Synthesis and properties of 5-diazoimidazoles and imidazolyl-5-diazonium salts

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Diazotization of 4-R-5-aminoimidazoles (R = CONHAr, CONHAlk, morpholinocarbonyl, or piperidinocarbonyl) with sodium nitrite in aqueous solutions of mineral acids afforded the corresponding 5-diazoimidazoles, whereas the reactions in concentrated tetrafluoroboric acid produced imidazolyl-5-diazonium salts. In the solid phase, diazonium salts are transformed into the corresponding diazo compounds.

Key words: diazotization, 5-diazoimidazoles, imidazolyl-5-diazonium salts, nitrosoamines, 3,7-dihydroimidazo[4,5-*d*]-1,2,3-triazin-4-ones.

Heterocyclic diazo compounds are highly reactive and are used for the preparation of new compounds, including those exhibiting biological activities. For example, 5-diazoimidazole-4-carboxamide serves as a precursor of the antitumor drugs dacarbazine[1] and temozolomide[2] employed in clinical practice.

Unlike the reactions of anthranilamides[3] giving rise to derivatives of annelated 1,2,3-triazin-4-ones, diazotization of aminoazoles containing the carbamoyl substituent in the *ortho* position with the respect to the amino group afforded the corresponding diazoazoles in the solid state.[4] In solutions, the resulting diazonium salts often lose the proton[5] and, hence, special conditions are required for the preparation of these compounds.[6,7] In addition, it is known that in aprotic media, diazoazoles, like aliphatic diazo derivatives, are involved in cycloaddition reactions, whereas diazonium salts of azoles react analogously to aromatic diazonium salts.[8] Nitrosoamines differ from both diazo compounds and diazonium salts in reactivity.[9] 1,2,3-Triazin-4-one derivatives are not subjected to the above-mentioned transformations.[3]

To study the behavior of imidazoles bearing the diazo function in reactions typical of this class of compounds, it is essential to prepare individual diazoimidazoles and imidazolyldiazonium salts and examine the conditions of their interconversions and cyclization giving rise to imidazotriazinones.

The introduction of the aryl or cycloalkyl substituents into the amide group of 5-diazoimidazole-4-carboxamide opens up considerable possibilities of solving this problem. In the present study, we synthesized new 4-(*N*-alkyl)- and 4-(*N*-aryl)-5-diazoimidazole-4-carboxamides and the corresponding diazonium salts in individual form and investigated the physicochemical properties of 2- and 5-diazoimidazoles.

We studied diazotization of 5-aminoimidazoles **1a—h** in different media. Under the conditions of strict temperature control (−5—0 °C), the reactions of amines **1a—d,f—h** with $NaNO_2$ in dilute HCl afforded solid individual 4-substituted 5-diazoimidazoles **2a—d,f—h** in 75—89% yields in spite of the fact that the latter can undergo cyclization to give imidazotriazinones **3** analogously to diazoimidazolecarboxamides **2i,j**.[10]

Under the same reaction conditions, aminoimidazole **1e** gave only the intramolecular cyclization product, *viz.*, 3-(*p*-ethoxycarbonylphenyl)-3,7-dihydroimidazo[4,5-*d*]-1,2,3-triazin-4-one (**3e**). In the IR spectrum of **3e**, absorption bands in the region of 2100—2300 cm^{-1} are absent and the absorption band of the C=O bond is observed at 1700 cm^{-1} (Table 1). Diazoimidazole **2e** was synthesized by diazotization of amine **1e** with ethyl nitrite in an aprotic medium.

Treatment of amines **1a—e** with crystalline $NaNO_2$ in 50% HBF_4 afforded the corresponding diazonium tetrafluoroborates **4a—e** in the solid state. The fact that diazonium salts **4f—l** were not isolated in the solid state neither under the analogous conditions nor upon the addition of sodium tetrafluoroborate or $SbCl_5$ to solutions of diazo compounds **2f—l** is, apparently, attributable to high solubility of these salts. Because of this, we used solutions of salts **4f—l** in dilute mineral or organic acids in subsequent studies.

