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Electron Spin Resonance and Electrochemical Studies of Some Mesoionic and Neutral 1,2,3,4-Oxa- and -Thiatriazoles and Their Alkylation Products

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Voltammetric studies of mesoionic 1,2,3,4-oxa- and -thiatriazoles confirmed that the former may be reduced irreversibly at potentials between −1.19 and −1.73 V *vs.* ferrocene in acetonitrile at scan rates between 0.05 and 1000 mV s^{-1}, whereas the latter are reduced reversibly under the same conditions. The corresponding radical anions were examined by ESR spectroscopy. Cationic alkylation products of the above compounds showed different electrochemical behaviour depending on the character of the heterocyclic ring. 1,2,3,4-Thiatriazolium ions were reduced reversibly. All coupling constants of the resulting neutral radicals were fully assigned using isotopic labelling. A cation with an 1,2,3,4-oxatriazolium ring reacted by cleavaging of an exocyclic C—S bond on electron uptake. The resulting alkyl radical was spin-trapped. © 1997 by John Wiley & Sons, Ltd.

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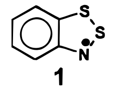
INTRODUCTION

Sulfur- and nitrogen-containing heterocyclic radicals with seven π-electrons are of continuing interest. In our group, 1,2,3-dithiazolyls (**1**) and 1,2,3,5-dithiadiazolyls (**2**) have been investigated.[1,2] 1,3,2,4-Dithiadiazolyls (**3**) are also well known.[3] With the aim of synthesizing molecular conductors, crystal structures of several derivatives of **2** have been determined, showing them to dimerize via a long-range sulfur–sulfur interaction.[4] Recently, a derivative of **2** which is monomeric even in the solid state has been reported.[5] Compounds **2** and **3** can conceptually be transformed into the isomeric thiatriazolyls **4** and **5** if one of the sulfur atoms in the ring is exchanged for an isolobal nitrogen function. 2,5-Dihydro-1,2,3,5-thiatriazol-5-yl radicals (**4**) have been prepared by Neugebauer *et al.*[6] In this paper, we report the generation and properties of neutral and anionic 2,3-dihydro-1,2,3,4-thiatriazol-2-yls (**5**) produced from cationic and mesoionic 1,2,3,4-thiatriazoles (**6**) by both chemical and electrochemical reduction. Simultaneously, a comparative electrochemical study was carried out with 5-phenyl-1,2,3,4-thiatriazole (**7**) and several mesoionic and cationic 1,2,3,4-oxatriazoles (**8**).

RESULTS AND DISCUSSION

Neutral compounds: 5-phenyl-1,2,3,4-thiatriazole (7) and the mesoions 8a, 8b, 6b, 6d and 6k

Compound **7** was reduced irreversibly at −2.00 V (Table 1). Considering that anions of **2** have been obtained by cyclic voltammetry,[7] this was not expected. Compound **7** probably decays rapidly through the loss of nitrogen. The mesoion **8a** has been investigated by polarography in the hitherto only work to be published on the electrochemistry of these types of compounds.[8]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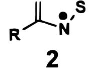
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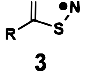
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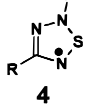
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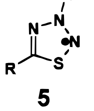
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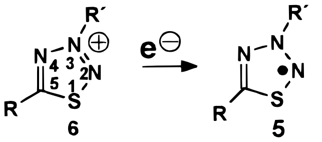

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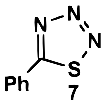
Cpd.	R	R′	Radical
6a	EtS	Et	**5a**
6b	O⁻	Ph	**5b**
6c	OEt	Ph	**5c**
6d	S⁻	Ph	**5d**
6e	SMe	Ph	**5e**
6f	SEt	Ph	**5f**
6g	SiPr	Ph	**5g**
6h	Ph	Me	**5h**
6i	Ph	Et	**5i**
6j	Ph	iPr	**5j**
6k	Ph	O⁻	**5k**
6l	SC_2D_5	Ph	**5l**
6m	SEt	C_6D_5	**5m**
6n	SEt	2-^{15}N	**5n**
6o	SEt	4-^{15}N	**5o**

None of the compounds studied contained sulfur, and they were all reduced irreversibly. The mesoionic thiatriazoles **6b** and **6d** are reduced reversibly. The reduction potentials depend on the nature of the exocyclic substituent (Table 2): for example, they are lower by *ca.* 200 mV for **6d**, which contains an exocyclic thiolate substituent. This behaviour is similar to the differences in reduction potentials between pyridine and benzenecarboxylic acid esters and thioacid esters.[9] Compound **6k**, which is an isomer of **6b**, is reduced irreversibly, probably owing to deoxygenation. This behaviour does not correspond with that observed in the case of pyridine *N*-oxide, where the stable radical anion was generated.[10]



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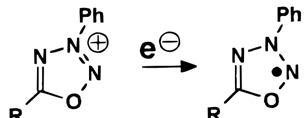

