Electrochemical Synthesis of Heterocyclic Compounds. XV.*

Anodic Synthesis of *s*-Triazolo[4,3-*a*]pyridine Derivatives

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Anodic oxidation of several heterocyclic hydrazones (*1a*–*9a*) prepared from 2-hydrazinopyridine of 2-hydrazino-4-nitropyridine and the corresponding aromatic aldehyde was performed in a CH₃CH–Et₄NClO₄ solution with the addition of 60 % HClO₄ on a platinum electrode, using controlled potentials. As a result of two-electron oxidative cyclizations, several *s*-triazolo[4,3-*a*]pyridine derivatives (*1b*–*9b*) were prepared in yields ranging from 55 to 92 %. A mechanism rationalizing the formation of the 3-phenyl-*s*-triazolo[4,3-*a*]pyridine, *1b*, has been studied by LSV, CPSV, RDE, coulometry and preparative scale electrolysis.

Oxidative cyclization of heterocyclic hydrazones is a widely used route for the preparation of *s*-triazoloazines or *s*-triazoloazoles and may be carried out with a variety of oxidizing agents,²⁻⁶ among the most widely used of which are bromine and metallic compounds.

We have previously reported⁷ a new route to 3-phenyl-3-triazolo[4,3-*a*]pyridine by electrochemical oxidation of benzaldehyde 2-pyridylhydrazone. However, we have found that the yield of products is dependent upon the solvent used. In order to gain a better understanding of the factors which influence the distribution of the products and to find the electrolysis conditions which give the highest yield of *s*-triazolo[4,3-*a*]pyridines we have now studied the anodic oxidation of a series of structurally different heterocyclic hydrazones. As a result, we can

report a convenient new synthesis of several *s*-triazolo[4,3-*a*]pyridine derivatives.

RESULTS AND DISCUSSION

Synthetic aspects. In order to optimize the yield of cyclic products (*1b*) anodic oxidations of benzaldehyde 2-pyridylhydrazone (*1a*) were performed in "neutral", basic and acidic media. Electrochemical oxidations were carried out on a platinum anode by controlled potential electrolysis in acetonitrile with tetraethylammonium perchlorate as supporting electrolyte in a divided cell. The electrolysis was complete after about 1–2 h, when the current dropped to 1–5 % of its starting value. The products *1b*, *1c* and *1d* were isolated, and hydrazide *1e* was detected by TLC. Two other products, pyridine (*1f*) and benzaldehyde (*1g*), were determined by means of GLC. The structures of all products obtained are shown in Scheme 1.

The results presented in Table 1 are mean values obtained from three electrolyses. The best yield of *1b* was obtained in acidic media in which electrolyses proceeded smoothly without inhibition of the electrode. The electrolysis, with the addition of pyridine as a base or in "neutral" media, resulted in a lower yield of *1b*, and the filming of the electrode occurred during the reaction.

Anodic oxidation of heterocyclic hydrazones prepared from 2-hydrazinopyridine (*1a*–*6a*) or 2-hydrazino-4-nitropyridine (*7a*–*9a*) and the corresponding aldehyde was typically performed in

* Part XIV. See Ref. 1.

Scheme 1.

an acetonitrile solution (100 ml) containing tetraethylammonium perchlorate (0.1 M) with the addition of 60 % perchloric acid (2 ml), using controlled potential electrolysis. All electrochemical syntheses were carried out in a divided cell on a Pt-gauze anode (3×5 cm) giving rise to *s*-triazolo[4,3-*a*]pyridine derivatives as shown in Scheme 2.

Voltammetric and preparative data for the anodic oxidation of heterocyclic hydrazones (1a–9a) are given in Table 2. RDE voltammograms, run in CH₃CN–0.1M Et₄NClO₄ with the addition of 60 % HClO₄, showed one wave. Coulometry at the applied potential showed that the overall electrode reaction was a two-electron oxidation in all cases examined.

