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Unexpected production of 2,4,6-triphenyl-1,3,5-triazine in the electroreduction of 3,4-diphenyl-1,2,5-thiadiazole 1-oxide. Theoretical estimation of reactive sites for 1-oxide and 1,1-dioxide 1,2,5-thiadiazoles

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Abstract

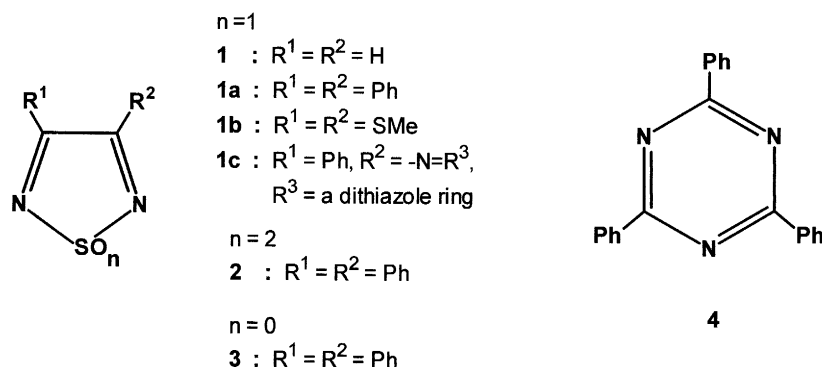
3,4-Diphenyl-1,2,5-thiadiazole 1-oxide (**1a**) in acetonitrile solution is electroreduced to 2,4,6-triphenyl-1,3,5-triazine and 3,4-diphenyl-1,2,5-thiadiazole. This behavior is very different from that of similar compounds with other oxidation states of the heterocyclic sulfur atom, such as the 1,1-dioxide derivative (**2**) and the aromatic 3,4-diphenyl thiadiazole parent ring. The Fukui functions were calculated for **1a** and **2** to estimate their reactivity, compare their reactive site, and rationalize the divergent electrochemical properties of **1a**. © 2000 Elsevier Science Ltd. All rights reserved.

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1,2,5-Thiadiazoles have been broadly applied in the areas of pharmaceutical, agricultural, industrial and polymer chemistry.^{1,2} In several of these applications, 1,1-dioxide and 1-oxide derivatives were employed. We have studied aspects of the physical-organic chemistry of several 1,1-dioxides,^{3–9} but similar work with 1-oxides is almost non-existent. We are not aware of any publication on the electrochemistry of 1-oxide derivatives. Theoretical molecular orbital calculations for **1** have been performed with a modified STO-3G* basis set,¹⁰ but the thiadiazole ring was constrained to be planar. A single-point 6-31G* energy was also calculated for the same molecule, using a fully optimized STO-3G* structure.¹¹ No theoretical estimations of reactive sites and reactivity have been attempted for the 1-oxide derivatives.

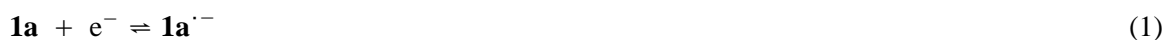
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We report here voltammetric and bulk electrolysis electroreduction experiments[†] of **1a** (Scheme 1), at ca. -1.5 V, in acetonitrile (ACN) solution. 2,4,6-Triphenyl-1,3,5-triazine (**4**) and 3,4-diphenyl-1,2,5-thiadiazole (**3**) were produced with ca. 30 and 50% yield, respectively. **4** Formation implies the opening of the heterocycle ring. Thus, the electroreduction of **1a** differs from that of **2**^{4,6} which, at more positive potentials (ca. -0.8 V) is reversibly reduced to a relatively stable radical anion. Compound **3**¹² is also electroreduced to a radical anion at more negative potentials (ca. -2.4 V).



Scheme 1.

A typical cyclic voltammogram of **1a** (Fig. 1, full line), presented several cathodic peaks (at -1.19 , -1.63 , -2.29 (shoulder), and -2.35 V). If the scan was reversed right after traversing the peak at -1.19 V, a corresponding anodic signal could be observed. The ratio of the anodic to the cathodic current intensities of the peaks ($R=I_{pa}/I_{pc}$) increased with the increase of the sweep rate, ν , and the switching potential, E_λ . The voltammetric current function for a one-electron reversible charge transfer, applied in the range of ν and E_λ for which $R > 0.7$ allowed the estimation of a diffusion coefficient ($D=2.8 \pm 0.1 \times 10^{-5}$ cm² seg⁻¹). It can be reasonably assumed that this monoelectronic, diffusion controlled, voltammetric couple at -1.19 V corresponds to the electroreduction of the substrate to the radical anion (Eq. (1)):



Subsequent reaction(s) must take place to account for the dependence of R with ν and E_λ .

