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New Dithio-*bis*-(diaroylmethanes) and Acetyl Diaroylchloromethyl Disulfides: Attractive Synthons and Precursors for the Liberation of Highly Reactive Dithiiranes or Thiosulfines

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Summary. In a new, feasible procedure five symmetrical *para*-substituted diaroylmethanes ((4-X–C_6H_4–CO)$_2$–CH_2; X = F, Cl, Br, CH_3, and CH_3O) are prepared, in most cases in very good yields. For purification and activation, they are converted into the copper(II) complexes of their enolates. Subsequently, three reaction steps with disulfur dichloride (S_2Cl_2), chlorine, and ethanethioic acid yield new CH-acidic dithio-*bis*-(diaroylmethanes), α-chlorosulfenic acid chlorides, and acetyl diaroylchloromethyl disulfides. The latter compounds are of interest for the liberation of highly reactive dithiirane/thiosulfine species. With thiomorpholine, α-chlorosulfenic acid chlorides give α-chlorosulfenic acid amides.

Keywords. Diaroylmethanes; Dithio-*bis*-(diaroylmethanes); α-Chlorosulfenic acid chlorides; Sulfenamides; Acetyl diaroylchloromethyl disulfides; Dithiiranes/thiosulfines.

Neue Dithio-*bis*-(diaroylmethane) und Acetyl-diaroylchlormethyl-disulfide: attraktive Synthone und Vorläufer zur Freisetzung hochreaktiver Dithiirane oder Thiosulfine

Zusammenfassung. In einem neuen, gut handhabbaren Verfahren werden in meist sehr guter Ausbeute fünf symmetrische *para*-substituierte Diaroylmethane ((4-X–C_6H_4–CO)$_2$–CH_2; X = F, Cl, Br, CH_3 und CH_3O) und daraus zur Reinigung und Aktivierung die Kupfer(II)komplexe ihrer Enolate dargestellt. Drei Reaktionsschritte mit Dischwefeldichlorid (S_2Cl_2), Chlor und Thioessigsäure führen der Reihe nach anschließend zu neuen CH-aciden Dithio-*bis*-(diaroylmethanen), α-Chlorsulfensäurechloriden und Acetyl-diaroylchlormethyl-disulfiden. Die letzteren Verbindungen sind zur Freisetzung von hochreaktiven Dithiiran/Thiosulfin-Spezies von Interesse. Mit Thiomorpholin geben α-Chlorsulfensäurechloride α-Chlorsulfensäureamide.

Introduction

Within a series of investigations in the field of reactive sulfurorganic compounds [1, 2], the present work reports the synthesis of a group of starting materials. Besides this intention, the new compounds are proposed to be used as attractive building blocks in other sectors of organic synthesis. Dithio-*bis*-(diaroylmethanes) seem to be versatile synthons for the construction of new and sensible sulfur functions. *Inter alia*, interesting possibilities for the synthesis of α,α′-dioxothiones [3], for the preparation of α-chlorosulfenic acid chlorides [4], and for the liberation of dithiiranes/thiosulfines [5, 6] can be seen.

Results and Discussion

A series of *para*-substituted benzoic acids was transformed into the known benzoic acid chlorides **1a**–**e** and benzoic acid methyl esters **2a**–**e**. By the application of high excesses of the recyclable reagents thionyl chloride and methanol, these preparations could be performed in very high yields.

Esters **2a**–**e** and ketones **3a**–**e** were used for the synthesis of five symmetrical *para*-substituted diaroylmethanes (**4a**–**e**, Scheme 1). Compared with the classical form of the ester condensation, the applied method has several advantages: low temperature, short reaction time, easy separation from starting products, and high yields. The method is an adaptation and modification of a procedure taken from the patent literature [7].

The use of the solvents *DMSO* and *THF* is responsible for the high reaction velocity and the mildness of the conditions. The central purification step is the isolation of the solid sodium enolates of **4a**–**e**. Unreacted starting material can be simply removed by washings with ether. Substituted diaroylmethanes (symmetrical or unsymmetrical compounds can be prepared by the method) find many applications in organic synthesis. In addition, there is a wide-spread use of substituted diaroylmethanes as efficient UV light absorbing components in sun-creams.

By reaction with copper(II) acetate hydrate in methanol, the sparingly soluble greenish complexes **6a**–**e** are formed. The reaction step is useful for the purification of β-diketones (liberation with hydrochloric acid). Here, it serves for the activation to a double substitution by disulfur dichloride (S_2Cl_2) [4].

From an inspection of the crude reaction mixtures by ^{1}H NMR spectroscopy, the reaction products which are obtained in the keto form only are judged to be very clean. In the course of recrystallizations, the amount of enol forms increases. For the methoxy substituted compound **7e**, the keto form dominates all the time.

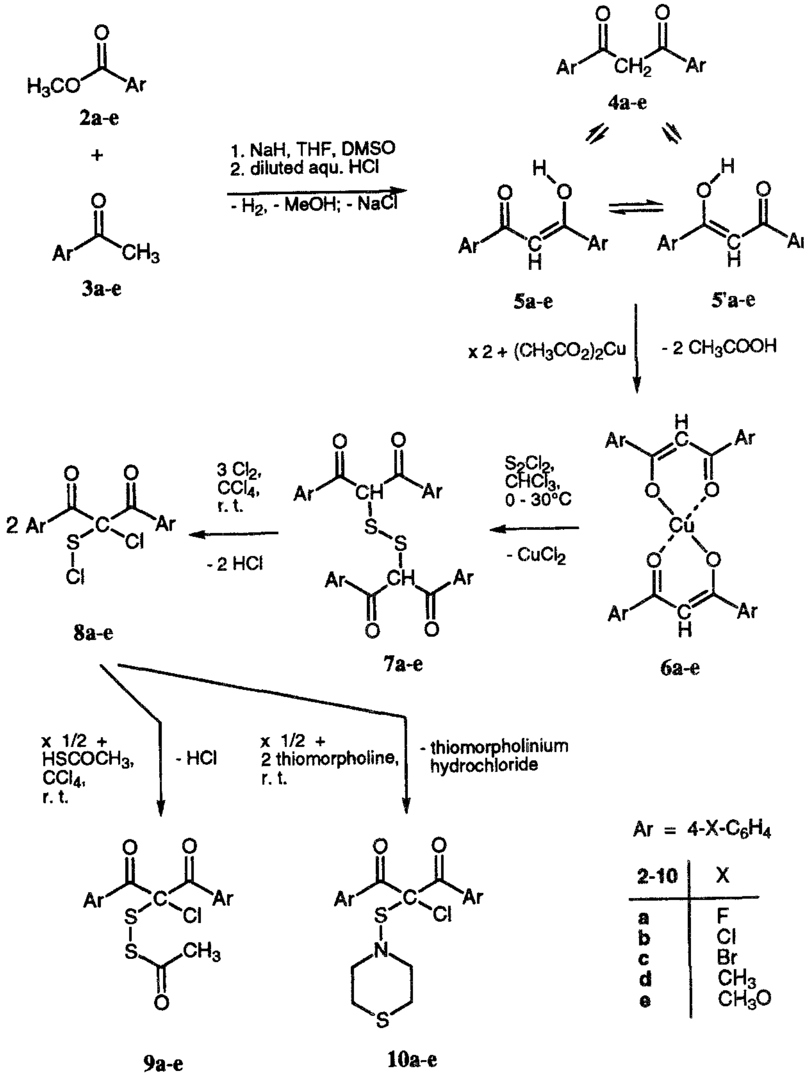
The new dithio-*bis*-(diaroylmethanes) **7a**–**e** should find several interesting applications in organic synthesis:

a. A new useful access to various heterocyclic systems with a sulfur functionality (*e.g.* transformation of **7a**–**e** into diazepines (with *o*-phenylenediamine *via* mild reduction and fission of the S–S-bond) [8–11].

b. Ring closure reactions at the two CH-acidic centres (*e.g.* with α,ω-dibromoalkanes) to form heterocycles with sulfur in the ring.

