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Electrochemical reduction of a herbicide metamitron (4-amino-3-methyl-6-phenyl-1,2,4-triazin-5(4*H*)-one) in buffered aqueous solutions occurs on the protonated 1,6-carbon-nitrogen double bond. The 2,3-double bond in the resulting 1,6-dihydrometamitron is electrochemically reduced at considerably more negative potentials. In reaction with borohydride the 2,3-double bond is reduced first. Reduction of the 1,6-double bond is very little influenced by replacing the 2,3-double bond by the -NHCH- grouping in 2,3-dihydrometamitron.

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The electron is the ultimate nucleophilic reagent and therefore electrochemical reductions often occur at a site which is preferred in nucleophilic additions. In most compounds which have been studied so far that possess several electroactive centers, these centers are linked by conjugation. In such systems, it is often difficult to distinguish the sequence of reactivities of individual centers, as the electron transfer occurs into the LUMO of the whole conjugated system. In some instances the nature of the product is decided by the site of protonation, which either precedes or succeeds the electron transfer.

In the case of the electrochemical reduction of the herbicide metamitron (4-amino-3-methyl-6-phenyl-1,2,4-triazin-5(4*H*)-one, **1**), widely used in the control of weeds in sugar and fodder beet production, the reduction of the protonated form of the 1,6-carbon-nitrogen double bond occurs at considerably more positive potentials than that of the protonated 2,3-azomethine bond (Figure 1). It is rather unusual that the reduction of the 1,6-bond in metamitron (**1**) occurs over the whole *pH*-range between 2 and

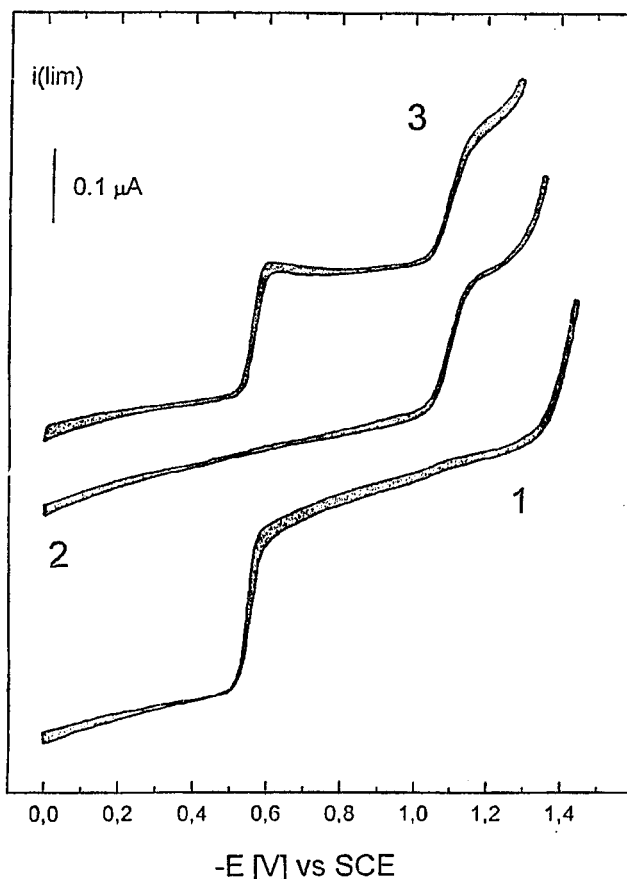
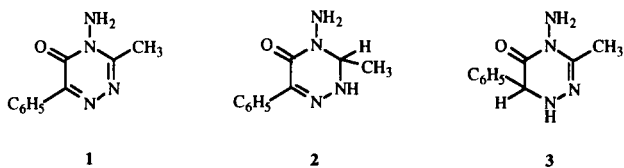


Figure 1. Polarographic curves of (1) dihydrometamitron, (2) 1,6-dihydrometamitron, and (3) 2,3-metamitron in acetate buffer *pH* 4.2 at concentrations  $3 \times 10^{-6}$  M.

8 at virtually the same potential as the reduction of the analogous bond in 2,3-dihydrometamitron (**2**) (Figure 1). Moreover, the half-wave potentials and their dependence on pH of the second reduction wave of metamitron (**1**) that corresponds to the reduction of the 2,3-bond, are identical with the half-wave potentials and their dependence on pH between pH 2 and 6 observed for 1,6-dihydrometamitron (**3**). This indicates that in metamitron the reactivity of the C=N bond in position 1,6 is very little affected by the presence and reduction of the C=N bond in position 2,3 and similarly the reactivity of the C=N bond in position 2,3 is only slightly affected by the reduction of the 1,6-bond.

Stability of  $\sigma$ -adducts has been compared only for 1,2,4-triazines that do not bear an oxo group in position 5. For such compounds the C-3 adducts were reported [1] to be less stable than C-5 adducts, while formation of C-6 adducts has been observed only for reactions of some nucleophiles.