The oxidation products (1b–9b) were isolated in good yields ranging from 55 to 92 % and, after purification, their elemental analyses, IR, NMR

and mass spectra were in agreement with the assigned structures.

The intramolecular cyclodehydrogenation of heterocyclic hydrazones leading to the *s*-triazolo[4,3-*a*]pyridines is usually performed using various oxidants. Our present anodic synthesis provides a useful, equally convenient alternative.

Mechanistic rationalization. The oxidations of benzylidene 2-pyridylhydrazone, 1a, were studied in some detail. All of the electrochemical studies were conducted using CH₃CN–0.1M Et₄NClO₄. 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 disc of platinum (diameter=1.0 or 3 mm) or a platinum bead electrode.

Current-potential curve of 1a, obtained with a

Table 1. Composition of the reaction mixture after oxidation of benzaldehyde-2-pyridylhydrazone, 1a.

Solution conditions	$E_{1/2}$ (V vs. SCE)	Applied potential (V vs. SCE)	<i>n</i> -Value	1b (%)	1c (%)	1d (%)	1e (%)	1f (%)	1g (%)
CH ₃ CN	0.82	1.4	2.2	62	10	—	traces	7	3
CH ₃ CN+ 60 % HClO ₄ (2 ml)	1.28	1.4	2.1	72	25	—	traces	traces	traces
CH ₃ CN+ pyridine (2 ml)	0.92	1.0	3.6	26	—	45	—	—	traces

Table 2. Conditions and results of electrochemical cyclodehydrogenation.

Conversion	RDE ^a voltammetry results, $E_{1/2}$ (V vs. SCE)	Applied potential (V vs. SCE)	n -Value ^b	Yield of product (%)	M.p. ^c (solvent)	Molecular formula or lit. m.p. (°C)	Elemental analysis		
							Calc./found	% C	% H % N
1a→1b	1.28	1.4	2.1	72	172–173° (A)	172–173 Lit. 8			
2a→2b	0.93	1.0	2.3	65	162–164° (A)	C ₁₃ H ₁₁ N ₃ ^d (209.13)	74.65 74.27	5.25 5.19	20.08 20.31
3a→3b	0.95	1.0	2.6	55	143–144° (A)	C ₁₃ H ₁₁ N ₃ ^e (209.13)	74.65 74.69	5.25 5.20	20.08 20.02
4a→4b	0.70	0.8	2.4	63	124–125° (A)	C ₁₃ H ₁₁ N ₃ O ^f (225.13)	68.01 68.35	4.88 5.01	18.65 18.79
5a→5b	0.85	1.2	2.4	60	166–168° (A)	C ₁₃ H ₁₅ N ₃ O ₃ ^g (285.15)	63.17 63.20	5.26 5.25	14.72 15.01
6a→6b	1.40	1.5	2.3	75	296–298° (B)	C ₁₂ H ₁₈ N ₄ O ₂ ^h (240.12)	60.01 59.98	3.33 3.30	23.32 23.81
7a→7b	1.10	1.2	2.2	90	162–163° (C)	C ₁₃ H ₁₀ N ₄ O ₃ ⁱ (270.13)	57.79 58.04	3.70 3.58	20.73 21.05
8a→8b	0.72	0.8	2.1	92	231–233° (D)	C ₁₄ H ₁₃ N ₅ O ₂ ^j (283.14)	59.38 59.03	4.59 4.37	24.79 24.45
9a→9b	0.91	1.0	2.3	83	181–182° (C)	C ₁₃ H ₁₄ N ₄ O ₅ ^k (330.15)	54.56 54.79	4.24 4.19	16.96 17.22

