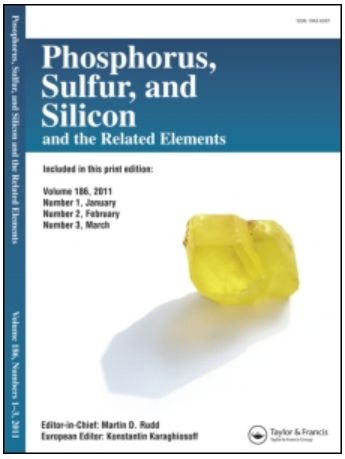

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ACYLSULFENIC ACIDS[1]

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ACYLSULFENIC ACIDS[1]

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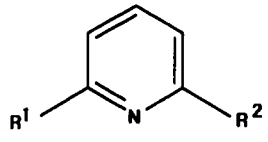
The synthesis of acylsulfenic acids and esters, their properties, reactions and spectral characteristics are described.

Key words: Acylsulfenic acids; complexes of; benzoylsulfenic acid; 2,6-di[(hydroxythio)-carbonyl]pyridine; oxidation of monothiocaboxylic acids.

INTRODUCTION

A representative (**1**) of the hitherto unknown class of acylsulfenic acids (compounds carrying a (hydroxythio) carbonyl group) has been discovered recently[2] as a metabolic intermediate[3] of the transformation —COOH→—COSH in a bacterial culture medium. Isolation and characterisation of (**1**) was possible only in form of its dimethyl ester (**2**)[4] the structure of which could be confirmed by an independent synthesis.[5] In this paper the synthesis of several compounds of the general structure R—CO—SOH (R = aryl or CH_3) as well as of their methyl esters will be described and their properties and spectral characteristics will be discussed.



	R^1	R^2
1	—CO—SOH	—CO—SOH
2	—CO—$SOCH_3$	—CO—$SOCH_3$
3	—CO—$SOCH_3$	—$COOCH_3$
4	—CO—SOH	—H
5	—CO—$SOCH_3$	—H
6	—$COOCH_3$	—$COOCH_3$
7	—CO—$SOCH_3$	—CO—SCl
8	—CO—SOC_2H_5	—CO—SOC_2H_5
9	—CO—SOC_2H_5	—$COOC_2H_5$
10	—CO—$SOCH_3$	—C(=CH_2)—OCH_3

RESULTS AND DISCUSSION

Synthesis Concepts

Several synthesis concepts which have been employed for aryl and alkyl sulfenic acids could also be envisaged for acylsulfenic acids, *viz.*

(a) Alkaline hydrolysis of the methyl esters[6] which can be obtained by reaction[5] of R—CO—SCl (from the thioanhydrides with Cl_2) with CH_3OH. Reaction of **2** with ethanolic KOH yielded, however, only products which after treatment[4] with CH_2N_2 were not sufficiently volatile for GC/MS analysis. Hence, the sulfenic acid which can easily be transformed to its methyl ester by treatment with CH_2N_2 and thus would have been detected by GC/MS was not formed.

(b) Hydrolysis of pyridine-2,6-di(carbonylsulfur chloride) with H_2O/pyridine or with ethanolic KOH yielded after treatment with CH_2N_2 only carboxylic and monothiocarboxylic esters.

(c) Alkaline hydrolysis of $(RCO—S—)_2$ (an oxidation product of RCOSH).[7] Treatment of $(Py\text{-}2\text{-}COS)_2$ yielded Py-2-COOH and Py-2-COSH only.

(d) Thermolysis of sulfoxides, *viz.* R—CO—SO—R′ → R—CO—SOH in analogy to a Chugayev reaction.[8] All attempts to oxidize the diethyl ester of **1** with a variety of oxidizing agents failed, however. This confirms earlier observations with S-benzyl-thiobenzoate.[9]

(e) Oxidation of the corresponding monothiocarboxylic acids.[10] This method proved to be successful with limitations. 3-chloroperbenzoic acid was the best choice since no formation of diacyl disulfides was observed in most cases.

