N-Arylation of azoles with low basicity by 1,4-dimethoxybenzene during undivided electrolysis

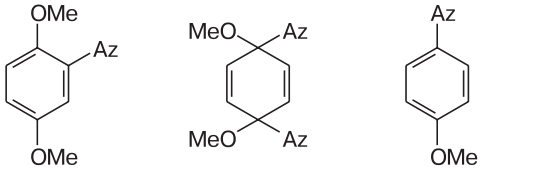
V. A. Chauzov, V. Z. Parchinskii, E. V. Sinel´shchikova, A. V. Burasov, B. I. Ugrak, N. N. Parfenov, and V. A. Petrosyan*

N. D. Zelinsky Institute of Organic Chemistry, Russian Academy of Sciences, 47 Leninsky prosp., 119991 Moscow, Russian Federation. Fax: +7 (095) 135 5328. E-mail: petros@ioc.ac.ru

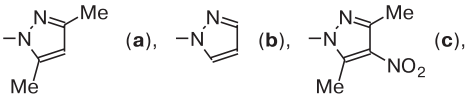
The reactions of 1,4-dimethoxybenzene with 4-nitropyrazole, 3,4-dinitro-5-methylpyrazole, 1,2,4-triazole, 3-nitro-1,2,4-triazole, and tetrazole were studied during undivided amperostatic electrolysis on a Pt electrode in MeCN, CH_2Cl_2, and MeOH. The main reaction products were 2-azolyl-1,4-dimethoxybenzenes and (or) 1,4-diazolyl-1,4-dimethoxycyclohexa-2,5-dienes. In all cases except 1,2,4-triazole, *N*-arylation occurs only in the presence of the Alk_4N^+ salts of azoles or 2,4,6-trimethylpyridine as a base. The mechanism of the reactions is discussed.

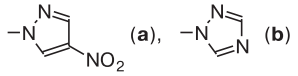
Key words: paired electrosynthesis, *N*-arylation, azoles, azole anions, 1,4-dimethoxybenzene.

The reactions of 1,4-dimethoxybenzene (DMB) with various azoles (pyrazoles, triazoles, and tetrazole) under amperostatic undivided electrolysis on Pt electrodes in MeCN and Alk_4N^+ salts of azoles or Bu_4NClO_4 as a supporting electrolyte afford[1—4] *ortho*-substitution products **1**, *ipso*-bisaddition products **2**, and, in some cases, *ipso*-substitution products **3**. We have established[1,2] for the first time the formation of bisadducts **2** among electrolysis products and the possibility of using azoles or their combination with 2,4,6-trimethylpyridine (*symm*-collidine, CL) instead of the corresponding anions in the starting reaction mixture.



1a—h **2a—d,f—h** **3a,b**

1, 2: Az =  (**a**), (**b**), (**c**), (**d**), (**e**), (**f**), (**g**), (**h**)

3: Az =  (**a**), (**b**)

It has recently been found[2] that the regularities which determine the yield and ratio of products **1** and **2** for 3,5-dimethylpyrazole (DMP), pyrazole (Pyr), and 3,5-dimethyl-4-nitropyrazole (DMNP) depend on the nature of the solvent (MeCN or CH_2Cl_2), basicity of the medium, and amount of the electricity passed and can be described by the stages presented in Scheme 1.

According to this scheme, the reaction of the H-bonded AzH·B azole complex (B = AzH, CL) with the DMB radical cation **4** affords intermediates **5** and **6**, which undergo further oxidation. The key stage determining the ratio of products **1** and **2** in the case of DMP and Pyr is the intramolecular rearrangement of the 1-azolyl-1,4-dimethoxyarenonium cation (**7**) to the 1-azolyl-2,5-dimethoxyarenonium cation (**8**). In this case, the cathodic process is related to the deprotonation of onium intermediates BH^+ formed during electrolysis.

In development of these works, we studied the regularities of *N*-arylation in systems containing DMB and relatively less basic and more acidic (compared to DMP and Pyr) azoles (Table 1), *viz.*, 4-nitropyrazole (NP), 3,4-dinitro-5-methylpyrazole (DNMP), 3-nitro-1,2,4-triazole (NTA), tetrazole (T), and 1,2,4-triazole (TA). The latter is similar in basicity to Pyr* but its acidity is

* The high basicity of TA is a result of the protonation of the N(4) atom rather than N(2) as in pyrazoles.[5] The accepted classification of azoles to compounds with high and low basicity is conventional and reflects the specific features of their electrochemical *N*-arylation.

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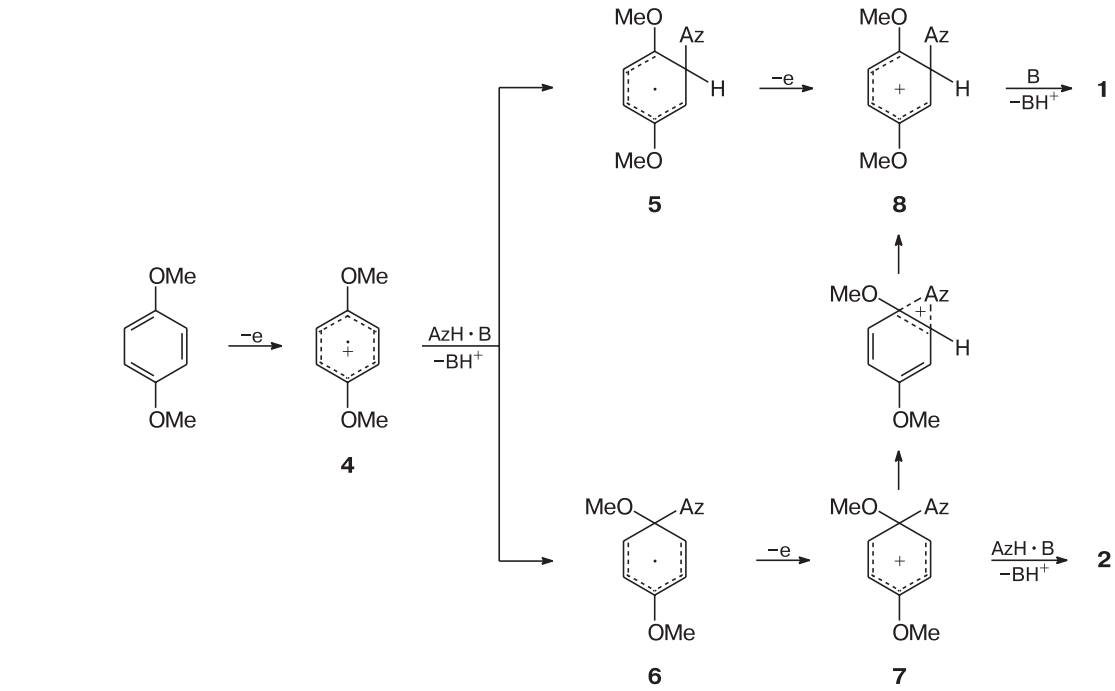
Scheme 1



B is AzH, CL

much higher and close to that of NP. In order to examine the composition of the electrolysis products, as in the previous studies,[1,2] we widely used NMR spectroscopic monitoring, which allowed us to detect hydrolytically labile compounds **2** in the final reaction mixture.

