Reduction of Thiocarbonyl Compounds with Lithium Diisopropylamide

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Dedicated to Professor *Hans-Ulrich Reissig*, Freie Univeristät Berlin, on the occasion of his 65th birthday

Treatment of 4,4-disubstituted 2-phenyl-1,3-thiazole-5(4*H*)-thiones with lithium diisopropylamide (LDA; LiN^iPr_2) in THF at −78° yielded the corresponding 1,3-thiazole-5(4*H*)-thioles in moderate yields. Sequential treatment with LDA and MeI under the same conditions led to the 5-methylsulfanyl derivatives. Similarly, reaction of some cycloalkanethiones as well as diaryl thioketones with LDA and MeI gave cycloalkyl methyl sulfides and diarylmethyl methyl sulfides, respectively. A reaction mechanism *via* H transfer from LDA to the thiocarbonyl C-atom *via* a six-membered transition state is proposed for this unprecedented reduction of the C=S bond.

1. Introduction. – For the synthesis of five-membered S-heterocycles, 1,3-dipolar cycloadditions with C=S compounds [1] or S-containing 1,3-dipoles [2] are of continuing interest. In the past, we have reported on various types of [2 + 3]-cycloadditions with 1,3-thiazole-5(4*H*)-thiones of type **1** (*cf. Scheme 1*) as a model for C=S dipolarophiles [3]. For example, reactions with thiocarbonyl ylides led to spirocyclic 1,3-dithiolanes [4], diazoalkanes reacted with **1** to give spirocyclic 2,5-dihydro-1,3,4-thiadiazoles [5], and reactions with azomethine ylides yielded spirocyclic 1,3-thiazolidines [6]. Differently substituted azomethine ylides have been generated *in situ* in the presence of **1** by various methods (*cf.* [7]), such as thermal ring opening of aziridines [6c][6d] or desilylation of *N*-[(trimethylsilyl)methyl]amino ethers [6e].

Within these studies, we have also tried to generate the *C*-unsubstituted *N*-methylazomethine ylide according to the protocol of *Roussi* and co-workers [8]. These authors reported that the treatment of trialkylamine *N*-oxides in THF with LDA at 0° in the presence of C=S dipolarophiles leads to the corresponding [2 + 3] cycloadducts (1,3-thiazolidine derivatives). For example, the reaction of trimethylamine oxide (**2**) with lithium diisopropylamide (LDA) in the presence of thiobenzophenone or adamantanethione, respectively, gave the corresponding *N*-methyl-1,3-thiazolidines **3** (*Scheme 1*). As a rationalization of the formation of five-membered N-heterocycles, the dehydration of the N-oxides to give an azomethine ylide as a reactive intermediate was proposed. Unexpectedly, the analogous treatment of a mixture of the 1,3-thiazole-5(4*H*)-thione **1a** and **2** with LDA at 0° carried out in our laboratories gave only the reduction product **4a**, and none of the expected cycloadduct could be detected.

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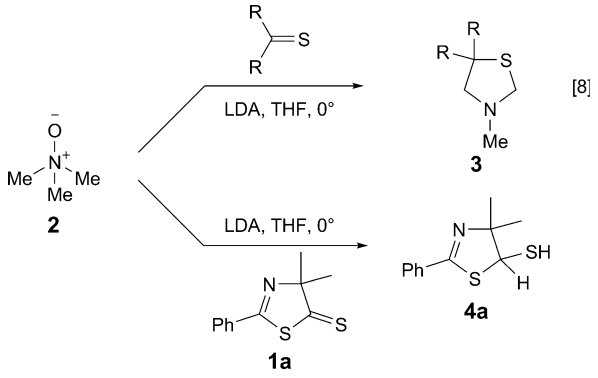
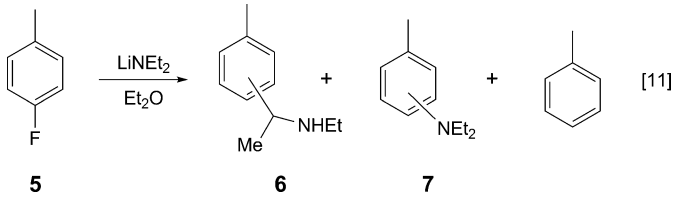
[1]) Part of the Ph. D. Thesis of *A. G.*, Universität Zürich, 2001; present address: *F. Hoffmann-La Roche Ltd.*, Grenzacherstrasse 124, CH-4070 Basel.

