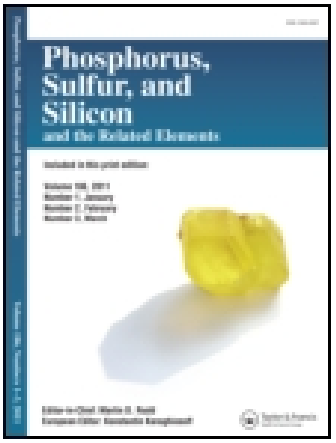


Phosphorus, Sulfur, and Silicon and the Related Elements
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gpss20

Preparation of New Dialkyl Benzene-, Biphenyl-, and Naphthalene-bis(α-oxoethanedithioates)

Jürgen Voss [a], Abraam Sarafidis [a], Andrzej Sawluk [a], Gunther Schmidt [a] & Gunadi Adiwidjaja [a]
[a] Department of Chemistry, University of Hamburg, Hamburg, Germany
Published online: 05 Nov 2010.

To cite this article: Jürgen Voss, Abraam Sarafidis, Andrzej Sawluk, Gunther Schmidt & Gunadi Adiwidjaja (2010) Preparation of New Dialkyl Benzene-, Biphenyl-, and Naphthalene-bis(α-oxoethanedithioates), Phosphorus, Sulfur, and Silicon and the Related Elements, 185:11, 2249-2276, DOI: 10.1080/10426500903575409

To link to this article: http://dx.doi.org/10.1080/10426500903575409

Phosphorus, Sulfur, and Silicon, 185:2249–2276, 2010

ISSN: 1042-6507 print / 1563-5325 online
DOI: 10.1080/10426500903575409

PREPARATION OF NEW DIALKYL BENZENE-, BIPHENYL-, AND NAPHTHALENE-BIS(α-OXOETHANEDITHIOATES)

Jürgen Voss, Abraam Sarafidis, Andrzej Sawluk, Gunther Schmidt, and Gunadi Adiwidjaja
Department of Chemistry, University of Hamburg, Hamburg, Germany

Novel arene-bis- and -tris(α-oxoethanedithioate) esters of the benzene, the biphenyl, and, in particular, the naphthalene series were prepared by reaction of the corresponding diazoacetyl or bromoacetyl derivatives with elemental sulfur in the presence of triethylamine in dry DMF, and subsequent direct alkylation of the produced dithiocarboxylate anions. The thiolation reaction of the diazoketones was significantly promoted by the addition of anhydrous calcium chloride (calcium chloride–activated thiolation, or CAT). Certain carbonyl-activated methylene and methyl compounds exhibiting no bromo or diazo substituents could be also transformed into dithioesters by the CAT reaction. The structure of three dithioesters was corroborated by X-ray structural analyses.

Supplemental materials are available for this article. Go to the publisher's online edition of* Phosphorus, Sulfur, and Silicon and the Related Elements *to view the free supplemental file.

Keywords Alkyl β-aryl-α-oxo-ethanedithioates; α-bromoketones; calcium chloride activation; α-diazoketones; thiolation

INTRODUCTION

The preparation of methyl α-oxo-dithiocarboxylates[1–3] was first described in 1978 by Mayer et al.[4] Phenacyl halides were used as starting compounds. Their reaction with a "thiolating mixture" consisting of elemental sulfur and triethylamine in an appropriate solvent led to arenedithioglyoxalate salts, which finally were methylated to the corresponding dithioesters.[4] Later on, aryl methyl ketones were shown to react with iodine/pyridine. The resulting pyridinium salts were thiolated, and the intermediate arenedithioglyoxalates were methylated to the dithioesters.[5] Hoepping and Mayer also described the formation of arenedithioglyoxalates by direct base-catalyzed (sodium *tert*-butylate) reaction of acetophenones with diethyl sulfide,[6] whereas Hansen and Heinemann obtained aromatic methyl α-oxo-dithiocarboxylates by reaction of acetophenones with sulfur dioxide in the

Received 28 September 2009; accepted 18 December 2009.
The Universität Hamburg, the Konrad-Adenauer-Stiftung (graduate scholarship A. S.), and the Fonds der Chemischen Industrie are gratefully acknowledged for financial support. We thank Prof. Dr. U. Behrens (X-Ray), Dr. Volker Sinnwell (NMR), and Manfred Didschun (preparations), Universität Hamburg, for their competent assistance.
Address correspondence to Prof. Dr. Jürgen Voss, Department of Chemistry, University of Hamburg, Martin-Luther-King-Platz 6, D-20146 Hamburg, Germany. E-mail: voss@chemie.uni-hamburg.de

presence of secondary amines and elemental sulfur, methylation of the intermediate 2-aryl-2-iminiodithioacetates $Ar-C(=NR_2)^+-CS_2^-$ under formation of the dithioesters $Ar-C(=NR_2)^+-CS_2Me$, and hydrolysis of the iminium group of the latter.[7] Also, benzaldehyde cyanohydrin can be transformed into an α-oxo-dithiocarboxylic ester[8], and the 2-benzoyl-1-methyl-1,3-dithiolium salts obtained from phenylglyoxal yield methyl phenyldithioglyoxalate by a cycloreversion reaction.[9]

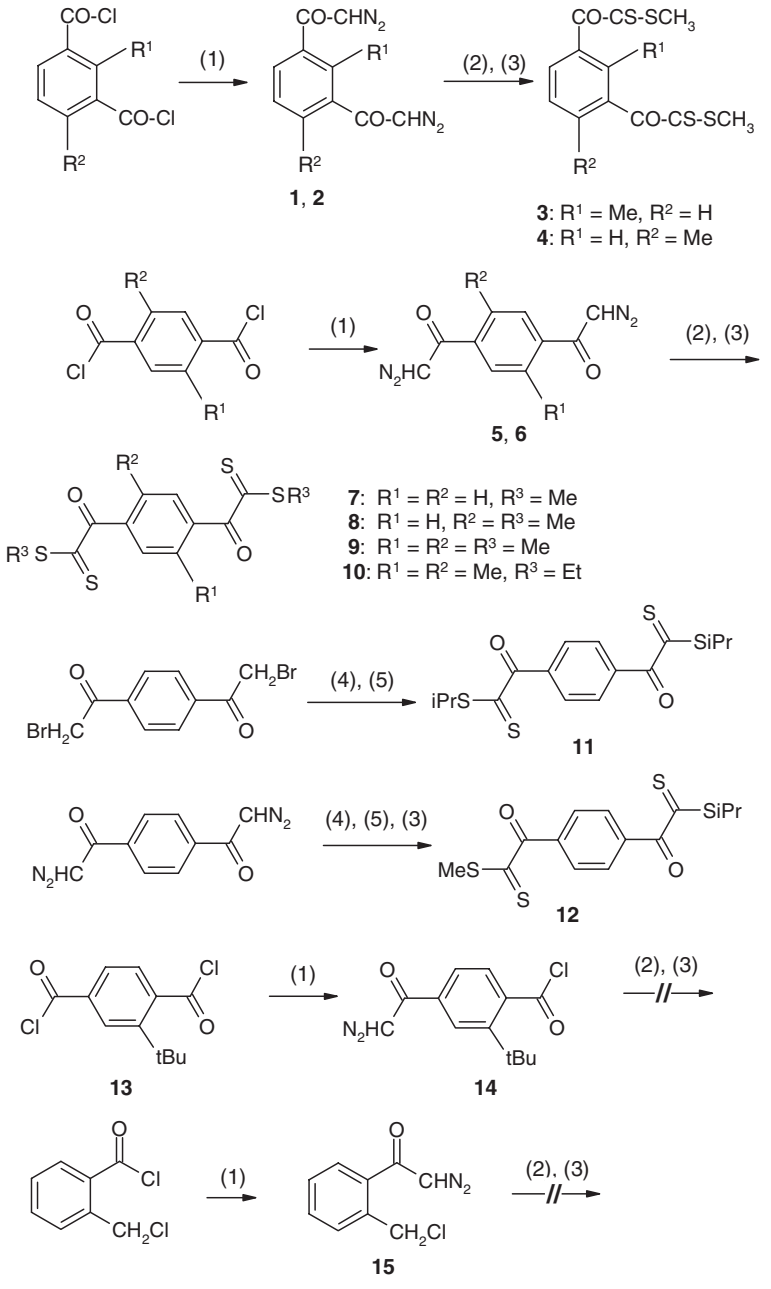
We have found out that α-oxo-dithiocarboxylate esters can be advantageously obtained from acyl chlorides as well, which are, in many cases, more easily available starting compounds compared with the corresponding α-haloacetophenones. The reaction of acid chlorides with diazomethane leads to diazoketones,[10] which can be thiolated with elemental sulfur in the presence of triethylamine.[1] Moreover, we have discovered that the thiolation of diazoketones is dramatically improved by the addition of anhydrous calcium chloride to the reaction mixture (calcium chloride activated thiolation reaction, or CAT reaction).[1] We have successfully applied this CAT reaction for the preparation of quite a number of aromatic and aliphatic alkyl α-oxo-dithiocarboxylates, including benzene-bis- and benzene-tris-dithioglyoxalates.[1]

In continuation of our EPR spectroscopic investigations on the radical anions of α-oxo-dithiocarboxylate esters,[2,11,12] the results of which will be published elsewhere, we needed further specimens of this class of compounds. We were, in particular, interested in the corresponding naphthalene derivatives, the preparation of which by various methods is reported here.

RESULTS AND DISCUSSION

First, we prepared benzene-bis-dithioglyoxalates with alkyl substituents at the benzene ring or a bulky *S*-isopropyl substituent, whose groups were expected to cause steric hindrance. This would possibly change the conformation, i.e., the torsion of the functional groups out of the plane of the benzene ring, whereas the known unsubstituted dimethyl ester **7**[1] exhibits a torsion angle of only 16° (see below).

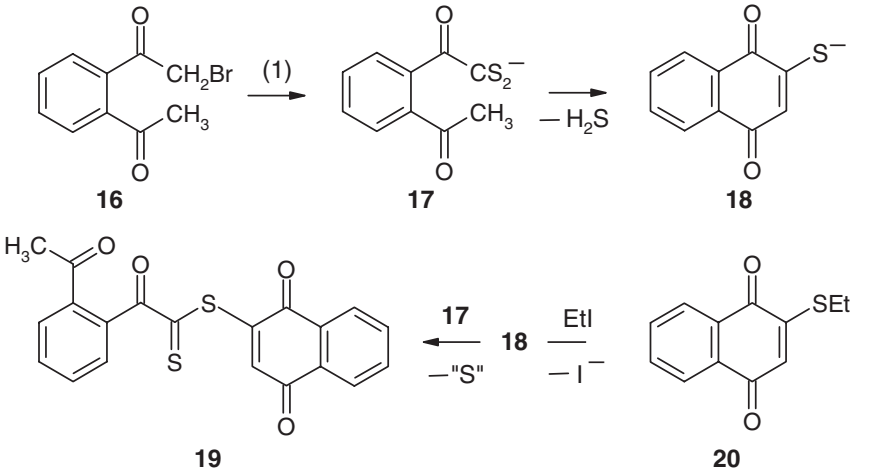
We applied the CAT route for the preparation of five new methylbenzene-bis-dithioglyoxalates. The reaction of 2- and 4-methylisophthaloyl dichloride, 2-methylterephthaloyl dichloride, and 2,5-dimethylterephthaloyl dichloride with diazomethane led to the bis-diazoketones **1**, **2**, **5**, and **6**. Thiolation under CAT conditions and subsequent alkylation with iodomethane or iodoethane gave the bis-dithioesters **3**, **4**, **8**, **9**, and **10** (Scheme 1). In view of the multiple steps during the course of the complex CAT reaction, and the presence of each two diazoketone groups in the starting molecules, expectedly the yields for the deciding last two steps of the five-step syntheses were quite acceptable (23%, 24%, 42%, 22%, and 9%, respectively) and satisfactory for our intended studies. The preparation of **8** via reaction of **5** with hydrogen bromide and thiolation of the resulting 1,4-bis(bromoacetyl)-2-methylbenzene was disadvantageous, since both steps gave low yields of only 14% each compared with the achieved 42% of **8** by the direct one-step thiolation of **5**. The 4% yield of 1,4-bis(bromoacetyl)-2,5-dimethylbenzene from **6** was even worse and thus not useful for the preparation of **9**. Diisopropyl 1,4-benzene-bis-dithioglyoxalate **11** was prepared via side-chain bromination of 1,4-diacetylbenzene, thiolation of the resulting bis-bromoketone, and alkylation with 2-iodopropane. We were also able to prepare the asymmetric 1,4-benzene-bis-dithioglyoxalate ester **12** with still 10% yield by successive alkylation of the dithioglyoxalate salt, first with the less reactive 2-iodopropane and then with iodomethane (Scheme 1). Obviously, due to the pronounced



Scheme 1 (1): CH_2N_2; (2): S_8, NEt_3, $CaCl_2$, DMF; (3): MeI, (4): S_8, NEt_3, DMF; (5): iPrI.

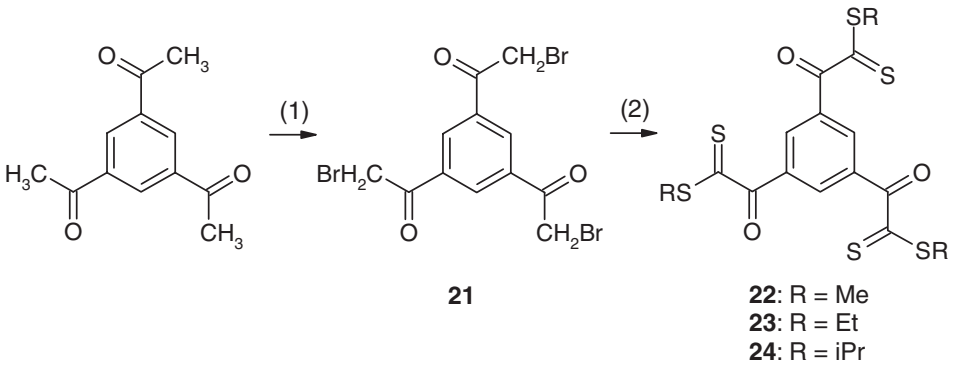
steric hindrance, the reaction of 2-*tert*-butylterephthaloyl dichloride (**13**, $R^1 = t$Bu, $R^2 =$ H) with diazomethane took place with only one acyl chloride function under formation of 2-*tert*-butyl-4-diazoacetylbenzoyl chloride **14**. The corresponding bis-dithioester was thus not available. Also, 2-(chloromethyl)diazoacetylbenzene **15**, which we obtained from 2-(chloromethyl)benzoyl chloride, did not react in a CAT reaction.

1,2-Bis(bromoacetyl)benzene is a delicate compound, and even its structure is not quite unequivocal.[13] We have found that a well defined monobromide **16** can be obtained by selective bromination of 1,2-diacetylbenzene. Its thiolation with subsequent ethylation led to two unexpected naphthoquinone derivatives **19** and **20** (Scheme 2). We assume the expected α-oxo-dithiocarboxylate **17** to be formed first. Intramolecular cyclization under elimination of hydrogen sulfide could then yield **18**, which reacts with either **17** to form **19** or with iodoethane to form **20**.



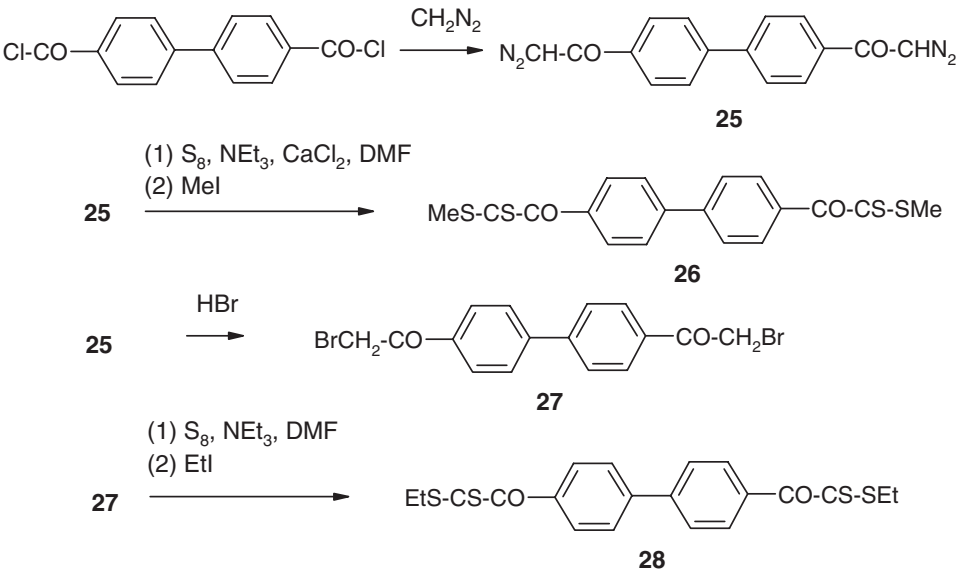
Scheme 2 (1): S_8, NEt_3, DMF.

Furthermore, we have prepared the benzene-1,3,5-tris-dithioglyoxalate esters **22**[6] (6%), **23** (2%), and **24** (0.4%) by thiolation of 1,3,5-tris(bromoacetyl)benzene **21** and subsequent alkylation (Scheme 3). Expectedly, only low yields were achieved. Although we have already reported on the EPR spectra of the radical anions and radical trianions of **22**,[11] we would like to make up for the preparation and full characterization of these fascinating compounds here.



