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ESR Detection of Aliphatic Dithioester Radical Anions by Photoreaction of Alkyl Disulfides

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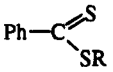
The radical anions of aromatic dithioesters have been obtained, and the corresponding ESR spectra were observed, by means of electrochemical reduction of the parent molecules:[2]



R = Me, Et, Pr^i, Bu^t, Ph

The spectra of the analogous aliphatic radical anions $RC(SR){=}S^{\bullet-}$, on the contrary, have never been reported. Most likely the reduction of the parent molecules does not yield a sufficiently high steady-state concentration to allow these radicals to be detected by ESR spectroscopy. We report here that the radical anions of aliphatic dithioesters can be obtained by photolysis of appropriate disulfides in an alkaline medium.

For instance, photolysis of MeSSMe in EtOH/EtOK yields an ESR spectrum corresponding to three different radicals whose relative proportions depend on the temperature and on the irradiation period. A sample spectrum is reported in Figure 1 together with the computer simulation. The structure of the radicals involved has been assigned as follows: (i) One of the ESR traces (that eventually disappears on raising the temperature above −60 °C) is clearly due to $MeSSMe^{\bullet-}$ (**1**) since the a_H splitting (5.35 G) and *g*-value (Table 1) are the same as previously reported[3,4] for this radical obtained in an independent manner. (ii) The second trace (about 40%), displaying a doublet (a_H = 14.25 G) of quartets (a_H = 1.25 G), was assigned to the dithioester radical anion **2** (Table 1):

2 **2**

(iii) The third trace (about 20%), exhibiting a septet (a_H = 0.75 G) due to six equivalent hydrogens, was assigned to the trithiocarbonate radical anion **3**:

3 **3**

The latter eventually becomes the only visible radical, particularly when the temperature is raised above −20 °C. It has also to be pointed out that radicals **1**–**3** appear after some time from the application of the photolysis: this is a clear indication that MeSSMe has to be firstly transformed into byproducts from which the radicals are subsequently produced.

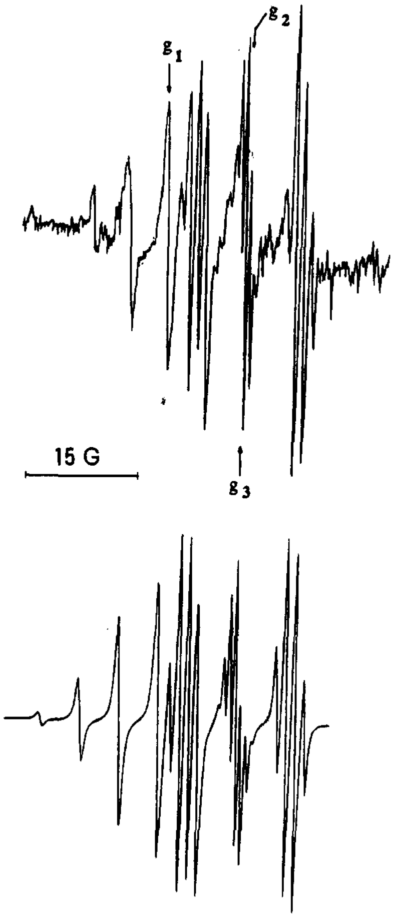


Figure 1. ESR spectrum of radicals **1**–**3** obtained by photolysis of MeSSMe in EtOH/EtOK at −93 °C. The computer simulation has been obtained with the parameters of Table 1 and with a relative intensity, respectively, of 2:2:1. The *g*-factors for each trace have been also indicated.

In previous works[3,4] we had shown that the spectrum of **1** ($MeSSMe^{\bullet-}$) can be obtained by photolysis of MeSH in EtOH/EtOK and it is a consequence of the coupling reaction of $MeS^{\bullet}$ with MeS^-. On the contrary the spectrum of **1** *cannot be obtained* by reduction[4] of MeSSMe with Na or K alloy. Accordingly, the delayed appearance, in the present case, of the spectrum of **1** (and the subsequent production of radicals **2** and **3**) requires a number of reaction steps which are summarized in Scheme 1.

