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ELECTROCHEMICAL RING-CONTRACTION OF FUSED [1,3,4] THIADIAZINIUM SALTS: PREPARATION OF FUSED PYRAZOLE DERIVATIVES.

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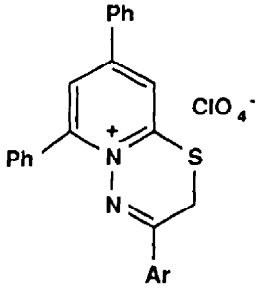
Abstract.- The electroreduction of several fused [1,3,4]-thiadiazinium salts on mercury pool cathode in an aprotic medium has been studied. In preparative experiments using dimethylformamide 0.2 M in lithium perchlorate as the electrolyte, the [1,3,4]-thiadiazinium salts **1-3** formed a mixture of the corresponding fused pyrazoles and ketimines. On the basis of results of preparative electrolyses (products and reaction potentials) and cyclic voltammograms a posible mechanism is proposed.

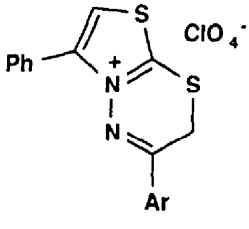
It has became increasingly apparent that the electrochemical reactions are a powerful tool in preparative heterocyclic chemistry. In spite of much work on the electrolytic formation of heteroaromatic systems from open-chain precursors very few studies have been devoted to the formation of heterocycles from a preformed ring by ring-contraction, all of them involve bond cleavage of oxygen-nitrogen, nitrogen-nitrogen or nitrogen-carbon bonds[1,2], there have been no reports dealing with ring-contraction based on a carbon-sulfur bond cleavage, to the best of our knowledge.

The preparation of pyrazoles from 6H-1,3,4-thiadiazines by sulfur extrusion is an important goal in heterocyclic chemistry, this conversion can be achieved by the action of tertiary phosphorus compounds[3], base-catalyzed rearrangement[4] or ultrasonic radiation[5].



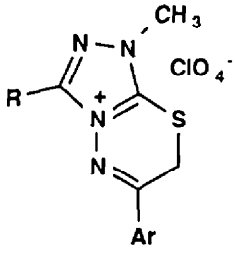
1

(a) Ar=C_6H_5
(b) Ar=4-CH_3O-C_6H_4
(c) Ar=4-Br-C_6H_4



2

(a) Ar=C_6H_5
(b) Ar=4-Br-C_6H_4

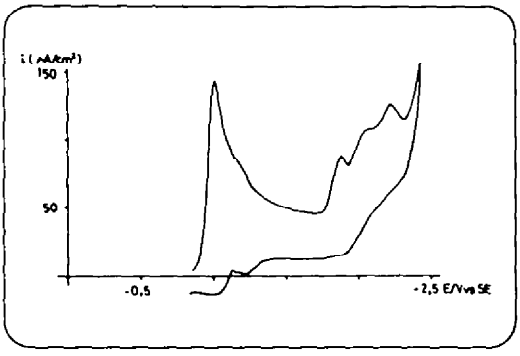


3

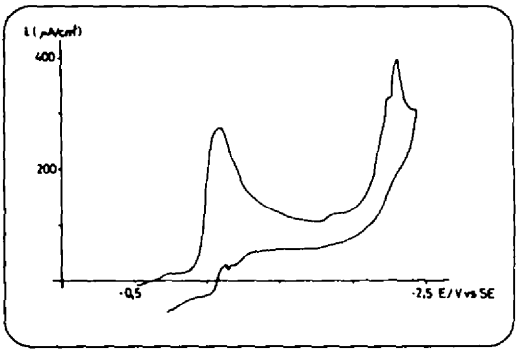
(a) R=SCH_3 Ar=C_6H_5
(b) R=SCH_3 Ar=4-CH_3O-C_6H_4
(c) R=H Ar=C_6H_5
(d) R=H Ar=4-CH_3O-C_6H_4

The present work is devoted to the study of several fused 1,3,4-thiadiazines such as: pyrido[2,1-*b*], thiazolo[2,3-*b*] and 1,2,4-triazolo[3,4-*b*][1,3,4]thiadiazines selected to investigate the influence of the fused heteroaromatic ring on the electrochemical sulfur extrusion of the 1,3,4-thiadiazine ring in order to prepare fused pyrazoles. This transformation is interesting from both synthetic and mechanistic viewpoints since it could be achievable under much milder reaction conditions than those used in hitherto-known methods.

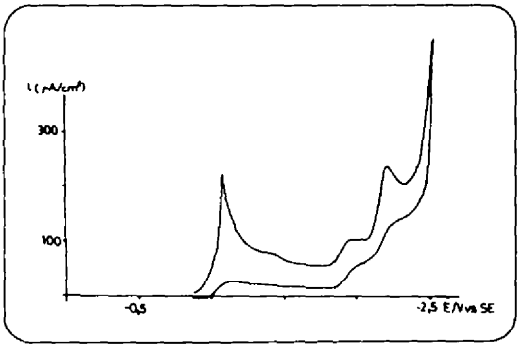
Cyclic Voltammogram of 1,3,4-Thiadiazinium Salts.



