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A new type of imine α-anion derived from 3-methyl-4-phenyl-1,2,5-thiadiazole 1,1-dioxide. Tautomerization and dimerization reactions

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epoc ABSTRACT: Proton abstraction from 3-methyl-4-phenyl-1,2,5-thiadiazole 1,1-dioxide (**1b**) in basic non-aqueous media generated a resonance-stabilized anion (**1b**$^-$) that added to **1b** producing a dimer, 3-phenyl-4-(4-phenyl-3-methylene-1,2,5-thiadiazolin-2-yl 1,1-dioxide)-4-methyl-1,2,5-thiadiazoline 1,1-dioxide (**2**). The anion and the dimer were also electrochemically generated by the cathodic reduction of **1b** in acetonitrile solution. The neutralization of basic ethanolic solutions containing **1b**$^-$ caused the precipitation of the tautomer of **1b**, 3-phenyl-4-methylene-1,2,5-thiadiazoline 1,1-dioxide (**3**). The anion **1b**$^-$, and the new compounds **2** and **3** were characterized and identified by NMR, IR and UV–VIS spectroscopic techniques. Their voltammetric behavior was also investigated. Copyright © 2001 John Wiley & Sons, Ltd.
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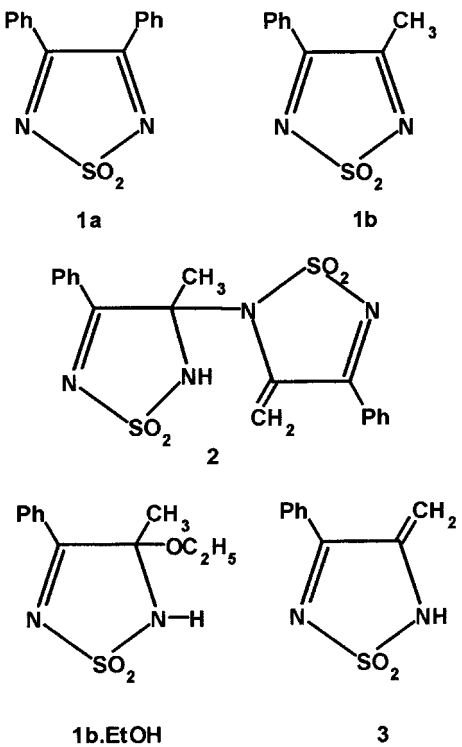
KEYWORDS: imine α-anion; 3-methyl-4-phenyl-1,2,5-thiadiazole 1,1-dioxide; isomerization; dimerization

INTRODUCTION

We have recently studied the equilibrium addition reaction of alcohols (ROH) to a C=N double bond of 3,4-diphenyl-1,2,5-thiadiazole 1,1-dioxide and 3-methyl-4-phenyl-1,2,5-thiadiazole 1,1-dioxide[1–4] (**1a** and **1b**; Scheme 1) to give the corresponding thiadiazoline compounds (e.g. **1b**·EtOH).

We have also studied the voltammetric properties of **1b** in acetonitrile (ACN) solution and those of several **1b**·ROH thiadiazolines in alcoholic solutions.[3,4] Spectroscopic and electrochemical results showed that the alcohol adds almost exclusively on the side of the molecule that bears the methyl substituent. Only in solutions of **1b** in pure EtOH or MeOH could the product of the addition on the phenyl side be observed by ^{1}H NMR in a less than 10% proportion.[5]

The strong electron-withdrawing characteristics of the $\rangle SO_2$ group confers a highly electropositive character to the heterocyclic carbon atoms of the thiadiazole 1,1-dioxide ring.[6] This facilitates nucleophilic additions to the C=N double bond, such as those mentioned above, and, in the case of **1b**, should also enhance the acidic character of the methyl protons and favor the formation of carbanions. This was investigated in this work.



Scheme 1

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EXPERIMENTAL

Solvents and reagents from the following sources were used: ACN, Mallinckrodt, spectroscopic grade; triethylamine (TEA), Sintorgan, p.a.; *tert*-butylamine (tBuA), Schuchardt München; EtOH, Merck, p.a.; TLC plates, Merck, silica gel 60 F_{254}; ACN-d_3, Sigma, 99 at.% D; EtOH-d_6, Merck, 99% min.; DMSO-d_6, Sigma, 99 at.% D; dimethylformamide (DMF), Mallinckrodt, A.R.; trifluoroacetic acid (TFA), Riedel-de Haën, 99%.