The addition of BF_3 etherate to a suspension of diazo compound **2a** in diethyl ether also afforded a solution. However, according to the results of IR spectroscopy, the solid residue obtained after the removal of the solvent consisted of *N*-(*p*-tolyl)azahypoxanthine (**3a**) and diazonium salt **4a**.

The structures of individual diazoimidazoles **2a—h** and diazonium salts **4a—e** were studied by ^1H NMR and IR

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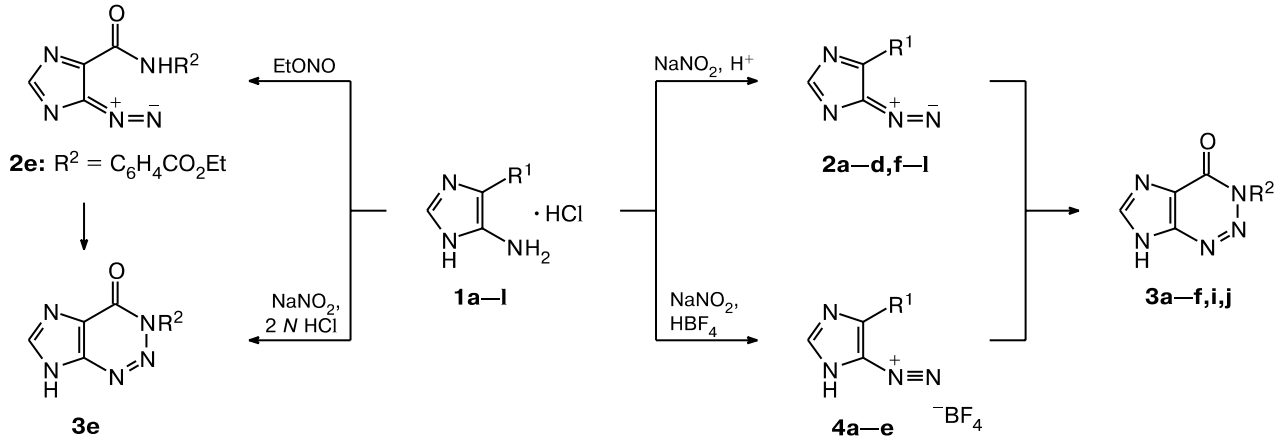
Scheme 1



1, 2, 4: R^1 = CONHTol-*p* (**a**), CONHTol-*o* (**b**), $CONHC_6H_4OMe$-*p* (**c**), $CONHC_6H_4Cl$-*p* (**d**), $CONHC_6H_4CO_2Et$-*p* (**e**), $CONHC_6H_{11}$-*cyclo* (**f**), morpholinocarbonyl (**g**), piperidinocarbonyl (**h**), CONHMe (**i**), $CONH_2$ (**j**), CO_2Et (**k**), NO_2 (**l**)
3: R^2 = Tol-*p* (**a**), Tol-*o* (**b**), C_6H_4OMe-*p* (**c**), C_6H_4Cl-*p* (**d**), $C_6H_4CO_2Et$-*p* (**e**), C_6H_{11}-*cyclo* (**f**), Me (**i**), H (**j**)

spectroscopy. The IR spectra of compounds **2a—h** (in KBr pellets) have a narrow intense stretching absorption band of the diazo group in the region of 2160—2180 cm^{-1}. In the spectra of compounds **4a—e** and salts **4i—k**, the stretching absorption band of the diazonium function is shifted to 2265—2280 cm^{-1} (KBr) and 2235—2265 cm^{-1} (H_2SO_4), respectively. The ^1H NMR spectra of diazoimidazoles **2a—h** have a singlet for the proton at the C(2) atom of the imidazole ring and signals characteristic of either aromatic protons or protons of the cycloalkyl fragment in the carboxamide substituent. In addition, the spectra of these compounds differ from those of salts **4a—e** (see Table 1) in that they do not show the signal for the proton at δ 13—14 corresponding to the NH group of the imidazole ring.

The ^1H NMR spectra (DMSO-d_6 and CF_3COOD) of diazoimidazoles **2** were compared with those of the corresponding diazonium salts **4** (see Table 1). In the spectra of the latter compounds, the signal for the proton bound to the second carbon atom of the imidazole ring is shifted downfield (δ 8.26—8.62) compared to that in the spectra of diazo compounds **2** (δ 7.61—7.74). This provides evidence that the electron density in heteroaromatic compounds is decreased, which is, apparently, responsible for an increase in the electrophilicity of the diazonium group and, as a consequence, for an increase in its reactivity.

