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PREPARATION OF UNSYMMETRICAL DISULFIDES BY USING SULFINES[1]

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Abstract—Acidolytic cleavage of unsymmetrically substituted dithioacetal monoxides, ArCH(SR)S(O)Me has been used to prepare linear unsymmetrical disulfides RSSMe. Disproportionation was suppressed by the addition of a small amount of benzyl mercaptan. The required starting materials were conveniently obtained from appropriately substituted sulfines ArC(=SO)SR and methyl lithium. The following disulfides were prepared: R = n-C_4H_9 (73.5%), n-C_7H_{15} (78%), Ph (77.3%), AcO$(CH_2)_{10}$ (81.5%).

The unsymmetrical dithioacetal PhCH(SEt)SC_7H_{15}-n gave upon oxidation with one equivalent of peracid a mixture of two dithioacetal monoxides which on treatment with $HClO_4$ led to three disulfides. This result is discussed in term of the mechanism of acidolysis.

The synthesis of unsymmetrical disulfides has attracted considerable attention as is evident from the number of new methods of preparation that have been reported for these compounds. Unsymmetrical disulfides have been prepared by the reaction of thiols[2] or silylated thiols[3] with sulfenyl halides, by reaction of thiols with sulfenimides,[4] sulfenyl thiocyanates,[5] sulfenyl hydrazides,[6] sulfenyl thiocarbonates,[7] thiosulfates (Bunte salts),[8,9] thiosulfonates,[10] thiolsulfinates,[11] alkylthio-dialkylsulfonium salts[12] and thionitrites.[13] The latter method seems to be most general, although it requires treatment of a thiol with a strict equimolar amount of dinitrogen tetroxide. In spite of the variety of methods mentioned above the synthesis of unsymmetrical disulfides is difficult due to the great propensity of these compounds to undergo disproportionation both under basic and acidic conditions.[14]

As part of our study of the synthetic utility of sulfines we recently described a convenient method for the preparation of dithioacetal monoxides from sulfines derived by monoxidation of dithiocarboxylic esters.[15] Previously, we used these dithioacetal monoxides in nucleophilic acylation reactions. This paper deals with their application in the synthesis of unsymmetrical disulfides.

The acidolysis of dithioacetal monoxides leading to aldehydes or ketones is well known.[16] However, little attention has been given to the specific nature of the disulfides formed as by-products during this carbonyl demasking process. The only examples known using an acidolytic cleavage of dithioacetal monoxides to prepare disulfides have been reported by Kishi *et al.*[17] (cyclic disulfide present in epidithiodiketopiperazines like gliotoxine) and Harrison *et al.*[18] (holomycin, a 5-membered ring disulfide).

The reaction sequence designed for the present study is pictured in Scheme 1. The required dithioester 1 was prepared either by alkylation of sodium dithio-*p*-toluate with the alkyl halide of choice, or from *p*-tolunitrile upon reaction with an appropriate thiol in the presence of HCl and subsequent treatment with hydrogen sulfide in pyridine. The ester 1 was converted into a mixture of *E*- and *Z*-sulfines (2) by oxidation with *m*-chloroperbenzoic acid.[19,20] The reaction of sulfines with an equimolar amount of methyllithium was performed at −78° in THF solution. Quenching with aqueous NH_4Cl-solution and extraction with ether yielded the crude dithioacetal monoxides (3). Since compounds of this type having a long alkyl chain appeared to be rather unstable in the crude state, they needed immediate purification. For example, we obtained a yield of 72% pure *n*-heptylthio(*p*-tolyl)-methyl methyl sulfoxide (3b) when the crude product, in ether solution, was dried over $MgSO_4/Na_2SO_4$ for 2 hr and then quickly chromatographed. However, the yield dropped to 40% when the crude product was stored overnight.

