6** allows the most correct explanation of the dependence of the ratio of yields of products **1a,b** and **2a,b** on the concentration of the pyrazole component during electrolysis of the highly basic pyrazole—DMB systems. If the rate of intramolecular rearrangement of **7a,b** producing the *ortho*-substitution products (**1a,b**, respectively) is independent of the concentration and nucleophilicity of the pyrazole coreactant, these factors certainly determine the rate of transformation of **7a,b** in the *ipso*-bisaddition products (**2a,b**, respectively) (see Scheme 6). Note that in some sense the rearrangement **7** ⟶ **6** can directly be proved experimentally, and this proof explains the exclusive formation of product **1b** in the electrolysis of the DMP—DMB mixture in the presence of chloroacetic acid (see Table 2, entry *10*). In fact, after short heating with chloroacetic acid in MeCN, a mixture of **1b** (0.24 mmol) and **2b** (0.51 mmol) obtained by electrolysis (at the DMP to DMB molar ratio equal to 1.5) contains only **1b** (0.47 mmol) and does not contain **2b**. In other words, under these conditions, compound **2b** is transformed by ~45% into compound **1b** and, likely, is hydrolyzed by ~55%. This purely chemical transformation **2b** ⟶ **1b** (Scheme 8) can be explained only by the rearrangement **7** ⟶ **6**.

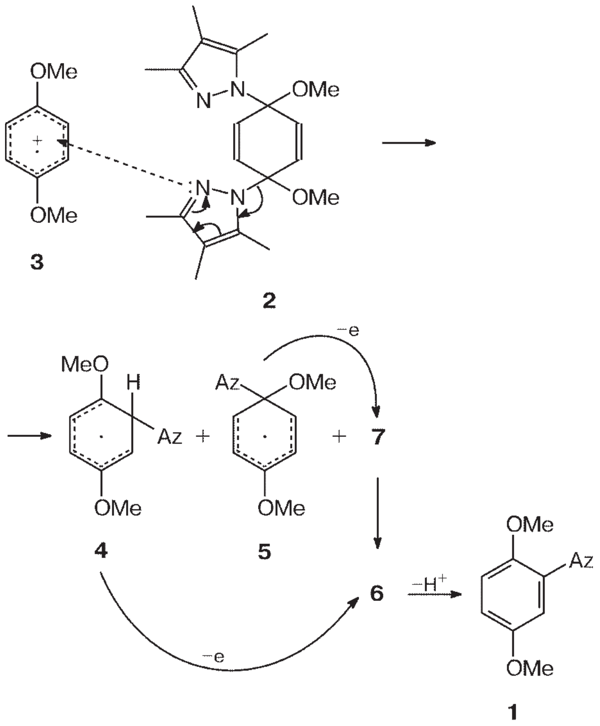
Taking into account the rearrangement **7** ⟶ **6** during *N*-arylation of highly basic pyrazoles, we can explain the specific features of electrolysis at the DMP/DMB molar ratio equal to 0.5. In this case, passing 1 *F* electricity results in the predominant formation of compound **2b** (see Table 2, entry *2*). The latter is evidently transformed into **1b** when the amount of electricity passed increased to 2 *F* (see Table 2, entry *1*). We assume that at the final stage of prolong electrolysis, when the initial DMP is almost completely consumed and the generation of radical cation **3** continues to occur, this intermediate can attack the N atom of the pyrazole group of **2b** to form compounds **7b**, **4b**, and **5b**. In the absence of DMP and other nucleophiles in the reaction mixture, these species are transformed into **6b** due to electrochemical oxidation and (or) intramolecular rearrangement. Compound **6b** is further deprotonated to give **1b** (Scheme 9).

Scheme 8



DH is proton donor

Scheme 9



Note the pronounced resemblance of the transformations **2a,b** ⟶ **1a,b** in Schemes 8 and 9. They differ only by the type of electrophilic reactants (proton donor DH or radical cation **3**) involved in the formation of arenonium cation **7a,b**.

Accomplishing the discussion of effects caused by the rearrangement **7** $\longrightarrow$ **6**, we note that its occurrence also explains the above mentioned influence of the replacement of the solvent (CH_2Cl_2 instead of MeCN) on the ratio of products **1a,b** and **2a,b**. The known ability of CH_2Cl_2 to stabilize efficiently radical cations[11] is evidently a result of the poor ionizing and polarizing properties inherent in this solvent (dielectric constants for MeCN and CH_2Cl_2 are 37 and 9, respectively). These properties substantially decrease the reactivity of ionic or dipolar nucleophiles present in an electrolyte solution. For the reactions considered, this is equivalent, in fact, to a decrease in the nucleophilicity of the pyrazole coreactant and, according to the above reasons, should favor the predominant formation of **1a,b** due to the rearrangement during *N*-arylation of highly basic pyrazoles in CH_2Cl_2.

The decrease in the yield of **1b** in the DMP—DMB system when MeOH is used instead of MeCN as a solvent (MeOH is close to MeCN in dielectric constant but simultaneously is much more basic and, evidently, more nucleophilic) is probably associated in part with the "switching off" of the rearrangement step because the formation of intermediates **5b** and further **7b** is hindered because of a multiply higher concentration of MeOH over that of DMP.

