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Electrochemical Synthesis of Heterocyclic Compounds. 17. Anodic Oxidation of Hydrazones in the Presence of Heteroaromatic and Schiff Bases[1]

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Anodic oxidation of a series of hydrazones in the presence of heteroaromatic and Schiff bases were performed in acetonitrile–tetraethylammonium perchlorate electrolyte solution at platinum using controlled potentials. As a result of four-electron oxidation several *s*-triazolo[4,3-*a*]pyridinium perchlorates (**1–9**), *s*-triazolo[4,3-*a*]quinolinium perchlorate (**10**), *s*-triazolo[3,4-*a*]isoquinolinium perchlorate (**11**), and *s*-triazolo[4,3-*a*]benzo[*f*]quinolinium perchlorate (**12**) were obtained in yields ranging from 30% to 90%. As a result of two-electron oxidation of [*p*-(*N*,*N*-dimethylamino)benzylidene]-*p*-nitrophenylhydrazine (A) in the presence of imidazole and 1,2,4-triazole the azo derivatives **13** and **14** were obtained with high yields. As a result of two-electron oxidation of hydrazone A in the presence of Schiff bases the new Schiff bases **15–20** were obtained in high yields. On the bases of the electroanalytical and preparative results it is concluded that the electrochemical oxidation of hydrazone A in the presence of heteroaromatic and Schiff bases occurs through the formation of cation B, which is attacked by base as a nucelophile. This excludes the possibility of annelation of the heteroaromatics through nitrilimine as an intermediate.

Continuing interest in electrochemical synthesis of heterocyclic compounds during the last decade is related to the wide range of applications of the electrolysis as a tool to induce ring-closure reactions.[2] In a previous paper,[3] we described the synthesis of *s*-triazolo[4,3-*a*]pyridinium salts by anodic oxidation of hydrazones in the presence of pyridine. As our working hypothesis, the formation of these products was explained in terms of the formation of the nitrilimine as an intermediate and subsequent 1,3-dipolar cycloaddition.[6] By using the same method, Jugelt and co-workers have recently reported several examples of the synthesis of *s*-triazolo[4,3-*a*]pyridinium and *s*-triazolo[4,3-*a*]quinolinium perchlorates.[4,5] In the present research we have examined anodic oxidation of hydrazones in the presence of various heteroaromatic and Schiff bases in order to gain a better understanding of these reactions. This report describes the results together with a discussion of the reaction mechanism.

Results and Discussion

Electrochemical Studies. The oxidations of [*p*-(*N*,*N*-dimethylamino)benzylidene]-*p*-nitrophenylhydrazine (A) were studied in some detail. All of the electrochemical studies were conducted by using acetonitrile–tetraethylammonium perchlorate (0.1 M) solution. A single compartment cell containing a saturated calomel electrode was employed, the counter electrode was a platinum sheet, and the working electrode was a polished disk of platinum (diameter = 1 or 3 mm).

Typical cyclic voltammograms for oxidation of [*p*-(*N*,*N*-dimethylamino)benzylidine]-*p*-nitrophenylhydrazine (A) and 1-(*p*-nitrophenyl)-3-[*p*-(*N*,*N*-dimethylamino)phenyl]-*s*-triazolo[4,3-*a*]pyridinium perchlorate (**1**), which is the final product after preparative electrolysis, are shown in Figure 1. Cyclic voltammogram of A exhibit two anodic waves at 0.59 and 1.27 V (Figure 1a). The first peak corresponds to the oxidation of the parent molecule and the second peak to the oxidation of A protonated by protons liberated along the first wave. Sweep reversal from the anodic to the cathodic side causes the appearance of one reduction peak at 0.43 V corresponding presumably to the reduction of the cation formed. Upon reversal of the scan direction after the first peak the same reduction peak was observed with peak separation $E_p^a - E_p^c = 160$ mV.[7] The shape of the cyclic voltammogram for A is essentially similar to those reported for a two-electron oxidation of *p*-(*N*,*N*-dimethylamino)phenol.[8,9] After addition of the pyridine as a base the potential of the first wave shifted to the cathodic side and wave doubled in height (Figure 1b). The reduction peak at 0.43 V disappeared, indicating further reaction of pyridine by the cation formed. The final product **1** is oxidized at 1.37 V (Figure 1c). This behavior permits selective oxidation of A in the presence of pyridine by using controlled potential electrolysis at the potential of the first wave. Cyclic voltammograms of A in the presence of the other heteroaromatic bases (runs 1–14 in Table I) show essentially identical shapes with those shown in Figure 1b.

The conclusions about the nature of the anodic peaks were substantiated by further voltammetric studies at a rotating disk electrode. The results of rotating disk voltammetry are shown in Figure 2. Current–potential curve of A shows the presence of two waves at 0.55 and 1.31 V, respectively, for oxidation in acetonitrile (Figure 2a). After the addition of pyridine as a base the first wave doubled in height (Figure 2b). After the addition of perchloric acid (Figure 2c) the first wave disappeared and the second wave increased. It is important to point out that the cyclic voltammogram of A run in the presence of perchloric acid showed the anodic peak at 1.27 V and one reduction peak around 0.43 V corresponding to the cation formed. Thus, the experiments described confirm that the first wave represents oxidation of the parent hydrazone, A, and the

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(1) Part 16 in this series: Saničanin, Ž.; Tabakovič, I. *Tetrahedron Lett.* **1986**, 407.
(2) Lund, H.; Tabakovič, I. *Adv. Heterocycl. Chem.* **1984**, *36*, 235.
(3) Tabakovič, I.; Crljenak, S. *Heterocycles* **1981**, *16*, 699.
(4) Jugelt, W.; Grubert, L. *Z. Chem.* **1985**, *25*, 408.
(5) Jugelt, W.; Grubert, L.; Paulss, V. *Z. Chem.* **1985**, *25*, 443.
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(7) The position of the peaks in cyclic voltammograms are dependent on "dryness" of acetonitrile changing by ±20 mV.
(8) Chatten, L. G.; Fleischmann, M.; Pletcher, D. *J. Electroanal. Chem.* **1986**, *18*, 175.
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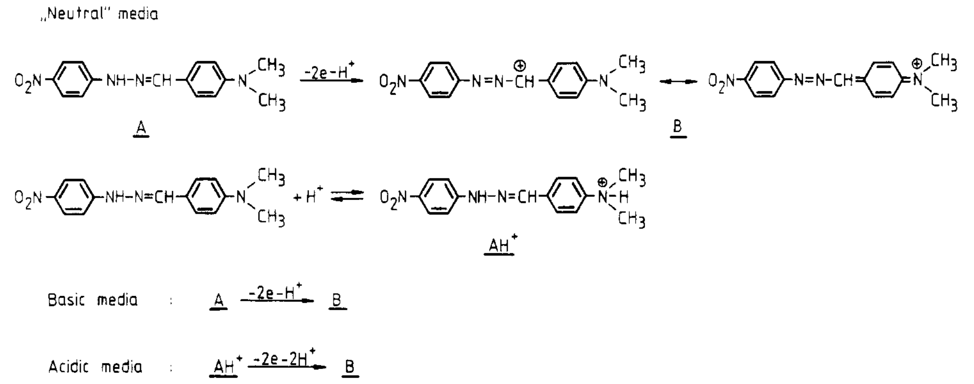
Table I. Electroanalytical Data[a]