^a Pt-electrode; 600 r.p.m.; substrate concentration 1 mM; compounds 1a–9a were run in CH₃CN–0.1 M Et₄NClO₄ in the presence of 60 % HClO₄ (C=0.1 M). ^b Determined by coulometry at controlled potential. ^c A=benzene–cyclohexane (1:1); B=CH₃CN; C=EtOH; D=EtOH–acetone (1:1). ^d IR (KBr): 3080, 2970, 1630, 1500, 1470, 1410, 1370, 1320, 1075, 1010, 830, 750, 740, 720, 700 cm⁻¹. ^e ¹H NMR (DMSO-*d*₆): δ =2.4 (s, 3H, CH₃), 6.8–8.5 (m, 8H, arom.) p.p.m. MS [IP 70 eV; *m/e* (% rel. int.)]: 209(100), 208(63), 194(6), 181(6), 143(6), 116(9), 92(23), 91(6), 90(6), 89(5), 66(6), 75(26). ^f IR (KBr): 3180, 2980, 1600, 1570, 1435, 1315, 1140, 990, 765, 755 cm⁻¹. ^g ¹H NMR (DMSO-*d*₆): δ =2.2 (s, 3H, CH₃), 6.8–8.05 (m, 8H, arom.) p.p.m. MS [IP 70 eV; *m/e* (% rel. int.)]: 209(100), 1435, 1315, 1140, 990, 765, 755 cm⁻¹. ^h ¹H NMR (DMSO-*d*₆): δ =3.9 (s, 3H, CH₃O), 6.9–8.6 (m, 8H, arom.) p.p.m. MS [IP 70 eV; *m/e* (% rel. int.)]: 209(100), 208(29), 207(5), 180(4), 117(6), 116(10), 106(4), 105(6), 92(5), 91(4), 90(8), 89(15), 78(8), 76(4), 66(5), 65(23). ⁱ IR (KBr): 3080, 3000, 2850, 1635, 1610, 1540, 1500, 1470, 1380, 1310, 1255, 1015, 835, 750, 730, 700 cm⁻¹. ^j ¹H NMR (DMSO-*d*₆): δ =3.9 (s, 3H, CH₃O), 6.9–8.6 (m, 8H, arom.) p.p.m. MS [IP 70 eV; *m/e* (% rel. int.)]: 225(100), 224(29), 211(15), 210(29), 182(10), 107(15), 84(41), 76(20). ^k IR (KBr): 3080, 3000, 1630, 1590, 1500, 1470, 1430, 1370, 1320, 1300, 1240, 1190, 1085, 1010, 880, 850, 750, 710 cm⁻¹. MS [IP 70 eV; *m/e* (% rel. int.)]: 285(45), 270(27), 242(5), 85(18), 84(56), 83(15), 69(65), 56(72), 55(76), 43(34), 42(56), 41(100), 40(13). ^l IR (KBr): 3100, 1640, 1600, 1570, 1540, 1490, 1440, 1420, 1350, 1270, 1150, 850, 770, 760 cm⁻¹. MS [IP 70 eV; *m/e* (% rel. int.)]: 240(100), 210(8), 194(4), 194(23), 193(10), 140(10), 92(15), 76(10), 66(10), 65(28). ^m IR (KBr): 3000, 1645, 1610, 1500, 1475, 1340, 1100, 1030, 820 cm⁻¹. MS [IP 70 eV; *m/e* (% rel. int.)]: 270(100), 255(6), 222(7), 221(16), 209(3), 179(13), 181(3), 119(5), 103(7), 76(5), 64(6), 63(34), 44(23), 43(7). ⁿ IR (KBr): 2910, 1640, 1605, 1500, 1345, 1300, 1190, 830 cm⁻¹. MS [IP 70 eV; *m/e* (% rel. int.)]: 283(59), 237(11), 210(9), 209(50), 193(10), 146(55), 145(100), 133(10), 132(84.5), 131(9), 180(16), 129(18), 115(11), 105(16), 103(19.5), 89(13), 78(23), 77(13), 65(8). ^o IR (KBr): 2940, 2840, 1640, 1590, 1350, 1305, 1230, 1130, 1005, 880, 855, 830 cm⁻¹. ^p ¹H NMR (DMSO-*d*₆) at 150°: δ =3.82 (s, 3H, CH₃O), 3.9 (s, 6H, CH₃O), 7.46 (s, 2H, H₂H₆), 7.85 (d, 1H, H₆, *J*=9.3 Hz); 8.25 (d, 1H, H₂), 9.78 (d, 1H, H₈, *J*=1.9 Hz). MS [IP 70 eV; *m/e* (% rel. int.)]: 330(100), 315(45), 287(7), 272(7), 257(12), 241(12), 165(7), 114(18), 72(6), 63(10).