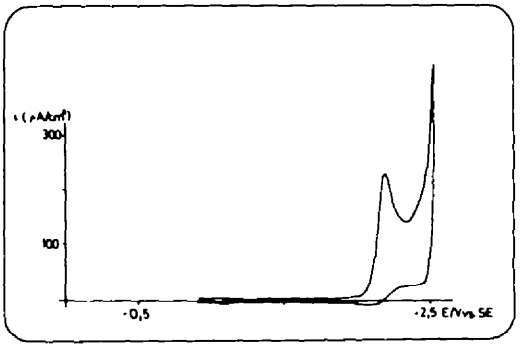
Cyclic Voltammogram of **1a** (8.3 10^{-4} M); dry DMF-$LiClO_4$; Hg electrode; 25°C; sweep rate: 100 mV s^{-1}.



Cyclic Voltammogram of **2a** (10^{-3} M); dry DMF-$LiClO_4$; Hg electrode; 25°C; sweep rate: 100 mV s^{-1}.



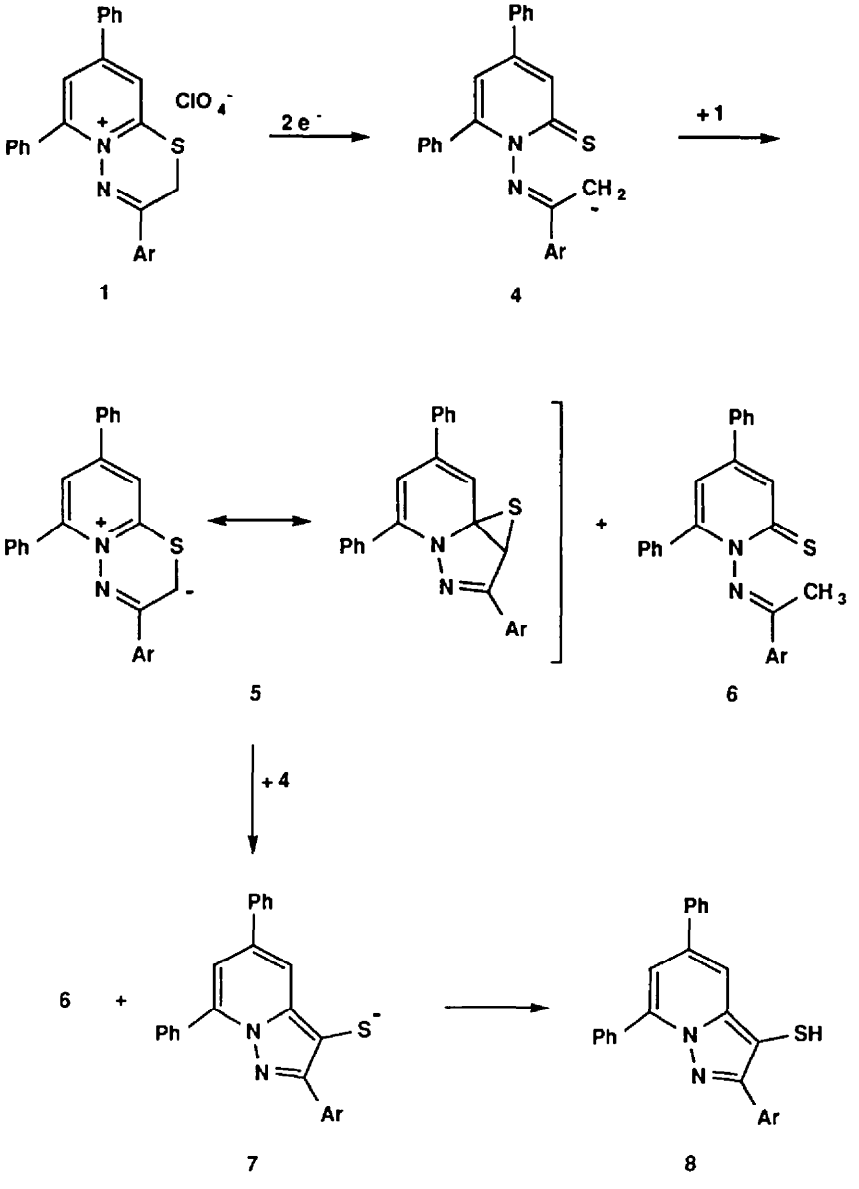
Cyclic Voltammogram of **3a** (10^{-3} M); dry DMF-$LiClO_4$; Hg electrode; 25°C; sweep rate: 100 mV s^{-1}.

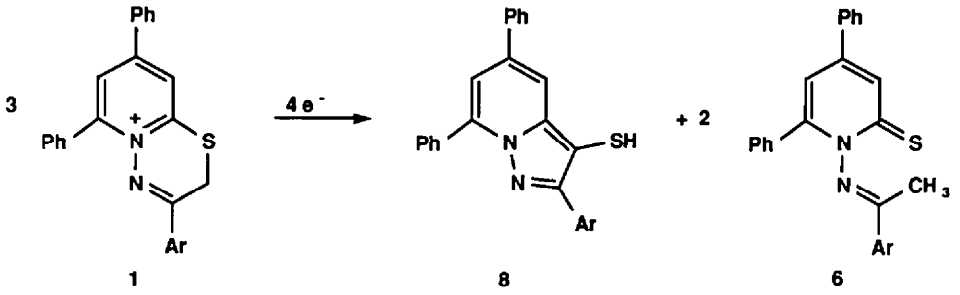


Cyclic Voltammogram of **12a** (8.8 10^{-4} M); dry DMF-$LiClO_4$; Hg electrode; 25°C; sweep rate: 100 mV s^{-1}.

