Reactivity of diazoazoles and azolediazonium salts in *C*-azo coupling reactions

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The comparative reactivity of heterocyclic diazo compounds and the corresponding diazonium salts in *C*-azo coupling reactions was studied using imidazole, pyrazole, and triazole derivatives as examples. The reactivities of pyrazole- and imidazole-derived diazonium salts are much lower than those of thiadiazole- and 1,2,4-triazole-derived diazonium salts but higher than those of pyrrole and indole diazo compounds.

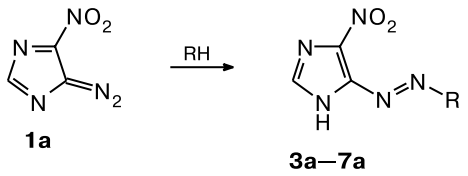
Key words: heterocyclic diazo compounds, diazonium salts, diazoimidazoles, diazopyrazoles, imidazolediazonium salts, pyrazolediazonium salts, 1,2,4-triazolediazonium salts, *C*-azo coupling, reactivity.

The *C*-azo coupling reaction characterizes the reactivity of aromatic diazonium salts. By varying the activity of the azo components, one can estimate qualitatively the reactivity of the diazonium derivative. Pycryldiazonium sulfate, which forms azo compounds with anisole and mesitylene, is known[1] to be among the most reactive aromatic compound in these reactions. The reactivity of heterocyclic diazonium salts varies over a very broad range. Thus the pyrrolediazonium salt does not react even with β-naphthol,[2] while the diazonium salts derived from isothiazole, benzothiazole, 1,2,4-triazole, and tetrazole give azo compounds with phenethole and mesitylene.[3] The highest reactivity is found for imidazole-2-diazonium salts obtained in 85% phosphoric acid, which undergo coupling with benzene,[4,5] apparently, through protonation of the imidazole ring. Heterocyclic diazo compounds with structures similar to quinonediazides and aliphatic diazo compounds react only with the most active azo components,[6—9] although often it is not defined what particular form, either diazo compound or the diazonium salt, takes part in the reaction. It is noteworthy that these forms can exist in the prototropic equilibrium.[10]

The purpose of the present study was to compare the reactivities of heterocyclic diazo compounds, *viz.*, 4-nitro-5-diazoimidazole (**1a**), ethyl 5-diazoimidazole- (**1b**), and 5-diazopyrazole-4-carboxylates (**1c**), and the corresponding diazonium salts **2a—c**, as well as 4,5-dicyanoimidazole-2-diazonium chloride (**2d**) and 1,2,4-triazole-3-diazonium sulfate (**2e**) under conditions that rule out prototropic interconversions. β-Naphthol, *N*,*N*-dimethylaniline, resorcinol, 1,3,5-trimethoxybenzene, 1,3-dimethoxybenzene, *m*- and *p*-cresol, anisole, mesitylene, xylene, toluene, and benzene were used as the ranking reagents.

Study of the reactions of diazo compounds **1a—c** with aromatic azo components has shown that the formation of azo coupling products depends on the nature of the substituent and the heterocycle structure. For example, diazoimidazole **1a** ($\delta_{H(2)}$ 7.72, ν(NN) = 2220 cm^{-1}) containing a strong electron-withdrawing group, forms azo compounds with β-naphthol, *N*,*N*-dimethylaniline, resorcinol, 1,3,5-trimethoxybenzene, and 1,3-dimethoxybenzene (**3a—7a**) (Scheme 1), whereas with anisole or *p*-cresol, no reaction was observed. As the reactivity of the azo component used in the reaction decreases, the time required for the formation of azo compounds substantially increases, while their yields decrease. The starting diazo compound is not completely converted into the final product, irrespective of the reaction time.

Scheme 1



1a **3a—7a**

R = 2-hydroxy-1-naphthyl (**3a**), 4-$Me_2NC_6H_4$ (**4a**), 2,4-$(OH)_2C_6H_3$ (**5a**), 2,4,6-$(MeO)_3C_6H_2$ (**6a**), 2,4-$(MeO)_2C_6H_3$ (**7a**)

Ethyl 5-diazopyrazole-4-carboxylate (**1c**) ($\delta_{H(3)}$ 8.34, ν(NN) = 2210 cm^{-1}) is also coupled with β-naphthol, *N*,*N*-dimethylaniline, resorcinol, 1,3,5-trimethoxyben-

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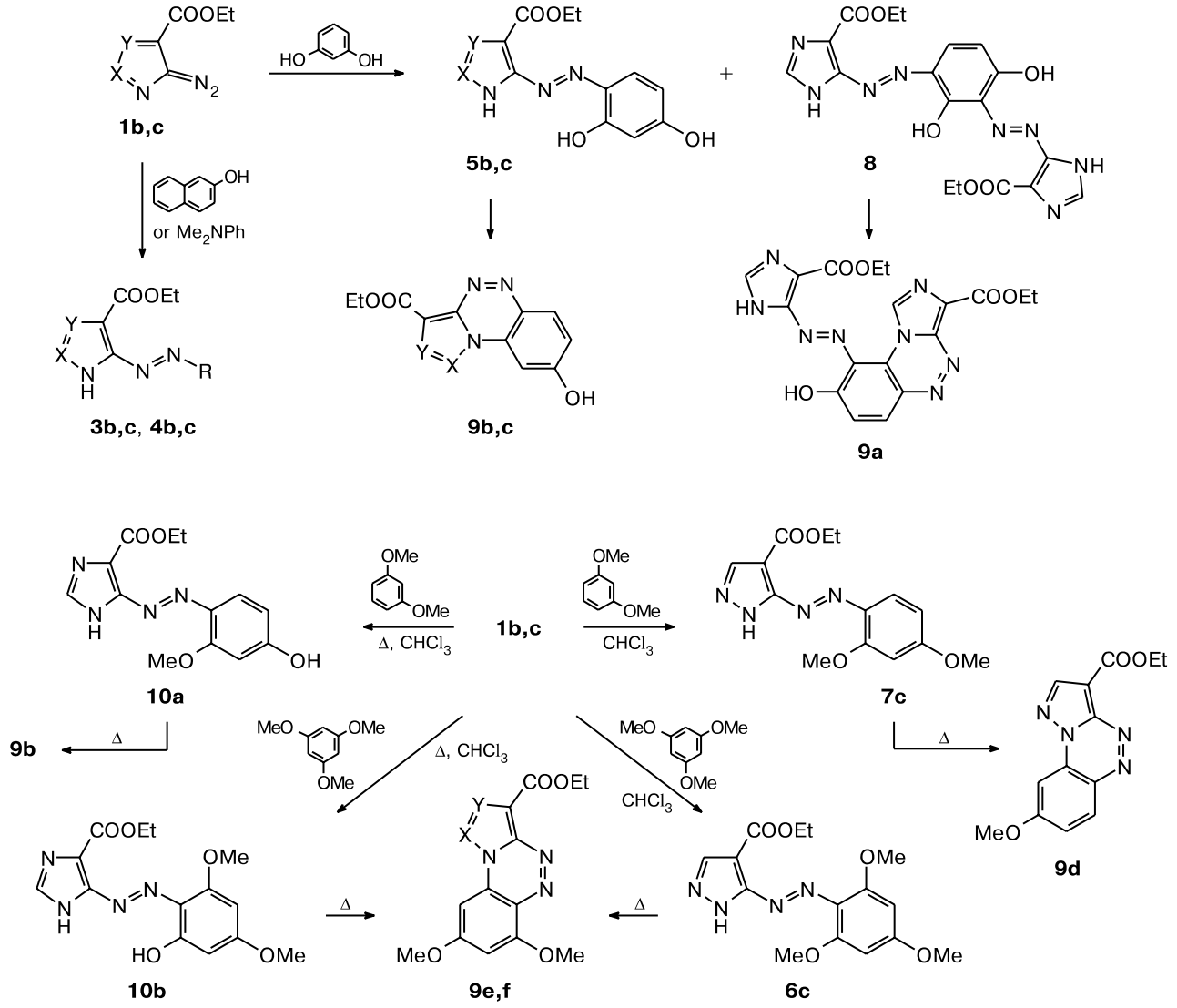
Scheme 2



X = CH, Y = N (**1b**, **3b—5b**, **9b,e**); X = N, Y = CH (**1c**, **3c—5c**, **9c,f**); R = 2-hydroxynaphthyl (**3b,c**), 4-$Me_2NC_6H_4$ (**4b,c**)

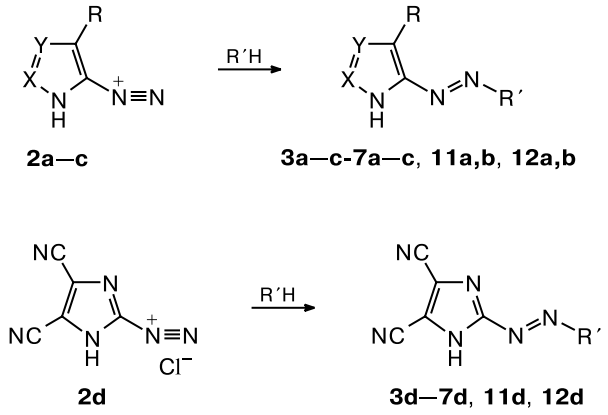
zene, and 1,3-dimethoxybenzene at room temperature to give azo compounds **3c—7c**, respectively (Scheme 2). Under similar conditions, ethyl 5-diazoimidazole-4-carboxylate (**1b**) ($\delta_{H(2)}$ 7.69, ν(NN) = 2190 cm^{-1}) reacts only with β-naphthol, *N*,*N*-dimethylaniline, and resorcinol, both mono (**5b**) and bis (**8**) azo coupling products being formed in the latter case. The structures of compounds **5b,c** and **8** were proved by physicochemical methods and by transforming them into the corresponding benzo(diazolo)triazines **9a—c**. Bis-azo coupling can be prevented by using a tenfold excess of the azo component.