Compound **1b** was synthesized and characterized according to a published procedure,[7] but the purification method was modified (the benzene recrystallization solvent was acidified with dry TFA) to prevent the formation of the dimer **2** (see Results). The yield of **1b** using the modified procedure was ≈50% vs. the literature-reported yield of 29%.[7] Standard methods were used for the purification of solvents and other reactants.

Spectroscopic measurements. ^{1}H and ^{13}C NMR spectra were obtained with a 200 MHz instrument. Conventional instruments were used for IR and UV–VIS spectroscopy, respectively. KBr pellets were used for the measurement of IR spectra. Teflon-stoppered quartz cells of 1 cm optical pathlength, placed in thermostated cell holders, were used for the UV–VIS spectral measurements. Reported molar absorptivities (ε) are accurate to ±2.5%.

Electrochemical measurements. Conventional cyclic voltammetric techniques were employed. A potentiostat, a three-module sweep generator and a pen recorder were used. An undivided, gas-tight, glass cell swept by purified nitrogen was used. The cell was kept in a dry box, where all experimental manipulations were made. The reference electrode, to which all potentials are referred, was Ag^+ (0.1 M ACN)/Ag. It was separated from the cell solution by a porous-glass plug. A 2 cm^2 Pt foil was the counter electrode and the working electrode was a Teflon-encapsulated vitreous carbon disk of 0.074 cm^2 geometric area.

1b. UV–VIS in dry ACN solution: λ_{max} (ACN) = 312 nm ($\varepsilon = 6.09 \times 10^3$ $M^{-1}cm^{-1}$). NMR spectra: ^{1}H, ACN-d_3, δ 2.67 (s, 3H) and 7.52–7.96 (m, 5H). ^{1}H, EtOH-d_6. (**1b**·EtOH-d_6), δ 1.78 (s, 3H) and 7.40–8.30 (m, 5H). ^{13}C, ACN-d_3, δ 18.3, 127.8–133.9, 167.5 and 170.5. ^{13}C, EtOH-d_6 (**1b**·EtOH-d_6), δ 26.9, 97.4, 127.0–135.4 and 178.3.

1b$^-$. NMR spectra: ^{1}H of the **1b**–EtOH–EtO$^-$ system ([**1b**] = 0.29 M; [EtONa-d_5] = 0.18 M in EtOH-d_6 solvent), δ: two equal intensity resonances at 4.37 and 4.87. ^{13}C of the **1b**–EtOH–EtO$^-$ system ([**1b**] = 0.588 M; [EtONa-d_5] = 0.370 M in EtOH-d_6 solvent), δ 112.9, 127.9–134.4, 148.1 and 173.1.

2. The UV–VIS spectrum of **2** (Fig. 1) is similar in ACN and EtOH solution. NMR spectra: ^{1}H, ACN-d_3, δ 1.76 (s, 3H), 2.34 (broad s, 0.4 H), 4.95 (deformed t, 2H) and 7.42–8.23 (m, 10 H). ^{13}C, ACN-d_3, δ 27.3, 72.4, 100.6, 126.5–133.5, 147.7, 170.7 and 184.0. The IR spectrum (KBr pellets) presents a band at 3450. The UV–VIS spectrum of **2** (Fig. 1) is similar in ACN and EtOH solution. The UV–VIS spectra of **2**$^-$, obtained by adding an excess of NaEtO to an ethanolic solution of **2**, does not differ greatly from that of the neutral molecule. The corresponding λ_{max} are as follows: **2** in EtOH, 255, 382 nm; **2** in EtOH + excess EtO$^-$, 250, 374 nm; **2** in ACN, 255, 385 nm.

3. UV–VIS: λ_{max} (ACN) = 303 nm ($\varepsilon = 4.00 \times 10^3$ $M^{-1}cm^{-1}$) and 432 nm ($\varepsilon = 9.50 \times 10^3$ $M^{-1}cm^{-1}$). NMR spectra: ^{1}H, DMSO-d_6, δ 4.92 (broad, 2H), 6.40 (s,1H) and 7.19–8.22 (m). ^{13}C, DMSO-d_6, δ 110.2, 128.2–132.3, 137.4 and 168.9. IR spectrum relevant bands: 3550, 3500, 3300, 3050, 2985, 1620, 1520, 1595, 1480, 1445, 1340, 1315, 1130 and 1040 cm^{-1}.