This mechanism is analogous to that reported in refs 3 and 4: the disproportion (step II) of $MeS^{\bullet}$ is a known process previously reported[5,6] under similar conditions, and the formation of $CH_2{=}S$, along with MeSH, accounts for the subsequent formation of the dithioester radical anion **2**, according to Scheme 2. Steps VI and VII are also supported by the following observations: (a) The use of MeOH/MeOK rather than EtOH/EtOK does not modify

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[1] In partial fulfillment of the requirements for the Ph.D. Thesis in Chemical Sciences of the University of Bologna.

[2] Voss, J.; Schlapkohl, K. *Tetrahedron* **1975**, *31*, 2892.

[3] Cremonini, M. A.; Lunazzi, L.; Placucci, G. *J. Chem. Soc. Perkin Trans. 2* **1992**, 451.

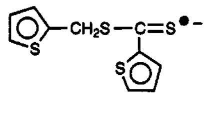
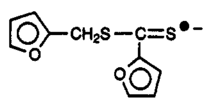
[4] Cremonini, M. A.; Lunazzi, L.; Placucci, G. *J. Org. Chem.* **1993**, *58*, 3805.

[5] Friswell, N. J.; Gowenlock, B. G. In *Advances in Free Radical Chemistry*; Williams, G. H., Ed.; Logos-Academic Press: New York, 1967; Vol. II, p 27.

[6] Lunazzi, L.; Placucci, G.; Grossi, L. *J. Org. Chem.* **1982**, *47*, 1367.

0022-3263/94/1959-3726$04.50/0

Table 1. ESR Parameters for Radicals 1−12

radical					
structure	no.	a_H splitting (G)	g-factor	t (°C)	solvent[a]
$MeSSMe^{\bullet-}$	**1**	5.35 (6H)	2.01342	−93	A, B
$MeSCH{=}S^{\bullet-}$	**2**	14.25 (1H) 1.25 (3H)	2.00697	−93	A, B
$(MeS)_2C{=}S^{\bullet-}$	**3**	0.75 (6H)	2.00712	−93	A, B
$EtSSEt^{\bullet-}$	**4**	6.00 (4H)	2.01330	−103	A
$EtSC(Me){=}S^{\bullet-}$	**5**	17.00 (3H)	2.00590	−103	A
nBuSC(CH$_2$Et)=S$^{\bullet-}$	**6**	10.75 (2H)	2.00596	−67	A, A′
$Pr^iSSPr^{i\bullet-}$	**7**	5.25 (2H)	2.01340	−80	A
$Me_2C{=}S^{\bullet-}$	**8**	18.60 (6H)	2.00520	−96	A
$MeOC(Ph){=}S^{\bullet-}$	**9**	1.10 (3H) 4.10 (2H ortho) 1.30 (2H meta) 5.50 (1H para)	2.00455	−36	B′
$EtOC(Ph){=}S^{\bullet-}$	**10**	0.90 (2H) 4.20 (2H ortho) 1.30 (2H meta) 5.10 (1H para)	2.00454	−37	A′
	**11** (70%)	1.25 (1H) 5.50 (1H) 6.05 (1H)	2.00580	−57	A′, B′
	11 (30%)	1.10 (1H) 5.20 (1H) 6.08 (1H)	2.00564	−57	A′, B′
	**12**	1.12 (1H) 5.50 (1H) 6.60 (1H)	2.00589	−68	A, A′

[a] A = EtOH/EtOK in cyclopropane, B = MeOH/MeOK in cyclopropane. A′ = EtOH/EtOK/HMPTA in cyclopropane; B′ = MeOH/MeOK/HMPTA in cyclopropane.