Diazoimidazole **1b** is coupled with polymethoxy derivatives of benzene in an aprotic solvent only on heating. Using spectroscopic techniques and chemical transformations into the corresponding benzo(imidazo)triazines **9b,e**, it was found that azo coupling is accompanied by demethylation of one methoxy group to give compounds **10a,b** (see Scheme 2).

A study of the reactivity of 4,5-dicyanoimidazole-2- (**2d**; ν(NN) = 2299 cm^{-1}), 4-nitro- (**2a**; $\delta_{H(2)}$ 8.43, ν(NN) = 2270 cm^{-1}) and 4-ethoxycarbonylimidazole-5-diazonium (**2b**; $\delta_{H(2)}$ 8.26, ν(NN) = 2265 cm^{-1}), 4-ethoxycarbonylpyrazole-5-diazonium (**2c**), and 1,2,4-triazole-3-diazonium (**2e**) salts with respect to azo coupling showed that the position of the diazonium group in the ring, unlike the nature of the heterocycle, does not affect much their reactivities. In the case of **2a—d**, coupling with β-naphthol, *N*,*N*-dimethylaniline, resorcinol, 1,3,5-trimethoxybenzene, and 1,3-dimethoxybenzene occurs rather smoothly at room temperature to give the

corresponding azo compounds **3a—d-7a—d**, whereas the reaction of salts **2a,b,d** with *m*- and *p*-cresol proceeds only on refluxing in glacial acetic acid for 3—5 h and gives azo compounds **11a,b,d** and **12a,b,d**, respectively (Scheme 3). Compounds **11c** and **12c** could not be prepared. None of the diazonium cations studied reacts with anisole or mesitylene under similar conditions.

Scheme 3

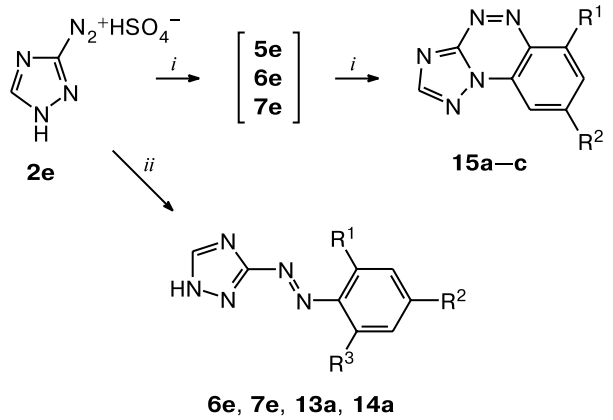


2a—7a, 11a, 12a: X = CH, Y = N, R = NO_2;
2b—7b, 11b, 12b: X = CH, Y = N, R = COOEt;
2c—7c: X = N, Y = CH, R = COOEt;

R′ = 2-hydroxy-1-naphthyl (**3a—d**), 4-$Me_2NC_6H_4$ (**4a—d**), 2,4-$(OH)_2C_6H_3$ (**5a—d**), 2,4,6-$(MeO)_3C_6H_2$ (**6a—d**), 2,4-$(MeO)_2C_6H_3$ (**7a—d**), 2-Me-4-OHC_6H_3 (**11a,b,d**), 2-Me-5-OHC_6H_3 (**12a,b,d**)

Whereas pyrazole- and imidazolediazonium salts exhibit comparable reactivities with respect to azo coupling, the 1,2,4-triazole-3-diazonium derivative **2e** ($\delta_{H(2)}$ 9.00, ν(NN) = 2275 cm^{-1}) is more reactive and reacts with anisole and mesitylene giving rise to azo compounds **13a** and **14a** (Scheme 4). In addition, upon the reaction of salt **2e** with hydroxy and polymethoxy benzene derivatives in 25% sulfuric acid, only benzo[2,1-*e*][1,2,4]triazolo[5,1-*c*]-*as*-triazines **15a—c**, resulting from intramolecular cyclization of the intermediate azo compounds **5e—7e**, were isolated as the final products. We were able to find conditions that allow one to avoid cyclization and to obtain 1,2,4-triazole azo derivatives **6e** and **7e**, which have not been described previously.

Scheme 4



i. 25% H_2SO_4. *ii*. 50% H_2SO_4.

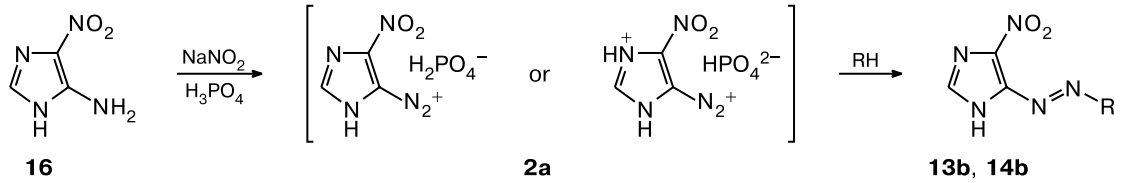
$R^1 = R^2 = R^3$ = OMe (**6e**); R^1 = H, $R^2 = R^3$ = OMe (**7e**); $R^1 = R^3$ = H, R^2 = OMe (**13a**); $R^1 = R^2 = R^3$ = Me (**14a**); R^1 = H, R^2 = OH (**15a**); $R^1 = R^2$ = OMe (**15b**); R^1 = H, R^2 = OMe (**15c**)

As an attempt to enhance the reactivity of diazonium salts by increasing the acidity of the medium,[8] we studied diazotization of 5-amino-4-nitroimidazole (**16**) in concentrated phosphoric acid and the subsequent coupling of the resulting diazonium salt with inert azo components such as anisole, mesitylene, *p*-xylene, and benzene. The reactions with anisole and mesitylene were found to give azo compounds **13b** and **14b**, whereas *p*-xylene and benzene did not react (Scheme 5).

The results obtained suggest that the reactivities of imidazolediazonium salts increase, possibly, due to protonation of the second N atom of the heterocycle. Nevertheless, the reactivity is still markedly lower than those of benzoimidazolediazonium salts able to form coupling products with inert azo components such as xylenes, toluene, and benzene, although it becomes comparable with the reactivity of 1,2,4-triazole-3-diazonium (**2e**).

Study of the reactions of 4,5-dicyanoimidazole-2-diazonium chloride (**2d**) with benzene and *p*-xylene at

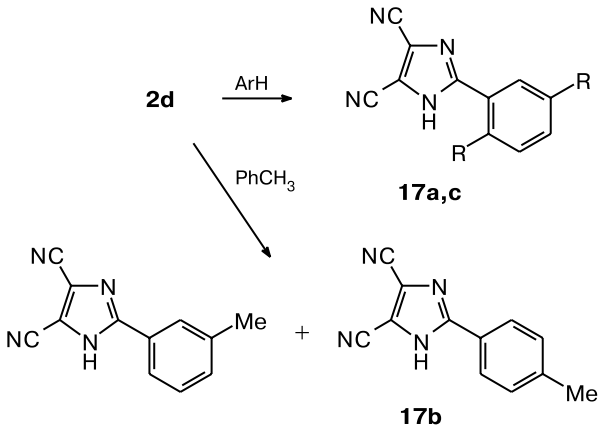
Scheme 5



R = 4-$MeOC_6H_4$ (**13b**), 2,4,6-$Me_3C_6H_2$ (**14b**)

60—70 °C has shown that in this case, no azo compounds are formed; instead, the reaction gives arylimidazoles **17a—c** (Scheme 6). The reaction with toluene gives a mixture of *meta*- and *para*-isomers in 1 : 1 ratio; however, only *para*-substituted product **17b** was isolated in a pure state.