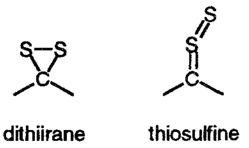
c. Preparation of reactive or sensible sulfur functionalities at the central carbon atom (*e.g.* preparation of α-chloro-sulfenylchlorides, of thiocarbonyl compounds, of precursors for the liberation of dithiiranes/thiosulfines). The last mentioned application was the stimulus for the present work.

Subsequently, the five different dithio-*bis*-(diaroylmethanes) **7a**–**e** [1] have been used for the synthesis of the α-chlorosulfenic acid chlorides **8a**–**e**. The reactions proceed with three chlorinating fissions in almost quantitative yields (Scheme 1). The ^{13}C NMR shifts of the central quarternary carbon atoms of **8a**–**e** show only small variations: $\delta = 90.55, 90.33, 90.31, 91.16$, and 91.37 ppm.



Scheme 1

After the careful removal of all traces of chlorine and a concentration of the solution, **8a–e** could be reacted with ethanethioic acid under very smooth conditions (within 5 min, Scheme 1). The products, a series of acetyl diaroylchloromethyl disulfides (**9a–e**), could be prepared in a pure form. They are needed for investigations in the field of dithiiranes/thiosulfines (Scheme 2).



Scheme 2

In comparison with similar compounds (*e.g.* derived from trichloromethane sulfenylchloride), **9a**–**e** have the advantage to give interception products without interfering rearrangements [1, 2, 6]. Interestingly, the ^{13}C NMR shifts of the central quarternary carbon atoms of **9a**–**e** show stronger variations ($\delta = 86.22, 85.88, 85.80, 87.20$, and 87.75 ppm) than their parent compounds. The structure of the reaction products is further confirmed (and an attack of ethanethioic acid at the C–Cl-group is excluded) by mass spectroscopical data (*e.g.* loss of S_2). A model for the reaction sequence $\mathbf{6} \rightarrow \mathbf{7} \rightarrow \mathbf{8} \rightarrow \mathbf{9}$ is available in the literature ($Ar = C_6H_5$) [4]. Reaction and work-up conditions have been changed for the present study. With thiomorpholine, the α-chlorosulfenic acid chlorides **8a**–**e** form α-chlorosulfenamides **10a**–**e** (Scheme 1). A part of the products was decomposed to a second type of compound with a central CH-group ($\delta(^1H) \approx 6.35$ ppm, $\delta(^{13}C) = 63.2$–63.4 ppm).

Experimental

NMR spectra were recorded on Bruker NMR spectrometers: AC 250F and AM 400WB (internal standards: *TMS* for ^{1}H NMR, $CDCl_3 = 77.00$ ppm for ^{13}C NMR). $CDCl_3$ was routinely filtered over Al_2O_3. Mass spectra were recorded using electron ionization (EI) on a Varian Mat 311A spectrometer. IR spectra were routinely taken from slurries (paraffin oil) and were recorded on a Perkin Elmer 1600 FTIR spectrometer. Melting points were measured with a Leica melting point microscope (PT100 sensor). Microanalysis was performed at the Institute of Physical Chemistry (Univ. Wien, Mikroanalytisches Laboratorium, Mag. *J. Theiner* and Mr. *S. Frenczko*). For TLC, silica gel 60 was purchased from Merck. $CHCl_3$ and CH_2Cl_2 were cleaned and dried by distillation from P_4O_{10}. Hexane was a fraction with boiling range 65–70 °C. Abbreviations: ar (aromatic), *L* (ligand), *M* (metal), qu (quarternary).

General procedure for the preparation of **1a**–**c**, **e**

Addition of an excess of thionyl chloride to the carboxylic acid, heating (later under magnetic stirring), removal of the remaining thionyl chloride by distillation at 760 torr, fractionated distillation of the product (150 mm *Vigreux* column) under vacuum.

4-Fluoro-benzoylchloride (**1a**; C_7H_4ClFO)

Thionylchloride (85.8 ml, 1.177 mol) and 35.03 g (0.250 mol) 4-fluoro-benzoic acid were heated for 2 h at 75 °C. The usual work-up yielded 37.48 g (94.6%) **1a** with b.p. 83–86 °C (20 torr), from this 33.88 g with b.p. 85–86 °C (20 torr).

4-Chloro-benzoylchloride (**1b**; $C_7H_4Cl_2O$)

Thionylchloride (85.3 ml, 1.17 mol) and 122.5 g (0.782 mol) 4-chloro-benzoic acid were heated under reflux for 36 h. The usual work-up yielded 119.8 g (0.685 mol, 88%) **1b** with b.p. 94.5 °C (9 torr).

4-Bromo-benzoylchloride (**1c**; C_7H_4BrClO)

Thionylchloride (42.9 ml, 0.588 mol) and 25.13 g (0.125 mol) 4-bromo-benzoic acid were heated to 75 °C for 3 h. The usual work-up yielded 24.70 g (90%) **1c** with b.p. 116 °C (10 torr) and m.p. 40–41 °C.

4-Methoxy-benzoylchloride (**1e**; $C_8H_7ClO_2$)

Thionylchloride (85.8 ml, 1.177 mol) and 38.04 g 4-methoxy-benzoic acid (0.250 mol) were heated to 75 °C for 3 h. The usual work-up yielded 38.37 g (0.223 mol, 89%) **1e** with b.p. 122 °C (9 torr).

General procedure for the preparation of **2a–e**

Within 30 min, the carboxylic acid chloride is added to a 100% excess of dry methanol (50 °C, magnetic stirring). Heating under reflux is continued for 2 h. The excess of methanol is distilled off at 760 torr. The product is purified by a fractionated distillation (150 mm mirrored *Vigreux* column).

4-Fluoro-benzoic acid methyl ester (**2a**; C_8H_7FO)

From 32.98 g **1a** (0.2080 mol) and 16.85 ml dry methanol (0.4160 mol), 29.17 g (0.189 mol, 91%) **2a** were obtained at 86 °C (16 torr).

4-Chloro-benzoic acid methyl ester (**2b**; $C_8H_7ClO_2$)

From 113.8 g (0.650 mol) **1b** and 41.7 g (1.30 mol) dry methanol, 106.6 g (0.625 mol, 96%) **2b** were obtained at 112 °C (15 torr, cooling water at 40 °C). On cooling, large colourless crystals (m.p.: 39–42 °C) were formed.

4-Bromo-benzoic acid methyl ester (**2c**; $C_8H_7BrO_2$)

From 24.14 g **1c** (0.110 mol, dropping funnel heated to 45 °C) and 8.91 ml dry methanol (0.220 mol), a cake of white crystals formed. Recrystallization from 15 ml dry methanol (under reflux) yielded 22.38 g **2c** (0.104 mol, 94.5%, m.p.: 77–78 °C) after vacuum drying (0.001 torr).

4-Methyl-benzoyl acid methyl ester (**2d**; $C_9H_{10}O_2$)

From 100.5 g (0.65 mol) **1d** and 41.7 g (1.30 mol) dry methanol, 86.4 g (0.595 mol, 88.5%) **2d** were obtained (b.p.: 106–107 °C, 15.5 torr; crystallizing).

4-Methoxy-benzoic acid methyl ester (**2e**; $C_9H_{10}O_3$)

From 38.12 g **1e** (0.223 mol) and 14.29 g methanol (0.446 mol), 33.71 g (0.203 mol, 91%) **2e** were obtained (b.p.: 130–132 °C, 13 torr; crystallizing).