In connection with the aforementioned easy disproportionation of unsymmetrical disulfides the acidolysis of dithioacetal monoxides (3) needs to be critically controlled. Kice and Ekman found during their investigation of acid-catalyzed disproportionation of unsymmetrical disulfides that such a reaction could be completely inhibited for a significant period of time by adding very small amounts of mercaptans.[14] Accordingly, the conversion of 3 to 4 and 5 was carried out in the presence of a small amount of benzyl mercaptan.[b] We used the strong acid catalyst perchloric acid, which enabled us to perform the reaction in a very short time, viz. not exceeding 10 min. The progress of the reaction was monitored by TLC. After completion of the reaction quenching with $NaHCO_3$ aq and chromatography gave the desired unsymmetrical disulfides (5) and *p*-tolualdehyde (4) in good yields. GLC analysis revealed that these disulfides were contaminated with negligible amounts (< 1%) of symmetrical disulfides RSSR.

The synthetic pathway described above was also applied for the preparation of 11,12-dithiatridecyl acetate (5d) which is of importance in connection with the study of the sex pheromone receptors of the European corn borer and the red-banded leaf-roller moths.[c] The full reaction sequence is outlined in Scheme 2. The required dithioester 1d was prepared from sodium dithio-*p*-toluate

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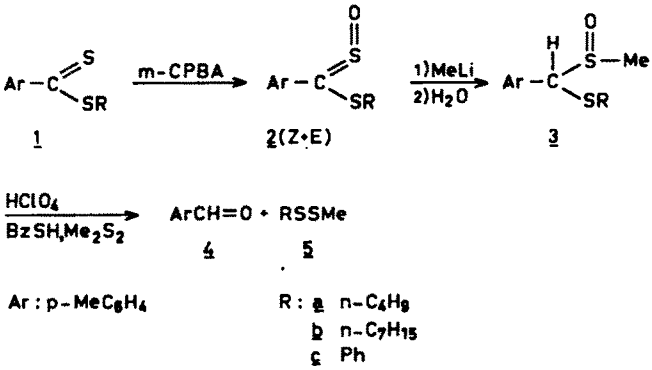
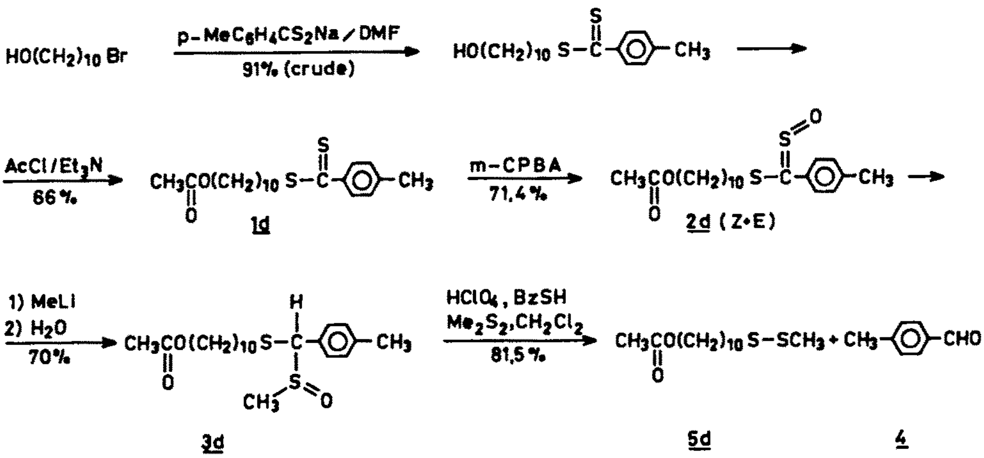
[b] A few mililters of Me_2S_2 were also added to hamper disulfide disproportionation during the work-up under slightly basic conditions. Experiments, in which this addition was omitted, led to unsymmetrical disulfides containing up to 4% of symmetrical disulfides RSSR.



Scheme 1.



Scheme 2.

and 10-bromodecanol[21] followed by acylation with acetyl chloride. Oxidation with *m*-chloroperbenzoic acid gave sulfine **2d** ($E + Z$), which upon a chemoselective reaction with methyl-lithium resulted in dithioacetal monoxide (**3d**). Acidolysis gave a mixture of the desired **5d** and *p*-tolualdehyde (**4**). Separation could only be achieved by chromatography on Bio-beads SX-12 (separation based on molecular size).