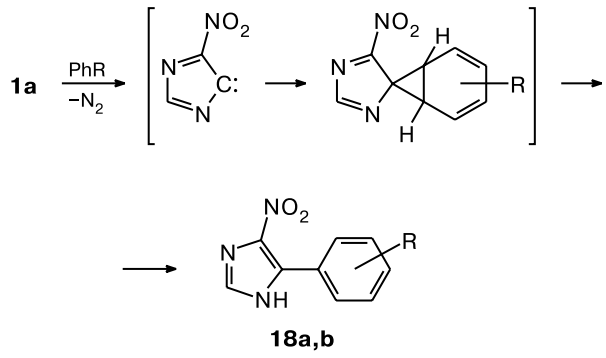
Scheme 6



R = H (**a**), Me (**c**)

It is noteworthy that the involvement of less reactive 4-nitro-5-diazoimidazole (**1a**) in similar transformations with benzene and toluene resulted in 5-aryl-4-nitro-substituted imidazoles **18a,b** in 38 and 23% yields, respectively, only after long-term refluxing (Scheme 7). The structure of the synthesized arylimidazoles was confirmed by physicochemical methods (Table 1).

Scheme 7



R = H (**a**), Me (**b**)

The different durations of the chemical transformations and different product yields can be attributed to different mechanisms leading to 2- and 5-aryl-substituted imidazoles. For example, the synthesis of compounds **17a—c** from salt **2d** follows an ionic mechanism, whereas the formation of compounds **18a,b** from diazoimidazole **1a** is preceded most likely by the formation of a carbene-type species. Thus, the form of the reacting diazo compound has a substantial influence on both the coupling reaction rate and the course of reactions with nitrogen evolution, although does not change the reaction routes.

In order to find out what class of organic substances the nitrogen-containing five-membered heterocycles containing a CNN fragment as a substituent resemble most closely and also to predict their behavior in typical chemical transformations, we analyzed a broad array of their properties, as well as calculated and spectroscopic characteristics. The stretching frequency of the diazo group increases in the following sequence: 3-diazopyrrole < 2-diazopyrrole < 3- and 4-diazopyrazoles < 4-diazoimidazole < 4-diazo-1,2,3-triazole < 2-diazoimidazole < 3-diazo-1,2,4-triazole < 5-diazotetrazole. On passing from diazoazoles to the corresponding diazonium salts, the stretching band for the functional group shifts by 70—140 cm^{-1}. A similar sequence of absorption frequencies of heterocyclic diazonium salt is as follows: pyrrole-3-diazonium salts < pyrazole-4-diazonium salts < imidazole-4-diazonium salts ≤ pyrazole-3-diazonium salts ≤ ≤ 1,2,3-triazole-4-diazonium salts = imidazole-2-diazonium salts = 1,2,4-triazole-3-diazonium salts. It is noteworthy that the $\nu(N_2^+)$ stretching frequency observed for the azolediazonium salts is similar to that of the diazonium group in aromatic diazonium salts. As regards their physicochemical characteristics, diazoazoles **1** we studied resemble more closely aromatic diazonium salts than aliphatic diazo compounds; therefore, they should tend to undergo transformations involving the terminal N atom of the diazo group. However, as compared with the azolediazonium and aromatic cations, diazo compounds **1** are expected to be almost inert in the reactions typical of aromatic diazonium compounds, whereas the activity of imidazolediazonium salts **2** in these transformations is comparable with that of aromatic salts, which is confirmed by our studies.

In addition, we detected a certain relationship between the chemical shift of the proton located in the azole ring and diazoazole reactivity (Fig. 1). It can be seen from Fig. 1 that the lower-field the position of the proton signal, the higher the activity of the diazonium derivative in *C*-azo coupling reactions. This type of proton behavior reflects the decrease in the electron density in the heterocyclic system, which finally increases the electrophilicity of the diazonium group and the reactivity of the diazo compound. Indeed, diazoimidazoles **1a,b** (δ_H 7.69 and 7.71) react only with the most reactive azo components, whereas triazole-3-diazonium salts **2e** (δ_H 9.0) and 4-nitroimidazole-5-diazonium salts **2a** (δ_H 8.43) react with a more extensive series of aromatic derivatives, and the ring protonation allows one to prepare azo compounds with simple arenes.

Table 1. Melting points, reaction times, yields and data of elemental analysis of the products

Compound	M.p. /°C	Reaction time (method)*	Yield (%)	Found / Calculated (%)			Molecular formula
				C	H	N	
3a	>300	5 days (*A*)	70	55.12	3.14	24.92	$C_{13}H_9N_5O_3$
		2 h (*B*)	82	55.13	3.20	24.73	
3b	228—229	14 days (*A*)	53	61.77	4.51	17.86	$C_{16}H_{14}N_4O_3$
		0.5 h (*B*)	85	61.93	4.55	18.05	
3c	210—212	4 days (*A*)	71	62.11	4.34	17.82	$C_{16}H_{14}N_4O_3$
		17 h (*B*)	90	61.93	4.55	18.05	
3d	261—263	10 days (*A*)	92	62.38	2.91	29.33	$C_{15}H_8N_6O$
		3 h (*B*)	98	62.50	2.80	29.15	
4a	>300	65 h (*A*)	60	50.52	4.54	32.38	$C_{11}H_{12}N_6O_2$
		10 min (*B*)	36	50.77	4.65	32.29	
4b	209—210	75 h (*A*)	53	58.66	6.07	24.19	$C_{14}H_{17}N_5O_2$
		15 min (*B*)	44	58.52	5.96	24.37	
4c	187—188	75 h (*A*)	59	58.43	5.97	24.48	$C_{14}H_{17}N_5O_2$
		10 min (*B*)	62	58.52	5.96	24.37	
4d	275—277	5 min	96	58.79	4.13	37.06	$C_{13}H_{11}N_7$
				58.86	4.18	36.96	
5a	238—240	14 days	74	43.22	2.75	27.79	$C_9H_7N_5O_4$
				43.38	2.83	28.10	
5b	220—221	25 days (*A*)	38	51.98	4.47	19.89	$C_{12}H_{12}N_4O_4$
		3 h (*B*)	62	52.17	4.38	20.28	
5c	182—183	1 h (*C*)	45	52.10	4.26	20.36	$C_{12}H_{12}N_4O_4$
		12 days (*D*)	67	52.17	4.38	20.28	
5d	283—285	10 h	85	52.06	2.35	33.14	$C_{11}H_6N_6O_2$
				51.97	2.38	33.06	
6a	>300	15 days (*A*)	68	46.87	4.22	22.93	$C_{12}H_{13}N_5O_5$
		4 h (*B*)	82	46.91	4.26	22.79	
6b	210—211	10 h (*B*)	62	53.98	5.40	16.87	$C_{15}H_{18}N_4O_5$
				53.89	5.43	16.76	
6c	230—231	3 h (*B*)	71	53.77	5.52	16.98	$C_{15}H_{18}N_4O_5$
				53.89	5.43	16.76	
6d	213—215	0.5 h (*B*)	83	53.76	3.88	26.97	$C_{14}H_{12}N_6O_3$
				53.85	3.87	26.91	
6e	156—158	0.5 h	76	50.04	5.11	26.37	$C_{11}H_{13}N_5O_3$
				50.19	4.98	26.60	
7a	>300	30 days (*A*)	32	47.78	3.94	25.34	$C_{11}H_{11}N_5O_4$
		6 h (*B*)	41	47.66	4.00	25.26	
7b	117—119	3 days (*B*)	54	55.22	5.36	18.34	$C_{14}H_{16}N_4O_4$
				55.26	5.30	18.41	
7c	220—222	4 h (*B*)	65	55.32	5.33	18.48	$C_{14}H_{16}N_4O_4$
				55.26	5.30	18.41	
7d	239—241	8 days (*A*)	51	55.24	3.64	29.86	$C_{13}H_{10}N_6O_2$
		1 h (*B*)	71	55.32	3.57	29.77	
7e	200—203	1 h	98	51.32	4.88	29.78	$C_{10}H_{11}N_5O_2$
				51.50	4.75	30.03	
9a	<300	3.5 h	32	51.18	3.92	26.27	$C_{18}H_{16}N_8O_5$
				50.95	3.80	26.40	
9b	<300	3.5 h (*A*)	59	55.94	4.00	21.83	$C_{12}H_{10}N_4O_3$
		5 h (*B*)	66	55.81	3.90	21.70	
9c	264—266	2 h	72	55.74	3.92	22.06	$C_{12}H_{10}N_4O_3$
				55.81	3.90	21.70	
9d	205—207	2 h	77	57.40	4.47	20.41	$C_{13}H_{12}N_4O_3$
				57.35	4.44	20.58	

(*to be continued*)

Table 1 (*continued*)