RESULTS AND DISCUSSION.

In order to learn about the cathodic behaviour of fused 1,3,4-thiadiazines derivatives, we have performed a voltammetric study in aprotic medium, studying one compound of each class **1a**, **2a**, and **3a** as well as that heteroaryl ketimines **6**. Experiments were carried out at a handing mercury drop electrode in dimethylformamide.





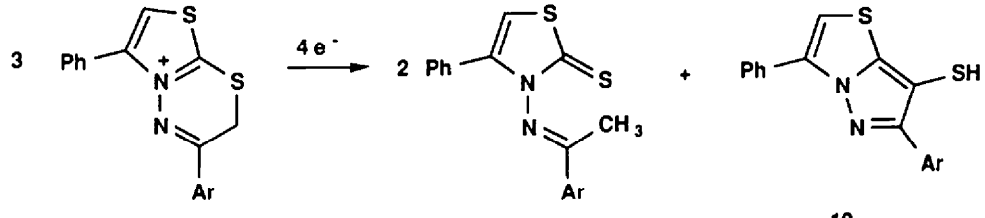
1 8 6

Cyclic voltammograms (CV´s) of compounds **1a-3a** show cathodic peaks but no anodic peak on the reverse scan. The first irreversible peak appears at -0.57, -0.67 and -0.60 *vs* SCE respectively corresponding to a two-electron process and the other irreversible peak appears at very negative potential (-1.75 V *vs* SCE). The fact that CV´s of ketimines **6a** and **12a** only show an irreversible cathodic peak at -1.42 and -1.70 V *vs* SCE respectively, clearly indicates that the first cathodic peak in the CV´s of compounds **1a-3a** correspond to an irreversible reduction of the endocyclic imminium bond. Taking account of these values preparative controlled-potential electrolyses (CPE) were carried out about -1.00V *vs* SCE.

Solutions of the appropriate bicyclic salts **1** (1mmol) were electrolyzed under a cathodic potential of -1.0 V *vs* SCE . The electron consumption suggest a process which involves 3 molecules and 4 electrons. When current started passing, the surface of the mercury cathode became red and after a short time the catholyte solution turned deep red.

From the mixture obtained after the work-up of the catholyte two products were obtained as crystalline solids. One of them was found to be the ketimine **6** resulting from the opening of the 1,3,4-thiadiazine portion whereas the other one was the corresponding pyrazolo[1,5-*a*]pyridine **8** (72-87%) resulting from the ring contraction of the 1,3,4-thiadiazine ring.

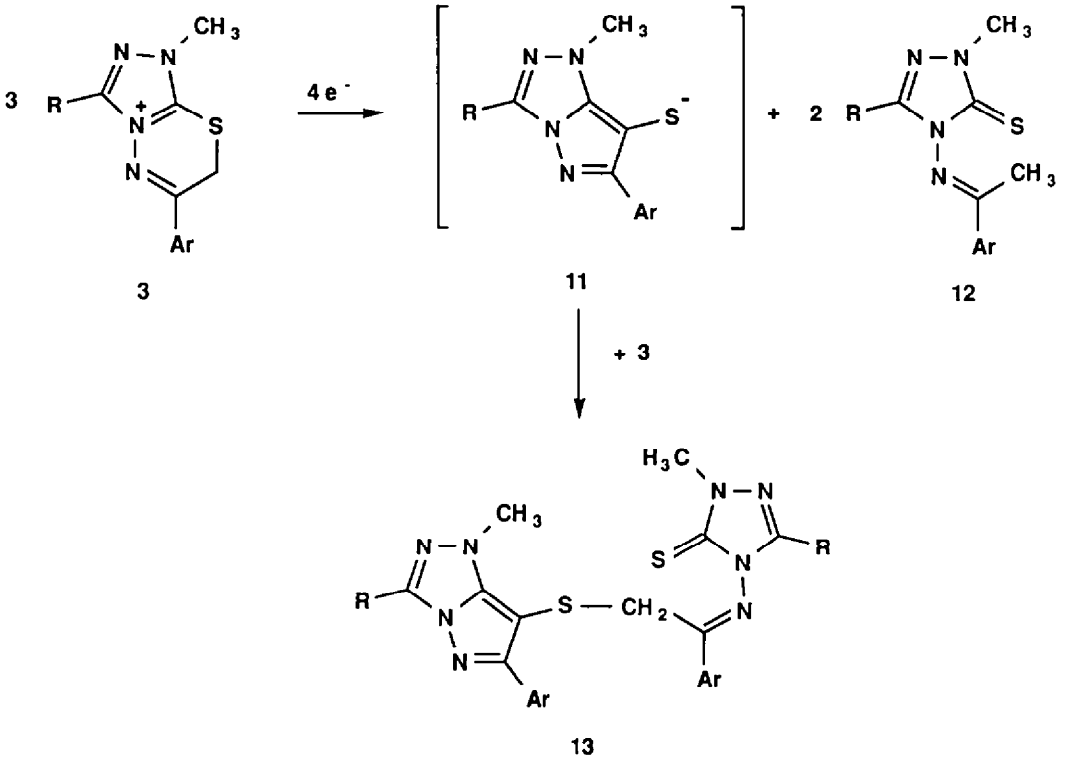
The conversion **1** → **6** + **8** presumably involves a first electrochemical step with two-electron transfer to give the anionic electrogenerated intermediate **4**. A second chemical step involving proton abstraction from **1** by the anionic compound **4** leads to **6** and the peripheral ylids **5** which can be represented as its valence tautomer with the thiirane ring. Finally, proton abstraction from **5** by the electrogenerated anion **4** leads to **7** which during the work-up was transformed into **8**.

