Arenium cation as the key intermediate of the electrosynthesis of *N*-(2,5-dimethoxyphenyl)azoles. A new approach to the synthesis of *N*-(dimethoxyphenyl)azoles

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Data on the effect of the acid-base properties of the medium on the yield and composition of the products of *N*-dimethoxyphenylation of azoles (pyrazole, triazole, their substituted derivatives, and tetrazole) upon galvanostatic electrolysis of azole—1,4-dimethoxybenzene mixtures in nucleophilic (MeOH) and neutral (MeCN) media were considered and the trends of this process were discussed. The generation of arenium cations (1,4-dimethoxy-1-azolylbenzenium in MeCN and 1,1,4-trimethoxybenzenium in MeOH) as the key intermediates of electrosynthesis of *N*-(dimethoxyphenyl)azoles, was proved experimentally. A new approach to the synthesis of *N*-(dimethoxyphenyl)azoles through electrosynthesis of 1,1,4,4-tetramethoxycyclohexa-2,5-diene by electrooxidation of 1,4-dimethoxybenzene in MeOH as the first step and the reaction of this quinone diketal with azoles as the second step was suggested. The efficiency of this route to *N*-(dimethoxyphenyl)azoles is comparable with the efficiency of the purely electrochemical one-step process.

Key words: 1,4-dimethoxybenzene, azoles, electrooxidation, *N*-(2,5-dimethoxyphenyl)azoles, arenium cation, 1,1,4,4-tetramethoxycyclohexa-2,5-diene.

N-Arylazoles represent a promising class of biologically active compounds possessing a broad spectrum of practical applications.[1] Meanwhile, the synthesis of these compounds has certain limitations, as nitrogen heterocycles are poorly suited to the use as partners for conventional arylating reagents.[2] This stimulated us to initiate the search for new, in particular, electrochemical approaches to the synthesis of *N*-arylazoles. Recently,[3—6] on the basis of the results of galvanostatic electrolysis of an azole—1,4-dimethoxybenzene (DMB) mixture in MeCN in an undivided cell, a probable mechanism for *N*-dimethoxyphenylation of azoles has been proposed (Scheme 1).

According to the drawn conclusions,[4—6] radical cation **1´** formed upon DMB oxidation can alternatively (steps **1´** → **2** or **1´** → **3**) react with a nucleophile represented here by the nonionized azole existing in solution as hydrogen-bonded Az—H·B complexes[5,6] (B is a base, which may be represented by most basic azoles or *sym*-collidine (CL) molecules added to the solution for electrolysis). In terms of the pK_a^{II} values (Table 1) characterizing the susceptibility of azoles (AzH) to protonation, they all were divided[4—6] into strongly and weakly basic ones. Although this classification is obviously arbitrary, this made it possible to relate the composition of the final reaction mixtures to the acid-base properties of initial azoles and thus to describe systematically the results of electrolysis.

Table 1. Azoles and their pK_a values (see Ref. 7)

Azole	pK_a^{I}	pK_a^{II}
Highly basic azoles		
3,5-Dimethylpyrazole (DMP)	15.0	4.1
Pyrazole (P)	14.2	2.5
1,2,4-Triazole (TA)	10.0	2.5
Lowly basic azoles		
3,5-Dimethyl-4-nitropyrazole (DMNP)	10.1	−0.5
4-Nitropyrazole (NP)	9.7	−2.0
3-Nitro-1,2,4-triazole (NTA)	6.0	−3.7
Tetrazole (T)	4.9	−2.7

Note. The pK_a^{I} and pK_a^{II} values correspond to the equilibria $Az^- + H^+ \rightleftharpoons AzH$ и $AzH + H^+ \rightleftharpoons AzH_2^+$, respectively.

The cathodic process includes deprotonation of the starting azoles and, partially, of onium compounds, resulting from the reaction of azoles or CL type bases with the protons generated in the anodic transformations of the reactants.

An important item of the process mechanism (see Scheme 1) is related to the hypothesis[5,6] of the presence

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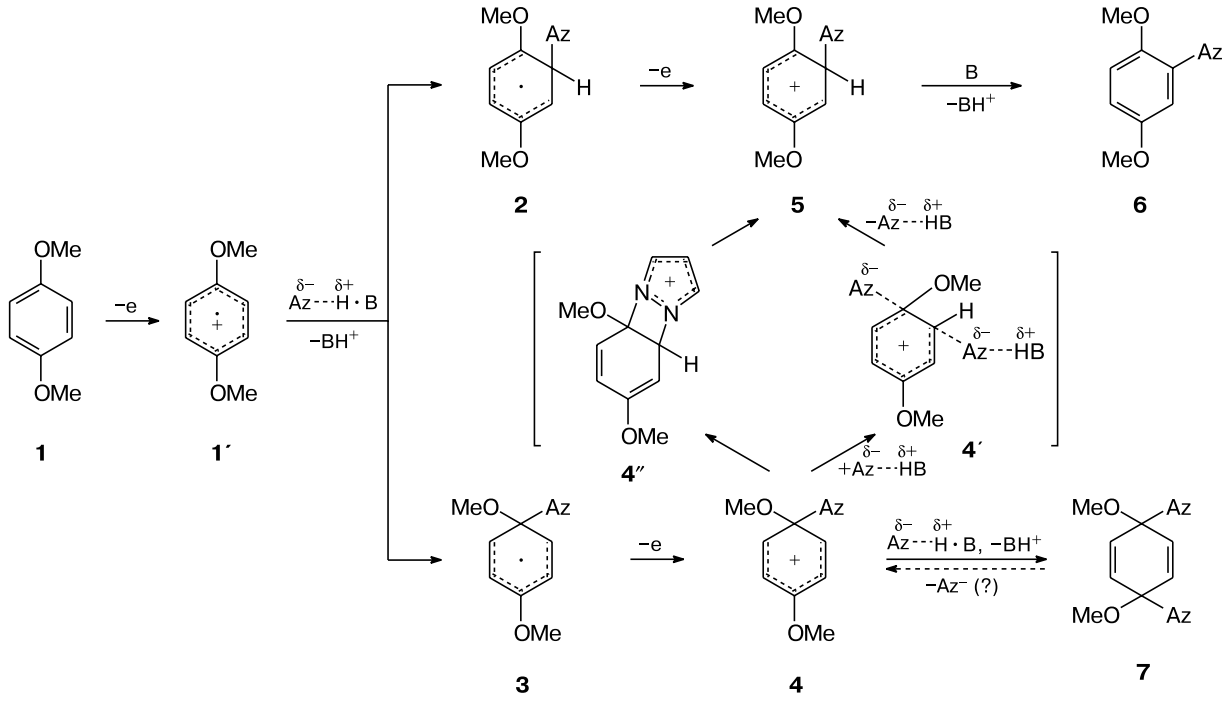
Scheme 1