Compound	M.p. /°C	Reaction time* (method)	Yield (%)	Found / Calculated (%)			Molecular formula
				C	H	N	
9e	243—245	3 h (*A*)	68	55.75	4.61	18.72	$C_{14}H_{14}N_4O_4$
		4 h (*B*)	57	55.63	4.67	18.53	
9f	230—231	3 h	80	55.79	4.63	18.39	$C_{14}H_{14}N_4O_4$
				55.63	4.67	18.53	
10a	153—155	3 days	87	53.86	4.94	19.52	$C_{13}H_{14}N_4O_4$
				53.79	4.86	19.30	
10b	163—167	3 h	57	52.41	4.94	17.12	$C_{14}H_{16}N_4O_5$
				52.50	5.04	17.49	
11a	198—200	4 month (*A*)	23	48.67	3.62	28.38	$C_{10}H_9N_5O_3$
		3.5 h (*B*)	74	48.59	3.67	28.33	
11b	235—238	4 month (*A*)	29	56.94	5.17	20.38	$C_{13}H_{14}N_4O_3$
		3 h (*B*)	82	56.93	5.14	20.43	
11d	278—281	1 h	46	57.01	3.12	33.43	$C_{12}H_8N_6O$
				57.14	3.20	33.32	
12a	>300	5 h (*B*)	33	48.64	3.71	28.51	$C_{10}H_9N_5O_3$
				48.59	3.67	28.33	
12b	208—210	4 month (*A*)	11	56.67	5.04	20.13	$C_{13}H_{14}N_4O_3$
		4.5 (*B*)	56	56.93	5.14	20.43	
12d	200—201	4 h	34	56.89	3.28	33.15	$C_{12}H_8N_6O$
				57.14	3.20	33.32	
13a	170—172	20 h	37	53.05	4.58	34.19	$C_9H_9N_5O$
				53.20	4.46	34.46	
13b	264—266	12 h (*A*)	72	48.32	3.78	28.14	$C_{10}H_9N_5O_3$
		20 h (*B*)	45	48.59	3.67	28.33	
14a	165—166	8 days	28	61.19	6.27	32.19	$C_{11}H_{13}N_5$
				61.38	6.09	32.53	
14b	205—208	50 h (*A*)	41	55.23	5.19	26.88	$C_{12}H_{13}N_5O_2$
		84 h (*B*)	36	55.59	5.05	27.01	
15a	181—183	0.5 h	68	51.16	2.84	37.18	$C_8H_5N_5O$
				51.34	2.69	37.42	
15b	179—180	0.25 h	98	52.11	4.06	30.05	$C_{10}H_9N_5O_2$
				51.95	3.92	30.29	
15c	174—178	1 h	96	53.58	3.68	34.64	$C_9H_7N_5O$
				53.73	3.51	34.81	
17a	243—244	48 days	83	68.18	3.18	28.74	$C_{11}H_6N_4$
				68.04	3.11	28.85	
17b	140—142	48 days	58	69.34	3.56	26.68	$C_{12}H_8N_4$
				69.22	3.87	26.91	
17c	132—134	48 days	42	70.11	4.39	25.13	$C_{13}H_{10}N_4$
				70.26	4.54	25.21	
18a	256—259	3 month	38	57.31	3.65	22.07	$C_9H_7N_3O_2$
				57.14	3.73	22.21	
18b	287—289	3 month	23	59.34	4.30	20.43	$C_{10}H_9N_3O_2$
				59.11	4.46	20.68	

* The preparation method (*A*, *B*, *C*, *D*) is given according to Experimental.

Thus, the experimental data we obtained on the reactivity of various diazoimidazole species are in good agreement with the regularities elucidated by analysis of spectroscopic characteristics. Studies of azo coupling of diazoazoles and the corresponding diazonium salts with a broad range of azo components have shown that the reactivities of the imidazole- and pyrazolediazonium salts are comparable with the reactivity of benzenediazonium chloride, while the 4-nitroimidazole-5-diazonium sulfate and phosphate are comparable with the most reactive diazonium salt, *viz.*, picryldiazonium sulfate, which has a predictive value for determining the scope of application of

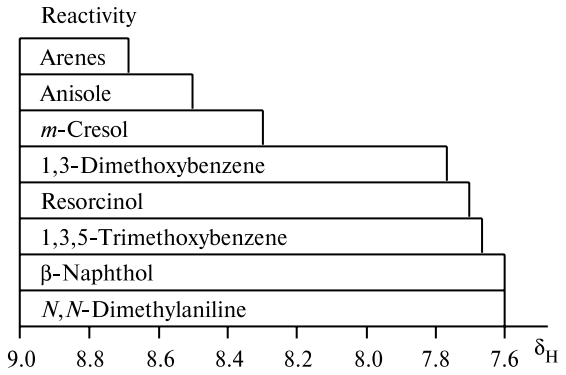


Fig. 1. Reactivity of diazoazoles in *C*-azo coupling with different azo components *vs.* chemical shift of the azole ring proton in the ^{1}H NMR spectra.

azole diazonium salts in other reactions. It was found that the imidazole derivatives occupy an intermediate position in the series of heterocyclic diazonium salts; their reactivities are much lower than those of the thiadiazole-[11] and 1,2,4-triazole-derived[7] diazonium salts, which react with inactive azo components, but are somewhat higher than those of pyrrole- and indole-derived[2] diazonium derivatives.

Experimental

Spectroscopic studies were performed using analytically and chromatographically pure samples. IR spectra of the synthesized compounds were recorded on a Specord IR-75 instrument (in KBr pellets and CaF_2 cells). UV spectra were measured on a Beckman-26 spectrophotometer. ^{1}H NMR spectra were recorded on a Bruker WR-250 instrument (250 MHz) in a DMSO-d_6—CCl_4 mixture (δ scale, internal Me_4Si). The reactions were monitored and the purity of the products was checked by TLC on Silufol UV-254 and Sorbfil UV-254 plates (silica gel STC-1A as the sorbent) using the following solvent systems: BuOH—AcOH—H_2O, 4 : 1 : 1 (I); $CHCl_3$—EtOH, 3 : 1 (II); and $CHCl_3$—EtOH, 10 : 1 (III).

The results of elemental analysis of the obtained compounds (C, H, N) correspond to calculated data. Their spectroscopic characteristics are listed in Table 2. The melting points were not corrected.

The starting diazoazoles and diazonium salts were prepared from the corresponding heterocyclic amines.[10] 4-Amino-5-nitroimidazole and ethyl 5-aminoimidazole-4-carboxylate were synthesized by known procedures.[12,13] 2-Amino-4,5-dicyanoimidazole, ethyl 5-aminopyrazole-4-carboxylate and 3-amino-1,2,4-triazole are commercially available.

4-R-5-(2-Hydroxy-1-naphthyl)azoimidazoles 3a,b and ethyl 5-(2-hydroxy-1-naphthyl)azopyrazole-4-carboxylate (3c) (general procedure). ***A.*** β-Naphthol (0.52 g, 3.6 mmol) was added with stirring at ~20 °C to a solution of diazo compound **1a—c** (3 mmol) in $CHCl_3$ or MeCN. The reaction mixture was kept until the starting diazoimidazole was completely converted (see Table 1). The solvent was evaporated *in vacuo* and the residue was washed with water and EtOH.

B. β-Naphthol (0.52 g, 3.6 mmol) was added with stirring at ~20 °C to a solution of 3 mmol of diazonium salt **2a—c** in 5 mL of glacial acetic AcOH. The reaction mixture was kept at ~20 °C (**2a,c**) or 70 °C (**2b**) until the starting diazonium salt disappeared (see Table 1). The precipitate was filtered off and washed with ether.

2-(2-Hydroxy-1-naphthyl)azoimidazole-4,5-dicarbonitrile (3d). β-Naphthol (0.49 g, 3.32 mmol (method *A*)) or (0.6 g, 4.17 mmol (method *B*)) was added with stirring at ~20 °C to a solution of diazo compound **1d** (0.5 g, 3.47 mmol) or diazonium salt **2d** (0.5 g, 2.77 mmol), respectively, in 10 mL of anhydrous MeCN. The reaction mixture was kept for 3 h (*A*) or for 10 days (*B*) until the starting compound disappeared, and the precipitate was filtered off.

4-R-5-[4-(*N*,*N*-Dimethylamino)phenyl]azoazoles 4a—c (general procedure). ***A.*** *N*,*N*-Dimethylaniline (0.46 mL, 3.6 mmol) was added with stirring at ~20 °C to a solution of diazo compound **1a—c** (3 mmol) in 10 mL of anhydrous MeCN or $CHCl_3$. The reaction mixture was kept until the starting diazoimidazole disappeared (see Table 1). The solvent was evaporated *in vacuo* to dryness, and the residue was recrystallized from 50% EtOH.