run	hydrazone $Ar_1NHN{=}CHAr_2$, Ar_1, Ar_2	base	E_p,[b] V	$i_l/w^{1/2}$,[c] $\mu A/(rps)^{1/2}$	n[d]
1	p-$NO_2C_6H_4$, p-$(CH_3)_2NC_6H_4$	pyridine	0.520	19.73	4.0
2	p-BrC_6H_4, p-$(CH_3)_2NC_6H_4$	pyridine	0.520	19.85	3.7
3	p-ClC_6H_4, p-$(CH_3)_2NC_6H_4$	pyridine	0.540	19.90	3.8
4	p-$NO_2C_6H_4$, C_6H_5	pyridine	1.210	21.10	3.4
5	p-$NO_2C_6H_4$, p-$NO_2C_6H_4$	pyridine	1.280	19.50	3.9
6	$p\infty NO_2C_6H_4$, p-$(CH_3)_2NC_6H_4$	2-methylpyridine	0.480	20.44	3.9
7		4-methylpyridine	0.505	20.50	3.9
8		4-cyanopyridine	0.580	21.15	4.2
9		4-acetylpiridine	0.560	20.68	3.9
10		quinoline	0.405	20.95	4.0
11		isoquinoline	0.480	20.73	3.9
12		benzo[*f*]quinoline	0.515	19.90	4.1
13		imidazolee	0.430	19.85	1.5
14		1,2,4-triazole	0.585	19.85	2.0
15		4-nitro-*N*-(3-hydroxy-4-methoxybenzilidene)aniline	0.575	10.68	2.1
16		4-methyl-*N*-(3,4-dimethoxybenzilidene)aniline	0.445		1.9
17		4-methyl-*N*-(4-methoxybenzylidene)aniline	0.475	10.69	2.0
18		4-acetyl-*N*-(4-methoxybenzylidene)aniline	0.545	11.04	2.0
19		4-bromo-*N*-(4-methoxybenzylidene)aniline	0.460	11.20	1.8
20		4-chloro-*N*-(4-methoxybenzylidene)aniline	0.470	11.13	1.9
21	ferocene		0.375	12.4	1.0

[a] Concentration of all hydrozones were 1 mM and bases 10 mM. [b] Peak potentials at 0.1 V s^{-1}. [c] Range of rotation rates: 100–3000 rpm: Pt anode ($2r$ = 1 mm). [d] Determined value of F mol^{-1} by coulometry performed in exhaustive preparative electrolysis at a controlled potential.

Scheme I



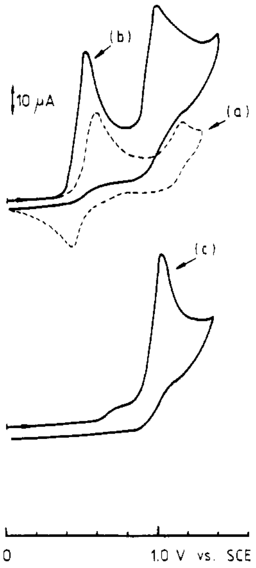


Figure 1. Cyclic voltammograms of 1 mM solution of hydrazone A in 0.1 M Et_4NClO_4–CH_3CN at a Pt electrode ($2r$ = 1 mm) with scan rate 0.1 V s^{-1}: (a) hydrazone A; (b) hydrazone A plus pyridine (c = 10 mM); (c) product 1.

second represent oxidation of the protonated hydrazone, AH^+. The current function, $i_L/(w^{1/2}C)$, obtained in the presence of pyridine was constant with rotation rates in the range from 100 to 10000 rpm and showed two-electron behavior by comparison of the values of the current function with that obtained for ferrocene, a compound known to undergo reversible one-electron oxidation (see Table I).

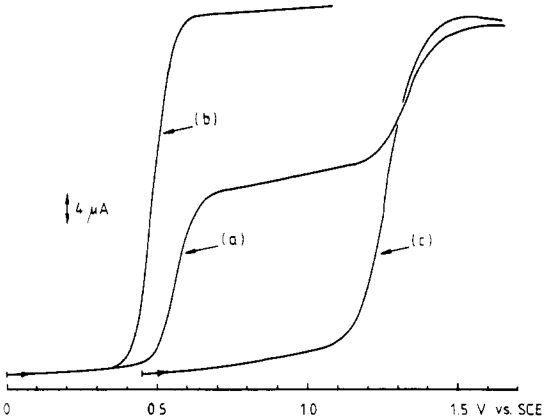


Figure 2. RDE voltammograms of 1 mM solution of hydrazone A in 0.1 M Et_4NClO_4–CH_3CN at a Pt electrode ($2r$ = 1 mm) with scan rate 0.03 V s^{-1} at rotation rate of 900 rpm: (a) hydrazone A; (b) hydrazone A plus pyridine (c = 10 mM); (c) hydrazone A plus $HClO_4$ (c = 2 mM).

The results of oxidation of A on voltammetric time scale in "neutral", basic, and acidic media can be explained according to the following Scheme I.

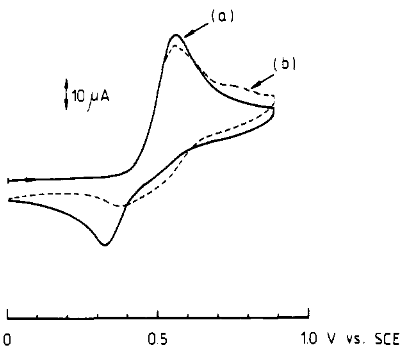


Figure 3. Cyclic voltammograms of 1 mM solution of hydrazone A in 0.1 M Et_4NClO_4–CH_3CN at a Pt electrode ($2r$ = 3 mm) with scan rate 0.1 V s^{-1}: (a) hydrazone A; (b) hydrazone A plus 4-nitro-*N*-(3-hydroxy-4-methoxybenzylidene)aniline (c = 5 mM).