Scheme 1

$$\text{(I)}\quad MeSSMe \xrightarrow{h\nu} 2\,MeS^{\bullet}$$

$$\text{(II)}\quad MeS^{\bullet} + MeS^{\bullet} \longrightarrow MeSH + CH_2{=}S$$

$$\text{(III)}\quad MeSH \xrightarrow{EtO^-} MeS^-$$

$$\text{(IV)}\quad MeS^{\bullet} + MeS^- \longrightarrow \underset{\mathbf{1}}{MeSSMe^{\bullet-}}$$

the observed spectrum, thus ruling out the participation to the reaction of the alkoxy moieties from the environment. (b) Addition of Bu^{t}OOBu^t enhances the intensity of the spectrum of **2** in that the radical Bu^{t}O$^{\bullet}$ (produced by photolysis of the peroxide) is known to be a much better H-abstractor than thiyl radicals (like MeS$^{\bullet}$), thus making step VII more efficient.

Reactions of Schemes 1and 2 are also required in order to explain the formation of radical **3** according to Scheme 3. A convincing indication which supports the sequence of Scheme 3 was obtained by studying the photolysis of EtSSEt. In this case only the two radicals EtSSEt$^{\bullet-}$ (**4**) and EtS-$^{\bullet}$CMe-S$^-$ (**5**) are observed (Table 1). When radical **5** is formed, a step like VIII yields a compound from which further H-abstraction is impossible. i.e.:

$$EtS^{\bullet} + \underset{\mathbf{5}}{EtS\text{-}^{\bullet}CMe\text{-}S^-} \longrightarrow (EtS)_2CMe\text{-}S^-$$

For the same reason photolysis of n-BuSSBu-n yields, in the same conditions, the radical anions **6**, n-BuSC(CH$_2$-Et)=S$^{\bullet-}$ (Table 1). The proposed sequences also allow one to predict that the dithioester radical anion cannot be observed when Pr^{i}SSPr^i is submitted to photolysis. In this case step VI of Scheme 2 yields in fact a byproduct from which further H-abstraction is impossible, i.e.:

$$Me_2CHS^{\bullet} + Me_2C^{\bullet}\text{-}S^- \longrightarrow Me_2CHS\text{-}C(Me_2)\text{-}S^-$$

Photolysis of Pr^{i}SSPr^i also confirms the occurrence of the disproportion process proposed in step II of Scheme 1. In addition to the expected radical Pr^{i}SSPr$^{i\bullet-}$ (**7**) we also observed, in fact, a second spectrum (Table 1) due to the radical anion of thioacetone **8** (Me$_2$C=S$^{\bullet-}$) which had been obtained in an independent way by Davies and Neville.[7] In our conditions[8] the presence of this radical is a consequence of steps II and V that, here, correspond to the following sequence:

$$Me_2CH\text{-}S^{\bullet} + Me_2CH\text{-}S^{\bullet} \longrightarrow Me_2CH\text{-}SH + Me_2C{=}S$$

$$Me_2C{=}S \xrightarrow[EtO^-]{h\nu} Me_2C{=}S^{\bullet-} \longleftrightarrow \underset{\mathbf{8}}{Me_2\dot{C}\text{—}S^-}$$

Again the intensity of **8** is enhanced by the presence of Bu^{t}OOBu^t.

On the other hand, photolysis of Bu^{t}SSBu^t does not yield any radical of this type: this is consistent with the proposed mechanism in that the disproportion process is not allowed in the case of Bu^{t}S$^{\bullet}$.

Finally, in order to have an additional and independent proof for the structural assignment of these new aliphatic dithioester radical anions, product analysis was carried

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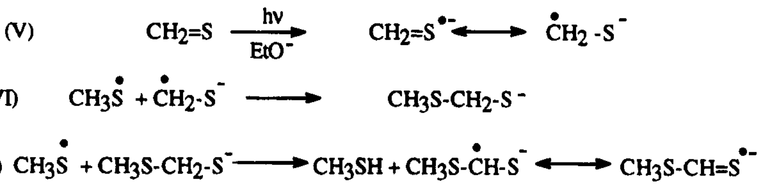
[7] Davies, A. G.; Neville, A. G. *J. Chem. Soc. Perkin Trans. 2* **1992**, 171.