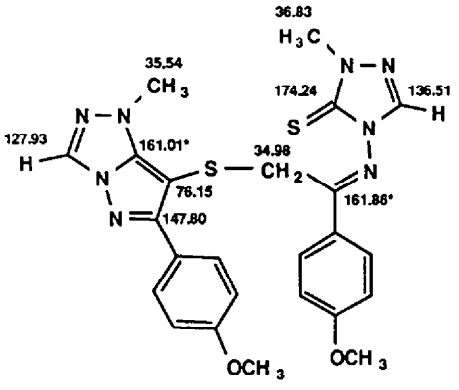


2 9 10

Similarly, when electroreductions of thiazolo[2,3-*b*][1,3,4]thiadiazinium perchlorates **2** were performed at -0.80 V for **2a**, -1.15 V for **2b** and -1.0 V *vs* SCE for **2c**, the electron consumption was 1.33 Faraday mol^{-1} and two products were isolated: the ketimine **9** and the pyrazolo[5,1-*c*]thiazole **10** (77-86% yield). This process takes place in a similar manner to the above mentioned for pyrido[2,1-*b*][1,3,4]thiadiazinium perchlorates **1**. In passing, it is worth mentioning that no general methods for the preparation of derivatives of the pyrazolo[5,1-*c*]thiadiazole ring system has hitherto been reported, it has only been mentioned that the reaction of pyrazoline-5-thiones with α-halocarbonyl compounds[6], or cyclization of 3-aminothiazolium salts by the action of acetic anhydride/sodium acetate[7] lead to pyrazolo[5,1-*b*]thiazole derivatives.

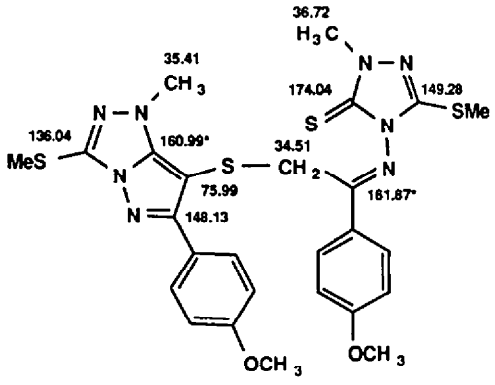
On the other hand, cathodic reductions of [1,2,4]-triazolo[3,4-*b*][1,3,4]thiadiazinium perchlorates **3** were carried out at -0.90 V *vs* SCE. The electricity consumption was 1 Faraday mol^{-1} and two products were isolated: the ketimine **12** and the pyrazolo[5,1-*c*][1,2,4]triazole **13** (63-78% yields). The formation of the later compound can be understood by the reaction of the thiolate **11** with the starting salt **3**. The reaction products were characterized on the basis of their elemental analysis and their MS and ^1H, ^{13}C NMR spectra. ^{13}C chemical shift for representative thiazolo[5,1-*c*][1,2,4]triazoles **13** are shown (values were assigned by decoupling methods, 2D H-C correlation techniques and by comparison with previously reported[8] values for fused pyrazolo-triazoles).





13 d

* Interchangeables



13 b

EXPERIMENTAL SECTION

All melting points were determined on a Kofler hot-plate melting point apparatus and are uncorrected. I.R. spectra were obtained as Nujol emulsions on a Nicolet FT-5DX spectrophotometer, NMR spectra were recorded on a Bruker AC-200 (200MHz). Mass spectra were recorded on a Hewlett-Packard 5993 C spectrometer. Microanalyses were performed on a Perkin-Elmer 240 C instrument.

ELECTROCHEMISTRY. Voltamperometric curves were registered with an Amel 553 potentiostat and a HQ Instruments 305 signal generator, coupled with a Philips PM 8133 x-y recorder. The working electrode was an handing mercury drop and the reference electrode was mercurous sulphate electrode (SE). The SSE system was anhydrous dimethylformamide 0.075 M in lithium percholate. Electrolyses were carried out in cells with compartment separated by a porous glass diaphragm. A mercury pool was used as the cathode and a platinum plate as the anode. The reference electrode was a SCE. Electrolyses were performed under controlled cathodic potential using an Amel 557 potentiostat and the amount of electricity was measured with an Amel 558 coulometer integrator coupled to the potentiostat. The values of the initial currents were about 100 mA and the electrolyses were continued until the current decreases to less than 1% of the starting value. The cell temperature was controlled at 25°C and nitrogen was bubbled through the catholyte solution for 10 min prior to electrolysis and above it during the experiment. For prevention of the accumulation of acid in the anode compartment, 1g of anhydrous sodium carbonate was put on the glass diaphragm.

Materials. Pyrido[3,2*a*][1,3,4]thiadiazinium salt[9] **1** and thiazolo[2,3-*b*][1,3,4]thiadiazinium salts[10] **2** were prepared as described in the literature.