Scheme 3 (1): Br_2, hv; (2): S_8, NEt_3, DMF.

Analogously, biphenyl-4,4′-dicarbonyl dichloride was transformed into the bis-diazoketone **25**. Its CAT reaction and methylation yielded 21% of the bis-dithioester **26**.



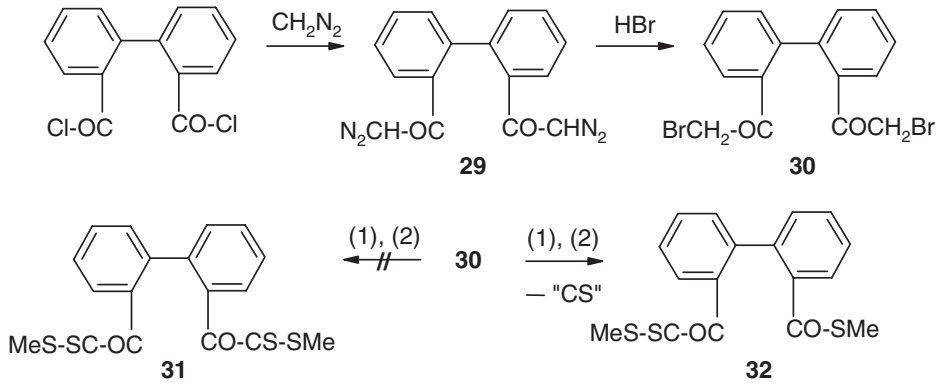
Scheme 4

Since, however, the corresponding ethylation with iodoethane did not give a satisfactory result, we chose the alternate two-step procedure. First the diazoketone **25** was reacted with hydrobromic acid[10] under formation of the corresponding bis-bromoketone **27**, which was then thiolated and ethylated to yield 36% of the bis-dithioester **28** (Scheme 4).

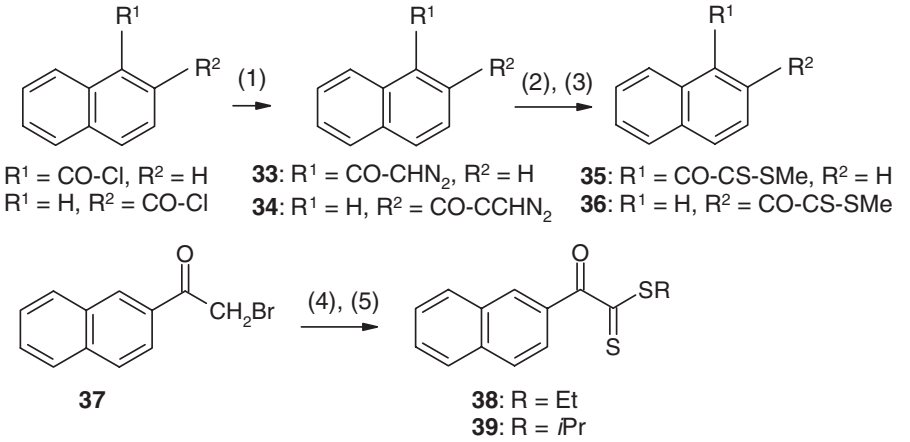
In the same way, biphenyl-2,2′-dicarbonyl dichloride was transformed into the bis-bromoketone **30** via the bis-diazoketone **29**. The thiolation of **30** with subsequent methylation did not, however, yield the desired bis-dithioester **31**. Instead, extrusion of one thiocarbonyl group occurred during the reaction, and only the asymmetric trithioester **32** was isolated, the structure of which was unequivocally proven by ^{1}H and ^{13}C NMR spectroscopy (Scheme 5). A similar extrusion of CS occurs during the reaction of 1,4-diacetylbenzene with thionyl chloride and subsequent methanolysis, which yields *O*-methyl 4-methoxycarbonylbenzene-(2-oxoethanethioate) instead of the expected *O*,*O*′-dimethyl 1,4-benzene-bis-(2-oxoethanethioate).[14]

Our priority aim of the present investigation was to synthesize α-oxo-dithioacetate esters of the naphthalene series. The two isomeric methyl naphthalenedithioglyoxylates **35**[5] and **36**[4,5] are known from the literature. We have prepared both these compounds by reaction of α- and β-naphthoyl chloride with diazomethane and subsequent CAT reaction of the diazoketones **33** and **34**, whereas the ethyl (**38**, 39%) and isopropyl (**39**, 36%) dithioesters of the β-naphthoyl series were prepared from 2-acetylnaphthalene via thiolation of 2-(bromoacetyl)naphthalene **37** (Scheme 6).

Considering the complexity of the thiolation reaction, we expected a marked decrease of the yields when we started to synthesize naphthalenes with two α-oxo-dithioacetate substituents.We were met with the first surprise when we subjected 1,3-bis(bromoacetyl)naphthalene **41**, which we obtained from the diazoketone **40**, to the thiolation reaction. Alkylation of the produced salt with iodomethane, iodoethane, or benzyl bromide did not yield the desired alkyl α-oxo-dithioacetates **42**, **43**, and **44**. Instead, the

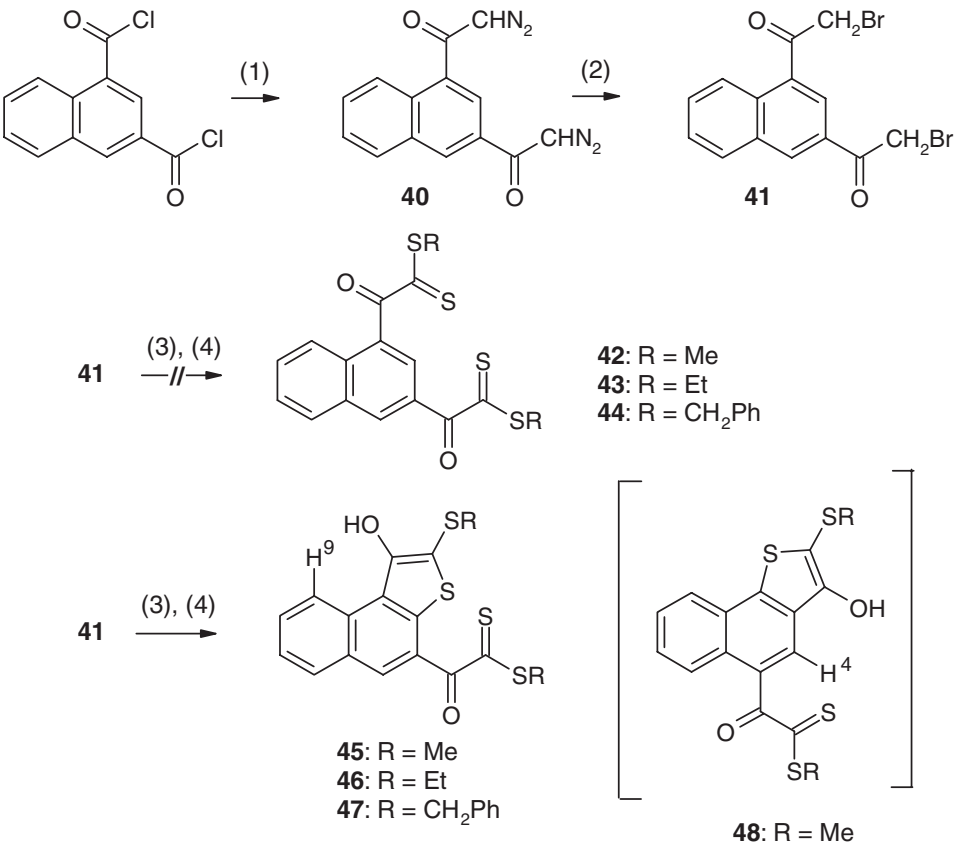


Scheme 5 (1): S_8, NEt_3, DMF; (2): MeI.



Scheme 6 (1): CH_2N_2; (2): S_8, NEt_3, $CaCl_2$, DMF; (3): MeI; (4) S_8, NEt_3, DMF; (5): RI.

isomeric thieno-annellated naphthalene derivatives **45**, **46**, and **47** were formed. All analytical and spectroscopic data are in agreement with the proposed structures. The presence of a hydroxy group is substantiated by the IR valence band at 3409 cm^{-1} and a signal at 10.40 ppm in the ^1H NMR spectrum of, e.g., **45**, whereas the signal due to 2-H is missing. Signals typical of Ar-S*CH*$_3$ groups appear at $\delta = 2.45$ ppm and $\delta = 21.72$ ppm in the ^1H and ^{13}C NMR spectra of **45**. Only one C=O and C=S ^{13}C NMR signal each is found at $\delta = 190.5$ and 230.5 ppm instead of two different ones expected for the bis-1,3-dithioester **42**. Corresponding spectroscopic results are observed for **46** and **47** (see the Experimental section). They indeed do not unequivocally exclude isomeric structures that could arise from intramolecular thiophene annellation by 3→4 (**48**) or 3→2 ring closure reactions, and we were not able to grow suitable crystals for an X-ray crystallographic structure determination. But fortunately, an NOE effect between the OH proton and the proton in the 8-position of the naphthalene moiety of **45** was observed. The assignment of 8-H (9-H of **45**) is definite due to its chemical shift $\delta = 9.35$ ppm and the doublet splitting $J_{H7,H8} = 8.6$ Hz, whereas the possible isomeric naphthothiophenes, e.g., **48**, could only exhibit NOEs between the OH proton and 2-H, or 4-H (singlet at $\delta = 8.10$ ppm) of **48**. The structures of



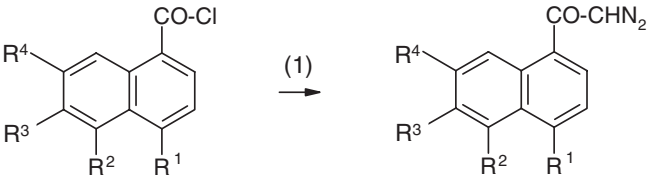
Scheme 7 (1): CH_2N_2; (2): HBr; (3): S_8, NEt_3, DMF; (4) RI.

45 and, by analogy, also of **46** and **47** can therefore be regarded as definitive. The formation of the thiophene ring can be understood by assuming first an intramolecular nucleophilic attack of the dithiocarboxylate group at the electron-deficient C-2 (two neighboring carbonyl groups!) of the naphthalene ring and concomitant 1,4-migration of the proton 2-H from carbon to oxygen under formation of the aromatic thiophene ring (Scheme 7).

1,4-Bis(diazoacetyl)naphthalene **49** was easily available from naphthalene-1,4-dicarbonyl dichloride. Its conversion into dimethyl 1,4-naphthalenedithioglyoxalate **58** by the CAT reaction failed. The two-step procedure via the intermediate dibromoketone **52** was, however, successful (Scheme 8).

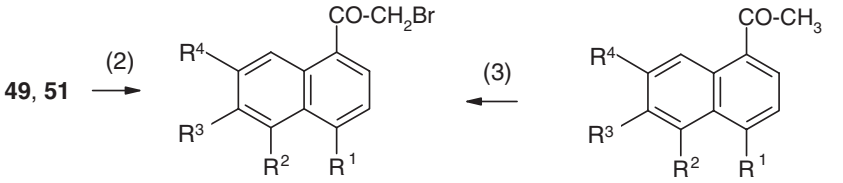
Similar results were observed in the 1,5-, 1,6-, and 1,7-naphthalene series. The bis-diazoketones **50** and **51** were not suitable for the CAT reaction, but 1,5-, 1,6-, and 1,7-bis(bromoacetyl)naphthalenes **53**, **54**, and **55**, which we prepared by bromination of 1,5- and 1,6-diacetylnaphthalene **56** and **57** or reaction of 1,7-bis(diazocetyl)naphthalene **51** with hydrogen bromide, could be successfully thiolated to form the dimethyl (**59**, **61**, **63**) and diethyl dithioesters (**60** and **62**), although with only moderate yields (Scheme 8).

1,8-Diacetylnaphthalene gave only decomposition products when we tried to brominate the methyl groups under various conditions.



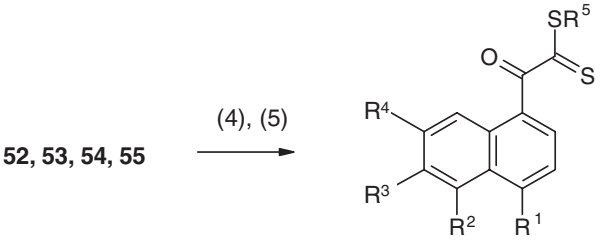
R^1 = CO-Cl, R^2–R^4 = H
R^1 = R^3 = R^4 = H, R^2 = CO-Cl
R^1–R^3 = H, R^4 = CO-Cl

49: R^1 = CO-CHN_2, R^2–R^4 = H
50: R^1 = R^3 = R^4 = H, R^2 = CO-CHN_2
51: R^1–R^3 = H, R^4 = CO-CHN_2



52: R^1 = CO-CH_2Br, R^2–R^4 = H
53: R^1 = R^3 = R^4 = H, R^2 = CO-CH_2Br
54: R^1 = R^2 = R^4 = H, R^3 = CO-CH_2Br
55: R^1–R^3 = H, R^4 = CO-CH_2Br

56: R^1 = R^3 = R^4 = H, R^2 = CO-CH_3
57: R^1 = R^2 = R^4 = H, R^3 = CO-CH_3



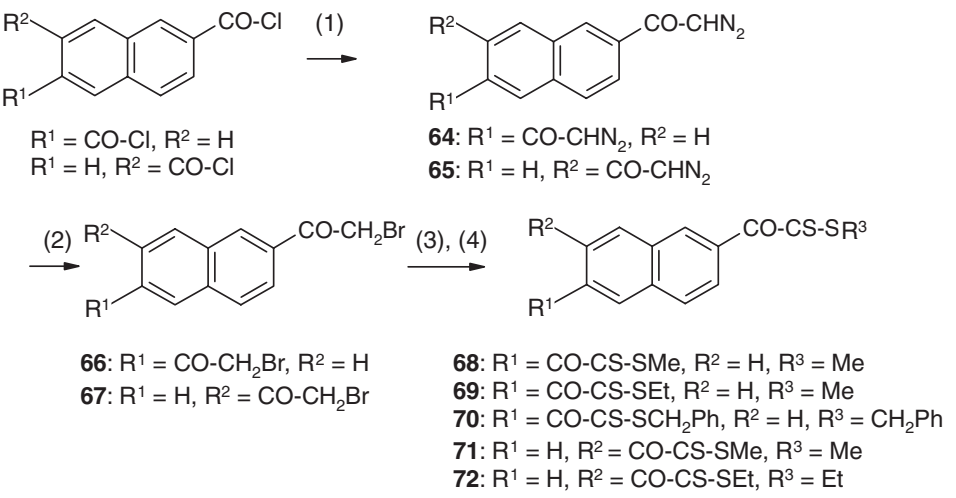
58: R^1 = CO-CS-SR^5, R^2 = R^4 = H, R^5 = Me
59: R^1= R^3 = R^4 = H, R^2 = CO-CS-SR^5, R^5 = Me
60: R^1 = R^3 = R^4 = H, R^2 = CO-CS-SR^5, R^5 = Et
61: R^1 = R^2 = R^4 = H, R^3 = CO-CS-SR^5, R^5 = Me
62: R^1 = R^2 = R^4 = H, R^3 = CO-CS-SR^5, R^5 = Et
63: R^1–R^3 = H, R^4 = CO-CS-SR^5, R^5 = Me

Scheme 8 (1): CH_2N_2; (2): HBr; (3): Br_2; (4): S_8, NEt_3, DMF; (5): R^5I.

Furthermore, we synthesized the five bis-dithioesters **68**, **69**, **70**, **71**, and **72** of 2,6- and 2,7-naphthalenediglyoxylic acid via the bis-diazoketones **64** and **65** and bis-bromoketones **66** and **67** (Scheme 9).

We performed single crystal X-ray structural analyses of **7** (Figure 1) and **71** (Figure 2). Selected bond lengths, bond angles, and torsion angles are compiled in Table I.

The conformations of the two compounds are slightly different. A torsion angle of 16.0° between the plane of the arene ring and the ketone plane (C2/C1/C11/O1) of **7** is found compared with only 5.3° for the corresponding torsion angle of **71** and 21.7° for the related methyl benzene-α-oxodithioacetate.[15] The arrangement of the dithioester and the ketone planes, on the other hand, is far from coplanar, irrespective of the loss of the



Scheme 9 (1): CH_2N_2; (2): HBr; (3): S_8, NEt_3, DMF; (4): R_3I.

resonance interaction between the two parts. Torsion angles O—C—C—S of 54.5° (**7**), 73.3° (**71**), and 69.4° (methyl benzene-α-oxodithioacetate) are observed. This is obviously due to steric repulsion between the sulfur atoms and the *ortho*- (**7**) and *peri*- (**71**) protons at the arene rings. Not unexpectedly, the two thiocarbonyl groups of **71** are rotated into opposite directions, which *anti*-orientation minimizes the total dipole moment of the molecule.