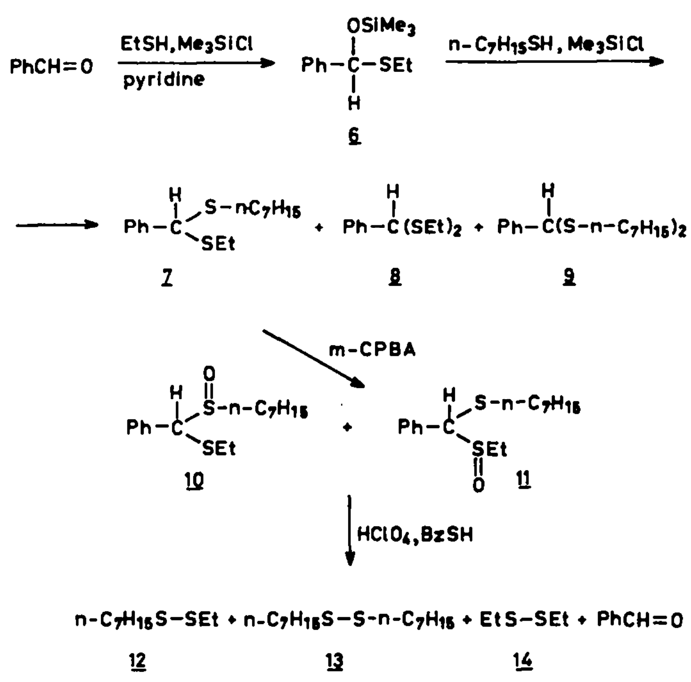
In design, the unsymmetrically substituted dithioacetal monoxides used in this synthetic approach can be prepared by oxidation of unsymmetrical dithioacetals. By adopting the method described by Ong and Chan[22] for symmetrical dithioacetals, O-trimethylsilyl hemithioacetal (**6**) was treated with *n*-heptanethiol in the presence of trimethylsilyl chloride. However, instead of a single compound **7** we obtained a mixture of three dithioacetals, namely **7**, **8** and **9** (Scheme 3).

This result can readily be explained by taking into account that hemithioacetal (**6**) will suffer from dissociation to starting thiol and aldehyde under the influence of traces of HCl arising from trimethylsilyl chloride. This leads to the situation that two mercaptans compete in the reaction with the aldehyde. In consequence, the required unsymmetrical dithioacetal (**7**) could be isolated in a yield of 30% only. Oxidation of **7** leads, as expected, to both isomeric monoxides **10** and **11**, separation of which is practically impossible. Treatment of this mixture with acid gave three disulfides, viz. **12**, **13** and **14** in comparable proportions (Scheme 3). Since the acidolysis was performed in the presence of benzyl mercaptan, disproportionation cannot account for the occurrence of the symmetrical disulfides (**13** and **14**). Therefore, they must be produced during the reaction with acid. Their formation can be rationalized on the basis of the mechanism of the acidolysis reaction as was recently put forward by us[24] (Scheme 4). Cleavage of the C–S bond in the protonated sulfoxide gives alkanesulfenic acid **15** and a thia-oxonium ion **16**. Recombination of these two species by reaction at the O atom of the sulfenic acid leads to sulfenic ester **17**, which is supposed to fragment spontaneously to aldehyde and disulfide. When a mixture of dithioacetal monoxides, viz. **10** and **11**, is present, two sulfenic acids and two thia-oxonium ions will arise. Rejoining of these intermediates within the same solvent cage as they were formed, thus without appreciable dissociation, would produce only one dilsulfide, viz. **12**. Apparently, this condition is not fulfilled. Free interchange of sulfenic acids takes place as can be deduced from the three disulfides isolated.