4-Nitro-5-[4-(*N*,*N*-dimethylamino)phenyl]azoimidazole (4a). ***B.*** *N*,*N*-Dimethylaniline (0.32 mL, 2.53 mmol) was added with stirring at ~20 °C to a solution of diazonium salt **2a** (0.5 g, 2.11 mmol) in 15% H_2SO_4. The reaction mixture was kept for 10 min. The precipitate was filtered off and an additional amount of the product was extracted from the filtrate with chloroform. The extract was concentrated *in vacuo* to dryness. The precipitate was recrystallized from 50% EtOH.

Ethyl 5-[4-(*N*,*N*-dimethylamino)phenyl]azoimidazole-4-carboxylate (4b) and 5-[4-(*N*,*N*-dimethylamino)phenyl]azopyrazole-4-carboxylate (4c). ***B.*** *N*,*N*-Dimethylaniline (0.46 mL, 3.61 mmol) was added with stirring at ~20 °C to diazonium salt **2b** (0.5 g, 3.01 mmol) in 10 mL of glacial AcOH. The reaction mixture was kept for 15 min. The solvent was evaporated, and the residue was recrystallized from 50% EtOH.

2-[4-(*N*,*N*-Dimethylamino)phenyl]- (4d) and **2-(2,4-dihydroxyphenyl)azoimidazole-4,5-dicarbonitrile (5d).** *N*,*N*-Dimethylaniline (0.42 mL, 3.32 mmol) or resorcinol (0.37 g, 3.32 mmol) was added with stirring at ~20 °C to a solution of diazonium salt **2d** (0.5 g, 2.77 mmol) in 10 mL of dry MeCN or $CHCl_3$. The reaction mixture was kept for 5 min or for 10 h, respectively, until the starting compound disappeared. The precipitate that formed was filtered off.

4-Nitro-5-(2,4-dihydroxyphenyl)azoimidazole (5a). Resorcinol (3.47 g, 4.3 mmol) was added with stirring at ~20 °C to a solution of diazo compound **1a** (0.5 g, 3.6 mmol) in 15 mL of $CHCl_3$ or MeCN. The reaction mixture we kept for 14 days. The precipitate was filtered off and recrystallized from EtOH.

Ethyl 5-(2,4-dihydroxyphenyl)azoimidazole- (5b) and 5-(2,4-dihydroxyphenyl)azopyrazole-4-carboxylates (5c). ***A.*** Resorcinol (3.31 g, 30.1 mmol) was added in portions with stirring at 10 °C over a period of 2 h to a solution of diazo compound **1b** (0.5 g, 3.01 mmol) in 25 mL of MeCN. The temperature was gradually brought to 20 °C and the reaction mixture was kept under these conditions for 25 days. The solvent was evaporated *in vacuo* and the residue was triturated with ether and filtered. The precipitate was recrystallized from acetone.

B. Resorcinol (0.4 g, 3.61 mmol) was added with stirring at ~20 °C to a solution of diazo compound **1b** (0.5 g, 3.01 mmol) in

Table 2. Spectroscopic characteristics of the products

Compound	IR, ν/cm^{-1}				^{1}H NMR, δ (*J*/Hz)
	NH	C=O	C=N, N=N	CN (NO_2)	
3a	3320	—	1630, 1610	1570 (1360)	6.72 (d, 1 H, H(4′), *J* = 9.7); 7.45—7.80 (m, 3 H, H(5′), H(6′), H(7′)); 7.88 (s, 1 H, H(2)); 7.95 (d, 1 H, H(3′), *J* = 9.7); 8.66 (d, 1 H, H(8′), *J* = 8.3); 13.92 (br.s, 1 H, OH); 15.90 (s, 1 H, NH)
3b	3350	1670	1610, 1590	—	1.42 (t, 3 H, $OCH_2C\underline{H}_3$, *J* = 7.0); 4.42 (q, 2 H, $OC\underline{H}_2CH_3$, *J* = 7.0); 6.97 (d, 1 H, H(4′), *J* = 9.4); 7.47 (dd, 1 H, H(6′), J_1 = 7.0, J_2 = 7.6); 7.61 (dd, 1 H, H(7′), J_1 = 8.6, J_2 = 7.0); 7.70 (d, 1 H, H(5′), *J* = 7.6); 7.97 (d, 1 H, H(3′), *J* = 9.4); 8.02 (s, 1 H, H(2)); 8.64 (d, 1 H, H(8′), *J* = 8.6); 9.71 (br.s, 1 H, OH); 15.55 (s, 1 H, NH)
3c	3430, 3380	1690	1630	—	1.40 (t, 3 H, $OCH_2C\underline{H}_3$, *J* = 7.0); 4.36 (q, 2 H, $OC\underline{H}_2CH_3$, *J* = 7.0); 6.73 (d, 1 H, H(4′), *J* = 9.5); 7.45 (dd, 1 H, H(7′), J_1 = 7.3, J_2 = 7.3); 7.58 (dd, 1 H, H(6′), J_1 = 7.0, J_2 = 7.3); 7.70 (d, 1 H, H(5′), *J* = 7.0); 7.91 (d, 1 H, H(3′), *J* = 9.5); 8.19 (s, 1 H, H(3)); 8.52 (d, 1 H, H(8′), *J* = 7.3); 10.20 (br.s, 1 H, OH); 15.86 (s, 1 H, NH)
3d	3180, 3430, 3535	—	1610, 1585	2220	5.95 (s, 1 H, OH); 6.81 (d, 1 H, H(3′), *J* = 9.5); 7.59 (dd, 1 H, H(6′), J_1 = 7.9, J_2 = 7.0); 7.59 (dd, 1 H, H(7′), J_1 = 7.0, J_2 = 8.2); 7.70 (d, 1 H, H(5′), *J* = 7.9); 7.95 (d, 1 H, H(4′), *J* = 9.5); 8.66 (d, 1 H, H(8′), *J* = 8.2); 15.03 (br.s, 1 H, NH)
4a	3440	—	1600	1560 (1340)	3.00, 3.12 (both s, 3 H each, NMe); 6.88 (d, 2 H, H(3′), H(5′), *J* = 9.3); 7.78 (s, 1 H, H(2)); 7.82 (d, 2 H, H(2′), H(6′), *J* = 9.3); 15.73 (br.s, 1 H, NH)
4b	3420	1685	1590	—	1.35 (t, 3 H, $OCH_2C\underline{H}_3$, *J* = 7.0); 3.07 (s, 6 H, NMe_2); 4.32 (q, 2 H, $OC\underline{H}_2CH_3$, *J* = 7.0); 6.84 (d, 2 H, H(3′), H(5′), *J* = 9.5); 7.78 (d, 2 H, H(2′), H(6′), *J* = 9.5); 7.79 (s, 1 H, H(2)); 14.72 (s, 1 H, NH)
4c	3430	1690	1580	—	1.31 (t, 3 H, $OCH_2C\underline{H}_3$, *J* = 7.0); 3.10 (s, 6 H, NMe_2); 4.24 (q, 2 H, $OC\underline{H}_2CH_3$, *J* = 7.0); 7.06 (d, 2 H, H(3′), H(5′), *J* = 9.4); 7.88 (d, 2 H, H(2′), H(6′), *J* = 9.4); 8.13 (s, 1 H, H(3)); 13.54 (s, 1 H, NH)
4d	3460	—	1595	2240, 2215	3.17 (s, 6 H, NMe_2); 6.83 (d, 2 H, H(3′), H(5′), *J* = 9.5); 7.82 (d, 2 H, H(2′), H(6′), *J* = 9.5); 14.83 (br.s, 1 H, NH)
5a	3420	—	1610, 1600	1560 (1345)	6.36 (d, 1 H, H(3′), *J* = 2.4); 6.58 (dd, 1 H, H(5′), J_1 = 8.9, J_2 = 2.4); 7.69 (d, 1 H, H(6′), *J* = 8.9); 7.93 (s, 1 H, H(2)); 9.24, 10.73 (both s, 1 H each, OH); 13.44 (br.s, 1 H, NH)
5b	3400	1705	1610, 1595	—	1.35 (t, 3 H, $OCH_2C\underline{H}_3$, *J* = 7.0); 4.36 (q, 2 H, $OC\underline{H}_2CH_3$, *J* = 7.0); 6.35 (d, 1 H, H(3′), *J* = 2.4); 6.56 (dd, 1 H, H(5′), J_1 = 8.9, J_2 = 2.4); 7.67 (d, 1 H, H(6′), *J* = 8.9); 7.93 (s, 1 H, H(2)); 9.09, 10.66 (both s, 1 H each, OH); 13.16 (br.s, 1 H, NH)
5c	3425	1700	1605, 1585	—	1.35 (t, 3 H, $OCH_2C\underline{H}_3$, *J* = 6.7); 4.30 (q, 2 H, $OC\underline{H}_2CH_3$, *J* = 6.7); 6.29 (s, 1 H, H(3′)); 6.51 (d, 1 H, H(5′), *J* = 8.4); 7.64 (d, 1 H, H(6′), *J* = 8.4); 8.03 (s, 1 H, H(3)); 9.29, 10.56 (both s, 1 H each, OH); 13.00 (br.s, 1 H, NH)
5d	3230	—	1600	2240, 2215	6.35 (d, 1 H, H(3′), *J* = 2.4); 6.44 (dd, 1 H, H(5′), J_1 = 9.2, J_2 = 2.4); 7.62 (d, 1 H, H(6′), *J* = 9.2); 10.36, 10.88 (both s, 1 H each, OH); 14.91 (br.s, 1 H, NH)
6a	3480	—	1590	1560 (1340)	3.85 (s, 6 H, 2 OMe); 3.91 (s, 3 H, OMe); 6.40 (s, 2 H, H(3′), H(5′)); 7.80 (s, 1 H, H(2)); 13.40 (s, 1 H, NH)
6b	3440	1690	1600, 1580	—	1.36 (t, 3 H, $OCH_2C\underline{H}_3$, *J* = 7.0); 3.83 (s, 6 H, 2 OMe); 3.89 (s, 3 H, OMe); 4.35 (q, 2 H, $OC\underline{H}_2CH_3$, *J* = 7.0); 6.33 (s, 2 H, H(3′), H(5′)); 7.74 (s, 1 H, H(2)); 14.79 (s, 1 H, NH)
6c	3510, 3455	1680	1590	—	1.19 (t, 3 H, $OCH_2C\underline{H}_3$, *J* = 6.7); 3.81 (s, 6 H, 2 OMe); 3.88 (s, 3 H, OMe); 4.17 (q, 2 H, $OC\underline{H}_2CH_3$, *J* = 6.7); 6.37 (s, 2 H, H(3′), H(5′)); 8.21 (s, 1 H, H(3)); 13.37 (br.s, 1 H, NH)
6d	3460, 3500	—	1590	2230	3.89 (s, 6 H, 2 OMe); 3.93 (s, 3 H, OMe); 6.32 (s, 2 H, H(3′), H(5′)); 14.97 (br.s, 1 H, NH)
6e	3450	—	1600, 1590	—	3.86 (s, 6 H, 2 OMe); 3.92 (s, 3 H, OMe); 6.38 (s, 2 H, H(3′), H(5′)); 8.81 (s, 1 H, H(5)); 13.39 (br.s, 1 H, NH)