The direct thiolation of activated methyl groups under formation of dithioesters has been studied by Hoepping and Mayer.[6] They used diethoxydisulfane in the presence of potassium *tert*-butoxide as a base to prepare α-oxodithiocarboxylates from acetophenones. In this way, they obtained **7** from 1,4-diacetylbenzene, and **22** in addition to two related

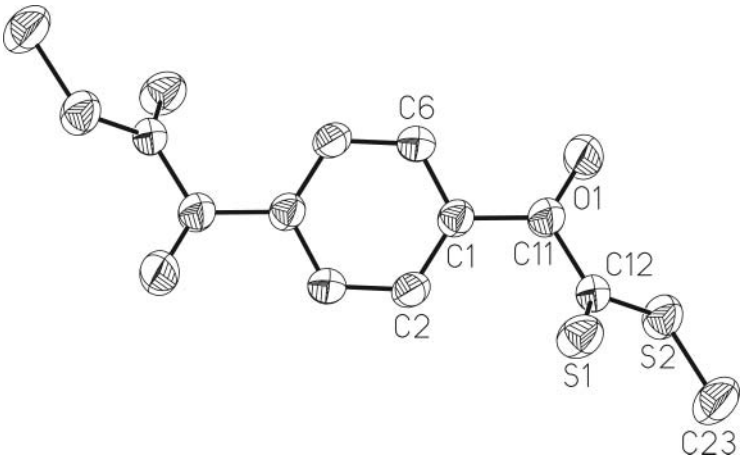


Figure 1 ORTEP view of the X-ray diffraction structure of **7**. Since the molecule exhibits a center of symmetry, the numbering is given for only one half of the atoms. Thermal ellipsoids are drawn at the 50% probability level. Hydrogen atoms are not shown.

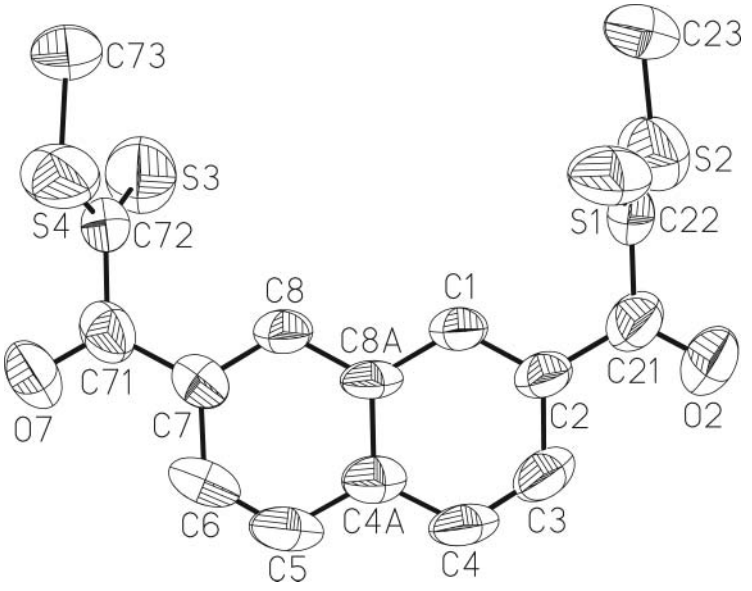


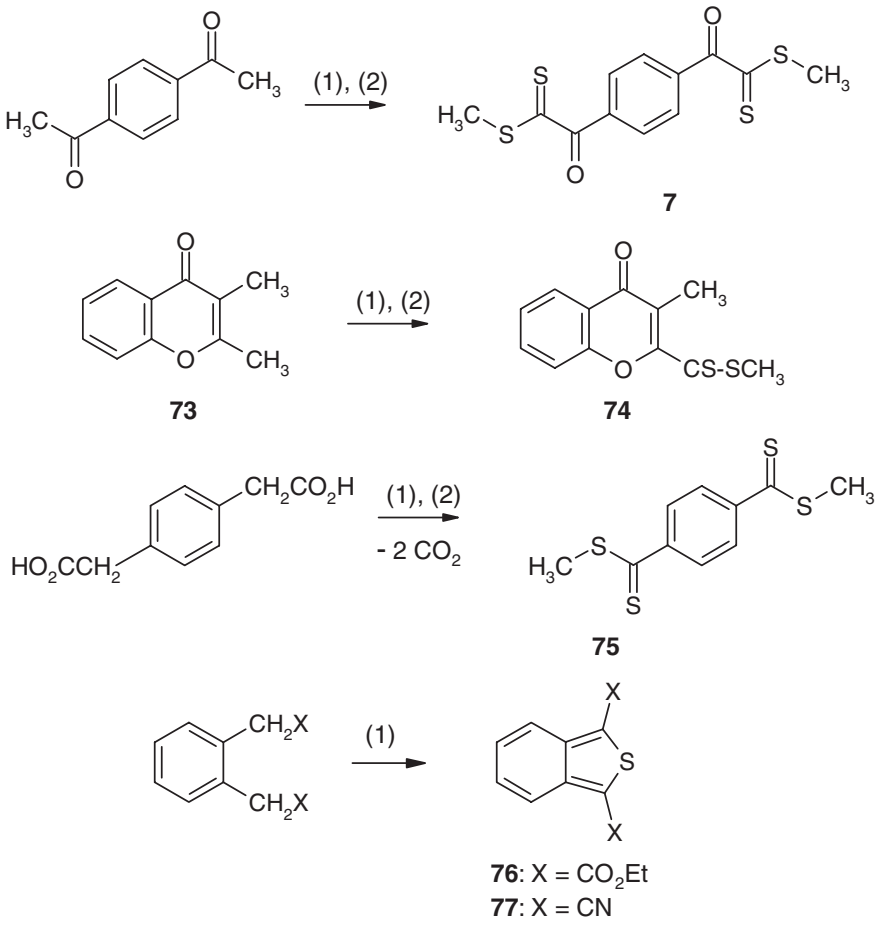
Figure 2 ORTEP view of the X-ray diffraction structure of **71** with atom numbering. Thermal ellipsoids are drawn at the 50% probability level. Hydrogen atoms are not shown.

bis-α-oxo-dithiocarboxylates from 1,3,5-triacetylbenzene. Certain methylarenes could also be transformed into the corresponding arenecarbodithioates.

We have studied the reaction of methyl and methylene compounds under the CAT conditions. When 1,4-diacetylbenzene was subjected to the CAT reaction, **7** was formed with 80% yield (Scheme 10). 2,3-Dimethylchromone **73** was totally resistant to thiolation in the absence of calcium chloride. However, the addition of the promoter led to a clean and selective reaction under formation of 92% of the dithioester **74** (Scheme 10).

Table I Selected bond lengths *d* (pm), angles α (°), and torsion angles θ (°) in **7**, **71**, and **74**

7		**71**		**74**	
	d		***d***		***d***
C1−C11	149.1	C2−C21	148.9	C2−C21	149.7
C11−C12	151.4	C21−C22	151.3	—	—
C11−O1	120.4	C21−O2	120.6	—	—
C12−S1	161.7	C22−S1	160.1	C21−S21	162.7
C12−S2	172.1	C22−S2	169.4	C21−S22	170.7
S2−C23	178.1	S2−C23	181.0	C22−S22	179.0
	α		α		α
S1−C12−S2	128.5	S1−C22−S2	128.9	S21−C21−S22	128.3
S1−C12−C11	120.6	S1−C22−C21	118.9	S21−C21−C2	119.6
S2−C12−C11	110.7	S2−C22−C21	112.3	S22−C21−C2	112.1
C12−S2−C23	103.3	C22−S2−C23	102.2	C22−S22−C21	102.9
	θ		θ		θ
C2−C1−C11−O1	16.0	C1−C2−C21−O2	5.3	C3−C2−C21−S21	−102.1
O1−C11−C12−S2	54.5	O2−C21−C22−S2	75.3	—	—
S1−C12−S2−C23	3.2	S1−C22−S2−C23	−2.9	S21−C21−S22−C22	2.3



Scheme 10 (1): S_8, NEt_3, $CaCl_2$, DMF; (2): Mel.

The reason for the activating effect of calcium chloride is not well understood, and even the mechanism of the thiolation reaction itself is not known in detail.[6,16] Obviously, first the cyclic sulfur molecule is cleaved by triethylamine under formation of open-chained sulfur species. These polysulfide zwitter-ions may then react both as nucleophiles or electrophiles, which attack the α-position of the carbonyl compound. In the absence of sulfur, calcium chloride does not react with diazoketones. In a control experiment, which we have performed, the diazoketone was recovered quantitatively from the reaction mixture. It is probable that the electrophilicity of the sulfur species is increased due to ion pairing between calcium ions and the anionic terminal of the sulfur chain. A similar effect has been observed for the base-catalyzed cleavage of sodium *S*-benzylthiosulfates to thioaldehydes.[17]

The structure of **74** is obvious from its analytical and spectroscopic data. It was corroborated by an X-ray structural analysis (Figure 3). Thus, the reagent unequivocally attacks the methyl group in the 2-position of **73**, which, due to the vinylogy principle, should exhibit a higher C-H-acidity as compared with the methyl substituents in the 3-position.

After a prolonged reaction time (seven days at ambient temperature), the thiolation of 1,4-benzenediacetic acid with subsequent methylation finally resulted in the formation of a

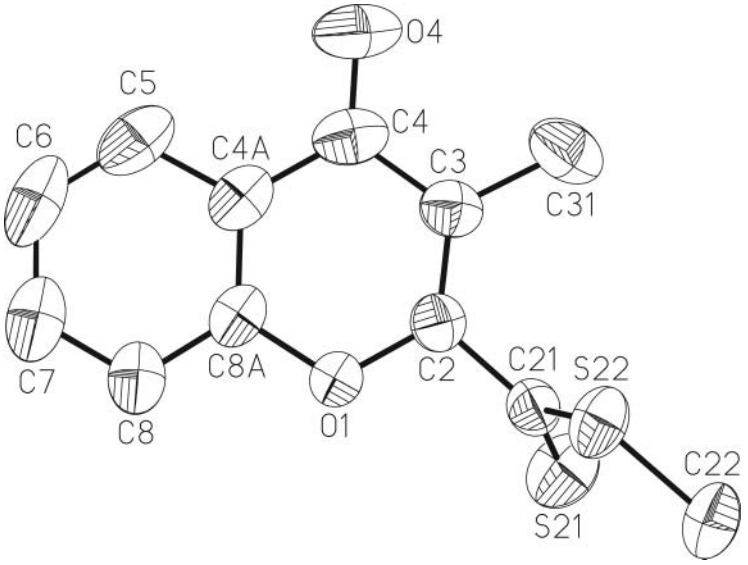


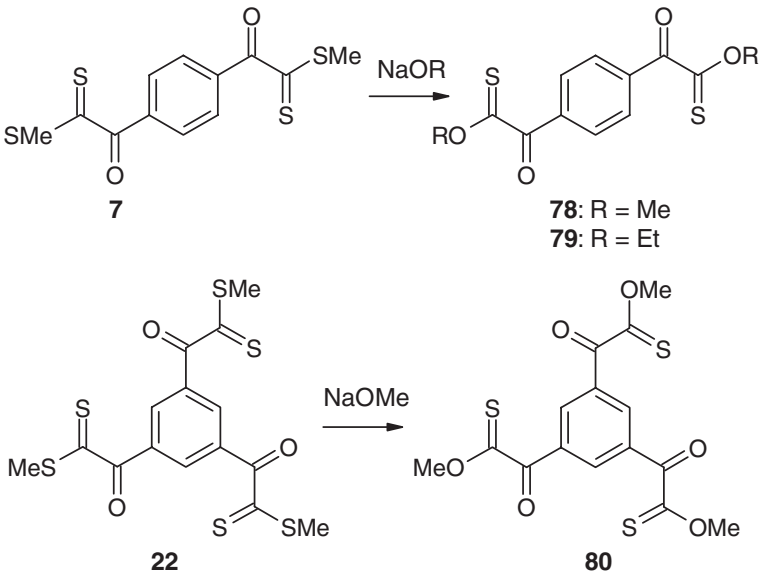
Figure 3 ORTEP view of the X-ray diffraction structure of **74** with atom numbering. Thermal ellipsoids are drawn at the 50% probability level. Hydrogen atoms are not shown.

product, which unexpectedly turned out to be dimethyl tetrathioterephthalate **75** (Scheme 10). In this case, the addition of calcium chloride did not accelerate the reaction. Obviously, first an attack of the electrophilic sulfur species at the activated methylene groups occurs, which is followed by decarboxylation of the intermediate in the basic reaction medium (Scheme 10). Diethyl 1,2-benzenediacetate and 1,2-benzenediacetonitrile are attacked at the methylene groups, too. Formally, one sulfur atom is simply introduced under elimination of hydrogen sulfide and intramolecular cyclization to form the interesting, bright yellow, and fluorescing benzo[c]thiophene derivatives **76**[18] and **77** (Scheme 10).

In pilot experiments, we have studied the transformation of the α-oxo-dithioesters **7** and **22** into the corresponding α-oxo-thionoesters. Acid-catalyzed transesterification failed. The reaction with sodium methoxide led, however, to the desired products **78** and **80**, although with low yields. Only trace amounts of the thiono-ethylester **79** were formed (Scheme 11).

CONCLUSION

The base-catalyzed reaction of diazoketones with elemental sulfur is significantly accelerated in the presence of anhydrous calcium chloride (CAT reaction). Bi- and trifunctional α-oxo-dithioesters, in particular in the naphthalene series, can be obtained by the CAT reaction or by thiolation of the corresponding bromoketones with subsequent alkylation. In certain cases, intramolecular cyclization under formation of annellated thiophenes occurs. Reaction of the α-oxo-dithioesters with sodium alkoxides leads to the corresponding α-oxo-thionoesters.



Scheme 11

EXPERIMENTAL

Corrected melting points (mp) were determined on an Electrothermal apparatus. IR spectra (ν in cm^{-1}, KBr pellets or films) were measured on a Perkin-Elmer FT-IR 1720X spectrometer. UV/Vis spectra [λ_{max} in nm, (lgε), MeOH] were recorded on a Perkin-Elmer 200 spectrometer. NMR spectra (δ in ppm vs. $SiMe_4$, J in Hz) were measured in $CDCl_3$ (if not stated otherwise) on Bruker AC 250 P (^{1}H: 250 MHz, ^{13}C: 63 MHz) and Bruker WM 400 (^{1}H: 400 MHz, ^{13}C: 100.6 MHz) spectrometers. H,H- or H,C-COSY experiments were performed when required. Mass spectra (EI, 70 eV; *m/z*; rel. intensities in% of the most intensive peak) were measured on a Varian MAT spectrometer. Thin layer chromatography (TLC) was performed on silica-coated Al foils (Kieselgel F_{254}, Merck, Darmstadt, Germany). Column chromatography (CC) was performed on Kieselgel 60 (70–230 mesh, Merck, Darmstadt, Germany).

X-Ray Structure Analyses

The crystal data of **7**, **71**, and **74**, and a summary of the experimental details are reported in Table II. The structures were solved by the direct method MULTAN[19] (**7** and **74**) or SHELXTL Plus[20] (**71**). All non-hydrogen atoms were localized. After refinement of these parameters, the hydrogen atoms were localized by differential Fourier synthesis.[21] They are not shown in Figures 1–3 for the sake of clarity. The final refinement was performed by least squares methods. In the case of **7**, an experimental correction for absorption[22] 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-746652 (**7**), No. CCDC-746651 (**71**), and No. CCDC 746650 (**74**). Copies of the data can be obtained free of charge upon application to CCDC, 12

Table II Crystal data and structure refinement for **7**, **71**, and **74**

Compound	**7**	**71**	**74**
Diffractometer	CAD 4 Enraf Nonius	Syntex $P2_1$	CAD 4-SDP Enraf Nonius
Radiation	Cu-K_α $\lambda = 1.54184$ Å	Mo-K_α $\lambda = 0.71073$ Å	Mo-K_α $\lambda = 0.71073$ Å
Temperature [K]	298	298	298
Empirical formula	$C_{12}H_{10}O_2S_4$	$C_{16}H_{12}O_2S_4$	$C_{12}H_{10}O_2S_2$
Formula weight	314.47	364.52	250.39
Crystal system	Monoclinic	Triclinic	Monoclinic
Space group	*C*2/*c*	*P*-1	$P2_1/n$
a [pm]	1424.5 (1)	904.0 (2)	898.2 (2)
b [pm]	433.55 (3)	968.4 (2)	1064.2 (1)
c [pm]	2357.0 (2)	1086.2 (2)	1267.9 (1)
α [°]	90.00	66.99 (2)	90.00
β [°]	100.67 (1)	78.04 (2)	96.08 (2)
γ [°]	90.00	88.74 (2)	90.00
V [pm^3]	$1.430 \cdot 10^9$	$0.854\ (3) \cdot 10^9$	$1.185 \cdot 10^9$
Z	4	2	4
$\rho_{calcd.}$ [g cm^{-3}]	1.46	1.42	1.40
μ [cm^{-1}]	59.6	5.58	4.19
F(000)	648	376	520
θ-limits [°]	2/70	2/25	2/24
h/*k*/*l*-limits	0, 17/0, 5/–28, 28		0, 10/0, 11/–14, 14
Reflections collected ($I > 3\sigma_1$)	1406	3042	1606
Number of parameters	104	201	147
R-Index	0.036	0.0707	0.031
R_w-Index ($w = {\sigma_1}^{-2}$)	0.030	0.067	0.028

Union Road, Cambridge CB2 IEZ, UK [Fax: (international) ++44–1223/336-033; E-mail: deposit@ccdc.cam.uk].

