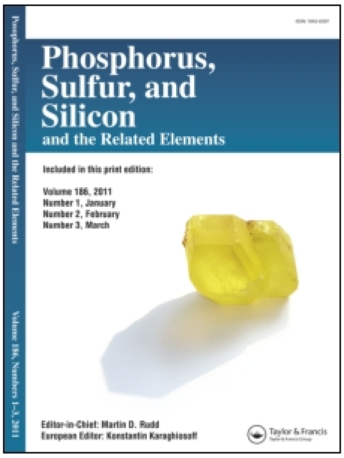


**Phosphorus, Sulfur, and Silicon and the Related Elements**
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

# Alkyl 2-Aryl-2-thioxoethanoates and -thioates: Preparation, Dimerization, and EPR Spectra of the Corresponding Radical Anions[1]

Jürgen Voss[a]; Andrzej Sawluk[a]; Gisela Lange[a]; Gunadi Adiwidjaja[b]
[a] Department of Chemistry, University of Hamburg, Hamburg, Germany [b] Department of Geosciences, University of Hamburg, Hamburg, Germany

**To cite this Article** Voss, Jürgen , Sawluk, Andrzej , Lange, Gisela and Adiwidjaja, Gunadi(2009) 'Alkyl 2-Aryl-2-thioxoethanoates and -thioates: Preparation, Dimerization, and EPR Spectra of the Corresponding Radical Anions1', Phosphorus, Sulfur, and Silicon and the Related Elements, 184: 5, 1206 — 1223

**To link to this Article: DOI:** 10.1080/10426500902855240

**URL:** http://dx.doi.org/10.1080/10426500902855240

*Phosphorus, Sulfur, and Silicon*, 184:1206–1223, 2009
Copyright © Taylor & Francis Group, LLC
ISSN: 1042-6507 print / 1563-5325 online
DOI: 10.1080/10426500902855240

# Alkyl 2-Aryl-2-thioxoethanoates and -thioates: Preparation, Dimerization, and EPR Spectra of the Corresponding Radical Anions[1]

**Jürgen Voss,[1] Andrzej Sawluk,[1,*] Gisela Lange,[1] and Gunadi Adiwidjaja[2]**
[1]Department of Chemistry, University of Hamburg, Hamburg, Germany
[2]Department of Geosciences, University of Hamburg, Hamburg, Germany

*The title compounds were prepared by reaction of the corresponding α-halocarboxylic or α-halothiolocarboxylic esters with tetraethylammonium thiosulfate and subsequent treatment of the resulting Bunte salts with sodium hydroxide in a two-phase system. Under elimination of sulfite, the deep-blue colored thiones were generated. These labile compounds could not always be isolated from the solutions in a pure state. Instead, frequently the [2+2]-dimers (dialkyl 2,4-diaryl-1,3-dithietane-2,4-carboxylates) or other follow-up products were obtained. Nevertheless, the EPR spectra of the monomer radical anions could be recorded even if solutions of the dimers were reduced by internal electrolysis. Additional EPR spectra were observed in several cases, which we assign to the radical anions of dialkyl 2,3-diaryl-2-butene-1,4-dioate radical anions originating from electron induced sulfur extrusion of the corresponding 1,3-dithietanes. Radical trianions were observed when a 1,4-benzene-bis-α-thioxoester or -thioxo-thiolester was electroreduced at a more negative electrode potential.*

**Keywords** Benzo[*c*]thiophenes; Bunte salts; 1,3-dithietanes; EPR spectroscopy; radical anions; 2-thioxocarboxylates

Received 28 December 2007; accepted 19 February 2008.

Dedicated to Professor Marian Mikołajczyk, CBMiM PAN in Łódź, Poland, on the occasion of his 70th birthday.

The University of Hamburg, the Konrad-Adenauer-Stiftung (gradute scholarship A. S.), the Deutsche Forschungsgemeinschaft, and the Fonds der Chemischen Industrie are gratefully acknowledged for their financial support. We thank Prof. Dr. U. Behrens, University of Hamburg, for his help concerning the X-ray structures.

Address correspondence to Prof. Dr. Jürgen Voss, University of Hamburg, Department of Chemistry–Organic Chemistry, Martin-Luther-King-Platz 6, D-20146 Hamburg, Germany. E-mail: voss@chemie.uni-hamburg.de

*A. Sawluk passed away on July 29, 1991.

## INTRODUCTION

We have performed electron paramagnetic resonance (EPR) spectroscopic studies on the radical anions of various monothio-$\alpha$-dicarbonyl compounds such as alkyl 2-arene-2-oxoethanedithioates,[2,3,4] $N,N$-disubstituted 2-aryl-2-thioxoethanamides,[5] and 2-aryl-2-thioxoethanethioamides[6] in order to gain insight into the electron distribution in these interesting species, which exhibit an inherent competition between a carbonyl group directly linked to a thiocarbonyl group. The related alkyl 2-aryl-2-thioxoethanoates **2** are not very well known, since they are considerably more labile than the corresponding stable $N,N$-disubstituted amides. According to our earlier results, they exhibit the same marked tendency to dimerize under [2+2]-cycloaddition and formation of 1,3-dithietanes,[7,8] which is observed in the case of monothiobenzile[9] and the monosubstituted *N-tert*-butyl-2-phenyl-2-thioxoethanamide.[10] Accordingly, they raise difficulties during their preparation and handling, and we had to find suitable methods for their preparation that would enable us to generate and study the corresponding radical anions by EPR spectroscopy.

## PREPARATIONS

In a preliminary note,[7] we have described the preparation of ethyl 2-phenyl-2-thioxoethanoate by base-catalyzed cleavage of the corresponding BUNTE-salt (organyl thiosulfate). The deep-blue oil dimerized within a short time even at low temperature or in solution under formation of the [2+2]-cycloadduct diethyl 2,4-diphenyl-1,3-dithietane-2,4-dicarboxylate. Its aliphatic counterpart ethyl 3,3-dimethyl-2-thioxobutanoate (**2k**, see Table I), which Metzner and coworkers have obtained by reaction of the oxo-ester with hydrogen sulfide, is more persistent, but during its preparation the corresponding dimer **3k** is also formed.[8,11]

We have prepared a series of further Bunte salts **1** from the corresponding alkyl 2-chloro- or 2-bromo-2-arylethanoates and -ethanethioates by use of tetraethylammonium thiosulfate, which is soluble in organic solvents and thus more suitable than sodium thiosulfate (Scheme 1).

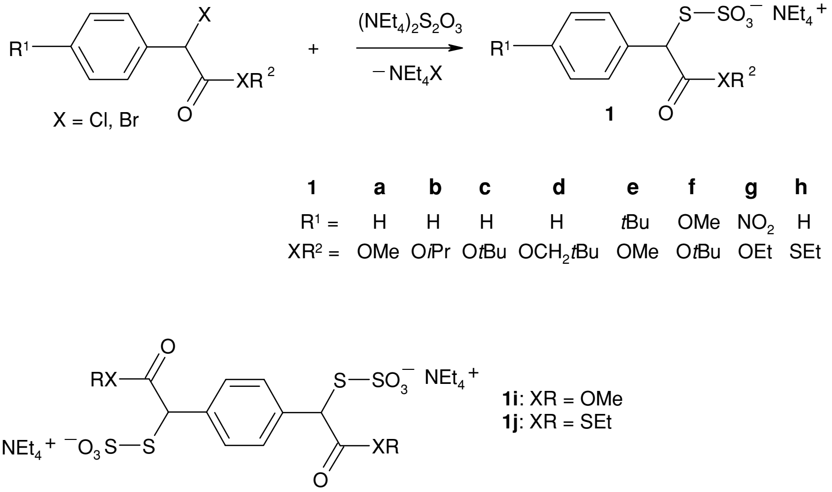
Three of the Bunte salts (**1g**, **1h**, and **1i)** were isolated as pure crystalline compounds and were spectroscopically characterized. The remaining ones were used for the fragmentation experiments without further purification.