RESULTS AND DISCUSSION

Behavior of 1b in basic (amines) aprotic (ACN) media. Spectroscopic characterization and electrochemistry of 2

ACN solutions of TEA and tBuA were employed. When TEA or tBuA was added to solutions of **1b** in ACN, the solutions rapidly acquired a pale yellow color. The UV–VIS spectra of these solutions (Fig. 1) depended on the [amine]/[**1b**] molar ratio (R). For small values of R (– –, Fig. 1), the 312 nm UV absorption band of **1b** was observed, together with two new maxima at 255 and 385 nm. The absorbance of the 312 nm band decreased with the increase in R and could not be observed for $R \geq 0.5$. The absorbance of the bands at 255 and 385 nm increased with increase in R, up to $R \approx 0.5$. Further increases in R did not change significantly the absorbance of these bands (⋯ and –·–, Fig. 1). The evaporation, at reduced pressure and room temperature, of both solvent and excess base from solutions with $R > 0.5$ produced a pale yellow solid, identified below as **2** (Scheme 1). A solution of the yellow solid presented UV absorption maxima at 255 and 385 nm (—, Fig. 1).

The decrease of the ca 310 nm UV band and the simultaneous increase of a UV absorption at ca 260 nm was recognized as characteristic of the conversion of a thiadiazole to the corresponding thiadiazoline derivative, as has been repeatedly observed in nucleophilic addition reactions to thiadiazole derivatives.[1,4]

However, the base to substrate molar ratio that was necessary to complete the reaction ($R \approx 0.5$), as observed by UV–VIS spectroscopy, was incompatible with an addition reaction of the amines to a C=N double bond of **1b**. In fact, TEA and tBuA were selected because of the

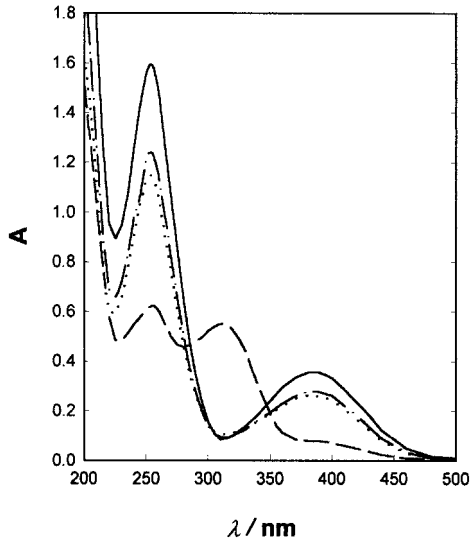


Figure 1. UV–VIS equilibrium spectra of solutions of **1b** and TEA in ACN. (– –) [**1b**] = 1.18×10^{-4} M, [TEA]/[**1b**] = 0.12; (···) [**1b**] = 1.165×10^{-4} M, [TEA]/[**1b**] = 0.6; (–·–) [**1b**] = 1.18×10^{-4} M, [TEA]/[**1b**] = 1.12. (—) Spectrum of an ACN solution of the yellow solid **2**. The UV–VIS spectra of $\mathbf{2}^-$ is, at the experimental resolution level, virtually identical with that of **2** (see spectroscopic data in Experimental section)

unlikeness of the addition reaction, since TEA does not have labile protons and tBuA is similar to the highly hindered *tert*-butyl alcohol, which does not add to **1b**.[4]

The reaction was postulated as a dimerization of **1b**, which was in agreement with the experimentally observed R for complete reaction, and with other experimental facts discussed below. The dimerization was initiated by the abstraction of a proton from **1b** [Eqn. (1)]. The $\mathbf{1b}^-$ anion formed added subsequently to another **1b** molecule [Eqn. (2)]. The dimeric anion is neutralized during work up procedures [Eqn. (3)]:

$$\mathbf{1b} + \mathrm{B}: \rightleftharpoons \mathbf{1b}^- + \mathrm{BH}^+ \quad (1)$$