Scheme 2.

rotating disc platinum electrode, shows the presence of two waves at +0.82 and 1.62 V, respectively, for oxidation in acetonitrile (Fig. 1a). The first wave corresponds to the oxidation of the parent molecule and the second to the *1a*

Fig. 1. RDE voltammograms of 1 mM solution of *1a* 0.1 M Et₄NClO₄-CH₃CN at rotation rate of 900 rev min⁻¹; Pt-electrode (2*r*=1 mm); (a) benzylidene-2-pyridylhydrazone, *1a*; (b) *1a* plus pyridine (*C*=0.001 M); (c) *1a* plus 60 % HClO₄ (*C*=0.001 M); (d) *1a* plus 60 % HClO₄ (*C*=0.01 M); (e) *1a* plus 60 % HClO₄ (*C*=0.1 M); (f) *1a* plus 60 % HClO₄ (*C*=0.1 M) plus H₂O (*C*=0.1 M).

protonated by protons liberated along the first wave. After the addition of pyridine as a base, the first wave doubled in height (Fig. 1b). The addition of perchloric acid (60 % in water) reduces the initial oxidation wave at 0.82 V and increases the more anodic wave (Fig. 1c). Thus, the experiments described confirm that the first wave represents oxidation of the parent hydrazone, *1a*, and the second represents oxidation of the protonated hydrazone. The current function, *i_L*/*w*^{1/2}*C*, obtained in the presence of perchloric acid was constant with a rotation rate in the range from 1.6 to 50 rev. s⁻¹, and showed two-electron behaviour by comparison of the values of the current function with that obtained for ferrocene, a compound known to undergo reversible one-electron oxidation. The reaction order (the log current-log concentration ratio) in the diffusion plateau region was about one.

Coulometry performed by exhaustive preparative electrolysis at a controlled potential for compound *1a* confirmed (*n*=2.1) that the wave shown in Fig. 1c corresponded to two electrons.

The effect of increasing acid concentration is shown in Figs. 1c, 1d and 1e; the major effect observed is the shift of the oxidation wave of the protonated hydrazone *1a* cathodically. The addition of water affects further cathodic movement of the wave (Fig. 1f). A similar effect was observed in the oxidation of 1-phenylpyrazolidin-

Table 3. Results of CPSV and LSV of *1a*.^a

CPSV ^b Logarithmic analysis		LSV ^d		
Number ^c	Slope (mV)	$E_p - E_p/2$ (mV)	$\partial E_p / \partial \log \nu$ ^e (mV)	$\partial E_p / \log C$ ^f (mV)
1	60 (2)	58	ca. 20	ca. -20
2	58 (2)			
3	83 (2)			

^a Concentration of *1a*, 1 mM; CH₃CN-0.1 M Et₄NClO₄ plus 60 % HClO₄ (C=0.1 M). ^b $\nu=0.15$ V s⁻¹; Pt-electrode (2r=3 mm). ^c 1=log [(1- i)/ i]; 2=log [(1- i)/ i]^{-2/3}; 3=log [(1- i)/ i]^{-2/3}-1/3]. ^d Platinum bead electrode. ^e Correlation coefficient: 0.994. ^f Correlation coefficient: 0.929; $\nu=0.1$ V s⁻¹.

3-one in acidic media.⁹

Using the same arguments the cathodic shift of the wave can be explained in terms of the Nernst equation and the equilibrium process according to Scheme 3.

Scheme 3.