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Cpd.	R	Radical
8a	O⁻	**9a**
8b	S⁻	**9b**
8c	SEt	**9c**

Mesoion **8b** shows an irreversible reduction at -1.19 V with a very small current, and a reversible signal at -1.53 V. The latter is similar to the reduction of **6b**. From the spectrocyclovoltammograms of **8b** (Fig. 1) and **6b** (Fig. 2), it is apparent that from both compounds a radical with the same UV–visible spectrum is formed. At potentials around -1.5 V, it shows absorptions at 310 and 375 nm and a flat band which extends to far above a wavelength of 500 nm. Since the reduction of **6b** is fully reversible, the spectrum can be ascribed to **5b**. In Fig. 1, on the contrary, at -1.19 V the spectrum of **8b** disappears and the spectrum of **6b** develops, giving **5b** on further reduction. The overall mechanism thus appears as in Scheme 1.

This mechanism (Scheme 1) explains the small current which accounts for the irreversible reduction of **8b** at -1.19 V. Compound **9b**, which is formed upon electron uptake of **8b**, rearranges to **5b** so swiftly that no oxidation peak for **5b** could be obtained at our scan rates. Since the reduction potential of **6b** is more negative than that of **8b**, **5b** losses its electron to **8b**, forming **6b**. Thus, electrons play only a catalytic role in this rearrangement. The thorough examination of the kinetics of this reaction with the help of fast cyclic voltammetry is the subject of further investigations and will be published elsewhere. Electrochemical reduction of **8b** and **6b** at -1.5 V *vs.* Ag/AgCl thus gave identical ESR spectra due to the same radical, **5b** (Table 3). In an electrolysis experiment, 40 mg of **8b** were reduced at -1.4 V *vs.* Ag/AgCl at a rotating platinum disc electrode in 1,2-dichloroethane in an undivided cell. After 3 days, the reaction mixture was worked up and chromatographed. A 7 mg amount of **6b** (18%) identical with the compound reported in Ref. 11 was isolated. Compound **8b** underwent the above reaction conditions unchanged when no current was applied.

Thermal rearrangements of this type have been reported for 1,2,3-oxadiazolethiolates,[12] 1,2,3,4-oxatriazolethiolates[11a] and 1,3,4-oxadiazolethiolates.[13] Also, photochemically induced or copper(I) ion-catalysed rearrangements of Δ^2-1,2,4-oxadiazolin-5-thiones have been described.[14] Electrochemically induced rearrangements of this type have not been reported previously.

Cations containing the 1,2,3,4-thiatriazole ring

Of the series of cations containing the 1,2,3,4-thiatriazole ring (**6a**, **6c**, **6e**–**j**), only **6a** is irreversibly reduced at -1.02 V (Table 2). Introduction of a phenyl

Table 1. Reduction potentials of neutral and mesoionic compounds in acetonitrile *vs.* Fc/Fc^+ with scan rate 200 mV s^{-1}

Compound	Reversibility	Potential (V)	Compound	Reversibility	Potential (V)
7	Irrev.	−2.00	**6b**	Rev.	−1.53
8a	Irrev.	−1.73	**6d**	Rev.	−1.27
8b	Irrev.	−1.19[a]	**6k**	Irrev.	−1.82

[a] Additionally reversibly reduced at −1.53 V.

Table 2. Reduction potentials of cationic compounds in acetonitrile *vs.* Fc/Fc$^+$ with scan rate 200 mV s^{-1}

Compound	Reversibility	Potential (V)	Compound	Reversibility	Potential (V)
8c	Irrev.	−0.49[a]	**6g**	Rev.	−0.68
6a	Irrev.	−1.02	**6h**	Rev.	−0.90
6c	Rev.	−0.76	**6i**	Rev.	−0.88
6e	Rev.	−0.69	**6j**	Rev.	−0.86
6f	Rev.	−0.69			

[a] Additionally reversibly reduced at −1.53 V.

group in position 3 or 5 yields compounds which may be reduced reversibly at potentials varying between −0.76 and −0.90 V *vs.* Fc/Fc$^+$. While no effect of the various 5-alkylthio substituents in **6e–g** on the reduction potential was observed, it is lowered significantly by increasing size of the 3-alkyl group for **6h–j**.

The 3-phenyl-substituted thiatriazolyls **5c**, **5e**, **5f** and **5g**, and those bearing a phenyl-substituent in position 5, thiatriazolyls **5h**, **5i** and **5j**, can be generated from their corresponding cations by reduction with zinc powder or sodiumdithionite[15] in toluene, as well as by electrochemical reduction. The half-lives of the radicals range between seconds and minutes. In Fig. 3 a representative example of the complex ESR spectra is shown. In the case of **5f**, isotopic exchange with ^{15}N in the ring positions 2 and 4, yielding **5n** and **5o**, and deuterations of the ethyl- (**5l**) or the phenyl moiety (**5o**) were performed in order to assign exactly all simulated coupling constants (Table 3). The ESR spectra document the sequence of nitrogen splitting constants a_N (N-2) > a_N (N-3) > a_N (N-4), i.e. the lowest splitting constant is attributed to the nitrogen atom N-4.