Under the conditions of ^1H NMR spectroscopic experiments in CF_3COOD, diazo compounds **2i—k** were transformed into diazonium salts **4i—k**. The NMR spectra of compounds **2i,j** in CF_3COOD have also signals for the protons corresponding to the imidazotriazinone structure **3i,j**, *i.e.*, intramolecular cyclization proceeds rather rapidly under these conditions. Dissolution of nitrodiazoimidazole **2l** in CF_3COOD did not lead to its transformation into diazonium salt **4l** (see Table 1). In the ^1H NMR spectrum in D_2SO_4 ($Me_4N^+I^-$ as the standard), the signal for the proton is shifted downfield, which is indicative of the transformation of compound **2l** into diazonium salt **4l**. The value of the shift δ given in Table 1 takes into account the chemical shift of $Me_4N^+I^-$ with respect to Me_4Si.

Earlier,[11,12] our studies of acid-base transformations in the series of diazoimidazoles demonstrated that products of the prototropic equilibrium between diazonium salts **4j,k,l** and diazo compounds **2j,k,l** were produced along with 4-substituted 5-nitrosoaminoimidazoles. In the present study, we investigated the equilibrium between diazoimidazoles **2** and the corresponding diazonium salts **4**, which were synthesized for the first time, by UV spectroscopy.

Analysis of the UV spectra of diazo compounds **2g,h**, which cannot undergo intramolecular cyclization, in chloroform, water, and 5—50% aqueous solutions of HBF_4 demonstrated that an increase in the concentration of the acid led to the shift of the absorption maximum from 320—326 to 295—296 nm, which is indicative of the formation of diazonium salts **4g,h**. This is evidence in favor of the occurrence of the acid-base equilibrium between the diazonium salts and diazo compounds. A change in pH of the solution can completely shift the equilibrium to either diazo compounds or diazonium salts. However, spectrophotometric study demonstrated that the group of spectral curves does not pass through an isobestic point, as in the case of compounds **2i—l**.[11,12] Consequently, the equilibrium mixture under study contained not only diazoimidazoles **2g,h** and the corresponding diazonium salts **4g,h** but also nitrosoamines as third components.

Diazo compounds **2a—d** in MeCN absorb at 330—338 nm, whereas the absorption maximum in the