Table II. Relative Rates for the Pseudo-First-Order Reaction between Cation B and Pyridine Derivatives[a]

nucleophile	E_p, V[b]	rel rate	rel rate from ref 11
4-cyanopyridine	0.010	1.0	1.0
4-acetylpyridine	0.030	4.7	
pyridine	0.070	108.1	100
4-methylpyridine	0.085	348.6	330

[a] Concentration of hydrazone A was 1 mM and pyridine derivatives 10 mM. [b] Peak potentials at v = 0.1 V s^{-1}.

Cyclic voltammograms of A obtained in the presence of Schiff bases show a somewhat different behavior. A typical cyclic voltammogram of A in the presence of 4-nitro-*N*-(3-hydroxy-4-methoxybenzylidene)aniline is shown in Figure 3. Addition of Schiff bases does not change the anodic peak potential and height of the wave of A. However, the cathodic peak at 0.43 V is reduced, indicating the nucleophilic attack of Schiff base on the resulting cation B. The current functions, $i_L/(w^{1/2}C)$, obtained at a rotating disk electrode in the presence of Schiff bases (runs 15–20 in Table I) were constant with rotation rates in the range from 100 to 3000 rpm and showed one-electron behavior on voltammetric time scale, which suggests that the Schiff base is not enough strong base to deprotonate the protonated hydrazone AH^+.

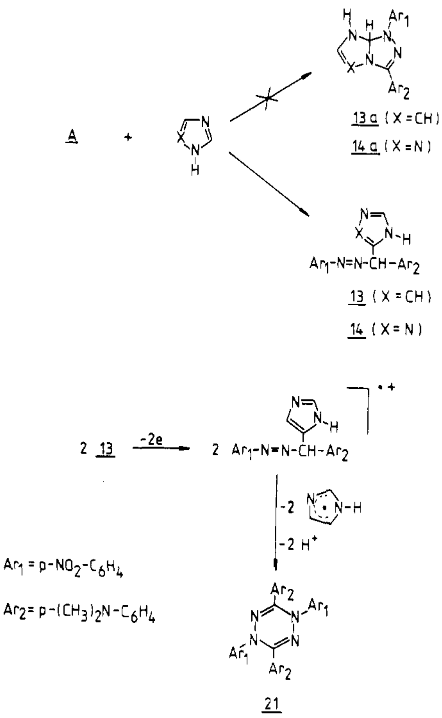
The electroanalytical data for different hydrazones in the presence of base are shown in Table I. The main feature of these results is a discrepancy in the n value determined by rotating disk voltammetry (n = 1 or 2) and coulometry performed in exhaustive preparative electrolysis (n = 2 or 4), except runs 13 and 14. It is obvious that on the voltammetric time scale the electrode reaction can be either one- or two-electron process, leading to the cation B, which is attacked by heteroaromatic or Schiff base as nucleophile. Thus as reactions takes place during exhaustive electrolysis, the apparent number of electrons transferred increases from limits n = 1 to n = 2 and from n = 2 to n = 4 (F mol^{-1}).

Providing that the nucleophilic attack occurs at the stage of the cation B it was possible to use shifts in oxidation potential to obtain relevant rate constants according to eq 1.[10] The value ΔE_p represents the difference in the peak

$$\Delta E_p = 0.0085 + 0.059 \log (k/a)^{1/2} \qquad a = Fv/RT \quad (1)$$

potential of A without a base and with a base present. The results are presented in Table II. It is noteworthy that the calculated relative rates are almost the same as the relative rates obtained for the pseudo-first-order reaction between 9,10-diphenylanthracene cation radical and pyridine derivatives.[11]

Scheme II



Anodic Oxidation of Hydrazones in the Presence of Pyridine, Quinoline, and Isoquinoline Derivatives. Anodic oxidation of hydrazones in the presence of the heteroaromatic bases were typically performed in acetonitrile solution containing tetraethylammonium perchlorate (0.1 M). Controlled potential electrolysis was used at the applied potential corresponding to the plateau of the wave of the current potential curve obtained with rotating disk electrode. All electrochemical synthesis were carried out in a divided cell at a Pt gauze anode (3 × 5 cm), giving rise to a good or high yields (30–90%) of fused *s*-triazolo perchlorates **1**–**12**.

Coulometry at the applied potential showed that the overall electrode reaction was four-electron oxidation in all cases examined. The oxidation products **1**–**12** were isolated after the electrochemical reaction, and after purification their elemental analysis and IR and NMR spectra were in agreement with the assigned structures (Table III).

Anodic Oxidation of Hydrazone A in the Presence of Imidazole and 1,2,4-Triazole. Anodic oxidations of [*p*-(*N*,*N*-dimethylamino)benzylidene]-*p*-nitrophenylhydrazine (A) in the presence of imidazole or 1,2,4-triazole were carried out at a platinum gauze anode in acetonitrile solution containing tetraethylammonium perchlorate by using a divided cell. Coulometry at controlled potential in exhaustive preparative electrolysis showed that the overall electrode reaction was two-electron oxidation. Products **13** and **14** precipitated during electrolysis and were isolated and identified by their melting points and spectra. The products *p*-nitro[((*p*-(*N*,*N*-dimethylamino)phenyl)-4-imidazolylmethyl)azo]benzene (**13**) and *p*-nitro[((*p*-(*N*,*N*-dimethylamino)phenyl)-3-(1,2,4-triazolyl)methyl)azo]benzene (**14**) were obtained in 82% and

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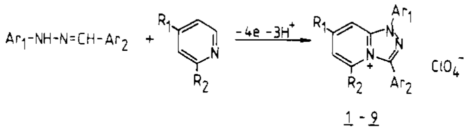
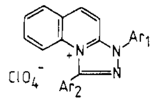
(11) Manning, G.; Parker, V. D.; Adams, R. N. *J. Am. Chem. Soc.* **1969**, *91*, 4584. Baizer, M. M.; Lund, H. *Organic Electrochemistry*; Marcel Dekker: New York, 1983; p 425.