(*to be continued*)

Table 2 (*continued*)

Compound	IR, ν/cm^{-1}				^{1}H NMR, δ (*J*/Hz)
	NH	C=O	C=N, N=N	CN (NO_2)	
7a	3500	—	1600	1560 (1350)	3.92, 4.01 (both s, 3 H each, OMe); 6.70 (dd, 1 H, H(5′), J_1 = 8.9, J_2 = 2.1); 6.81 (d, 1 H, H(3′), J = 2.1); 7.71 (d, 1 H, H(6′), J = 8.9); 7.85 (s, 1 H, H(2)); 13.43 (br.s, 1 H, NH)
7b	3440	1690	1600, 1580	—	1.36 (t, 3 H, $OCH_2C\underline{H}_3$, J = 7.0); 3.85, 3.89 (both s, 3 H each, OMe); 4.35 (q, 2 H, $OC\underline{H}_2CH_3$, J = 7.0); 6.87 (dd, 1 H, H(5′), J_1 = 8.6, J_2 = 2.4); 6.98 (d, 1 H, H(3′), J = 2.4); 7.73 (d, 1 H, H(6′), J = 8.6); 7.91 (s, 1 H, H(2)); 13.54 (br.s, 1 H, NH)
7c	3510	1700	1590, 1570	—	1.35 (t, 3 H, $OCH_2C\underline{H}_3$, J = 7.0); 3.90, 3.98 (both s, 3 H each, OMe); 4.36 (q, 2 H, $OC\underline{H}_2CH_3$, J = 7.0); 6.68 (dd, 1 H, H(5′), J_1 = 8.6, J_2 = 2.4); 6.80 (d, 1 H, H(3′), J = 2.4); 7.67 (d, 1 H, H(6′), J = 8.6); 8.29 (s, 1 H, H(3)); 14.22 (br.s, 1 H, NH)
7d	3440	—	1580	2230	3.94, 4.03 (both s, 3 H each, OMe); 6.57 (dd, 1 H, H(5′), J_1 = 9.2, J_2 = 2.4); 6.73 (d, 1 H, H(3′), J = 2.4); 7.74 (d, 1 H, H(6′), J = 9.2); 13.20 (br.s, 1 H, NH)
7e	3425	—	1590	—	3.90, 3.99 (both s, 3 H each, OMe); 6.58 (dd, 2 H, H(5′), J_1 = 8.8, J_2 = 2.2); 6.71 (dd, 1 H, H(3′), J = 2.2); 7.68 (d, 1 H, H(6′), J = 8.8); 8.46 (s, 1 H, H(5)); 13.39 (br.s, 1 H, NH)
9a	3400	1720	1600	—	1.41 (m, 6 H, 2 $OCH_2C\underline{H}_3$); 4.44 (m, 4 H, 2 $OC\underline{H}_2CH_3$); 7.36 (d, 1 H, H(7), J = 9.2); 8.12 (s, 1 H, H(2′)); 8.51 (d, 1 H, H(6), J = 9.2); 9.56 (s, 1 H, H(1)); 14.03 (br.s, 1 H, OH); 14.54 (br.s, 1 H, NH)
9b	—	1700	1600	—	1.40 (t, 3 H, $OCH_2C\underline{H}_3$, J = 7.0); 4.44 (q, 2 H, $OC\underline{H}_2CH_3$, J = 7.0); 7.29 (dd, 1 H, H(7), J_1 = 8.9, J_2 = 2.1); 7.69 (d, 1 H, H(9), J = 2.1); 8.42 (d, 1 H, H(6), J = 8.9); 9.18 (s, 1 H, H(1))
9c	—	1715	1610	—	1.39 (t, 3 H, $OCH_2C\underline{H}_3$, J = 7.0); 4.41 (q, 2 H, $OC\underline{H}_2CH_3$, J = 7.0); 7.37 (dd, 1 H, H(7), J_1 = 9.3, J_2 = 2.3); 7.61 (d, 1 H, H(9), J = 2.3); 8.55 (d, 1 H, H(6), J = 9.3); 8.71 (s, 1 H, H(2)); 11.95 (br.s, 1 H, OH)
9d	—	1695	1600	—	1.39 (t, 3 H, $OCH_2C\underline{H}_3$, J = 7.0); 4.06 (s, 3 H, OMe); 4.41 (q, 2 H, $OC\underline{H}_2CH_3$, J = 7.0); 7.45 (dd, 1 H, H(7), J_1 = 9.2, J_2 = 2.1); 7.92 (d, 1 H, H(9), J = 2.1); 8.53 (d, 1 H, H(6), J = 9.2); 8.82 (s, 1 H, H(2))
9e	—	1700	1605	—	1.40 (t, 3 H, $OCH_2C\underline{H}_3$, J = 7.0); 4.00, 4.07 (both s, 3 H each, OMe); 4.43 (q, 2 H, $OC\underline{H}_2CH_3$, J = 7.0); 6.81 (s, 1 H, H(9)); 7.45 (s, 1 H, H(7)); 9.18 (s, 1 H, H(1))
9f	—	1685	1610	—	1.39 (t, 3 H, $OCH_2C\underline{H}_3$, J = 6.9); 4.08, 4.14 (both s, 3 H each, OMe); 4.42 (q, 2 H, $OC\underline{H}_2CH_3$, J = 6.9); 6.87 (d, 1 H, H(9), J = 2.6); 7.29 (d, 1 H, H(7), J = 2.6); 8.67 (s, 1 H, H(2))
10a	3415	1710	1610, 1585	—	1.32 (t, 3 H, $OCH_2C\underline{H}_3$, J = 7.0); 3.91 (s, 3 H, OMe); 4.31 (q, 2 H, $OC\underline{H}_2CH_3$, J = 7.0); 6.46 (dd, 1 H, H(5′), J_1 = 8.8, J_2 = 2.4); 6.60 (d, 1 H, H(3′), J = 2.4); 7.58 (d, 1 H, H(6′), J = 8.8); 7.79 (s, 1 H, H(2)); 10.37 (s, 1 H, OH); 14.35 (br.s, 1 H, NH)
10b	3430	1710	1610	—	1.36 (t, 3 H, $OCH_2C\underline{H}_3$, J = 7.0); 3.85, 3.90 (both s, 3 H each, OMe); 4.36 (q, 2 H, $OC\underline{H}_2CH_3$, J = 7.0); 6.09 (s, 1 H, H(5′)); 6.18 (s, 1 H, H(3′)); 7.90 (s, 1 H, H(2)); 13.38 (br.s, 1 H, OH); 14.79 (s, 1 H, NH)
11a	3400	—	1585	1560 (1340)	2.65 (s, 3 H, Me); 6.30 (br.s, 1 H, OH); 6.71 (d, 1 H, H(5′), J = 8.9); 6.75 (s, 1 H, H(3′)); 7.70 (d, 1 H, H(6′), J = 8.9); 7.76 (s, 1 H, H(2)); 13.28 (br.s, 1 H, NH)
11b	3280	1700	1585, 1570	—	1.35 (t, 3 H, $OCH_2C\underline{H}_3$, J = 7.1); 2.63 (s, 3 H, Me); 4.36 (q, 2 H, $OC\underline{H}_2CH_3$, J = 7.1); 6.75 (dd, 1 H, H(5′), J_1 = 8.9, J_2 = 2.2); 6.81 (d, 1 H, H(3′), J = 2.2); 7.64 (d, 1 H, H(6′), J = 8.9); 8.30 (s, 1 H, H(2)); 10.20 (br.s, 1 H, OH); 14.43 (br.s, 1 H, NH)
11d	3440, 3245	—	1585	2225	2.61 (s, 3 H, Me); 6.69 (dd, 1 H, H(5′), J_1 = 9.2, J_2 = 1.8); 6.77 (d, 1 H, H(3′), J = 1.8); 7.69 (d, 1 H, H(6′), J = 9.2); 10.49 (s, 1 H, OH); 11.30 (br.s, 1 H, NH)