Table 1. Spectroscopic characteristics of compounds **2—4**

Compound	IR, ν/cm^{-1}					^{1}H NMR (DMSO-d$_6$, δ, *J*/Hz)
	NH	N_2^+ or $=N^+=N^-$	C=O	BF_4	C=N	
2a	3290	2170	1670	—	—	10.46 (br.s, 1 H, NH); 7.74 (d, 2 H, Ar, *J* = 8.2); **7.72** (s, 1 H, Im); 7.16 (d, 2 H, Ar, *J* = 8.2); 2.28 (s, 3 H, Me)
2b	3330	2170	1665	—	—	10.54 (s, 1 H, NH); **7.71** (s, 1 H, Im); 7.65—7.23 (m, 4 H, Ar); 2.18 (s, 3 H, Me)
2c	3330	2160	1660	—	—	
2d	3275	2175	1670	—	—	10.82 (br.s, 1 H, NH); 7.90 (d, 2 H, Ar, *J* = 8.8); **7.74** (s, 1 H, Im); 7.42 (d, 2 H, Ar, *J* = 8.8)
2f	—	2170	1650	—	—	8.49 (m, 1 H, N<u>H</u>C$_6$H$_{11}$); **7.64** (s, 1 H, Im); 3.74 (m, 1 H, NHC$_6$<u>H</u>$_{11}$); 1.91—1.30 (m, 10 H, NHC$_6$<u>H</u>$_{11}$)
2g	—	2180	1620	—	—	**7.64** (s, 1 H, Im); 4.37 (m, 2 H, CH_2); 3.65 (m, 6 H, 3 CH_2)
2h	—	2170	1630	—	—	**7.61** (s, 1 H, Im); 4.27 and 3.60 (both m, 2 H each, CH_2); 1.56 (m, 6 H, 3 CH_2)
2i	3320	2170	1650	—	—	8.63 (m, 1 H, N<u>H</u>Me); **7.62** (s, 1 H, Im); 2.77 (d, 3 H, NHC<u>H</u>$_3$, *J* = 4.9)
2j	3350, 3290	2180	1695	—	—	8.01 and 7.83 (both br.s, 1 H each, NH_2); **7.61** (s, 1 H, Im)
2k	—	2190	1720	—	—	**7.69** (s, 1 H, Im); 4.36 (q, 2 H, OC<u>H</u>$_2$Me, *J* = 7.0); 1.33 (t, 3 H, OCH$_2$C<u>H</u>$_3$, *J* = 7.0)
2l	—	2220	1540, 1360 (NO_2)		—	**7.72** (s, 1 H, Im)
3a	3440	—	1700	—	1620, 1590	14.33 (br.s, 1 H, NH); 8.40 (s, 1 H, Im); 7.42 and 7.35 (both d, 2 H each, Ar, *J* = 8.0); 2.45 (s, 3 H, Me)
3b	3420	—	1705	—	1600, 1590	14.38 (br.s, 1 H, NH); 8.45 (s, 1 H, Im); 7.48—7.32 (m, 4 H, Ar); 2.11 (s, 3 H, Me)
3c	3470	—	1715	—	1620, 1595	14.23 (br.s, 1 H, NH); 8.39 (s, 1 H, Im); 7.45 and 7.06 (both d, 2 H each, Ar, *J* = 8.8); 3.86 (s, 3 H, OMe)
3d	3460	—	1710	—	1605, 1595	14.22 (br.s, 1 H, NH); 8.43 (s, 1 H, Im); 7.61 and 7.57 (both d, 2 H each, Ar, *J* = 9.3)
3e	3410	—	1700, 1680	—	1610, 1595	14.20 (br.s, 1 H, NH); 8.44 (s, 1 H, Im); 8.15 and 7.74 (both d, 2 H each, Ar, *J* = 8.5); 4.38 (q, 2 H, OC<u>H</u>$_2$CH$_3$, *J* = 7.0); 1.40 (t, 3 H, OCH$_2$C<u>H</u>$_3$, *J* = 7.0)
3f	3390	—	1630	—	1600, 1590	13.57 (br.s, 1 H, NH); 8.53 (s, 1 H, Im); 3.74 (m, 1 H, CH); 1.88—1.10 (m, 10 H, 5 CH_2)
3i	3425	—	1710	—	1600, 1590	12.56 (br.s, 1 H, NH); 8.49 (s, 1H, Im); 3.97 (s, 3 H, Me) 9.53 (s, 1 H, Im); 4.38 (s, 3 H, Me)*
3j	3420	—	1690	—	1605, 1600	14.81 (br.s, 2 H, 2 NH); 8.49 (s, 1 H, Im) 9.49 (s, 1 H, Im)*
4a	3510, 3470, 3310	2265	1670	1080	—	13.37 (br.s, 1 H, NH); 10.56 (s, 1 H, NH); **8.59** (s, 1 H, Im); 7.47 and 7.39 (both d, 2 H each, Ar, *J* = 8.2); 2.42 (s, 3 H, Me)
4b	3500, 3450, 3300	2260	1670	1075	—	13.38 (br.s, 1 H, NH); 10.61 (s, 1 H, NH); **8.62** (s, 1 H, Im); 7.58—7.43 (m, 4 H, Ar); 2.23 (s, 3 H, Me)
4c	3380, 3260, 3200	2255	1660	1070	—	13.87 (br.s, 1 H, NH); 10.55 (s, 1 H, NH); **8.59** (s, 1 H, Im); 7.51 and 7.12 (both d, 2 H each, Ar, *J* = 8.8); 3.85 (s, 3 H, OMe)
4d	3470, 3350, 3330	2280	1670	1080	—	14.03 (br.s, 1 H, NH); 9.71 (s, 1 H, NH); **8.57** (s, 1 H, Im); 7.64 and 7.31 (both d, 2 H each, Ar, *J* = 8.8)
4e	3470, 3350, 3330	2270	1680, 1660	1080	—	14.21 (br.s, 1 H, NH); 10.31 (s, 1 H, NH); **8.59** (s, 1 H, Im); 8.16 and 7.80 (both d, 2 H each, Ar, *J* = 8.2); 4.38 (q, 2 H, OC<u>H</u>$_2$Me, *J* = 7.0); 1.37 (t, 3 H, OCH$_2$C<u>H</u>$_3$, *J* = 7.0)
4g						**8.30** (s, 1 H, Im); 4.12 and 4.06 (both m, 4 H each, CH_2)*
4i	3440	2235	1650	—	—	**8.29** (s, 1 H, Im); 3.20 (s, 3 H, Me)*
4j		2240		—	—	**8.30** (s, 1 H, Im)*
4k	3450	2265	1705	1070	—	**8.26** (s, 1 H, Im); 4.70 (q, 2 H, OC<u>H</u>$_2$Me, *J* = 7.0); 1.53 (t, 3 H, OCH$_2$C<u>H</u>$_3$, *J* = 7.0)*
4l				—	—	**7.99** (s, 1 H, Im)* or **8.43** (s, 1 H, Im)**