The cleavage reaction (Scheme 2) was performed in a two-phase solvent mixture by stirring an aqueous solution of the organyl thiosulfate

**TABLE I EPR Spectroscopic Proton HFS Coupling Constants $a^{H}_{\mu}$ (mT) and $g$-Factors of the Radical Anions of $\alpha$-Thioxo-Esters and -thioesters $p$-$R^1$-$C_6H_4$-CS-CO-$XR^2$ ($2^-$)**

| | $R^1$ | $XR^2$ | $a^{H}_{2,6}$ | $a^{H}_{3,5}$ | $a^{H}_{4}$ | $a^{H}_{R^2}$ | $g$ |
|---|---|---|---|---|---|---|---|
| **2a** | H | OMe | 0.184 | 0.068 | 0.204 | 0.075 | 2.01037 |
| **2c** | H | O*t*Bu | 0.200 | 0.075 | 0.216 | — | [a] |
| **2d** | H | $OCH_2$-*t*Bu | 0.185 | 0.065 | 0.204 | 0.085 | 2.01032 |
| **2e** | *t*Bu | OMe | 0.184 | 0.072 | — | 0.074 | 2.01030 |
| **2f** | MeO | O*t*Bu | 0.190 | 0.070 | 0.023[b] | — | 2.00984 |
| **2g** | $NO_2$ | OEt | 0.11 | 0.32 | (1.05)[c] | [d] | [a] |
| **2h** | H | SEt | 0.161 | 0.068 | 0.165 | 0.029 | 2.01098 |
| **2i** | CS-CO-OMe | OMe | 0.235 | 0.235 | — | [d] | 2.00513 |
| **2i**$^{3-e}$ | CS-CO-OMe | OMe | 0.184 | 0.068 | — | 0.075<br>0.020[f] | 200996 |
| **2j**$^{3-e}$ | CS-CO-SEt | SEt | 0.161 | 0.060 | – | 0.030 | 2.01091 |
| **2k** | [g] | OEt | – | – | (0.025)[h] | 0.075 | 2.01045 |

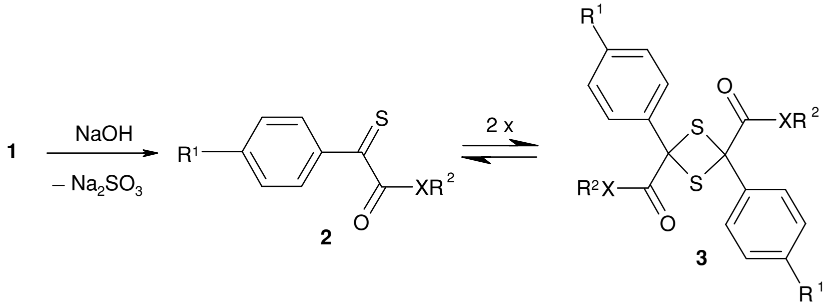
[a] Not determined.
[b] $a^{H}_{4-OMe}$.
[c] $a^{N}_{NO2}$.
[d] Not resolved.
[e] Radical trianion, observed at $E_{red} = -2.0$ V, see text.
[f] $a^{H}_{4-COOMe}$.
[g] **2k** = *t*Bu-CS-CO-OEt.
[h] $a^{H}_{tBu}$.



| 1 | a | b | c | d | e | f | g | h |
|---|---|---|---|---|---|---|---|---|
| $R^1$ = | H | H | H | H | *t*Bu | OMe | $NO_2$ | H |
| $XR^2$ = | OMe | O*i*Pr | O*t*Bu | $OCH_2$*t*Bu | OMe | O*t*Bu | OEt | SEt |

**1i**: XR = OMe
**1j**: XR = SEt

**SCHEME 1**



**SCHEME 2**

**1** with diethyl ether or trichloromethane and sodium hydroxide. In most cases, the organic phase turned blue and was then separated. Removal of the ether at low temperature gave the thiones **2** as blue oils or crystals (**2f**). Most of them dimerized under decolorization within minutes or after a few hours at 20°C or even below 0°C except the crystalline **2f**, which can be stored for a week in the dark at −23°C. The stabilization of **2f** is obviously due to the +M effect of the *para*-methoxy substituent. We have recrystallized the resulting colorless solids in several cases and obtained the pure dialkyl 2,4-diaryl-1,3-dithietane-2,4-dicarboxylates **3b**, **3c**, **3d**, **3e**, and **3f** and the -bis-thiolocarboxylate **3h**.

According to their NMR spectra, several dithietanes were formed as a mixture of two stereoisomers, the ratios of which depended on the bulkiness of the alkyl group. The pure *trans*-stereoisomers of **3b** and **3c** could be isolated by fractionizing crystallization. Their configurations were revealed by X-ray structural analyses. An ORTEP plot of **3b** is shown in Figure 1.

The nitro derivative **2g** could not be extracted into the ether phase. It was generated by stirring a solution of **1g** in dry DMF with powdered sodium hydroxide. The resulting deep-blue solution was directly used for the EPR measurement. Also the bifunctional Bunte salts dimethyl benzene-1,4-bis(α-thiosulfatoacetate) (**1i**) and *S*, *S*-diethyl benzene-1,4-bis(α-thiosulfatoacetothioate) (**1j**) led to water-soluble products. The thiones **2i** and **2j** were therefore generated by fragmentation with powdered sodium hydroxide in dry acetonitrile. The resulting solutions were directly used for the internal electroreduction and EPR measurement.

Dialkyl α,α′-dibromo-1,2-benzenediacetates (**4**), on the other hand, did not even lead to Bunte salts. Instead, they reacted with tetraethylammonium thiosulfate under formation of the known dimethyl benzo[c]thiophene-1,3-dicarboxylate (**5a**)[12] and the unknown diethyl

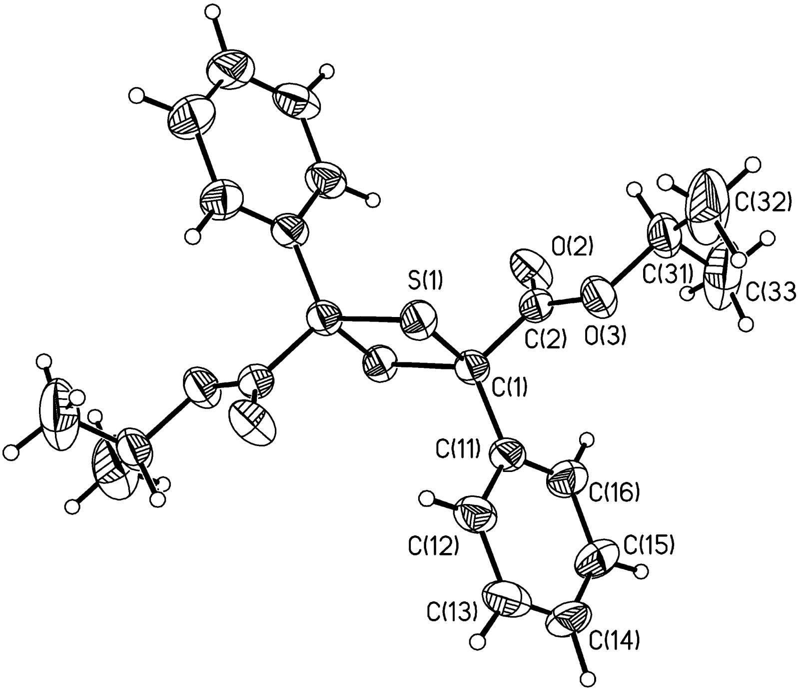
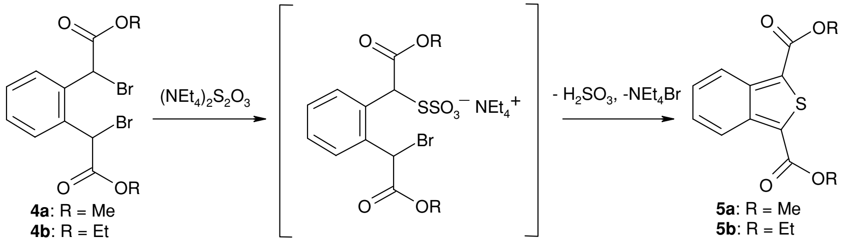