B = AzH, collidine

of a rearrangement of arenium cations **4** → **5**. This was assumed to occur for strongly basic azoles as intramolecular β-alkylation through transition state **4″**, whereas for weakly basic azoles incapable of such transformation, this occurs as intermolecular interaction through the transition state **4′** by the *cine*-substitution mechanism.

Apart from the *ortho*-substitution products of type **6**, the final reaction mixture contained *ipso*-bis-addition products **7**; the yield of products **6** increased continuously during the electrolysis, while the yield of products **7** passed through a maximum. According to the available data,[5,6] this is due to the fact that product **7** is converted during electrolysis into **6** along the path **7** → **4** → **5** → **6**. Note that in this case, the step **4** → **7** (see Scheme 1) should be reversible, although the driving force of the back reaction (**7** → **4**) has remained obscure, together with the reasons for dependence of the yield and ratio of products **6** and **7** on the acid-base properties of the initial azoles and the medium.[4–6]

Therefore, this work aims at the development of the views on *N*-dimethoxyphenylation of azoles and experimental substantiation of the steps involving the arenium cation as the key intermediate of the process. It should be emphasized that some of these issues have already been addressed in the study of electrochemical *N*-dimethoxyphenylation in MeOH.[8] Therefore, here we compare the results of azole *N*-dimethoxyphenylation in MeCN and MeOH.

The study was performed with azoles (see Table 1) selected out of those studied previously[4–6] (for convenient comparison of the results).

Results and Discussion

As noted above, the transformations **7** → **4** → **5** → **6** (see Scheme 1) take place during the electrochemical *N*-dimethoxyphenylation of azoles only in the case where the step **4** → **7** is reversible. To substantiate this conclusion, it is pertinent to consider data on the influence of the acid-base properties of the medium on the ratio of products **6** and **7** in the reaction medium. It can be seen from the data presented in Table 2 that in the electrolysis involving pyrazole (P), the addition of CL as a base to the initial reaction mixture sharply increases the yield of the *ipso*-bis-addition product **7**. Conversely, the AcOH additives decrease the yield of this product and simultaneously increase the yield of the *ortho*-substituted product **6**. The addition of stronger chloroacetic acid gives only product **6**. A similar effect has been described previously[3] for electrolysis involving DMP*.

This result is quite surprising: generally, the addition of acids should induce protonation of any species that

* Here and below, in substantiation of the conclusions of this work, apart from the newly obtained results, we used some experimental data obtained previously[3–5] and interpreted them from a new standpoint.

Table 2. Effect of acid and base additives on the yield and composition of the products of electrolysis of an azole—DMB mixture[a]

Entry	Azole	pK_a^I (pK_a^{II})	Additive	Current yield[b] (%)	
				6	**7**
1	P	14.2	—	3	28
2	P	(2.5)	CL	<2	38
3	P		AcOH	13	17
4	P		$ClCH_2COOH$	25	—
5	DMP[c]	15	—	28	30
6	DMP[c]	(4.06)	CL	15	42
7	DMP[c]		AcOH	38	14
8	DMP[c]		$ClCH_2COOH$	63	—
9	NP[c]	9.64	—	<2	—
10	NP[c]	(−2.0)	CL	4	52
11	T[c]	4.9	—	4	—
12	T[c]	(−2.68)	CL	50	29

[a] Reactant ratio: 1.5 moles of azole, 1 mol of DMB, 0.5 mole of the additive. Conditions of electrolysis: Pt electrodes, MeCN, I = 50 mA, Q = 2 F per mole of DMB, 0.022 M Bu_4NClO_4 supporting solution.