General Procedure for the Preparation of 6-Substituted 1-Methyl-7H-[1,3,4]triazolo[1,2,4]triazolo-[3,4-b]thiadiazin-3-ium Perchlorates 3

To a solution of the corresponding 4-amino1-methyl-5-thioxo-4,5-dihydro[1,2,4]triazole[11] (10 mmol) in methanol (40 ml), the appropriate phenacyl bromide (10 mmol) was added. The reaction mixture was refluxed for 24 h. After cooling, the solvent was partially removed under reduced pressure at room temperature. The concentrated solution was then stored at 0°C overnight and the precipitated solid was collected by filtration and recrystallized from methanol to give the corresponding [1,2,4]triazolo[3,4-*b*]thiadiazinium bromides. A mixture of the fused[1,3,4]thiadiazinium bromide (10 mmol), ethanol (25 ml) and 70% perchloric acid (10 ml) was stirred at room temperature for 2 h. The precipitated solid was isolated by filtration and purified by recrystallization from ethanol to give **3** as crystalline solids. The following derivatives **3** were obtained:

(3a) 6-Phenyl-3-methylthio (84%), m.p. 185-187°C (colourless prisms). Found: C, 38.39; H, 3.56; N, 14.62. $C_{12}H_{13}ClN_4O_4S_2$ requires: C, 38.24; H, 3.48; N, 14.86; i.r. (Nujol):1557, 1415, 1319, 1296, 1087, 1002, 917, 866, 803, 764 and 685 cm^{-1}; ^{1}H-n.m.r. δ (DMSO-d_6): 2.80 (s, 3H, CH_3S), 4.15 (s, 3H, CH_3N), 4.80 (s, 2H, CH_2), 7.40-8.50 (m, 5H); ^{13}C-n.m.r. δ ($CDCl_3$+TFA): 16.6 (CH_3S), 27.6 (CH_2), 41.7 (CH_3N), 132.3 (C_o), 133.7 (C_m), 135.4 (C_i), 138.3 (C_p), 148.7 (C_6), 161.0 (C_3), 161.9 (C_{8a}); m/z (%): 276 (M^+-$HClO_4$, 2), 263 (5), 244 (10), 211 (5), 201 (4), 172 (15), 161 (20), 160 (10), 145 (10), 142 (15), 129 (16), 128 (13), 118 (10), 104 (15), 103 (100), 102 (36).

(3b) 6-(4-Methoxyphenyl)-3-methylthio (85%), m.p. 212-214°C (colourless prisms). (Found: C, 38.54; H, 3.61; N, 13.70. $C_{13}H_{15}ClN_4O_5S_2$ requires: C, 38.38; H, 3.72; N, 13.77; i.r. (Nujol): 1608, 1585, 1552, 1511, 1319, 1302, 1268, 1189, 1109, 917, 860, 855, 821, 736 and 679 cm^{-1}; ^{1}H-n.m.r. δ (DMSO-d_6): 2.75 (s, 3H, CH_3S), 3.41 (s, 3H, CH_3N), 3.89 (s, 3H, CH_3O), 4.60 (s, 2H, CH_2), 7.19 (d, 2H, J=8.9 Hz), 8.03 (d, 2H, J=8.9 Hz); ^{13}C-n.m.r. δ (DMSO-d_6): 13.22 (CH_3S), 23.38 (CH_2), 37.93 (CH_3N), 55.74 (CH_3O), 114.87 (C_m), 123.47 (C_i), 130.21 (C_o), 145.73 (C_6), 153.26 (C_3), 157.67 (C_p), 163.53 (C_{8a}); m/z (%): 307 (M^+-ClO_4, 10), 306 (M^+-$HClO_4$, 20), 305 (74), 275 (13), 274 (81), 273 (13), 259 (10), 241 (11), 202 (3), 187 (10), 174 (15), 173 (15), 172 (100), 161 (17), 133 (20), 132 (19), 129 (30), 102 (12).

(3c) 6-Phenyl (82%), m.p. 262-264°C (colourless prisms). (Found: C, 40.19; H, 3.58; N, 16.73. $C_{11}H_{11}ClN_4O_4S$ requires: C, 39.95; H, 3.35; N, 16.94); i.r. (Nujol): 3126, 1597, 1546, 1523, 1302, 1234, 1189, 1089, 985, 832, 753 and 685 cm^{-1}; ^{1}H-n.m.r. δ (DMSO-d_6): 3.98 (s, 3H, CH_3N), 4.62 (s, 2H, CH_2), 7.44-7.67 (m, 3H), 7.80-8.03 (m, 2H), 9.57 (s, 1H, H-3);^{13}C-n.m.r. δ (DMSO-d_6): 22.24 (CH_2), 36.46 (CH_3N), 126.57 (C_o), 127.61 (C_m), 130.08 (C_i), 131.75 (C_p), 140.81 (C_3), 143.31 (C_6), 157.46 (C_{8a}); m/z (%) 230 (M^+-$HClO_4$, 5), 217 (28), 216 (45), 198 (100), 197 (23), 189 (5), 156 (10), 143 (30), 127 (18), 126 (25), 117 (30), 115 (20), 104 (21), 103 (74), 77 (10).