Approximately the same value for the coupling constants of N-4 has been established for the 1,3,2,4-dithiadiazolyls **3**.[3] This clearly indicates that the spin distribution in **3** and **5** is affected relatively little by the exchange of the sulfur in ring position 3 of radical **3** with the —NR′— function in radical **5**.

Radical **3** has been reported to undergo a photochemically induced rearrangement into **2**.[3b] Considering

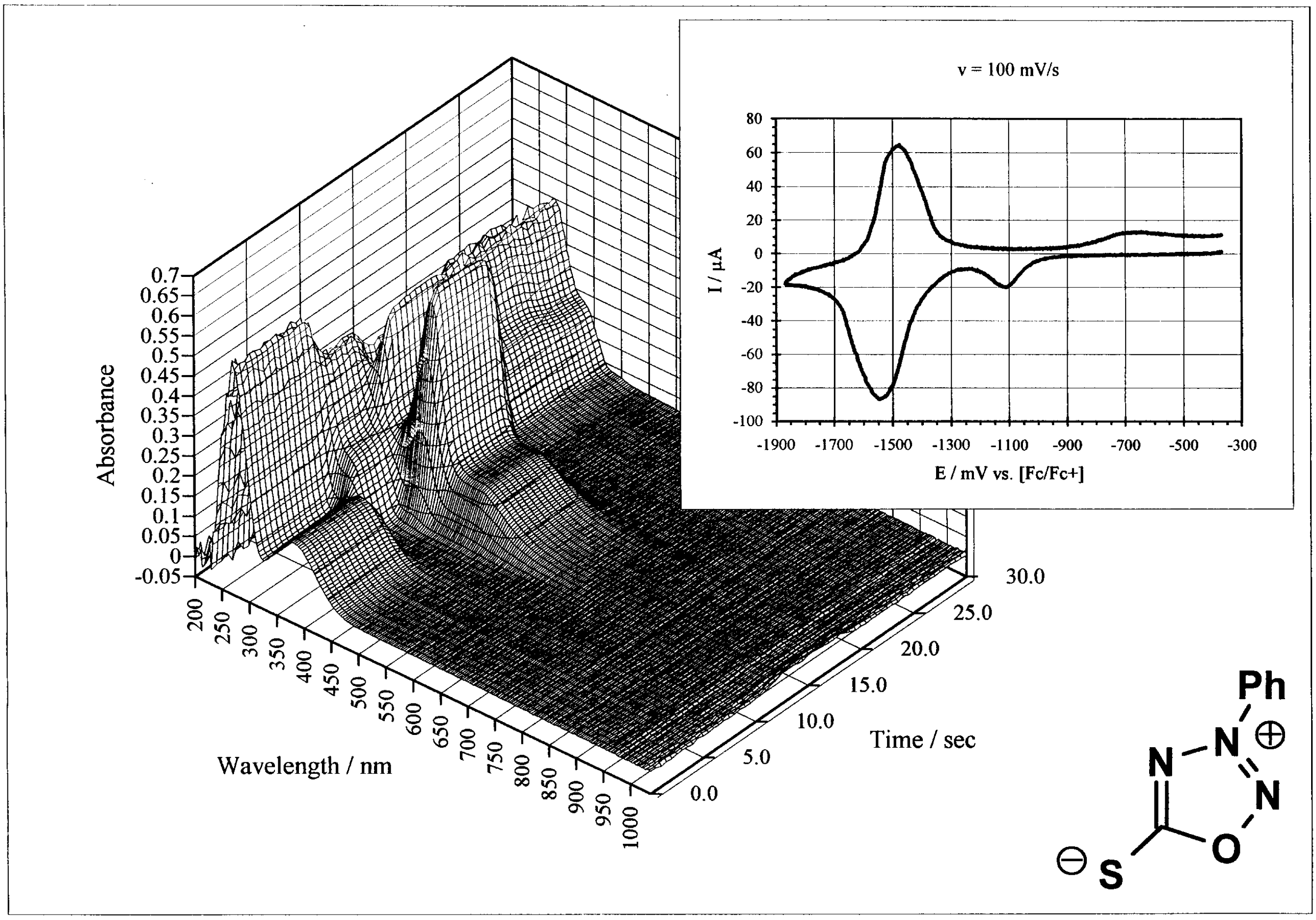


Figure 1. Spectrocyclovoltammogram of 3.7 mM **8b** in acetonitrile (0.1 M *n*-Bu$_4$NBF$_4$) using an Au–LIGA structure as the working electrode.