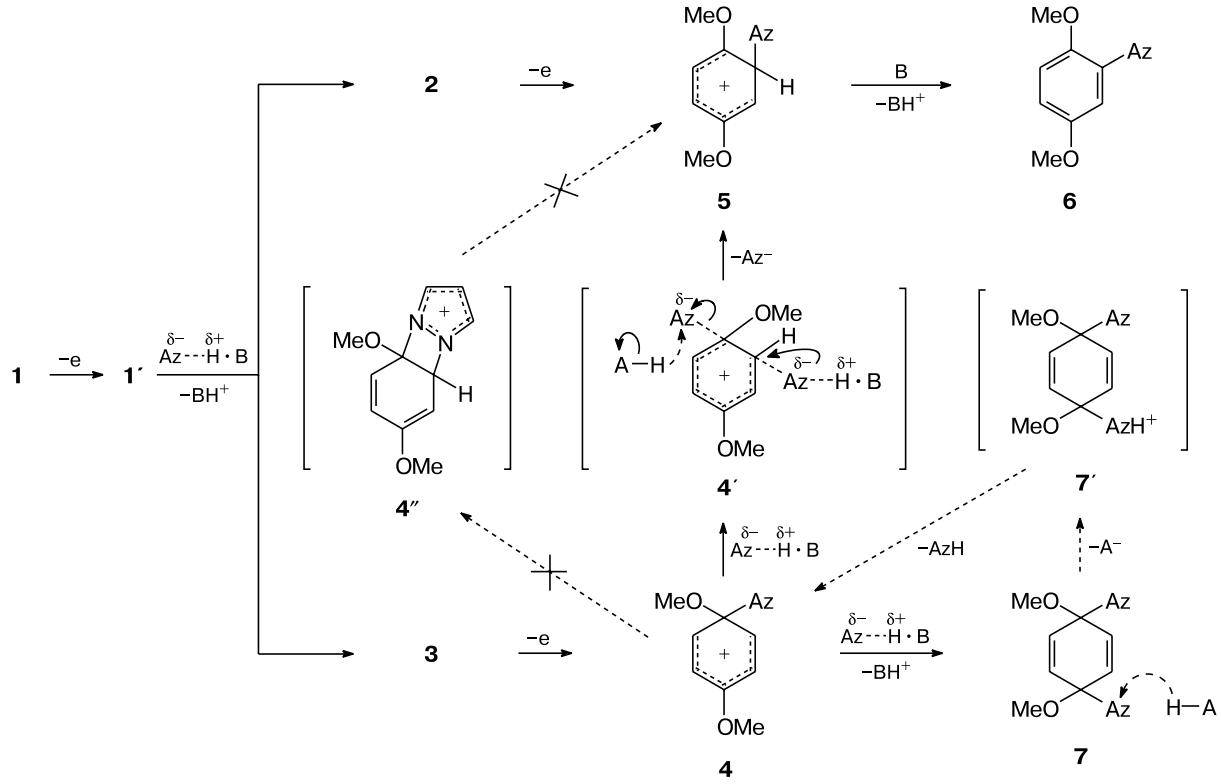
[b] Under the experiment conditions, the material and current yields coincide.

[c] See Refs 3—5.

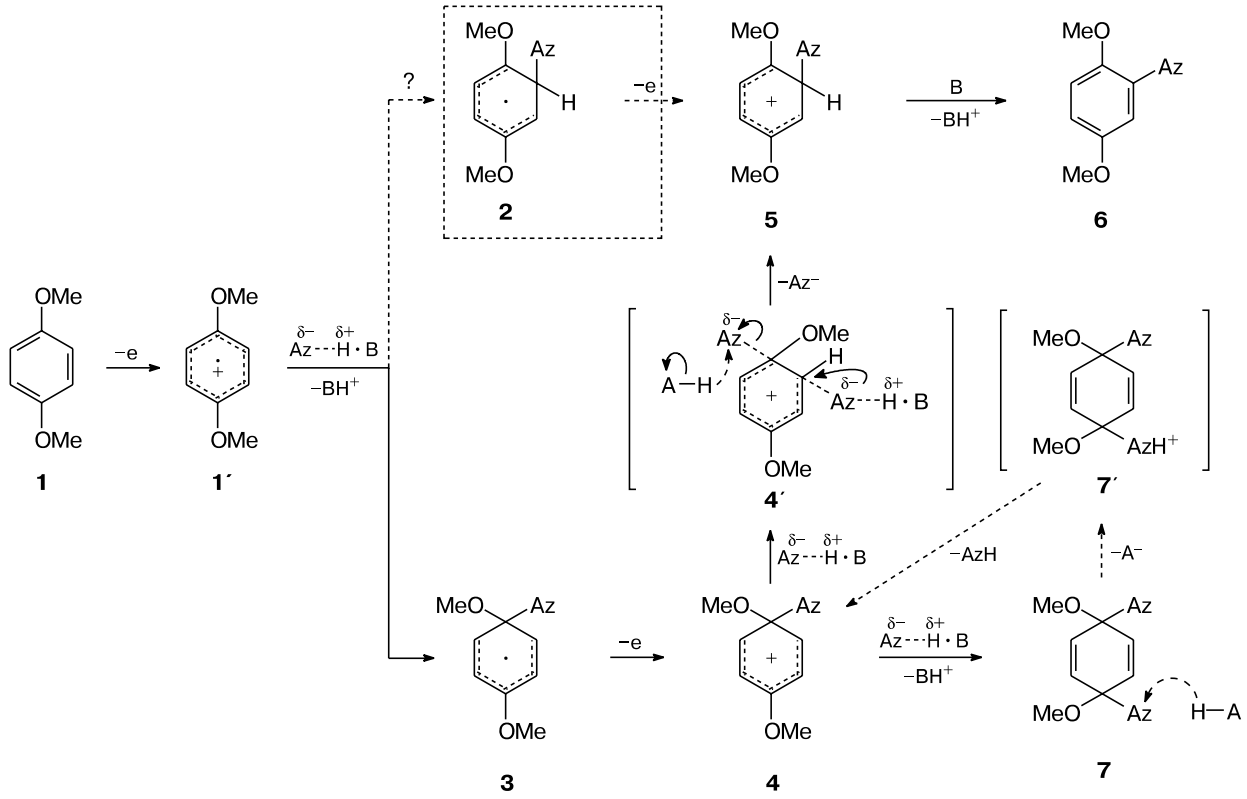
exhibit nucleophilic properties and, consequently, retard the process. This was actually the case when a considerable excess of an acid with respect to the azole was added; however, this was not the case with a considerably deficient amount (see Table 2). In our opinion, the effect observed upon the addition of acids into the mixture for electrolysis is attributable to the electrophilic assistance from the acid molecule A—H to the elimination of the azole fragment from the product molecule **7**, thus promoting steps **7** → **7′** → **4** (Scheme 2). As a result, transformation **4** → **7** becomes reversible and, as a consequence, the yield of **6** in the electrolysis products grows and the yield of **7** drops (see Table 2). The CL additive as a base induces the opposite effect as it makes the step **4** → **7** fully irreversible thus increasing the yield of product **7**.