(3d) 6(4-Methoxyphenyl) (79%), m.p. 244-246°C (colourless prisms). (Found: C, 40.19; H, 3.52; N, 15.41. $C_{12}H_{13}ClN_4O_5S$ requires: C, 39.95; H, 3.63; N, 15.53); i.r (Nujol): 3120, 1608, 1540, 1517, 1314, 1274, 1240, 1183, 1092, 1030, 1016, 849, 829 and 730 cm^{-1}; ^{1}H-n.m.r. δ (DMSO-d_6): 3.87 (s, 3H, CH_3N),

4.00 (s, 3H, CH_3O), 4.62 (s, 2H, CH_2), 7.17 (d, 2H, J=9.0 Hz), 8.04 (d, 2H,J=9.0 Hz), 9.74 (s, 1H, H-3); ^{13}C-n.m.r. δ (DMSO-d_6): 23.59 (CH_2), 37.81 (CH_3N), 55.71 (CH_3O), 114.81 (C_m), 123.55 (C_i), 130.21 (C_o), 142.10 (C_3), 144.76 (C_i), 158.43 (C_p), 163.45 (C_{8a})

Preparative Electrolysis Procedure.

The solvent-supporting electrolyte system (SSE) was formed by adding lithium perchlorate (0.63 g, 5mmol) in dry dimethylformamide (25 ml). into the anodic chamber of a divided cell was placed a solution of sodium carbonate (1g) in SSE (5 ml) and a solution of the appropiate fused [1,3,4]thiadiazinium perchlorate **1**, **2** or **3** (1mmol) in SSE (20 ml) was placed into the cathodic chamber. Electrolyses were performed under controlled cathodic potential, after the electricity of 1.33 F/mol for compounds **1** and **2** or 1.00 F/mol for compounds **3** was passed the catholyte was separated from the mercury by decantation and then poured into cold water (150 ml). The resultant mixture was keept at 0°C overnight.

The precipitated solid was collected by filtration, washed with cold methanol (10 ml) and recrystallized from the appropiate solvent to give the corresponding fused pyrazoles **8**, **10** or **13**. From the filtrate, the corresponding ketimines **6**, **9** or **12** were isolated. The following fused pyrazoles were obtained:

(8a) Ar = C_6H_5 (87%), m.p. 129-130°C (yellow crystals from dichloromethane/ethanol, 1:1). (Found: C, 79.52; H, 4.63; N, 7.25. $C_{25}H_{18}N_2S$ requires: C, 79.33; H, 4.79; N, 7.40; i.r. (Nujol): 1630, 1540, 1506, 1330, 1228, 1076, 1019, 917, 872, 758 and 690 cm^{-1}; ^{1}H-n.m.r. δ ($CDCl_3$): 7.02 (d, 1H, J=2.0 Hz), 7.23-7.28 (m, 3H), 7.35-7.54 (m, 9H), 7.76-7.80 (m, 2H), 7.97-8.02 (m, 2H), (SH proton was not observed); ^{13}C-n.m.r. δ ($CDCl_3$): 99.25 (C_3), 112.52, 113.37, 126.78, 127.83, 128.12, 128.31, 128.38, 128.42, 128.68, 128.96, 129.51, 132.21, 132.67, 138.12, 138.38, 140.36, 145.94, 155.37; m/z (%): 378 (M^+, 35), 377 (100), 346 (10), 274 (28), 230 (34), 203 (53), 202 (38), 192 (11), 160 (10), 128 (11), 103 (8).

(8b) Ar = 4-CH_3O-C_6H_4 (72%), m.p. 110-112°C (yellow prisms from ethanol). (Found: C, 76.35; H, 5.19; N, 6.59. $C_{26}H_{20}N_2OS$ requires: C, 76.44; H, 4.93; N, 6.86; i.r. (Nujol): 1636, 1608, 1526, 1327, 1304, 1287, 1250, 1175, 1030, 860, 832, 758 and 700 cm^{-1}; ^{1}H-n.m.r. δ ($CDCl_3$): 3.70 (s, 3H, CH_3O), 7.00 (d, 1H, J=2 Hz), 7.36-7.55 (m, 12H), 7.77-7.82 (m, 2H), 7.95-7.99 (m, 2H); ^{13}C-n.m.r. δ ($CDCl_3$): 55.07 (CH_3O), 98.36 (C_3), 112.35, 113.08, 113.26, 124.87, 126.77, 127.05, 128.05, 128.35, 128.90, 129.46, 129.85, 132.73, 137.81, 138.17, 140.19, 145.95, 155.10, 159.73; m/z (%): 376 (M^+-32, 15), 277 (10), 264 (20), 263 (100), 230 (18), 219 (35), 204 (10), 203 (14), 202 (33), 135 (25), 133 (25), 115 (33), 103 (17), 77 (21).

(8c) Ar = 4-Br-C_6H_4 (82%), m.p. 199-200°C (yellow prisms from chloroform/benzene 1:1). (Found: C, 65.83; H, 4.01; N, 6.19. $C_{25}H_{17}BrN_2S$ requires: C, 65.65; H, 3.75; N, 6.12; i.r. (Nujol): 1631, 1597, 1534, 1506, 1212, 1070, 1007, 860, 826, 764 and 690 cm^{-1}; ^{1}H-n.m.r. δ ($CDCl_3$): 7.12 (d, 1H, J=2 Hz), 7.16-7.20 (m, 2H), 7.45-7.51 (m, 6H), 7.60 (d, 1H, J=2 Hz), 7.65-7.70 (m, 4H), 7.86-7.90 (m, 2H), (SH proton was not observed); ^{13}C-n.m.r. δ ($CDCl_3$): 97.89 (C_3), 112.57, 113.95, 122.51, 126.95, 128.16, 128.56, 129.05, 129.42, 129.63, 129.82, 130.57, 132.45, 138.23, 138.90, 140.28, 145.56, 154.62, (C aryl linked to C2 was not observed); m/z (%): 458 (M^++2, 5), 456 (M^+, 5), 426 (82), 425 (72), 424 (100), 423 (45), 276 (27), 219

(16), 203 (17), 202 (26), 172 (66), 171 (20), 157 (7), 155 (7), 139 (14), 115 (21), 102 (16), 77 (24).