1,3-bis-(4-Fluoro-phenyl)-propane-1,3-dione (**4a**; $C_{15}H_{10}F_2O_2$, 260.240)

Compound **4a** was prepared from 5.09 g (33 mmol) **2a**, 4.14 g (30 mmol) **3a**, and 1.33 g 55–65% NaH dispersion (33.3 mmol) in 10 g (9.1 ml) dry *DMSO* and 10 g (11.2 ml) dry *THF*. The synthesis was analogous to the preparation of **4d**. For work-up, 4.10 g 32% hydrochloric acid (1.31 g HCl = 0.36 mmol HCl) were added after dilution with distilled water. The yield of **4a** was 5.57 g (71.3%, identified by transformation to **7a**); Ref. [12]: 16%, m.p.: 109 °C (water/methanol); Ref. [13]: 50%.

1,3-bis-(4-Chloro-phenyl)-propane-1,3-dione (**4b**; $C_{15}H_{10}Cl_2O_2$, 293.149)

Compound **4b**, was prepared from 33.78 g (198 mmol) **2b** (solid), 27.83 g (180 mmol) **3b**, and 7.98 g 55–65% NaH dispersion (200 mmol) in 60 g (54.6 ml) dry *DMSO* and 60 g (67.2 ml) dry *THF*. The synthesis was analogous to the preparation of **4d** (the suspension of the starting compounds **2b** and **3b** in *DMSO* and *THF* had to be warmed up in order to dissolve **2b** completely). For work-up, 24.6 g 32% hydrochloric acid (7.86 g HCl = 0.216 mol HCl) were added after dilution with distilled water. The yield of **4b** was 42.60 g (80.7%, m.p.: 155–159 °C); Ref. [14]: 55%, m.p.: 160–161 °C; Ref. [15]: 85%.

1,3-bis-(4-Bromo-phenyl)-propane-1,3-dione (**4c**; $C_{15}H_{10}Br_2O_2$, 382.051)

Compound **4c** was prepared from 14.19 g (66 mmol) **2c** (solid), 11.94 g (60 mmol) **3c**, and 2.66 g 55–65% NaH dispersion (66.7 mmol) in 20 g (18.2 ml) dry *DMSO*, and 20 g (22.4 ml) dry *THF*. The synthesis was analogous to the preparation of **4d** (the suspension of the starting compounds **2c** and **3c** in dry *DMSO* (8 ml from the above amount) and dry *THF* (8 ml from the above amount) had to be warmed up in order to dissolve the starting compounds completely). For work-up, 8.20 g 32% hydrochloric acid (2.62 g HCl = 72 mmol HCl) were added after dilution with distilled water. The yield of **4c** was 18.60 g (81.1%, m.p.: 191.5–194.5 °C); Ref. [12]: 15%, m.p.: 184 °C; Ref. [16]: 42%.

1,3-Di-(4-tolyl)-propane-1,3-dione (**4d**; $C_{17}H_{16}O_2$, 252.313)

A solution of 24.78 g (165 mmol) **2d** (solid) and of 20.13 g (150 mmol) molecular sieve dried **3d** (liquid) in 10 ml dry *THF* and 10 ml dry *DMSO* was added dropwise (1–2 drops/s) within 50 min under vigorous magnetic stirring and under a stream of argon to a suspension of 4 g (166 mmol) NaH (from 6.67 g 55–65% NaH dispersion) in 45 ml dry *THF* and 35 ml dry *DMSO* at 3–5 °C (cooling in an ice-water bath). After the addition stirring was continued, and the temperature was raised to 20 °C within 30 min. Finally, the reaction mixture was stirred at 30 °C for 50 min. The reaction mixture was transferred to a 250 ml round bottomed flask and the solvents were removed *in vacuo* (temperature of the water bath not above 40 °C). A dark-brown fluid was formed that turned into a brown solid (sodium enolate). The solid was scrupulously digested with 120 ml dry ether and sucked off. This procedure was repeated with a 60 ml and a 40 ml portion of dry ether. Remaining ether was removed from the sand-coloured sodium enolate *in vacuo* (at 30 °C). After crushing of lumps, the solid was poured in one portion into a beaker with 400 ml ice-water. Immediately afterwards, 20.5 g 32% hydrochloric acid (6.56 g HCl = 0.18 mol HCl) were added under vigorous magnetic stirring. Flakes of a very bright solid were formed. The mother liquor remained acid. The product was sucked off, washed with 100 ml distilled water and evacuated overnight in a desiccator ($CaCl_2$ *sicc*, oil pump). The yield was 34.7 g (83.4%, characterized by the transformation to **7d**; Ref. [14]: 53%, m.p.: 127–128 °C; Ref. [15]: 90%.

1,3-bis-(4-Methoxy-phenyl)-propane-1,3-dione (**4e**; $C_{17}H_{16}O_4$, 284.312)

Compound **4e** was prepared from 10.97 g (66 mmol) **2e** (solid), 9.01 g (60 mmol) **3e**, and 2.66 g 55–65% NaH dispersion (66.7 mmol) in 20 g (18.2 ml) dry *DMSO* and 20 g (22.4 ml) dry *THF*. From these amounts, 8 ml *DMSO* and 8 ml *THF* were used for the dissolution (under slight warming) of **2e** and **3e**. The synthesis was analogous to the preparation of **4d**. For work-up, 8.20 g 32% hydrochloric acid (2.62 g HCl = 72 mmol HCl) were added after dilution with distilled water. The yield of **4e** was 12.77 g (74.8%, m.p.: 111.5–113.5 °C); Ref. [14]: 48%, m.p.: 116–117 °C; Ref. [15]: 75%; Ref. [17]: 58%, m.p.: 131–138 °C.

Copper(II)-1,3-bis-(4-fluorophenyl)-1,3-propanedionate (*M*:*L* = 1:2)
(**6a**; $C_{30}H_{18}CuF_4O_4$, 582.010)

Within 5 min, a freshly prepared solution of 9.76 g (37.50 mmol) diketone **4a** in 500 ml hot methanol (> 60 °C) was added to a solution of 9.00 g (45.10 mmol) copper(II) acetate ($(CH_3CO_2)_2Cu \cdot H_2O$) in 3000 ml hot methanol (> 60 °C) under magnetic stirring. Immediately, a pale yellowish-greenish precipitate of compound **6a** was formed. Without stirring the solution was allowed to cool down to 40 °C. After filtration, further material could be collected by concentrating the hot mother liquor in two steps to 1/3 of its volume. The combined precipitates were washed twice with methanol and dried at 80 °C. After further drying (0.01 torr, 60 °C, 3 h), 10.80 g **6a** (18.56 mmol, 99.0%) were obtained as flakes of very fine, pale yellowish-greenish crystals; m.p.: 289–292 °C (Ref. [13]: 244–245 °C). Due to electrostatic phenomena, the transfer of the dried product can become difficult (similar for **6b**–**e**). IR: ν = 1610.0, 1600.5, 1556.5, 1538.5, 1446.0, 1220.4, 1156.4, 1091.3, 1060.5, 1012.1, 840.6, 773.0 cm^{-1}.

Copper(II)-1,3-bis-(4-chlorophenyl)-1,3-propanedionate ($M{:}L = 1{:}2$)
(**6b**; $C_{30}H_{18}Cl_4CuO_4$, 647.829)

Compound **6b** was prepared similar to **6a** from 11.00 g (37.52 mmol, in 400 ml methanol) **4b** and 9.00 g (45.00 mmol, in 3000 ml methanol) copper(II) acetate. Yield: 11.10 g (91.3%) as flakes of very fine yellowish-greenish crystals; m.p.: 347–354 °C; IR: $\nu = 1588.0$ (ar C–C), 1533.6, 1312.9, 1091.0, 1012.2, 842.2, 775.8 cm^{-1}; $C_{30}H_{18}Cl_4CuO_4$ (647.829); calc.: C 55.62, H 2.80; found: C 55.33; H 2.63.