It is important that the composition of the final reaction mixture depends also on the acid-base properties of azoles. This is well illustrated by the results of earlier studies. A mixture of products **7** and **6** obtained by electrolysis involving T is easily converted into product **6** during separation or even storage.[5] Conversely, the partial transformation of the products **7** → **6** formed upon electrolysis involving the least acidic DMP requires not only addition of an acid but also heating of the reaction mixture.[4]

Scheme 2



Scheme 3



Data presented in Table 2 can serve as yet another example; it can be seen that electrolysis of a mixture of DMB with strongly basic azoles gives products **6** and **7** and the CL additives do not affect much their yield (*cf.* entries *5* and *6*). Conversely, electrolysis of a mixture of DMB and weakly basic azoles gives almost no *N*-arylation products whose formation requires the addition of CL to the mixture for electrolysis (see Table 2; *cf.* entries *9* and *10*, *11* and *12*). These results indicate, most likely, that most acidic azoles can also serve as the acid A—H to catalyze the back transformation **7** → **4**. Most efficient in this respect is T, *i.e.*, the most acidic azole, which explains, in particular, an increased (as compared with NP) content of product **6** in the final reaction mixture (see Table 2; *cf.* entries *10* and *12*).

While developing these views, one can easily conclude that the acid components A—H of the reaction mixture catalyze also the *cine*-substitution **4** → **5** through electrophilic assistance to the elimination of the azole function from the *ipso*-position of intermediate **4′** (see Scheme 2). Therefore, the views on the **4** → **5** rearrangement pathways of arenium cations were corrected. We refuted the conclusions drawn earlier[4–6] stating that the **4** → **5** rearrangement of strongly basic azoles proceeds through intermediates **4″** * (see Scheme 2) and arrived at the conclusion that this rearrangement for both strongly and weakly basic azoles can occur irreversibly as a *cine*-substitution (Scheme 3).

The foregoing leads to the conclusion concerning the crucial role of acid catalysis in the mechanism of azole *N*-dimethoxyphenylation. In addition, it follows from these data that the competing *ortho*- and *ipso*-reactions of the arenium cation **4** with the azole nucleophile are the key stages of the mechanism. Whereas the former reaction is reversible due to electrophilic assistance of the A—H acid components of the reaction mixture to the elimination of the azole residue from the *ipso*-position of intermediate **7′**, the latter reaction, which follows a *cine*-substitution mechanism, is irreversible, the more so, in view of the relatively fast deprotonation of cation **5** to give the final product (see Scheme 3, **5** → **6**).

The presence of two reaction pathways for the intermediate arenium cation (**5** ← **4** → **7**) leads to the conclusion that during electrolysis, the target product **6** can be

* The acid additives for the electrolysis involving strongly basic azoles are expected to hamper the formation of a cyclic transition state. However, this is not the case; conversely, the yield of product **6** increases in the presence of acids (see Table 2).

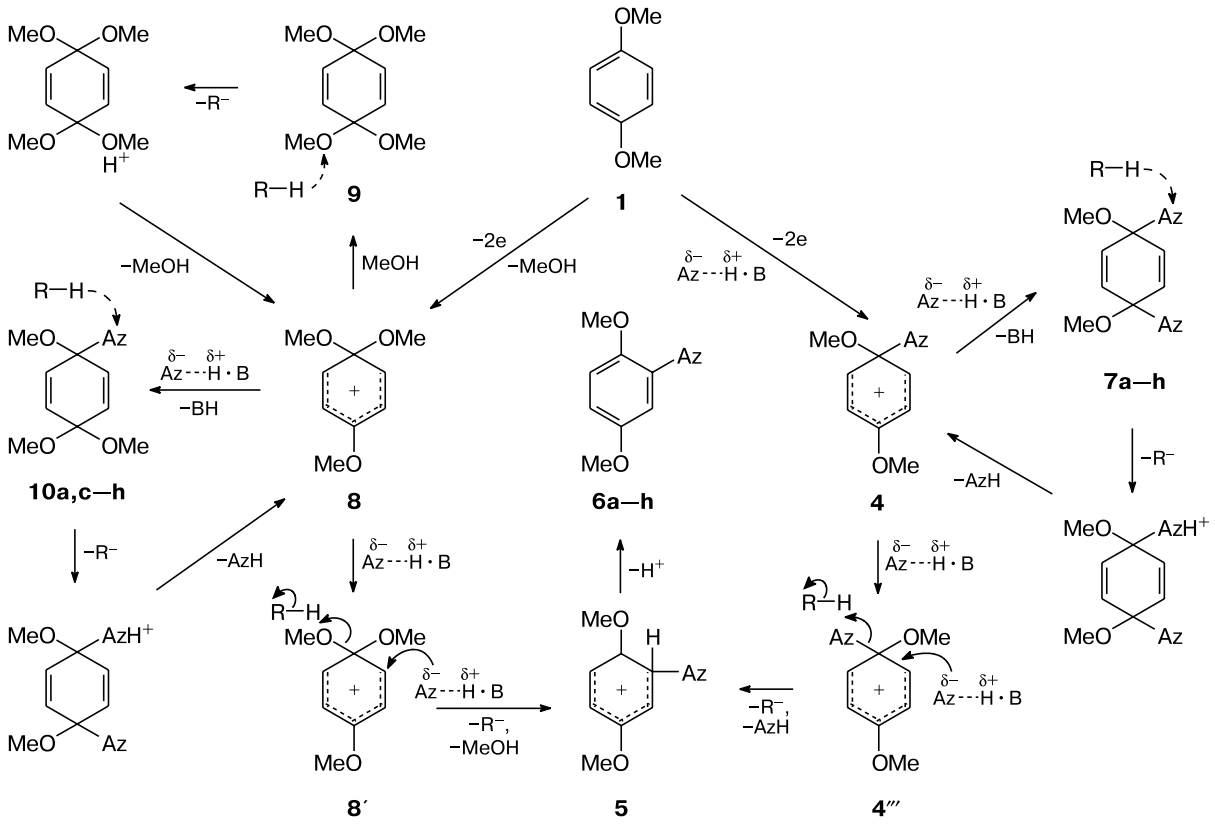
formed either through the sequence **1** → **1′** → **3** → **4** → → **5** → **6** or through the sequence **1** → **1′** → **3** → **4** → **7** → → **4** → **5** → **6**. Either of the pathways includes the irreversible transformation of arenium cations **4** → **5**; thus, the initially formed *ipso*-bisaddition **7** product can be gradually converted during electrolysis to **6**, because the step **4** → **7** is reversible (see above).