$$\mathbf{1b} + \mathbf{1b}^- \rightleftharpoons \mathbf{2}^- \quad (2)$$

$$\mathbf{2}^- + \mathrm{H}^+ \rightleftharpoons \mathbf{2} \quad (3)$$

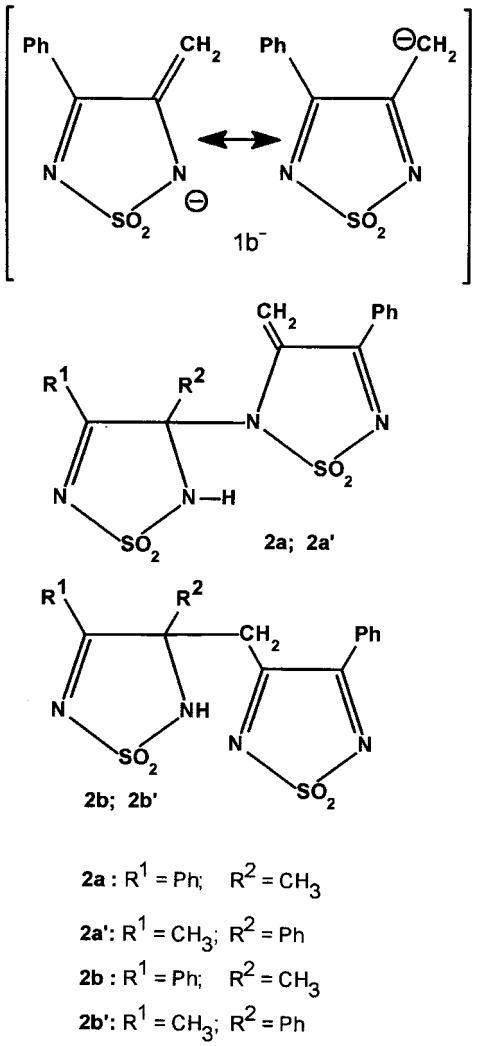
Gradual yellowing and similar spectral changes are observed in **1b** solutions in nominally dry ACN solvent[4] to which no base had been added. The yellowing process is faster the higher is the residual water content of the ACN solvent. Apparently the monomeric residual water[8] in the ACN solvent is a strong enough base to displace Eqn. (1) sufficiently to the right. Freshly prepared uncolored solutions of **1b** in very dry ACN are also observed to develop rapidly a yellow color if placed in contact with silica in TLC plates. The yellowing process is prevented by the addition of dry TFA to **1b**–ACN solutions.

The yellow compound formed on the TLC plates from ACN solutions of **1b** was isolated using preparative TLC (it had a smaller R_f than **1b**). It was found to be spectroscopically (UV–VIS, IR) and chromatographically (TLC) identical with **2**.

Compound **2** decomposed slowly in solution, reverting partially to **1b** and forming other unidentified (TLC) products. Thus, recrystallization purification was not practical, and chromatographically (TLC) pure samples of **2** were used to confirm its structure by ^{1}H and ^{13}C NMR and IR spectroscopy. The spectroscopic results are discussed below, along with other chemical and electrochemical evidence.

The delocalized negative charge in $\mathbf{1b}^-$ (Scheme 2) implies the possibility of several alternative structures for $\mathbf{2}^-$: the attacking site of the $\mathbf{1b}^-$ nucleophile might be the $—CH_2^-$ or the $\rangle N^-$ group, and the attacking group might bond to any of the two electron-deficient heterocyclic carbon atoms of **1b**. The resulting structures are indicated in Scheme 2 as **2a**, **2a′**, **2b** and **2b′**.

The structure **2a**, identical with that identified in Scheme 1 as **2**, was found to be consistent with the spectral data:



Scheme 2

(a) All structures in Scheme 2 contain thiadiazoline moiety, which is responsible for the 255 nm UV band. But only the **a**-type structures also have an eneimine [CH_2=C;—C(Ph)=N—] functional group that might absorb at 385 nm. The disappearance of the UV band at ca 310 nm rules out the **b**-type structures, which have a thiadiazole group. Furthermore, a change in the UV spectra is expected for **2b**-type structures if EtOH is added to their solutions in ACN (as a consequence of the addition reaction of EtOH to the thiadiazole C=N bond[1–4]). This was not observed experimentally.

(b) The downfield shift of the methyl ^{13}C NMR signal from 18.3 ppm in **1b**[1] to 27.3 ppm in **2** suggested that the nucleophilic addition of $\mathbf{1b}^-$ took place on the methyl side of **1b**, as is the case for the addition of alcohols.[3,4] This favors structures **2a** and **2b**.

(c) The ^1H NMR resonance at 4.95 ppm (2H), indicated a $=CH_2$ group (as in **a**-type structures). In contrast, **b**-type structures should have given a signal from a $—CH_2—$ group (at ca 2 ppm) that was only observed as a minor component (ca 10%) (see Supporting information).