Results and Discussion

An undivided electrolysis. The results presented below for the electrolysis of systems containing DMB and low-basic azoles are compared with those for DMP, Pyr, and DMNP obtained by us previously[2] (Table 2).

Table 1. The pK_a values of some azoles[5] and collidine

Azole[a]	pK_a		Azole[a]	pK_a	
	I[b]	II[c]		I[b]	II[c]
DMP	15	4.06	TA	10.04	2.45
Pyr	14.21	2.48	NTA	5.98	−3.65
DMNP	10.65	−0.45	T	4.90	−2.68
NP	9.64	−2.00	Imidazole	14.4	6.99
DNMP	—[d]	—	CL	—	7.43

[a] DMP is 3,5-dimethylpyrazole, Pyr is pyrazole, DMNP is 3,5-dimethyl-4-nitropyrazole, NP is 4-nitropyrazole, DNMP is 3,4-dinitro-5-methylpyrazole, TA is 1,2,4-triazole, NTA is 3-nitro-1,2,4-triazole, T is tetrazole, CL is collidine.
[b] Azole under study.
[c] Conjugate acid.
[d] The pK_a value is unknown but evidently close to pK_a of 3,4-dinitropyrazole (5.48).

The general comparison of the results of electrolysis for the highly basic azoles (DMP, Pyr, TA) and azoles with low basicity (DMNP, NP, NTA, DNMP, and T) indicates that in the absence of basic additives the *N*-arylation of azoles of the latter group occurs very limply, and the formation of minor (in most cases, <2%) amounts of substitution products **1** is probably determined by the arylation of the azole anions formed by the direct deprotonation[6] of the azoles on the Pt cathode (see Table 2, *cf.* entries *7*, *9*, *17*, *33* and *1*, *20*, *22*) rather than to the direct arylation of the azoles (as in the case of DMP, Pyr, and TA). In turn, the addition of CL to the electrolyte slightly affects the change in the total current efficiency (CE) of *N*-arylation products **1** and **2** for the first group of azoles, while in the case of low-basic azoles, when CL or the Alk_4N^+ salts of azoles are added, the total CE of compounds **1** and **2** multiply increases (see Table 2, *cf.* entries *2*, *21*, *23* and *8*, *10*, *15*, *34*, *35*).

A change in the electrolysis conditions has different effects on the ratio of products **1** and **2** for azoles with low and high basicity. This is illustrated by the results of *N*-arylation of DMP and NP. For example, in the electrolysis with DMP, an increase in the basicity of the medium due to the addition of CL favors the formation of **2a** and hinders the formation of **1a**, and an increase in the acidity of the medium (the addition of AcOH) has an

opposite effect. By contrast, in the electrolysis with NP, an increase in the basicity of the medium upon replacement of CL by the NP salt (the basicity of CL is lower than that of the NP anion, see Table 1) increases the CE of product **1d**, decreases the CE of **2d**, and leads to the *ipso*-substitution product **3a** (see Table 2, *cf*. entries *10*, *15*, and *16*). The addition of AcOH to a mixture of NP and CL results, evidently, in the protonation of the latter, decreases the nucleophilicity of the NP complex with CL, and thus hinders *N*-arylation (see Table 2, *cf*. entries *10* and *12*).

In turn, in the electrolysis with DMP by passing 2 F electricity at the DMP : DMB = 0.5 molar ratio or with CH_2Cl_2 as a solvent instead of MeCN, **1a** is formed predominantly, while in the electrolysis with NP under similar conditions only a decrease in the CE of product **2d** was observed (see Table 2, *cf*. entries *1* and *4*, *5* and *6*, *10* and *12*, and *13* and *14*).

The results obtained in the electrolysis with NTA are similar on the whole to those for NP, namely, compounds **1g** and **2g** are formed in low CE in the presence of CL, and if CL is replaced by the NTA salt, their total CE noticeably increases, primarily due to product **1g** (see Table 2, entries *31* and *32*). It is of interest that in the case of DNMP, the only *N*-arylation product is **1e**, whose CE are the same for electrolysis in the presence

Table 2. Yields of products of the electrochemical *N*-arylation of azoles by 1,4-dimethoxybenzene (DMB) as functions of the electrolysis conditions[a] (results of the known works[2,3] necessary for comparison are included)