Copper(II)-1,3-bis-(4-bromophenyl)-1,3-propanedionate ($M{:}L = 1{:}2$)
(**6c**; $C_{30}H_{18}CuBr_4O_4$, 825.633)

Compound **6c** was prepared similar to **6a** from 14.33 g (37.52 mmol, dissolved/suspended in 5000 ml methanol) **4c** and 9.00 g (45.00 mmol, in 3000 ml methanol) copper(II) acetate. Yield: 13.45 g (86.8%) as flakes of very fine yellowish-greenish crystals; m.p. >350 °C; IR: $\nu = 1586.3$ (ar C–C), 1531.1, 1310.0, 1225.9, 1184.4, 1104.2, 1072.1, 1008.5, 841.7, 794.0, 774.6, 665.6 cm^{-1}; $C_{30}H_{18}Br_4CuO_4$ (825.633); calc.: C 43.64, H 2.20; found: C 43.08, H 1.91.

Copper(II)-1,3-di-(4-tolyl)-1,3-propanedionate ($M{:}L = 1{:}2$)
(**6d**; $C_{34}H_{30}CuO_4$, 566.156)

Compound **6d** was prepared similar to **6a** from 9.47 g (37.52 mmol, in 400 ml methanol) **4d** and 9.00 g (45.00 mmol, in 3000 ml methanol) copper(II) acetate. Yield: 9.22 g (86.8%) as flakes of very fine yellowish-greenish crystals; m.p.: 287–291 °C (Ref. [18]: 99%, m.p.: 295.5 °C); IR: $\nu = 1609.4$, 1588.0 (ar C–C), 1533.8, 1492.3, 1314.0, 1182.2, 1062.6, 1018.2, 942.1, 840.0, 756.6 cm^{-1}.

Copper(II)-1,3-bis-(4-methoxyphenyl)-1,3-propanedionate ($M{:}L = 1{:}2$)
(**6e**; $C_{34}H_{30}CuO_8$, 630.153)

Compound **6e** was prepared similar to **6a** from 10.67 g (37.52 mmol, in 400 ml methanol) **4e** and 9.00 g (45.00 mmol, in 3000 ml methanol) copper(II) acetate. Yield: 10.49 g (88.8%) as flakes of very fine yellowish-greenish crystals; m.p.: 288–294 °C (Ref. [19]: m.p.: 300 °C); IR: $\nu = 1604.2$, 1589.3 (ar C–C), 1539.3, 1492.5, 1325.1, 1307.4, 1263.3, 1228.4, 1175.9, 1031.2, 840.2, 782.1 cm^{-1}.

Dithio-bis-(bis-(4-fluorobenzoyl)-methane) (**7a**; $C_{30}H_{18}F_4O_4S_2$, 582.584)

8.984 g (15.4 mmol) copper complex **6a** (ground in a mortar) were transferred into the reaction flask, dried for 30 min *in vacuo* (at 50 °C), and suspended in 600 ml dry $CHCl_3$ (argon flushed before). To the cooled suspension (at 0 °C, in an ice-salt bath of −3 to −5 °C) a solution of 1.574 mmol S_2Cl_2 (15.74 ml 1 *M* S_2Cl_2 in CH_2Cl_2 and 440 ml dry $CHCl_3$, argon flushed before) was added dropwise under argon and with vigorous magnetic stirring over 3 h. After the addition, the magnetic stirring was continued for 1 h at 0 °C. Within 30 min, the reaction mixture was allowed to warm up to 10 °C, within further 30 min to 20 °C. After filtration (rinsing of the filter cake with 200 ml dry $CHCl_3$), the clear yellowish solution was concentrated *in vacuo* at 35 °C. Crystallization was initiated by the addition of hexane. Yield: 3.267 g (36.4%) white crystals of **7a** from two crops; m.p.: 131–148 °C (in another run starting from 0.2185 g **6a**, **7a** was formed in 70.3% crude yield; recrystallizations from CCl_4/hexane); IR: $\nu = 1697.7$ ($\nu_{C=O}$), 1681.3, 1668.0, 1598.7 ($\nu_{\mathrm{arC\text{-}C}}$), 1506.3, 1252.0, 1242.1, 1160.6, 1006.7, 979.5, 842.2 cm^{-1}; ^1H NMR (250 MHz): $\delta = 6.44$ (s, 2H, H–C–S), 7.12 (m, 8H, ar *meta*), 8.03 (m, 8H, ar *ortho*) ppm; ^{13}C NMR (62.9 MHz): $\delta = 65.14$ (H–C–S), 116.23 (*meta*-C, $^3J_{CF} = 22.1$ Hz), 131.27 (*ipso*-C, $^5J_{CF} = 2.95$ Hz), 131.98 (*ortho*-C, $^4J_{CF} = 9.5$ Hz), 166.33 (C–F, $^2J_{CF} = 257.6$ Hz), 189.92 (C=O) ppm; MS (190 °C): *m/e* = 319 (1, $(F\text{–}C_6H_4\text{–}CO)_2CS^+$), 290 (3), 272 (2), 260 (60), 259 (42, $(F\text{–}C_6H_4\text{–}CO)_2CH^+$), 165 (37, $C_9H_6FO_2^+$), 123 (100, $F\text{–}C_6H_4\text{–}CO^+$), 95 (57), 75 (13), 69 (24), 57 (33), 56 (20), 43 (42); $C_{30}H_{18}F_4O_4S_2$ (582.58); calc.: C 61.85, H 3.11, S 11.1; found: C 62.37, H 3.13, S 10.93.

Dithio-bis-(bis-(4-chlorobenzoyl)-methane) (**7b**; $C_{30}H_{18}Cl_4O_4S_2$, 648.403)

Compound **7b** was prepared analogously to the synthesis of **7a** from 7.392 g (11.41 mmol) **6b** and 11.64 mmol S_2Cl_2 (from 11.64 ml 1 *M* S_2Cl_2 in CH_2Cl_2). During the work-up, the solvents were removed from the filtrated reaction solution *in vacuo* (the evaporation had to be controlled carefully because of a tendency of the crude product to form a voluminous foam; this behaviour was shown by all crude products **7a**–**e**). The crude yield was almost quantitative; recrystallizations (from $CHCl_3$/hexane) gave 1.992 g (26.9%) **7a** of high purity and an additional crop of 1.981 g (26.8%, sufficient purity for further synthesis). M.p.: 132–134 °C; IR: $\nu = 1681.1$ ($\nu_{C=O}$), 1664.0, 1585.3 ($\nu_{ar\,C-C}$), 1564.1, 1278.1, 1261.3, 1092.2, 980.0, 846.3, 817.7 cm^{-1}; ^1H NMR (250 MHz): $\delta = 6.42$ (s, 2H, H–C–S), 7.44 (d, 8H, ar *ortho*, $^3J_{AB} = 8.5$ Hz), 7.93 (d, 8H, ar *meta*, $^3J_{AB} = 8.5$ Hz) ppm; ^{13}C NMR (62.9 MHz): $\delta = 65.06$ (H–C–S), 129.38 (ar C–H), 130.52 (ar C–H), 133.10 (ar qu C), 141.02 (ar qu C), 190.22 (C=O) ppm; MS (220 °C): *m*/*e* = 322 (3, $(Cl-C_6H_4-CO)_2CS^+$), 294 (23), 293 (28), 292 (39), 291 (39, $(Cl-C_6H_4-CO)_2CH^+$), 183 (11), 181 (33, $C_9H_6ClO_2^+$), 141 (54), 140 (13), 139 (100, $Cl-C_6H_4-CO^+$), 113 (21), 11 (65), 75 (31), 69 (47), 64 (16); $C_{30}H_{18}Cl_4O_4S_2$ (648.40); calc.: C 55.57, H 2.80, S 9.89; found: C 54.84, H 2.64, S 9.87.