(d) Two ^{13}C NMR resonances, attributed to carbon atoms in $\rangle C$=N— groups, are experimentally observed in the 170–180 ppm range. **b**-Type structures have three carbon atoms in similar groups, whereas **a**-type structures have two. The ^{13}C NMR resonance at 100.6 ppm, assigned to $=CH_2$ in an **a**-type structures, has no obvious assignment in **b**-type structures, since the carbon atom in the $—CH_2—$ group should resonate at ca 35–40 ppm.

A cyclic voltammogram of **2** in ACN solution [Fig. 2(b)] showed peaks at −1.75 V (first cathodic sweep), +0.58 V (first anodic sweep) and −0.57 V (second cathodic sweep). The cathodic peak at −1.75 V is characteristic of thiadiazoline reduction,[9] while the remaining peaks might be associated with other electrophores in the molecule, such as the eneimine [CH_2=C—C(Ph)=N—] group.

We have reported[3] that the cyclic voltammogram of **1b** in ACN solution, particularly at high concentrations of **1b**, indicates a radical–substrate dimerization process. However, attempts to isolate the dimer from the products of the bulk electrolysis of **1b** in ACN solutions at ca −1.06 V were unsuccessful. A complex and unstable mixture of products was obtained on work-up.

We have now found that the voltammogram of the catholyte [Fig. 2(a)], scanned immediately after completion of the bulk electroreduction of **1b** (i.e., after the disappearance of the voltammetric signal of **1b** at ca −0.9 V), is nearly identical with the cyclic voltammogram of **2** [Fig. 2(b)]. Furthermore, the UV–VIS spectrum of this completely electrolyzed solution is very similar (except for a weak shoulder absorption at ca 500 nm) to the spectrum of **2** shown in Fig. 1. Hence, it must be concluded that **2** is one of the products of the electrolysis of **1b** in ACN.

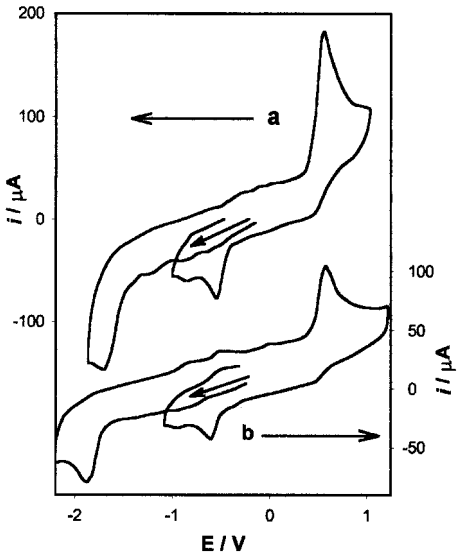


Figure 2. (a) Cyclic voltammogram of a 21.6 mM solution of **1b** in ACN after exhaustive electrolysis at −1.06 V. v = 0.2 V s^{-1}. (b) Cyclic voltammogram of an ACN solution of a sample of **2** obtained from a preparative chromatographic run (see text)

A mechanism for the electrolytic formation of **2** can be postulated as follows:

$$\mathbf{1b} + e^- \rightleftharpoons \mathbf{1b}^{-\cdot} \quad (4)$$

$$\mathbf{1b}^{-\cdot} + \mathbf{1b} \rightleftharpoons \mathbf{1b}H^{\cdot} + \mathbf{1b}^- \quad (5)$$

$$\mathbf{1b}H^{\cdot} + \mathbf{1b}^{-\cdot} \rightleftharpoons \mathbf{1b} \cdot H_2 + \mathbf{1b}^- \quad (6)$$

Subsequently, the $\mathbf{1b}^-$ anion [Eqns (5) and (6)] and the substrate **1b** dimerize [Eqn. (2)]. The experimentally measured charge consumed per mole of **1b** electrolyzed (0.4 mol e^-/mol **1b**),[3] is in agreement with the global electrolysis reaction [Eqns ((4)–(6)) and (2)]:

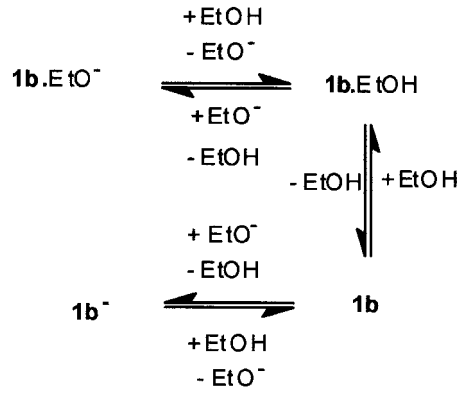
$$5\ \mathbf{1b} + 2\ e^- \rightleftharpoons 2\ \mathbf{2}^- + \mathbf{1b} \cdot H_2 \quad (7)$$

The postulated thiadiazoline **1b**. H_2 was not identified and has not been reported in the literature.