Entry	Azole[b]	Azole : DMB (mol) (amount of electricity per mole of DMB/F)	Solvent	Additive[c] (moles per mole of DMB)	Current efficiencies of products (%)	
					1	**2**
1	DMP[2]	1.5 (2)	MeCN	—	28	30
2	DMP[2]	1.5 (1)	MeCN	CL (0.5)	15	42
3	DMP[2]	1.5 (2)	MeCN	AcOH (1.5)	38	14
4	DMP[2]	1.5 (2)	CH_2C_l	—	45	—
5	DMP[2]	1.5 (2)	MeCN	—	35	—
6	DMP[2]	0.5 (1)	MeCN	—	22	19
7	DMNP[2]	1.5 (2)	MeCN	—	10	—
8	DMNP[2]	1.5 (2)	MeCN	CL (0.5)	<2	24
9	NP	1.5 (2)	MeCN	—	<2	—
10	NP	1.5 (2)	MeCN	CL (0.5)	4	52
11	NP	1.5 (2)	CH_2Cl_2	CL (0.5)	—	10
12	NP	1.5 (2)	MeCN	CL (0.5) AcOH (0.5)	<2	—
13	NP	0.5 (2)	MeCN	CL (0.5)	—	13
14	NP	0.5 (1)	MeCN	CL (0.5)	—	22
15	NP	1.0 (2)	MeCN	—	10 [d,e]	29
16	NP	1.25 (2)	MeCN	—	8 [f]	43
17	DNMP	1.5 (2)	MeCN	—	<2	—
18	DNMP	1.5 (2)	MeCN	CL (0.5)	6	—
19	DNMP	1.0 (2)	MeCN	—	6 [g]	—
20	Pyr[2]	1.5 (2)	MeCN	—	<2	23
21	Pyr[2]	1.5 (2)	MeCN	CL (0.5)	<2	38
22	TA	1.5 (2)	MeCN	—	7	40
23	TA	1.5 (2)	MeCN	CL (0.5)	2	56
24	Pyr[2]	1.5 (2)	MeCN	AcOH (1.5)	13	17
25	Pyr[2]	1.5 (2)	CH_2Cl_2	—	40	—
26	TA	1.5 (2)	MeCN	AcOH (1.5)	8	33
27	TA	1.5 (2)	CH_2Cl_2	—	—	7
28	Pyr[2]	0.5 (2)	MeCN	—	—	<2
29	TA	0.5 (2)	MeCN	—	— [h]	—
30	TA	0.5 (2)	MeCN	—	—	19
31	NTA	1.5 (2)	MeCN	CL (0.5)	3	10
32	NTA	1.0 (2)	MeCN	—	28 [i]	18
33	T	1.5 (2)	MeCN	—	4 [j]	—
34	T[3]	1.0 (2)	MeCN	—	88 [j,k]	—

(*to be continued*)

Table 2 (*continued*)

Entry	Azole[b]	Azole : DMB (mol) (amount of electricity per mole of DMB/F)	Solvent	Additive[c] (moles per mole of DMB)	Current efficiencies of products (%)	
					1	**2**
35	T	1.5 (2)	MeCN	CL (0.5)	50[j]	29[j]
36	T	1.5 (2)	CH_2Cl_2	CL (0.5)	52[j]	21[k]
37	T	0.5 (2)	MeCN	CL (0.5)	15[j]	—
38	T	0.5 (2)	MeCN	CL (0.5)	7[l]	—
39	DMP**2**	1.5 (2)	MeOH	—	9[m]	—
40	T	1.5 (2)	MeOH	CL (0.5)	20[j,n], 52[j,o]	—
41	T	1.5 (2)	MeOH	CL (0.5)	5[j,p], 30[j,o,p,q]	—
42	NTA	1.5 (2)	MeOH	CL (0.5)	5[r], 18[o]	—
43	DNMP	1.5 (2)	MeOH	CL (0.5)	3[s], 16[o]	—
44	NP	1.5 (2)	MeOH	CL (0.5)	—[t,u], 7[o]	7
45	TA	1.5 (2)	MeOH	CL (0.5)	<2[v], 10[o]	11

[a] Electrolysis was carried out *vs*. an 0.022 *M* solution of Bu_4NClO_4 (0.5 moles per mole of DMB).
[b] DMP is 3,5-dimethylpyrazole, DMNP is 3,5-dimethyl-4-nitropyrazole, NP is 4-nitropyrazole, DNMP is 3,4-dinitro-5-methylpyrazole, Pyr is pyrazole, TA is 1,2,4-triazole, and NTA is 3-nitro-1,2,4-triazole, and T is tetrazole.
[c] CL is collidine.
[d] Me_4N^+ salt of NP (0.5 moles per mole of DMB) was used instead of Bu_4NClO_4.
[e] The reaction mixture contains 1-(4-methoxyphenyl)-4-nitropyrazole (**3a**), 8% yield.
[f] Me_4N^+ salt of NP (0.25 moles per mole of DMB) was used instead of Bu_4NClO_4, the yield of compound **3a** being 4%.
[g] Bu_4N^+ salt of DNMP (0.5 moles per mole of DMB) was used instead of Bu_4NClO_4.
[h] The yield of 1-(4-methoxyphenyl)-1,2,4-triazole (**3b**) was 12%.
[i] Me_4N^+ salt of NTA (0.5 moles per mole of DMB) was used instead of Bu_4NClO_4.
[j] A mixture of the *N*-isomers.
[k] Bu_4N^+ salt of T (0.5 moles per mole of DMB) was used instead of Bu_4NClO_4.
[l] One *N*-isomer.
[m] The yield of 1,1,4,4-tetramethoxycyclohexa-2,5-diene (**12**) was 52%.
[n] A mixture of the *N*-isomers of 1,1,4-trimethoxy-4-tetrazolylcyclohexa-2,5-diene (**10h**) is also formed (38% yield).
[o] After additional heating (5 h, 110 °C).
[p] Tetrazole was added to the reaction mixture after the end of electrolysis before MeOH was distilled off (70 °C, 20 Torr, 30 min).
[q] A mixture of the isomers of **10h** is also formed (43% yield).
[r] After the solvent was distilled off (70 °C, 20 Torr, 30 min), the yield of 1,1,4-trimethoxy-4-(3-nitrotriazol-1-yl)cyclohexa-2,5-diene (**10g**) was 13%.
[s] After the solvent was distilled off (70 °C, 20 Torr, 30 min), the yield of 1,1,4-trimethoxy-4-(5-methyl-3,4-dinitropyrazol-1-yl)cyclohexa-2,5-diene (**10e**) was 13%.
[t] After the solvent was removed (20 °C), the yield of **12** was 12% and the yield of 1,1,4-trimethoxy-4-(4-nitropyrazol-1-yl)cyclohexa-2,5-diene (**10d**) was 3%.
[u] After the solvent was distilled off (70 °C, 20 Torr, 30 min), the yield of **12** 6% and the yield of **10d** was 11%.
[v] After the solvent was removed (20 °C) or distilled off (70 °C, 20 Torr, 30 min), the yield of **12** was 21% and the yield of 1,1,4-trimethoxy-4-(1,2,4-triazol-1-yl)cyclohexa-2,5-diene (**10f**) was 38%.

of both CL and DNMP salt (see Table 2, *cf*. entries *18* and *19*).