**FIGURE 1** ORTEP view of the dithietane **3b**. Thermal ellipsoids are drawn at the 50% probability level. Selected bond lengths (pm) and bond angles (°): S1–C1: 1.836, S1–C1′: 1.839, C1–S1–C1′: 86.4, S1–C1–S1′: 93.6.

ester (**5b**) (Scheme 3), the structure of which was proved by an X-ray structure analysis (Figure 2).

This result was not unexpected, since **5a** is also formed by reaction of **4a** with potassium disulfide via sulfur extrusion of the intermediate 3,4-benzodithiane.[12] Probably, mono-Bunte salts are formed from **4** in the



**SCHEME 3**

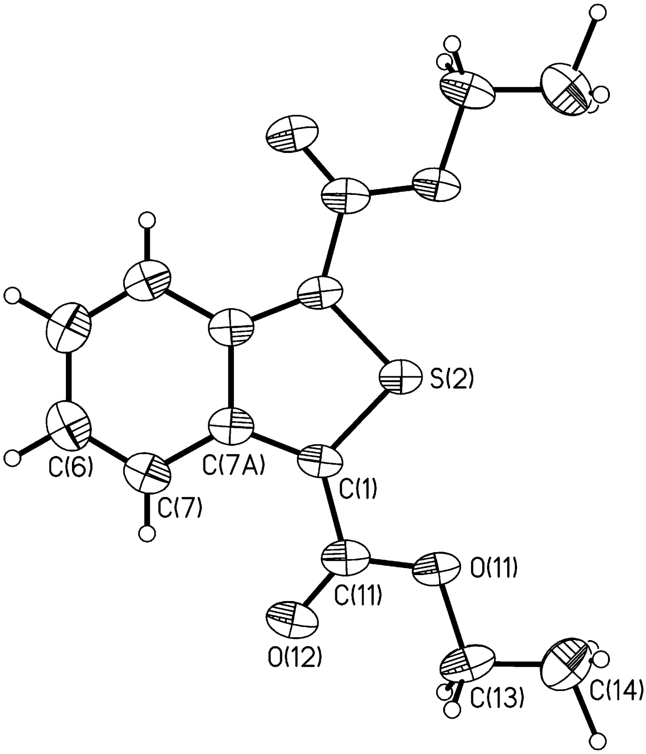


**FIGURE 2** ORTEP view of the benzo[*c*]thiophene **5b**. Thermal ellipsoids are drawn at the 50% probability level. Selected bond lengths (pm) and bond angles (°): S–C1: 1.706, C1–C7a: 1.395, C7–C7a: 1.406, C6–C7: 1.344, C5–C6: 1.431, C2–S–C3: 92.5, S–C1–C7a: 112.4, C2–C7a–C4a: 111.4.

first step. Subsequently, intramolecular cyclization under elimination of sulfite and bromide to form **5** occurs (Scheme 3).

## EPR SPECTROSCOPIC RESULTS

Radical anions of the $\alpha$-thioxo-esters and $\alpha$-thioxo-thioloesters **2** were generated by internal electroreduction in dry acetontrile or DMF. Suitable reduction potentials for the single electron transfer steps were determined during the EPR measurements by controlled potential sweeps at intervals of 50 mV between 0.0 and −2.0 V. Resolved EPR spectra were recorded at −35°C. Experimental EPR spectra of the methyl 2-phenyl-2-thioxophenylethanoate (**2a**) and ethyl

2-phenyl-2-thioxophenylethanethioate (**2h**) radical anions along with the computer simulations are for example shown in Figure 3.

The proton hyperfine structure (HFS) coupling constants $a_\mu^{\mathrm{H}}$ and $g$-factors are compiled in Table I. In most cases, a straightforward assignment based on the comparison of substituted derivatives was possible.

In cases where the thiones were not stable enough for isolation, the blue-colored acetonitrile solutions obtained by stirring of the Bunte salts **1** with solid sodium hydroxide powder could be directly used for the electroreductive generation of the radical anions.

The pattern of the proton HFS coupling constants reflects a spin density distribution in $\mathbf{2}^{\cdot -}$, which one would expect for arene radical anions with electron-withdrawing substituents. It can be reproduced by HMO calculations.[13] Application of the McConnell equation, $a_\mu^{\mathrm{H}} = -2.7 \cdot \rho_\mu^\pi$, gives $a_{\mathrm{para}}^{\mathrm{H}} = 0.212$ mT, $a_{\mathrm{ortho}}^{\mathrm{H}} = 0.169$ mT, $a_{\mathrm{meta}}^{\mathrm{H}} = 0.013$ mT in reasonable agreement with the experimental values (Table I). The ratio $a_{\mathrm{ortho}}^{\mathrm{H}}/a_{\mathrm{para}}^{\mathrm{H}}$ is close to 1. This is indicative of a particularly strong spin-attracting effect of the substituent.[14] We have observed this effect in related arene radical anions such as Ph-CO-CS-SR[3,4] as well. The coupling constants $a_\mu^{\mathrm{H}}$ of the aromatic protons in the thiolester $\mathbf{2h}^{\cdot -}$ are significantly lower compared with the data found for the corresponding ester radical anions, e.g., $\mathbf{2a}^{\cdot -}$. This tendency was found in the Ar-CO-CO-XR (X = O, S) series as well and has been attributed to an increased spin density in the functional group -CO-CO-SR,[4] an argument that should apply to the -CS-CO-XR functionality too. As usual,[4] the protons of the SEt group in $\mathbf{2h}^{\cdot -}$ exhibit smaller coupling constants compared with the OEt protons.

The *para*-nitro substituent of $\mathbf{2g}^{\cdot -}$ totally dominates the spin density distribution, which therefore completely deviates from $\mathbf{2a}^{\cdot -}$. The *para*-methoxy substituent of $\mathbf{2f}^{\cdot -}$, on the other hand, does not significantly disturb the spin density distribution.

In several cases, additional EPR spectra with quite different spectroscopic parameters (Table II) appeared at higher fields ($g \approx 2.0036$) when more negative reduction potentials were applied. Figure 4 shows an example.