Scheme 1



The use of LDA as a strong base in organic synthesis, *e.g.*, for the deprotonation of CH-acidic compounds, is well-known [9]. Less well known is the use of LDA as a reducing agent [10], *e.g.*, in the reduction of nitro arenes to the corresponding anilines and azoxy arenes *via* a single-electron transfer (SET) mechanism [10a]. Furthermore, treatment of 4-fluorotoluene (**5**) with lithium diethylamide ($LiNEt_2$) in Et_2O led to a mixture of the *meta*- and *para*-isomers of ethyl(2-tolylethyl)amine, **6**, and *N*,*N*-diethyltoluidine, **7**, as well as toluene [11] (*Scheme 2*). The formation of **6** was rationalized by a hydride transfer from $LiNEt_2$ to the intermediate aryne, followed by nucleophilic addition of the aryl anion at the formed imine. However, to the best of our knowledge, there is no hydride transfer reaction of LDA known.

Scheme 2

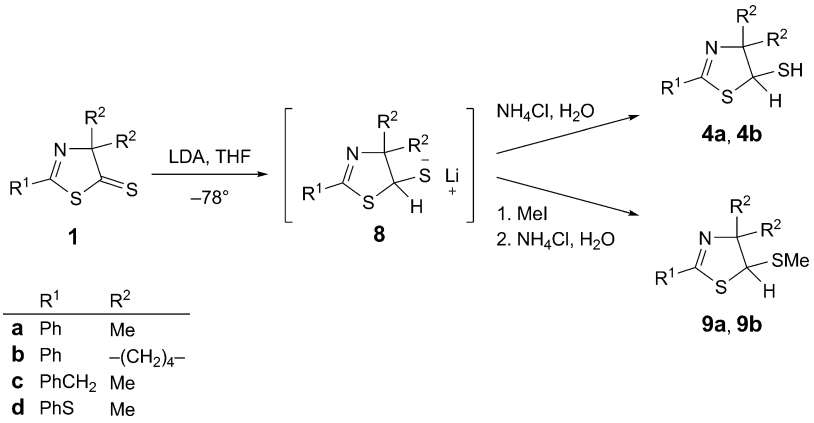


The aim of the present study was to evaluate the ability of LDA as a hydride-transfer reagent in thiocarbonyl chemistry.

2. Results and Discussion. – As mentioned above, treatment of a mixture of equimolar amounts of 4,4-dimethyl-2-phenyl-5(4*H*)-thione (**1a**) and trimethylamine *N*-oxide (**2**) in THF at 0° with 3.5 equiv. of LDA led to the corresponding 4,5-dihydro-1,3-thiazole-5-thiole **4a** [12], which was isolated in 40% yield, as the major product. This surprising result motivated us to investigate reactions of C=S-containing compounds with LDA. First, the reaction with **1a** was repeated in the absence of the *N*-oxide **2** at −78° by using 1.6 equiv. of LDA. Under these conditions, only one product, **4a**, was formed, which, after treatment with an aqueous 20% NH_4Cl solution,

was isolated in 69% yield. An analogous result was obtained with 2-phenyl-3-thia-1-azaspiro[4.4]non-1-ene-4-thione (**1b**; 63% yield of **4b**; *Scheme 3*). This outcome hints at a carbophilic addition of a hydride ion onto **1**, leading to an intermediate thiolate **8**. Therefore, **1a** and **1b**, respectively, in THF at $-78°$ were treated with 1.6 equiv. of LDA. After stirring for 15 min, 1 equiv. of MeI was added, the mixture was allowed to warm to room temperature, and then poured onto ice. Usual workup gave the corresponding 5-methylsulfanly derivatives **9a** [13] and **9b** in 68 and 80% yield, respectively. Unfortunately, the analogous reactions with 2-benzyl- and 2-(phenylsulfanyl)-1,3-thiazol-5(4*H*)-thione, **1c** and **1d**, respectively, failed.

Scheme 3



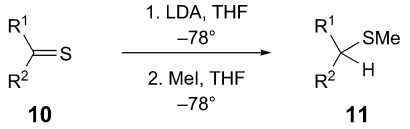
	R^1	R^2
a	Ph	Me
b	Ph	$-(CH_2)_4-$
c	$PhCH_2$	Me
d	PhS	Me

With the aim of excluding the possibility that the H-atom at C(5) of the reduction products **4** and **9** stems from the solvent, the reaction with **1a** was repeated in (D_8)THF with freshly prepared LDA, as well as with the commercially available 2M LDA solution in THF. In both cases, the formed **4a** did not contain any D-atom. Therefore, we concluded that LDA acted as a hydride donor in this reaction.