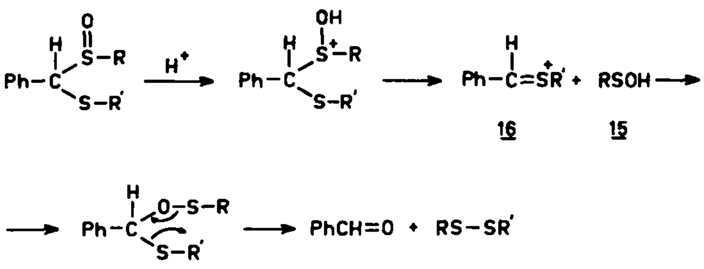
Consequently, exclusive formation of an unsymmetrical disulfide can only be accomplished when a single well-defined dithioacetal monoxide is used as starting material. This basic requirement can be fulfilled by preparing these precursors from an appropriate sulfine as illustrated in Scheme 1.

EXPERIMENTAL

NMR spectra were recorded on an EM 390 spectrometer using TMS as an internal standard. The mass spectral measurements were performed on a Varian MS 1B mass spectrometer.



Scheme 3.



Scheme 4.

Dithioesters

The dithioesters **1a** and **1b** were obtained from the reaction of *p*-tolunitrile with the corresponding thiol in the presence of HCl, followed by the reaction with H_2S in pyridine, according to Marvel *et al.*[25]

*n-Butyl dithio-*p*-toluate* (**1a**) was purified by distillation (b.p. 140–142° at 1 mm Hg), yield 72%. NMR ($CDCl_3$) δ 0.96 (t, 3 H), 1.2–2.0 (m, 4 H), 2.33 (s, 3 H), 3.33 (t, 2 H), 7.1 and 7.85 (AA'BB' "q", 4 H).

*n-Heptyl dithio-*p*-toluate* (**1b**) was also purified by distillation (b.p. 156–158° at 0.06 mm Hg), yield 61%. NMR ($CDCl_3$) δ 0.9 (t, 3 H), 1.1–1.85 (m, 12 H), 2.4 (s, 3 H), 2.6 (t, 2 H), 7.28 and 8.0 (AA'BB' "q", 4 H).

*Sodium dithio-*p*-toluate* was prepared according to Becke and Hagen[26] from *p*-chloromethyltoluene, NaOMe and S and purified as follows. The crude product, obtained after aqueous work-up, was dissolved in acetone and the insoluble ppt of NaOH was filtered off. Acetone was evaporated and the residue was washed with benzene to give pure sodium dithio-*p*-toluate.

Sulfines

Synthesis of sulfines was performed by oxidation of the corresponding dithio-*p*-toluates with *m*-chloroperbenzoic acid (*m*-CPBA).[19,20] The sulfine **2c** has been described previously.[15]

n-Butylthio p*-tolyl sulfine* (**2a**), yield 86%, *E–Z* ratio 2.5:1. Purification by column chromatography on Kieselgel 60 (70–230 mesh). The unchanged dithioester was eluted with benzene, the *E*-isomer with $CHCl_3$–CCl_4 (1:1), the *Z*-isomer with $CHCl_3$. NMR ($CDCl_3$) *E*-isomer δ 0.85 (t, 3 H), 1.05–1.8 (m, 4 H), 2.37 (s, 3 H), 2.55 (t, 2 H), 7.2 and 8.02 (AA'BB', 4 H); *Z*-isomer δ 0.85 (t, 3 H), 1.1–1.85 (m, 4 H), 2.38 (s, 3 H), 3.03 (t, 2 H), 7.01–7.35 (m, 4 H), Peak matching M found: 240.243 ± 0.003; for $C_{12}H_{16}OS_2$ M calc.: 240.2453.

n-Heptylthio p*-tolyl sulfine* (**2b**), yield 65%. *E–Z* ratio 2:1. Purification by column chromatography. The unchanged dithioester was eluted with benzene, the *E*-isomer also with benzene, the *Z*-isomer with benzene–ether 2:1.