* In CF_3COOD.
** In D_2SO_4.

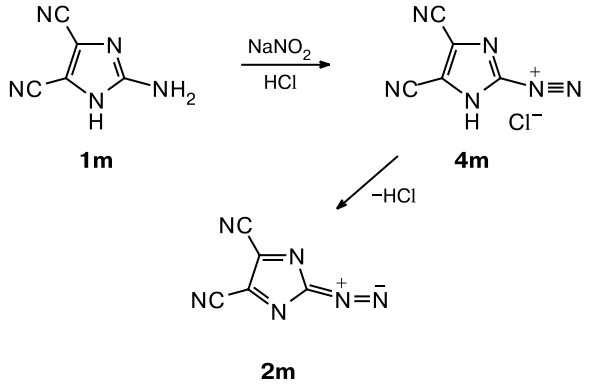
spectra in concentrated HBF_4 is shifted to 293—296 nm, which corresponds to the absorption maximum in the spectra of crystalline diazonium salts **4a—d** in MeCN. Therefore, the diazo compounds in concentrated acids are transformed into the corresponding diazonium salts. However, we failed to carry out the reverse transformation of diazonium salts **4a—e**, which readily undergo cyclization to azahypoxanthine derivatives **3a—e**, into the corresponding diazo compounds **2a—e** by gradually decreasing the concentration of the acid in a UV cell. The reason is that the presence of water even in insignificant amounts leads to the rapid transformation of the diazonium salts into the diazo compounds followed by the transformation into the imidazotriazinone ring. Thus, the IR spectrum of salt **4a** washed with a minimum amount of water shows an absorption band at 2265 cm^{-1} along with a more intense band at 2170 cm^{-1} corresponding to diazo compound **2a**, whereas these diazonium salts in an equimolar mixture of water and 4-(arylcarbamoyl)imidazole-5-diazonium tetrafluoroborates **4a—e** are very rapidly transformed into 3-arylimidazotriazin-4-ones **3a—e**.

It should be noted that solid 5-imidazolyldiazonium salts **4a—e** and diazo compounds **2a—e** are also very unstable on storage in the dark at room temperature. After one month, they undergo cyclization to imidazotriazinones in quantitative yields. In the IR spectra of the diazonium salts and diazo compounds recorded within 14 days after their preparation, the intensities of the stretching absorption bands of the diazonium and diazo groups decreased and a new absorption band appeared at 1700—1715 cm^{-1}, which corresponds to the C=O bond of the triazinone structure. After one month, the absorption bands of the diazonium or diazo group as well as of the amide carbonyl group at 1660—1680 cm^{-1} completely disappeared.