From a crop with a high percentage of enol form: ^{13}C NMR (100.6 MHz): $\delta = 102.96$ (qu C–S), 127.97 (ar C–H), 131.00 (ar C–H), 133.91 (ar qu C), 137.91 (ar qu C), 193.34 (C=O/C–OH) ppm.

Dithio-bis-(bis-(4-bromobenzoyl)-methane) (**7c**; $C_{30}H_{18}Br_4O_4S_2$, 826.207)

Compound **7c** was prepared similar to **7a** from 9.420 g (11.41 mmol) **6c** and 11.64 mmol S_2Cl_2 (11.64 ml 1 *M* S_2Cl_2 in CH_2Cl_2). Fractional crystallization of the product from the filtrated and concentrated reaction mixture ($CHCl_3$/hexane) gave several pure crops of 4.092 g (43.4%) **7c**. M.p.: 145–161.5 °C; IR: $\nu = 1693.4$ ($\nu_{C=O}$), 1667.7, 1582.0 ($\nu_{ar\,C-C}$), 1564.4, 1275.4, 1250.0, 1177.9, 1069.6, 998.6, 977.5, 834.1 cm^{-1}; ^1H NMR (250 MHz): $\delta = 6.51$ (s, 2H, H–C–S), 7.49 (d, 8H, ar *meta*, $^3J_{AB} = 8.4$ Hz), 7.78 (d, 8H, ar *ortho*, $^3J_{AB} = 8.4$ Hz) ppm; ^{13}C NMR (62.9 MHz): $\delta = 64.95$ (H–C–S), 129.87 (ar qu C), 132.39 (ar C–H), 132.39 (ar C–H), 133.48 (ar qu C), 190.41 (C=O) ppm; MS (240 °C): *m*/*e* = 410 (2, $(^{79}Br-C_6H_4-CO)_2CS^+$), 380 (20), 379 (18, $(^{79}Br-C_6H_4-CO)_2CH^+$), 301 (3), 256 (9), 185 (100), 183 (98, $^{79}Br-C_6H_4-CO^+$), 157 (49), 155 (50, $^{79}Br-C_6H_4^+$), 97 (16), 89 (11), 76 (44), 75 (38), 69 (66); $C_{30}H_{18}Br_4O_4S_2$ (826.21); calc.: C 43.61, H 2.20, S 7.76; found: C 43.37, H 2.03, S 7.80.

Enol form: ^1H NMR (250 MHz, mixed with keto form): $\delta = 7.32$ (d, 8H, ar *meta*, $^3J_{AB} = 8.4$ Hz), 7.56 (d, 8H, ar *ortho*, $^3J_{AB} = 8.4$ Hz), 14.82 (s, 2H, OH) ppm; ^{13}C NMR (62.9 MHz, C–S signal miss.): $\delta = 126.46$ (ar qu C), 130.96 (ar C–H), 131.13 (ar C–H), 134.33 (ar qu C), 193.48 (C=O/C–OH) ppm.

Dithio-bis-(di-(4-toluyl)-methane) (**7d**; $C_{34}H_{30}O_4S_2$, 566.730)

Compound **7d** was prepared similar to **7a** from 8.740 g (15.44 mmol) **6d** and 15.74 mmol S_2Cl_2 (15.74 ml 1 *M* S_2Cl_2 in CH_2Cl_2). The filtrated and concentrated reaction mixture (yellowish solution) formed a cake of a crystalline crude product by cooling to 0 °C. It was recrystallized from hot (40–50 °C) $CHCl_3$ and hexane (main component) yielding 5.309 g (60.7%) **7d**. From the mother liquor, an additional crop of 0.6704 g (7.6%) could be obtained. M.p. of the major crop: 150–179 °C; IR: $\nu = 1677.6$ ($\nu_{C=O}$), 1662.5, 1602.8 ($\nu_{ar\,C-C}$), 1281.0, 1266.0, 1179.4, 982.5, 814.3 cm^{-1}; ^1H NMR (250 MHz): $\delta = 2.37$ (s, 12H, CH_3), 6.33 (s, 2H, H–C–S), 7.21 (d, 8H, ar *meta*, $^3J_{AB} = 8.3$ Hz), 7.87 (d, 8H, ar *ortho*, $^3J_{AB} = 8.3$ Hz) ppm; ^{13}C NMR (62.9 MHz): $\delta = 21.69$ (q, CH_3), 65.75 (H–C–S), 129.34 (ar C–H), 129.55 (ar C–H), 132.60 (*ipso*-C), 145.03 (*para*-C), 191.19 (C=O) ppm; MS: *m*/*e* = 282 (42, $(H_3C-C_6H_4-CO)_2CS^+$), 252 (26, $C_{17}H_{16}O_2^+$), 251 (29), 161 (11, $C_{10}H_9O_2^+$), 120 (12), 119 (100, $H_3C-C_6H_4-CO^+$), 91 (55, $C_7H_7^+$), 69 (28), 65 (23, $C_5H_5^+$), 64 (14); $C_{34}H_{30}O_4S_2$ (566.73); calc.: C 72.06, H 5.34, S 11.31; found: C 71.64, H 5.26, S 11.78.

Dithio-bis-(bis-(4-methoxybenzoyl)-methane) (**7e**; $C_{34}H_{30}O_8S_2$, 630.727)

Compound **7e** was prepared from 7.190 g (11.41 mmol) **6e** and 11.64 mmol S_2Cl_2 (11.64 ml 1 *M* S_2Cl_2 in CH_2Cl_2) similar to the synthesis of **7a**. The filtrated and evaporated reaction mixture formed an oil.

Dissolution in hot ethanol and cooling gave two crops of clean **7e** with 4.707 g (65.4%); an additional crop was obtained from the mother liquor (0.5822 g, 8.1%). M.p. (main crops): 79–81 °C; IR: $\nu = 1681.5$ ($\nu_{C=O}$), 1659.5, 1651.4, 1594.9 ($\nu_{arC\text{-}C}$), 1573.4, 1510.0, 1315.8, 1256.1, 1168.0, 1024.7, 845.6 cm^{-1}; ^{1}H NMR (250 MHz): $\delta = 3.83$ (s, 12H, OCH$_3$), 6.23 (s, 2H, H–C–S), 6.87 (d, 8H, ar *meta*, $^3J_{AB} = 8.9$ Hz), 7.96 (d, 8H, ar *ortho*, $^3J_{AB} = 8.9$ Hz) ppm; ^{13}C NMR (100.6 MHz): $\delta = 55.47$ (q, OCH$_3$), 65.64 (H–C–S), 114.03 (*meta*-C), 127.96 (*ipso*-C), 131.61 (*ortho*-C), 164.14 (*para*-C), 190.11 (C=O) ppm; MS: *m/e* = 314 (9, (H$_3$CO–C$_6$H$_4$–CO)$_2$CS$^+$), 284 (52, C$_{17}$H$_{16}$O$_4^+$), 283 (22), 177 (10, C$_{10}$H$_9$O$_3^+$), 136 (20), 135 (100, H$_3$CO–C$_6$H$_4$–CO$^+$), 109 (10), 108 (48, C$_7$H$_8$O$^+$), 107 (21), 92 (23), 77 (37, C$_6$H$_5^+$), 69 (12), 64 (18); C$_{34}$H$_{30}$O$_8$S$_2$ (630.73); calc.: C 64.75, H 4.79, S 10.17; found: C 64.19, H 4.76, S 11.03.