NMR ($CDCl_3$) *E*-isomer δ 0.75 (t, 3 H), 1.0–1.8 (m, 10 H), 2.36 (s, 3 H), 2.57 (t, 2 H), 7.2 and 8.05 (AA'BB', 4 H); (*Z*-isomer δ 0.81 (t, 3 H), 1.05–1.9 (m, 10 H), 2.34 (s, 3 H), 3.04 (t, 2 H), 7.05–7.35 (m, 4 H). Peak matching *M* found: 282.292 ± 0.003; for $C_{15}H_{22}OS_2$ M calc.: 282.2922.

Dithioacetal monoxides

General procedure. To a stirred soln of the sulfine of choice (5 mmole) in THF (40 ml) at −78° and under an inert atmosphere MeLi in ether (5 mmole) was added dropwise with a syringe. After 10 min at −78° the mixture was poured in 120 ml sat NH_4Cl aq. The aqueous layer was extracted with ether, the combined organic layers were dried for 2 hr over a mixture of $MgSO_4$ and Na_2SO_4 with a small amount of $NaHCO_3$ and concentrated. The crude mixture was chromatographed on Kieselgel 60 (70–230 mesh).

*n-Butylthio-(*p*-tolyl)-methyl sulfoxide* (**3a**). The crude product was purified by column chromatography. Impurities were eluted with benzene, and the sulfoxide **3a** with benzene–acetone (5:1), yield 50% as a mixture of diastereosomers (ratio 1:1). NMR ($CDCl_3$) δ 0.9 (t, 3 H), 1.1–1.8 (m, 4 H), 2.3 (s, 3 H), 2.22 and 2.4 (s, s, 3 H; two diastereomers), 2.5–2.95 (t, t, 2 H; two diastereomers), 4.68 and 4.8 (s, s, 1 H; two diastereomers), 6.95–

7.35 (m, 4 H). Peak matching for the peak $[M–CH_3SO]^+$ *m/e* found: 193.195 ± 0.003; for $C_{12}H_{17}S$ *m/s* calc.: 193.1956.

n-Heptylthio-(p-tolyl)-methyl methyl sulfoxide (3b). The crude product was purified by column chromatography. Impurities were eluted with benzene, and the sulfoxide 3b with benzene–acetone (5:1), yield 72% as a mixture of diastereomers (ratio 1:1). NMR ($CDCl_3$) δ 0.88 (t, 3 H), 1.05–1.95 (m, 10 H), 2.18 and 2.3 (s, s, 3 H, two diastereomers), 2.34 (s, 3 H), 2.52–3.0 (t,t, 2 H, two diastereomers), 4.68 and 4.75 (s, s, 1 H, two diastereomers), 6.95–7.35 (m, 4 H). Peak matching for the peak $[M–CH_3SO]^+$ *m/e* found: 235.241 ± 0.003; for $C_{15}H_{23}S$ *m/e* calc.: 235.2426.

Phenylthio-(p-tolyl)-methyl methyl sulfoxide (3c) has been described previously.[15]

Preparation of unsymmetrical disulfides

General procedure. To a stirred soln of 3 (4 mmole), benzyl mercaptan (4 mg) and Me_2S_2 (3–5 ml) in $CHCl_2$ (40 ml), 70% $HClO_4$ aq (100 mg) in THF (6 ml) was added in one portion at room temp. The mixture was stirred and monitored by TLC. When TLC revealed the absence of starting sulfoxide (after *ca.* 10 min) the soln was shaken twice with 5% $NaHCO_3$ aq. The organic layer was washed with water and dried over $MgSO_4$. After evaporation the products were separated by column chromatography or preparative TLC.

n-Butyl methyl disulfide (5a). After column chromatography on Kieselgel 60 (70–230 mesh), elution with hexane–benzene (3:1) gave 5a in a yield of 73.5%. NMR ($CDCl_3$) δ 0.9 (t, 3 H), 1.15–1.9 (m, 4 H), 2.38 (s, 3 H), 2.68 (t, 2 H). Peak matching M found: 136.217 ± 0.003; for $C_5H_{12}S_2$ M calc.: 136.2171.

n-Heptyl methyl disulfide (5b). After column chromatography elution with hexane–benzene (3:1) gave 5b in a yield of 73%. Using preparative TLC with hexane–benzene (5:1) as developing solvent gave a yield of 78%. NMR ($CDCl_3$) δ 0.9 (t, 3 H), 1.15–1.9 (m, 10 H), 2.38 (s, 3 H), 2.68 (t, 2 H). Peak matching M found: 178.267 ± 0.003; for $C_8H_{18}S_2$M calc.: 178.2660.