Table III. Products of Anodic Oxidation of Hydrazones in the Presence of Heteroatomic Bases



1-9

compd	Ar_1	Ar_2	R_1	R_2	yield, %	mp, °C (solv)	IR (KBr) ν, cm^{-1}	^1H NMR ($DMSO-d_6$/TMS) δ
						Pyridines		
1	$p-NO_2C_6H_4$	$p-(CH_3)_2NC_6H_4$	H	H	80	280–282 [lit.[3] 280–282] (CH_3CN/benzene)		
2	$p-BrC_6H_4$	$p-(CH_3)_2NC_6H_4$	H	H	55	232–234 (CH_3CN/benzene)	1640 (C=N), 1600 (C=C), 1520, 1375 (NO_2), 1090 (ClO_4^-)	3.12 (s, 6 H, $(CH_3)_2N$), 6.8–99.2 (m, 12 H, Ar)
3	$p-ClC_6H_4$	$p-(CH_3)_2NC_6H_4$	H	H	65	144–146 (CH_3CN/benzene)	1640 (C=N), 1600 (C=C), 1520, 1375 (NO_2), 1085 (ClO_4^-)	3.13 (s, 6 H, $(CH_3)_2N$), 6.9–9.2 (m, 12 H, Ar)
4	$p-NO_2C_6H_4$	C_6H_5	H	H	30	268–269 (CH_3CN/benzene)	1640 (C=N), 1600 (C=C), 1525, 1355 (NO_2), 1100 (ClO_4^-)	7.1–9.2 (m, 13 H, Ar)
5	$p-NO_2C_6H_4$	$p-NO_2C_6H_4$	H	H	40	303–305 (CH_3CN/benzene)	1640 (C=N), 1595 (C=C), 1525, 1355 (NO_2), 1100 (ClO_4^-)	7.1–9.2 (m, 13 H, Ar)
6	$p-NO_2C_6H_4$	$p-(CH_3)_2NC_6H_4$	H	CH_3	63	148–150 (CH_3CN/benzene)	1630 (C=N), 1600 (C=C), 1530, 1380 (NO_2), 1100 (ClO_4^-)	2.65 (s, 3 H, CH_3), 3.0 (s, 6 H, $(CH_3)_2N$), 6.8–9.2 (m, 11 H, Ar)
7	$p-NO_2C_6H_4$	$p-(CH_3)_2NC_6H_4$	CH_3	H	88	145–147 (CH_3CN/benzene)	1640 (C=N), 1600 (C=C), 1515, 1340 (NO_2), 1090 (ClO_4^-)	2.7 (s, 3 H, CH_3), 3.13 (s, 6 H, $(CH_3)_2N$), 6.9–9.1 (m, 11 H, Ar)
8	$p-NO_2C_6H_4$	$p-(CH_3)_2NC_6H_4$	CN	H	62	335–338 (CH_3CN/benzene)	2250 (C≡N), 1640 (C=N), 1605 (C=C), 1520, 1375 (NO_2), 1090 (ClO_4^-)	3.1 (s, 6 H, $(CH_3)_2N$), 7.1–8.3 (m, 11 H, Ar)
9	$p-NO_2C_6H_4$	$p-(CH_3)_2NC_6H_4$	CH_3CO	H	82	142–144 (CH_3CN/benzene)	1680 (CH_3CO), 1640 (C=N), 1510, 1340 (NO_2), 1080 (ClO_4^-)	2.1 (s, 3 H, CH_3CO), 3.12 (s, 6 H, $(CH_3)_2N$), 6.9–9.1 (m, 11 H, Ar)



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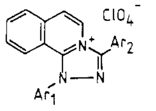

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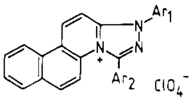


12

compd	Ar_1	Ar_2	yield, %	mp, °C (solv)	IR (KBr) ν, cm^{-1}	^1H NMR ($DMSO-d_6$/TMS) δ
				Quinolines		
10	$p-NO_2C_6H_4$	$p-(CH_3)_2NC_6H_4$	64	278–279 [lit.[5] 278–280] (CH_3CN/benzene)	1640 (C=N), 1610 (C=C), 1515, 1360 (NO_2), 1100 (ClO_4^-)	3.1 (s, 6 H, $(CH_3)_2N$), 6.8–8.9 (m, 14 H, Ar)
11	$p-NO_2C_6H_4$	$p-(CH_3)_2NC_6H_4$	67	199–201 [lit.[5] 203–204] (CH_3CN/benzene)	1640 (C=N), 1600 (C=O), 1520, 1350 (NO_2), 1090 (ClO_4^-)	3.13 (s, 6 H, $(CH_3)_2N$), 6.9–8.9 (m, 14 H, Ar)
12	$p-NO_2C_6H_4$	$p-(CH_3)_2NC_6H_4$	94	236–237	1630 (C=N), 1590 (C=C), 1515, 1360 (NO_2), 1090 (ClO_4^-)	3.11 (s, 6 H, $(CH_3)_2N$), 7.70–9.45 (m, 16 H, Ar)

[a] Satisfactory analysis (±0.35% for C, H, N) were reported for all products.

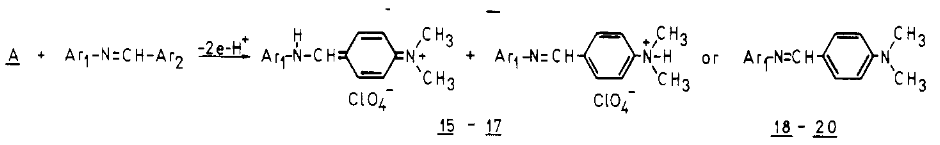
86%, respectively, according to Scheme II. Jugelt and co-workers[5] proposed the cycloadducts **13a** and **14a** as a products of the oxidation of hydrazone A in the presence of imidazole or 1,2,4-triazole, but it was found that these were **13** and **14** instead. The structure of the products **13** and **14** was deduced from high-resolution mass spectral and NMR data. Mass spectral data and elemental analysis of **13** indicated the formula $C_{18}H_{18}N_6O_2$, with molecular peak at 350.148448 (measured; 350.149116 calculated). ^1H NMR spectra showed four sharp singlets at 7.26 (H_5 imidazolyl), 7.39 (H_2 imidazolyl), 7.92 (CH), and 10.28 (NH) ppm, which was exchanged by addition of D_2O. The NMR spectra also showed characteristic patterns for $p-NO_2C_6H_4$ and $p-(CH_3)_2NC_6H_4$ structures (see Experimental Section). It is important to note that Jugelt attributed the "doublet" at 8.44 ppm (J = 10 Hz) to the CH=CH structure **13a** in the proposed formula on the Scheme II. However, for such type of structure one could expect coupling constant between 1 and 2 Hz.