The same EPR spectra were also observed when the corresponding dialkyl 2,4-diaryldithietane-1,3-dicarboxylates **3a**, **3d**, and **3e** were subjected to internal electroreduction. Tentatively, we assign these EPR spectra to the radical anions of dialkyl 2,3-diarylbut-2-enedioates ($\mathbf{6}^{\cdot -}$). The low $g$-factors and small line-widths are indicative of the absence of sulfur (heavy-atom effect) in the molecules. Furthermore, HFS couplings with the protons of each two equivalent arene moieties are observed. This fact implies conjugation between the two arene

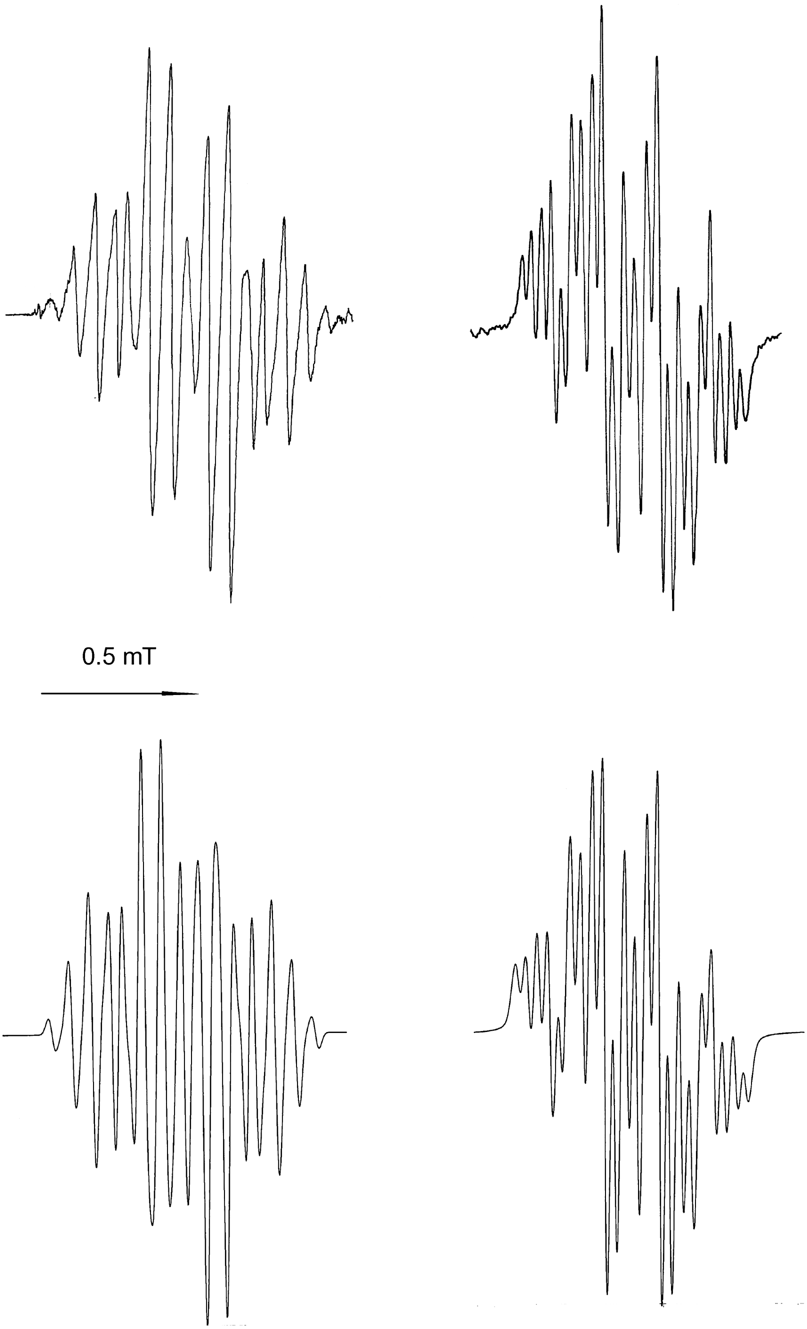


**FIGURE 3** EPR spectra (top: experimental, bottom: simulated) of the radical anions **2a**$^{\cdot-}$ (left) and **2h**$^{\cdot-}$ (right).

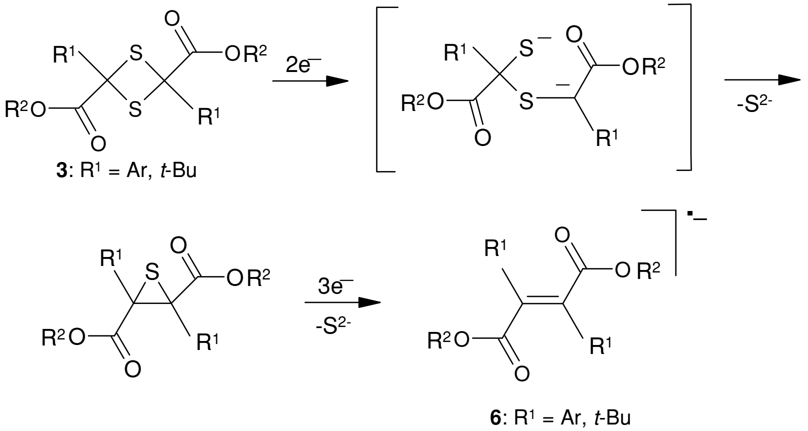
**TABLE II EPR Spectroscopic Proton HFS Coupling Constants $a^{H}_{\mu}$ (mT) and *g*-Factors of the Dialkyl But-2-enedioate Radical Anions $R^2O{-}CO{-}CR^1{=}CR^1{-}CO{-}OR^2$ ($6^{\cdot -}$)**

| | $R^1$ | $R^2$ | $a^{H}_{2',2'',6',6''}$ | $a^{H}_{3',3'',5',5''}$ | $a^{H}_{4',4''}$ | $g$ |
|---|---|---|---|---|---|---|
| **6a** | Ph | Me | 0.113 | 0.047 | 0.123 | 2.00363 |
| **6d** | Ph | *t*BuCH$_2$ | 0.114 | 0.047 | 0.121 | 2.00363 |
| **6e** | 4-*t*Bu-C$_6$H$_4$ | Me | 0.114 | 0.046 | – | 2.00363 |
| **6k** | *t*Bu | Et | | | 0.028$^{a}$ | 2.00500 |

$^{a}a^{H}_{tBu}$

rings, which is possible in **6** but not in **3**. The alkenes **6** could be formed by electron-induced sulfur extrusion from the 1,3-dithietanes **3**. We assume that first two electrons are transferred to **3** under ring opening. Elimination of a sulfide anion from the intermediate dianion would lead to a thiirane. Finally, the well known reductive thiirane desulfurization[15] yields the alkene derivative **6** (Scheme 4).