The water present in acetonitrile acts as a base because of the fact that acetonitrile is a very weak base compared with water.¹⁰

In order to learn more about the mechanism for conversion *1a*→*1b*, we have used the diagnostic criteria given by Andrieux and Savéant for cyclization reaction^{11,12} using linear sweep voltammetry (LSV). Peak potentials on a small platinum bead electrode were measured for concentrations, from 0.2 to 2 mM at $\nu=0.15$ V s⁻¹, and sweep rate variations in the range of sweep rate from 0.05 to 1 V s⁻¹. The results are presented in Table 3.

The data given are the result of linear least squares analysis of over 15 voltammograms. It is worth noting that cyclic voltammetry of *1a* does not show reversibility for the sweep range from 0.02 to 80 V s⁻¹, indicating a fast chemical reaction which follows electron transfer.¹³

It is seen that the rate of variation of E_p with log ν is 20 mV dec⁻¹ and the variation of the peak potential with the concentration is also 20 mV dec⁻¹. According to the diagnostic criteria previously established, three mechanistic schemes are possible: e-c-D-p-p, e-c-p-D-p and e-D-c-p-p

(the capital letter designates the rate determining step, e=electron transfer on the electrode, d=a solution electron transfer, c=cyclization step and p=deprotonation). The formation of products *1c*, *1d* and *1e*, in preparative electrolysis of *1a* under various solvent conditions (see Scheme 1), is a good indication that the cyclization reaction in conversion *1a*→*1b* occurs after the second electron has been transferred. This observation ruled out the first two mechanistic possibilities. The remaining possibility was e-D-c-p-p, involving a solution electron transfer as a rate-deter-

Fig. 2. LS and CPS voltammograms of *1a* (C=1 mM) with 60 % HClO₄ added (C=0.1 M); Pt-electrode (2r=3 mm); $\nu=0.15$ V s⁻¹.

mining step.

Further mechanistic study of the reaction $1a \rightarrow 1b$ was done by application of convolution potential sweep voltammetry (CPSV).¹⁴ The technique of semi-integral analysis using the equation given by Vanden Born and Evans¹⁵ applied to convolute i-E curves was described recently.¹⁶ The linear sweep and the convoluted voltammogram are shown in Fig. 2.

The logarithmic analysis described by Savéant *et al.*¹⁷ were applied over the wave of the $I-E$ curve, and the resulting slopes are given in Table 3. Comparison of the CPSV slope values in Table 3 shows that analysis number 2, with an experimental value of 58 mV, is closest to the theoretical values (58.6 mV).

The conversion of protonated $1a \rightarrow 1b$ involves a loss of two electrons and three protons and a carbon-nitrogen bond formation. The values of $\partial e_p / \partial \log v = 20$ mV and $\partial E_p / \partial \log C = 20$ mV point to the occurrence of a second order rate-determining step (D-step) by comparison with diagnostic criteria for LSV¹¹ and CPSV.¹⁷ Scheme 4 presents an overall picture of many of the mechanistic possibilities.

Oxidation of protonated benzaldehyde 2-

pyridylhydrazone (RH_2^+) is initiated by the rapid, reversible formation of radical-dication (RH_2^{2+}) which deprotonates as an acidic species leading to the formation of radical-cation (RH^+). A pair of RH^+ disproportionates in solution giving the parent compound $1a$ (RH), which is protonated in acidic media, and dication (RH^{2+}). Our kinetic data obtained from LSV and CPSV approximately fit a second order rate low. According to the diagnostic criteria,^{11,12} three reaction steps, after the rate-determining step, are included: (i) cyclization of dication (c-step), (ii) deprotonation (p-step) and (iii) deprotonation (p-step). Hence, since diagnostic criteria presented by Andrieux and Savéant¹¹ do not cover all possible mechanisms, it seems reasonable to propose that the relatively high acidity of RH^{2+} favours deprotonation leading to the cation (R^+). Also it is possible that the coulombic repulsion in the stage of dication is unfavourable to the cyclization. The cation (R^+) deprotonates, leading to the nitrilimine (R). One can anticipate that the intermediate nitrilimine (R) may either cyclize as a 1,5-dipolar species into 3-phenyl-*s*-triazolo[4,3-*a*]pyridine, $1b$, or may be trapped by acetonitrile in a concurrent

Scheme 4.