The saturated solution of **13** was further oxidized by controlled potential electrolysis performed at 0.6 V vs SCE. The process was followed by cyclic voltammetry. The cyclic voltammograms of **13** without the charge passed and at the end of the electrolysis are shown in Figure 4.

Cyclic voltammograms with constant conditions were obtained as an function of charge passed, and the results indicated that for constant potential electrolysis the wave at 0.6 V vs SCE decreased at a rate corresponding to the cousmmption of 1.1 F mol^{-1} (Figure 5).

It is obvious that the radical cation of **13** formed at 0.6 V vs SCE undergoes chemical reactions and the most probable reactions are illustrated in Scheme II, involving cleavage of C–C bond, deprotonation, and dimerization of nitrilimine, as a possible intermediate, leading to the 1,4-

Table IV. Products of Anodic Oxidation of Hydrazone A in the Presence of Schiff Bases[a]



compd	Ar_1	Ar_2	yield, %	mp, °C (solv)	IR (KBr) ν, cm^{-1}	^1H NMR (DMSO-d_6/TMS) δ
15	p-$NO_2C_6H_4$	3-OH-4-$OCH_3C_6H_3$	84		1640 (C=N), 1610 (C=C), 1580, 1320 (NO_2), 1085 (ClO_4^-)	3.02, 3.27 [s, s, 6 H (5:5), $(CH_3)_2N$], 6.45–8.55 (m, 8 H, Ar), 9.07 (s, 1 H, NH), 9.65 (s, 1 H, CH)
	p-$NO_2C_6H_4$	3,4-$OCH_3C_6H_3$	54	195–197 (CH_3CN/H_2O)		
	p-$NO_2C_6H_4$	4-$OCH_3C_6H_4$	41			
16	p-$CH_3C_6H_4$	3,4-$OCH_3C_6H_4$	67		1650 (C=N), 1600 (C=C), 1040 (ClO_4^-)	2.37 (s, 3 H, CH_3), 3.07, 3.26 [s, s, 6 H (3:7) $(CH_3)_2N$], 6.8–8.3 (m, 8 H, Ar), 8.97 (s, 1 H, NH), 9.74 (s, 1 H, CH)
	p-$CH_3C_6H_4$	3-OH-4-$OCH_3C_6H_3$	68	116–118 (CH_3CN/H_2O)		
	p-$CH_3C_6H_4$	4-$OCH_3C_6H_4$	63			
17	C_6H_5	3-OH-4-$OCH_3C_6H_3$	80	80–83 (CH_3CN/H_2O)	1640 (C=N), 1600 (C=C), 1100 (ClO_4^-)	3.07, 3.27 [s, s, 6 H (6:4) $(CH_3)_2N$], 6.7–8.3 (m, 9 H, Ar), 9.02 (s, 1 H, NH), 9.65 (s, 1 H, CH)
	C_6H_5	4-$OCH_3C_6H_4$	87			
18	p-$CH_3COC_6H_4$	3-OH-4-$OCH_3C_6H_3$	63	177–178 (CH_3CN/H_2O)	1660 (C=O), 1630 (C=N), 1600 (C=C)	2.54 (s, 3 H, CH_3CO), 3.0 (s, 6 H, $(CH_3)_2N$), 6.55–8.05 (m, 8 H, Ar), 8.24 (s, 1 H, CH)
	p-$CH_3COC_6H_4$	4-$OCH_3C_6H_4$	76			
19	p-BrC_6H_4	4-$OCH_3C_6H_4$	63	156–158 (CH_3CN/H_2O)	1620 (C=N), 1535 (C=C)	3.03 (s, 6 H, $(CH_3)_2N$), 6.52–7.90 (m, 8 H, Ar), 8.25 (s, 1 H, CH)
20	p-ClC_6H_4	3-OH-4-$OCH_3C_6H_3$	80	145–146 (CH_3CN/H_2O)	1620 (C=N), 1595 (C=C)	3.08 (s, 6 H, $(CH_3)_2N$), 6.65–8.00 (m, 8 H, Ar), 8.35 (s, 1 H, CH)

[a] Satisfactory analysis (±0.35% for C, H, N) were reported for all products.

dihydro-1,2,4,5-tetrazine derivative **21** in 92% yield. There are numerous examples which indicate such fate of radical cation.[12]

The cyclic voltammogram of **21** show the formation of a stable radical cation according to the peak potential separation ($E_p^a - E_p^c$) of ca. 60 mV and constant current function ($i_p/v^{1/2}$) with sweep rate. Mass spectra of **21** showed molecular peak at 564, and ^1H NMR spectra showed a singlet at 2.95 ppm for $(CH_3)_2N$ protons and a AA′BB′ type of structure for aromatic protons from 6.4 to 8.1 ppm.

Anodic Oxidation of Hydrazone A in the Presence of Schiff Bases. Anodic oxidations of [p-(N,N-dimethylamino)benzylidene]-p-nitrophenylhydrazine (A) in the presence of Schiff bases were performed at a platinum gauze anode in acetonitrile solution containing tetraethylammonium perchlorate in a divided cell at controlled potential usually set at 0.1 V more positive potential than E_p value given in Table I. The electrolysis was terminated after the current decayed smoothly to background with passage of 1.8–2.1 F mol^{-1}. The products depended on the isolation procedure. Protonated Schiff bases **15**–**17** were obtained directly (method A); imines **18**–**20** were obtained after addition of $NaHCO_3$ solution (method B). The products **15**–**17** were deprotonated with $NaHCO_3$ solution to the corresponding Schiff bases. The structure of all Schiff bases were also confirmed by their independent synthesis. Coulometry at the applied potential showed that the overall electrode reaction was two-electron oxidation in all cases examined. Spectral and elemental analysis data were in agreement with assigned structures (see Table IV).