Finishing the discussion of the mechanistic aspects of *N*-arylation of pyrazoles, we have to concentrate attention on the problem of stability of the products under the anodic oxidation conditions. In our opinion, the latter noticeably affects both the composition of the target products and its dependence on the amount of electricity passed. Comparison of the structures of arylation products **1** and **2** shows that a relatively high oxidation potential can be expected only for **2**, which is confirmed, to some extent, by the oxidation potential of a similar structure of 1,1,4,4-tetramethoxycyclohexa-2,5-diene presented in Table 1. On the contrary, the structure of products **1** allows us to assume relatively low oxidation potentials for them. In the absence of electron-acceptor groups in the pyrazole substituents, it seems probable that the oxidation potentials of these compounds are comparable or even lower than that for DMB. Indeed, the CV curves of solutions of **1b** contain three oxidation peaks, whose potentials (see Table 1) are comparable to those of the first and subsequent peaks in the CV curves of DMB. This implies that *ortho*-substitution products **1** formed by amperostatic electrolysis can undergo electrochemical transformations to a noticeable extent. The lower yields of **1a** are evidently due to its easier oxidation compared to that of **1b** (see Table 2). In fact, the molecule of the latter is non-complanar due to the repulsion between the *ortho*-methoxy group in the phenyl ring and methyl groups in the pyrazole ring, which virtually transforms the pyrazole ring into a withdrawing substituent.

For evaluation of preparative aspects of *N*-arylation of pyrazoles, note that **1** and **2** are compounds, whose syntheses by the classical methods of the organic chemistry are difficult, and therefore, the proposed one-step method for their preparation from available initial substances seems useful. However, products **2** form, as a rule, in a mixture with **1** and are hydrolytically unstable in most cases. That is why, their isolation in the individual form is difficult. Therefore, the electrochemical *N*-arylation of pyrazoles is of greatest interest as a method for synthesis of products of the type **1** by the undivided amperostatic electrolysis of reaction mixtures containing a considerable DMB excess (see Table 2, entry *1*), with acid additives (entries *9* and *10*), or using CH_2Cl_2 as solvent (entries *11* and *19*). Note, however, that the first route is accompanied by the intense anodic oxidation of DMB and affords a great amount of resins. Two other methods have no these disadvantages and were used as most appropriate to prepare **1** in the individual form (see Experimental).

Experimental

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

Redox characteristics of the objects under study were determined by the CV method in a glass cell, whose temperature was maintained constant (25 °C), using a PI-50-1.1 potentiostat with a PR-8 programmer. A Pt wire 1 mm in diameter coated with a Teflon shell was used as the working electrode. The reference electrode was Ag/0.1 *M* $AgNO_3$. The supporting electrolyte was 0.1 *M* Bu_4NClO_4 in the solvent used.

Amperostatic electrolysis of solutions of DMB (2 mmol) in reaction mixtures (45 mL) with different compositions was carried out in a glass undivided cell with a constant temperature (20—21 °C) using a magnetic stirrer and axial cylindrical Pt electrodes with surface areas of 12.3 cm^2 (cathode) and 37.2 cm^2 (anode) in an argon atmosphere at the controlled current (I = 50 mA), passing 1 or 2 F electricity per mole of DMB (see Table 2). After cessation of electrolysis, the solvent was distilled off on a rotary evaporator at the temperature $\leq$100 °C (25 Torr), and the residue was analyzed by ^1H NMR. Reactants and solvents for this experiment, its apparatus design, and typical experimental procedure were similar to those described previously.[1] The spectral characteristics of compounds **1b**, **2a—c** used for their identification and the procedure for determination of the current yield of **1** and **2** (calculation per two-electron transformation of DMB) based on the spectral data without their isolation from solution were published previously.[1]

A porous glass diaphragm was used for electrolysis with divided cathodic and anodic spaces. The cell volume and ratios of surface areas of the Pt electrodes were approximately the same as those for undivided electrolysis. In experiment with the changed polarity of electrodes, their potential was monitored by a potentiostat of the CV setup.

Silufol UV-245 plates were used for TLC.

Below we describe the experiments with isolation of the target products, which confirm the validity of conclusions about their structure based on the spectral data.

1,4-Dimethoxy-2-(pyrazol-1-yl)benzene (1a). After the solvent was distilled off (20—35 °C, 25 Torr), the residue (see Table 2, entry *19*) was treated with water (10 mL) and benzene (20 mL). The organic layer was separated, washed with water, and dried with anhydrous Na_2SO_4. After chromatographic purification (silica gel, benzene as eluent), compound **1a** was obtained as a dense yellow oil in 32% yield (0.131 mg). Found (%): C, 64.22; H, 6.16; N, 13.35. $C_{11}H_{12}N_2O_2$. Calculated (%): C, 64.69; H, 5.92; N, 13.72. ^{1}H NMR, δ: 3.79 and 3.84 (both s, 6 H, 2 MeO); 6.40 (t, 1 H, CH pyraz.); 6.84 (dd, 1 H, CH arom.); 7.10 (d, 1 H, CH arom.); 7.30 (d, 1 H, CH arom.); 7.60 and 8.15 (both d, 2 H, CH pyraz.).

2-(3,5-Dimethoxypyrazol-1-yl)-1,4-dimethoxybenzene (1b). After the treatment of the reaction mixture (see Table 2, entry *10*), compound **1b** was obtained in 43% yield (201 mg) using a similar procedure. The product was a dense yellow oil and slowly crystallized on staying. Found (%): C, 67.23; H, 6.90; N, 12.12. $C_{13}H_{16}N_2O_2$. Calculated (%): C, 67.22; H, 6.94; N, 12.06. The ^{1}H NMR spectrum of compound **1b** was analogous to that described previously.[1]

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