Behavior of 1b in strong by basic media. Characterization of $\mathbf{1b}^-$

A more strongly basic medium than that provided by the ACN solution of the amines should be necessary to obtain the anion $\mathbf{1b}^-$ in high enough concentration for its characterization.

Alkoxide anions were considered adequate for that purpose. However, in the commonly used *tert*-butoxide–DMSO system only dimerization was observed. The relatively slow breakage of the C—H bond provides



Scheme 3

adequate conditions for the dimerization reaction [Eqn. (2)], since it implies a slow build-up of the $\mathbf{1b}^-$ concentration in the presence of the **1b** substrate.

To cope with this limitation, EtOH was used as a solvent. Since **1b** forms almost quantitatively the thiadiazoline **1b**·EtOH in EtOH solution, the concentration of the substrate **1b** would be very low.

It was also expected that in a basic ethanolic solution the NH proton of the thiadiazoline **1b**·EtOH would be rapidly abstracted (Scheme 3, left). A similar reaction has been observed previously[1] in solutions of **1a**·EtOH in EtOH, to which NaEtO was added.

The UV–VIS spectrum of a ca 1×10^{-4} M solution of **1b** in EtOH, to which an ethanolic solution of NaEtO had been added (to a final concentration of ca 0.1 M), changed gradually [Fig. 3(a) and (b)]. After a lapse of about 2 h, the band of **1b**·EtOH at 265 nm shifted to 248 nm, a band at 360 nm developed and reached maximum intensity and the solution acquired a light yellow color. During these changes, an isosbestic point was observed at 275 nm [Fig. 3(a)]. Similar spectral and color changes were observed when ethanolic solutions of **1a** were treated with NaEtO, as mentioned above.[1] **1b**·EtO^- (Scheme 3, left) is responsible for the absorption bands at 248 and 360 nm.

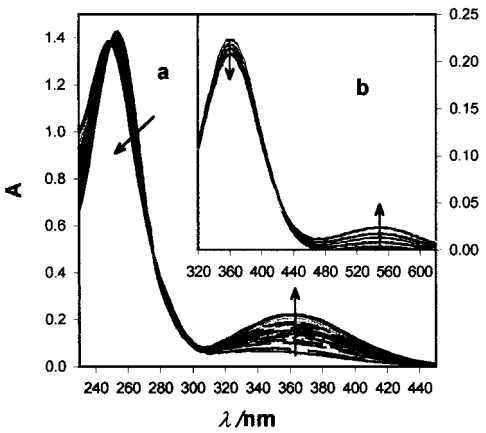


Figure 3. Time evolution of the UV–VIS spectra of a solution of **1b** in EtOH– NaEtO. [**1b**] = 1.34×10^{-4} M. [NaEtO] = 0.117 M. (a) Spectra recorded at selected times during the first 2 h after NaEtO addition. (b) As (a) during the first 48 h after NaEtO addition. Arrows indicate the absorption intensity and wavelength changes with time

The **1a**–EtOH–EtO^- system did not change further. However, during a 2-day lapse after the addition of NaEtO to the solution of **1b** in EtOH, the intensity of the band at 360 nm decreased, a low-intensity absorption band at 550 nm developed and an isosbestic point at 425 nm was observed [Fig. 3(b)]. The solution gradually turned to a purple color.

The change is justified below as being due to the formation of the $\mathbf{1b}^-$ anion. The reaction of the excess EtO^- with the low equilibrium concentration of **1b** caused a slow displacement of all equilibria (Scheme 3) to the right, forming the purple $\mathbf{1b}^-$ anion that absorbs light at 550 nm.