The results of *N*-arylation of T is noteworthy in that the CE of **1h** (forms as a mixture of two *N*-isomers in a ratio of ~3 : 2) is very high and the overall CE of the *N*-arylation product reaches 90% in most cases. This noticeably exceeds the CE of the *N*-arylation products not only for the low-basic azoles but even for the most reactive highly basic DMP (see Table 2, *cf*. entries *1*, *2* and *34*, *35*). What is also unusual in this case is that the obtained mixture of *N*-isomers of **1h** and **2h** is transformed into an almost pure mixture of *N*-isomers of **1h** after brief heating (in particular, during distillation of the solvent). Perhaps, it is for this reason that the relative concentration of **2h** can differ substantially (not the total CE of **1h** and **2h**) in parallel experiments. With CH_2Cl_2 as the solvent, the total yield of **1h** and **2h** and their ratio remain virtually unchanged, and electrolysis with an excess of DMB affords a mixture of *N*-isomers of **1h** in low yields (see Table 2, entries *36* and *37*). The latter fact and the predominant consumption of one of the isomers at the final stages of electrolysis (see Table 2, entry *38*), as in the case of Pyr and TA, indicate, most likely, the easiness of electrooxidation of product **1h**. The distinction in behavior of DMP and T during electrolysis in MeOH is of interest. In the case of DMP,

compound **1a** is formed in a low CE (9%), and the main reaction product is the oxidative *ipso*-bismethoxylation product of DMB, *viz.*, 1,1,4,4-tetramethoxycyclohexa-2,5-diene, in 52% CE (see Table 2, entry *39*),[2] whereas in the case of T we obtained a mixture of *N*-isomers (~2 : 1) of **1h** (20% CE) and 1,1,4-trimethoxy-4-tetrazolylcyclohexa-2,5-diene (38% CE) (see Table 2, entry *40*). The formation of products of this type, *viz.*, ketal derivatives of *para*-quinone, upon *N*-arylation in MeOH was observed for other azoles with low basicity as well (see Table 2, entries *42—45*). Since these results are important for understanding the mechanisms of formation of products **1** and **2**, the corresponding experimental data will be considered below together with the discussion of these problems.

The electrochemical behavior of TA resembles in part that of Pyr with similar basicity. During electrolysis with Bu_4NClO_4 as the supporting electrolyte, TA efficiently reacts with DMB in the absence of basic additives to form product **2f** predominantly, and the CE of the latter, as in the case of Pyr, increases when CL is added (see Table 2, entries *20—23*). However, the conditions favoring the formation of product **1** in the case of DMP and Pyr (the addition of AcOH or electrolysis in CH_2Cl_2) do not afford the desired result in the electrolysis with TA (see Table 2, entries *24—27*). In turn, electrolysis with an excess of DMB (TA : DMB = 0.5), which also affords predominantly **1** in the case of DMP, is accompanied here by the formation of *ipso*-substitution product **3b*** (see Table 2, *cf.* entries *5*, *28*, and *29*) rather than **1f**. However, it is of note that it is the *ipso*-bisaddition product **2f** that is presumably the precursor of **3b**, because only **2f** was found in the reaction mixture when a halved amount of electricity (1 F) was passed (see Table 2, entry *30*). As for the absence or a low content of **1f** among the reaction products in all experiments with TA, this is reasoned, most probably, by its easy electrooxidation, as in the case of **1b** during *N*-arylation of Pyr.[2]

Thus, a whole series of distinctions, which follows from a comparison of the data of *N*-arylation of azoles with high and low basicity, needs Scheme 1 presented above to be refined. This will allow the correct description of the regularities of *N*-arylation of the last-mentioned azoles.

Electrolysis in a divided cell. The previously established[2] *N*-arylation of such a highly basic azole as DMP during electrolysis in the anodic compartment of a divided cell confirmed unambiguously the possibility of direct reaction of the nonionized form of DMP with radical cation **4** (see Scheme 1). This procedure, which allows the elucidation of the object of the electrophilic attack by **4**, can also be useful for azoles with low basicity (NP, NTA), whose electrolysis in the presence of CL differs from that in the presence of the salt of the corresponding azole. By the way, this fact indicated that NP and NTA form complexes with CL but remain in the nonionized form. The corresponding experiment was performed for NP, and the conditions of entry *10* were chosen as model with the only distinction that the double amount of CL was used to prevent the deactivation of the pyrazole component of the reaction mixture (anodic electrolysis is accompanied by proton generation). In the qualitative respect, the results obtained are comparable with those of the experiment in the undivided cell, although the composition of the reaction products somewhat differed. This can be explained by the objective difference in experimental conditions. For example, electrolysis of the NP—DMB—CL system gave a mixture of **1d** и **2d** in 9 and 37% CE respectively (*cf.* entry *10* in Table 2). Note that only resin-like products are formed upon electrolysis of the NP—DMB system in the absence of CL in the anodic compartment of the divided cell. On the whole, our experiments additionally substantiate the hypothesis[1,2] about the involvement of the nonionized AzH • B complexes as nucleophilic coreactants in the electrochemical *N*-arylation of azoles.

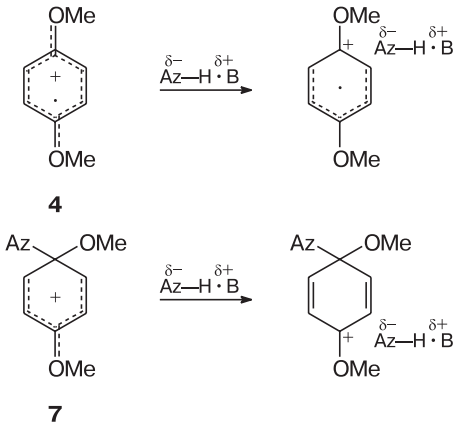
Regularities of *N*-arylation of azoles with low basicity. The above presented, often contradictory experimental results can be explained if we introduce several concepts concerning the stage of interaction of the azole nucleophile (see Scheme 1) with intermediates bearing a positive charge, such as radical cation **4** and arenonium cation **7**.

Based on the concept about the substantial difference in electrophilicity of the *ortho*- and *ipso*-positions of these intermediates, we believe that the involvement of the azole anion is preferential for *ortho*-substitution, whereas *ipso*-substitution can involve both the azole anion and a complex of nonionized azole. This point needs to be discussed in more detail. The presence of methoxy groups in intermediates **4** and **7** undoubtedly favor the localization of the positive charge mainly on the *ipso*-carbon atoms of the ring. For these reasons, the *ipso*-attack on ions **4** or **7** by the azole nucleophile requires relatively small energy expenses. This process occurs, evidently, even when these ions come close to the nonionized azole complex (dipole), as is shown in Scheme 2, and the more so when they approach to the azole anion.