The most promising procedure consists in an oxidation of the respective monothiocarboxylic acid with 3-chloroperbenzoic acid at about −15°C in dry CH_2Cl_2 saturated with N_2. This method is obviously limited to compounds which are not affected otherwise by the reagent. Thus, from furan-2-monothiocarboxylic acid only decomposition products could be obtained (cf., e.g. References 11–13). Free acylsulfenic acids can be obtained in substance only if they can be crystallized from the reaction mixture at low temperatures. All attempts of purification by chromatography (silicagel, sephadex LH-20), recrystallization or salt formation (K^+, $(C_2H_5)_3N$, pyridine) lead to partial or complete decomposition. In those cases where the free acids could not be separated from the reaction mixture the latter was treated with CH_2N_2 in order to obtain the more stable methyl esters.

Acylsulfenic Acids and their Methyl Esters

2,6-Di[(hydroxythio)carbonyl]pyridine (**1**) could be obtained in purest form. It is a pale yellow substance which can be stored for several months at −20°C if air and moisture are rigorously excluded. At room temperature decomposition under evolution of H_2S can be noticed after several days. If heated **1** decomposes without melting. It is readily soluble in polar solvents as acetone, CH_3OH, $(CH_3)_2SO$ or dioxan, slightly soluble in H_2O and insoluble in hexane, $CHCl_3$ or ether. Solutions decompose at room temperature with elimination of S and formation of pyridine-2,6-dicarboxylic acid. Treatment with a solution of CH_2N_2

in CH_2Cl_2 leads to the dimethyl ester **2** and to small amounts of 6-(methoxythio)carbonylpyridine-2-carboxylic acid methyl ester[4] (**3**) and 2-(1-methoxyethenyl)-6-(methoxythio)carbonyl-pyridine (**10**).

The only other free acid which could be obtained by crystallisation at low temperatures was benzoyl sulfenic acid (**11**) which could be transformed to its methyl ester **12** by treatment with CH_2N_2. 2-(Methoxythio)carbonyl pyridine (**5**) could be separated from the reaction mixture after treatment with CH_2N_2 by reversed phase HPLC. In the same way 2-(methoxythio)carbonyl-thiophene (**13**) could be obtained, a rather unstable compound since CH_3CN/H_2O solutions (prepared for HPLC) decompose with elimination of S after several hours. Oxidation of monothioacetic acid with subsequent treatment with CH_2N_2 yields a mixture which according to GC/MS analysis contained acetylsulfenic acid methyl ester (**14**), diacetyl disulfide and 3-chlorobenzoic acid methyl ester. Attempts to obtain **14** in pure form by distillation (normal pressure or vacuum) or chromatography (silicagel or sephadex LH-20) lead to partial or complete decomposition. Partial removal of 3-chlorobenzoic acid was possible by cooling the solution to −20°C. Spectroscopic data of **14** had to be determined from the remaining mixture and subtraction of the spectra of the pure contaminants.

Metal Complexes of Acylsulfenic Acids

Acylsulfenic acids form complexes with various metals. Compounds carrying only one sulfenic acid group react with Met^{3+} only, the Fe^{3+} complexes being especially stable. **1** which carries 2 sulfenic acid groups forms complexes with Met^{2+} as well as with Met^{3+}.