Much more concentrated solutions were prepared for NMR spectroscopic measurements. The ^{1}H NMR of a solution of **1b** in EtOH–d_6, to which NaEtO-d_5 had been added ([**1b**] = 0.29 M; [EtONa-d_5] = 0.18 M), was measured. The clear initial solution turned light yellow and then purple minutes after the addition of NaEtO-d_5. The spectrum presented (in addition to the signals of **1b**·EtOH), two signals of equal intensity at $\delta = 4.37$ and 4.87 ppm that were assigned to the protons of the $CH_2^{\delta-}$ group of the $\mathbf{1b}^-$ anion. The position of these signals and their separation were similar to those of comparable enolate anions.[10] An appreciable increase in the intensity of the signal at $\delta = 5.51$ ppm (corresponding to the OH protons of the residual EtOH content of the EtOH-d_6 solvent) was also observed. This indicated the transfer of protons to the EtO^- ion. Furthermore, the concentration ratio $[\mathbf{1b}^-]/([\mathbf{1b}\cdot EtOH] + [\mathbf{1b}^-])$, as measured by the integration of the respective ^{1}H NMR signals (corrected according to the number of protons involved), corresponded to the experimental ratio of (mol EtO^- added)/(mol **1b** initially present).

The ^{13}C NMR spectrum of $\mathbf{1b}^-$ (in the **1b**–EtOH–EtO^- system, [**1b**] = 0.588 M; [EtONa–d_5] = 0.370 M; EtOH–d_6 solvent), presented a signal for the heterocyclic carbon on the phenyl side at $\delta = 173.1$, only slightly shifted from the corresponding signal of **1b**. A large upfield shift was found for the heterocyclic carbon on the methyl side ($\delta = 148.1$ for $\mathbf{1b}^-$ vs. 167.5 for **1b**). A resonance at $\delta = 112.9$ ppm was assigned to —C—$CH_2^{\delta-}$.

The formation of **1b**·EtO^- and $\mathbf{1b}^-$ was also suggested by cyclic voltammetric experiments. In the accepted mechanism for the voltammetric electroreduction of **1b** in ethanolic solution,[3] one of the observed cathodic peaks (peak IIIc) is assigned to the electroreduction of **1b**·EtOH. Peak IIIc disappeared immediately upon addition of excess NaEtO to ethanolic solutions of **1b**. The disappearance of peak IIIc was caused by the reaction $\mathbf{1b}\cdot EtOH + EtO^- \rightleftharpoons \mathbf{1b}\cdot EtO^- + EtOH$ (Scheme 3). Upon further standing, the solution acquired

a purple color (formation of $\mathbf{1b}^-$, Scheme 3), and all voltammetric signals disappeared.

Characterization of 3

An orange solid (**3**, Scheme 1) precipitated from a fresh, purple **1b**–EtOH–EtO^- solution when it was acidified with anhydrous TFA.

The following features of the spectral data for **3** were considered structurally important: the 4.92 ppm (2H, —C═CH_2) and the 6.40 ppm (1H, —N*H*) ^{1}H NMR signals, the ^{13}C NMR spectrum, which is similar, but clearly distinguishable, to that of $\mathbf{1b}^-$ and the 1040 cm^{-1} C–N stretching IR band.

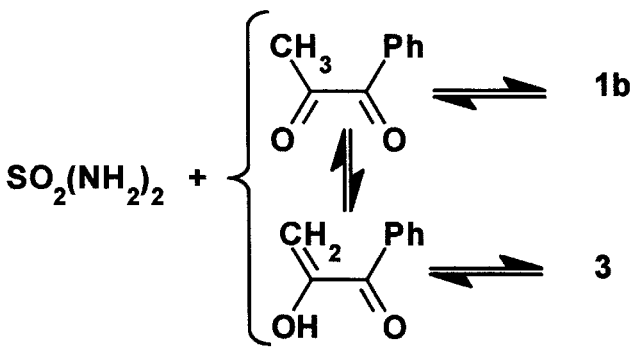
Compound **3** was found to be chromatographically (TLC) and spectroscopically (UV–VIS, IR) identical with a previously unreported by-product that we isolated from the yellow crude crystals obtained in the synthesis of **1b**. The formation of **3** during the synthesis of **1b** from sulfamide and 1-phenyl-1,2-propanedione in refluxing acid medium (HCl in EtOH) can be rationalized if the keto–enol equilibrium for the precursor diketone is considered (Scheme 4).

The practical observation of the acid–base and tautomeric equilibria

The anion $\mathbf{1b}^-$ is related by acid–base equilibrium to **3** and to **1b**, which are in turn associated with a tautomeric equilibrium. The equilibrium between **3** and $\mathbf{1b}^-$, involving an N-bonded proton of **3**, could be observed voltammetrically in DMF solution (**3** is not soluble in ACN).