[8] The ESR spectra corresponding to the thioaldehyde radical anions (CH$_2$=S$^{\bullet-}$ and MeCH=S$^{\bullet-}$) produced, respectively, by photolysis of MeSSMe and EtSSEt were not detected since they rapidly reacted further to yield the corresponding dithioester radical anions **2** and **5**. Owing to the greater steric hindrance, the subsequent coupling reaction of Me$_2$C=S$^{\bullet-}$ (**8**) is, conversely, slow enough as to yield a steady-state concentration sufficient for ESR detection.

Scheme 2



$$\text{(V)}\quad \mathrm{CH_2{=}S} \xrightarrow[\mathrm{EtO^-}]{h\nu} \mathrm{CH_2{=}S^{\bullet-}} \longleftrightarrow \mathrm{\dot{C}H_2\text{-}S^-}$$

$$\text{(VI)}\quad \mathrm{CH_3\dot{S}} + \mathrm{\dot{C}H_2\text{-}S^-} \longrightarrow \mathrm{CH_3S\text{-}CH_2\text{-}S^-}$$

$$\text{(VII)}\quad \mathrm{CH_3\dot{S}} + \mathrm{CH_3S\text{-}CH_2\text{-}S^-} \longrightarrow \mathrm{CH_3SH} + \mathrm{CH_3S\text{-}\dot{C}H\text{-}S^-} \longleftrightarrow \mathrm{CH_3S\text{-}CH{=}S^{\bullet-}}$$

2

Scheme 3

$$\text{(VIII)}\quad \mathrm{MeS^{\bullet}} + \mathrm{MeS\text{-}^{\bullet}CH\text{-}S^-}\ (\mathbf{2}) \longrightarrow \mathrm{(MeS)_2CH\text{-}S^-}$$

$$\text{(IX)}\quad \mathrm{(MeS)_2CH\text{-}S^-} + \mathrm{MeS^{\bullet}} \longrightarrow \mathrm{MeSH} + \underset{\mathbf{3}}{\mathrm{(MeS)_2C^{\bullet}\text{-}S^-}}$$

out. After photolysis of MeSSMe in EtOH/EtOK, the alkaline solution was neutralized with acetic acid and the presence of $\mathrm{MeSCH_2SH}$ (decay product of radical **2** by H-abstraction from the environment) and of $\mathrm{(MeS)_2CHSH}$ (decay product of radical **3**) was detected by GC-mass spectrometry. To check that decay actually occurred *via* H-abstraction, photolysis of MeSSMe was repeated in $\mathrm{CD_3OD/CD_3OK}$. After neutralization with acetic acid, the presence of MeSCHDSH ($M^+ = 95$) as well as of MeSCHD ($M^+ - 33 = 62$, due to loss of SH) was observed.

Phenylmethanethiol $\mathrm{PhCH_2SH}$ had been reported[9] to behave in a different way with respect to the other thiols $\mathrm{RCH_2SH}$ (R = H or alkyl groups) when submitted to photolysis in an alkaline solution since the ESR spectrum of thiobenzaldehyde radical anion ($\mathrm{PhCH{=}S^{\bullet-}}$), rather than the spectrum of the corresponding disulfide radical anion, had been obtained. It was thus conceivable to expect a different behavior also for the photolysis of benzyl disulfide, $\mathrm{PhCH_2SSCH_2Ph}$. Contrary to the previous cases, a reaction with the environment was indeed observed since the radicals $\mathrm{MeOCPh{=}S^{\bullet-}}$ (**9**) or $\mathrm{EtOCPh{=}S^{\bullet-}}$ (**10**) were detected, respectively, when using MeOH/MeOK or EtOH/EtOK. These radicals could be easily identified (Table 1) since they have essentially the same spectral parameters as those obtained by electrochemical reduction [2] of the parent molecules.