(10a) Ar = C_6H_5 (86%), m.p. 187-188°C (yellow prisms from ethanol). (Found: C, 66.13; H, 4.23; N, 8.91. $C_{17}H_{12}N_2S_2$ requires: C, 66.20; H, 3.92; N, 9.08; i.r. (Nujol): 3120, 3092, 1580, 1557, 1297, 1161, 1059, 821, 776, 742 and 702 cm^{-1}. ^{1}H-n.m.r. δ ($CDCl_3$): 6.83 (s, 1H), 7.18-7.21 (m, 3H), 7.46-7.50 (m, 4H), 7.79-7.83 (m, 2H), 8.04-8.09 (m, 2H); ^{13}C-n.m.r. δ ($CDCl_3$): 99.32 (C_7), 108.03, 127.02, 127.63, 128.05, 128.26 (CHx2), 128.58, 129.25, 132.03, 135.10, 148.04, 157.25; m/z (%): 308 (M^+, 27), 307 (49), 206 (16), 205 (58), 204 (97), 135 (11), 134 (100), 102 (41), 89 (14), 77 (21).

(10b) Ar = 4-Br-C_6H_4 (77%), m.p. 190-191°C (yellow prisms from ethanol). (Found: C, 52.63; H, 2.93; N, 7.05. $C_{17}H_{11}BrN_2S_2$ requires: C, 52.72; H, 2.86; N, 7.23; i.r. (Nujol): 3120, 1597, 1552, 1495, 1291, 1161, 1070, 1008, 832, 770, 736, 720 and 707 cm^{-1}; ^{1}H-n.m.r. δ ($CDCl_3$): 6.90 (s, 1H), 7.17-7.25 (m, 2H), 7.45-7.60 (m, 5H), 8.08-8.13 (m, 2H), (SH proton was not observed); ^{13}C-n.m.r. δ ($CDCl_3$): 108.36, 122.34, 127.09, 128.13, 128.68, 129.37, 129.47, 130.54, 130.61, 135.29, 147.98, 156.80, (C_7 was not observed); m/z (%): 388 (M^++2, 6), 386 (M^+, 6), 356 (61), 354 (62), 306 (13), 205 (29), 204 (30), 172 (13), 134 (77), 128 (13), 102 (100), 77 (17).

(13a) Ar =C_6H_5, R = CH_3S (72%), m.p. 203-205°C (colourless prisms from ethanol). (Found: C, 52.25; H, 4.58; N, 20.17. $C_{24}H_{24}N_8S_4$ requires: C, 52.15; H, 4.38; N, 20.27; i.r. (Nujol): 1602, 1568, 1318, 1248, 1188, 1146, 1072, 854, 776, 710 and 696 cm^{-1}; ^{1}H-n.m.r. δ ($CDCl_3$): 2.53 (s, 3H, CH_3S), 2.67 (s, 3H, CH_3S), 3.41 (s, 3H, CH_3N), 3.58 (s, 3H, CH_3N), 3.79 (s, 2H, CH_2), 7.36-7.45 (m, 6H), 7.86-7.97 (m, 4H); ^{13}C-n.m.r. δ ($CDCl_3$): 13.80 (CH_3S), 14.20 (CH_3S), 34.70 (CH_2), 35.40 (CH_3N), 36.80 (CH_3N), 127.80, 128.20, 128.35 (CHx2), 128.50, 128.85, 132.00, 132.15, 133.40, 136.15, 148.10, 149.25, 160.85, 161.80, 174.10; m/z (%): 552 (M^+, 3), 551 (3), 550 (6), 278 (10), 277 (6), 245 (16), 244 (47), 224 (12), 175 (34), 172 (25), 161 (69), 160 (13), 149 (11), 142 (15), 128 (16), 104 (58), 102 (100), 98 (16).

(13b) Ar = 4-CH_3O-C_6H_4, R = CH_3S (63%), m.p. 178-180°C (colourless prisms from ethanol). (Found: C, 50.81; H, 4.55; N, 18.20. $C_{26}H_{28}N_8O_2S_4$ requires: C, 50.96; H, 4.61; N, 18.28; i.r. (Nujol): 1608, 1510, 1506, 1319, 1308, 1251, 1177, 1105, 1030, 842, 730 and 690 cm^{-1}; ^{1}H-n.m.r. δ ($CDCl_3$): 2.51 (s, 3H, CH_3S), 2.65 (s, 3H, CH_3S), 3.44 (s, 3H, CH_3N), 3.61 (s, 3H, CH_3N), 3.74 (s, 2H, CH_2), 3.85 (s, 6H, 2xCH_3O), 6.82-6.93 (m, 4H), 7.78-7.92 (m, 4H); ^{13}C-n.m.r. δ ($CDCl_3$): 13.70 (CH_3Sx2), 34.51 (CH_2), 35.42 (CH_3N), 36.72 (CH_3N), 55.19 (CH_3O), 55.36 (CH_3O), 76.00, 113.62 (CHx2), 124.85, 125.81, 129.26, 130.23, 136.04, 148.13, 149.28, 160.07, 160.68, 162.12, 162.68, 174.04; m/z (%): 612 (M^+, 5), 611 (3), 610 (5), 306 (15), 305 (24), 274 (21), 241 (6), 174 (11), 173 (26), 172 (100), 133 (15), 129 (25), 102 (10).