A voltammogram of a solution of **3** in DMF is shown in Fig. 4(a). The orange solution presented cathodic peaks at ca −0.9 and −1.5 V in the first cathodic sweep, an anodic peak at ca 0.1 V in the reverse anodic sweep and a cathodic peak at ca −0.2 V in the second cathodic sweep.

As can be observed [Fig. 4(b)–(f)], alternative additions of excess alkali (NaEtO in EtOH solution) or



Scheme 4

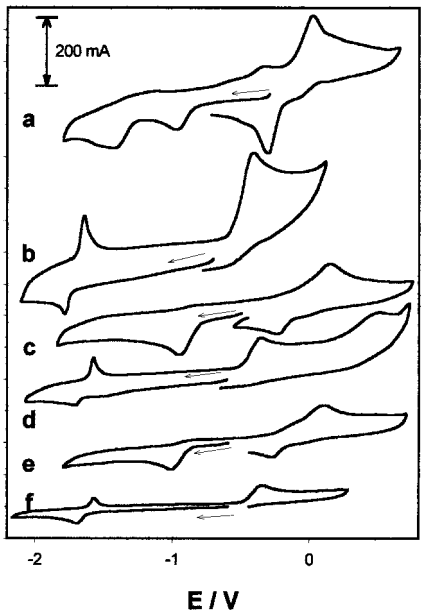


Figure 4. (a) Cyclic voltammogram of **3** in DMF solution. [**3**] = 5.61 mM, supporting electrolyte, 0.11 M $NaClO_4$; v = 0.2 V s^{-1}. (b)–(f) Cyclic voltammograms of the same solutions in the same conditions after the following succesive additions: (b) 50 μl of 1 M NaEtO solution in EtOH (solution A), (c) 80 μl of 1 M TFA solution in DMF (solution B), (d) 90 μl of solution A, (e) 100 μl of solution B, (f) 110 μl of solution A

acid (TFA in DMF solution) caused a nearly reproducible change in the voltammogram. Successive voltammograms in basic medium [Fig. 4(b), (d) and (f)] or acidic medium [Fig. 4(c) and (e)] are very similar. Furthermore, the color of the solution changed repeatedly from bright blue in the basic medium to brown–orange in the acid medium. It seemed reasonable to assume that the amphiprotic anion $\mathbf{1b}^-$ (Scheme 2) is the bright blue species, whereas in neutral or acidic solutions the substrate exists mainly as **3**.

As for the **1b** ⇌ $\mathbf{1b}^-$ acid–base equilibrium, as mentioned above, the addition of tert- butoxide anions to **1b** in DMSO solution leads to the formation of **2**. Since the rate of formation of $\mathbf{1b}^-$ by proton abstraction from the C—H bond of **1b** is presumably slow, the $\mathbf{1b}^-$ anion is formed in the presence of a relatively high concentration of **1b**. This favours the dimerization reaction [Eqn. (2)].

The tautomeric equilibrium **1b** ⇌ **3** is practically displaced towards **1b** in ACN and towards **3** in DMF solution. In protic solvents the participation of thiadiazoline addition compounds is unavoidable, but the presence of **3**, besides those of $\mathbf{1b}^-$ and **1b**·EtOH, was observed in a ^{1}H NMR spectrum recorded immediately after a molar excess of solid **1b** was dissolved in a solution of NaEtO-d_5 in EtOH-d_6 solvent (analytical concentrations: $[\mathbf{1b}]_0$: 0.557 M, $[EtO^-]_0$: 0.37 M). In contrast with the extremely slow, reactive dissolution process of **1b** in EtOH solvent to form the thiadiazoline adduct, **1b** dissolved and reacted

rapidly in the basic EtOH solvent: the signal of **1b** was not observed in the first ^{1}H NMR spectrum. After ≈2 h the ^{1}H NMR spectrum was identical with that obtained when NaEtO-d_5 was added to a ethanolic solution of **1b**·EtOH (see above: Behavior of **1b** in strongly basic media).

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Supporting information: ^{1}H and ^{13}C NMR spectra of **1b**, **1b**·EtOH, **1b**$^-$, **2** and **3** and a discussion of peripheral results, are available at the EPOC website at http://www.wiley.com/epoc.

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