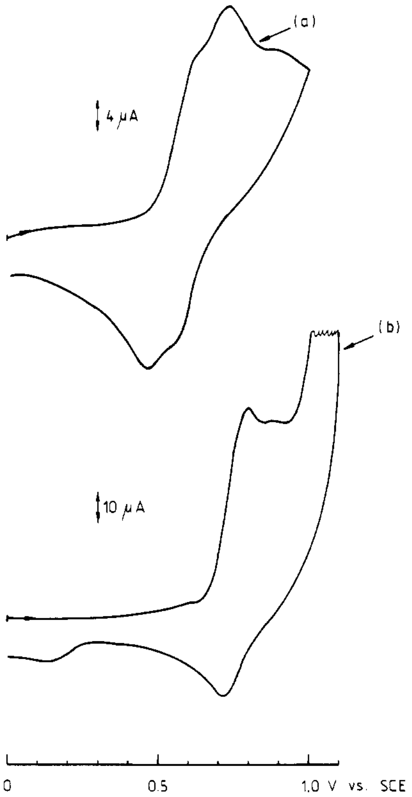


Figure 4. Cyclic voltammograms in 0.1 M Et_4NClO_4 solution in CH_3CN/CH_2Cl_2 (1:1) at a Pt electrode (2r = 3 mm) with scan rate 0.1 V s^{-1}: (a) saturated solution of **13** in the beginning of electrolysis at 0 F mol^{-1}; (b) solution after exhaustive electrolysis at 1.1 F mol^{-1}.

Oxidation of hydrazone A in the presence of 4-methyl-N-(4-methoxybenzylidene)aniline at 0.58 V vs SCE gave a new protonated Schiff base, e.g., 4-methyl-N-[4-

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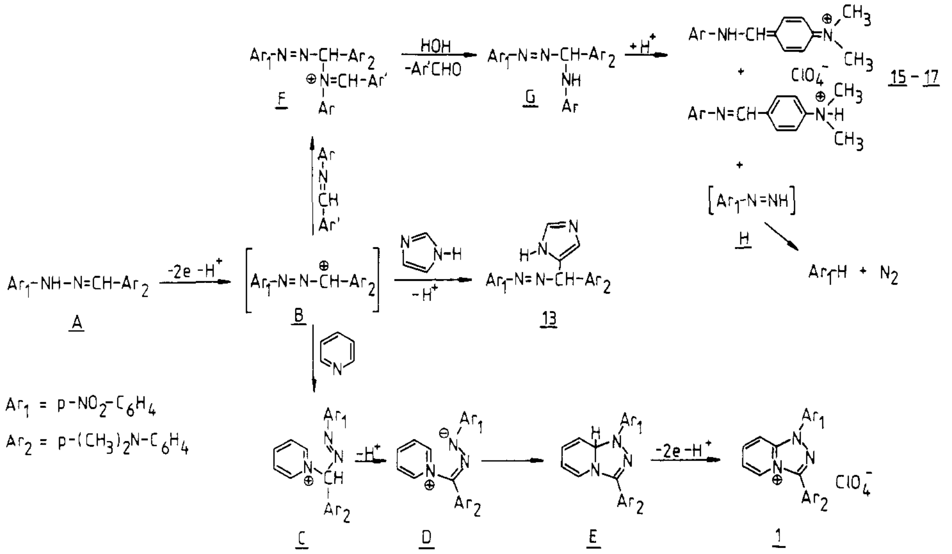
[12] For comprehensive review of such reactions the following texts are presented: Adams, R. N. *Electrochemistry at Solid Electrodes*; Marcel Dekker: New York, 1969. Torii, S. *Electroorganic Synthesis*; Kodansha Ltd.: Tokyo, 1985.

Scheme III



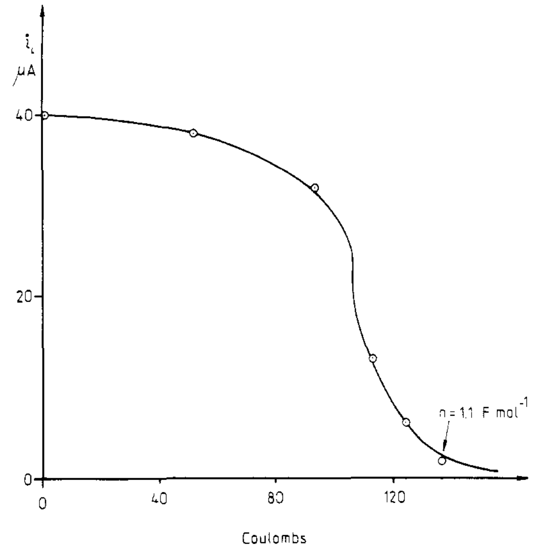


Figure 5. Coulometry for oxidation at 0.5–0.6 V of saturated solution of **13** (450 mg/100 mL) in 0.1 M Et_4NClO_4 solution in CH_3CN/CH_2Cl_2 (1:1) at a Pt electrode.

(*N,N*-dimethylamino)benzylidene]aniline (**16**) in 67% yield. NMR spectra showed two singlets at 3.26 and 3.07 ppm, which can be attributed to the two protonated forms in ratio 7:3. This ratio is dependent on the structure of protonated Schiff base formed and ranges from 7:3 to 6:4. GLC analysis of the reaction mixture confirmed the presence of nitrobenzene and *p*-anisaldehyde as the reaction products. The yield of product **16** is dependent on Schiff base present and ranges from 63% to 67% (see Table IV).

It is important to point out that the anodic oxidation of hydrazone A in the presence of Schiff bases gives rise to the new Schiff bases and does not give triazolium salts as expected product of the 1,3-dipolar cycloaddition between Schiff base as a dipolarophile and the nitrilimine as a possible intermediate.

Mechanistic Rationalization. The most likely mechanism of the oxidation of hydrazone A in the presence of heteroaromatic and Schiff bases, which would fit the observed electrochemical and preparative results, can be described in the form of Scheme III.

Oxidation of hydrazone A is initiated by the rapid formation of cation B through two electron and one proton loss. Pyridine as a nucleophile attacks the cation B leading to the new cation C. It seems that the nucleophilic attack of pyridine molecule is a faster reaction than the deprotonation reaction. The cation C as an acidic species deprotonates by other pyridine molecule leading to a 1,5-dipolar species which may cyclize to E. It is supposed that the intermediate E is oxidizable species at the applied potential which is further oxidized through two electron and one proton loss to the final product **1**.

In the presence of imidazole cation B as an electrophile attacks the imidazole molecule in position 4 or 5, as the most probable places for the electrophilic attack,[13] leading through deprotonation to the product **13**.