By contrast, the *ortho*-attack in the interaction of intermediates **4** or **7** with a nucleophile needs the localization of the positive charge on one of the *ortho*-positions. This is associated with substantial polarization of these intermediates leading to the formation of an energetically less favorable structure. This structure is evidently formed with the lowest expenses when intermedi-

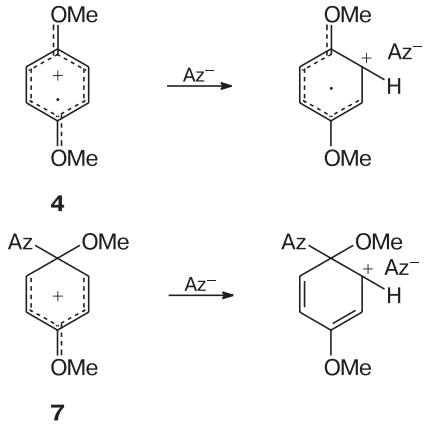
* The formation of *ipso*-substitution products **3a,b** will be discussed elsewhere.

Scheme 2



ates **4** or **7** approach to the anion, as is shown in Scheme 3, and its formation is much more difficult when they approach to a dipole (nonionized azole complex).

Scheme 3



Note, however, that this assumption explains only the specific feature of the *ortho*-attack of ions **4** and **7** because the "pantophagy" of their *ipso*-position should result in all cases in the formation of compounds **6**, **7**, and further **2** (see Scheme 1). This forced us to introduce the second concept about the irreversibility of the *ortho*-attack on **4** and **7** and reversibility (equilibrium character) of the *ipso*-attack. The lower the nucleophilicity and basicity of Az^- and the higher acidity of AzH, the higher the reversibility. In fact, this differentiates the nucleophilic attacks of the *ipso*- and *ortho*-positions, determining the former as the kinetically controlled and the latter as the thermodynamically controlled process. The data presented in the Section on undivided electrolysis and in Table 2 agree with both concepts. For example, in the case of NP and NTA, the use of the Alk_4N^+ salt of azole as the azole component instead of the AzH • CL complex results in the appearance (or an increase in the relative content) of **1** in the electrolysis products (see Table 2, *cf.* entries *10* and *15*, *31* and *32*).

At the same time, unlike the data of electrolysis involving the NP or NTA complexes with CL, in electrolysis with complexes of DNMP or T with CL the corresponding compounds **1e,h** are the main or even single products. The use of a DNMP—DNMP salt mixture gives the same result (see Table 2, *cf.* entries *18*, *19* and *34*, *35*). We believe that complexes of less acidic azoles (TA, NP, NTA) (see Table 1) with CL, like complexes of highly basic azoles,[2] are nonionized. In the case of more acidic azoles (DNMP, T), the Az—H bond in the Az—H • B complex is likely much more polar, up to the formation of the tight $Az^-H \cdot B^+$ ion pair. This conclusion can be favored to some extent by the fact that solutions of mixtures of DNMP or T with CL in MeCN exhibit higher electric conductivity than solutions of TA, NP, or NTA mixtures with CL in MeCN.* Of course, this cannot serve as the direct proof for the ionic structure of the DNMP and T complexes with CL but can indicate its rather easy ionization upon approaching to cationic intermediate **4** or **7**. In turn, the latter explains the differences in the experimental results mentioned above.

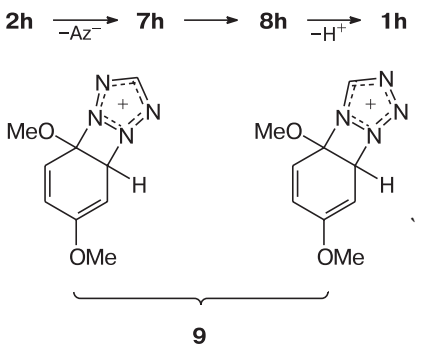
An increase in the acidity of the azoles upon introduction of nitro groups into the ring is accompanied by a decrease in their nucleophilicity due to a considerable shift of the electron density from the N atoms of the rings to the nitro groups. This manifests in a decrease in the total CE of products **1** and **2** on going, *e.g.*, from DMP to DMNP, from NP to DNMP, and from TA to NTA (see Table 2, *cf.* entries *1* and *7*, *10* and *18*, *23* and *31*). In turn, the high total current efficiencies of **1h** and **2h** (see Table 2, entries *34—36*) for the most acidic azole studied, T, evidently point to the unexpectedly high nucleophilicity of the corresponding anion. This is associated, most likely, with the specificity of delocalization of the negative charge in the latter, *viz.*, mainly on the contiguous N atoms, which are, on the whole, the object of the electrophilic attack (α-effect). Note that an increase in nucleophilicity caused by this type of effect predetermines, most likely, the possibility of involvement of triazoles and pyrazoles in the process considered. This conclusion can be confirmed by the experimental fact that imidazole, which is more basic than isomeric Pyr but does not contain contiguous N atoms (see Table 1), does not virtually react with DMB under

* This is indicated, for example, by the fact that during amperostatic electrolysis of a mixture of DNMP or T with CL the resistance of the cell is almost independent of the presence or the absence of a supporting electrolyte; however, it increases ~10-fold during electrolysis of mixtures of TA, NP, or NTA with CL in the absence of the supporting electrolyte.

conditions similar to those used in entries *20*, *21*, and *24* (see Table 2).

According to our data,[2] in the electrochemical *N*-arylation of DMP and Pyr, the rearrangement of the arenonium cations **7** → **8** makes a considerable contribution to the formation of **1** (see Scheme 1). However, such a rearrangement seems highly improbable for the low-basic azoles studied in this work. This follows, for example, from the fact that changes in the solvent and in the acidic-basic properties of the medium (see above) do not affect the yield and the ratio of the electrolysis products.[2] Nevertheless, the exceptional easiness of the transformation of a mixture of compounds **1h** и **2h**, which is formed upon electrolysis with T, into product **1h** after brief heating or even upon storage at ~20 °C can be explained only by the rearrangement **7h** → **8h** (Scheme 4).