Such a different reaction pathway can be explained, in our opinion, by the occurrence of the initial steps of the reaction sequence described in ref 10, i.e.:

$$\mathrm{PhCH_2SSCH_2Ph} \xrightarrow{\mathrm{R\bar{O}}} \mathrm{Ph\bar{C}HSSCH_2Ph}$$

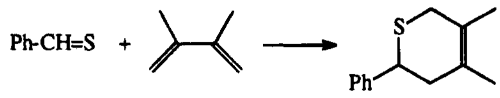
$$\mathrm{Ph\bar{C}HSSCH_2Ph} \longrightarrow \mathrm{PhCH{=}S} + \mathrm{PhCH_2\bar{S}}$$

The thiobenzaldehyde undergoes subsequently to a Cannizzaro-type reaction,[11] yielding the thioesters that, in our photolytic conditions, generate the observed radical anions **9** (R = Me) or **10** (R = Et) by a well-known single electron transfer (SET) process:

$$2\,\mathrm{PhCH{=}S} \xrightarrow{\mathrm{RO^-}} \mathrm{PhCH_2SH} + \mathrm{Ph\text{-}C(OR){=}S}$$

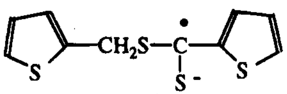
$$\mathrm{Ph\text{-}C(OR){=}S} \xrightarrow[e^-]{h\nu} \mathrm{Ph\text{-}C(OR){=}S^{\bullet-}}$$

A first indication favoring this mechanism is the observation that these ESR spectra (contrary to the case of the other disulfides) appear *immediately* after the irradiation is applied, since now the thioesters are already present, having been formed by reaction with $\mathrm{RO^-}$. This could be actually proved by product analysis (GC-mass spectrometry) which showed that the thioesters $\mathrm{PhC(OR){=}S}$ (R = Me or Et) are indeed generated *before* photolysis (on the contrary thioesters were never observed in the case of the other disulfides, either in the absence or in the presence of irradiation). The concomitant formation of thiobenzaldehyde, which is also predicted to occur *before* photolysis, could be proved too. As PhCH=S is too unstable to be directly detected[12] by product analysis, we added to the reaction mixture a diene (2,3-dimethyl-1,3-butadiene) which allowed us to observe the corresponding cycloaddition[12] product, according to the reaction:



An additional proof of the presence of thiobenzaldehyde was also achieved by the observation, in appropriate conditions,[13] of the well-known[9] ESR spectrum of its radical anion (superimposed to the spectra of **9** or **10**) which appears immediately after the application of the irradiation.

The reason why benzyl disulfide, contrary to the other disulfides $\mathrm{RCH_2SSCH_2R}$ (R ≠ Ph), follows the proposed reaction pathway should be attributed to the formation of the carbanion $\mathrm{PhCH_2SSCHPh^{(-)}}$ which is greatly stabilized by conjugation with the phenyl group. Indeed when the phenyl moiety is substituted by less-conjugating rings (e.g. by thiophene), the reaction reverts to that previously reported, yielding the dithioester radical anion **11**, both in EtOH/EtOK and in MeOH/MeOK.



11

This radical (Table 1) is expected to exist as a pair of *E,Z* conformers owing to the restricted rotation about the thiophene-C• bond, as observed in analogous cases.[14] As reported in Figure 2, two such conformers were indeed observed with a 70:30 intensity ratio. The analogous

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[9] Casarini, D.; Lunazzi, L.; Placucci, G.; Ishida, T.; Ishii, A.; Okazaki, R. *J. Org. Chem.* **1988**, *53*, 1582.

[10] Ikehira, H.; Tanimoto, S. *Bull. Chem. Soc. Jpn.* **1984**, *57*, 1423.

[11] Ashby, E. C.; Coleman, D.; Gamasa, M. *J. Org. Chem.* **1982**, *52*, 4079.

[12] Vedejs, E.; Stults, J. S.; Wilde, R. G. *J. Am. Chem. Soc.* **1988**, *110*, 5452.