All the foregoing casts doubt on the practicability of obtaining product **6** along the route **1′** → **2** → **5** → **6** (see Scheme 3) involving impracticable step **1′** → **2**,[4,5] the more so, because it is impossible to obtain **7** as the second product by this route. In our opinion, in most cases, steps **1′** → **2** → **5** → **6** can be neglected when describing the mechanism of electrosynthesis of *N*-(dimethoxyphenyl)azoles.

These conclusions are in good agreement with azole *N*-dimethoxyphenylation data in MeOH,[8] which, however, has specific features due to the simultaneous presence of two competing nucleophiles, namely, MeOH molecules and azoles, in the reaction mixture. This affected the structure of the intermediate arenium cation, which was 1,1,4-trimethoxyarenium **8** (Scheme 4), instead of 1-(azol-1-yl)-1,4-dimethoxyarenium **4**, and the structures of the *ipso*-substitution products: instead of 1,4-di(azol-1-yl)-1,4-dimethoxycyclohexa-2,5-dienes **7**, the reaction gave 1,1,4,4-tetramethoxycyclohexa-2,5-diene (**9**) and 1-(azol-1-yl)-1,1,4-trimethoxycyclohexa-2,5-dienes **10**.

Generally, taking into account the above results and resorting to published data,[8] *N*-dimethoxyphenylation of azoles in neutral (MeCN) and nucleophilic (MeOH) media can be described by Scheme 4. It can be seen that both in neutral and nucleophilic media, the competing *ortho*- and *ipso*-reactions of arenium cations **4** and **8** with the azole nucleophile are the key steps of the process and make the crucial contribution to the formation of the *ortho*-substitution product **6**. For example, it follows from the available results[8] that the higher the acidity of the reaction mixture that undergoes electrolysis, the higher the content of *ipso*-bisaddition **10** and *ortho*-substitution **6** products in the final solution and the lower the content of the *ipso*-bisaddition product **9**. Conversely, electrolysis

Scheme 4



6, **7**, **10:** Az = 3,5-dimethylpyrazol-1-yl (**a**), pyrazol-1-yl (**b**), 1,2,4-triazol-1-yl (**c**), 4-nitropyrazol-1-yl (**d**), 3,5-dimethyl-4-nitropyrazol-1-yl (**e**), 3-nitro-1,2,4-triazol-1-yl (**f**), tetrazol-1-yl (**g**), tetrazol-2-yl (**h**)

involving strongly basic DMP and P unable to perform acid catalysis results in a predominant content of product **9** in the reaction mixture.[8]

Thus, acid catalysis plays an important role in the electrochemical *N*-dimethoxyphenylation of azoles both in MeCN (see above) and in MeOH by providing (see Scheme 4) electrophilic assistance to elimination of the azole residue from products **7** and **10**, the methoxy group from product **9** and, which is equally important, the methoxy group from intermediate **8´**.

In conformity with the drawn conclusions,[8] we believe that in the electrolysis of the azole—DMB mixture, the role of the acid catalyst can be played by not only acids specially added to the reaction mixture or most acidic azoles but also by the onium species formed upon the reactions of azoles with the protons generated during the anodic reactions.

The above general trends of electrochemical *N*-dimethoxyphenylation of azoles (see Scheme 4) are presented based on the view of generation of arenium cations (**4**, **8**) as the key intermediates, which undergo various, in particular, acid-catalyzed transformations along the way to the target products. The proposed mechanism (see Scheme 4) may be validated by obtaining independent experimental evidence for generation of arenium cations **4** and **8**.

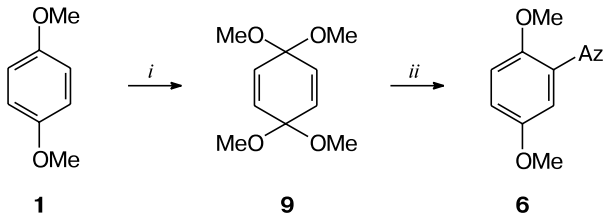
Meanwhile, such evidence can be gained from characteristic features of this process mechanism (see Scheme 4). It can be seen that, except for the early steps (**1** → **4** or **1** → **8**), all other steps are purely chemical. This means that if the proposed steps (including the generation of arenium cations **4** and **8**) are correct, then having removed the electrochemical steps, we gain the possibility of purely chemical synthesis of target product **6** from quinone bisketal **9** through steps **9** → **8** → **5** → **6** and from *ipso*-bisaddition products **10** (**7**) through steps **10** (**7**) → **8** (**4**) → **5** → **6**.

Note that we have already carried out experiments of this type without perception. As noted above, upon electrolysis with T, the mixture of final products **7** and **6** is readily converted into product **6** during storage.[5] A similar conversion of components **7** and **6** of the reaction mixture obtained after electrolysis involving the least acidic DMP (see Table 1) required[4] not only AcOH additives but also heating for several hours, *i.e.*, more rigorous conditions. Thus it follows that azoles behave as better (T) or poorer (DMP) leaving groups depending on their structure. These results alone point to the feasibility of the purely chemical transformation **7** → **4** → **5** → **6**, thus confirming the generation of arenium cation **4**.