(*to be continued*)

Table 2 (*continued*)

Compound	IR, ν/cm^{-1}				^{1}H NMR, δ (*J*/Hz)
	NH	C=O	C=N, N=N	CN (NO_2)	
12a	3320	—	1640, 1600	1540 (1380)	2.74 (s, 3 H, Me); 7.60 (d, 1 H, H(6′), J = 2.6); 8.23 (dd, 1 H, H(4′), J_1 = 2.6, J_2 = 7.4); 8.65 (s, 1 H, H(2)); 9.00 (d, 1 H, H(3′), J = 7.4); 10.01 (br.s, 1 H, OH); 13.36 (br.s, 1 H, NH)
12b	3250	1695	1600, 1570	—	1.42 (t, 3 H, $OCH_2C\underline{H}_3$, J = 7.0); 2.35 (s, 3 H, Me); 4.41 (q, 2 H, $OC\underline{H}_2CH_3$, J = 7.0); 6.87 (d, 1 H, H(3′), J = 8.5); 7.18 (dd, 1 H, H(4′), J_1 = 1.5, J_2 = 8.5); 7.65 (d, 1 H, H(6′), J = 1.5); 7.99 (s, 1 H, H(2)); 11.93 (br.s, 1 H, OH); 14.15 (br.s, 1 H, NH)
12d	3420, 3235	—	1590	2230	2.59 (s, 3 H, Me); 6.65 (d, 1 H, H(3′), J = 9.0); 7.69 (s, 1 H, H(6′)); 7.81 (d, 1 H, H(4′), J = 9.0); 10.64 (s, 1 H, OH); 12.07 (br.s, 1 H, NH)
13a	3430	—	1590	—	3.89 (s, 3 H, OMe); 7.13 (d, 2 H, H(2′), H(6′), J = 8.9); 7.95 (d, 2 H, H(3′), H(5′), J = 8.9); 8.63 (s, 1 H, H(5)); 14.31 (br.s, 1 H, NH)
13b	3425	—	1600	1565 (1345)	3.91 (s, 3 H, OMe); 7.19 (d, 2 H, H(2′), H(6′), J = 8.9); 7.92 (s, 1 H, H(2)); 7.94 (d, 2 H, H(3′), H(5′), J = 8.9); 13.24 (br.s, 1 H, NH)
14a	3430	—	1595, 1575	—	2.31 (s, 3 H, Me); 2.36 (s, 6 H, 2 Me); 7.03 (s, 2 H, H(3′), H(5′)); 8.68 (s, 1 H, H(5)); 14.16 (br.s, 1 H, NH)
14b	3420	—	1600	1550 (1340)	2.22, 2.32, 2.49 (all s, 3 H each, Me); 7.06 (s, 2 H, H(3′), H(5′)); 7.99 (s, 1 H, H(2)); 13.60 (br.s, 1 H, NH)
15a	—	—	1605, 1590	—	6.38 (d, 1 H, H(9), J = 2.2); 6.49 (dd, 1 H, H(7), J_1 = 9.2, J_2 = 2.2); 7.68 (d, 1 H, H(6), J = 9.2); 8.89 (s, 1 H, H(2)); 10.71 (br.s, 1 H, OH)
15b	—	—	1600, 1580	—	3.88 (s, 6 H, OMe); 6.14 (s, 2 H, H(7), H(9)); 8.94 (s, 1 H, H(2))
15c	—	—	1600, 1585	—	3.91 (s, 3 H, OMe); 6.51 (d, 1 H, H(9), J = 2.2); 6.58 (dd, 1 H, H(7), J_1 = 9.0, J_2 = 2.2); 7.76 (d, 1 H, H(6), J = 9.0); 8.91 (s, 1 H, H(2))
17a	3450	—	1580	2235	7.49 (m, 3 H, H(3), H(4), H(5)); 8.00 (m, 2 H, H(2), H(6)); 14.65 (br.s, 1 H, NH)
17b	3430	—	1590	2220	2.54 (s, 3 H, Me); 7.33 (d, 2 H, H(3), H(5), J = 9.0); 7.87 (d, 2 H, H(2), H(6), J = 9.0); 14.46 (br.s, 1 H, NH)
17c	3445	—	1600	2225	2.35, 2.46 (both s, 3 H each, Me); 7.15—7.22 (m, 2 H, H(3), H(4)); 7.42 (s, 1 H, H(6)); 13.94 (br.s, 1 H, NH)
18a	3440	—	1585	1530 (1350)	7.48—7.67 (m, 5 H, Ph); 7.90 (s, 1 H, H(2)); 13.45 (br.s, 1 H, NH)
18b	3435	—	1580	1545 (1350)	—

5 mL of glacial AcOH. After 3 h, the solvent was evaporated and the residue was recrystallized from acetone.

C. Resorcinol (0.4 g, 3.61 mmol) was added with stirring at ~20 °C to a solution of diazonium salt **2b,c** (0.5 g, 2.45 mmol) in 6 *M* HCl. The mixture was kept for 1—1.5 h and the precipitate was filtered off and recrystallized from acetone.

D. Resorcinol (0.33 g, 3.01 mmol) was added at ~20 °C to a solution of diazo compound **1c** (0.5 g, 3.01 mmol) in 15 mL of MeCN. The reaction mixture was kept for 12 days. The solvent was evaporated *in vacuo* and the residue was triturated with ether and filtered. The precipitate was recrystallized from acetone.

4-Nitro-5-(2,4,6-trimethoxyphenyl)azoimidazole (6a), 2-(2,4,6-trimethoxyphenyl)azoimidazole-4,5-dicarbonitrile (6d), 4-nitro-5-(2,4-dimethoxyphenyl)azoimidazole (7a), 2-(2,4-dimethoxyphenyl)azoimidazole-4,5-dicarbonitrile (7d). ***A.*** 1,3,5-Trimethoxybenzene (0.56 g, 3.3 mmol) or 1,3-dimethoxybenzene (0.43 mL, 3.3 mmol) was added with stirring at ~20 °C to a solution of diazo compound **1a** or diazonium salt **2d** (3.0 mmol) in 15 mL of $CHCl_3$ or anhydrous MeCN. The reaction mixture was kept under these conditions until the diazo compound disappeared (see Table 1). The precipitate was filtered off and recrystallized from the corresponding solvent.

B. 1,3,5-Trimethoxybenzene (0.56 g, 3.3 mmol) or 1,3-dimethoxybenzene (0.43 mL, 3.3 mmol) was added to a mixture of diazonium salts **2a**,**d** (3.0 mmol) in 10 mL of glacial AcOH. The reaction mixture was kept at 70 °C until the starting compound disappeared (see Table 1). The precipitate was filtered off and washed with ether.

Ethyl 5-(2,4,6-trimethoxyphenyl)- (6b) and 5-(4-hydroxy-2,6-dimethoxyphenyl)azoimidazole-4-carboxylate (10b). Ethyl 5-diazoimidazole-4-carboxylate (**1b**) (0.5 g, 3.0 mmol) was dissolved in 5 mL of conc. AcOH, 1,3,5-trimethoxybenzene (0.56 g, 3.3 mmol) was added, and the mixture was left at ~20 °C for ~18 h. The solvent was evaporated and the dry residue containing compounds **6b** and **10b** was dissolved in a slight amount of EtOH and separated by column chromatography ($CHCl_3$—EtOH, 3 : 1). The yield of compound **6b** was 0.62 g (62%), that of compound **10b** was 0.14 g (15%).