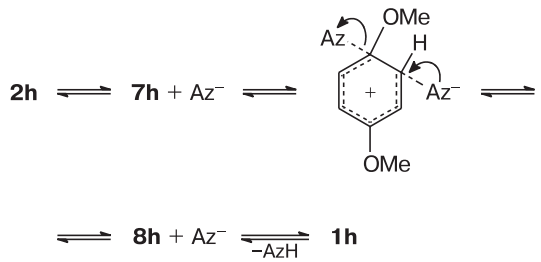
Scheme 4



Note. Here and in Schemes 5—7 Az is the tetrazole residue (a mixture of *N*-isomers).

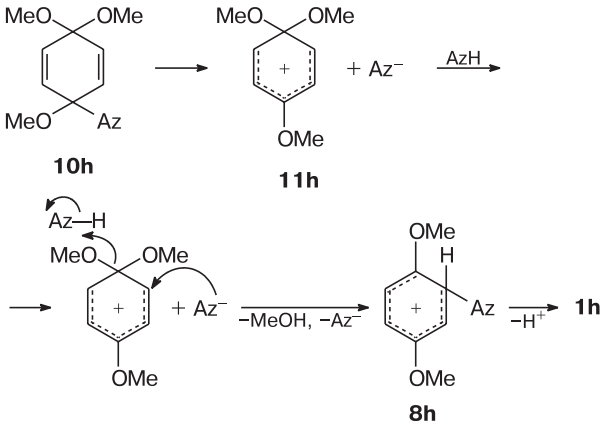
Earlier[2] we concluded that during electrolysis with highly basic azoles such a rearrangement occurs as the intramolecular *ortho*-arylation of the adjacent N atom in azole. However, in the case of T with very low basicity (see Table 1), the existence of the four-membered transition state **9** (see Scheme 4) casts some doubt. In fact, a similar rearrangement is not observed (see Table 2, entries *22*, *26*, and *27*) for electrolysis with TA, which is much more basic than T (see Table 1). For this reason, rearrangement **7h** → **8h** in the electrolysis with T occurs, most likely, in a different manner, for example, as an intermolecular *cine*-substitution (Scheme 5).

Scheme 5



The fact that one of the *N*-arylation products of T in MeOH (Scheme 6), *viz.*, 1,1,4-trimethoxy-4-tetrazolylcyclohexa-2,5-diene (**10h**) (see above), can also be transformed into **1h** but upon prolong heating (5 h, 110 °C) is an argument in favor of Scheme 5. The much more drastic conditions of this rearrangement as compared with the transformation **2h** → **1h** can be explained by the necessity to eliminate such a poorly leaving group as methoxyl in the stage of *cine*-substitution.

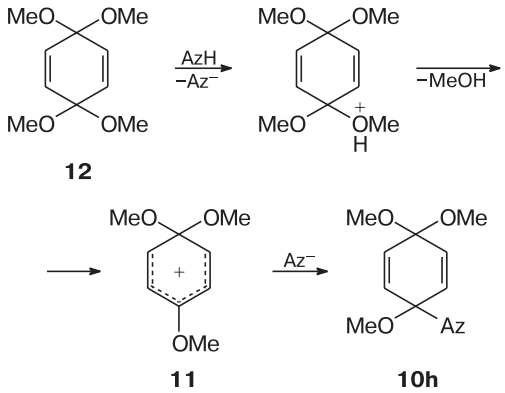
Scheme 6



The results of undivided electrolysis in MeOH provide a very helpful information for the understanding of the regularities of *N*-arylation of azoles. First, note that under these conditions the higher CE of product **1h** compared to that of product **1a** is evidently due to the higher nucleophilicity of the T•CL complex compared to that of the DMP•CL complex (see Table 2, *cf.* entries *39* and *40*). As for product **10**, its formation according to Scheme 1 could formally be explained by different selectivities of two consecutive *ipso*-reactions of intermediates **4** and **7** with the nucleophiles present in the solution (MeOH and T•CL complex). However, we managed to show that in this case yet another route of formation of compound **10h** is possible, and this route is not directly related to the electrochemically generated electrophilic intermediates. It is shown experimentally (see Table 2, entry *41*) that under mild conditions (30 min, 70 °C) the virtually quantitative and irreversible exchange interaction occurs between T and the product of electrochemical methoxylation of DMB, *viz.*, 1,1,4,4-tetramethoxycyclohexa-2,5-diene (**12**), to form compound **10h**. A possible route of this transformation includes the formation of cation **11** due to acid catalysis performed by T (Scheme 7). In this case, further heating of the reaction mixture also produces product **1h** according to Scheme 6.

Note that according to the published data[7] the transformation of cyclohexadiene **12** into *ortho*-substituted DMB derivatives under the action of nucleophilic reagents (alcohols, thiols, *etc.*) is catalyzed by H-acids or Lewis acids and often requires prolong heating.

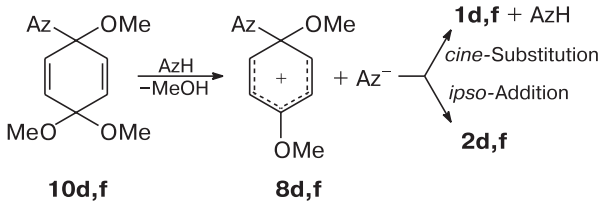
Scheme 7



The specific feature of this reaction is the use of the azole—CL (3 : 1) system, which provides both acid catalysis (AzH) and the presence of an efficient nucleophile (AzH • CL) even under mild conditions. In addition, the intermediate formation of the *ipso*-substitution product **10** has been established for the first time for similar processes. Thus, when the T—CL—DMB system is used in MeOH, not only compound **10h**, but also cyclohexadiene **12** can be the real primary product of the electrochemical reaction.