Analogous conclusions can be drawn from the results of an experiment described in our publication.[8] Heating of the reaction mixture formed after electrolysis of an azole—DMB mixture in MeOH, which contained products **6**, **9**, and **10**, always caused a decrease in the contents (down to zero) of *ipso*-bisaddition **9** and **10** products with a simultaneous increase in the *ortho*-substituted product **6**. It is quite obvious that temperature rise facilitates the acid-catalyzed elimination of the methoxy and azole groups from structures **8´**, **9**, **10** (see Scheme 4). Therefore, it can be concluded that in MeOH, as in MeCN, the electrochemical (see Scheme 4) and purely chemical processes comprise the same steps **9** (**10**) → **8** → **5** → **6**.

The above-noted possibility of chemical transformation of tetramethoxycyclohexadiene **9**, which is more readily available than products **7** and **10**, into the target *ortho*-substituted product **6** creates prerequisite for the preparation of arylazoles *via* a two-step synthesis (Scheme 5).

Scheme 5



1 **9** **6**

i. Electrochemical step, MeOH, −2 e, −2 H^+;
ii. Chemical step, AzH.

The method comprises electrooxidation of 1,4-dimethoxybenzene in MeOH by a known procedure[9] to give quinone diketal **9** (yield 70%) as the first step and purely chemical reaction of diketal **9** with azoles to give product **6** as the second step.

The reaction of quinone diketal **9** with azoles was carried out by fusing the reactants together for 5 h at 110 °C, if necessary, with basic (CL) or acidic (AcOH) additives to the reaction mixture. If the final reaction mixture contained the *ipso*-addition products, it was heated for additional 5 h at 110 °C. The results are summarized in Table 3.

The possibility of implementing this process has been already shown in our previous work:[10] fusion together of bisketal **9** with 3-nitro-1,2,4-triazole (or tetrazole) induces irreversible reaction between them, resulting in 1,4-dimethoxy-2-(3-nitro-1,2,4-triazol-1-yl)benzene (a mixture of isomeric 1,4-dimethoxy-2-(tetrazol-1-yl)- and 1,4-dimethoxy-2-(tetrazol-2-yl)benzens).

However, our experiments on two-step synthesis of *N*-(dimethoxyphenyl)azoles (see Table 3) showed that, on the one hand, the product composition and yield depend on the structure of the azole and, on the other hand, they depend on the acid-base properties of the medium. For example, fusion of strongly basic DMP with bisketal **9** does not result in the formation of any products, only the addition of AcOH and heating of the reaction mixture

Table 3. Yields of the products of chemical reaction of azoles with quinone diketal **9**[a]

Entry	Azole	pK_a^I (pK_a^{II})	Additive[b]	Yield[c] (%)			
				6	**7**	**10**	**11**[d]
1	DMP	15	—	—	—	—	—
2	DMP	(4.1)	AcOH	72	—	—	—
3	Imid-azole	14.4 (7.0)	AcOH	—	—	—	—
4	P	14.2	—	—	58	37	—
5[e]	P	(2.5)	—	32	—	—	—
6	P		AcOH	65	—	—	—
7	TA	10	—	4	12	56	—
8	TA	(2.5)	AcOH	70	—	—	—
9	DMNP	10.1	—	33	—	—	36
10	DMNP	(−0.5)	CL	—	—	—	—
11	DMNP		AcOH	12	—	—	33
12	NP	9.7	—	44	—	—	44
13	NP	(−2.0)	CL	4	28	47	—
14[e]	NP		—	11	44	15	—
15	NP		AcOH	37	—	—	—
16	NTA	6.0	CL	69	—	28	—
17[e]	NTA	(−3.7)	CL	90	—	—	—
18	T	4.9	—	66	—	—	20
19	T	(−2.7)	CL	52	—	13	—

[a] Fusion for 5 h at 110 °C of a solid **9**—azole mixture in a 1 mmol : 1.5 mmol ratio.
[b] 0.5 mmol.
[c] In relation to bisketal **9**.
[d] 1,2,4-Trimethoxybenzene.
[e] Additional heating for 5 h at 110 °C.

once again initiate the efficient reaction between the components to yield the *ortho*-substitution product **6** (see Table 3, *cf.* entries *1* and *2*). Less basic P or TA do react with bisketal **9** on fusion, giving rise to products **7** and **10**, although almost no *ortho*-substitution products **6** are present (see Table 3, entries *4* and *7*). The AcOH additives change crucially the situation, compound **6** becoming the major reaction product (see Table 3, entries *6* and *8*). The whole set of these results attests unambiguously to an important role of acid catalysis in the mechanisms of both purely electrochemical and the two-step methods for the synthesis of *N*-(dimethoxyphenyl)azoles.

Unlike strongly basic azoles (DMP, P, and TA), more acidic, weakly basic azoles (DMNP, NP, NTA, and T) not only act as nucleophiles but also perform acid catalysis (electrophilic assistance to demethoxylation of quinone diketal **9**). Fusion of these azoles with bisketal **9** gives predominantly the corresponding *ortho*-substitution products **6** (see Table 3, entries *9*, *12*, and *18*); an additional heating of the reaction mixture also gives only products **6** (see Table 3, footnote *d*).

Thus, the *ipso*-addition products can be detected in reactions with such azoles only when the experiments are carried out with CL additives, which decrease the acid

Table 4. Yields of *ortho*-substitution product **6** (in relation to the DMB taken) in one-step and two-step syntheses

Azole	Yield (%)	
	One-step method[a]	Two-step method[b]
DMP	57	50
P	18	46
TA	10	50
NP	0	31
NTA	18	48
T	52	46

[a] The maximum yields obtained with the azole—DMB—additive (CL or AcOH) composition of choice (see Refs 3—5).
[b] Overall yield with allowance for the 70% yield of product **9** in the first step.

catalytic properties of weakly basic azoles (see Table 3, entries *13*, *16*, and *19*). In addition, DMNP, which resembles most closely in properties (see Table 3) strongly basic azoles, is absolutely unable to perform acid catalysis in the presence of CL additives. This arrests the reaction of quinone diketal **9** with DMNP; hence, none of the desired products is formed (see Table 3, entry *10*).