Methyl phenyl disulfide (5c). After column chromatography (hexane–benzene 3:1) yield 77.3%. NMR ($CDCl_3$) δ 2.4 (s, 3 H), 7–7.6 (m, 5 H).

Peak matching M found: 156.187 ± 0.003; for $C_7H_8S_2$M calc.: 156.1876.

Preparation of 11,12-*dithiatridecyl acetate* (5d). 10-*Bromodecanol*-1 was obtained[21] from 1,10-decandiol and gaseous HBr in the presence of $CaCl_2$. Column chromatography (benzene–EtOH 3:1) gave the product contaminated with starting diol (yield *ca* 40%). This product was used without further purification in the next reaction.

10-*Hydroxydecyl dithio*-p-*toluate.* 10-bromodecanol-1 (4.5 g, 19 mmol) and sodium dithio-*p*-toluate (3.61 g, 19 mmole) were dissolved in dimethoxyethane (50 ml). The soln was stirred and refluxed for 1 hr. When GLC revealed complete consumption of the starting material, NaBr was filtered off and the solvent removed. Water and ether were added and the layers were separated. The aqueous layer was extracted with ether. The combined etheral layers were washed with water, dried over $MgSO_4$ and concentrated to give 5.63 g (91%) of crude 10-hydroxydecyl dithio-*p*-toluate. This compound was used without further purification in the reaction with acetyl chloride.

10-*Acetoxydecyl dithio*-p-*toluate* (1d). 10-Hydroxydecyl dithio-*p*-toluate (3.85 g, 11.88 mmole) and acetyl chloride (1.57 g, 20 mmole) were dissolved in ether (50 ml) and Et_3N (2.02 g, 20 mmole) was added dropwise while stirring. After 0.5 hr $Et_3N \cdot HCl$ was filtered off. The filtrate was washed with water, dried over $MgSO_4$ and concentrated to give 4.23 g of the crude product. After column chromatography ($CHCl_3$–CCl_4 5:2) the yield of pure 1d was 2.868 g (66%). NMR ($CDCl_3$) δ 1.1–1.85 (m, 16 H), 2.0 (s, 3 H), 3.3 (t, 2 H), 4.0 (t, 2 H), 7.0–7.95 (m, 4 H).

Peak matching M found: 366.351 ± 0.003; for $C_{20}H_{30}O_2S_2$ M calc.: 366.3498.

10-*Acetoxydecyl* p-*tolyl sulfine* (2d). To a stirred soln of 1d (2.86 g, 7.8 mmole) in ether (50 ml) a soln of 85% *m*-CPBA (1.56 g, 7.8 mmole) in ether (30 ml) was added dropwise at 0°. The mixture was stirred for 30 min (negative KI test) and then shaken twice with 200 ml 5% $NaHCO_3$ aq and once with water. After drying and concentrating the crude product was purified by column chromatography (hexane–acetone 20:1). 0.37 g of unreacted 1d was recovered, yield of sulfine 2d (*E–Z* ratio 2:1) 2.128 g (71.4%; based on consumed substrate 81%). NMR ($CDCl_3$) δ 1.15–1.9 (m, 16 *H*), 2.05 (s, 3 H), 2.36 (s, 3 H), 2.57 and 3.05 (t, t, 2 H, two diastereomers), 4.0 (t, 2 H), 7.2–8.2 (m, 4 H).

Peak matching M found: 282.344 ± 0.003; for $C_{20}H_{30}O_3S_2$ M calc.: 282.3447.