Electrolysis of the AzH—DMB—CL systems with DNMP and NTA in MeOH (see Table 2, entries *43* and *42*) is characterized by the same regularities. The main electrolysis products are compounds **10e,g** (CE 13% for each) and **1e,g** (CE 5 and 3%, respectively). As in the case of T, heating of the obtained reaction mixtures (5 h, 110 °C) results in the transformation of **10e,g** into **1e,g** in ~100% yield (see Table 2, entries *43* and *42*), which is in accord with Scheme 6. No diene **12** was formed in the cases considered (as in the electrolysis of T). Less acidic NP and TA behave in a different manner (see Table 1): the main electrolysis products are compounds **10d,f** (CE 3 and 38%) and **12** (CE 12 and 28%, respectively); the formation of product **1** was observed only in the case of TA (CE ~1% (**1d**)) (see Table 2, entries *44* and *45*). Changes in the composition of the reaction mixtures during distillation of the solvent (70 °C, 20 Torr, 30 min) are observed only for NP, namely, cyclohexadiene **12** is partially transformed by the azole into **10d** (CE 11%). Under more drastic conditions (5 h, 110 °C), similar transformations are observed in both cases, *viz.*, the formation of products **1d,f** (CE 7 and 10%, respectively) and **2d,f** (7 and 11%, respectively). According to the CE in the case of NP, the major part of diene **12** is primarily transformed by the azole into **10d** (see Scheme 7) and then into a mixture of **1d** и **2d**, while in the case of TA only product **10f** can likely undergo such a transformation. These results can be explained in terms of Scheme 8, which differs from Scheme 6 in the alternative formation of products **2d,f** due to both the insufficient nucleophilicity of the azole component for the exclusive *ortho*-(but not *ipso*-) attack and the relatively low acidity of NP and TA stabilizing compounds **10d,f** and **2d,f**.

Scheme 8



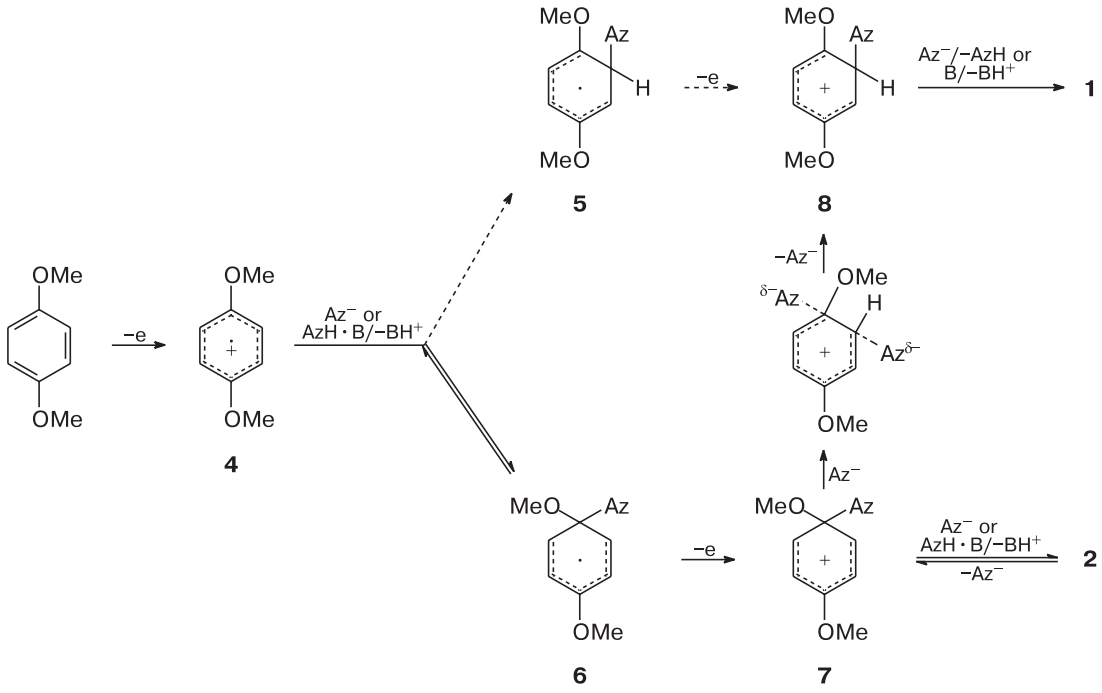
The results presented demonstrate first of all the specific features of electrochemical *N*-arylation of azoles with low basicity in MeOH, which affords solvolysis products **10** and **12**. Nevertheless, some of these results are very useful for the understanding of the general regularities of the process considered. For example, the transformations of **12** into **10** and then into **1** (see Schemes 6 and 7), which were experimentally confirmed for the most acidic azoles, are a serious argument in favor of the above assumptions about the reversibility of the *ipso*-attack of electrophilic intermediates **4** and **7** by the azole nucleophiles and the irreversibility of their *ortho*-attack. The fact that heating of compounds **10d,f** for the least polar NP and TA complexes with CL produces mixtures of **1d,f** and **2d,f** confirms, most likely, the second assumption about the preferential occurrence of the *ortho*-attack of cation **7** (and, probably, radical cation **4**) only in the presence of the azole anion or a sufficiently polar AzH • CL complex.

Thus, as applied to azoles with low basicity (acidic), Scheme 1 proposed by us previously for the electrochemical *N*-arylation of highly basic azoles by DMB should be refined taking into account the above assumptions (see Schemes 4—7) about the reversibility of some stages* and the possibility of the intermolecular mechanism of rearrangement of the arenonium ions **7** → **8** (Scheme 9).

To finish the discussion of the possible mechanisms of *N*-arylation of the azoles (see Schemes 1 and 9), we

* Note that the reversibility of these stages is also real for highly basic azoles when electrolysis is carried out in the presence of acids, *e.g.*, AcOH.[2]

Scheme 9



note that the assumption on the possibility of formation of *ortho*-arylation products **1** due to the intra- or intermolecular transformations **7** → **8** agrees completely with the experimental results. This transformation in the final stage of electrolysis allows us to believe (at least formally) that the stage commonly accepted for similar processes (methoxylation, cyanation, *etc.*), *viz.*, *ortho*-attack of radical cation **4** by a nucleophile, can be excluded. Moreover, the relatively high rate of the *ipso*-attack of arenionim cations **7** by the nucleophile compared to the *ortho*-attack observed in several cases assumes that the *ipso*-attack in the case of radical cation **4** followed by the fast oxidation of intermediate **6** (on the electrode or by ion **4** acting as a mediator) is also preferential. For these reasons, the stages of the *ortho*-attack of radical cation **4** with the formation of radical **5** followed by its subsequent oxidation are designated in Scheme 9 by dotted arrows as theoretically possible but presently having no necessary experimental substantiation.