The peak at -2.35 V was assigned to the electroreduction of **3** ($E_{1/2}=-2.39$ ¹²) by comparative cyclic voltammetry (a cyclic voltammogram of a sample of **3** is included in Fig. 1, broken line). Furthermore, **3** was also a product of the bulk electroreduction of **1a** (see below). From the relative current intensities of the voltammetric peaks of **1a** and **3** (Fig. 1), and the experimental concentration of the respective substrates, it can be estimated that ca. 50% of the voltammetrically generated **1a**^{·-} transforms into **3**.

Bulk electrolysis experiments, at -1.50 V, of a solution of **1a** in ACN were performed. The electrolysis products, identified as follows, were: (a) **4**. Compound **4** is practically insoluble in the electrolytic

[†] Voltammetric experiments were performed in an undivided, gas-tight, glass cell swept by purified nitrogen. The cell was kept and manipulated within a dry box. The reference electrode (r.e.) was Ag⁺ (0.1 M ACN)/Ag separated from the cell solution by a porous-glass plug. A 5 cm² Pt foil was the counter electrode (c.e.) and the working electrode (w.e.) was a Teflon[®] encapsulated vitreous carbon disk of 0.074 cm². Bulk electrolysis experiments were carried out in a divided cell. A sinterized glass plate separated the anodic and the cathodic compartments. The w.e. (cathode) was a vitreous carbon rod (0.3 cm diameter and 1.5 cm length), the c.e. was an 8 cm² Pt foil. The w.e. described above for voltammetry was also included into the cathodic compartment. The electrolysis was interrupted at selected time intervals and cyclic voltammograms, using this w.e., were run to measure the concentration of substrate.

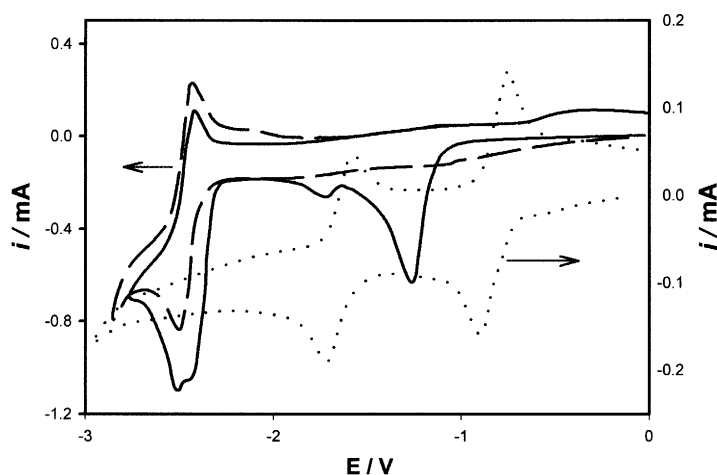


Fig. 1. Cyclic voltammograms, current function vs potential for ACN solutions of **1a**, **2**, and **3**. Supporting electrolyte: 0.20 M TEAP. $\nu=0.2 \text{ V seg}^{-1}$. (—): [**1a**]=10.8 mM; (.....): [**2**]=3.41 mM; (— — —): [**3**]=3.36 mM

solution and precipitated as a white solid. It was identified by IR,¹³ UV–visible spectroscopies¹⁴ and GC–MS. Its mp was 233.5–234.5°C (lit.: 235.0–235.4°C¹⁴). The yield was ca. 30%. (b) Compound **3**, identified by GC–MS in a chloroformic extract of the electrolyzed solution. The yield of **3**, as measured by the current intensity of its voltammetric peak after exhaustive electrolysis, was in the 40–48% range. (c) Benzonitrile, identified by GC. (d) Benzil, identified by GC–MS and (e) a minor unidentified product (GC–MS).