(Hydroxythio)carbonyl benzene (**11**) dissolved in CH_2Cl_2 was shaken with aqueous solutions of various metal salts. Fe^{3+} lead to a violet, Ga^{3+} to a yellow color of the organic phase, Co^{2+}, Ni^{2+}, Zn^{2+} and Cu^{2+} did not show any reaction. Treatment with an aquous solution of $NaHCO_3$ in order to remove unreacted **11** and traces of 3-chlorobenzoic acid still present from the synthesis resulted in a decomposition of the Ga complex (decoloration), while the Fe complex was stable. It can be obtained as a violet-black powder by concentration of the solution. It is readily soluble in CH_2Cl_2, acetone and ethyl acetate, slightly soluble in H_2O, CH_3OH and C_2H_5OH and insoluble in hexane. Attempts to obtain crystals for an X-ray analysis failed because of a decomposition of the complex in solution when kept at room temperature. The molecular mass (515) as determined by field desorption mass spectrometry (FD–MS) allows to calculate a Fe^{3+}—to ligand ratio of 1:3 thus demonstrating the structural relationship to hydroxamic acid. This is confirmed by the IR-spectrum (CsI) which shows that Fe^{3+} is bound by the two oxygen atoms of the —CO—SO— group. Instead of the C=O—bond at 1676 cm^{-1} observed for **12** there exist two bands at 1499 and 1481 cm^{-1} (symmetrical and antisymmetrical vibration), a shift which is also observed for hydroxamates which is caused by a weakening of the C=O-bond due to the complexation. This weakening of the C=O-bond is accompanied by a strengthening of the C—N-bond (resulting in a shift to larger wave numbers) of hydroxamates. In an analogous manner the C—S—bond (971 cm^{-1}) is shifted as compared to that of **12** (906 cm^{-1}). A strong band at 877 cm^{-1} can be attributed

to the S—O vibration as it is observed in the IR-spectra of other acylsulfenate complexes also. A final structure proof was provided by dissolving the complex in CH_2Cl_2, adding CH_2N_2 and diluted H_2SO_4. After complete decoloration of the solution the formation of **12** as main product could be demonstrated by GC/MS, accompanied by traces of benzoic acid methyl and ethyl ester (decomposition products of **11**).

In an analogous way the Fe^{3+} complex of 2-(hydroxythio)carbonylthiophene could be obtained as a violet powder (also the reactions with other metal salts parallel those of **11**). The molecular mass (533) determined by FD-MS shows again a metal-to-ligand ratio of 1:3. The characteristic IR-bands (CsI) are 1520 and 1462 (C=O), 909 (C—S) and 875 cm^{-1} (S—O). Treatment with CH_2N_2 and diluted H_2SO_4 yields **13** and traces of the methyl and ethyl esters of thiophene-2-carboxylic acid. Solutions of **4** and of acetylsulfenic acid if treated with Fe^{3+} as described above turned violet but attempts to isolate the complexes in substance failed (decomposition).

As had been observed for pyridine-2,6-di(monothio)carboxylic acid[14,15] complexes with a series of metals can be obtained from **1**. They form precipitates insoluble in all common organic solvents. The violet Fe^{3+} (regarding a possible redox reaction Fe^{2+}/Fe^{3+} see Reference 14) and the yellow Ga^{3+} and Zn^{2+} complexes were investigated in some detail. Treatment with CH_2N_2 and diluted H_2SO_4 yield in each case **2** and traces of its decomposition products as, e.g. **3** and **6**. However, it was impossible to obtain mass spectra with any of the following techniques: EI, CI, FD, FAB. The presence of the respective metals could be shown by photoelectron spectroscopy. The strong IR bands in the vicinity of 1510 cm^{-1} (Fe^{3+}: 1506, Ga^{3+}: 1502, Zn^{2+}: 1518; the S—O bands can be found at 871, 864 and 890 cm^{-1}, resp.) indicate that the carbonyl group is involved in the binding of the cation (cf. above) and not the sulfur as in the case of the di-monothiocarboxylic acid[14] where the carbonyl band lies at 1605 cm^{-1}. This observation suggests a polymeric structure in accordance with the insolubility and involatility of the complexes.

Spectroscopic Characterisation of the Acylsulfenic Acids and their Methyl Esters

IR-Spectra (see Table 1)

1 shows a broad band with a maximum at 3269 cm^{-1} typical for H-bonded OH. Accordingly, the CO band is split due to intra- and intermolecular H-bonding (typical for solid samples). The position of the carbonyl band of the esters depends strongly on the nature of the substituent and hence it is not characteristic of the sulfenic ester group *per se*. It occurs, however, always at lower wave numbers than the corresponding carboxylic acid esters and at higher wave numbers than for the monothiocarboxylic acid S-esters. More characteristic are the C—S band in the vicinity of 900 cm^{-1} and the vibrations of the S—O—R moiety the position of which is influenced somewhat by the nature of R.