Experimental

^{1}H 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.

Tetrabutylammonium perchlorate was prepared by the exchange reaction of the corresponding bromide with $NaClO_4$ followed by recrystallization from EtOH. Tetraalkylammonium salts of azoles were synthesized by a general procedure[3] using commercial DMB, TA, NTA, and T with 98—99% purity (Lancaster), and NP and DNMP were prepared according to a previously described procedure.[8] Acetonitrile was purified and dried by boiling with and distillation from $KMnO_4$ and double distillation from P_2O_5 followed by distillation from calcined K_2CO_3.

Amperostatic electrolysis of DMB (2 mmol) in 45 mL of reaction mixtures with different compositions was carried out under argon at the controlled current (I = 50 mA), passing 1 or 2 F electricity per mole of DMB (see Table 2). After termination of the electrolysis, the solvent was distilled off on a rotary evaporator at the temperature ≤70 °C (25—30 Torr), and the residue was analyzed by ^{1}H NMR. Electrolysis was performed under conditions similar to those described previously.[1] For spectroscopic characteristics used for identification of the series of compounds **1** and **2** and the procedure for the determination of the current efficiencies of **1** and **2** (calculated per two-electron transformation of DMB) without their isolation from a solution, see Ref. 1.

A porous glass diaphragm was used for electrolysis with divided cathodic and anodic compartments. The cell volume and surface areas of the Pt electrodes were approximately the same as those for undivided electrolysis.

The examples of experiments given below describe isolation of the target products, which corroborate the conclusions about their nature drawn from the spectroscopic data.

In entry *10* (see Table 2), the residue after distillation of the solvent (20—35 °C, 25 Torr) was triturated with ether and the ethereal extract was concentrated *in vacuo*. After chromatographic purification of the residue on silica gel using benzene as the eluent, **1,4-dimethoxy-1,4-di(4-nitropyrazol-1-yl)cyclohexa-2,5-diene (2d)** was obtained in 42% yield (220 mg) with m.p. 110 °C. Found (%): C, 46.40; H, 3.95; N, 23.12. $C_{14}H_{14}N_6O_6$. Calculated (%): C, 46.41; H, 3.89; N, 23.2. The

^{1}H NMR spectrum of cyclohexadiene **2d** was identical with that described previously.[1]

Compounds **1e,g** were obtained analogously (see Table 2, entries *18* and *32*).

1,4-Dimethoxy-2-(5-methyl-3,4-dinitropyrazol-1-yl)benzene (1e). The yield was 20 mg (4%). Found (%): C, 46.60; H, 3.90; N, 18.10. $C_{12}H_{12}N_4O_6$. Calculated (%): C, 46.76; H, 3.92; N, 18.18. ^{1}H NMR, δ: 2.60 (s, 3 H, Me); 3.80, 3.83 (both s, 3 H, 2 MeO); 7.04—7.17 (m, 3 H, C_6H_3).

1,4-Dimethoxy-2-(3-nitro-1,2,4-triazol-1-yl)benzene (1g). The yield was 95 mg (19%), 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, 3 H, 2 MeO); 7.05—7.30 (m, 3 H, C_6H_3); 9.13 (s, 1 H, $C_2HN_4O_2$).

The spectroscopic (^{1}H NMR) characteristics of compounds used for the identification and determination of their content in reaction mixtures are presented below.

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

1,4-Dimethoxy-2-(tetrazol-1 and -2-yl)benzenes (1h) (mixture of *N*-isomers, 3 : 2). ^{1}H NMR, δ: 3.76—3.89 (four s, 6 H, 2 MeO); 7.05—7.32 (m, 3 H, C_6H_3); 8.96, 9.59 (both s, 1 H, CHN(4)) (*cf.* Ref. 3).

1,4-Dimethoxy-1,4-di(tetrazol-1- and -2-yl)cyclohexa-2,5-dienes (2h) (mixture of mainly two isomers, 3 : 2). ^{1}H NMR, δ: 3.28, 3.40 (both s, 6 H, 2 MeO); 6.79, 6.81 (both s, 4 H, C_6H_4); 9.56, 9.70 (both s, 2 H, CHN(4)).

1-(4-Methoxyphenyl)-1,2,4-triazole (3f). ^{1}H NMR, δ: 3.82 (s, 3 H, MeO); 7.05, 7.72 (both d, 4 H, C_6H_4); 8.04, 9.01 (both s, 2 H, $C_2H_2N_3$) (*cf.* Ref. 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, 3 MeO); 6.31 (br.s, 4 H, C_6H_4); 8.10, 8.92 (both s, 2 H, $C_3H_2N_3O$).

1,1,4-Trimethoxy-4-(5-methyl-3,4-dinitropyrazol-1-yl)cyclohexa-2,5-diene (10e). ^{1}H NMR, δ: 2.70 (s, 3 H, Me); 3.30, 3.32, 3.62 (all s, 9 H, 3 MeO); 4.93—6.20 (m, 4 H, C_6H_4).

1,1,4-Trimethoxy-4-(1,2,4-triazol-1-yl)cyclohexa-2,5-diene (10f). ^{1}H NMR, δ: 3.20, 3.25, 3.30 (all s, 9 H, 3 MeO); 6.25, 6.35 (both d, 4 H, C_6H_4); 7.80, 8.52 (both s, 2 H, $C_2H_2N_3$).

1,1,4-Trimethoxy-4-(3-nitrotriazol-1-yl)cyclohexa-2,5-diene (10g). ^{1}H NMR, δ: 3.20, 3.25, 3.60 (all s, 9 H, 3 MeO); 5.07—6.16 (m, 4 H, C_6H_4); 8.60 (s, 1 H, $C_2HN_4O_2$).

1,1,4-Trimethoxy-4-(tetrazol-1- and -2-yl)cyclohexa-2,5-diene (10h) (mixture of *N*-isomers, 2 : 1). ^{1}H NMR, δ: 3.20—3.30, 3.60 (all br.s, 9 H, 3 MeO); 4.97—6.15 (m, 4 H, C_6H_4); 8.50, 8.84 (both s, 1 H, CHN(4)).

1,1,4,4-Tetramethoxycyclohexa-2,5-diene (12). ^{1}H NMR, δ: 3.20 (s, 12 H, 4 MeO); 6.00 (s, 4 H, C_6H_4).

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