Ethyl 5-(2-hydroxy-4,6-dimethoxyphenyl)azoimidazole-4-carboxylate (10b). Ethyl 5-diazoimidazole-carboxylate (**1b**) (0.5 g, 3.0 mmol) was dissolved in 10 mL of dry $CHCl_3$, 1,3,5-tri-

methoxybenzene (0.56 g, 3.3 mmol) was added, and the mixture was kept for 3 h at 60 °C. The solvent was evaporated *in vacuo*, the residue was suspended in Et_2O, and the yellow precipitate was filtered off.

4-R-5-(2,4,6-Trimethoxyphenyl)- (6b,c) and 4-R-5-(2,4-dimethoxyphenyl)azoimidazoles (7b,c) (general procedure). 1,3,5-Trimethoxybenzene (0.56 g, 3.3 mmol) or 1,3-dimethoxybenzene (0.43 mL, 3.3 mmol) was added with stirring at ~20 °C to a solution of 3 mmol of diazo compound **1b,c** (method *A*) or diazonium salt **2b,c** (method *B*) in 5 mL of glacial AcOH. The reaction mixture was kept under these conditions until the reaction was completed (see Table 1), and the precipitate was filtered off.

3-(2,4,6-Trimethoxyphenyl)- (6e) and 3-(2,4-dimethoxyphenyl)azo-1,2,4-triazole (7e). Crystalline $NaNO_2$ (0.49 g, 7.14 mmol) was added with vigorous stirring at 0 °C to a solution of 3-amino-1,2,4-triazole (0.5 g, 5.95 mmol) in 3 mL of 50% H_2SO_4. The reaction mixture was kept for 15 min under the same conditions, then 1,3,5-trimethoxybenzene (1.2 g, 7.14 mmol) or 1,3-dimethoxybenzene (0.93 mL, 7.14 mmol) was added, and the precipitate that formed was filtered off.

Ethyl 5-(4-hydroxy-2-methoxyphenyl)azoimidazole-4-carboxylate (10a). 1,3-Dimethoxybenzene (0.43 mL, 3.3 mmol) was added dropwise to a solution of diazo compound **1b** (0.5 g, 3.0 mmol) in 10 mL of anhydrous $CHCl_3$. The reaction mixture was kept at 60 °C for several days. The orange precipitate was filtered off.

Benzo[*e*]imidazo- (9a,b,e) and benzo[*e*]pyrazolo[5,1-*c*][1,2,4]triazines (9c,d,f). Azo compound **5b,c, 6b** (method *A*), **6c, 7c, 8**, or **10a**,**b** (method *B*) (2 mmol) was dissolved in 10 mL of conc. AcOH and *p*-toluenesulfonic acid (0.2 mmol) was added. The reaction mixture was kept at 80—90 °C (see Table 1), two-third of the solvent was distilled off *in vacuo* and the solution was cooled. The precipitate was filtered off and recrystallized from EtOH.

4-R-5-(4-Hydroxy-2-methylphenyl)azoimidazoles 11a,b and 4-R-5-(5-hydroxy-2-methylphenyl)azoimidazoles 12a,b (general procedure). ***A.*** *m*-Cresol or *p*-cresol (0.35 mL, 3.3 mmol) was added dropwise to a solution of diazoimidazole **1a,b** (3.0 mmol) in 10 mL of anhydrous $CHCl_3$. The reaction mixture was kept at ~20 °C until the reaction was completed (see Table 1). The orange-colored precipitate was filtered off and recrystallized from a $CHCl_3$—acetone mixture (10 : 1).

B. A solution of diazonium salt **2a**,**b** (3.0 mmol) and *m*-cresol or *p*-cresol (0.35 mL, 3.3 mmol) in 5 mL of conc. AcOH was kept at 80—90 °C until the initial diazoimidazole disappeared (see Table 1). In the case of synthesis of compounds **11a**,**b**, the orange-colored precipitate was filtered off and recrystallized from a $CHCl_3$—acetone mixture (10 : 1). In the synthesis of azo derivatives **12a**,**b**, the solvent was evaporated *in vacuo* and the residue was recrystallized from EtOH.

2-(4-Hydroxy-2-methylphenyl)- (11d) and 2-(5-hydroxy-2-methylphenyl)azoimidazole-4,5-dicarbonitrile (12d). *m*- or *p*-Cresol (0.36 g, 3.32 mmol) was added with stirring at ~20 °C to a solution of diazonium salt **2d** (0.5 g, 2.77 mmol) in 10 mL of anhydrous MeCN. The reaction mixture was kept at 80 °C for 1 h and 4 h, respectively. The solvent was evaporated *in vacuo* and the residue was recrystallized from EtOH.

3-(4-Methoxyphenyl)- (13a) and 3-(2,4,6-trimethylphenyl)azo-1,2,4-triazole (14a). An aqueous solution of $NaNO_2$ (0.49 g, 7.14 mmol) was added dropwise at 0 °C to a vigorously stirred solution of 3-amino-1,2,4-triazole (0.5 g, 5.95 mmol) in 5 mL of 30% H_2SO_4. The reaction mixture was kept under the same conditions for 15 min, and then anisole (0.82 mL, 7.14 mmol) or mesitylene (1.0 mL, 7.14 mmol) was added. The mixture was kept until the starting diazotriazole disappeared (see Table 1) and the precipitate was filtered off.

4-Nitroimidazole-5-diazonium phosphate (2a). Finely ground sodium nitrite (0.67 g, 9.77 mmol) was added at −10 °C over a period of 10 min to a vigorously stirred solution of 4-amino-5-nitroimidazole **16** (0.5 g, 3.91 mmol) in 5 mL of concentrated orthophosphoric acid. The temperature was raised to 0 °C during 0.5 h and then to +10 °C during 1 h. The mixture was stirred until the sodium nitrite grains disappeared. The product was not isolated but used immediately for the reaction with anisole and mesitylene.

4-Nitro-5-(4-methoxyphenyl)- (13b) and 4-nitro-5-(2,4,6-trimethylphenyl)azoimidazole (14b). ***A.*** Anisole (0.38 mL, 2.34 mmol) or mesitylene (0.33 mL, 2.34 mmol) was added to diazo solution of yellow-green salt **2a** and the temperature was raised to 20 °C, the mixture was stirred for 12 or 50 h, respectively and diluted with water, and the precipitate was filtered off and reprecipitated with water from ethanol.

B. Diazoimidazole **1a** (0.5 g, 3.6 mmol) was dissolved in 5 mL of glacial AcOH, then 1 mL of conc. H_2SO_4 and anisole (0.5 mL, 4.37 mmol) or mesitylene (0.62 mL, 4.37 mmol) were added successively at ~20 °C, the mixture kept for 20 or 84 h, respectively. The precipitate was filtered off and recrystallized from EtOH.

8-Hydroxybenzo[2,1-*e*]- (15a), 6,8-dimethoxybenzo[2,1-*e*]- (15b) and 8-methoxybenzo[2,1-*e*][1,2,4]triazolo[5,1-*c*]-*as*-triazine (15c). An aqueous solution of $NaNO_2$ (0.49 g, 7.14 mmol) was added dropwise at 0 °C to a vigorously stirred solution of 3-amino-1,2,4-triazole (0.5 g, 5.95 mmol) in 5 mL of 30% H_2SO_4. The reaction mixture was kept under the same conditions for 15 min, resorcinol (0.79 g, 7.18 mmol) (or 1,3,5-trimethoxybenzene (1.2 g, 7.14 mmol), or 1,3-dimethoxybenzene (0.93 mL, 7.14 mmol)) was added. After 20—60 min, the precipitate was filtered off.

Synthesis of 2-arylimidazole-4,5-dicarbonitriles 17a—c and 4-nitro-5-arylimidazoles 18a,b (general procedure). 4,5-Dicyanoimidazole-2-diazonium chloride (**2d**) or 4-nitro-5-diazoimidazole (**1a**) was suspended in benzene, toluene, or *p*-xylene. The reaction mixture was kept at about 60—70 °C (for **2d**) or at the arene boiling point (for **1a**) until the starting diazo compound disappeared (see Table 1). The solvent was evaporated *in vacuo* and the residue was triturated with *tert*-butyl methyl ether and crystallized from acetone.

MS **18b**, m/z (I_{rel} (%)): 204 (5.57); 203 (40.32); 183 (35.81); 103 (37.74); 92 (38.79); 91 (100); 77 (45.68); 65 (36.71).

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