10-*Acetoxydecylthio-(p-tolyl)-methyl methyl sulfoxide* (3d). To a stirred soln of 2d (2.128 g, 5.57 mmole) in THF under N_2-atmosphere MeLi (3.5 ml, 5.6 mmole) was added dropwise with a syringe at −78°. The mixture was stirred at this temp. for 15 min and then poured in 120 ml sat NH_4Cl aq. Ether was added and the layers were separated. The aqueous layer was extracted with ether. The combined organic layers were dried over $MgSO_4$ with a small amount of $NaHCO_3$ (for about 2 hr) and the solvent was removed. The crude compound was purified by column chromatography (hexane–acetone 4:3) to give 1.55 g (70%) of pure 3d, as a mixture of diastereomers (ratio 1:3). NMR ($CDCl_3$) δ 1.2–1.9 (m, 16 H), 2.0 (t, 3 H), 2.2 and 2.4 (s, s, 3 H, two diastereomers), 2.3 (s, 3 H), 2.75 (t, 2H), 4.0 (s, 3 H), 4.68 and 4.78 (s, s, ratio 1:3, 1 H), 7.0–7.3 (m, 4 H).

Peak matching for the peak $[M–CH_3SO]^+$ *m/e* Found: 335.293 ± 0.003; for $C_{20}H_{31}O_2S$; *m/e* Calc. 335.2951.

Acidolysis of 3d. Sulfoxide 3d (1.5 g, 3.77 mmole), Me_2S_2 (5 ml) and benzyl mercaptan (4 mg) were dissolved in CH_2Cl_2 (40 ml). 70% $HClO_4$aq (100 mg) in THF (6 ml) was added in one portion while stirring at room temp. The mixture was stirred for 10 min (TLC showed no starting material) and then shaken twice with 5% $NaHCO_3$aq. The organic layer was washed with water, dried over $MgSO_4$ and the solvent was removed. The disulfide 5d was separated from 4 by using high pressure column chromatography (Chromatospac-Prep 100, produced by Jobin Yvon) with the aid of Bio-Beads SX-12 and $CHCl_3$ as an eluent (piston pressure 3.8 bar, elution pressure 1.6 bar what gave elution rate of about 20 ml/min). 5d was obtained as the first fraction with the yield of 0.854 g (81.5%). NMR ($CDCl_3$) δ 1.1–1.85 (m, 16 H), 2.0 (s, 3 H), 2.38 (s, 3 H), 2.68 (t, 2 H), 4.0 (t, 2 H).

Peak matching M found: 278.320 ± 0.003; for $C_{13}H_{26}O_2S_2$ M calc.: 278.3185.

Unsymmetrical dithioacetal monoxide via O-*trimethylsilyl hemithioacetal*

O-*Trimethylsilyl* S-*ethyl benzalhemithioacetal* (6) was prepared according to Chan and Ong[23] from benzaldehyde, ethyl mercaptan and trimethylchlorsilane in pyridine.

Reaction of 6 *with n-heptyl mercaptan.* Hemithioacetal 6 (2.2 g, 9.1 mmole), n-heptyl mercaptan (1.214 g, 9.1 mmole) and a few drops of Me_3SiCl were stirred at room temp. in $CHCl_3$ (15 ml) for 4 hr. The solvent was removed and the residue (2.636 g) was fractionated. The second fraction (b.p. *ca.* 134° at 0.3 mm Hg) was collected to give 0.72 g (30%) of 7. NMR ($CDCl_3$) δ 0.9 (t, 3 H), 1.15–1.72 (t + m, 13 H), 2.4–2.7 (t + q, 4 H), 4.9 (s, 1 H), 7.15–7.60 (m, 5 H).

Acidolysis of the mixture of 10 *and* 11. Acidolysis was performed according to the general procedure described for the synthesis of unsymmetrical disulfides. After usual work-up GLC analysis of the crude product revealed presence of three disulfides 12, 13 and 14 in comparable proportions.

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