The cation B is liable to nucleophilic attack by Schiff base present leading to the iminium-type compound F, which is hydrolyzed by water present, leading through loss of aldehyde to amino compound G, which is protonated by protons liberated in anodic oxidation and cleaved presumably in concerted reaction yielding final products **15–17** and (*p*-nitrophenyl)diimide H, which may to a considerable extent decompose to form nitrogen and nitrobenzene.[14]

In conclusion we can say that the electrochemical oxidation of hydrazone A in the presence of heteroaromatic and Schiff bases is occurring through the formation of cation B, which is attacked by base as a nucleophile. This excludes the possibility of annelation of the heteroaromatics through nitrilimine as an intermediate.

Experimental Section

Materials. Acetonitrile (Merck) was purified by refluxing over potassium permanganate for 1 h, followed by distillation over P_2O_5.[15] Tetraethylammonium perchlorate (Eastman) was recrystallized twice from water, then dried in an oven at 110 °C, and kept in a desiccator over P_2O_5. Hydrazones were prepared by refluxing of corresponding hydrazine and aldehyde in ethanol and Schiff bases by refluxing of corresponding aniline and aldehyde in ethanol. All starting materials gave, after purification, a correct spectra.

Apparatus and Procedures. All melting points are uncorrected. The IR spectra (KBr pellets) were recorded on a Perkin-Elmer M-377 spectrophotometer, and the NMR spectra were recorded on Perkin-Elmer R 12 A and Bruker AC 250 spectrometers using tetramethylsilane as an internal standard. Mass

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[13] Grimmet, M. R. *Adv. Heterocycl. Chem.* **1970**, *12*, 103.
[14] Cohen, S. G.; Nicholson, J. *J. Org. Chem.* **1965**, *30*, 1162.
[15] Clark, D.; Fleichmman, M.; Pletcher, D. *J. Electroanal. Chem.* **1972**, *53*, 165.

spectra were recorded on Hitachi Perkin-Elmer RMV-6L and AEI MS 902 mass spectrometers. GLC analysis was performed with a Perkin-Elmer F-11 equipped with a flame ionization detector at a constant temperature (100 °C) using 10% Carbowax 20 M on Chromosorb W column.

The voltammetric measurements were performed in a 25-cm^3 conical cell fitted with a platinum disk electrode, 1 or 3 mm in diameter, a platinum as a counter electrode, and a saturated calomel electrode (SCE). The current–potential curves were monitored with a Gould X–Y 3054 recorder using HI-TEK potentiostat (type DT 2101) and HI-TEK PPR 1 wave form generator. For rotating disk electrode studies a Tacussel rotating electrode type EDI and MO 10 K were employed. Precise control of the rotation speed was ensured by independent servo control electronic units type Asservitex 3000 and 10000. Preparative controlled potential electrolysis was carried out by means of an Amel 550-SU potentiostat. During the electrolysis an electronic integrator was used to recorded the quantity of electricity passed.

General Procedure for Preparation of Products 1–12 by Oxidation of Hydrazones in the Presence of Heteroaromatic Bases. Into the anodic compartment of the divided cell with Pt gauze anode (3 × 5 cm) and an Ni cathode filled with a 0.1 M solution of Et_4NClO_4 in acetonitrile (100 mL) were added the hydrazone (2 mmol) and heteroaromatic base (20 mmol). The potential was maintained at a fixed value with initial currents generally 200–300 mA. Electrolysis was usually discontinued when the current dropped to 10–15 mA. The solution was evaporated to ca. 10 mL and 100 mL of benzene was added. The precipitate was filtered and dissolved in ca. 5 mL of acetonitrile. Into this solution was added 150 mL of water containing few drops of $HClO_4$. The precipitated products **1–12** were isolated by filtration and recrystallized from the appropriate solvent (see Table III).

General Procedure for Preparation of Products 13 and 14 by Oxidation of Hydrazone A in the Presence of Imidazole and 1,2,4-Triazole. Into the anodic compartment of the divided cell with Pt gauze anode (3 × 5 cm) and an Ni cathode filled with a 0.1 M solution of Et_4NClO_4 in acetonitrile (100 mL) were added the hydrazone A (1 mmol) and heteroaromatic base (10 mmol). The anode potential was usually set at 0.4 V vs SCE in the beginning of the electrolysis and was increased gradually during the electrolysis up to 0.55 V vs SCE, and electrolysis was terminated after the initial current (300–400 mA) decayed smoothly to 10–15 mA. The products **13** or **14** precipitated during the electrolysis, isolated by filtration, and recrystallized from acetonitrile and acetone, giving analytically pure samples.

p-Nitro[((*p*-(*N*,*N*-dimethylamino)phenyl)-4-imidazolylmethyl)azo]benzene (**13**): 82% yield at 1.9 F mol^{-1}; mp 235–237 °C; IR (KBr) 2920, 1600, 1590, 1540, 1500, 1480, 1360, 1327, 1005, 830, 815 cm^{-1}; MS, *m*/*e* (relative intensity) 350 (85.3), 323 (41.4), 322 (43.9), 147 (14.6), 146 (100), 145 (70.7), 129 (9.7), 102 (12.1), 91 (97), 90 (9.7), 77 (12.1), 76 (73); NMR (DMSO-d_6) 3.06 (s, 6 H, $(CH_3)_2N$), 7.26 (s, 1 H, H_5 imidazolyl), 7.92 (s, 1 H, CH); 10.28 (s, 1 H, NH), 6.73 and 7.26 (two doublets, 4 H, J = 10 Hz, *p*-$(CH_3)_2NC_6H_4$), 7.37 and 8.14 (two doublets, 4 H, J = 10 Hz *p*-$NO_2C_6H_4$) ppm. Anal. Calcd for $C_{18}H_{18}N_6O_2$: C, 61.71; H, 5.14; N, 24.00. Found: C, 61.55; H, 5.18; N, 24.12.

p-Nitro[((*p*-(*N*,*N*-dimethylamino)phenyl)-3-(1,2,4-triazolyl)methyl)azo]benzene (**14**): 86% yield at 2.0 F mol^{-1}; mp 225–227 °C; IR (KBr) 2920, 1600, 1570, 1495, 1480, 1405, 1350, 1310, 1265, 1130, 1105, 995, 955, 840, 820 cm^{-1}; MS, *m*/*e* (relative intensity) 351 (68.2), 283 (35.5), 282 (97.9), 253 (7.2), 236 (16.0), 207 (9.1), 147 (42.3), 146 (100), 145 (98.1), 131 (13.0), 106 (33.8), 90 (7.2), 77 (7.2); NMR (DMSO-d_6) 2.96 (s, 6 H, $(CH_3)_2N$), 8.40 (s, 1 H, H_5 triazolyl), 8.93 (s, 1 H, CH), 10.25 (s, 1 H, NH), 6.71 and 7.10 (two doublets, 4 H, J = 10 Hz, *p*-$(CH_3)_2NC_6H_4$, 7.34 and 8.13 (two doublets, 4 H, J = 10 Hz, *p*-$NO_2C_6H_4$). Anal. Calcd for $C_{17}H_{17}N_7O_2$: C, 58.12; H, 4.84; N, 27.92. Found: C, 58.30; H, 4.86; N, 27.51.