Dithio-bis-(dibenzoylmethane) (**7f**)

The NMR spectra of **7f** [4] were recorded for comparison with the new compounds **7a**–**e**. ^{1}H NMR (250 MHz): $\delta = 6.51$ (s, 2H, H–C–S), 7.44 (dd, 8H, ar *meta*), 7.57 (t, 2H, ar *para*, $^3J = 7.3$ Hz), 8.00 (d, 8H, ar *ortho*, $^3J = 7.5$ Hz) ppm; ^{13}C NMR (62.9 MHz): $\delta = 65.34$ (H–C–S), 128.17 (ar C–H), 128.90 (ar C–H), 132.96 (*ipso*-C), 134.04 (*para*-C), 191.51 (C=O) ppm.

Preparation of **8a**–**e**; *general procedure*

1 mmol dithio-*bis*-(diaroylmethane) **7a**–**e** is transferred to a 100 ml round-bottomed flask and is suspended/dissolved in 40 ml dry CCl$_4$ (for **7c** in 50 ml dry CCl$_4$ and 10 ml dry CH$_2$Cl$_2$). Under vigorous magnetic stirring, a stream of dry Cl$_2$ (CaCl$_2$) is bubbled through the suspension/solution at r.t. until clear, yellow solution is obtained (5–10 min). Chlorine gas that is not absorbed in the reaction flask is destroyed (security washing bottle, washing bottle with an aqueous sodium sulfite solution). Now, a strong stream of dry argon (CaCl$_2$) is bubbled through the reaction solution until most of the chlorine is expelled (very weak yellowish colour, about 15–20 min). Finally, the solution is concentrated *in vacuo* (8 torr) to about 1/8 of its volume (30 °C water bath).

Complete removal of the solvent *in vacuo* for reactions on a 0.15 mmol scale gave almost quantitative crude yields. From ^{1}H NMR and ^{13}C NMR spectroscopy, the purities were estimated to be higher than 95%.

After their preparation, compounds **8a**–**e** were immediately used for the syntheses described below. After a solution of **8b** had been evaporated for IR spectroscopy (neat, between NaCl plates), the oil was rinsed with CDCl$_3$. No remarkable decomposition could be detected by ^{1}H NMR spectroscopy. Both spectra showed a small impurity attributed to an RSH species.

Bis-(4-fluorobenzoyl)-chloromethanesulfenyl chloride (**8a**; C$_{15}$H$_8$Cl$_2$F$_2$O$_2$S, 361.190)

IR (neat): $\nu = 3188.3$, 3110.9, 3079.4, 1697.3 ($\nu_{C=O}$), 1660.2, 1597.1 ($\nu_{arC\text{-}C}$), 1507.1, 1410.9, 1244.4, 1160.6, 1009.9, 854.2 cm^{-1}; ^{1}H NMR (250 MHz): $\delta = 7.05$ (m, 4H, ar *meta*), 8.01 (m, 4H, ar *ortho*) ppm; ^{13}C NMR (62.9 MHz): $\delta = 90.55$ (Cl–C–SCl), 116.34 (*meta*-C, $^3J_{CF} = 22.2$ Hz), 128.59 (*ipso*-C, $^5J_{CF} = 3.1$ Hz), 132.88 (*ortho*-C, $^4J_{CF} = 9.8$ Hz), 166.47 (C–F, $^2J_{CF} = 259.7$ Hz), 186.26 (C=O) ppm.

Bis-(4-chlorobenzoyl)-chloromethanesulfenyl chloride (**8b**; C$_{15}$H$_8$Cl$_4$O$_2$S, 394.099)

IR (neat): $\nu = 3095.2$, 3042.0, 1695.0 ($\nu_{C=O}$), 1662.3, 1587.5 ($\nu_{arC\text{-}C}$), 1567.0, 1488.3, 1401.8, 1257.0, 1216.2, 1095.2, 1011.7, 845.7, 734.6 cm^{-1}; ^{1}H NMR (250 MHz): $\delta = 7.34$ (d, 4H, ar *ortho*, $^3J_{AB} = 6.9$ Hz), 7.91 (d, 4H, ar *meta*, $^3J_{AB} = 6.9$ Hz) ppm; ^{13}C NMR (62.9 MHz): $\delta = 90.33$ (Cl–C–SCl), 129.34 (ar C–H), 130.42 (ar qu C), 131.19 (ar C–H), 141.71 (ar qu C), 186.46 (C=O) ppm.

Bis-(4-bromobenzoyl)-chloromethanesulfenyl chloride (**8c**; C$_{15}$H$_8$Br$_2$Cl$_2$O$_2$S, 483.001)

IR (neat): $\nu = 3094.4$, 3036.4, 1697.3 ($\nu_{C=O}$), 1660.3, 1583.0 ($\nu_{arC\text{-}C}$), 1564.1, 1485.1, 1396.7, 1255.7, 1216.8, 1182.2, 1074.0, 1008.6, 842.7 cm^{-1}; ^{1}H NMR (250 MHz): $\delta = 7.51$ (d, 4H, ar *meta*, $^3J_{AB} = 7.9$ Hz), 7.81 (d, 4H, ar *ortho*, $^3J_{AB} = 7.9$ Hz) ppm; ^{13}C NMR (62.9 MHz): $\delta = 90.31$ (Cl–C–SCl), 130.70 (ar qu C), 130.82 (ar qu C), 131.18 (ar C–H), 132.36 (ar C–H), 186.64 (C=O) ppm.

Di-(4-toluyl)-chloromethanesulfenyl chloride (**8d**; $C_{17}H_{14}Cl_2O_2S$, 353.263)

IR (neat): $\nu = 3035$, 2953.1, 2921.4, 2865.4, 1693.4 ($\nu_{C=O}$), 1651.9, 1603.1 ($\nu_{ar\,C\text{-}C}$), 1569.8, 1265.1, 1224.6, 1182.4, 1004.9, 840.4, 711.7 cm^{-1}; ^{1}H NMR (250 MHz): $\delta = 2.315$ (s, 6H, CH_3), 7.14 (d, 4H, ar *meta*, $^3J_{AB} = 8.2$ Hz), 7.86 (d, 4H, ar *ortho*, $^3J_{AB} = 8.2$ Hz) ppm; ^{13}C NMR (62.9 MHz): $\delta = 21.70$ (q, CH_3), 91.16 (Cl–C–SCl), 129.54 (ar C–H), 129.75 (*ipso*-C), 130.03 (ar C–H), 146.06 (*para*-C), 187.41 (C=O) ppm.

Bis-(4-methoxybenzoyl)-chloromethanesulfenyl chloride (**8e**; $C_{17}H_{14}Cl_2O_4S$, 385.262)

IR (neat): $\nu = 3078.4$, 3011.1, 2968.6, 2936.1, 2841.2, 1684.4 ($\nu_{C=O}$), 1646.3, 1597.8 ($\nu_{ar\,C\text{-}C}$), 1571.4, 1511.4, 1316.0, 1266.8, 1234.6, 1171.4, 1027.0, 848.3, 732.3 cm^{-1}; ^{1}H NMR (250 MHz): $\delta = 3.79$ (s, 6H, OCH_3), 6.81 (d, 4H, ar *meta*, $^3J_{AB} = 8.9$ Hz), 7.97 (d, 4H, ar *ortho*, $^3J_{AB} = 8.9$ Hz) ppm; ^{13}C NMR (62.9 MHz): $\delta = 55.49$ (q, OCH_3), 91.37 (Cl–C–SCl), 114.09 (*meta*-C), 124.92 (*ipso*-C), 132.52 (*ortho*-C), 164.64 (*para*-C), 186.46 (C=O) ppm.