Preparations

A fivefold stoichiometric amount (related to the respective acid chloride as substrate) of *N*-methyl-*N*-nitrosourea was used as starting material for the preparation of ethereal solutions of diazomethane and their reaction with the acid chlorides to form the diazoketones according to the literature.[10]

Warning: Diazomethane is explosive, carcinogenic, and toxic. Diazoketones decompose upon heating under explosion. α-Haloketones are lacrimatory. Suitable precautions must be taken while working with these compounds!

Please see the Supplemental Materials (available online) for complete spectroscopic data.

Diazoketones[10]

1,3-Bis(diazoacetyl)-2-methylbenzene (1). The reaction of 2-methylisophthaloyl dichloride[23] (4.8 g, 0.022 mol) in diethyl ether (100 mL) with CH_2N_2 gave **1** as a yellow powder (2.1 g, 42%), mp 113–115°C. ^{1}H NMR (250 MHz): 2.50 (s, 3 H, CH_3), 5.50 (s, 2 H, CHN_2), 7.30 (t, $J = 8.9$, 1 H, 5-H), 7.42 (d, $J = 9.0$, 2 H, 4/6-H).

1,3-Bis(diazoacetyl)-4-methylbenzene (2). The reaction of 4-methylisophthaloyl dichloride[24] (10.8 g, 0.050 mol) in diethyl ether (180 mL) with CH_2N_2 gave **2** as a yellow powder (8.8 g, 77%), mp 120–122°C. ^{1}H NMR (250 MHz): 2.55 (s, 3 H, CH_3), 5.62 (s, 1 H, 1-CHN_2), 5.90 (s, 1 H, 3-CHN_2), 7.30 (d, J = 8.0, 1 H, 5-H), 7.62 (d, J = 8.0, 1 H, 6-H), 7.82 (s, 1 H, 2-H). ^{13}C NMR (63 MHz): 20.37 (CH_3), 54.32 (CHN_2), 125.56 (C-5), 128.61 (C-6), 131.92 (C-2), 134.34 (C-4), 137.86 (C-1), 142.07 (C-3), 184.98 (C=O). Anal. calcd. for $C_{11}H_8N_4O_2$ (228.21): C, 57.89; H, 3.53; N, 24.55; Found: C, 57.91; H, 3.47; N, 23.58.

1,4-Bis(diazoacetyl)-2-methylbenzene (5). The reaction of 2-methylterephthaloyl dichloride[25] (6.0 g, 0.027 mol) in diethyl ether (100 mL) with CH_2N_2 gave **5** as a yellow powder (3.1 g, 52%), mp 126–130°C. ^{1}H NMR (250 MHz): 2.50 (s, 3 H, CH_3), 5.50 (s, 1 H, 1-CHN_2), 5.90 (s, 1 H, 4-CHN_2), 7.30–7.70 (m, 3 H, H_{Ar}).

1,4-Bis(diazoacetyl)-2,5-dimethylbenzene (6). The reaction of 2,5-dimethylterephthaloyl dichloride[25,26] (6.3 g, 0.027 mol) in diethyl ether (270 mL) with CH_2N_2 gave **6** as yellow leaflets (5.6 g, 89%), mp 155°C (decomp.). ^{1}H NMR (250 MHz): 2.40 (s, 6 H, CH_3), 5.55 (s, 2 H, CHN_2), 7.72 (s, 2 H, 3/6-H). ^{13}C NMR (63 MHz): 19.84 (CH_3), 56.50 (CHN_2), 129.99 (C-3/6), 134.02 (C-2/5), 139.53 (C-1/4), 189.06 (C=O).

2-tert-Butyl-4-(diazoacetyl)benzoyl chloride (14). Into a stirred, boiling solution of 2-*tert*-butyl-1,4-dimethylbenzene[27] (8.2 g, 0.050 mol) in pyridine (50 mL), $KMnO_4$ (38 g, 0.24 mol) was added in small portions. The mixture was stirred at 20°C for 14 h. The MnO_2 was filtered off and washed with hot H_2O (30 mL). The filtrates were concentrated to 10 mL under vacuum. Conc. aq. HCl (2 mL) was added under cooling. The precipitated acid was washed with ice-cold H_2O, dissolved in NaOH, and again precipitated with dil. HCl to yield 2-*tert*-butylterephthalic acid[28,29] (6.8 g, 61%) as white crystals, mp 240–246°C.

This acid (6.4 g, 0.029 mol) and PCl_5 (14.0 g, 0.074 mol) were heated to 100°C until the evolution of HCl ceased (ca. 6 h). The $POCl_3$ was removed under vacuum. The residue was dissolved in ligroin, filtered, and concentrated in a vacuum to yield 2-*tert*-butylterephthaloyl dichloride[28] **13** (6.0 g, 81%) as a red-brown oil.

The reaction of **13** (1.1 g, 0.004 mol) in diethyl ether (45 mL) with CH_2N_2 gave **14** as a yellow oil (1.0 g, 86%). ^{1}H NMR (250 MHz): 1.45 (s, 9 H, CH_3), 5.90 (s, 1 H, CH), 7.60 (m, 2 H, H_{Ar}), 7.95 (m, 1 H, H_{Ar}).

2-(Chloromethyl)-1-(diazoacetyl)benzene (15). The reaction of 2-(chloromethyl)benzoyl chloride[30] (28.0 g, 0.14 mol) in diethyl ether (150 mL with diazomethane) gave **15** as yellow crystals (6.0 g, 21%), mp 40–42°C (lit.[30]: bp 135°C/Torr). ^{1}H NMR (250 MHz): 4.90 (s, 2 H, CH_2), 5.70 (s, 1 H, CHN_2), 7.25–7.75 (m, 4 H, 3/4/5/6-H). ^{13}C NMR (63 MHz): 43.95 (CH_2), 56.74 (CHN_2), 127.56 (C-5), 128.45 (C-6), 131.09 (C-4), 131.44 (C-1), 136.28 (C-3), 137.04 (C-2), 192.18 (C=O). Anal. calcd. for $C_9H_7ClN_2O$ (194.62): C, 55.54; H, 3.62; Cl, 18.22; N, 14.39; Found: C, 55.64; H, 3.55; Cl, 18.13; N, 14.24.

4,4′-Bis(diazoacetyl)biphenyl (25). The reaction of biphenyl-4,4′-dicarbonyl dichloride[31] (6.0 g, 0.021 mol) in diethyl ether (150 mL) with CH_2N_2 gave **25** as a yellow powder (5.6 g, 89%), mp 163–168°C (lit.[31] mp 165°C). ^{1}H NMR (250 MHz): 5.95 (s, 2 H, CHN_2), 7.60–7.75 (m, 4 H, 2/2′/6/6′-H), 7.80–7.90 (m, 4 H, 3/3′/5/5′-H). ^{13}C NMR (63 MHz): 54.36 (CHN_2), 127.40 (C-2/2′/6/6′), 127.77 (C-3/3′/5/5′), 136.19 (C-1/1′), 144.01 (C-4/4′), 185.15 (C=O).

2,2′-Bis(diazoacetyl)biphenyl (29). The reaction of biphenyl-2,2′-dicarbonyl dichloride[32,33] (18.4 g, 0.066 mol) in diethyl ether (500 mL) with CH_2N_2 gave **29** as a

yellow powder (18.0 g, 94%), mp 129–130°C [lit.[33]: mp 134–135°C (benzene, decomp.)]. ^{1}H NMR (250 MHz): 5.50 (s, 2 H, CHN_2), 7.10–7.20 (m, 2 H, 4/4′-H), 7.35–7.40 (m, 4 H, 5/5′/6/6′-H), 7.55–7.60 (m, 2 H, 3/3′-H). ^{13}C NMR (100 MHz): 56.82 (CHN_2), 127.56 (C-5/5′), 127.88 (C-4/4′), 130.72 (C-6/6′), 131.69 (C-2/2′), 137.75 (C-1/1′), 139.31 (C-2/2′), 189.46 (C=O).

1-(Diazoacetyl)naphthalene (33). The reaction of 1-naphthoyl chloride (Fluka, 10.0 g, 0.052 mol) in diethyl ether (52 mL) with CH_2N_2 gave **33** (9.3 g, 84%) as a yellow powder, mp 52°C (lit.[34]: 55°C). ^{1}H NMR (250 MHz): 5.70 (s, 1 H, CHN_2), 7.40–7.62 (m, 4 H, H_{Ar}), 7.82–8.00 (m, 2 H, H_{Ar}), 8.50 (d, J = 7.4, 1 H, 2-H). ^{13}C NMR (63 MHz): 57.22 (CHN_2), 124.50 (C-6), 125.41 (C-7), 126.35 (C-3), 126.54 (C-5), 127.53 (C-4), 128.34 (C-8), 129.80 (C-4a), 131.88 (C-2), 133.85 (C-8a), 135.53 (C-1), 189.56 (C=O).

2-(Diazoacetyl)naphthalene (34). The reaction of 2-naphthoyl chloride (Fluka, 15.0 g, 0.078 mol) in diethyl ether (80 mL) with CH_2N_2 gave **34** (9.6 g, 62%) as yellow crystals, mp 82–84°C [lit.[35]: 73–75°C (hexane/Et_2O)]. ^{1}H NMR (250 MHz): 6.05 (s, 1 H, CHN_2), 7.50–7.61 (m, 2 H, H_{Ar}), 7.80–7.92 (m, 4 H, H_{Ar}), 8.25 (s, 1 H, 1-H). ^{13}C NMR (63 MHz): 54.36 (CHN_2), 123.06 (C-6), 126.87 (C-7), 127.62 (C-5), 127.80 (C-8), 128.21 (C-4), 128.56 (C-3), 129.34 (C-1), 132.55 (C-4a), 134.02 (C-8a), 135.44 (C-2), 186.20 (C=O). Anal. calcd. for $C_{12}H_8N_2O$ (196.20): C, 73.45; H, 4.10; N, 14.27; Found: C, 73.91; H, 4.18; N, 13.79.

1,3-Bis(diazoacetyl)naphthalene (40). Naphthalene-1,3-dicarboxylic acid[36] (5.0 g, 0.023 mol) and PCl_5 (11.4 g, 0.055 mol) were heated to reflux for 6 h. The $POCl_3$ was removed in a vacuum to yield naphthalene-1,3-dicarbonyl dichloride (5.20 g, 89%) as yellowish needles, mp 106°C (ligroin). Anal. calcd. for $C_{12}H_6Cl_2O_2$ (253.08): C, 56.95; H, 2.39; Cl, 28.02; Found: C, 56.94; H, 2.18; Cl, 27.95.

Reaction of this acid chloride (5.20 g, 0.021 mol) in diethyl ether (50 mL) with CH_2N_2 gave **40** as a yellow powder (4.30 g, 78%), mp 127°C (decomp.). ^{1}H NMR (250 MHz): 5.85 (s, 1 H, 3-CHN_2), 6.10 (s, 1 H, 1-CHN_2), 7.50–7.70 (m, 2 H, 6/7-H), 7.95 (d, J = 8.0, 1 H, 5-H), 8.05 (s, 1 H, 4-H), 8.15 (s, 1 H, 8-H), 8.55 (s, 1 H, 2-H). ^{13}C NMR (63 MHz): 54.67 (3-CHN_2), 57.61 (1-CHN_2), 123.03 (C-6), 125.72 (C-7), 127.56 (C-5), 129.74 (C-8), 129.82 (C-4), 130.80 (C-4a), 131.80 (C-2), 132.70 (C-8a), 133.16 (C-3), 136.16 (C-1), 185.06 (3-C=O), 191.15 (1-C=O). MS: 264 (3) [M^+], 208 (33) [M^+ –2 N_2], 195 (27) [M^+−CHN_2,−N_2], 167 (15) [M^+−$COCHN_2$,−N_2], 152 (100) [$C_{12}H_8^+$], 139 (34) [$C_{11}H_7^+$], 126 (15) [M^+−2 $COCHN_2$], 76 (24) [$C_6H_4^+$], 63 (26). Anal. calcd. for $C_{14}H_8N_4O_2$ (264.24): C, 63.64; H, 3.05; N, 21.20; Found: C, 63.35; H, 3.03; N, 19.54.

1,4-Bis(diazoacetyl)naphthalene (49). The reaction of naphthalene-1,4-dicarbonyl dichloride[37] (6.60 g, 0.026 mol) in diethyl ether (120 mL) with CH_2N_2 gave **49** as a light yellow powder (5.95 g, 88%), mp 155–157°C. ^{1}H NMR (250 MHz): 5.70 (s, 2 H, CHN_2), 7.55–7.65 (m, 4 H, 5/6/7/8-H), 8.43 (bs, 2 H, 2/3-H). ^{13}C NMR (63 MHz): 57.80 (CHN_2), 124.94 (C-6/7), 125.46 (C-5/8), 127.70 (C-2/3), 129.48 (C-4a/8a), 137.94 (C-1/4), 188.84 (C=O). Anal. calcd. for $C_{14}H_8N_4O_2$ (264.24): C, 63.64; H, 3.05; N, 21.20; Found: C, 63.40; H, 2.97; N, 20.46.

1,5-Bis(diazoacetyl)naphthalene (50). The reaction of naphthalene-1,5-dicarbonyl dichloride[38] (5.20 g, 0.021 mol) in diethyl ether (50 mL) with CH_2N_2 gave **50** as a yellow powder (4.50 g, 83%), mp 165°C. ^{1}H NMR (250 MHz): 5.70 (s, 2 H, CHN_2), 7.55–7.80 (m, 6 H, H_{Ar}).

1,7-Bis(diazoacetyl)naphthalene (51). The reaction of naphthalene-1,7-dicarbonyl dichloride[39] (1.40 g, 0.0060 mol) in diethyl ether (80 mL) with CH_2N_2 gave

51 as a yellow powder (1.20 g, 86%), mp 156–158°C. ^{1}H NMR (250 MHz): 5.80 (s, 1 H, 7-CHN_2), 6.15 (s, 1 H, 1-CHN_2), 7.10–7.20 (m, 2 H, H_{Ar}), 7.90–8.10 (m, 3 H, H_{Ar}), 8.95 (s, 1 H, 8-H). ^{13}C NMR (63 MHz): 54.69 (CHN_2), 124.08 (C-3), 125.14 (C-4), 126.74 (C-5), 126.85 (C-6), 129.04 (C-2), 131.94 (C-8), 135.76 (C-7), 135.87 (C-1), 182.93 (C=O). MS: 252 (13), 237 (31), 236 (3) [M^+-N_2], 208 (47) [$M^+-2\ N_2$], 195 (26) [M^+-N_2, $-CHN_2$], 180 (13) [$M^+-2\ N_2$,−CO], 167 (12) [$M^+-COCHN_2$,$-N_2$], 152 (100) [$C_{12}H_8^+$], 139 (37) [$C_{11}H_7^+$], 126 (14) [$M^+-2\ COCHN_2$], 76 (27) [$C_6H_4^+$], 63 (28).

2,6-Bis(diazoacetyl)naphthalene (64). The reaction of naphthalene-2,6-dicarbonyl dichloride[40] (13.2 g, 0.052 mol) in diethyl ether (100 mL) with CH_2N_2 gave **64** as a yellow powder (10.0 g, 78%), mp 200°C (decomp.). ^{1}H NMR (250 MHz): 5.30 (s, 2 H, CHN_2), 7.90–8.30 (m, 4 H, H_{Ar}), 8.05 (s, 2 H, 1/5-H).

2,7-Bis(diazoacetyl)naphthalene (65). The reaction of naphthalene-2,7-dicarbonyl dichloride[40,41] (5.4 g, 0.022 mol) in diethyl ether (100 mL) with CH_2N_2 gave **65** as a yellow powder (4.9 g, 87%), mp 200°C (decomp.). ^{1}H NMR (250 MHz): 6.10 (s, 2 H, CHN_2), 7.90–8.00 (m, 4 H, 3/4/5/6-H), 8.30 (s, 2 H, 1/8-H). ^{13}C NMR (63 MHz): 54.68 (CHN_2), 125.36 (C-4/5), 128.59 (C-3/6), 128.75 (C-1/8), 131.77 (C-4a), 131.81 (C-8a), 137.24 (C-2/7), 185.60 (C=O). Anal. calcd. for $C_{14}H_8N_4O_2$ (264.24): C, 63.64; H, 3.05; N, 21.20; Found: C, 63.35; H, 3.02; N, 20.40.

Bromoketones from Diazoketones[10]

1,4-Bis(bromoacetyl)-2-methylbenzene. The reaction of **5** (1.10 g, 0.005 mol) with aq. HBr (47%, 43 mL) in diethyl ether (500 mL) gave the bromoketone as a white powder (0.22 g, 14%), mp 92–96°C. ^{1}H NMR (250 MHz): 2.55 (s, 3 H, CH_3), 4.38 (s, 2 H, CH_2), 4.42 (s, 2 H, CH_2), 7.70–7.90 (m, 3 H, 3/5/6-H). ^{13}C NMR (63 MHz): 21.04 (CH_3), 30.63 (CH_2), 33.35 (CH_2), 126.27 (C-5), 128.74 (C-6), 132.82 (C-3), 136.14 (C-2), 139.28 (C-4), 138.82 (C-1), 190.70 (C=O), 194.21 (C=O).