[13] Addition of *tert*-butyl peroxide favors the formation of thiobenzaldehyde radical anion (thus enhancing its ESR spectrum) in that the $\mathrm{Bu^tO^{\bullet}}$ radical abstracts an hydrogen atom from the phenylmethanethiolate $\mathrm{PhCH_2S^-}$ formed, simultaneously with PhCH=S, from the carbanion $\mathrm{PhCH_2SSCHPh^{(-)}}$ as proposed in ref 10.

[14] Borghi, R.; Cremonini, M. A.; Lunazzi, L.; Placucci, G. *J. Org. Chem.* **1991**, *56*, 6337.

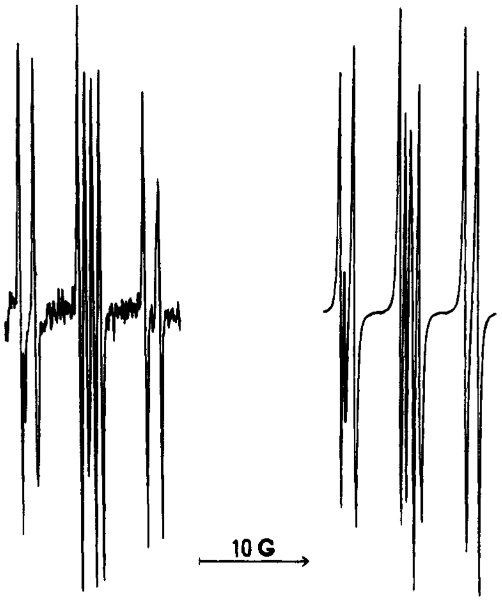
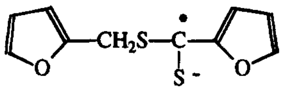


Figure 2. Experimental (left) and simulated (right) ESR spectrum of radical **11**, showing the presence of two rotational conformers in a 7:3 ratio. The parameters used for the simulation are reported in Table 1.

radical **12** was also detected when replacing the phenyl group by the less-conjugating furan moiety. In the latter case the *E,Z* rotational conformers yielded spectra too similar to be properly resolved, so that only a single set of parameters are reported in Table 1 for **12**.



(12)

Conclusions

Direct ESR evidence for a number of aliphatic dithioester radical anions, that cannot be otherwise produced, has been obtained by photolyzing the appropriate disulfides in an alkaline medium. The various steps of this process have been elucidated by the ESR observation of concomitant radicals produced in the reaction, as well as by a product analysis which also involved isotopic substitution. In the case of benzyl disulfide a different pathway, requiring the formation of a stabilized carbanion as well as a reaction with the environment, is followed.

Experimental Section

Most of the disulfides employed were commercially available. The disulfide precursor of radical **11** (Thiophene-2-yl disulfide)[15] and of radical **12** (furan-2-yl disulfide)[16] were obtained as described in the literature.

The ESR spectra were obtained by photolyzing the samples in the cavity of an ESR spectrometer (Varian E104) by means of a carefully focused 500-W high-pressure Hg lamp, using suprasil quartz tubes. The samples were prepared by dissolving the disulfides in ROH/ROK (see Table 1) adding cyclopropane as solvent. Some samples (Table 1) also contained small amount of HMPTA (hexamethylphosphourus triamide) that helped in dissolving the disulfide. The solutions were carefully degassed and sealed *in vacuo*. It is worthwhile to outline that when benzyl disulfide is dissolved in ROH/ROK a reddish color develops immediately, as often observed when stabilized carbanions are formed. On the contrary in all the other cases the alkaline solutions remained colorless.

Acknowledgment. This work was carried out with the financial support of MURST and CNR, Rome.

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(15) Mieolszynski, J. L.; Aberkane, O.; Schneider, M.; Paquer, D.; Born, M.; Park, G. *Sulfur Lett.* **1988**, *8*, 31.

(16) Firouzabadi, H.; Mohammadpour-Baltork, I. *Bull. Chem. Soc. Jpn.* **1992**, *65*, 1131.