Procedure for Preparation of 1,4-Dihydro-1,2,4,5-tetrazine 21 by Oxidation of 13. Into the anodic compartment of the divided cell with Pt gauze anode (3 × 5 cm) and an Ni cathode filled with 0.1 M solution of Et_4NClO_4 in acetonitrile/methylene chloride (1:1) (100 mL) was added 450 mg (1.28 mmol) of **13** was added. The anode potential was set at 0.5 V vs SCE in the beginning of the electrolysis and was increased gradually during the electrolysis up to 0.6 V, and the electrolysis was terminated after the initial current (120–150 mA) decayed smoothly to 10 mA. During the electrolysis the starting compound **13** was gradually dissolving. The solution was evaporated to ca. 10 mL, and 100 mL of 5% aqueous $NaHCO_3$ solution was added. The precipitated product **21** was isolated by filtration and recrystallized from ethanol: 92% yield of **21** at 1.1 F mol^{-1}; mp 313–314 °C; IR (KBr) 2920, 1610, 1595, 1530, 1510, 1370, 1345, 1330, 1310, 1295, 1200, 1115, 1000, 850, 820 cm^{-1}; MS, *m*/*e* (relative intensity) 564 (100), 537 (12.5), 536 (44.6), 477 (35.7), 476 (98.6), 461 (9.8), 428 (5.3), 310 (14.2), 309 (71.4), 291 (71), 268 (8.1), 149 (42.8), 145 (16.0), 131 (32.1), 130 (21.4), 122 (14.6), 97 (23.2); NMR ($CDCl_3$) 2.95 (s, 12 H, $(CH_3)_2N$), 6.55 and 7.2 (AA′BB′ system, 8 H, *p*-$(CH_3)_2NC_6H_4$), 7.2 and 8.0 (AA′BB′ system, 8 H, *p*-$NO_2C_6H_4$) ppm. Anal. Calcd for $C_{30}H_{28}N_6O_4$: C, 67.16; H, 5.22; N, 15.67. Found: C, 67.45; H, 5.25; N, 15.33.

General Procedure for Preparation of Products 15–20 by Oxidation of Hydrazone A in the Presence of Schiff Bases. Into the anodic compartment of the divided cell with Pt gauze anode (3 × 5 cm) and an Ni cathode filled with 0.1 M solution of Et_4NClO_4 in acetonitrile (100 mL) were added the hydrazone A (2 mmol) and Schiff base (10 mmol). The anode potential was set at 0.1 V more positive potential than E_p value given in Table I, with initial currents of 250–350 mA. Electrolysis was discontinued until the current dropped to 10–15 mA. The isolation of products was performed by two methods. **Method A.** The solution was evaporated to ca. 10 mL, and 100 mL of benzene was added. The precipitate was filtered and dissolved in ca. 5 mL of acetonitrile. Into this solution was added 50 mL of water containing few drops of $HClO_4$. The precipitated products **15–17** were isolated by filtration and recrystallized from the appropriate solvent (see Table IV).

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Registry No. **1**, 78893-12-6; **2**, 115095-10-8; **3**, 115095-12-0; **4**, 115095-14-2; **5**, 115095-16-4; **6**, 115095-18-6; **7**, 115095-20-0; **8**, 115095-22-2; **9**, 115095-24-4; **10**, 107426-16-4; **11**, 115095-26-6; **12**, 115095-28-8; **13**, 115095-29-9; **14**, 115095-30-2; **15**, 115095-31-3; **16**, 115117-28-7; **17**, 69338-40-5; **18**, 38131-68-9; **19**, 15485-29-7; **20**, 15486-62-1; O_2N-*p*-C_6H_4N=CHC_6N_4-*p*-OMe, 15450-66-5; H_3C-*p*-C_6H_4N=CHC_6H_4-*p*-OMe, 3246-78-4; C_6H_5N=CHC_6H_4-*p*-OMe, 836-41-9; H_3CCO-*p*-C_6H_4N=CH-C_6H_4-*p*-OMe, 23596-02-3; O_2N-*p*-C_6H_4NHN=CHC_6H_4-*p*-$N(CH_3)_2$, 3155-30-4; Br-*p*-C_6H_4NHN=CHC_6H_4-*p*-$N(CH_3)_2$, 27246-80-6; Cl-*p*-C_6H_4NHN=CHC_6H_4-*p*-$N(CH_3)_2$, 115095-35-7; O_2N-*p*-C_6H_4NHN=CHC_6H_5, 3078-09-9; O_2N-*p*-C_6H_4NHN=CHC_6H_4-*p*-NO_2, 3155-22-4; Br-*p*-C_6H_4N=CHC_6H_4-*p*-OMe, 15485-23-1; 2-methoxy-5-[[(4-nitrophenyl)imino]methyl]phenol, 115095-32-4; 1,2-dimethoxy-4-[[(4-nitrophenyl)imino]methyl]benzene, 74650-17-2; 1,2-dimethoxy-4-[[(4-methylphenyl)imino]methyl]benzene, 67101-90-0; 2-methoxy-5-[[(4-methylphenyl)imino]methyl]phenol, 115095-33-5; 2-methoxy-5-[(phenylimino)methyl]phenol, 75638-30-1; 2-methoxy-5-[[(4-acetylphenyl)imino]methyl]phenol, 115095-34-6; pyridine, 110-86-1; 2-methylpyridine, 109-06-8; 4-methylpyridine, 108-89-4; quinoline, 91-22-5; isoquinoline, 119-65-3; benzo[*f*]quinoline, 85-02-9; imidazole, 288-32-4; 1,2,4-triazole, 288-88-0; 2-methoxy-5-[[(4-chlorophenyl)imino]methyl]phenol, 115095-36-8; 4-cyanopyridine, 100-48-1; 4-acetylpyridine, 1122-54-9.