Generally, the reaction of quinone diketal **9** with azoles requires rather fine tuning of reaction conditions: the medium should be sufficiently acidic (to enable acid catalysis) but not too much to avoid complete suppression of the nucleophilic properties of azoles. This is well illustrated by the data presented in Table 3. For example, in the presence of AcOH, the nucleophilic properties of DMNP and NP decrease and, as a consequence, the yield of products **6** decreases (see Table 3, *cf.* entries *9* and *11*; *12* and *15*).

Generally, the results attest to obvious similarity of the mechanisms of the chemical step of the two-step synthesis of *N*-(dimethoxyphenyl)azoles to the mechanism of the one-step electrosynthesis presented in Scheme 4. In our opinion, this attests unambiguously to intermediate generation of arenium cations **8** or **4**.

The results of one-step and two-step syntheses are compared in Table 4.

An interesting feature of the two-step synthesis is the fact that in some cases, the reaction products were found to contain 1,2,4-trimethoxybenzene (**11**). Its absence in the final reaction mixtures in our previous experiments[4—6] can be attributed to the presence of three electron-donating substituents and, as a consequence, low oxidation potential of **11**. Therefore, compound **11** completely burned-out during galvanostatic electrolysis to give resinous products.* This accounts for the rather low current yields of *N*-(dimethoxyphenyl)azoles upon their electro-

* When somewhat higher current density is used, pronounced resinification takes place even during electrolysis involving DMP.

synthesis,[4—6] because most of electricity was consumed for the oxidation of trimethoxybenzene **11**.

A special place in the series of studied azoles is occupied by imidazole, which is similar to DMP in acidity and is much more basic than DMP (see Table 3). However, the heterocyclic nucleus of this compound does not contain two adjacent nitrogen atoms (no α-effect); therefore, imidazole has relatively low nucleophilcity, which is too low for efficient interaction with quinone diketal **9** to give desired products (see Table 3, entry *3*).

Experimental

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

The tetramethylammonium salt of NTA was synthesized by a known procedure.[9] Commercial DMB, DMP, T, TA, P, NTA, NP, and DMNP were used (Lancaster, 98—99% purity).

One-step electrosynthesis. Electrochemical experiments (see Table 2) were carried out by a reported procedure[3—5] according to which DMB (2 mmol) was subjected to galvanostatic electrolysis (I = 50 mA) in MeCN in a 50-mL undivided cell with Pt-electrodes in the presence of azole (3 mmol) by passing 2 F of electricity per mole of DMB (see Tables 2, 4). A 0.022 M solution of Bu_4NClO_4 was used as the supporting electrolyte; if necessary, acids (0.5 mmol) (AcOH, $ClCH_2COOH$) or bases (CL) were added. After completion of the electrolysis, the solvent was distilled off on a rotary evaporator at ~20 °C (25—30 Torr) and the residue was analyzed by ^{1}H NMR. The yields of electrolysis products were determined in relation to the two-electron transformation of the taken DMB by comparison of the integral intensities of the unambiguously identified and, most often, singlet signals of the products (azole and aromatic CH protons, MeO-group protons) and the signals from the tetrabutylammonium cation of the supporting salt with a known concentration (CH_2 and Me group protons). The spectroscopic characteristics of the compounds are given below.

Two-step synthesis. At the first step, bisketal **9** was prepared by galvanostatic electrolysis of DMB in MeOH by a reported procedure[6] using an undivided cell with Pt electrodes. The yield of bisketal **9** was 70%. At the second step, compound **9** (1 mmol) reacted with azole (1.5 mmol). In some cases (see Table 2), CL or AcOH additives (0.5 mmol) were used. The reactant mixture prepared in the above-indicated proportion was heated in a drying oven at 110 °C. After heating for 5 h (or 10 h if necessary), the reaction mixture was analyzed by ^{1}H NMR. The yield of the products (in relation to taken bisketal **9**) was determined by comparing the integral intensities of the unambiguously identified signals in the ^{1}H NMR spectra of products with the total integral intensity of the CH protons of the azole groups (detailed procedure was described previously[4]).

The spectroscopic (^{1}H NMR) characteristics used for identification and determined percentages of compounds **6**, **7**, **9**, and **10** in reaction mixtures are presented below.

2-(3,5-Dimethylpyrazol-1-yl)-1,4-dimethoxybenzene (6a). ^{1}H NMR, δ: 2.14, 2.20 (both s, 6 H, Me); 3.70, 3.78 (both s, 6 H, MeO); 5.90 (s, 1 H, azole CH); 6.80—7.07 (m, 3 H, CH arom.).

1,4-Dimethoxy-2-(pyrazol-1-yl)benzene (6b). ^{1}H NMR, δ: 3.79, 3.84 (both s, 6 H, MeO); 6.40 (t, 1 H, azole CH , J = 9.1 Hz); 6.84 (dd, 1 H, CH arom., J_1 = 3.1 Hz, J_2 = 10.0 Hz); 7.10, 7.30 (both d, 1 H each, CH arom., J = 3.1 Hz); 7.60, 8.15 (both d, 1 H each, azole CH , J = 9.1 Hz).

1,4-Dimethoxy-2-(1,2,4-triazol-1-yl)benzene (6c). ^{1}H NMR, δ: 3.80, 3.90 (both s, 6 H, MeO); 6.94—7.35 (m, 3 H, C_6H_3); 8.04, 8.85 (both s, 2 H, $C_2H_2N_3$).

1,4-Dimethoxy-2-(4-nitropyrazol-1-yl)benzene (6d). ^{1}H NMR, δ: 3.79, 3.91 (both s, 6 H, MeO); 7.04—7.20, 7.31 (both m, 3 H, CH arom.); 8.03, 9.02 (both s, 2 H, azole CH).