(13c) Ar =C_6H_5, R = H (78%), m.p. 177-179°C (colourless prisms from methanol). (Found: C, 57.18; H, 4.47; N, 24.27. $C_{22}H_{20}N_8S_2$ requires: C, 57.37; H, 4.38; N, 24.33; i.r. (Nujol): 1602, 1557, 1529, 1331, 1302, 1234, 1155, 1098, 1068, 1019, 979, 866, 843, 781 and 719 cm^{-1}; ^{1}H-n.m.r. δ ($CDCl_3$): 3.65 (s, 3H, CH_3N), 3.66 (s, 3H, CH_3N), 3.84 (s, 2H, CH_2), 6.96 (s, 1H), 7.33-7.47 (m, 6H), 7.71-7.75 (d, 2H, J=7.0 Hz), 7.87-7.92 (m, 2H), 8.16 (s, 1H); ^{13}C-n.m.r. δ ($CDCl_3$): 35.60 (CH_2), 35.60 (CH_3N), 36.87 (CH_3N), 76.46, 128.04, 128.13, 128.23, 128.36, 128.49, 129.11, 132.03, 132.10, 133.52, 136.42, 147.77, 161.00,

161.87, 175.10; m/z (%): 461 (M^+, 2), 231 (32), 229 (14), 198 (15), 186 (5), 128 (30), 126 (100), 115 (17), 104 (21), 99 (16), 77 (26).

(13d) Ar = 4-CH_3O-C_6H_4, R = H (63%), m.p. 193-196°C (colourless prisms from ethanol). (Found: C, 55.13; H, 5.47; N, 21.38. $C_{24}H_{24}N_8O_2S_2$ requires: C, 55.37; H, 4.65; N, 21.52; i.r. (Nujol): 1608, 1591, 1562, 1512, 1336, 1308, 1263, 1177, 1087, 1019, 974, 838, 815 and 798 cm^{-1}; ^{1}H-n.m.r. δ ($CDCl_3$): 3.66 (s, 3H, CH_3N), 3.86 (s, 3H, CH_3N), 3.67 (s, 2H, CH_2), 3.84 (s, 3H, CH_3O), 3.86 (s, 3H, CH_3O), 6.83 (d, 2H, J=8.9 Hz), 6.85 (d, 2H, J=8.9 Hz), 6.94 (s, 1H), 7.74 (d, 2H, J=8.9 Hz), 7.84 (d, 2H, J=8.9 Hz), 8.16 (s, 1H); ^{13}C-n.m.r. δ ($CDCl_3$):34.98 (CH_2), 35.54 (CH_3N), 36.83 (CH_3N), 55.20 (CH_3O), 55.43 (CH_3O), 76.15, 113.68, 113.75, 124.48, 125.56, 127.93, 129.53, 130.12, 136.51, 147.80, 160.24, 161.01, 161.86, 162.82, 174.24; m/z (%): 520 (M^+, 2), 518 (2), 354 (2), 262 (12), 261 (25), 260 (17), 259 (40), 229 (25), 228 (76), 213 (21), 173 (12), 148 (10), 134 (36), 133 (26), 129 (30), 126 (100), 115 (35), 114 (14), 91 (11).

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References.

1.- Baizer, M. M.; Lund H. *"Organic Electrochemistry"* Ed. Marcel Dekker Inc., New York, **1983.**

2.- Lund, H.; Tabacovic, I. *Adv. Heterocycl. Chem.* **1984**, 36, 235

3.- Pfeiffer, W. D.; Bulka, E. *Synthesis* **1977**, 485

4.- Schmidt, R. R.; Huth, H. *Tetrahedron Lett.* **1975**, 33; Molina, P.; Arques,A.; Ferao, A. *Synthesis* **1982**, 645; Molina, P.; Arques, A.; Velasco M. D.; Villalgordo, J.M. *Synthesis* **1988**, 729; Molina, P.; Tarraga, A.; Garcia, C *Heterocycles* **1988**, 27, 733.

5.- Pfeiffer, W. D.; Bulka, E.; Miethchen, R. *Z. Chem.* **1987**, 27, 296.

6.- Peseke, K. *Z. Chem.* **1976**, 16, 52; Peseke, K.; Vogel, C.; Blaesch, J.; Kollhof, K. H. *J. Prakt. Chem.* **1982**, 324, 639.

7.- Koga, H.; Hirobe, M.; Okamoto, T. *Chem. Pharm. Bull.* **1974**, 22, 482

8.- Faure,R.; Vicent, E.J.; Elguero, J. *Org. Magn. Resonance*, **1977**, 9, 508; Alajarin, M.; Molina, P.; Tarraga, A.; Vilaplana, M.J.; Foces-Foces, M.C.; Cano, F.H.; Claramunt, R.M.; Elguero, J. *Bull. Chem. Soc. Jpn.* **1985**, 58, 735.

9.- Molina, P.; Arques, A.; Ferao, A. *Synthesis* **1982**, 645.

10.- Molina, P.; Arques, A.; Velasco, M. D.; Villalgordo, J. M. *Heterocycles* **1987**, 26, 1323.

11.- Becker, H. G. O.; Timpe, H. J. *J. Prakt Chem.* **1973**, 315, 97.