Preparation of **9a–e**; *general procedure*

148.9 µl (2 mmol = 158.6 mg, 96% content) ethanethioic acid is added within 30 seconds to a freshly prepared solution of diaroyl-chloromethanesulfenyl chloride **8a–e** (2 mmol, CCl_4) under magnetic stirring. After 2 min at r.t., the reaction mixture is heated to 50 °C for 5 min. The solvent and unreacted ethanethioic acid are evaporated *in vacuo*. The recrystallized products (*vide infra*) were stored at 4 °C. In the course of several weeks no decomposition could be detected.

Acetyl-(bis-(4-fluorobenzoyl)-chloromethyl)-disulfide (**9a**; $C_{17}H_{11}ClF_2O_3S_2$, 400.842)

For crystallization from a synthesis that follows the general procedure, the crude product is dissolved in 1.25 ml ether and 0.75 ml toluene. Storage at 4 °C leads to crystallization. The crystals are washed twice with 1 ml portions of hexane. After filtration and evaporation of the solvents (0.1 torr), 464.8 mg white crystals are collected; yield of the recrystallized product: 58%. A second crop gives another 99.1 mg (12%). 340.4 mg from the first crop are again recrystallized (1.25 ml toluene/4 ml hexane/cooling): m.p.: 111–113 °C; R_f (SiO_2, acetic acid ester:hexane = 1:4) = 0.29; IR: $\nu = 1741.9$ ($\nu_{C=O}$), 1668.2, 1588.8 ($\nu_{ar\,C\text{-}C}$), 1239.5, 1160.5, 1102.9, 852.6 cm^{-1}; ^{1}H NMR (250 MHz): $\delta = 2.41$ (s, 3H, H_3C–C=O), 7.02 (m, 4H, ar *meta*), 7.97 (m, 4H, ar *ortho*) ppm; ^{13}C NMR (62.9 MHz): $\delta = 28.98$ (q, H_3C–C=O), 86.22 (Cl–C–SS), 115.98 (*meta*-C, $^3J_{CF} = 22.1$ Hz), 129.22 (*ipso*-C, $^5J_{CF} = 3.2$ Hz), 132.85 (*ortho*-C, $^4J_{CF} = 9.7$ Hz), 166.00 (C–F, $^2J_{CF} = 258.4$ Hz), 185.65 (C=O), 190.98 (S–C=O) ppm; MS (150 °C): $m/e = 358$ (1, $M-C_2H_2O$), 336 (4, $M-S_2$), 294 (18, $M-C_2H_2OS_2$), 123 (100, $F-C_6H_4-CO^+$), 95 (45), 43 (65); $C_{17}H_{11}ClF_2O_3S_2$ (400.84); calc.: C 50.94, H 2.77, S 16.00; found: C 50.88, H 2.67, S 15.90.

Acetyl-(bis-(4-chlorobenzoyl)-chloromethyl)-disulfide (**9b**; $C_{17}H_{11}Cl_3O_3S_2$, 433.752)

For crystallization from a synthesis that follows the general procedure, the crude product is dissolved in ether. Slow evaporation of the solvent under cooling leads to crystallization. The crystals are washed twice with 1 ml portions of hexane. After filtration and evaporation of solvents, 680.9 mg white crystals are collected; yield of the recrystallized products: 79%. A second crop gives another 45.5 mg (5%) 503.9 mg from the first crop are again recrystallized (2.75 ml toluene/5.5 ml hexane/cooling): m.p.: 126.5–127.5 °C; R_f (SiO_2, acetic acid ester:hexane = 1:4) = 0.35; IR: $\nu = 1738.9$ ($\nu_{C=O}$), 1667.1, 1585.8 ($\nu_{ar\,C\text{-}C}$), 1566.4, 1247.7, 1214.8, 1176.2, 1091.3, 1007.4, 997.2, 846.1, 738.0, 725.8 cm^{-1}; ^{1}H NMR

(250 MHz): $\delta = 2.41$ (s, 3H, H_3C–C=O), 7.32 (d, 4H, ar *meta*, $^3J_{AB} = 9.0$ Hz), 7.87 (d, 4H, ar *ortho*, $^3J_{AB} = 9.0$ Hz) ppm; ^{13}C NMR (62.9 MHz): $\delta = 29.00$ (q, H_3C–C=O), 85.88 (Cl–C–SS), 129.06 (ar C–H), 131.13 (ar qu C), 131.32 (ar C–H), 140.91 (ar qu C), 185.91 (C=O), 190.92 (S–C=O) ppm; MS (110 °C): *m/e* = 432 (0.3, M^+), 390 (8, M–C_2H_2O), 368 (45, M–S_2), 328 (5), 326 (5, M–$C_2H_2OS_2$), 291 (2), 185 (4), 183 (5), 141 (30), 139 (100, Cl–C_6H_4–CO^+), 111 (40, $C_6H_4Cl^+$), 75 (21), 64 (11), 43 (64); $C_{17}H_{11}Cl_3O_3S_2$ (433.75); calc.: C 47.07, H 2.56, S 14.78; found: C 47.06, H 2.46, S 14.30.

Acetyl-(bis-(4-bromobenzoyl)-chloromethyl)-disulfide (**9c**; $C_{17}H_{11}Br_2ClO_3S_2$, 522.654)

For crystallization from a synthesis that follows the general procedure, the crude product is dissolved in toluene; hexane is added. The crystals are washed twice with 1 ml portions of hexane. After filtration and evaporation of solvents (0.1 torr), 886.0 mg crystals (whitish powder) are collected; yield of the recrystallized product: 85%. A second crop gives another 7.7 mg (1%). 551.3 mg from the first crop are again recrystallized (8 ml toluene/8 ml hexane/cooling): m.p.: 148–150 °C; R_f (SiO_2, acetic acid ester:hexane = 1:4) = 0.36; IR: $\nu = 1736.4$ ($\nu_{C=O}$), 1666.7, 1581.8 ($\nu_{ar\,C\text{-}C}$), 1562.7, 1377.6, 1247.3, 1215.7, 1177.2, 1106.7, 1072.7, 1005.9, 995.5, 844.0, 727.9, 717.8 cm^{-1}; ^{1}H NMR (250 MHz): $\delta = 2.41$ (s, 3H, H_3C–C=O), 7.49 (d, 4H, ar *meta*, $^3J_{AB} = 8.4$ Hz), 7.78 (d, 4H, ar *ortho*, $^3J_{AB} = 8.4$ Hz) ppm; ^{13}C NMR (62.9 MHz): $\delta = 29.00$ (q, H_3C–C=O), 85.80 (Cl–C–SS), 129.83 (ar qu C), 131.34 (ar C–H), 131.54 (ar qu C), 132.07 (ar C–H), 186.11 (C=O), 190.90 (S–C=O) ppm; MS (240 °C): *m/e* = 480 (2), 478 (1, M–C_2H_2O), 458 (7), 456 (3, M–S_2), 418 (19), 416 (24), 414 (12, M–$C_2H_2OS_2$), 186 (14), 185 (86), 184 (14), 183 (88, Br–C_6H_4–CO^+), 157 (66), 155 (64, $C_6H_4Br^+$), 76 (55), 75 (44), 64 (22), 50 (22), 43 (100); $C_{17}H_{11}Br_2ClO_3S_2$ (522.65); calc.: C 39.07, H 2.12, S 12.27; found: C 39.44, H 2.07, S 11.80.