2-(3,5-Dimethyl-4-nitropyrazol-1-yl)-1,4-dimethoxybenzene (6e). ^{1}H NMR, δ: 2.36, 2.48 (both s, 6 H, Me); 3.78, 3.85 (both s, 6 H, MeO); 6.70—7.20 (m, 3 H, CH arom.).

Compounds **6f** and **6g** (as a mixture with **6h**) were isolated from the reaction mixture according to procedures given below.

1,4-Dimethoxy-2-(3-nitro-1,2,4-triazol-1-yl)benzene (6f). The reaction mixture obtained after heating of bisketal **5**, NTA, and CL (10 h, 110 °C) was dissolved in ethanol (5 mL) and mixed with a 2 M aqueous solution of NaOH (15 mL). After crystallization of the separated oil in a refrigerator, the precipitate was filtered off, washed with water (3×10 mL), dried on a watch glass (2 h, 110 °C), and triturated with hexane. Drying in air gave 205 mg (82%) of compound **6f**, m.p. 118 °C. Found (%): C, 48.10; H, 3.99; N, 22.50. $C_{10}H_{10}N_4O_4$. Calculated (%): C, 48.00; H, 4.03; N, 22.39. ^{1}H NMR, δ: 3.82, 3.92 (both s, 6 H, MeO); 7.05—7.30 (m, 3 H, C_6H_3); 9.13 (s, 1 H, $C_2HN_4O_2$).

1,4-Dimethoxy-2-(tetrazol-1-yl)benzene (6g) and **1,4-dimethoxy-2-(tetrazol-2-yl)benzene (6h)** (isomer mixture, 3 : 2). A mixture of bisketal **5**, T, and CL prepared in the same proportions as described above was converted, after heating in a drying oven (10 h, 110 °C) and a workup similar to that described above, into 120 mg (58%) of a **6g** + **6h** mixture, m.p. 65 °C. ^{1}H NMR, δ: 3.76—3.89 (4 s, 6 H, MeO); 7.05—7.32 (m, 3 H, C_6H_3); 8.96, 9.59 (both s, 1 H, CHN_4).

1,4-Dimethoxy-1,4-di(pyrazol-1-yl)cyclohexa-2,5-diene (7b) (isomer mixture). ^{1}H NMR, δ: 3.13, 3.20 (both s, 6 H, MeO); 6.53, 6.64 (both s, 4 H, CH arom.); 6.27, 6.33, 7.44, 7.93 (all m, 2 H each, azole CH).

1,4-Dimethoxy-1,4-di(1,2,4-triazol-1-yl)cyclohexa-2,5-diene (7c) (isomer mixture). ^{1}H NMR, δ: 3.20, 3.30 (both s, 6 H, MeO); 6.59, 6.70 (both s, 4 H, CH arom.); 7.88, 7.92, 8.61, 8.72 (all s, 4 H, azole CH).

1,4-Dimethoxy-1,4-di(4-nitropyrazol-1-yl)cyclohexa-2,5-diene (7d) (isomer mixture). ^{1}H NMR, δ: 3.28, 3.33 (both s, 6 H, MeO); 6.60, 6.73 (both s, 4 H, CH arom.); 8.11, 8.17, 8.94, 9.00 (all s, 4 H, azole CH).

1,1,4,4-Tetramethoxycyclohexa-2,5-diene (9). ^{1}H NMR, δ: 3.20 (s, 12 H, MeO); 6.00 (s, 4 H, CH arom.).

1,1,4-Trimethoxy-4-(pyrazol-1-yl)cyclohexa-2,5-diene (10b). ^{1}H NMR, δ: 3.20, 3.23, 3.31 (all s, 9 H, MeO); 6.18, 6.38 (both d, 4 H, CH arom., J = 12.5 Hz); 6.28 (m, 1 H, azole CH); 7.80 (d, 1 H, azole CH , J = 2.7 Hz); 7.90 (d, 1 H, azole CH, J = 4.5 Hz).

1,1,4-Trimethoxy-4-(1,2,4-triazol-1-yl)cyclohexa-2,5-diene (10c). ^{1}H NMR, δ: 3.20, 3.25, 3.30 (all s, 9 H, MeO); 6.25, 6.35 (both d, 4 H, CH arom., J = 12 Hz); 7.80, 8.52 (both s, 2 H, $C_2H_2N_3$).

1,1,4-Trimethoxy-4-(4-nitropyrazol-1-yl)cyclohexa-2,5-diene (10d). ^{1}H NMR, δ: 3.20, 3.23, 3.30 (all s, 9 H, MeO); 6.31 (br.s, 4 H, CH arom.); 8.10, 8.92 (both s, 2 H, $C_3H_2N_3O$).

1,1,4-Trimethoxy-4-(3-nitro-1,2,4,-triazol-1-yl)cyclohexa-2,5-diene (10f). ^{1}H NMR, δ: 3.20, 3.25, 3.60 (all s, 9 H, MeO); 5.07—6.16 (m, 4 H, CH arom.); 8.60 (s, 1 H, $C_2HN_4O_2$).

1,1,4-Trimethoxy-4-(tetrazol-1-yl)cyclohexa-2,5-diene (10g) and **1,1,4-trimethoxy-4-(tetrazol-2-yl)cyclohexa-2,5-diene (10h)** (isomer mixture 2 : 1). ^{1}H NMR, δ: 3.20—3.30, 3.60 (all br.s, 9 H, MeO); 4.97—6.15 (m, 4 H, CH arom.); 8.50, 8.84 (both s, 1 H, CHN_4).

1,2,4-Trimethoxybenzene (11). ^{1}H NMR, δ: 3.70—3.90 (three s, 9 H, MeO); 6.31 (dd, 1 H, CH arom., J = 6.1 Hz, J = 3.2 Hz); 6.45 (d, 1 H, H arom., J = 3.2 Hz); 6.73 (d, 1 H, CH arom., J = 6.1 Hz).

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