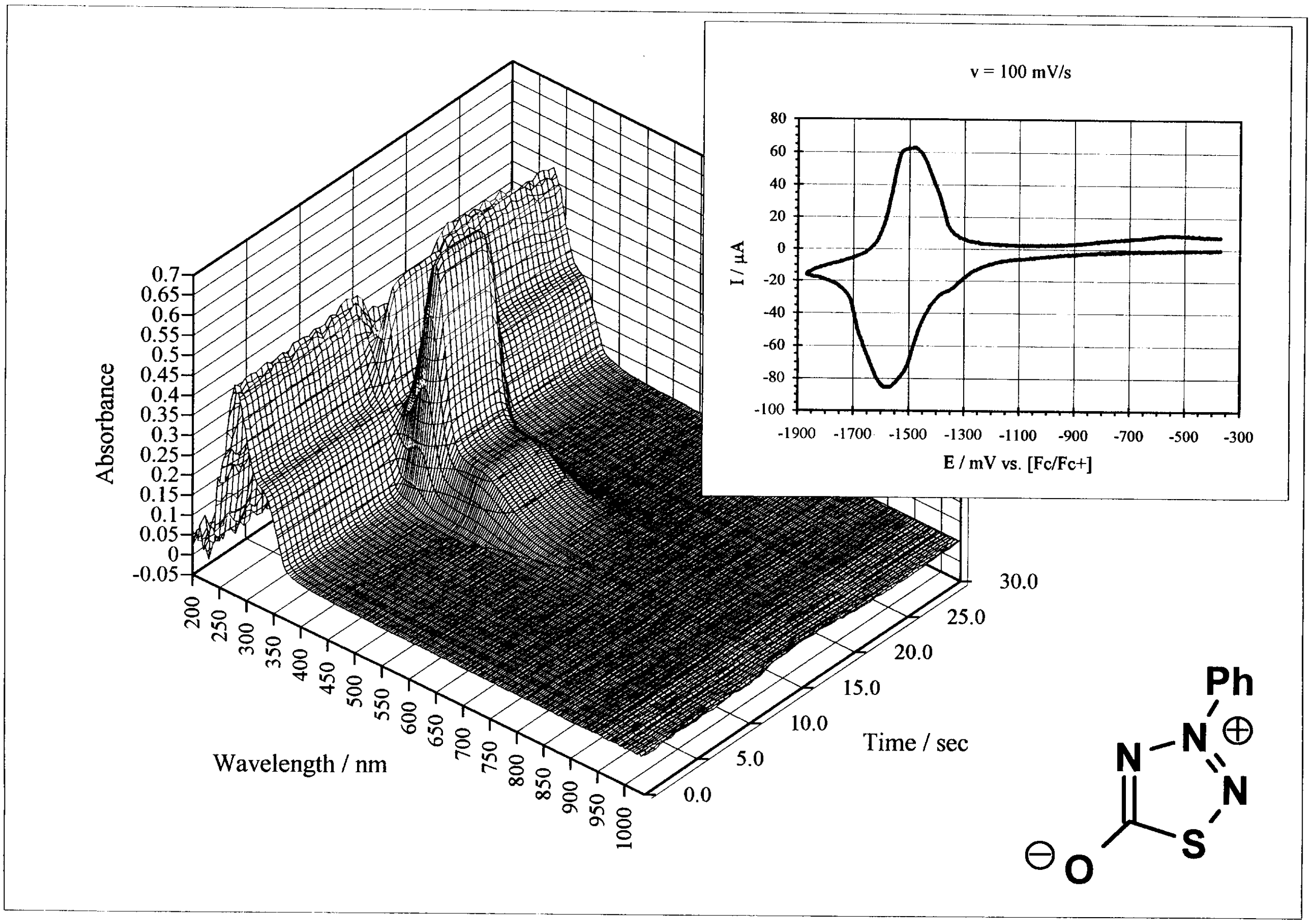
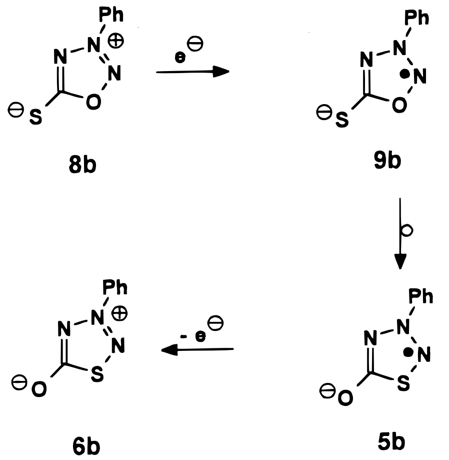


Figure 2. Spectrocyclovoltammogram of 3.9 mM **7b** in acetonitrile (0.1 M n-Bu$_4$NBF$_4$), showing the same radical anion UV–visible spectrum as in Fig. 1.

the electronic similarity between **3** and the thiatriazolyls **5**, such a rearrangement might also be expected to occur for **5**. Up to now, this has not been observed. This may be due to the relatively short lifetime of **5** compared with **3**, since the rearrangement of **3** proceeds at a fairly slow rate.