^1H- and ^{13}C-NMR Spectra

The CO—$SOCH_3$-signal can be found between 3.8 and 3.9 ppm. In the ^{13}C-spectra the CO signal is observed in the vicinity of 190–195 ppm. The

CH_3-signal at 66 ppm lies characteristically lower than that of $COOCH_3$ (52 ppm), probably due to a deshielding caused by the partially positive sulfur R—$C(O^-)=S^+OR$).

Mass Spectra

The fragmentation pattern both of the free acylsulfenic acids (R—CO—SOH) and of their esters (cf. Reference 16) is rather straightforward showing the loss of ·SOH (·SOR) followed by the elimination of CO. Ions due to the loss of ·OR are of low intensity if recognizable at all. Species of the structure RS^+ resulting from a rather complex rearrangement process can be observed with low abundance (1–2% rel. int.). In the case of disubstituted pyridine derivatives (**3**, **7–10**) the fragmentation of the sulfenic ester group always exceeds that of the other substituent in intensity.

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EXPERIMENTAL PART

Instruments Mass spectra: EI: Kratos MS 25 with Carlo Erba HRGC 500, Varian MAT 212 with Varian GC 3700, Finnigan 3200 with GC 9100; GC Columns: FS-SE-54 or BP 10. FD: Varian-MAT 731. Exact mass measurements (indicated by elemental formulas): Finnigan MAT HSQ 30. NMR: Bruker AM-300. IR: Perkin–Elmer 283. GC/IR: FTIR-Spectrometer FTS-40 Digilab with Carlo Erba GC 6000, Column FS-Pb-2. UV: Beckmann Spectrophotometer 25. Photoelectron spectra: Leybold–Heraeus LHS-10. GC: Carlo Erba HRGC 4160, column FS–SE–52. HPLC: Knauer FR-30 (Nucleosil 7 C_{18}, Macherey & Nagel, Düren). Column Chromatography: Silicagel 0.040-0.063 mm, Merck, Darmstadt; Sephadex LH-20, Pharmacia, Freiburg.

2,6-Di[(hydroxythio)carbonyl]pyridine (**1**) To a solution of 1 g (3.6 mmol) pyridinium pyridinium-2,6-dicarbothioate[17] in 200 ml CH_2Cl_2 saturated with N_2 a solution of 1.24 g (7.2 mmol) 3-chloroperbenzoic acid (MCPBA) in 20 ml CH_2Cl_2 was added slowly (1 ml/min) at ~ −15°C (cooling with an ice/NaCl bath). After 1 hr the orange color of the solution had disappeared and a yellow precipitate was observed. After stirring for 1 hr under continuous cooling the precipitate was filtered off, washed with CH_2Cl_2 to remove 3-chlorobenzoic acid (MCBA) and dried under cooling with ice i.v. Yield 565 mg (68%). UV (CH_3OH) (λ nm, log ε) 293 (3.76), 238 (3.86). IR: see Table 1. ^{1}H-NMR (DMSO-d_6): 8.10 and 8.40 ppm (A_2X system): aromatic H, 9.1 (broad): SOH. ^{13}C-NMR (DMSO-d_6): 123.5, 141.1 and 149.1 (C-3, C-4, C-2), 196.3 ppm (CO). Mass Spectrum (*m/z*, rel. int.) 231 (19) $C_7H_5NO_4S_2$: M^+, 213 (40) $C_7H_3NO_3S_2$: $[M - H_2O]^+$, 182 (18) $C_7H_4NO_3S$: $[M - {}^{\cdot}SOH]^+$, 154 (67) $C_6H_4NO_2S$: $[M - {}^{\cdot}COSOH]^+$, 105 (100): *m/z* 154 − ·SOH, 77 (58): *m/z* 105 − CO.