Scheme 5.

cyclization of nitrilimine as a 1,3-dipolar species giving 1-(2-pyridyl)-3-phenyl-5-methyl-1,2,4-triazol, **1c**. The final step in the formation of the fused triazolo-compounds is generally considered to involve nitrilimine as intermediates based on kinetic measurement data^{18,19} or on trapping with 1,3-dipolarophiles.^{6,20,21} Our results suggest also that the nitrilamine is the final intermediate in the electrochemical reaction $1a \rightarrow 1b$.

The possible formation of all products during anodic oxidation of **1a** under various solution conditions can be explained in terms of nitrilimine as an intermediate according to Scheme 5.

The intermediate nitrilimine (R) formed in "neutral" media as well as in the presence of perchloric acid preferentially undergoes the cyclization leading to **1b** (62 and 72 % yield, respectively). The slower 1,3-dipolar cycloaddition process leading to **1c**, and the nucleophilic attack of water leading to hydrazide **1e** are overrun by a faster nucleophilic attack of ring nitrogen to give a cyclic product **1b**. The hydrazide **1e** is further oxidized at the applied potential ($E_{1/2}$ of **1e** is 0.75 V vs. SCE) giving rise to pyridine, **1f**, and benzaldehyde, **1g**, as side products. The same type of cleavage of hydrazones performed by anodic oxidation has already

been observed.²² However, it seems that in basic media, with pyridine present, intermolecular 1,3-cycloaddition is faster than the intramolecular 1,5-cycloaddition reaction leading to the higher yield of **1d** (45 % more than of **1b** (26 %)). One can envisage the formation of 1-(2-pyridyl)-3-phenyl-*s*-triazolo[4,3-*a*]pyridinium perchlorate, **1d**, through the formation of an intermediate bicyclic compound which is further oxidized at the applied potential by the loss of two electrons and one proton, giving rise to **1d**. This type of reaction has been used for annelation of pyridine rings *via* the anodic oxidation of some aldehyde hydrazones in the presence of pyridine.²³

EXPERIMENTAL

Materials. Acetonitrile (Merck) was purified by refluxing over potassium permanganate for 1 h, followed by distillation over P_2O_5 .²⁴ 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 . Heterocyclic hydrazones (**1a**–**9a**) were prepared by refluxing 2-hydrazinopyridine or 2-hydrazino-4-nitropyridine and corresponding aldehyde in ethanol. All heterocyclic hydrazones

gave, after purification, a correct elemental analysis.

Apparatus and procedures. All melting points are uncorrected. The IR spectra (KBr pellets) were recorded on a Perkin-Elmer M-377 spectrophotometer, the NMR spectra were recorded on a Perkin-Elmer R 12A spectrometer using tetramethylsilane as an internal standard, and mass spectra were recorded on a Hitachi Perkin-Elmer RMV-6L mass spectrometer. 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 apparatus and cells for voltammetry, coulometry and preparative electrolysis have been described earlier.²⁵ The procedure used for CPSV was described recently.¹⁶ The platinum electrode used in the voltammetric experiments was cleaned by keeping it for *ca.* 60 s in DMF, then rinsing it with acetone and drying it with paper tissue. This procedure was repeated prior to each measurement.

General procedure for preparation of s-triazolo-[4,3-a]pyridine derivatives (2b–9b). 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 Et₄NClO₄ and 2 ml HClO₄ (60 %) in acetonitrile (200 ml) the heterocyclic hydrazone (2a–9a) was added (0.3–0.5 g). The potential was maintained at a fixed value (see Table 2) with initial currents generally 200–900 mA. Electrolysis was usually discontinued when the current dropped to 10–20 mA, which generally took 1–3 h. The solution was evaporated to *ca.* 10 ml and saturated aqueous sodium hydrogen carbonate (150 ml) was added. The pH of the solution was adjusted at about 10 by the addition of a 3N NaOH solution. After standing about 48 h at room temperature, the precipitated cyclization product (2b–9b) was isolated by filtration and recrystallized from the appropriate solvent (see Table 2).