1,4-Bis(bromoacetyl)-2,5-dimethylbenzene. The reaction of **6** (2.7 g, 0.012 mol) with aq. HBr (47%, 60 mL) in diethyl ether (100 mL) gave the bromoketone as a yellowish-white powder (0.15 g, 4%), mp 136–140°C. ^{1}H NMR (250 MHz): 2.50 (s, 6 H, CH_3), 4.40 (s, 4 H, CH_2), 7.50 (s, 2 H, 3/6-H). ^{13}C NMR (63 MHz): 20.60 (CH_3), 33.34 (CH_2), 131.84 (C-3/6), 136.54 (C-2/5), 137.63 (C-1/4), 194.05 (C=O).

4,4′-Bis(bromoacetyl)biphenyl (27). The reaction of **25** (14.4 g, 0.050 mol) with aqu. HBr (47%, 250 mL) in diethyl ether (600 mL) gave **27** as a yellow powder (16.3 g, 83%), mp 211–215°C [lit.[42]: mp 220–222°C (benzene, decomp.)]. ^{1}H NMR (250 MHz): 4.50 (s, 4 H, CH_2), 7.75 (d, $J = 8.3$, 4 H, 2/2′/6/6′-H), 8.10 (d, $J = 8.2$, 4 H, 3/3′/5/5′-H). ^{13}C NMR (63 MHz): 30.59 (CH_2), 127.14 (C-2/2′/6/6′), 129.11 (C-3/3′/5/5′), 133.61 (C-4/4′), 145.62 (C-1/1′), 190.61 (C=O). MS: 396 (10) [M^+], 394 (4) [M^+], 303 (81) [M^+-CH_2Br], 301 (100) [M^+-CH_2Br], 257 (11), 180 (23) [M^+-CH_2Br,$-COCH_2Br$], 166 (37), 165 (66), 152 (35) [$M^+-2\ COCH_2Br$], 151 (45), 126 (9), 104 (10) [$C_7H_4O^+$], 76 (10) [$C_6H_4^+$], 63 (28).

2,2′-Bis(bromoacetyl)biphenyl (30). The reaction of **29** (3.0 g, 0.010 mol) with aq. HBr (47%, 50 mL) in diethyl ether (500 mL) gave **30** as yellow crystals (2.7 g, 69%), mp 87–88°C (EtOH) [lit.[43]: 100–102°C (MeOH)]. ^{1}H NMR (250 MHz): 4.06 (A-part of AB-system, 2 H, $J = 11.3$, CH_2), 4.32 (B-part of AB-system, 2 H, $J = 11.3$, CH_2), 7.20 (m, 2 H, 5/5′-H), 7.40–7.60 (m, 4 H, 4/4′/6/6′-H), 7.70–7.75 (m, 2 H, 3/3′-H), ^{13}C NMR (63 MHz): 33.68 (CH_2), 128.08 (C-4/4′), 128.94 (C-5/5′), 130.91 (C-6/6′), 132.05 (C-3/3′),

135.51 (C-1/1′), 140.42 (C-2/2′), 194.57 (C=O). Anal. calcd. for $C_{16}H_{12}Br_2O_2$ (396.09): C, 48.52; H, 3.05; Br, 40.35; Found: C, 49.50; H, 3.16; Br, 39.60.

1,3-Bis(bromoacetyl)naphthalene (41). The reaction of **40** (4.3 g, 0.016 mol) with aq. HBr (47%, 91 mL) in diethyl ether (400 mL) gave **41** as a yellow powder (5.3 g, 89%), mp 119°C. ^{1}H NMR (250 MHz): 4.60 (s, 2 H, 3-CH_2), 4.65 (s, 2 H, 1-CH_2), 7.70 (ddd, J = 1.2, 7.6, 8.0, 1 H, 6-H), 7.78 (ddd, J = 1.2, 7.9, 8.3, 1 H, 7-H), 8.05 (d, J = 7.9, 1 H, 5-H), 8.45 (s, 1 H, 4-H), 8.60 (d, J = 8.3, 1 H, 8-H), 8.65 (s, 1 H 2-H). ^{13}C NMR (63 MHz): 30.01 (3-CH_2), 33.69 (1-CH_2), 126.01 (C-6), 126.23 (C-7), 128.03 (C-5), 129.67 (C-4a), 130.41 (C-8), 131.53 (C-4), 132.87 (C-8a), 133.22 (C-3), 133.55 (C-1), 135.83 (C-2), 190.33 (3-C=O), 193.86 (1-C=O). MS: 372 (1) [M^+], 370 (5) [M^+], 368 (1) [M^+], 276 (49) [M^+-CH_2Br], 274 (79) [M^+-CH_2Br], 168 (34) [$M^+-COCH_2Br,-Br$], 154 (35) [$M^+-COCH_2Br,-CH_2Br$], 140 (53) [$C_{11}H_8^+$], 139 (81) [$C_{11}H_7^+$], 126 (100) [$M^+-2\ COCH_2Br$], 95 (18) [CH_2Br^+], 93 (17) [CH_2Br^+]. Anal. calcd. for $C_{14}H_{10}Br_2O_2$ (370.04): C, 45.44; H, 2.72; Br, 43.19; Found: C, 45.45; H, 2.73; Br, 42.32.

1,4-Bis(bromoacetyl)naphthalene (52). The reaction of **49** (3.2 g, 0.012 mol) with aq. HBr (47%, 60 mL) in diethyl ether (350 mL) gave **52** as a yellow powder (3.4 g, 76%), mp 136°C. ^{1}H NMR (250 MHz): 4.50 (s, 4 H, CH_2), 7.60–7.70 (m, 2 H, 6/7-H), 7.80 (s, 2 H, 2/3-H), 8.35–8.42 (m, 2 H, 5/8-H). ^{13}C NMR (63 MHz): 33.85 (CH_2), 125.19 (C-6/7), 125.78 (C-5/8), 128.85 (C-2/3), 130.88 (C-4a/8a), 137.39 (C-1/4), 194.58 (C=O). Anal. calcd. for $C_{14}H_{10}Br_2O_2$ (370.05): C, 45.44; H, 2.72; Br, 43.18; Found: C, 45.97; H, 2.80; Br, 43.76.

1,7-Bis(bromoacetyl)naphthalene (55). The reaction of **51** (1.2 g, 0.005 mol) with aq. HBr (47%, 25 mL) in diethyl ether (140 mL) gave **55** as a beige powder (1.4 g, 83%), mp 121°C. ^{1}H NMR (250 MHz): 4.60 (s, 2 H, 7-CH_2), 4.65 (s, 2 H, 1-CH_2), 7.70 (t, J = 8.2, 1 H, 3-H), 7.95 (d, J = 8.3, 1 H, 4-H), 8.05–8.20 (m, 3 H, 2/5/6-H), 9.45 (s, 1 H, 8-H) ^{13}C NMR (63 MHz): 31.27 (7-CH_2), 33.29 (1-CH_2), 125.24 (C-3), 127.28 (C-4), 128.69 (C-5), 129.54 (C-6), 130.02 (C-4a), 130.04 (C-2), 132.95 (C-8a), 133.55 (C-7), 133.96 (C-1), 136.42 (C-8), 191.54 (7-C=O), 193.91 (1-C=O). MS: 372 (4) [M^+], 370 (8) [M^+], 368 (4) [M^+], 278 (13) [M^+-CH_2Br], 277 (99) [M^+-CH_2Br], 276 (14) [M^+-CH_2Br], 275 (100) [M^+-CH_2Br], 197 (13) [$M^+-CH_2Br,-Br$], 168 (35) [$M^+-COCH_2Br,-Br$], 154 (38) [$M^+-COCH_2Br,-CH_2Br$], 140 (43) [$C_{11}H_8^+$], 139 (43) [$C_{11}H_7^+$], 126 (48) [$M^+-2\ COCH_2Br$]. Anal. calcd. for $C_{14}H_{10}Br_2O_2$ (370.04): C, 45.44; H, 2.72; Br, 43.19; Found: C, 46.00; H, 2.96; Br, 42.98.

2,6-Bis(bromoacetyl)naphthalene (66). The reaction of **64** (7.0 g, 0.028 mol) with aq. HBr (47%, 140 mL) in diethyl ether (400 mL) gave **66** as a light yellow powder (6.3 g, 63%), mp 225–227°C. ^{1}H NMR (250 MHz): 4.60 (s, 4 H, CH_2), 8.10–8.15 (m, 4 H, 3/4/7/8-H), 8.55 (s, 2 H, 1/5-H) ^{13}C NMR (63 MHz): 30.57 (CH_2), 125.47 (C-4/8), 130.39 (C-3/7), 130.58 (C-1/5), 133.71 (C-4a/8a), 134.96 (C-2/6), 191.08 (C=O).

2,7-Bis(bromoacetyl)naphthalene (67). The reaction of **65** (4.8 g, 0.018 mol) with aq. HBr (47%, 60 mL) in diethyl ether (500 mL) gave **67** as a yellow powder (5.0 g, 73%), mp 139–142°C. ^{1}H NMR (250 MHz): 4.60 (s, 4 H, CH_2), 8.00 (d, J = 8.5, 2 H, 4/5-H), 8.20 (d, 2 H, J = 8.5, 2 H, 3/6-H), 8.70 (s, 2 H, 1/8-H). ^{13}C NMR (63 MHz): 30.41 (CH_2), 127.33 (C-4/5), 128.89 (C-3/6), 131.67 (C-4a), 132.38 (C-1/8), 138.18 (C-8a), 144.05 (C-2/7), 190.86 (C=O). MS: 372 (5) [M^+], 370 (11) [M^+], 368 (5) [M^+], 278 (14) [M^+-CH_2Br], 277 (98) [M^+-CH_2Br], 276 (14) [M^+-CH_2Br], 275 (100) [M^+-CH_2Br], 197 (4) [$M^+-CH_2Br,-Br$], 180 (25), 154 (57) [$M^+-COCH_2Br,-CH_2Br$], 126 (42) [$M^+-2\ COCH_2Br$]. Anal. calcd. for $C_{14}H_{10}Br_2O_2$ (370.04): C, 45.44; H, 2.72; Br, 43.19; Found: C, 45.80; H, 2.62; Br, 43.00.

Bromoketones from Ketones

1,3,5-Tris(bromoacetyl)benzene (21). 1,3,5-Triacetylbenzene[44] (24.8 g, 0.100 mol) was dissolved in AcOH (100%). Br_2 (48.0 g, 0.300 mol) was added with caution. The reaction was started by irradiation with an electric bulb (60 W). The mixture soon decolorized and began to boil. After cooling, the produced HBr was removed by suction. The solution was diluted with sufficient water. The precipitate was filtered off, washed with $NaHCO_3$-solution until neutral, and dried in a desiccator over P_2O_5 to yield **21** (38.8 g, 88%), mp 110–112°C (lit.[44]: mp 111°C), which could be used in the next step without further purification. IR: 1690 (C=O). ^{1}H NMR: 5.90 (s, 6 H, CH_2), 8.83 (s, 3 H, 2/4/6-H). Anal. calcd. for $C_{12}H_9Br_3O_3$ (440.91): C, 32.69; H, 2.06; Br, 54.37; Found: C, 32.72; H, 1.95; Br, 56.00.

1,5-Bis(bromoacetyl)naphthalene (53). 1,5-Diacetylnaphthalene **56**[45] (3.5 g, 0.017 mol) was dissolved in AcOH (100%, 120 mL). A solution of Br_2 (5.3 g, 0.033 mol) in AcOH (10 mL) was added. When the red color had disappeared, a colorless precipitate formed, which was recrystallized from AcOH/AcOEt to yield **53** as colorless crystals (3.3 g, 52%), mp 175°C [lit.[45]: 181–182°C (AcOEt)]. ^{1}H NMR (250 MHz): 4.60 (s, 4 H, CH_2), 7.70 (dd, J = 8.3/7.8, 2 H, 3/7-H), 8.00 (d, J = 7.9, 2 H, 5/8-H), 8.80 (d, J = 8.5, 2 H, 2/6-H).

1,6-Bis(bromoacetyl)naphthalene (54). 1,6-Diacetylnaphthalene **57**[46] (7.3 g, 0.035 mol) was dissolved in AcOH (100%, 70 mL). A solution of Br_2 (11.0 g, 0.069 mol) in AcOH (20 mL) was added. When the red color had disappeared, a colorless precipitate formed, which was recrystallized from AcOH/AcOEt to yield **54** as beige colored powder (6.5 g, 51%), mp 124–128°C. ^{1}H NMR (250 MHz): 4.60 (s, 4 H, CH_2), 7.60 (t, J = 7.8, 1 H, 3-H), 8.05–8.25 (m, 3 H, 2/4/8-H), 8.60 (s, 1 H, 5-H), 8.80 (d, J = 8.5, 1 H, 7-H). ^{13}C NMR (100 MHz): 30.64 (6-CH_2), 33.30 (1-CH_2), 125.55 (C-3), 126.72 (C-4), 126.81 (C-8), 130.99 (C-7), 131.12 (C-2), 131.88 (C-4a), 132.34 (C-8a), 133.27 (C-6), 133.29 (C-1), 135.38 (C-5), 190.94 (6-C=O), 193.82 (1-C=O). MS: 372 (5) [M^+], 370 (10) [M^+], 368 (5) [M^+], 278 (14) [M^+-CH_2Br], 277 (98) [M^+-CH_2Br], 276 (14) [M^+-CH_2Br], 275 (100) [M^+-CH_2Br], 197 (48) [$M^+-CH_2Br,-Br$], 154 (46) [$M^+-COCH_2Br,-CH_2Br$], 140 (28) [$C_{11}H_8^+$], 139 (27) [$C_{11}H_7^+$], 126 (40) [$M^+-2\ COCH_2Br$], 91 (20) [$C_7H_7^+$]. Anal. calcd. for $C_{14}H_{10}Br_2O_2$ (370.04): C, 45.44; H, 2.72; Br, 43.19; Found: C, 45.92; H, 2.64; Br, 42.31.

α-Oxo-dithioesters by CAT Reaction of Diazoketones (General Prodedure)

A mixture of S_8 (3 equivalents), NEt_3 (3 equivalents), and dry $CaCl_2$ (1.1 equivalents) in dry DMF (100 mL if 0.1 mol of the diazoketone were used) was stirred at 20°C for 30 min. Then the diazoketone (1 equivalent) was added portionwise. Stirring was continued at 20°C (if not stated otherwise) at least until the evolution of N_2 ceased. Since the progress of the reaction could not be directly monitored by TLC, reaction times of up to 48 h were applied. The mixture was cooled down to −10°C, and MeI or EtI (0.4 equivalents) was added. After another 28 h stirring at 20°C, the reaction mixture was poured into ice-water and neutralized with dil. HCl. The products were extracted with sufficient $CHCl_3$. The extracts were washed five to 10 times with H_2O to remove the DMF completely, dried over Na_2SO_4, and evaporated under vacuum. The residues were pre-purified by flash chromatography ($CHCl_3$) and finally purified by recrystallization and/or column chromatography (CC) with

suitable solvents and eluents. The α-oxo-dithioesters are deeply colored and more or less foul-smelling compounds, which can be stored without decomposition in a refrigerator for months.

Dimethyl 2-methyl-1,3-benzene-bis(α-oxoethanedithioate) (3). Thiolation of **1** (2.1 g, 0.009 mol) gave **3** as red crystals (0.7 g, 24%), mp 133–135°C ($CHCl_3$/hexane). ^{1}H NMR (250 MHz): 2.55 (s, 3 H, CH_3), 2.80 (s, 6 H, SCH_3), 7.30 (t, J = 8.3, 1 H, 5-H), 7.60 (d, J = 8.9, 2 H, 4/6-H). ^{13}C NMR (63 MHz): 18.45 (CH_3), 18.58 (SCH_3), 124.61 (C-5), 132.95 (C-4/6), 137.12 (C-1/3), 138.42 (C-2), 189.96 (C=O), 229.74 (C=S). MS: 328 (1) [M^+], 237 (10) [$M^+-CS_2CH_3$], 162 (7), [$M+-COCS_2CH_3,-SCH_3$], 160 (14), 158 (7), 85 (66), 83 (100), 47 (24). Anal. calcd. for $C_{13}H_{12}O_2S_4$ (328.50): C, 47.53; H, 3.68; S, 39.04; Found: C, 46.19; H, 4.49; S, 38.72.

Dimethyl 4-methyl-1,3-benzene-bis(α-oxoethanedithioate) (4). Thiolation of **2** (3.5 g, 0.015 mol) gave **4** as red crystals (1.2 g, 23%), mp 63°C ($CHCl_3$/hexane). ^{1}H NMR (250 MHz): 2.60 (s, 3 H, CH_3), 2.80 (s, 6 H, SCH_3), 7.35 (d, J = 8.9, 1 H, 5-H), 7.90 (d, J = 8.8, 1 H, 6-H), 8.2 (s, 1 H, 2-H). ^{13}C NMR (100 MHz): 18.39 (CH_3), 18.77 (1-SCH_3), 21.53 (3-SCH_3), 130.23 (C-5), 131.99 (C-6), 132.76 (C-1), 133.72 (C-2), 134.37 (C-3), 146.70 (C-4), 189.04 (1-C=O), 189.64 (3-C=O), 230.09 (1-C=S), 230.10 (3-C=S). MS: 328 (7) [M^+], 281 (1) [M^+-SCH_3], 237 (100) [$M^+-CS_2CH_3$], 209 (20) [$M^+-COCS_2CH_3$], 162 (8), [$M^+-COCS_2CH_3,-SCH_3$], 118 (24) [$M^+-COCS_2CH_3,-CS_2CH_3$], 90 (28) [$M^+-2\ COCS_2CH_3$]. Anal. calcd. for $C_{13}H_{12}O_2S_4$ (328.50): C, 47.53; H, 3.68; S, 39.04; Found: C, 47.13; H, 3.52; S, 39.11.