2,6-Di[(methoxythio)carbonyl]pyridine (**2**) Treatment of **1** with a solution of CH_2N_2 in CH_2Cl_2 gave **2** identical in all respects with the material obtained by treatment of pyridine-2,6-di(carbonylsulfur chloride) with CH_3OH.[5] Spectral data may be found in Reference 5.

Pyridine-2-monothiocarboxylic acid A suspension of 2 g (14.5 mmol) of pyridine-2-thiocarboxylic acide amide in 290 ml 0.05N NaOH (14.5 mmol) was heated for 3 hrs to 65°C. The yellowish green solution thus obtained was extracted with 290 ml $CHCl_3$. The aquous phase was underlaid with 290 ml $CHCl_3$, saturated with N_2 and acidified (pH 1-2) with diluted H_2SO_4. After shaking the organic phase was dried and evaporated i.v. to dryness. Yield: 0.54 g (27%) of an orange solid. MS: DCI (CH_4) *m/z* 140 ($[M + H]^+$), 106 ($[M + H - H_2S]^+$).

TABLE I

Characteristic IR absorptions of acyl sulfenic acid and their esters

Cpd.	Medium	CO	C—CO	C—S	S—O-R(H)	
1	KBr	1651 1670 1680	1283	936	818	784
2	KBr	1709	1282	907	979	731
3	KBr	1698	1295	927	991	717
7	KBr	1694	1282	897	987	726
5	film	1690	1228	920	992	729/741
8	KBr	1707	1281	892	1015	740
9	film	1692	1285	891	1016	735
13	film	1660	1204	886	982	723
12	film	1676	1212	906	988	736
14	gas	1717	1138	934	1007	740

Thiophene-2-monothiocarboxylic acid To a solution of 13 g KOH (0.23 mol) in 80 ml ethanol saturated with H_2S 10 ml (0.09 mol) of thiophene-2-carboxylic acid chloride were added dropwise under cooling with ice/NaCl. After stirring for 1 hr, and occasional addition of H_2S to maintain an excess, precipitated KCl was filtered off. The solution was evaporated i.v. to dryness and the residue was dissolved in 300 ml H_2O. From the aquous solution the monothiocarboxylic acid was obtained as described above. Yield: 10.8 g (83%) of a yellow oil. MS: CI (i-C_4H_{10}) m/z 201 ($[M + C_4H_9]^+$), 145 ($[M + H]^+$), 111 ($[M + H - H_2S]^+$).

Furan-2-monothiocarboxylic acid was prepared as described for the thiophene derivative. Yield: 81% of a yellow oil. After treatment with CH_2N_2 two peaks were observed by GC/MS analysis, *viz.* furan-2-monothiocarboxylic acid S-ester (main product, m/z 142: M^+, 95: $[M - {}^{\cdot}SCH_3]^+$) and O-ester (m/z 142: M^+, 111: $[M - {}^{\cdot}OCH_3]^+$).

2-[(Methoxythio)carbonyl]-pyridine (**5**) To a cooled (ice/NaCl) solution of 540 mg (3.9 mmol) of pyridine-2-monothiocarboxylic acid in 40 ml CH_2Cl_2 saturated with N_2 a solution of 670 mg (3.9 mol) MCPBA in 10 ml CH_2Cl_2 was added dropwise. The mixture was stirred under continued cooling for 2 hrs. After removal of MCBA the solution was treated under cooling with a stream of CH_2N_2 until the deep yellow color persisted. After 30 min the solvent was removed. The remaining reddish brown oil was chromatographed on silica-gel with $CHCl_3$ and subsequently purified by reversed phase HPLC with CH_3CN/H_2O 4:3. CH_3CN was removed i.e., the remaining aquous phase was extracted with CH_2Cl_2, the extract was dried and the solvent was removed. Yield: 45 mg (7%) of a pale yellow oil. UV (CH_2Cl_2) (λ nm, log ε): 276 (3.70), 270 (sh), 231 (3.95). IR: see Table 1. ^{1}H-NMR ($CDCl_3$): 8.53 (H-6), 7.87 (H-4), 7.85 (H-3), 7.50 (H-5), 3.85 ppm (CH_3), ^{13}C-NMR ($CDCl_3$): 196.1 (CO), 150.7 (C-2), 148.8 (C-6), 137.6 (C-4), 128.7 (C-5), 119.1 (C-3), 65.8 (CH_3). MS (m/z, rel. int.): 169 (22) $C_7H_7NO_2S$: M^+, 138 (5) C_6H_4NOS ($[M - {}^{\cdot}OCH_3]^+$), 106 (70) C_6H_4NO ($[M - {}^{\cdot}SOCH_3]^+$), 78 (100): m/z 106 − CO.