Density functional theory (DFT) calculations were performed for **5d** and **5h**. The geometry of the two radicals was optimized by means of B3LYP/3–21G. Single-point calculations were made using 6–31G*. Average deviations of the calculated hyperfine coupling constants (hfccs) from measured values are usually smaller than 0.04 mT.[16] Compounds **5d** and **5h** were calculated to be planar, or nearly planar. For **5h**, the calculated and measured coupling constants matched very well (Table 3). This can be regarded as proof of the cyclic nature of the radicals **5**, as open-chain structures have been discussed, and ruled out, for their closed-shell counterparts, **6**.[17] For radical **5d**, absolute values of the calculated hfccs for the protonated and non-protonated radical are shown in Table 3. They do not differ much except for $a_{\text{N-3}}$. The calculated results are generally in better accord with the measured values of the hfccs for the protonated radical anion. The cyclic voltammograms and ESR spectra of **6b** and **6d** showed no change on adding 1 mmol l^{-1} trifluoroacetic acid (TFA) or TFA-d_1. The conclusion has to be drawn that the radical anions are protonated also in the absence of acids.



Scheme 1. Electrochemically induced rearrangement of **8b** into **6b**.

5-Ethylthio-3-phenyl-1,2,3,4-oxatriazolium ion

Compound **8c**, synthesized by ethylation of **8b**, shows an irreversible reduction at −0.49 V. The follow-up product of the irreversible reduction is reduced at −1.53 V, this value being identical with that of the reversible reduction of **8b**. This indicates that radical **9c**

Table 3. Experimental and calculated (in italics; prot. are the calculated values for the protonated radical anion) isotropic hyperfine coupling constants (mT) and *g*-factors of neutral and anionic 1,2,3,4-thiatriazolyls (5) in toluene or DMF (anions) at 298 K[a]

Compound	a_{N-2}	a_{N-3}	a_{N-4}	$a_{H-2',6'}$	$a_{H-4'}$	$a_{H-3',5'}$	$a_{\alpha-H}$	g-Factor
5b	0.891	0.534	0.102	0.216	0.211	0.058		2.0038
5c	1.045	0.647	0.020	0.164	0.164	0.054		2.0037
5d	0.950	0.531	0.055	0.170	0.190	0.055		2.0041
calc.	*1.07*	*0.38*	*0.04*	*0.20*	*0.25*	*0.07*		
prot.	*1.09*	*0.54*	*0.06*	*0.19*	*0.19*	*0.08*		
5e	1.050	0.576	0.025	0.151	0.151	0.045		2.0041
5f	1.051	0.578	0.027	0.150	0.150	0.048		2.0041
5g	1.053	0.576	0.025	0.148	0.148	0.047		2.0041
5h	1.054	0.696	0.091	0.065	0.073		0.434	2.0039
calc.	*1.067*	*0.686*	*0.103*	*0.077*	*0.080*		*0.401*	
5i	1.054	0.693	0.090	0.063	0.073		0.304	2.0039
5j	1.052	0.695	0.089	0.070	0.080		0.160	2.0039
5l	1.051	0.576	0.026	0.149	0.149	0.046		2.0041
5m	1.051	0.574						2.0041
5n	1.498	0.577	0.025	0.151	0.151	0.047		2.0041
5o	1.051	0.576	0.035	0.148	0.148	0.046		2.0041

[a] Linewidths are 0.025–0.045 ml.

undergoes cleavage of the ethyl—S bond, to yield mesoion **8b**. No sign of the existence of **9c** is found with the scan rates employed (10–1000 mV s^{-1}). Hence **9c** must have a lifetime of less than 0.1 s. The final proof for the decay of **9c** into **8b** and an ethyl radical was the trapping of the latter with 2-methyl-2-nitrosopropane (cf. Scheme 2). The resulting ESR spectrum consisted of a 1 : 1 : 1 triplet of 1 : 2 : 1 triplets, and the coupling constants and *g*-factors matched perfectly with those taken from the literature for *tert*-butylethylnitroxide (**10**)[18] (Fig. 4).