Interestingly, the EPR spectra of the monomers were also observed when the dimeric dithietanes were used as starting compounds for the internal electroreduction. Obviously an equilibrium between the monomers and the dimers exists in the polar solvent (Scheme 2), or the radical anions of the latter are cleaved under formation of the monomers. In fact, the 1,3-dithietanes **3** tend to cleave at elevated temperatures, which is perceptible by the light-blue color that develops upon warming. Since very low concentrations of paramagnetic



SCHEME 4

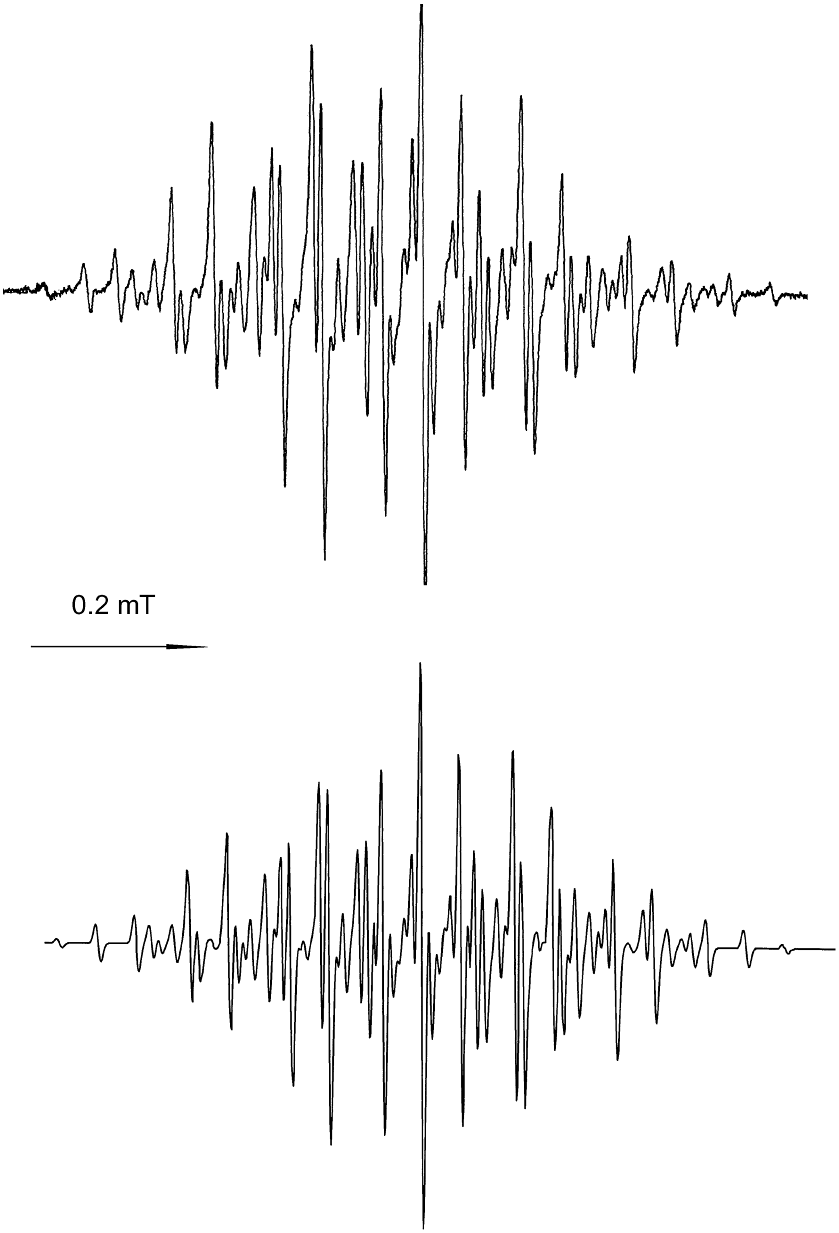
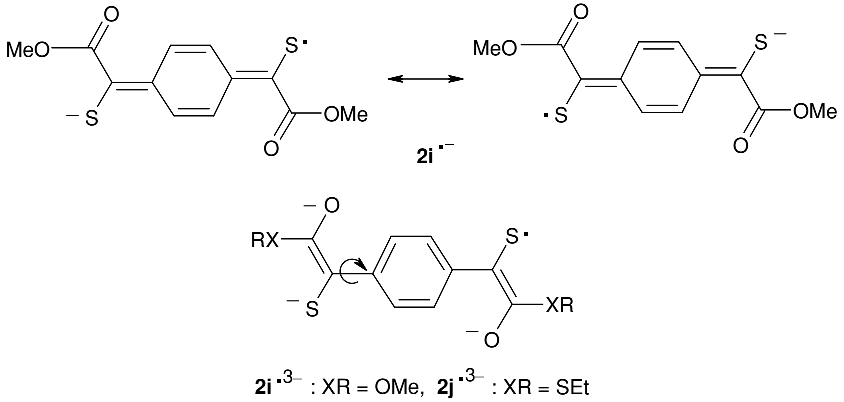


**FIGURE 4** EPR Spectrum (top: experimental, bottom: simulated) of the radical anion 6a$^-$.

species can be detected by EPR spectroscopy, even trace amounts of the monomers would lead to the observed result. This observation opens up the valuable possibility of generating radical anions of the elusive thione species from the much more stable dimers.

Two different EPR spectra are also observed after electroreduction of the bis-$\alpha$-thioxo-ester **2i**. First ($E_{\text{red}} \approx -1\text{V}$) an intense quintet resulting from HFS coupling with four equivalent protons [$a_{\mu}^{\text{H}}(\text{exp.}) = 0.250$ mT, $a_{\mu}^{\text{H}}(\text{HMO}) = 0.227$ mT] appears at $g = 2.005013$. The second, more complex spectrum with $g = 2.00996$ is observed at $E_{\text{red}} \approx -2\text{V}$. An interpretation of these EPR spectra is not straightforward. Neither of the two can be assigned to a butenedioate radical anion of type **6**. Instead, the quintet may be best assigned to the expected radical anion $\mathbf{2i}^{\cdot-}$. Since the spin is symmetrically delocalized over the whole molecule (Scheme 5) and thus over two thiocarbonyl groups, the $g$-factor is lower as compared with the corresponding monofunctional radical anions of type $\mathbf{2a}^{\cdot-}$–$\mathbf{2h}^{\cdot-}$, and the four aromatic protons are of course equivalent. The second spectrum, which is produced at more negative reduction potential, is tentatively assigned to the radical trianion $\mathbf{2i}^{3-}$. It exhibits an asymmetric spin density distribution, which resembles the one found in the *para*-substituted radical monoanion $\mathbf{2e}^{\cdot-}$ (see the proton HFS coupling constants in Table I). We assume that the spin label group, in terms of the EPR time scale, is coplanar with the ring, so that spin delocalization is possible. By contrast, the other, doubly negatively charged functional group is twisted out of the ring plane (Scheme 5).



**SCHEME 5**

Internal electroreduction ($E_{\text{red}} \approx -2$V) of the bis-thiolester **2j** resulted in the formation of the radical trianion **2j**$^{3-}$. Its EPR spectrum strikingly resembles the spectrum of **2h**$^{\cdot -}$, which is explained in the same way as for **2i**$^{3-}$.

EPR spectra of radical trianions have also been observed in the related series of bifunctional $\alpha$-oxo-thiono- and $\alpha$-oxo-dithioesters.[3]

## EXPERIMENTAL

Corrected melting points (mp) were determined with an Electrothermal-Schmelzpunktsapparatur. Boiling points (bp) were determined during distillation. Thin layer chromatography (TLC) was performed on Al foils coated with $SiO_2$ $F_{254}$ (Merck, Darmstadt). The spots were detected by the extinction of the fluorescence or by spraying with the iodine/sodium azide reagent.[16] Column chromatography (CC) was performed on Kieselgel 60 (Merck, Darmstadt), 0.063–0.200 mm (70–230 mesh). Eluents [$CH_2Cl_2$, petroleum ether (PE)] were distilled prior to use. Solvents were purified and dried by standard laboratory procedures.[17] Removal of solvents was performed in a vacuum rotary evaporator.