Acetyl-(di-(4-toluyl)-chloromethyl)-disulfide (**9d**; $C_{19}H_{17}ClO_3S_2$, 392.915)

For crystallization from a synthesis that follows the general procedure, the crude product is dissolved in a small amount of toluene. The addition of cyclohexane under cooling leads to crystallization. The crystals are washed twice with 1 ml portions of hexane. After filtration and evaporation of solvents (0.1 torr), 367.6 mg cream-coloured crystals are collected; yield of the recrystallized product: 55.9%. A second crop gives another 134.0 mg (20%). 294.9 mg from the first crop are again recrystallized (2 ml toluene/9 ml hexane/cooling): m.p.: 125–127 °C; R_f (SiO_2, acetic acid ester:hexane = 1:4) = 0.27; IR: $\nu = 1738.3$ ($\nu_{C=O}$), 1667.2, 1602.0 ($\nu_{ar\,C\text{-}C}$), 1568.1, 1255.5, 1239.9, 1224.7, 1189.8, 1178.3, 1104.4, 1029.0, 1002.2, 843.3, 713.0, 704.5 cm^{-1}; ^{1}H NMR (250 MHz): $\delta = 2.30$ (s, 6H, CH_3), 2.40 (s, 3H, H_3C–C=O), 7.11 (d, 4H, ar *meta*, $^3J_{AB} = 8.4$ Hz), 7.83 (d, 4H, ar *ortho*, $^3J_{AB} = 8.4$ Hz) ppm; ^{13}C NMR (62.9 MHz): $\delta = 21.65$ (q, CH_3), 28.88 (q, H_3C–C=O), 87.20 (Cl–C–SS), 129.29 (ar C–H), 130.15 (ar C–H), 130.36 (*ipso*-C), 145.20 (*para*-C), 186.72 (C=O), 191.53 (S–C=O) ppm; MS (170 °C): *m/e* = 350 (0.5, M–C_2H_2O), 328 (3), 286 (6, M–$C_2H_2OS_2$), 271 (2), 251 (2), 119 (100, H_3C–C_6H_4–CO^+), 91 (43, $C_7H_7^+$), 65 (15, $C_5H_5^+$), 43 (29); $C_{19}H_{17}ClO_3S_2$ (392.92); calc.: C 58.08, H 4.36, S 16.32; found: C 58.47, H 4.43, S 16.22.

Acetyl-(bis-(4-methoxybenzoyl)-chloromethyl)-disulfide (**9e**; $C_{19}H_{17}ClO_5S_2$, 424.914)

For crystallization from a synthesis that follows the general procedure, the crude product is dissolved in a small amount of toluene. The addition of hexane under cooling leads to crystallization. The crystals are washed twice with 1 ml portions of hexane. After filtration and evaporation of solvents (0.1 torr), 618.0 mg cream-coloured crystals are collected; yield of the recrystallized product: 73%. A second crop gives another 54.2 mg (6%): 294.9 mg from the first crop are again recrystallized (6 ml toluene/8 ml hexane/cooling): m.p.: 123–125 °C; R_f (SiO_2, acetic acid ester:hexane = 1:4) = 0.09; IR: $\nu = 1737.0$ ($\nu_{C=O}$), 1673.0, 1651.5, 1597.6 ($\nu_{ar\,C\text{-}C}$), 1263.4, 1235.7, 1184.3, 1167.8, 1104.0, 1034.1, 848.5 cm^{-1}; ^{1}H NMR (250 MHz): $\delta = 2.40$ (s, 3H, H_3C–C=O), 3.79 (s, 6H, OCH_3), 6.79 (d, 4H, ar *meta*, $^3J_{AB} = 9.1$ Hz), 7.93 (d, 4H, ar *ortho*, $^3J_{AB} = 9.1$ Hz) ppm; ^{13}C NMR (62.9 MHz): $\delta = 28.89$ (q, H_3C–C=O), 55.49 (q, OCH_3), 87.75 (Cl–C–SS), 113.87 (*meta*-C), 125.63 (*ipso*-C), 132.56 (*ortho*-C), 164.09

(*para*-C), 185.79 (C=O), 191.70 (S–C=O) ppm; MS (200 °C): *m/e* = 362 (5), 360 (15, M–S_2), 318 (22, M–$C_2H_2OS_2$), 136 (13), 135 (100, $H_3CO–C_6H_4–CO^+$), 108 (34), 107 (18, $C_7H_7O^+$), 92 (12), 77 (22.5, $C_6H_5^+$), 43 (25); $C_{19}H_{17}ClO_5S_2$ (424.91); calc.: C 53.71, H 4.03, S 15.09; found: C 53.29, H 4.03, S 14.29.

Acetyl-dibenzoylchloromethyl-disulfide (**9f**; $C_{15}H_{10}ClO_3S_2$, 337.816)

^{1}H NMR (250 MHz): $\delta = 2.42$ (s, 3H, H_3C–C=O), 7.33 (dd, 4H, ar *meta*), 7.47 (t, 2H, ar *para*, $^3J = 7.3$ Hz), 7.93 (d, 4H, ar *ortho*, $^3J = 7.8$ Hz) ppm; ^{13}C NMR (62.9 MHz): $\delta = 28.99$ (q, H_3C–C=O), 86.55 (Cl–C–SS), 128.57 (*meta*-C), 130.00 (*ortho*-C), 132.94 (*ipso*-C), 134.04 (*para*-C), 187.09 (C=O), 191.34 (S–C=O) ppm.

Reactions of 0.15 **8a–e** *with 0.30 mmol thiomorpholine in* CCl_4*:*
examination of the solutions by ^{13}*C NMR*

Thiomorpholine

^{13}C NMR (62.9 MHz): $\delta = 28.03$ (SCH_2), 47.59 (NCH_2) ppm.

Bis-(4-fluorobenzoyl)-chloro-methanesulfenthiomorpholide (**10a**; $C_{19}H_{16}ClF_2NO_2S_2$, 427.911)

^{13}C NMR (62.9 MHz): $\delta = 28.46$ (SCH_2), 59.25 (NCH_2), 88.26 (CCl), 115.91 (CH, $^3J = 115.9$ Hz), 129.71 (C-1), 132.63 (CH, $^4J = 9.4$ Hz), 165.82 (C-4, $^2J = 257.9$ Hz), 187.43 (C=O) ppm.

Bis-(4-chlorobenzoyl)-chloro-methanesulfenthiomorpholide (**10b**; $C_{19}H_{16}Cl_3NO_2S_2$, 460.821)

^{13}C NMR (62.9 MHz): $\delta = 28.50$ (SCH_2), 59.28 (NCH_2), 87.92 (CCl), 129.05 (CH), 131.17 (CH), 131.65 (C-1), 140.59 (C-4), 187.74 (C=O) ppm.

Bis-(4-bromobenzoyl)-chloro-methanesulfenthiomorpholide (**10c**; $C_{19}H_{16}ClBr_2NO_2S_2$, 549.723)

^{13}C NMR (62.9 MHz): $\delta = 28.53$ (SCH_2), 59.32 (NCH_2), 88.6 (CCl), 129.50 (C-1), 131.23 (CH), 132.08 (CH), 132.40 (C-4), 187.96 (C=O) ppm.

Di-(4-toluyl)-chloro-methanesulfenthiomorpholide (**10d**; $C_{21}H_{22}ClNO_2S_2$, 419.984)

^{13}C NMR (62.9 MHz): $\delta = 28.50$ (SCH_2), 59.28 (NCH_2), 87.92 (CCl), 129.34 (CH), 129.55 (CH; maybe 129.95 or 129.24), 130.95 (C-1), 144.83 (C-4), 188.52 (C=O) ppm.

Bis-(4-methoxybenzoyl)-chloro-methanesulfenthiomorpholide (**10e**; $C_{21}H_{22}ClNO_4S_2$, 451.983)

^{13}C NMR (62.9 MHz): $\delta = 28.42$ (SCH_2), 59.12 (NCH_2), 89.96 (CCl), 113.78 (CH-3), 132.28 (CH-2), 126.62 (C-1), 163.83 (C-4), 187.53 (C=O) ppm.

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