Our studies indicated, in agreement with the literature [2], that borohydride attacks metamitron at the C-3 carbon and yields 2,3-dihydrometamitron (**2**). It seems that the presence of the 5-oxo group does not affect the electron deficiency at C-3, reported [3] to be the highest in the 1,2,4-triazine ring. On the other hand, the first electrochemical reduction step of metamitron in aqueous buffers occurs at the 1,6-azomethine bond and yields 1,6-dihydrometamitron (**3**). The electrochemical reduction is preceded by a protonation of the C=N bond and is facilitated by the phenyl group in position 6. This reduction mechanism differs, however, from that recently reported by Olmedo *et al.* [4].

The difference between the chemical and electrochemical reduction can hence be due to a preferential protonation of N-1. Alternatively, the difference may be due to steric requirements of  $\text{BH}_4^-$  resulting in the preference of the attack on C-3 over that on a more crowded C-6. Finally, an orientation of metamitron (**1**) at the electrode surface may prefer an attack on the 1,6-bond. To distinguish between these alternative reduction paths, comparison with attacks of other nucleophiles on metamitron and related compounds is in progress.

## EXPERIMENTAL

Controlled potential electrolysis of metamitron (**1**) (4-amino-3-methyl-6-phenyl-1,2,4-triazin-5(4H)-one) was carried out using a stirred mercury pool electrode at -1.1 V (SCE) using PAR 173 and 175 (EG&G Instruments, Princeton, NJ) as potentiostat. A Pt-grid was used as counter-electrode, the reference electrode was SCE.

4-Amino-3-methyl-6-phenyl-1,6-dihydro-1,2,4-triazin-5(1H)-one (**2**).

To a solution of 1 g (0.005 mole) of metamitron (**1**) in 50 ml of acetonitrile were added 200 ml of an aqueous solution of 0.1 molar acetate buffer pH 4.7. Electrolysis at -1.1 V was carried out in an argon atmosphere until 953 Coulombs passed (theoretical consumption: 946 Coulombs). The white precipitate which formed (550 mg, 55%) was separated by filtration and recrystallization from methanol, mp 193.5°;  $^1\text{H}$  nmr (DMSO- $d_6$ ):  $\delta$  2.04 (s, 3H,  $\text{CH}_3$ ), 4.64 (s, 1H,  $\text{H}_6$ ), 5.00 (s, 2H,  $\text{NH}_2$ ), 6.91 (s, 1H, NH), 7.30-7.33 (m, 5H,  $\text{C}_6\text{H}_5$ );  $^{13}\text{C}$  nmr (DMSO- $d_6$ ):  $\delta$  17.1 ( $\text{CH}_3$ ), 60.6 ( $\text{C}_6$ ), 127.7 ( $\text{C}'_4$ ), 127.8 ( $\text{C}_{3,5}$ ), 127.8 ( $\text{C}_{2,6}$ ), 136.5 ( $\text{C}_1$ ), 146.6 ( $\text{C}_3$ ), 165.3 ( $\text{C}_5$ ).

Anal. Calcd. for  $\text{C}_{10}\text{H}_{12}\text{N}_4\text{O}$ : C, 58.29; H, 5.87; N, 27.19. Found: C, 58.23; H, 5.87; N, 27.61.

4-Amino-3-methyl-6-phenyl-2,3-dihydro-1,2,4-triazin-5(2H)-one or 4-Amino-3-methyl-6-phenyl-3,4-dihydro-1,2,4-triazin-5(2H)-ol (**3**) [5].

To a solution of 1 g (0.005 mole) of metamitron (**1**) in 100 ml of methanol was gradually added 0.3 g (0.008 mole) of solid sodium borohydride and stirred for 48 hours at room temperature (gas evolution). Methanol was distilled off, 600 mg (60%) of white crystals were washed with 5 ml of water and recrystallized from ethanol, mp 134-136° (lit [5] 135°);  $^1\text{H}$  nmr (DMSO- $d_6$ ):  $\delta$  1.40 (d,  $J^3$  5.91 Hz = 3H,  $\text{CH}_3$ ), 4.84 (d,  $^3J_{\text{HH}} = 5.89$  Hz, 1 H, CH), 4.94 (s, 2 H,  $\text{NH}_2$ ), 7.32 (m, 3 H,  $\text{C}'_{3,4,5}$  H), 7.78 (d,  $^3J_{\text{HH}} = 7.19$  Hz, 2 H,  $\text{C}'_{2,6}$  H), 8.83 (s, 1 H, OH);  $^{13}\text{C}$  nmr (DMSO- $d_6$ ):  $\delta$  15.9 ( $\text{CH}_3$ ), 68.4 ( $\text{C}_3$ ), 127.3 ( $\text{C}'_4$ ), 127.5 ( $\text{C}'_{3,5}$ ), 127.7 ( $\text{C}'_{2,6}$ ), 134.6 ( $\text{C}_1$ ), 135.9 ( $\text{C}_5$ ), 156.7 ( $\text{C}_6$ ).

Anal. Calcd. for  $\text{C}_{10}\text{H}_{12}\text{N}_4\text{O}$ : C, 58.29; H, 5.87; N, 27.19. Found: C, 57.78; H, 5.95; N, 26.57.

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