Unexpectedly, elemental analysis and IR spectroscopy demonstrated that diazotization of 2-aminoimidazole-4,5-dicarbonitrile (**1m**) with sodium nitrite in dilute HCl afforded 4,5-dicyanoimidazole-2-diazonium salt (**4m**; ν_{NN} = 2290 cm^{-1}) rather than 2-diazoimidazole-4,5-dicarbonitrile (**2m**; ν_{NN} = 2250 cm^{-1}), as has been reported earlier.[13] Recrystallization of salt **4m** from dry acetonitrile or its storage in the solid state in the dark at room temperature for 2—3 days gave diazo compound **2m** (Scheme 2). In our opinion, this transformation accounts for some differences in the reactivity, which have been observed earlier by other research groups.[14,15]

To summarize, under the conditions used for diazotization, the diazonium salts and diazo compounds were isolated in individual form.

Scheme 2



Experimental

Spectroscopic studies were carried out with the use of analytically and chromatographically pure samples. The IR spectra were recorded on a Specord IR-75 instrument (in KBr pellets and CaF_2 cells). The UV spectra were measured on a Beckman-26 spectrophotometer. The ^1H NMR spectra were recorded on a Brucker WR-250 instrument (250 MHz) (δ scale, Me_4Si as the internal standard). The course of the reactions and purities of the compounds were monitored by TLC on Silufol UV-254 and Sorbifil UV-254 plates (silica gel CTX-1A as the sorbent) in the Bu^nOH—AcOH—H_2O (4 : 1 : 1) and $CHCl_3$—EtOH (3 : 1 and 10 : 1) solvent systems.

The results of elemental analysis of the compounds for C, H, N, and Cl are consistent with the calculated data. The melting points (Table 2) were not corrected. The spectroscopic characteristics of the compounds are given in Table 1.

The starting 5-aminoimidazole-4-carboxamide[16] (**1j**), 5-aminoimidazole-4-(*N*-methyl)carboxamide[17,18] (**1i**), 5-aminoimidazole-4-(*N*-aryl)carboxamides[19] **1a—e**, 5-aminoimidazole-4-(*N*-cycloalkyl)carboxamides[19] **1f—h**, 5-amino-4-nitroimidazole[20] (**1l**), and ethyl 5-aminoimidazole-4-carboxylate[21] (**1k**) were synthesized according to procedures described earlier. 2-Amino-4,5-dicyanoimidazole (**1m**) was commercially available.

5-Diazoimidazole-4-[*N*-(*p*-tolyl)]carboxamide (2a), 5-diazoimidazole-4-[*N*-(*o*-tolyl)]carboxamide (2b), 5-diazoimidazole-4-[*N*-(*p*-methoxyphenyl)]carboxamide (2c), and 4-[*N*-(*p*-chlorophenyl)]-5-diazoimidazolecarboxamide (2d) (general procedure). A cooled solution of $NaNO_2$ (0.08 g, 1.2 mmol) in water (2 mL) was added portionwise with vigorous stirring to a suspension of 5-aminoimidazole-4-(*N*-aryl)carboxamide hydrochloride **1a—d** (1 mmol) in 1 *N* HCl (6 mL, 2 mmol) at 0 °C. The reaction mixture was stirred at this temperature for 5—10 min. The precipitate that formed was filtered off, washed with Et_2O, and dried *in vacuo*.

5-Diazoimidazole-4-[*N*-(*p*-ethoxycarbonylphenyl)]carboxamide (2e). Ethyl nitrite (0.4 mL, 4.8 mmol) was added to a mixture of 5-aminoimidazole-4-[*N*-(*p*-ethoxycarbonylphenyl)]carboxamide (**1e**) (1 g, 3.2 mmol) and dry dioxane (50 mL) saturated with HCl and cooled to 0 °C. The reaction mixture was stirred with cooling for 2 h. The precipitate that formed was filtered off. The filtrate was concentrated *in vacuo*. The residue was suspended in Et_2O (5 mL), filtered off, and dried *in vacuo*.