2-[(Methoxythio)carbonyl]-thiophene (**13**) was synthesized as described above from 1 g (6.9 mmol) thiophene-2-monothiocarboxylic acid in 30 ml CH_2Cl_2 and 1.2 g (6.9 mmol) MCPBA in 15 ml CH_2Cl_2. Yield: 65 mg (5%) of a pale yellow oil. UV (CH_2Cl_2) (λ nm, log ε): 253 (3.95), 293 (3.99), IR: see Table 1. ^{1}H-NMR ($CDCl_3$): 7.68 (H-3), 7.57 (H-5), 7.11 (H-4), 3.91 ppm (CH_3). ^{13}C-NMR ($CDCl_3$): 187.4 (CO), 137.2 (C-2), 132.9 (C-5), 129.6 (C-3), 128.1 (C-4), 67.3 (CH_3). MS (m/z, rel. int.) 174 (4): M^+, 115 (2): $[M - COOCH_3]^+$, 111 (100): $[M - {}^{\cdot}SOCH_3]^+$, 83 (14): m/z 111 − CO.

(Methoxythio)carbonylbenzene (benzoylsulfenic acid methyl ester) (**12**) was synthesized as described above from 1.17 g (8.5 mmol) monothiobenzoic acid in 30 ml CH_2Cl_2 and 1.46 g (8.5 mmol) MCPBA in 15 ml CH_2Cl_2. Yield: 78 mg (7%) of a pale yellow oil. UV (CH_2Cl_2) (λ nm, log ε) 240 (4.04), 272 (3.75). IR: see Table 1. ^{1}H-NMR ($CDCl_3$) 7.71 (H-2 + H-6), 7.58 (H-4), 7.45 (H-3 + H-5), 3.90 ppm (CH_3). ^{13}C-NMR ($CDCl_3$): 195.1 (CO), 134.0 (C-1 + C-4), 129.1 (C-3 + C-5), 126.0 (C-2 + C-6), 66.9 (CH_3). MS (m/z, rel. int.): 168 (1) $C_8H_8O_2S$: M^+, 109 (2) C_6H_5S, 105 (100) C_7H_5O: $[M - {}^{\cdot}SOCH_3]^+$, 77: $C_6H_5^+$.

(Hydroxythio)carbonylbenzene (benzoylsulfenic acid) (**11**) The reaction mixture (see above) was cooled for 12 hrs with CH_3OH/Dry Ice, the precipitated MCBA was removed by filtering, the filtrate was concentrated to 10 ml and kept in the cold bath for another 6 hrs. MCBA was removed again and the filtrate was evaporated to dryness and the residue was dried i.v. for 2 hrs. The pink solid thus obtained (400 mg) still contained small amounts of MCBA. IR: see Table 1. ^{1}H-NMR ($CDCl_3$): 7.75 (H-2 + H-6), 7.59 (H-4), 7.45 (H-3 + H-5), 5.5 ppm (broad): OH. ^{13}C-NMR ($CDCl_3$): 199.5 (CO), 134.3 (C-1), 133.1 (C-4), 129.1 (C-3 + C-5), 126.0 (C-2 + C-6). MS (*m/z*, rel. int.) 154 (10): M^+, 105 (100): C_6H_5CO, 77 (75): $C_6H_5^+$.