IR spectra were measured as KBr pellets or films on Perkin-Elmer spectrometers 297 and 399. $^1$H NMR spectra were measured in $CDCl_3$ on Varian T 60 and EM 360, and Bruker WH 270 and EM 400 spectrometers. UV/VIS spectra were recorded in methanol (Uvasol) on a Perkin-Elmer 200 spectrometer. Mass spectra were measured on a Varian MAT CH 7 spectrometer.

EPR spectra were obtained on a Bruker 420s spectrometer (X-band) equipped with a Bruker Gaussmeter and a microwave counter as described earlier.[4,14,18] The radical anions were generated by internal electroreduction at room temperature or at −35°C as described previously.[14,18]

## X-Ray Structure Analyses

The crystal data of **3b**, **3c**, and **5b** and a summary of the experimental details are given in Table III. Data collection was performed with a CAD 4 SDP (Enraf Nonius) diffractometer with graphite-monochromated Cu-$K_\alpha$ radiation (Ni-filter, $\lambda$ = 1.54184 Å) in the $\theta/2\theta$ scan mode at 298 K. The structures were solved by the direct method MULTAN.[19] All non-hydrogen atoms were localized. After refinement of these parameters, the hydrogen atoms were localized by differential Fourier synthesis.[20] The final refinement was performed by least squares

**TABLE III Crystal Data and Structure Refinement for 3b, 3c, and 5b**

| Compound | **3b** | **3c** | **5b** |
|---|---|---|---|
| Empirical formula | $C_{22}H_{24}O_4S_2$ | $C_{24}H_{28}O_4S_2$ | $C_{14}H_{14}O_4S$ |
| Formula weight | 416.56 | 444.62 | 278.31 |
| Crystal system | monoclinic | monoclinic | orthorhombic |
| Space group | $P2_1/n$ | $P2_1/n$ | *Cmma* |
| $a$ [pm] | 870.2 (1) | 1213.8 (1) | 696.3 (1) |
| $b$ [pm] | 1973.9 (1) | 1139.7 (1) | 2204.5 (1) |
| $c$ [pm] | 640.9 (1) | 899.5 (1) | 876.7 (1) |
| $\beta$ [°] | 106.35 (1) | 105.84 (1) | |
| $V$ [pm$^3$] | $1.056 \times 10^9$ | $1.197 \times 10^9$ | $1.346 \times 10^9$ |
| $Z$ | 2 | 2 | 4 |
| $\rho_{\text{calcd.}}$ [g cm$^{-3}$] | 1.31 | 1.23 | 1.37 |
| $\mu$ [cm$^{-1}$] | 24.1 | 21.5 | 21.5 |
| $F(000)$ | 440 | 472 | 584 |
| $\theta$-limits [°] | 2/70 | 2/70 | 2/70 |
| $h/k/l$-limits | 0, 10/0, 24/−7, 7 | 0, 14/0, 13/−10, 10 | 0, 8/0, 26/0, 10 |
| Reflections collected ($I > 3\sigma_I$) | 1855 | 1773 | 646 |
| Number of parameters | 176 | 193 | 77 |
| $R$-Index | 0.035 | 0.031 | 0.049 |
| $R_w$-Index ($w = \sigma_I^{-2}$) | 0.030 | 0.030 | 0.055 |

methods. Experimental correction for absorption[21] was performed in addition to the usual Lorentz correction for polarization. Crystallographic data have been deposited with the Cambridge Crystallographic Data Centre as supplementary publications No. CCDC-667725 (**3a**), CCDC-667726 (**3b**), and CCDC-667727 (**5b**). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 IEZ, UK [Fax: (international) +44–1233/336–033; E-Mail: deposit@ccdc.cam.uk].

## Preparations

Ethyl 3,3-dimethyl-2-thioxobutanoate (**2k**) and diethyl trans-2,4-di-tert-butyldithietane-1,3-dicarboxylate (**3k**) were prepared according to the literature.[8,11]

## Bunte Salts (1): General Procedure

A solution of the corresponding alkyl 2-bromo- or 2-chloro-2-arylethanoate (4 mmol) and tetraethylammonium thiosulfate[22] (4 mmol) was heated to reflux in abs. ethanol (30 mL) under monitoring by TLC. A reaction time of 12 h was applied in cases difficult to survey. Removal of the solvent left the Bunte salts as oils or crystals. The Bunte salts **1g**, **1h**, and **1i** were purified by crystallization from a suitable solvent. The other ones were used in the following reactions without further purification.

### *Tetraethylammonium S-(Methoxycarbonyl-phenylmethyl) Thiosulfate (1a)*

Salt **1a** was obtained from methyl 2-chloro-2-phenylethanoate[23] as a yellow oil.

### *Tetraethylammonium S-(Isopropyloxycarbonyl-phenylmethyl) Thiosulfate (1b)*

Salt **1b** was obtained from isopropyl 2-chloro-2-phenylethanoate[23] as a yellow oil.

### *Tetraethylammonium S-(tert-Butyloxycarbonyl-phenylmethyl) Thiosulfate (1c)*

Salt **1c** was obtained from *tert*-butyl 2-chloro-2-phenylethanoate[24] as colorless crystals.

### *Tetraethylammonium S-(Neopentyloxycarbonyl-phenylmethyl) Thiosulfate (1d)*

Salt **1d** was obtained from neopentyl 2-chloro-2-phenylethanoate[23] as a yellow oil.

### *Tetraethylammonium S-[Methoxycarbonyl-(4-tert-butylphenyl)methyl] Thiosulfate (1e)*

Salt **1e** was obtained from methyl 2-bromo-2-(4-*tert*-butylphenyl) ethanoate[25] as a yellow oil.

### *Tetraethylammonium S-[tert-Butyloxycarbonyl-(4-methoxyphenyl)methyl] Thiosulfate (1f)*

Salt **1f** was obtained from *tert*-butyl 2-bromo-2-(4-methoxyphenyl) ethanoate[26] as a yellow solid.

### *Tetraethylammonium S-[Methoxycarbonyl-(4-nitrophenyl)methyl] Thiosulfate (1g)*

Salt **1g** was obtained from ethyl 2-chloro-2-(4-nitrophenyl) ethanoate[27] as colorless crystals (19%), mp 84–85°C (EtOAc/hexane). IR (KBr): $\nu$ 1740 (C=O), 1530 ($NO_2$), 1350 ($NO_2$), 1230 (C—O) $cm^{-1}$. $^1H$ NMR (60 MHz): $\delta = 1.22$ (m, 15H, $CH_3$), 3.25 (q, 8H, $NCH_2$), 4.12 (q, 2H, $OCH_2$), 5.28 (s, 1H, CH), 7.64 (d, 2H, 2′/6′-H), 8.09 (d, 2H, 3′/5′-H).

Anal. Calcd. for $C_{18}H_{30}N_2O_7S_2$ (450.58): C, 47.98; H, 6.71; N, 6.22; S, 14.23; Found: C, 48.14; H, 6.75; N, 6.21; S, 14.09%.

### *Tetraethylammonium S-(Ethylthiocarbonyl-phenylmethyl) Thiosulfate (1h)*

The reaction of 2-chloro-2-phenylethanoyl chloride (Merck, Darmstadt, 15.0 g, 0.079 mol) with ethanethiol (4.92 g, 0.079 mol) and triethyl amine (8.02 g, 0.079 mol) in dry diethyl ether (100 mL) according to a standard laboratory method[17] gave *S*-ethyl 2-chloro-2-phenylethanethioate (13.5 g, 80%), which was used without further purification to yield **1h** as hygroscopic colorless crystals (14.9 g, 56%), mp 85–90°C ($CHCl_3$/EtOAc). IR (KBr): $\nu$ 1680 (C=O) cm$^{-1}$. $^1$H NMR (60 MHz): $\delta = 1.20$ (m, 15H, $CH_3$), 2.83 (q, 2H, $SCH_2$), 3.20 (q, 8H, $NCH_2$), 5.28 (s, 1H, CH), 7.23 (m, 5H, arom-H). Anal. Calcd. for $C_{18}H_{31}NO_4S_3$ (421.65): C, 51.27; H, 7.41; N, 3.32; S, 22.81; Found: C, 51.59; H, 7.51; N, 3.38; S, 22.41%.