4-(*N*-Cyclohexyl)-5-diazoimidazolecarboxamide (2f). A cooled solution of $NaNO_2$ (0.34 g, 4.9 mmol) in water (3 mL) was added portionwise with vigorous stirring to a solution of

Table 2. Yields, melting points, retention factors, and elemental analysis data for the compounds synthesized

Compound	Yield (%)	M.p. /°C	R_f (eluent)	Found / Calculated (%)				Molecular formula
				C	H	N	Cl	
2a	89	85—86	0.71 (*a*)	57.88	4.32	30.34	—	$C_{11}H_9N_5O$
				58.15	3.99	30.82		
2b	80	94—95	0.66 (*a*)	57.95	4.36	30.51	—	$C_{11}H_9N_5O$
				58.15	3.99	30.82		
2c	84	97—99	0.70 (*a*)	54.04	3.94	28.47	—	$C_{11}H_9N_5O_2$
				54.32	3.73	28.79		
2d	75	140—142	0.68 (*a*)	48.12	2.67	27.94	14.53	$C_{10}H_6ClN_5O$
				48.50	2.44	28.28	14.32	
2e	17	67—69	0.57 (*a*)	54.62	3.94	24.67	—	$C_{13}H_{11}N_5O_3$
				54.74	3.89	24.55		
2f	77	76—77	0.80 (*a*)	54.51	6.35	31.72	—	$C_{10}H_{13}N_5O$
				54.78	5.98	31.94		
2g	82	64—65	0.59 (*a*)	46.17	4.42	33.73	—	$C_8H_9N_5O_2$
				46.38	4.38	33.80		
2h	81	55—56	0.62 (*a*)	52.76	5.42	34.05	—	$C_9H_{11}N_5O$
				52.68	5.40	34.13		
3a	83 (***A***)	213—215	0.56 (*b*)	58.11	4.02	30.88	—	$C_{11}H_9N_5O$
	87 (***B***)			58.15	3.99	30.82		
3b	88 (***A***)	207—209	0.47 (*a*)	58.03	4.07	30.67	—	$C_{11}H_9N_5O$
	80 (***B***)			58.15	3.99	30.82		
3c	79 (***A***)	201—205	0.43 (*a*)	54.24	3.76	28.92	—	$C_{11}H_9N_5O_2$
	82 (***B***)			54.32	3.73	28.79		
3d	84 (***A***)	219—221	0.63 (*b*)	48.62	2.51	28.14	14.53	$C_{10}H_6ClN_5O$
	80 (***B***)			48.50	2.44	28.28	14.32	
3e	79 (***A***)	218—220	0.70 (*b*)	54.65	3.93	24.61	—	$C_{13}H_{11}N_5O_3$
	75 (***B***)			54.74	3.89	24.55		
3f	71	187—189	0.46 (*b*)	54.85	6.03	32.02	—	$C_{10}H_{13}N_5O$
				54.78	5.98	31.94		
4a	98	77—79	0.55 (*c*)	41.48	3.02	22.00	—	$C_{11}H_{10}N_5O \cdot BF_4$
				41.94	3.20	22.23		
4b	92	94—96	0.78 (*c*)	41.54	3.11	21.93	—	$C_{11}H_{10}N_5O \cdot BF_4$
				41.94	3.20	22.23		
4c	91	128—130	0.82 (*c*)	39.58	3.33	20.77	—	$C_{11}H_{10}N_5O_2 \cdot BF_4$
				39.91	3.04	21.16		
4d	89	65—66	0.64 (*c*)	35.35	2.44	20.51	10.12	$C_{10}H_7ClN_5O \cdot BF_4$
				35.81	2.10	20.88	10.57	
4e	91	60—61	0.75 (*c*)	41.54	3.37	18.30	—	$C_{13}H_{12}N_5O_3 \cdot BF_4$
				41.85	3.24	18.77		
4m	96	148—150	0.82 (*a*)	33.35	0.58	46.23	19.47	C_5HN_6Cl
				33.26	0.56	46.55	19.64	

* The following solvent systems were used: *a*, $CHCl_3$—EtOH (3 : 1); *b*, $CHCl_3$—EtOH (10 : 1); *c*, Bu^nOH—AcOH—H_2O (4 : 1 : 1).

5-aminoimidazole-4-(*N*-cyclohexyl)carboxamide hydrochloride (**1f**) (1 g, 4.1 mmol) in 1 *N* HCl (23 mL, 8.2 mmol) at 0 °C. The reaction mixture was stirred at this temperature for 15—20 min and then extracted with chloroform. The extract was concentrated *in vacuo* and the oily residue was triturated with *tert*-butyl methyl ether to form a bright-yellow precipitate.