(Methoxythio)carbonylmethane (acetylsulfenic acid methyl ester) (**14**) was synthesized from 1.07 g (14.5 mmol) monothioacetic acid in 40 ml CH_2Cl_2 and 2.49 g (14.5 mmol) MCPBA in 30 ml CH_2Cl_2 and treatment with CH_2N_2 as described above. The reaction mixture was cooled for 12 hrs with CH_3OH/Dry Ice, the precipitated MCBA was removed by filtering, the filtrate was concentrated to 10 ml under cooling with ice and afterwards kept for 6 hrs at −75°C. MCBA was removed again and the solvent was evaporated. Yield: 960 mg of an orange yellow oil containing 50% 14, 39% diacetyldisulfide and 11% MCBA methyl ester. IR: see Table I. ^{1}H-NMR ($CDCl_3$): 3.81 ($SOCH_3$), 2.14 ppm (CH_3CO). ^{13}C-NMR ($CDCl_3$): 192.3 (CO), 66.8 ($SOCH_3$)), 24.1 ppm (CH_3CO). MS (*m/z*, rel. int.): 106 (112): M^+, 63 (6): $^+SOCH_3$, 43 (100) CH_3CO^+.

Tris(benzoylsulfenato)iron (III) To a freshly prepared solution of **11** freed from MCBA as described above (starting from 2.35 g monothiobenzoic acid) under vigorus stirring a solution of 4.6 g $FeCl_3$. $6H_2O$ in 30 ml H_2O was added whereupon the solution turned violet. After stirring for 30 min at room temperature the organic phase was washed twice with 10 ml of a saturated $NaHCO_3$ solution and was dried. Evaporation of the solvent yielded 1.12 g (13%) of a blackish violet powder. Mp 134–135°C. UV (CH_2Cl_2) (λ nm, log ε) 503 (3.74), 305 (4.20), 237 (4.49), IR: see text. FD-MS: *m/z* 515 (M^+). Through a solution of 2 mg of the iron complex in 10 ml CH_2Cl_2 CH_2N_2 was bubbled until a color change was observed. Then under vigorous stirring 1 ml 5% H_2SO_4 was added and the addition of CH_2H_2 was continued until complete decoloration of the solution was achieved. Evaporation of the solvent after drying of the solution yielded a yellow oil which was subjected to GC/MS. The main product (see text) was **12**.

[Tris(2-thienylcarbonylsulfenato)]iron (III) was prepared as described above from 1.2 g freshly oxidized thiophene-2-monothiocarboxylic acid and 2.2 g $FeCl_3$. $6H_2O$ in 15 ml H_2O. Due to the lower stability of the complex the organic phase was washed twice with 20 ml 1M $NaHCO_3$ and twice with H_2O. Yield: 500 mg (11%) of a blackish-violet powder. Mp 164–165°C. UV (CH_2Cl_2) (λ nm, log ε) 512 (3.72), 334 (4.35), 261 (4.41). IR: see text. FD-MS: *m/z* 533 (M^+), 111 ($C_4H_3SCO^+$). Treatment with CH_2N_2 as described above yielded **13** as the main product (see text).

Complexes of **1** To solutions of 50 mg (0.22 mmol) of **1** in 5 ml acetone aquous solutions of 0.22 mmol of the respective metal salts were added (60 mg $FeSO_4 \cdot 7H_2O$, 62 mg $ZnSO_4 \cdot 7H_2O$, or 92 mg $Ga_2(SO_4)_3$ in 1 ml H_2O). The solutions turned yellow for Zn and Ga and violet for Fe. After keeping for 12 hrs at O°C the precipitates were filtered off, washed with H_2O and acetone and dried for 15 hrs. i.v. Yields: 10.2 mg Fe-complex (violet powder), 11.5 mg Zn-complex and 10.3 mg Ga-complex (yellow powders). The samples did not melt below 300°C. IR: see text. Treatment with CH_2N_2 as described above yielded **2** as the main product (see text).

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