### *Bis(tetraethylammonium) S,S′-Benzene-1,4-bis(methoxycarbonyl-phenylmethyl) Bis(thiosulfate) (1i)*

Dimethyl 1,4-benzenediacetate[28] was brominated with NBS.[17] The resulting dimethyl $\alpha,\alpha'$-dibromo-1,4-benzenediacetate was used without further purification to yield **1i** as colorless crystals (40%), mp 175–177°C (EtOH/$Et_2O$). IR (KBr): $\nu$ 1750 (C=O), 1230 (C–O) cm$^{-1}$. $^1$H NMR (400 MHz): $\delta = 1.22$ (t, 24H, $CH_3$), 3.25 (q, 16H, $NCH_2$), 3.65 (s, 6H, $OCH_3$), 5.00 (s, 2H, CH), 7.35 (m, 4H, arom-H). Anal. Calcd. for $C_{28}H_{52}N_2O_{10}S_4$ (704.99): C, 47.70; H, 7.43; N, 3.97; S, 18.19; Found: C, 46.30; H, 7.37; N, 4.01; S, 17.63%.

### *Bis(tetraethylammonium) S,S′-Benzene-1,4-bis(ethylthiocarbonyl-phenylmethyl) Bis(thiosulfate) (1j)*

1,4-Benzenediacetic acid (Fluka, 2.91 g, 0.015 mol) was treated with $SOCl_2$ (19.6 g, 0.165mol) and NCS (10.3 g, 0.078 mol).[17] Reaction of the resulting $\alpha,\alpha'$-dichloro-1,4-benzenediacetyl chloride with ethanethiol (1.92 g, 0.031 mol) and $NEt_3$ (3.03 g, 0.030 mol) (see preparation of **1h**) led to *S*,*S′*-diethyl $\alpha,\alpha'$-dichloro-1,4-benzenediacetothioate (4.00 g, 76%), which was used without further purification to yield **1j** as a colorless oil.

## Bunte Salt Fragmentation: General Procedure

The Bunte salt **1** (1–2 g) was dissolved in a sufficient amount of $H_2O$ (not more than 60 mL). After the addition of diethyl ether (20 mL) and aqueous NaOH (2N, 5 mL), the mixture was vigorously stirred. The organic phase turned blue to violet and was separated after 15 min. The extraction was repeated until the ether remained nearly colorless. In certain cases, further addition of NaOH was appropriate since more blue product was formed. The ether layer was washed with $H_2O$, dried over $Na_2SO_4$, and vacuum-evaporated at low temperature. The remaining blue-colored oils or crystals were directly used for the generation of the radical anions by internal electroreduction.

### *tert-Butyl 2-Phenyl-2-thioxoethanoate (2c)*

Thione **2c** was obtained from **1c** as blue crystals. $^1$H NMR (60 MHz): $\delta = 1.45$ [s, 9H, $C(CH_3)_3$], 7.2–7.7 (m, 5H, arom-H).

### *tert-Butyl 2-(4-Methoxyphenyl)-2-thioxoethanoate (2f)*

Thione **2f** was obtained from **1f** with 48% yield as dark-blue crystals. $^1$H NMR (60 MHz); $\delta = 1.46$ [s, 9H, $C(CH_3)_3$], 3.84 (s, 3H, $OCH_3$), 6.9–7.6 (AA′BB′-system, 8H, arom-H).

### *Di-tert-butyl trans-2,4-Diphenyl-1,3-dithietane-2,4-dicarboxylate (3c)*

Yield 48%, mp 164°C (PE). IR (KBr): $\nu = 1720$ (C=O) cm$^{-1}$. $^1$H NMR (60 MHz): $\delta = 1.37$ [s, 18H, $C(CH_3)_3$], 7.2–7.7 (m, 10H, arom-H). MS (70 eV): *m/z (%)* 343 (9) [$M^+$–$CO_2t$Bu], 222 (5) [$C_6H_5CSCO_2t$Bu$^+$], 122 (17), 121 (100) [$C_6H_5CS^+$], 77 (24) [$C_6H_5^+$]. Anal. Calcd. for $C_{24}H_{28}O_4S_2$ (444.61): C, 64.83; H, 6.35; S, 14.42; Found: C, 64.77; H, 6.43 S, 14.53%.

### *Dimethyl trans-2,4-Bis(4-tert-butylphenyl)-1,3-dithietane-2,4-dicarboxylate (3e)*

Yield 30%, colorless oil. IR (KBr): $\nu = 1730$ (C=O), 1230 (C–O) cm$^{-1}$. $^1$H NMR (60 MHz): $\delta = 1.32$ [s, 18H, $C(CH_3)_3$], 3.78 (s, 6H, $OCH_3$), 7.4 (d, 4H, arom-H), 7.58 (d, 4H, arom-H); Anal. Calcd. for $C_{26}H_{32}O_4S_2$ (472.67): C, 66.07; H, 6.82; S, 13.57; Found: C, 63.27; H, 6.69; S, 14.15%.

### *Di-tert-butyl trans-2,4-Bis(4-methoxyphenyl)-1,3-dithietane-2,4-dicarboxylate (3f)*

Yield 48%, mp 153°C (PE). IR (KBr): $\nu = 1760$ (C=O), 1230 (C–O) cm$^{-1}$. $^1$H NMR (60 MHz): $\delta = 1.37$ [s, 18H, $C(CH_3)_3$], 3.84 (s, 6H, $OCH_3$), 6.9–7.6 ($A_2B_2$-system, 8H, arom-H). MS (70 eV): *m/z (%)* 403 (3) [$M^+$–$CO_2t$Bu], 252 (10) [$CH_3OC_6H_4CSCO_2t$Bu$^+$], 151 (100) [$CH_3OC_6H_4CS^+$], 107 (2) [$CH_3OC_6H_4^+$]. Anal. Calcd. for $C_{26}H_{32}O_6S_2$ (504.67): C, 61.88; H, 6.39; S, 12.71; Found: C, 61.68; H, 6.40; S, 12.86%.

### S,S-Diethyl trans- and cis-2,4-Diphenyl-1,3-dithietane-2,4-dicarbothioate (3h)

Yield 60%, mp 107–109°C (EtOAc/PE). IR (KBr): $\nu = 1650$ (C = O), $\text{cm}^{-1}$. $^1$H NMR (60 MHz); *trans*-isomer: $\delta = 1.20$ (t, 6H, $CH_3$), 2.86 (q, 4H, $SCH_2$), 7.4–7.6 (m, 10H, arom-H); *cis*-isomer: 1.32 (t, 6H, $CH_3$), 2.98 (q, 4H, $SCH_2$), 7.4–7.6 (m, 10H, arom-H). MS (70 eV): *m/z* (%) 331 (5) [$M^+$–COSEt], 210 (6) [$C_6H_5CSCOSEt^+$], 121 (100) [$C_6H_5CS^+$]. Anal. Calcd. for $C_{26}H_{32}O_4S_2$ (420.64): C, 57.11; H, 4.79; S, 30.49; Found: C, 56.85; H, 4.78; S, 30.43%.