Dimethyl 2-methyl-1,4-benzene-bis(α-oxoethanedithioate) (8). Thiolation of **5** (1.63 g, 0.0071 mol) gave **8** as dark red crystals (0.98 g, 42%), mp 63–65°C ($CHCl_3$/hexane). ^{1}H NMR (250 MHz): 2.50 (s, 3 H, CH_3), 2.75 (s, 6 H, SCH_3), 7.50–7.90 (m, 3 H, 3/5/6-H). ^{13}C NMR (100 MHz): 18.40 (SCH_3), 18.76 (SCH_3), 20.85 (CH_3), 127.06 (C-5), 130.73 (C-3), 132.96 (C-6), 135.22 (C-2), 139.35 (C-4), 139.54 (C-1), 189.50 (C=O), 189.75 (C=O), 229.73 (C=S), 230.01 (C=S). MS: 328 (5) [M^+], 237 (100) [$M^+-CS_2CH_3$], 209 (11) [$M^+-COCS_2CH_3$], 146 (25), [$M^+-2\ CS_2CH_3$], 118 (66) [$M^+-COCS_2CH_3,-CS_2CH_3$], 91 (36) [$C_7H_7^+/CS_2CH_3^+$], 90 (28) [$M^+-2\ COCS_2CH_3$], 89 (32). Anal. calcd. for $C_{13}H_{12}O_2S_4$ (328.50): C, 47.53; H, 3.68; S, 39.04; Found: C, 47.51; H, 3.64; S, 39.12.

Dimethyl 2,5-dimethyl-1,4-benzene-bis(α-oxoethanedithioate) (9). Thiolation of **6** (1.0 g, 0.004 mol) gave **9** as red-violet crystals (0.3 g, 22%), mp 200–204°C ($CHCl_3$/hexane). ^{1}H NMR (250 MHz): 2.42 (s, 6 H, CH_3), 2.80 (s, 6 H, SCH_3), 7.35 (s, 2 H, 3/6-H). ^{13}C NMR (100 MHz): 18.63 (SCH_3), 20.37 (CH_3), 133.29 (C-3/6), 136.19 (C-1/4), 137.28 (C-2/5), 190.12 (C=O), 230.40 (C=S). MS: 342 (2) [M^+], 251 (100) [$M^+-CS_2CH_3$], 223 (7) [$M^+-COCS_2CH_3$], 160 (24), [$M^+-2\ CS_2CH_3$], 132 (60) [$M^+-COCS_2CH_3,-CS_2CH_3$], 104 (18) [$M^+-2\ COCS_2CH_3$], 91 (35) [$C_7H_7^+/CS_2CH_3^+$], 78 (17) [$C_6H_6^+$], 77 (12) [$C_6H_5^+$]. Anal. calcd. for $C_{14}H_{14}O_2S_4$ (342.50): C, 49.09; H, 4.12; S, 37.44; Found: C, 48.97; H, 4.11; S, 37.47.

Diethyl 2,5-dimethyl-1,4-benzene-bis(α-oxoethanedithioate) (10). Thiolation of **6** (1.2 g, 0.005 mol) gave **10** as red crystals (0.15 g, 9%), mp 129–132°C ($CHCl_3$/hexane). MS: 370 (3) [M^+], 265 (100) [$M^+-CS_2C_2H_5$], 237 (9) [$M^+-COCS_2C_2H_5$], 160 (24), [$M^+-2\ CS_2C_2H_5$], 132 (57) [$M^+-COCS_2C_2H_5,-CS_2C_2H_5$], 104 (15) [$M^+-2\ COCS_2C_2H_5$], 103 (18), 78 (12) [$C_6H_6^+$], 77 (11) [$C_6H_5^+$]. Anal. calcd. for $C_{16}H_{18}O_2S_4$ (370.58): C, 51.86; H, 4.90; S, 34.61; Found: C, 51.57; H, 5.02; S, 34.66.

S-Isopropyl S′-methyl 1,4-benzene-bis(α-oxoethanedithioate) (12). The thiolation mixture obtained from 1,4-bis(diazoacetyl)benzene[47] (0.50 g, 0.0032 mol) was

first treated with 2-iodopropane (0.82 g, 0.0048 mol) for 2 h and subsequently with MeI (0.45 g, 0.0032 mol). Careful CC (two times with toluene) removed the two accompanying symmetric dithioesters **7** and **11** to give pure **12** as red oil (0.11 g, 10%). IR: 1680 (C=O), 1250 (C=S). ^{1}H NMR (250 MHz): 1.50 (d, $J = 7.5$, 6 H, CHCH_3), 2.84 (s, 3 H, SCH_3), 4.25 (sept, $J = 7.5$, 1 H, CH) 8.00 (s, 4 H, 2/3/5/6-H). Anal. calcd. for $C_{14}H_{14}O_2S_4$ (342.53): C, 49.09; H, 4.12; S, 37.45; Found: C, 49.42; H, 4.58; S, 37.51.

Dimethyl 4,4′-biphenyl-bis(α-oxoethanedithioate) (26). Thiolation of **25** (2.15 g, 0.007 mol) gave **26** as a salmon-colored powder (0.55 g, 21%), mp 152°C ($CHCl_3$/hexane). ^{1}H NMR (250 MHz): 2.80 (s, 6 H, CH_3), 7.70 (d, $J = 8.9$, 4 H, 2/2′/6/6′-H), 8.10 (d, $J = 8.9$, 4 H, 3/3′/5/5′-H). ^{13}C NMR (63 MHz): 18.41 (CH_3), 127.49 (C-2/2′/6/6′), 131.26 (C-3/3′/5/5′), 132.59 (C-4/4′), 145.22 (C-1/1′), 190.70 (C=O), 230.83 (C=S). MS: 390 (6) [M^+], 299 (100) [$M^+-CS_2CH_3$], 271 (1), [$M^+-COCS_2CH_3$]. Anal. calcd. for $C_{18}H_{14}O_2S_4$ (390.57): C, 55.36; H, 3.61; S, 32.84; Found: C, 55.57; H, 3.46; S, 32.76.

Methyl 1-naphthalene-α-oxoethanedithioate (35). Thiolation of **33** (14.0 g, 0.096 mol) gave **35** as red crystals (1.5 g, 25%), mp 100–101°C ($CHCl_3$/hexane, lit.[4] mp 100–101°C). ^{1}H NMR (250 MHz): 2.84 (s, 3 H, CH_3), 7.44 (t, $J = 7.7$, 1 H, 3-H), 7.50–7.70 (m, 2 H, 6/7-H), 7.85–7.95 (m, 2 H, 5/8-H), 8.30 (d, $J = 8.3$, 1 H, 4-H), 8.82 (d, $J = 8.2$, 1 H, 2-H). ^{13}C NMR (100 MHz): 18.74 (CH_3), 123.97 (C-6), 125.92 (C-7), 126.77 (C-3), 128.63 (C-4), 128.68 (C-4), 130.43 (C-4a), 131.32 (C-8a), 132.62 (C-8), 133.88 (C-1), 134.56 (C-2), 191.50 (C=O), 232.20 (C=S). MS: 246 (11) [M^+], 231 (1) [M^+-CH_3], 155 (100) [$M^+-CS_2CH_3$], 127 (78) [$M^+-COCS_2CH_3$], 126 (12) [$C_{10}H_6^+$], 101 (6), 91 (6) [$CS_2CH_3^+$], 77 (11) [$C_6H_5^+$], 75 (7). Anal. calcd. for $C_{13}H_{10}OS_2$ (246.35): C, 63.38; H, 4.09; S, 26.03; Found: C, 63.09; H, 4.00; S, 25.82.

Methyl 2-naphthalene-α-oxoethanedithioate (36). Thiolation of **34** (14.0 g, 0.096 mol) gave **36** as red crystals (2.3 g, 42%), mp 74–76°C ($CHCl_3$/hexane). ^{1}H NMR (250 MHz): 2.90 (s, 3 H, CH_3), 7.50–7.62 (m, 2 H, H_{Ar}), 7.83–8.20 (m, 4 H, H_{Ar}), 8.48 (s, 1 H, 1-H). ^{13}C NMR (100 MHz): 18.46 (CH_3), 124.87 (C-6), 127.01 (C-7), 127.87 (C-5), 128.55 (C-8), 129.26 (C-4), 129.85 (C-3), 130.12 (C-4a), 132.18 (C-8a), 133.29 (C-1), 136.08 (C-2), 190.94 (C=O), 231.40 (C=S). MS: 246 (11) [M^+], 155 (100) [$M^+-CS_2CH_3$], 127 (75) [$M^+-COCS_2CH_3$], 101 (7), 91 (5) [$CS_2CH_3^+$], 77 (9) [$C_6H_5^+$], 63 (5). Anal. calcd. for $C_{13}H_{10}OS_2$ (246.35): C, 63.38; H, 4.09; S, 26.03; Found: C, 63.36; H, 4.03; S, 25.92.

α-Oxo-dithioesters from Bromoketones and Other Substrates (General Procedure)

A mixture of S_8 (3 equivalents) and NEt_3 (3 equivalents) in dry DMF (100 mL if 0.1 mol of bromoketone were used) was stirred at 20°C for 30 min. Then a solution of the bromoketone (1 equivalent) or other substrate in DMF (30 mL) was slowly dropped in. Stirring was continued at 20°C for 30 min. The mixture was cooled down to 5°C. After the addition of the respective iodoalkane (3 equivalents), the mixture was stirred at 20°C for at least 1 h. The formation of the dithioester was monitored by thin layer chromatography (TLC, $CHCl_3$). Finally, the reaction mixture was poured into ice-water and neutralized with dil. HCl. The products were extracted with sufficient $CHCl_3$. The extracts were washed 10 times with H_2O to remove the DMF completely, then dried over Na_2SO_4 and evaporated under vacuum. The residues were purified by CC ($CHCl_3$) and finally purified by recrystallization and/or CC with suitable solvents and eluents.

Diisopropyl 1,4-benzene-bis(α-oxoethanedithioate) (11). Thiolation of 1,4-bis(bromoacetyl)benzene[44,47] (6.4 g, 0.020 mol) gave **11** as carmine red crystals (0.27 g, 3.7%), mp 115–117°C (CH_2Cl_2/hexane). IR: 1660 (C=O). ^{1}H NMR (250 MHz): 1.50 (d,

$J = 7.5$, 12 H, CH_3), 4.20 (sept, $J = 7.4$, 2 H, CH_2), 8.00 (s, 4 H, 2/3/5/6-H). Anal. calcd. for $C_{16}H_{18}O_2S_4$ (370.57): C, 51.85; H, 4.89; S, 34.60; Found: C, 51.52; H, 4.85; S, 34.87.

1,4-Naphthoquinone-2-yl 2-acetylbenzene-α-oxoethanedithioate (19). A solution of 1,2-diacetylbenzene (Fluka, 1.0 g, 0.006 mol) in $CHCl_3$ (13 mL) and a separate solution of Br_2 (0.5 g, 0.006 mol) in $CHCl_3$ (6 mL) were cooled to –25°C and mixed together in the cold environment. After warming to +20°C, the red color disappeared at once. The reaction mixture was washed with icy water and $NaHCO_3$-solution. The solvent was removed in a vacuum at low temp. The remaining 1-acetyl-2-(bromoacetyl)benzene **16** (1.45 g, 0.006 mol) was thiolated without further purification to yield **19** (0.47 g, 21%) as red crystals, mp 253°C ($CHCl_3$/hexane, decomp.). IR: 1700 (C=O), 1650 (C=O), 1600 (C=C), 1240 (C=S). UV/VIS: 527 (3.18), 282 (4.37), 246 (4.18), 206 (4.60). ^{1}H NMR (250 MHz): 1.87 (s, 3 H, CH_3), 6.93 (s, 1 H, CH), 7.66–8.03 (m, 8 H, H_{Ar}). MS: 380 (6) [M^+], 233 (100), 189 (11), 147 (11), 76 (10) [$C_6H_4^+$]. Anal. calcd. for $C_{20}H_{12}O_4S_2$ (380.44): C, 63.14; H, 3.18; S, 16.86; Found: C, 61.55; H, 3.09; S, 16.78. In addition, 2-ethylthio-1,4-naphthoquinone **20** was obtained after ethylation and careful separation by CC (eluents: 1. diethyl ether, 2. $CHCl_3$) as yellow crystals (0.09 g, 7%), mp 141–142°C [toluene/hexane; lit.[48]: 141–142°C ($CHCl_3$)]. IR: 1680 (C=O), 1660 (C=O), 1600 (C=C). UV/VIS: 416 (3.54), 290 (4.09), 258 (4.45), 205 (4.56). ^{1}H NMR (250 MHz): 1.37 (t, $J = 7.5$, 3 H, CH_3), 3.00 (q, $J = 7.5$, 2 H, CH_2), 6.75 (s, 1 H, CH), 7.83–8.04 (m, 4 H, H_{Ar}), in agreement with lit.[48] MS: 218 (33) [M^+], 189 (14) [$M^+-C_2H_5$], 147 (23), 76 (14) [$C_6H_4^+$], 45 (100).

Trimethyl 1,3,5-benzene-tris(α-oxoethanedithioate) (22). Thiolation of **21** (6.4 g, 0.020 mol) gave **22** as deep violet crystals (0.48 g, 5.6%), mp 98°C (CH_2Cl_2/hexane; lit.[6]: mp 96°C). IR: 1660 (C=O). ^{1}H NMR (250 MHz): 2.86 (s, 9 H, CH_3), 8.63 (s, 3 H, 2/4/6-H). Anal. calcd. for $C_{15}H_{12}O_3S_6$ (432.64): C, 41.64; H, 2.79; S, 44.46; Found: C, 41.58; H, 2.65; S, 44.61.

Triethyl 1,3,5-benzene-tris(α-oxoethanedithioate) (23). Thiolation of **21** (6.4 g, 0.020 mol) gave **23** as violet crystals (0.19 g, 2%), mp 65°C (CH_2Cl_2/hexane). IR: 1660 (C=O). ^{1}H NMR (250 MHz): 1.46 (t, $J = 7.5$, 9 H, CH_3), 3.50 (q, $J = 7.5$, 6 H, CH_2), 8.76 (s, 3 H, 2/4/6-H). Anal. calcd. for $C_{18}H_{18}O_3S_6$ (474.70): C, 45.54; H, 3.82; S, 40.52; Found: C, 45.59; H, 3.75; S, 40.45.

Triisopropyl 1,3,5-benzene-tris(α-oxoethanedithioate) (24). Thiolation of **21** (6.4 g, 0.020 mol) gave **24** as carmine red crystals (0.044 g, 0.43%), mp 95°C (CH_2Cl_2/hexane). IR: 1660 (C=O). ^{1}H NMR (250 MHz): 1.52 (d, $J = 7.5$, 18 H, CH_3), 3.50 (sept, $J = 7.5$, 3 H, CH), 8.65 (s, 3 H, 2/4/6-H). Anal. calcd. for $C_{21}H_{24}O_3S_6$ (516.80): C, 48.80; H, 4.68; S, 37.22; Found: C, 48.88; H, 4.55; S, 37.10.

Diethyl 4,4′-biphenyl-bis(α-oxoethanedithioate) (28). Thiolation of **27** (4.0 g, 0.010 mol) gave **28** as a salmon-colored powder (1.5 g, 36%), mp 73–76°C ($CHCl_3$/hexane). ^{1}H NMR (250 MHz): 1.50 (t, $J = 7.5$, 6 H, CH_3), 3.45 (q, $J = 7.4$, 4 H, CH_2), 7.70 (d, $J = 8.3$, 4 H, 2/2′/6/6′-H), 8.05 (d, $J = 8.3$, 4 H, 3/3′/5/5′-H). ^{13}C NMR (100 MHz): 11.61 (CH_3), 29.05 (CH_2), 126.87 (C-2/2′/6/6′), 130.51 (C-3/3′/5/5′), 131.98 (C-4/4′), 144.58 (C-1/1′), 189.20 (C=O), 229.85 (C=S). MS: 418 (0.5) [M^+], 313 (100) [$M^+-CS_2C_2H_5$], 285 (2), [$M^+-COCS_2C_2H_5$], 180 (64) [$M^+-CS_2C_2H_5$,$-COCS_2C_2H_5$], 152 (26), [M^+-2 $COCS_2C_2H_5$], 105 (5), 77 (9) [$C_6H_5^+$]. Anal. calcd. for $C_{20}H_{18}O_2S_4$ (418.62): C, 57.38; H, 4.33; S, 30.64; Found: C, 57.00; H, 4.10; S, 30.00.