5-Diazoimidazole-4-carboxylic acid morpholide (2g) and 5-diazoimidazole-4-carboxylic acid piperidide (2h) (general procedure). A cooled solution of $NaNO_2$ (0.36 g, 5.2 mmol) in water (3 mL) was added portionwise with vigorous stirring to a solution of amine **1g,h** (1 g, 4.3 mmol) in 1 *N* HCl (24 mL, 8.6 mmol) at 0 °C. The reaction mixture was stirred at this temperature for 15—20 min. The yellow precipitate that formed was filtered off, washed with Et_2O, and dried *in vacuo*. An additional amount of the diazo compound was extracted from an acidic filtrate in $CHCl_3$ and the extract was concentrated *in vacuo*.

3-(*p*-Tolyl)-3,7-dihydroimidazo[4,5-*d*]-1,2,3-triazin-4-one (3a), 3-(*o*-tolyl)-3,7-dihydroimidazo[4,5-*d*]-1,2,3-triazin-4-one (3b), 3-(*p*-methoxyphenyl)-3,7-dihydroimidazo[4,5-*d*]-1,2,3-

triazin-4-one (3c), and 3-(*p*-chlorophenyl)-3,7-dihydroimidazo[4,5-*d*]-1,2,3-triazin-4-one (3d) (general procedure). 4-Arylcarbamoylimidazole-5-diazonium tetrafluoroborate (**4a—d**, method ***A***) or 5-diazoimidazole-4-(*N*-aryl)carboxamide (**2a—d**, method ***B***) (1 g) was suspended in water (15 mL). The reaction mixture was kept at 30 min. The precipitate that formed was filtered off, crystallized from EtOH, and dried.

3-(*p*-Ethoxycarbonylphenyl)-3,7-dihydroimidazo[4,5-*d*]-1,2,3-triazin-4-one (3e). ***A.*** 4-(*p*-Ethoxycarbonylphenyl)carbamoylimidazole-5-diazonium tetrafluoroborate (**4e**) (1 g, 2.68 mmol) was suspended in water (15 mL). The reaction mixture was kept for 30 min. The precipitate that formed was filtered off, crystallized from EtOH, and dried.

B. A cooled solution of $NaNO_2$ (0.27 g, 3.9 mmol) in water (3 mL) was added portionwise with vigorous stirring to a suspension of 5-aminoimidazole-4-[*N*-(*p*-ethoxycarbonylphenyl)]carboxamide hydrochloride (**1e**) (1 g, 3.2 mmol) in 1 *N* HCl (18 mL, 6.4 mmol) at 0 °C. The reaction mixture was kept for 5 min, The precipitate that formed was filtered off, crystallized from EtOH, and dried *in vacuo*.

3-Cyclohexyl-3,7-dihydroimidazo[4,5-*d*]-1,2,3-triazin-4-one (3f). 5-Diazoimidazole-4-(*N*-cyclohexyl)carboxamide (**2f**) (1 g, 4.6 mmol) was suspended in a 1 *N* NH_3 solution (5 mL). The reaction mixture was kept for 1 h and then the solution was cleared with activated carbon. The precipitate that formed was filtered off and the filtrate was concentrated *in vacuo*. The residue was crystallized from EtOH and dried.

4-[*N*-(*p*-Tolyl)carbamoyl]imidazole-5-diazonium (4a), 4-[*N*-(*o*-tolyl)carbamoyl]imidazole-5-diazonium (4b), 4-[*N*-(*p*-methoxyphenyl)carbamoyl]imidazole-5-diazonium (4c), 4-[*N*-(*p*-chlorophenyl)carbamoyl]imidazole-5-diazonium (4d), and 4-[*N*-(*p*-ethoxycarbonylphenyl)carbamoyl]imidazole-5-diazonium (4e) tetrafluoroborates (general procedure). Crystalline $NaNO_2$ (2.4 mmol) was added with stirring to a suspension of 5-aminoimidazole-4-(*N*-aryl)carboxamide hydrochloride **1a—e** (1 mmol) in 50% HBF_4 (ρ = 1.41 g cm^{-3}) (5 mL) at −5 °C. The reaction mixture was kept for 3—5 min. The precipitate that formed was filtered off and dried *in vacuo*.

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