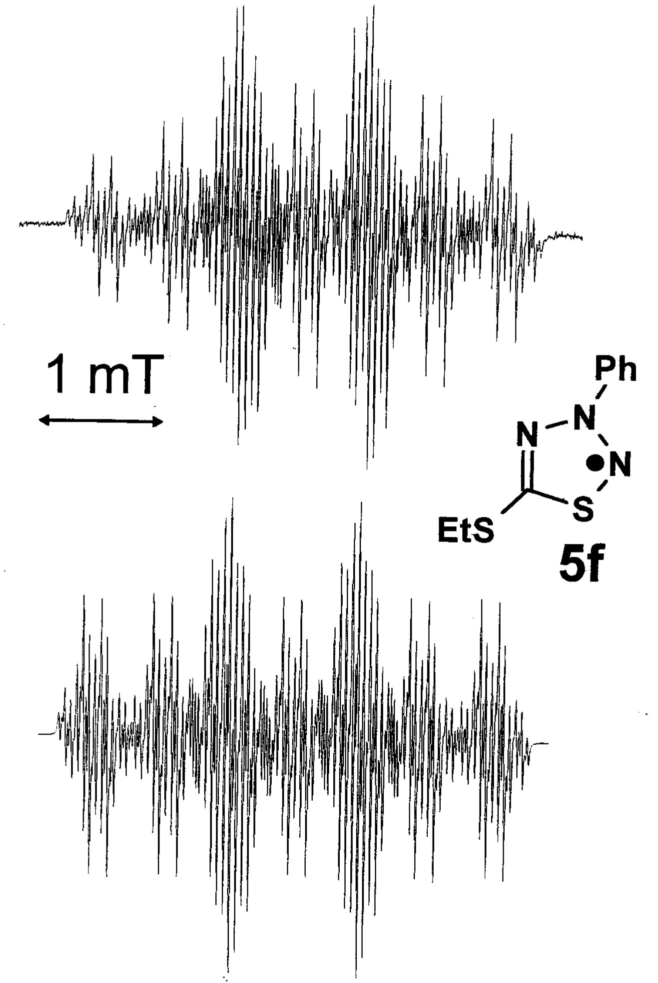


Figure 3. ESR spectrum of radical **5f** in toluene together with a simulation (bottom; linewidth 0.017 mT) using the data shown in Table 3.

Similar cleavages have been documented for the radical anions of esters of benzoic[9a] and pyridine-based[9b] acids and thioic acids. Surprisingly, in the latter cases the carbonyl–sulfur bond, C(O)—SR, was cleaved. In contrast, in the case of esters C(O)O—R, cleavage of the alkyl–oxygen bond was observed, yielding the corresponding carboxylates. Up to now it has not been possible to identify **6b**as a decay product from **5c**, which results from cleavage of the O—Et bond.

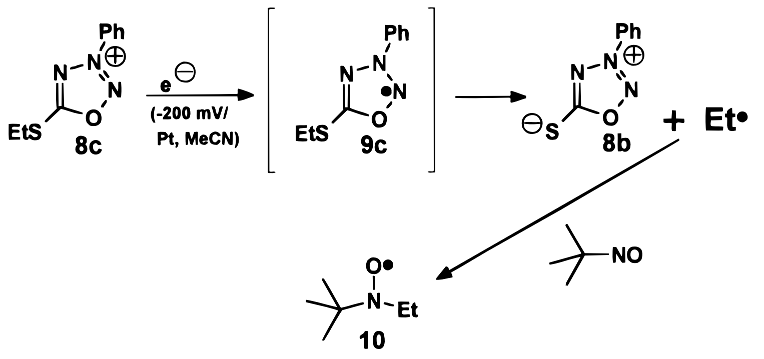
CONCLUSION

Mesoionic, neutral and cationic 1,2,3,4-thiatriazoles are reduced at potentials between −0.5 and −1.5 V *vs.* Fc/Fc^+, most of them reversibly, yielding stable radicals **5**. In contrast, none of the 1,2,3,4-oxatriazoles studied gave stable radicals **9**. In two cases, decay products of radicals **9** were identified, either by spectroelectrochemistry or by a spin-trap experiment. Radical **9b** rearranged to a 1,2,3,4-thiatrizole whereas **9c** decomposed by cleavage an exocyclic sulfur–ethyl bond.

EXPERIMENTAL

Spectra

ESR spectra were recorded using ERS 300 (ZWG, Berlin, Germany) and ESP 300 E (Bruker, Karlsruhe, Germany) X-band spectrometers. All measurements



Scheme 2. Spin-trap experiment with electrochemically reduced **8c** using *tert*-nitrosopropane as trapping reagent.

were carried out at room temperature with a rectangular cavity and 100 kHz field modulation. For calculating the *g*-factors, the magnetic field and the microwave frequency were measured with an NMR magnetometer and a ProNova 3120 frequency counter, respectively. ESR spectra were simulated using a Bruker simulation program on an Aspect 2000 computer using Gaussian lineshapes. Cyclic voltammetry was performed either with an ECM 700 (ZWG) or a Model 273A potentiostat/galvanostat (EG&G Princeton Applied Research, Princeton, NJ, USA in acetonitrile which was 0.1 M in tetrabutylammonium tetrafluoroborate *vs.* Ag/AgCl.

In situ spectroelectrochemical measurements were carried out with a capillary cell based on a gold LIGA structure, which has been described previously.[19a,b] The spectra were recorded with a fast scanning diode-array spectrometer (J&M Analytische Mess- und Regeltechnik, Aalen, Germany), triggered by or own program using a DA–AD plug-in board to simultaneously drive a potentiostat built in our own laboratory, and to record the current data.