Methyl 2-(2′-methylthiocarbonyl)biphenyl-α-oxoethanedithioate (32). Thiolation of **30** (2.7 g, 0.06 mol) gave **32** as a red oil (0.7 g, 35%). ^{1}H NMR (250 MHz): 2.40 (s, 3 H, $COSCH_3$), 2.60 (s, 3 H, CS_2CH_3), 7.00 (d, $J = 8.0$, 1 H, 3′-H), 7.35–7.50

(m, 6 H, H_{Ar}), 7.70 (d, $J = 8.0$, 1 H, 3-H). ^{13}C NMR (63 MHz): 16.64 ($COSCH_3$), 18.77 (CS_2CH_3), 123.84, 127.19, 128.24, 128.37, 129.69, 131.01, 131.29, 131.98 (8 CH_{Ar}), 134.82, 141.32, 142.31, 145.57 (4 C_{qAr}), 190.09 (C=O), 195.98 (C=O), 230.57 (C=S).

Ethyl 2-naphthalene-α-oxoethanedithioate (38). Thiolation of **37**[49] (3.0 g, 0.012 mol) gave **38** as a red oil (1.6 g, 39%). ^1H NMR (250 MHz): 1.48 (t, $J = 7.5$, 3 H, CH_3), 3.50 (q, $J = 7.5$, 2 H, CH_2), 7.55–7.70 (m, 2 H, 6/7-H), 7.85–7.95 (m, 3 H, 4/5/8-H), 8.10 (dd, $J = 2.0$, 8.9, 1 H, 3-H), 8.50 (s, 1 H, 1-H). ^{13}C NMR (100 MHz): 11.65 (CH_3), 29.13 (CH_2), 124.30 (C-3), 126.41 (C-6), 127.26 (C-5), 127.93 (C-8), 128.64 (C-7), 129.26 (C-4), 129.53 (C-4a), 131.60 (C-8a), 132.65 (C-1), 135.47 (C-2), 190.10 (C=O), 230.40 (C=S). MS: 260 (16) [M^+], 231 (3) [$M^+-C_2H_5$], 199 (2) [$M^+-SC_2H_5$], 155 (100) [$M^+-CS_2C_2H_5$], 127 (70) [$M^+-COCS_2C_2H_5$]. Anal. calcd. for $C_{14}H_{12}OS_2$ (260.37): C, 64.58; H, 4.65; S, 24.63; Found: C, 64.59; H, 4.67; S, 24.54.

Isopropyl 2-naphthalene-α-oxoethanedithioate (39). Thiolation of **37**[49] (4.0 g, 0.016 mol) gave **39** as a red oil (1.5 g, 36%). MS: 274 (5) [M^+], 186 (12), 155 (100) [$M^+-CS_2C_3H_7$], 127 (57) [$M^+-COCS_2C_3H_7$], 126 (13), 77 (7) [$C_6H_5^+$]. Anal. calcd. for $C_{15}H_{14}OS_2$ (260.37): C, 65.65; H, 5.14; S, 23.37; Found: C, 65.60; H, 5.04; S, 23.25.

Methyl 1-Hydroxy-2-methylthio-naphtho[2,1-b]thiophene-4-(α-oxoethanedithioate) (45). Thiolation of **41** (2.5 g, 0.007 mol) gave **45** (0.33 g, 13%) as an orange powder, mp 184–187°C. IR: 3409 (OH), 3062, 2916, 1639 (C=O), 1615, 1562, 1416, 1312, 1247 (C=S), 1209, 1089, 1003, 973, 837, 760, 691, 579, 523, 435. ^1H NMR (400 MHz, DMSO-d_6): 2.45 (s, 3 H, SCH_3) 3.00 (s, 3H, CS_2CH_3), 7.70 (ddd, $J = 1.2$, 7.0, 8.4, 1 H, 7-H), 7.90 (ddd, $J = 1.2$, 7.0, 8.5, 1 H, 8-H), 8.25 (d, $J = 8.2$, 1 H, 6-H), 8.60 (s, 1H, 5-H), 9.35 (d, $J = 8.6$, 1H, 9-H), 10.40 (s, 1 H, OH). ^1H NMR (250 MHz, $CDCl_3$): 2.40 (s, 3 H, SCH_3), 2.95 (s, 3H, CS_2CH_3), 6.75 (s, 1 H, OH), 7.55 (ddd, $J = 1.2$, 7.0, 8.4, 1 H, 7-H), 7.80 (ddd, $J = 1.2$, 7.0, 8.5, 1 H, 8-H), 7.95 (d, $J = 8.2$, 1 H, 6-H), 8.40 (s, 1H, 5-H), 9.15 (d, $J = 8.6$, 1 H, 9-H). ^{13}C NMR (100 MHz, DMSO-d_6): 19.45 (CS_2CH_3), 21.72 (2-SCH_3), 111.95 (C-2), 123.15 (C-1), 123.49 (C-9), 126.22 (C-7), 127.13, 129.57 (2 C_{qu}), 130.61 (C-8), 130.75 (C-6), 131.38, 132.19 (2 C_{qu}), 134.82 (C-5), 153.10 (C_{qu}), 190.54 (C=O), 230.46 (C=S). MS: 364 (28) [M^+], 273 (100) [$M^+-CS_2CH_3$], 245 (37) [$M^+-COCS_2CH_3$], 230 (25) [$M^+-COCS_2CH_3,-CH_3$], 169 (11), 158 (30) [$C_{10}H_6S^+$], 126 (21) [$C_{10}H_6^+$] 125 (24) [$C_{10}H_5^+$], 91 (34) [$CS_2CH_2CH_3^+$]. Anal. calcd. for $C_{16}H_{12}O_2S_4$ (364.52): C, 52.72; H, 3.32; S, 35.18; Found: C, 52.06; H, 3.24; S, 34.65.

Ethyl 1-hydroxy-2-ethylthio-naphtho[2,1-b]thiophene-4-(α-oxoethanedithioate) (46). Thiolation of **41** (2.8 g, 0.011 mol) gave **46** (0.3 g, 10%) as orange crystals, mp 140°C. MS: 392 (38) [M^+], 363 (14) [$M^+-C_2H_5$], 331 (2) [$M^+-SC_2H_5$], 287 (100) [$M^+-CS_2C_2H_5$], 259 (24) [$M^+-COCS_2C_2H_5$], 230 (30) [$M^+-COCS_2C_2H_5,-C_2H_5$], 158 (21) [$C_{10}H_6S^+$], 126 (15) [$C_{10}H_6^+$], 76 (8) [$C_6H_4^+$]. Anal. calcd. for $C_{18}H_{16}O_2S_4$ (392.58): C, 55.07; H, 4.11; S, 32.67; Found: C, 54.64; H, 4.26; S, 33.19.

Benzyl 1-hydroxy-2-benzylthio-naphtho[2,1-b]thiophene-4-(α-oxoethanedithio ate) (47). Thiolation of **41** (2.0 g, 0.005 mol) gave **47** (0.16 g, 6%) as orange red crystals, mp 173–175°C. MS: 516 (2) [M^+], 425 (1) [M^+-CH_2Ph], 349 (7) [$M^+-CS_2CH_2Ph$], 258 (3) [$M^+-CS_2CH_2Ph,-CH_2Ph$], 230 (3) [$M^+-COCS_2CH_2Ph,-CH_2Ph$), 121 (19), 91 (100) [$C_7H_7^+$], 77 (8) [$C_6H_5^+$], 65 (12) [$C_5H_5^+$]. Anal. calcd. for $C_{28}H_{20}O_2S_4$ (515.72): C, 65.08; H, 3.90; S, 24.82; Found: C, 64.13; H, 3.66; S, 23.69.

Dimethyl 1,4-naphthalene-bis(α-oxoethanedithioate) (58). Thiolation of **52** (3.4 g, 0.009 mol) gave **58** (0.7 g, 22%) as red crystals, mp 130–131°C

($CHCl_3$/hexane). ^1H NMR (250 MHz): 2.80 (s, 6 H, CH_3), 7.60–7.68 (m, 2 H, 6/7-H), 7.75 (s, 2 H, 2/3-H), 8.45–8.55 (m, 2 H, 5/8-H). ^{13}C NMR (63 MHz): 18.85 (CH_3), 126.02 (C-6/7), 127.97 (C-5/8), 128.64 (C-2/3), 131.32 (C-4a/8a), 136.43 (C-1/4), 189.77 (C=O), 229.82 (C=S). MS: 364 (7) [M^+], 273 (100) [$M^+-CS_2CH_3$], 245 (15), [$M^+-COCS_2CH_3$], 198 (12) [$M^+-COCS_2CH_3,-SCH_3$], 182 (23), [$M^+-2\ CS_2CH_3$], 154 (62) [$M^+-COCS_2CH_3,-CS_2CH_3$], 126 (56) [$M^+-2\ COCS_2CH_3$], 91 (35) [$CS_2CH_3^+$]. Anal. calcd. for $C_{16}H_{12}O_2S_4$ (364.53): C, 52.72; H, 3.32; S, 35.19; Found: C, 52.27; H, 3.22; S, 35.27.

Dimethyl 1,5-naphthalene-bis(α-oxoethanedithioate) (59). Thiolation of **53** (3.3 g, 0.009 mol) gave **59** (0.9 g, 28%) as a yellow-orange powder, mp 209–211°C ($CHCl_3$/hexane). ^1H NMR (250 MHz): 2.85 (s, 6 H, CH_3), 7.60 (dd, $J = 7.3, 7.6$, 2 H, 3/7-H), 7.95 (d, $J = 7.3$, 2 H, 4/8-H), 9.00 (d, $J = 8.8$, 2 H, 2/6-H). ^{13}C NMR (63 MHz): 18.84 (CH_3), 126.52 (C-3/7), 131.49 (C-4a/8a), 131.73 (C-2/6), 131.76 (C-1/5), 132.34 (C-4/8), 188.98 (C=O), 229.81 (C=S). MS: 364 (0.4) [M^+], 273 (28) [$M^+-CS_2CH_3$], 198 (4) [$M^+-COCS_2CH_3,-SCH_3$], 154 (44) [$M^+-COCS_2CH_3,-CS_2CH_3$], 126 (83) [$M^+-2\ COCS_2CH_3$], 91 (100) [$CS_2CH_3^+$], 76 (7) [$C_6H_4^+$]. Anal. calcd. for $C_{16}H_{12}O_2S_4$ (364.53): C, 52.72; H, 3.32; S, 35.19; Found: C, 51.66; H, 3.22; S, 35.16.

Diethyl 1,5-naphthalene-bis(α-oxoethanedithioate) (60). Thiolation of **53** (3.3 g, 0.009 mol) gave **60** (0.9 g, 28%) as red crystals, mp 130°C ($CHCl_3$/hexane). MS: 392 (9) [M^+], 288 (17), 287 (100) [$M^+-CS_2C_2H_5$], 259 (4) [$M^+-COCS_2C_2H_5$], 182 (4) [$M^+-2\ CS_2C_2H_5$], 154 (42) [$M^+-COCS_2C_2H_5,-CS_2C_2H_5$], 126 (37) [$M^+-2\ COCS_2C_2H_5$]. Anal. calcd. for $C_{18}H_{16}O_2S_4$ (392.59): C, 55.07; H, 4.11; S, 32.67; Found: C, 54.66; H, 4.03; S, 32.72.

Dimethyl 1,6-naphthalene-bis(α-oxoethanedithioate) (61). Thiolation of **54** (3.5 g, 0.009 mol) gave **61** (1.1 g, 34%) as a violet powder, mp 135–137°C ($CHCl_3$/hexane). ^1H NMR (250 MHz): 2.85 (s, 3 H, 6-CH_3), 2.90 (s, 3 H, 1-CH_3), 7.50 (t, $J = 8.3$, 1 H, 3-H), 8.00 (d, $J = 8.2$, 1 H, 2-H), 8.10–8.20 (m, 2 H, 4/8-H), 8.50 (s, 1 H, 5-H), 8.80 (d, $J = 8.6$, 1 H, 7-H). ^{13}C NMR (100 MHz): 18.45 (6-CH_3), 18.80 (1-CH_3), 125.25 (C-3), 126.53 (C-4), 127.86 (C-8), 130.86 (C-4a), 131.91 (C-8a), 132.82 (C-6), 133.03 (C-2), 133.94 (C-1), 134.66 (C-7), 135.77 (C-5), 190.11 (6-C=O), 190.52 (1-C=O), 230.61 (6-C=S), 231.08 (1-C=O). MS: 364 (5) [M^+], 273 (100), [$M^+-CS_2CH_3$], 245 (2) [$M^+-COCS_2CH_3$], 154 (45) [$M^+-COCS_2CH_3,-CS_2CH_3$], 126 (40) [$M^+-2\ COCS_2CH_3$], 91 (10) [$CS_2CH_3^+$], 63 (12). Anal. calcd. for $C_{16}H_{12}O_2S_4$ (364.53): C, 52.72; H, 3.32; S, 35.18; Found: C, 52.71; H, 3.03; S, 35.90.

Diethyl 1,6-naphthalene-bis(α-oxoethanedithioate) (62). Thiolation of **54** (2.9 g, 0.008 mol) gave **62** (1.0 g, 31%) as red crystals, mp 85–87°C ($CHCl_3$/hexane). MS: 392 (7) [M^+], 287 (100) [$M^+-CS_2C_2H_5$], 259 (7) [$M^+-COCS_2C_2H_5$], 154 (59) [$M^+-COCS_2C_2H_5,-CS_2C_2H_5$], 126 (53) [$M^+-2\ COCS_2C_2H_5$], 77 (9) [$C_6H_5^+$]. Anal. calcd. for $C_{18}H_{16}O_2S_4$ (392.59): C, 55.07; H, 4.11; S, 32.67; Found: C, 55.12; H, 4.01; S, 32.81.

Dimethyl 1,7-naphthalene-bis(α-oxoethanedithioate) (63). Thiolation of **55** (1.4 g, 0.004 mol) gave **63** (0.6 g, 45%) as a violet powder, mp 90–93°C ($CHCl_3$/hexane). ^1H NMR (250 MHz): 2.85 (s, 3 H, 7-CH_3), 2.90 (s, 3 H, 1-CH_3), 7.60 (t, $J = 8.2$, 1 H, 3-H), 7.90–8.00 (m, 2 H, 4/5-H), 8.05–8.15 (m, 2 H, 2/6-H), 9.35 (s, 1 H, 8-H). ^{13}C NMR (100 MHz): 17.92 (7-CH_3), 18.25 (1-CH_3), 125.07 (C-3), 126.70 (C-4), 128.68 (C-5), 129.40 (C-4a), 130.73 (C-6), 131.68 (C-8a), 131.79 (C-7), 132.53 (C-2), 133.38 (C-8), 135.61 (C-1), 190.05 (2 C=O), 230.16 (2 C=S). MS: 364 (13) [M^+], 273 (100), [$M^+-CS_2CH_3$], 245 (11) [$M^+-COCS_2CH_3$], 182 (10) [$M^+-2\ CS_2CH_3$], 154 (71) [$M^+-COCS_2CH_3,-CS_2CH_3$],

126 (65) [$M^+-2\ COCS_2CH_3$], 91 (16) [$CS_2CH_3^+$]. Anal. calcd. for $C_{16}H_{12}O_2S_4$ (364.53): C, 52.72; H, 3.32; S, 35.18; Found: C, 52.73; H, 3.26; S, 35.18.

Dimethyl 2,6-naphthalene-bis(α-oxoethanedithioate) (68). Thiolation of **66** (4.0 g, 0.010 mol) gave **68** (1.2 g, 31%) as red needles, mp 225–230°C ($CHCl_3$/hexane). ^{1}H NMR (250 MHz): 2.90 (s, 6 H, CH_3), 8.00–8.10 (m, 4 H, 3/4/5-H), 8.50 (s, 2 H, 1/5-H). ^{13}C NMR (63 MHz): 18.47 (CH_3), 126.03 (C-4/8), 130.29 (C-3/7), 132.43 (C-1/5), 132.89 (C-4a/8a), 134.79 (C-2/6), 190.98 (C=O), 230.18 (C=S). MS: 364 (4) [M^+], 273 (100), [$M^+-CS_2CH_3$], 245 (3) [$M^+-COCS_2CH_3$], 182 (14) [$M^+-2\ CS_2CH_3$], 154 (92) [$M^+-COCS_2CH_3,-CS_2CH_3$], 126 (72) [$M^+-2\ COCS_2CH_3$], 91 (27) [$CS_2CH_3^+$], 63 (6). Anal. calcd. for $C_{16}H_{12}O_2S_4$ (364.53): C, 52.72; H, 3.32; S, 35.18; Found: C, 52.76; H, 3.32; S, 35.35.

Diethyl 2,6-naphthalene-bis(α-oxoethanedithioate) (69). Thiolation of **66** (1.2 g, 0.003 mol) gave **69** (0.33 g, 25%) as violet crystals, mp 113–117°C ($CHCl_3$/hexane). MS: 392 (4) [M^+], 287 (100) [$M^+-CS_2C_2H_5$], 272 (17) [$M+-CS_2C_2H_5,-CH_3$], 259 (4) [$M^+-COCS_2C_2H_5$], 182 (15) [$M^+-CS_2C_2H_5$], 154 (62) [$M^+-COCS_2C_2H_5,-CS_2C_2H_5$], 126 (41) [$M^+-2\ COCS_2C_2H_5$], 105 (4), 77 (9) [$C_6H_5^+$]. Anal. calcd. for $C_{18}H_{16}O_2S_4$ (392.59): C, 55.07; H, 4.11; S, 32.67; Found: C, 54.91; H, 4.21; S, 32.74.