Oxidation of benzaldehyde-2-pyridylhydrazone, 1a, in "neutral" and acidic media. The electrolysis of 1a (0.3 g) was carried out in the same way as described in the general procedure, using controlled potential with or without the addition of perchloric acid (see Table 1). Electrolysis without the addition of perchloric acid, *e.g.* in "neutral" media, was accompanied by the passivation of the platinum electrode. The process was interrupted several times during the electrolysis and the electrode was washed in HNO₃ (1:1), water and acetone in order to "activate" it. After electrolysis at controlled potential, acetonitrile was evaporated to a volume of *ca.* 10 ml and saturated aqueous

sodium hydrogen carbonate (150 ml) was added. The products 1b and 1c were isolated by extraction with chloroform (4×30 ml). After evaporation of the solvent the residue was subjected to column chromatography on a silica gel column using chloroform as an eluant. The compound 1c, 1-(2-pyridyl)-3-phenyl-5-methyl-1,2,4-triazol, appeared as a first fraction. After evaporation of the solvent the compound 1c and recrystallization from benzene–cyclohexane (1:2) gave m.p. 54–55 °C. Anal. Found: C. 71.64; H. 5.21; N. 24.01. Calc. for C₁₄H₁₂N₄: C. 71.20; H. 5.08; N. 23.71. IR (KBr): 2920, 1590, 1570, 1520, 1460, 1430, 1380, 1350, 1310, 1270, 1175, 1140, 1120, 1090, 1040, 995, 960, 925, 780, 730, 700, 665 cm⁻¹. ¹H NMR (60 MHz, CDCl₃): δ 2.9 (3H, s, CH₃); 7.1–8.5 (9H, m, arom.). MS IP 70 eV, *m/e* (% rel. int): 236(100), 235(24), 169(17), 195(63), 194(89), 149(33), 147(70), 133(91), 117(28), 105(43), 104(57), 103(24), 93(33), 92(35), 91(22), 76(54), 65(37).

The second fraction after evaporation of the solvent and recrystallization from benzene–cyclohexane (1:1) gave 1b with m.p. 172–173 °C (Lit.⁸ m.p.=172–173 °C).

Oxidation of benzaldehyde-2-pyridylhydrazone, 1a, in basic media. The electrolysis of 1a (0.3 g) was carried out in the same way as described in the general procedure, using controlled potential with the addition of 2 ml of pyridine (see Table 1). During the electrolysis, passivation of the electrode occurred and the process was interrupted several times during the electrolysis and the electrode was washed in HNO₃ (1:1), water and acetone. After electrolysis, acetonitrile was evaporated to a volume of *ca.* 5 ml and water (100 ml), containing a few drops of perchloric acid, was added. After standing 5 days at room temperature the precipitated product 1d was isolated by filtration and after recrystallization from CH₃CN–H₂O (2:1), acidified with a few drops of perchloric acid giving m.p. 245–247 °C. Anal. Found: C. 55.01 H. 3.51; N. 15.07. Calc. for C₁₇H₁₃N₄ClO₄: C. 54.85; H. 3.48; N. 15.05. IR (KBr): 3100, 1640, 1590, 1570, 1500, 1470, 1440, 1340, 1320, 1290, 1100, 780, 700, 630 cm⁻¹. ¹H NMR (60 MHz, DMSO-*d*₆): δ 7.3–8.8 (13 H, m, arom.).

The mother liquor was extracted with chloroform (3×40 ml) and after evaporation of the solvent and recrystallization from benzene–cyclohexane, (1:1), it gave 1b with m.p. 172–173 °C (Lit.⁸ m.p.=172–173 °C).

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