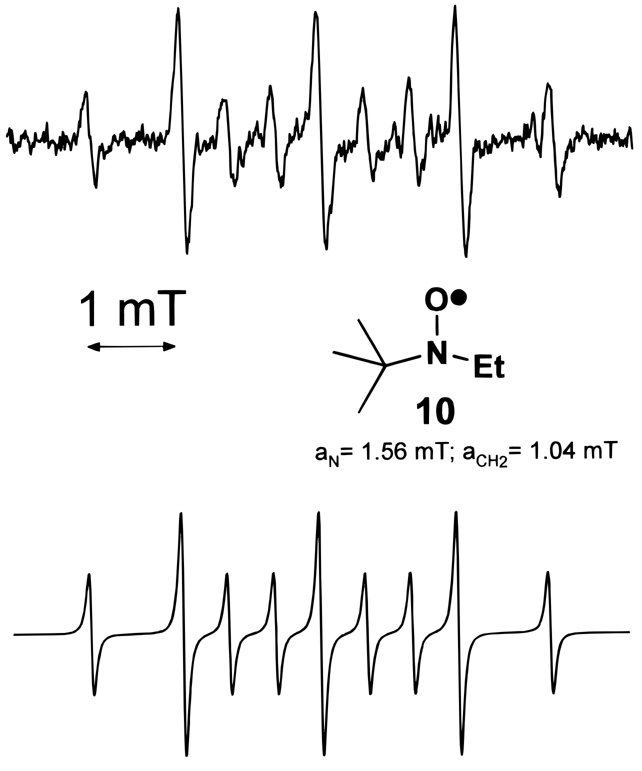


Figure 4. Experimental (top) and simulated[18] (bottom) ESR spectrum of *tert*-butylethylnitroxide (**10**) generated during the reduction of **8c** in the presence of 2-methyl-2-nitrosopropane.

NMR spectra were measured with a Bruker AC 200 T instrument. For the spin-trap experiment, an *in situ* EC-ESR cell as described in Ref. 19c was used.

Solvents and supporting electrolytes were of electrochemical grade purchased from Fluka and used without further purification. For ESR spectra using electrochemical reduction, dichloromethane or DMF (radical anions) were the solvent. For cyclic voltammetry and ESR, the concentration of the compounds was approximately 1 mM and the concentration of the spin-trap was 10 mM. All solutions were thoroughly purged with nitrogen prior to use. All compounds refused to be reversibly oxidized up to +1.5 V. In this context, the term reversible applies to scan rates between 0.05 and 1 V s^{-1}.

Compounds

The following compounds have been described previously: **7**,[20] **8a**,[21] **8b**,[11] **8c**,[11] **6a**,[20] **6b**,[11] **6c**,[11] **6d**,[11] **6i**[20] and **6k**.[22]

5-Isopropylthio-3-phenyl-1,2,3,4-thiatriazolium trifluormethanesulfonate (**6g**) and 3-isopropyl-5-phenyl-1,2,3,4-thiatriazolium trifluormethanesulfonate (**6j**) were obtained by the following method: to 0.5 mmol of **7** or **6d**, respectively, in 1 ml of CH_2Cl_2, 1 mmol of isopropyl trifluormethanesulfonate[23] was added. After 24 h the solution was cooled to −8 °C. The products crystallized on slow addition of chilled diethyl ether and light petroleum (b.p. 30–50 °C). **6g**: yield 64%; m.p. 92–93 °C ^1H NMR ($CDCl_3$), 1.56 ppm (6H, d, $J = 6.8$ Hz, 2 CH_3), 4.22 [1H, septet, $J = 6.8$ Hz, $(H_3C)_2CH$], 7.59–7.75 (3H, m, 3-, 4-, 5-H in Ph), 8.24 (2H, d, $J = 7.2$ Hz, 2-, 6-H); ^{13}C NMR ($CDCl_3$), 22.32 ppm (2 CH_3), 43.83 [$(H_3C)_2CH$], 123.06 (3-, 5-C in Ph), 130.57 (2-, 6-C), 134.61 (4-C), 139.74 (1-C), 191.13 [SC(═N)S]. **6j**: yield 52%; m.p. 98–99 °C; ^1H NMR ($CDCl_3$), 1.91 ppm (6H, d, $J = 6.6$ Hz, 2 CH_3), 5.66 [1H, septet, $J = 6.6$ Hz, $(H_3C)_2CH$], 7.56–7.77 (3H, m, 3-, 4-, 5-H in Ph), 8.12 (2H, d, $J = 7.0$ Hz, 2-, 6-H); ^{13}C NMR ($CDCl_3$), 21.91 ppm (2 CH_3), 70.80 [$(H_3C)_2CH$], 123.41 (1-C in Ph), 129.98 (3-, 5-C), 130.28 (2-, 6-C), 136.24 (4-C), 187.47 [PhC(═N)S)].

The triflates of **6g** and **6j** did not give a satisfactory elemental analyses. Therefore, they were converted into the perchlorates in the following way: to 0.3 mmol of the triflate in 2 ml of CH_2Cl_2 0.5 mmol of lithium perchlorate in 2 ml of diethyl ether were added. The solution was cooled to −8 °C and the perchlorates crystallized on slow addition of chilled diethyl ether and light petroleum. **6g**: yield 85%; m.p. 128–129 °C. Found: C, 35.67; H, 3.55; N, 12.36; S, 18.44. $C_{10}H_{12}N_3ClO_4S_2$ requires C, 35.55; H, 3.58; N, 12.44; S, 18.98%. **6j**: yield 90%; m.p. 121–122 °C. Found: C, 39.39; H, 3.99; N, 13.56; S, 10.55. $C_{10}H_{12}N_3ClO_4S$ requires C, 39.28; H, 3.96; N, 13.74; S, 10.49%.