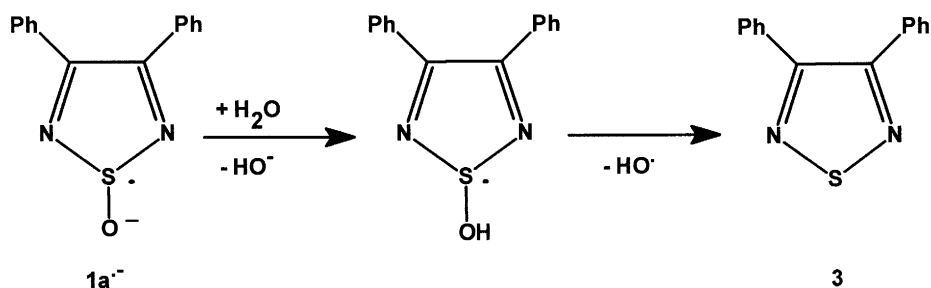
The concentration of **1a** was measured at selected times during the electrolysis using the current intensity of its voltammetric peak at -1.19 V . The calculated number of electrons per mole of **1a** electrolyzed was 0.4.

The dotted line in Fig. 1 corresponds to a typical cyclic voltammogram of **2** in ACN solution. Compound **2** is reduced to a radical anion and to a dianion in two successive, reversible voltammetric peaks.^{4,6} The bulk electrolysis of **2** in ACN solution, at the potential of the first charge transfer, produces a strongly colored solution containing, presumably, the radical anion. The solution is stable under the dry N_2 atmosphere of the cell.

When the electroreduction of **1a** was carried out in a 0.60 M water solution in ACN, **3** was the main product. The formation of a precipitate of **4** was not observed, although **4** was chromatographically detected as a minor component. Conversely, when the concentration of **1a** was increased (decreasing the relative amount of residual water available to $\mathbf{1a}^{\cdot-}$), the relative yield of **3** decreased. Thus, **3** was probably formed (Scheme 2) by reaction of the radical anion with residual water. The proposed structure for $\mathbf{1a}^{\cdot-}$ and the mechanism of Scheme 2 are in accordance with the calculated values of the Fukui functions (see below).

It might be recalled that the 1-oxide thiadiazole **1c** (Scheme 1) has been reported to deoxygenate smoothly to the thiadiazole by thermolysis at 250°C, while a 1,1-dioxide compound, otherwise structurally identical to **1c**, was stable at 280°C.¹⁵

The unexpected formation of the triazine from $\mathbf{1a}^{\cdot-}$ involves the loss of the >SO group and the opening of the ring at the heterocyclic C–C bond. At this stage, the mechanism of **4** formation can only be a matter of speculation, although a cleavage of the N–S bond of $\mathbf{1a}^{\cdot-}$, followed by an attack of the resulting nucleophilic radical anion on a molecule of **1a** appear as reasonable initial steps. A detailed study of the



Scheme 2.

distribution of the products as a function of the conditions of the electrolysis is underway to clarify the mechanism.

Reactivity and reactive sites for **1a** and **2** were estimated through the calculation[‡] of the Fukui functions¹⁷ in an attempt to rationalize the different electroreduction behavior.

Bond lengths and bond angles for **1a** were in good agreement with those calculated,¹¹ or measured by X-ray diffraction for similar molecules (**1b**,¹⁰ **1c**¹⁵). Table 1 shows the net atomic charges and the condensed Fukui functions f^+ , f^- and f^0 (for a nucleophilic or an electrophilic attack, or for a radical reaction, respectively), for the heterocyclic atoms of **1a** and **2**. Positive values of the condensed Fukui functions, and adequate charges (i.e. positive for a nucleophilic attack) indicates preferential reactivity for the type of reaction in question. The results predicted, as expected, the N atoms as preferred sites for electrophilic attacks. Less obviously, the preferred site for a nucleophilic attack or for the formation of a radical anion, as judged by the f^+ and the f^0 values of the positively charged atoms, were the heterocyclic C atoms for **2** and the S atom for **1a**.

Table 1

Compound	Heterocyclic Atom	charge	$f^+ \times 100$	$f^- \times 100$	$f^0 \times 100$
1a	O	-0.69	6.9	4.2	5.6
	S	1.08	11.1	4.4	7.7
	N	-0.72	14.8	4.4	9.6
	C	0.12	7.4	0.8	3.3
2	O	-0.61	6.0	3.5	4.7
	S	1.63	5.1	1.5	3.2
	N	-0.61	8.7	4.6	6.1
	C	0.25	11.2	0.9	6.0

[‡] Ab-initio HF/3-21G** and HF/6-31G** Hartree-Fock LCAO molecular orbital (MO) calculations were performed for the neutral molecule, the radical anion and the radical cation of **1a** and **2** with the Gaussian 94W series of programs.¹⁶ RHF single determinantal wavefunctions were used for closed-shell systems and UHF for the open shell systems, with orbitals being the solutions of the Roothaan equations. The equilibrium conformation of the neutral molecule was calculated by the gradient method.

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