Dibenzyl 2,6-naphthalene-bis(α-oxoethanedithioate) (70). Thiolation of **66** (2.1 g, 0.010 mol) gave **70** (0.8 g, 28%) as salmon-colored powder, mp 167–170°C ($CHCl_3$/hexane). MS: 516 (1) [M^+], 349 (18) [$M^+-CS_2CH_2Ph$], 182 (3) [$M^+-2\ CS_2CH_2Ph$], 154 (17) [$M^+-COCS_2CH_2Ph,-CS_2CH_2Ph$], 126 (10) [$M^+-2\ COCS_2CH_2Ph$], 91 (100) [$C_7H_7^+$], 65 (12) [$C_6H_5^+$]. Anal. calcd. for $C_{28}H_{20}O_2S_4$ (516.73): C, 65.08; H, 3.90; S, 24.82; Found: C, 64.72; H, 3.79; S, 24.93.

Dimethyl 2,7-naphthalene-bis(α-oxoethanedithioate) (71). Thiolation of **67** (2.8 g, 0.008 mol) gave **71** (0.74 g, 27%) as violet crystals, mp 140–143°C ($CHCl_3$/hexane). ^{1}H NMR (250 MHz): 2.90 (s, 6 H, CH_3), 7.95 (d, J = 8.3, 2 H, 4/5-H), 8.15 (d, J = 8.5, 2 H, 3/6-H), 8.50 (s, 2 H, 1/8-H). ^{13}C NMR (100 MHz): 18.49 (CH_3), 128.09 (C-4/5), 131.12 (C-4a), 131.35 (C-8a), 134.65 (C-1/8), 138.44 (C-2/7), 189.96 (C=O), 230.48 (C=S). MS: 364 (2) [M^+], 273 (100), [$M^+-CS_2CH_3$], 154 (51) [$M^+-COCS_2CH_3,-CS_2CH_3$], 126 (49) [$M^+-2\ COCS_2CH_3$], 91 (15) [$CS_2CH_3^+$], 63 (6). Anal. calcd. for $C_{16}H_{12}O_2S_4$ (364.53): C, 52.72; H, 3.32; S, 35.18; Found: C, 52.64; H, 3.37; S, 36.02. See X-ray structure above and Figure 2.

Diethyl 2,7-naphthalene-bis(α-oxoethanedithioate) (72). Thiolation of **67** (2.0 g, 0.005 mol) gave **72** (0.3 g, 14%) as violet crystals, mp 88°C ($CHCl_3$/hexane). MS: 287 (23) [$M^+-CS_2C_2H_5$], 259 (3) [$M^+-COCS_2C_2H_5$], 154 (52) [$M^+-COCS_2C_2H_5,-CS_2C_2H_5$], 126 (100) [$M^+-2\ COCS_2C_2H_5$], 105 (26), 76 (52) [$C_6H_4^+$]. Anal. calcd. for $C_{18}H_{16}O_2S_4$ (392.59): C, 55.07; H, 4.11; S, 32.67; Found: C, 54.84; H, 4.15; S, 32.67.

Diethyl benzo[c]thiophene-1,3-dicarboxylate (76). Thiolation of diethyl 1,2-benzenediacetate[50] (1.00 g, 0.004 mol) gave **76** (0.35 g, 32%) as fluorescing yellow crystals, mp 152–153°C ($CHCl_3$/hexane); mp, spectroscopic, and analytical data are in agreement with the literature.[18]

Benzo[c]thiophene-1,3-dicarbonitrile (77). Thiolation of 1,2-benzenediacetonitrile[50] (0.62 g, 0.004 mol) in the presence of $CaCl_2$ gave **77** (0.10 g, 13%) as fluorescing yellow needles, mp 175–176°C ($CHCl_3$/hexane) [lit.[51]: 179–180°C; lit.[52]: 183°C (benzene)]. UV/VIS: 382 (4.01), 371 (4.05), 328 (3.88), 313 (3.76), 299 (3.64), 230 (4.45). ^{1}H NMR (250 MHz): 7.50–7.60 (m, 2 H, 4/7-H), 7.85–7.95 (m, 2 H, 5/6-H). ^{13}C NMR (63 MHz): 106.33 (C-1/3), 112.23 (CN), 120.91 (C-4/7), 129.04 (C-5/6), 142.22 (C-3a/7a).

MS: 184 (100) [M^+], 157 (10) [M^+—HCN]. Anal. calcd. for $C_{10}H_4N_2S$ (184.22): C, 65.20; H, 2.19; N, 15.21; S, 17.41; Found: C, 65.10; H, 2.11; N, 15.22; S, 17.35.

Dimethyl 1,4-benzene-bis(α-oxoethanedithioate) (7). Thiolation of 1,4-diacetylbenzene (Fluka) (1.13 g, 0.007 mol) in the presence of $CaCl_2$ gave **7** (1.76 g, 80%); mp, IR, and ^{1}H NMR spectra are in agreement with an authentic sample.[1]

Methyl 3-methyl-4H-chromone-2-carbodithioate (74). Thiolation of 2,3-dimethyl-4*H*-chromone (**73**)[53] (1.13 g, 0.0065 mol) in the presence of $CaCl_2$ gave **74** (1.49 g, 92%) as red crystals, mp 106–107°C (MeOH/petroleum ether). IR: 1630 (C=O), 1610 (C=O), 1050 (C=S). UV/VIS: 509 (1.98), 310 (4.14), 265 (4.29), 220 (4.43), 205 (4.40). ^{1}H NMR (250 MHz): 2.10 (s, 3 H, CH_3), 2.82 (s, 3 H, SCH_3), 7.41 (m, 2 H), 7.76 (m, 1 H), 8.21 (m, 1 H, 5-H). Anal. calcd. for $C_{12}H_{10}O_2S_2$ (250.39): C, 57.58; H, 4.03; S, 25.62; Found: C, 57.75; H, 3.92; S, 25.67. See X-ray structure above and Figure 3.

Dimethyl benzene-1,4-bis-carbodithioate (75). Thiolation of 1,4-benzenediacetic acid (Fluka) (0.1 g, 0.5 mmol) for a prolonged reaction time of 8 days gave dimethyl benzene-1,4-bis-carbodithioate **75** (0.05g, 38%), which was purified by CC (CCl_4) and recrystallization from $CHCl_3$/hexane. ^{1}H and ^{13}C NMR: in agreement with an authentic sample.[54] Anal. calcd. for $C_{10}H_{10}S_4$ (258.45): C, 46.47; H, 3.90; S, 49.63; Found: C, 46.38; H, 3.90; S, 49.56.

O,O′-Dimethyl 1,4-benzene-bis(α-oxoethanethioate) (78). A solution of **7** (0.37 g, 0.0012 mol) in $CHCl_3$ (100 mL) was cooled to –10°C. A solution of Na (0.054 g, 0.0023 mol) in dry MeOH (10 mL) and $CHCl_3$ (50 mL) was added under vigorous stirring. After 30 min, the reaction mixture was warmed up to 20°C. The brown precipitates were repeatedly filtered off. The filtrate was concentrated in a vacuum below 20°C and filtrated once more. The clear residue was purified by repeated CC on SiO_2 (1. $CHCl_3$, 2. toluene) and recrystallization from pentane/$CHCl_3$ (2×) to yield **78** as light yellow crystals (71 mg, 21%), mp 120–122°C. IR: 1670 (C=O). ^{1}H NMR (250 MHz): 4.33 (s, 6 H, CH_3), 8.03 (s, 4 H, 2/3/5/6-H). Anal. calcd. for $C_{12}H_{10}O_4S_2$ (282.29): C, 51.05; H, 3.57; S, 22.71; Found: C, 50.09; H, 3.47; S, 23.47.

O,O′-Diethyl 1,4-benzene-bis(α-oxoethanethioate) (79). The diethylester **79** was prepared as described for **78** by use of NaOEt instead of NaOMe. Repeated CC on SiO_2 (3× $CHCl_3$) gave **79** as a yellow oil (4 mg, 1%), IR: 1670 (C=O). ^{1}H NMR (250 MHz): 1.51 (t, J = 7.5 Hz, 6 H, CH_3), 4.78 (q, J = 7.5 Hz, 4 H, CH_2), 8.10 (s, 4 H, 2/3/5/6-H). MS: 104 (100), 77 (18), Anal. calcd. for $C_{14}H_{14}O_4S_2$ (310.34): C, 54.18; H, 4.55; S, 20.66; Found: C, 54.23; H, 4.58; S, 20.80.

O,O′,O″-Trimethyl 1,3,5-benzene-tris(α-oxoethanethioate) (80). The trimethylester **80** was prepared from **22** (0.45 g, 0.001 mol) as described for **78**. Repeated CC on SiO_2 (3× $CHCl_3$) gave **80** as a yellow oil (23 mg, 5%), IR: 1670 (C=O). ^{1}H NMR (250 MHz): 4.31 (s, 9 H, CH_3), 8.62 (s, 3 H, 2/4/6-H). Anal. calcd. for $C_{15}H_{12}O_6S_3$ (384.45): C, 46.86; H, 3.15; S, 25.02; Found: C, 46.72; H, 3.08; S, 25.50.

REFERENCES

1. Activated thioesters Part 9. For Part 8, seeA. Sawluk and J. Voss, *Synthesis*, **968** (1986).
2. A. Sarafidis, Darstellung von bifunktionellen aromatischen α-Oxo-dithiocarbonsäureestern und ESR-spektroskopische Untersuchung ihrer Radikalanionen [Preparation of Bifunctional Aromatic α-Oxo-dithiocarboxylic Esters and ESR Spectroscopic Investigation of Their Radical Anions], PhD thesis, University of Hamburg, Hamburg, Germany, 1993.

3. 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, Hamburg, Germany, 1987.
4. R. Mayer, H. Viola, and B. Hopf, *Z. Chem.*, **18,** 90 (1978).
5. D. Villemin and F. Thibault-Starzyk, *Synlett*, 148 (1993).
6. A. Hoepping and R. Mayer, *Bull. Soc. Chim. Belges*, **103,** 389 (1994).
7. J. Hansen and F. W. Heinemann, *Phosphorus, Sulfur, and Silicon*, **118,** 155 (1996).
8. J. Ramachandran, D. V. Ramana, S. R. Ramadas, and C. N. Pillai, *Proc. Ind. Acad. Sci., Chem. Sci.*, **89,** 283 (1980); *Chem. Abstr.*, **94,** 139395 (1981).
9. E. Vedejs, M. J. Amost, J. M. Dolphin, and J. Eustache, *J. Org. Chem.*, **45,** 2601 (1980).
10. Autorenkollektiv, *Organikum, Organisch-chemisches Grundpraktikum*, 19th ed. (Johann Ambrosius Barth, Leipzig, Berlin, Heidelberg, 1993), p. 577.
11. A. Sawluk and J. Voss, *Angew. Chem.*, **101,** 927 (1989); *Angew. Chem. Int. Ed. Engl.*, **28,** 906 (1989).
12. J. Gassmann, H. Günther, K. Osternack, A. Sawluk, K. Thimm, and J. Voss, *Magn. Reson. Chem.*, **32,** 624 (1994).
13. J. O. Halford and B. Weissmann, *J. Org. Chem.*, **17,** 1646 (1952).
14. H. Günther and J. Voss, *J. Chem. Res.*, (S) 68 (1987), (M) 775 (1987).
15. W. Rach, G. Kiel, and G. Gattow, *Z. Anorg. Allg. Chem.*, **569,** 137 (1989).
16. W. Thiel, R. Mayer, and H. Viola, *Z. Chem.*, **28,** 233 (1988).
17. G. W. Kirby, A. W. Lochead, and G. N. Sheldrake, *J. Chem. Soc., Chem. Commun.*, 922 (1984).
18. J. Voss, A. Sawluk, G. Lange, and G. Adiwidjaja, *Phosphorus, Sulfur, and Silicon*, **184,** 1206 (2009).
19. G. Germain, P. Main, and M. M. Woolfson, *Acta Crystallogr.*, **A27,** 368 (1971).
20. G. M. Sheldrick, SHELXTL PLUS-Release 4.21N, Siemens Crystallographic Research System. Analytical X-ray Instr., Inc., 1990.
21. B. A. Frenz, *Structure Determination Package*, College Station, Texas (1982).
22. P. Coppens, L. Leiserowitz, and D. Rabinovich, *Acta Crystallogr.*, **18,** 1035 (1965).
23. V. P. Ivanov, R. G Karpenko, F. M. Stoyanovich, V. I. Suskina, A. B. Shapiro, and E. G. Rozantsev, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 646 (1971); *Chem. Abstr.*, **75,** 48855 (1971).
24. H. Ooyama, T. Morita, T. Masumizu, T. Shibata, and T. Wada, Jpn. Pat., 63,179,859, (1988); *Chem. Abstr.*, **110,** 2894 (1989).
25. T. D. Dang, C. S. Wang, W. E. Click, H. H. Chuah, T. T. Tsai, D. M. Husband, and F. E. Arnold, *Polymer*, **38,** 621 (1997).
26. H. de Diesbach, *Helv. Chim. Acta*, **6,** 539 (1923).
27. E. E. Burgoyne, T. G. Klose, and D. K. Watson, *J. Org. Chem.*, **20,** 1508 (1955).
28. K.-H. Etzbach, R. Sens, and S. Beckmann (BASF A.G., Germany), Eur. Pat., 62553 (1994); *Chem. Abstr.*, **122**, 242307 (1995).
29. I. I. Bil'kis, E. V. Pateleeva, A. P. Tananakin, and V. D. Shteingarts, *Russ. J. Org. Chem. (transl. from Zh. Org. Khim.)*, **33,** 652 (1997); *Chem. Abstr.*, **128,** 270279 (1998).
30. (a) I. G. Hinton and F. G. Mann, *J. Chem. Soc.*, 599 (1959); (b) I. G. Hinton, F. G. Mann, and A. Vanterpool, *J. Chem. Soc.*, 610 (1959).
31. T. S. Work, *J. Chem. Soc.*, **142,** 1315 (1940).
32. F. Bell and P. H. Robinson, *J. Chem. Soc.*, **129,** 1695 (1927).
33. T. B. Smith and C. W. Muth, *Proc. W. Virginia Acad. Sci.*, **25,** 42 (1953); *Chem. Abstr.*, **49,** 42805 (1955).
34. H. Schubert and L. Selisko, *J. Prakt. Chem.*, **16,** 1 (1962).
35. R. Pellicciari, M. Curini, and N. Spagnoli, *Arch. Pharmaz.*, **317,** 38 (1984).
36. E. F. Bradbrook and R. P. Linstead, *J. Chem. Soc.*, 1739 (1936).
37. R. Scholl and H. Neumann, *Ber. Dt. Chem. Ges.*, **55,** 118 (1922).
38. G. Lock, *Monatsh. Chem.*, **81,** 850 (1950).

39. H. Frischkorn and G. Roesch (Hoechst A.-G., Germany), *Ger. Offen.*, 2621169 (1977); *Chem. Abstr.*, **88**, 75314 (1978).
40. D. N. Burdge and N. L. Allphin, *J. Chem. Engn. Data*, **8,** 457 (1963).
41. K. R. Erunlu, *Justus Liebigs Ann. Chem.*, **724,** 208 (1969).
42. H. Schubert, H. J. Lorenz, and R. Fischer, *J. Prakt. Chem.*, **22,** 140 (1963).
43. E. Ghera, Y. Gaoni, and S. Shoua, *J. Am. Chem. Soc.*, **98,** 3627 (1976).
44. P. Ruggli and E. Gassenmeier, *Helv. Chim. Acta*, **22,** 496 (1939).
45. F. Mayer, A. Mombour, W. Lassmann, W. Werner, P. Landmann, and E. Schneider, *Liebigs Ann. Chem.*, **488,** 259 (1931).
46. W. Carruthers and R. Pooranamoorthy, *J. Chem. Soc. Perkin Trans.1*, 1181 (1973).
47. W. C. J. Ross, *J. Chem. Soc.*, 752 (1950).
48. E. L. McInnis, B. Grant, and E. Arcelo, *Tetrahedron Lett.*, **22,** 3807 (1981).
49. T. Immediata and A. R. Day, *J. Org. Chem.*, **5,** 512 (1940).
50. C. W. Muth, D. O. Steiniger, and Z. B. Papanastassiou, *J. Am. Chem. Soc.*, **77,** 1006 (1955).
51. W. Volz, Herstellung und Reaktionen von Benzo[c]thiophenen [Preparation and Reactions of Benzo[c]thiophenes], PhD thesis, University of Hamburg, Hamburg, Germany, 1990.
52. R. R. Amaresh; M. V. Lakhshmikantham, J. W. Baldwin, M. P. Cava, R. M. Metzger, and R. D. Rogers, *J. Org. Chem.*, **67,** 2453 (2002).
53. A. Nishinaga, H. Ando, K. Maruyama, and T. Mashino, *Synthesis*, 839 (1992).
54. J. Voss, W. Schmüser, and K. Schlapkohl, *J. Chem. Res., (M)* 1801 (1977).