Compound **6l** was synthesized by applying the alkylation procedure described above to **6d** using perdeuteroethyl triflate. Perdeuteroethyl triflate was prepared from silver triflate and perdeuteroethyl iodide.[24] Compound **6m** was prepared according to the general synthesis of **6d**, starting from phenylhydrazine deuterated in the aromatic ring, which was made from aniline (Ph-d_5) and sodium nitrite.[25] Compound **6n** was synthesized like **6d**,[11] using sodium [^{15}N]nitrite in the nitrosation of phenyldithiocarbazate. Compound **6o** was made like **6m** using [2-^{15}N]phenylhydrazine made from aniline and sodium [^{15}N]nitrite.[25]

5-Methylthio-3-phenyl-1,2,3,4-thiatriazolium tetrafluoroborate (**6e**), 5-ethylthio-3-phenyl-1,2,3,4-thiatriazolium tetrafluoroborate (**6f**) and 3-methyl-5-phenyl-1,2,3,4-thiatriazolium tetrafluoroborate (**6h**) were prepared from **7** and **6d** by alkylation with the appropriate Meerwein salts, the procedure being similar to published ethylations with triethyloxonium tetrafluoroborate.[11] **6e**: yield 77%; m.p. 146–147 °C. Found: C, 32.38; H, 2.62; N, 14.04; S, 21.60. $C_8H_8BF_4N_3S_2$ requires C, 32.34; H, 2.71; N, 14.14; S, 21.58%. ^{1}H NMR [acetone-d_6–TFA (100:1)], 3.14 ppm (3H, s, CH_3), 7.76–7.92 (3H, m, 3-, 4-, 5-H in Ph), 8.47 (2H, d, $J = 7.2$ Hz, 2-, 6-H); ^{13}C NMR [acetone-d_6–TFA (100:1)], 18.75 ppm (CH_3), 124.47 (3-, 5-C in Ph), 131.66 (2-, 6-C), 135.61 (4-C), 141.26 (1-C), 193.72 [SC(=N)S]. **6f**: yield 82%; m.p. 91–92 °C. Found C, 34.61; H, 3.18; N, 13.46; S, 20.40. $C_9H_{10}BF_4N_3S_3$ requires C, 34.62; H, 3.21; N, 13.46; S, 20.51%. ^{1}H NMR ($CDCl_3$), 1.59 ppm (3H, t, $J = 7.4$ Hz, CH_3), 3.61 (2H, q, $J = 7.4$ Hz, CH_2), 7.63–7.80 (3H, m, 3-, 4-, 5-H in Ph), 8.28–8.34 (2H, d, $J = 7.7$ Hz, 2-, 6-H); ^{13}C NMR ($CDCl_3$), 12.7 ppm (CH_3), 31.4 (CH_2), 123.0 (3-, 5-C in Ph), 130.6 (2-, 6-C), 135.1 (4-C), 139.7 (1-C), 191.5 [SC(=N)S]. **6h**: yield 46%; m.p. 176–177 °C. Found: C, 36.32; H, 3.05; N, 15.78; S, 12.09. $C_8H_8BF_4N_3S$ requires C, 36.26; H, 3.04; N, 15.85; S, 12.10%. ^{1}H NMR [acetone-d_6–TFA (100:1)], 5.19 ppm (3H, s, CH_3), 7.69–7.91 (3H, m, 3-, 4-, 5-H in Ph), 8.28 (2H, d, $J = 7.2$ Hz, 2-, 6-H); ^{13}C NMR (acetone-d_6–TFA), 51.65 ppm (CH_3), 124.80 (1-C in Ph), 130.85 (3-, 5-C), 131.26 (2-, 6-C), 137.10 (4-C), 188.64 [PhC(=N)S)].

Compound **8a** was prepared from **8b** by a hitherto unpublished method: to 1 mmol of **8b** in 5 ml of dry CH_2Cl_2 at 0 °C, 6 mmol of MCPBA in 20 ml of CH_2Cl_2 were added in a slurry over a period of 60 min. The mixture was stirred at room temperature for 60 min, washed with saturated brine, a solution of 2 g of Na_2S in 30 ml of water and again with brine, dried over Na_2SO_4 and evaporated to dryness. The product was chromatographed on silica gel with diethyl ether–pentane (1:1) and crystallized to yield 100 mg (61%) of **8a**, which had spectroscopic data identical with those reported.[21]

Compound **8a** could not be alkylated by alkyl oxonium salts or triflates; **6b** refused to be alkylated by alkyl triflates; **8b** decomposed in the presence of isopropyl triflate.

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