### Dimethyl Benzo[c]thiophene-1,3-dicarboxylate (5a)

Dimethyl $\alpha,\alpha'$-dibromo-1,2-benzenediacetate (**4a**)[29] (441 mg, 1.52 mmol) and tetraethylammonium thiosulfate[22] (1128 mg, 3.03 mmol) were refluxed in ethanol (30 mL) overnight. Irrespective of a yellow precipitate, the solvent was removed. The oily residue was dissolved in $CHCl_3/H_2O$ and extracted with another two portions of $CHCl_3$. The extract was dried over $Na_2SO_4$. After removal of the solvent, the residue was purified by CC ($CHCl_3$) to yield yellow crystals of **5a** (230 mg, 61%), mp 160°C ($CHCl_3$/PE), lit.[12]: mp 160°C. IR (KBr): $\nu = 1710$ (C=O), $\text{cm}^{-1}$. $^1$H NMR (60 MHz): $\delta = 4.00$ (s, 6H, $OCH_3$), 7,1–8.7 (m, 4H, arom-H). Anal. Calcd. for $C_{12}H_{10}O_4S$ (250.27): C, 57.59; H, 4.03; S, 12.81; Found: C, 58.09; H, 3.99; S, 13.08%.

### Diethyl Benzo[c]thiophene-1,3-dicarboxylate (5b)

Compound **5b** was obtained as described for **5a** from diethyl $\alpha,\alpha'$-dibromo-1,2-benzenediacetate (**4b**)[30] (600 mg, 1.86 mmol) and tetraethylammonium thiosulfate[22] (1400 mg, 3.03 mmol). Yield: 330 mg (63%) yellow crystals, mp 152–153°C ($CHCl_3$/PE). IR (KBr): $\nu =$ 1680 (C = O), $\text{cm}^{-1}$. UV/VIS (MeOH): $\lambda_{\max}$ (log $\varepsilon$) 381 (4.20), 334 (3.96), 319 (3.83), 248 (4.66), 219 (4.46), 302 (4.40) nm. $^1$H NMR (60 MHz): $\delta = 1.43$ (t, 6H, $CH_3$), 4.45 (q, 4H, $OCH_2$), 7,1 – 8.7 (m, 4H, arom-H). Anal. Calcd. for $C_{14}H_{14}O_4S$ (278.33): C, 60.42; H, 5.07; S, 11.52; Found: C, 60.41; H, 5.20; S, 11.46%.

## REFERENCES

[1] EPR Studies on Carboxylic Esters, Part 18. For Part 17, see J. Voss and R. Edler, *J. Chem. Res.*, 226 (2007).

[2] A. Sawluk, *Darstellung von Phenylendiglyoxylsäurederivaten und ESR-spektroskopische Untersuchung der Radikalanionen [Preparation of Phenylenediglyoxylic Acid Derivatives and ESR Spectroscopic Investigation of the Radical Anions]*, PhD thesis, University of Hamburg, Germany, 1987. A. Sawluk passed away on July 29th 1991.

[3] A. Sawluk and J. Voss, *Angew. Chem.,* **101,** 927 (1989); *Angew. Chem., Int. Ed. Engl.*, **28,** 906 (1989).

[4] J. Gassmann, H. Günther, K. Osternack, K. Thimm, and J. Voss, *Magn. Reson. Chem.*, **32,** 624 (1994).

[5] W. Schmüser and J. Voss, *J. Chem. Res. (S)*, 149 (1978); *J. Chem. Res. (M)*, 1901 (1978).

[6] H. Günther, *Synthese, Struktur und Reaktionen aktivierter Thiocarbonsäureester und -amide. – ESR-spektroskopische Untersuchungen ihrer Radikalanionen. [Synthesis, Structure and Reactions of Activated Thiocarboxylic Esters and Amides. – ESR Spectroscopic Studies of their Radical Anions]*, PhD thesis, University of Hamburg, Germany, 1980.

[7] K. Thimm and J. Voss, *Tetrahedron Lett.*, 537 (1975).

[8] P. Metzner, J. Vialle, and A. Vibet, *Tetrahedron*, **34,** 2289 (1978).

[9] C. Bak and K. Praefcke, *Z. Naturforsch.*, **B35,** 372 (1980).

[10] K. Thimm, W. Schmüser, and J. Voss, *J. Chem. Res. (S)*, 244, *J. Chem. Res. (M)*, 2837 (1977).

[11] P. Metzner, J. Vialle, and A. Vibet, *Tetrahedron Lett.*, 4295 (1976).

[12] G. Cignarella and G. Cordella, *Tetrahedron Lett.*, 1871 (1973); *Gazz. Chim. Ital.*, **104,** 455 (1974).

[13] R. Cannings, *Simple Huckel Molecular Orbital, SHMO*, an iterative online program (http://www.chem.ucalgary.ca/SHMO/), based on: A. Rauk, *Orbital Interaction Theory of Organic Chemistry*, Chapters 3 and 5 (Wiley Interscience, Chichester, 1994).

[14] J. Voss and F.-R. Bruhn, *Liebigs Ann. Chem.*, 1931 (1979).

[15] C. G. Venier, Small-ring compounds of sulphur and selenium, In: *Organic Compounds of Sulphur, Selenium, and Tellurium. Specialist Periodical Reports* (Royal Soc. Chem., London, 1981), Vol. 6, pp. 207, 210.

[16] E. Chargaff, C. Levine, and C. Green, *J. Biol. Chem.*, **175,** 67 (1948).

[17] Autorenkollektiv, *Organikum*, 16th ed. (VEB Deutscher Verlag der Wissenschaften, Berlin, 1986).

[18] R. Edler and J. Voss, *Chem. Ber.*, **122,** 187 (1989).

[19] G. Germain, P. Main, and M. M. Woolfson, *Acta Cryst.*, **A27,** 368 (1971).

[20] B. A. Frenz, *Structure Determination Package*, College Station, TX (1982).

[21] A. C. T. North, D. C. Phillips, and F. S. Mathews, *Acta Cryst.*, **A24,** 351 (1968).

[22] B. Hahn, B. Köpke, and J. Voss, *Liebigs Ann. Chem.*, 10 (1981).

[23] A. B. H. Funcke, R. F. Rekker, M. J. E. Ernsting, and W. T. Nauta, *Arzneimittelforsch.,* **6,** 60 (1956).

[24] F. Rolla, *J. Org. Chem.*, **47,** 4327 (1982).

[25] J. W. Epstein, H. J. Brabander, W. J. Fanshawe, C. M. Hofmann, T. C. McKenzie, S. S. Safir, A. C. Osterberg, D. B. Cosulich, and F. M. Lovell, *J. Med. Chem.*, **24,** 481 (1981).

[26] H. Gotthardt, M. C. Weisshuhn, and B. Christl, *Chem. Ber.*, **109,** 740 (1976).

[27] M. Makosza, K. Sienkiewicz, and K. Wojciechowski, *Synthesis*, 850 (1990).

[28] A. F. Titley, *J. Chem. Soc.*, **130,** 2571 (1930).

[29] G. Cignarella and A. Vigevani, *Gazz. Chim. Ital.*, **98,** 1474 (1968).

[30] C. De Luca, A. Inesi, and L. Rampazzo, *J. Chem. Soc., Perkin Trans 2*, 1821 (1983).