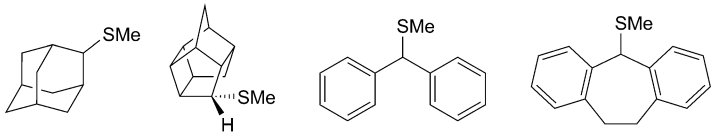
Encouraged by these results, we attempted to extend the scope of this reduction process to thioketones. Because of the easier workup and purification, the presumably formed thiolate should be trapped *via* methylation. First, two cycloaliphatic thioketones, adamantanethione (**10a**) [14] and pentacyclo[5.4.$0^{2,6}$.$0^{3,10}$.$0^{5,9}$]undecane-8-thione (**10b**) [15], in THF/heptane/ethylbenzene at $-78°$ were treated with *ca.* 1.25 equiv. of LDA for 10 min. Then, excess MeI was added at the same temperature, the mixture was stirred for another 10 min, and the reaction was quenched by addition of H_2O. The yields of the methyl sulfanyl derivatives **11** were estimated on the basis of ^{1}H-NMR spectra of the crude mixture to be in the range of 70–80%. After chromatographic purification, **11a** [16] and **11b** were obtained in 42 and 47% yield, respectively (*Scheme 4*). We propose that the MeS group of **11b** is *endo*-oriented as the result of an *exo*-addition, in analogy to other nucleophilic additions with pentacyclo[5.4.$0^{2,6}$.$0^{3,10}$.$0^{5,9}$]undecan-8-one [15a][17].

Surprisingly, 1,1,3,3-tetramethylindane-2-thione did not react under the same conditions, and performing the reaction at $-40°$ with 3 equiv. of LDA provided a

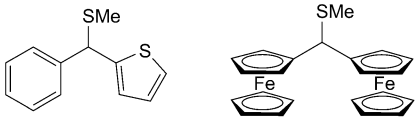
Scheme 4



10 11



11a 11b 11c 11d



11e 11f

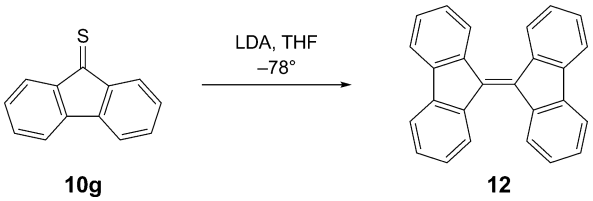
complex mixture containing traces of the expected sulfide and numerous by-products. Similarly, neither di(*tert*-butyl)thioketone nor 2,2,4,4-tetramethyl-3-thioxocyclobutanone did undergo a reaction with LDA. Most likely, steric hindrance is the reason for the failure.

Next, the reaction with aromatic thioketones was examined. Treatment of thiobenzophenone (**10c**) [18] as well as thiodibenzosuberone (**10d**) [19] with *ca.* 1.25 equiv. of LDA and subsequent treatment of the initial product with MeI led to the corresponding methylsulfanyl derivatives. **11c** [20] and **11d**, respectively (in 52 and 41% yield, resp.; *Scheme 4*). On the other hand, the analogous reaction of the hetarylthioketones phenyl(thiophen-2-yl)methanethione (**10e**) [21] and di(selenophen-2-yl)methanethione [22] led to complex mixtures of diverse products, and, only in the case of **10e**, the corresponding methylsulfanyl derivative **11e** was obtained in a very low yield (9%). Finally, the reduction of diferrocenylthioketone (**10f**) was performed successfully by using 3.2 equiv. of LDA and 6.5 equiv. of MeI. After chromatographic workup, the hitherto unknown diferrocenylmethyl methyl sulfide **11f** was obtained in 37% yield.

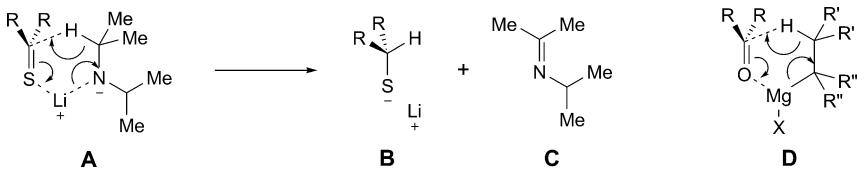
9*H*-Fluorene-9-thione (**10g**) [18][23] is a prominent representative of aromatic thioketones, known as a superdipolarophilic agent [2]. However, the attempted reduction of **10g** with LDA failed, and only traces of the desired methylsulfanyl derivative were detected in the crude mixture by ^{1}H-NMR spectroscopy. The major product was the known bisfluorenylidene (= 9-(9*H*-fluoren-9-ylidene)-9*H*-fluorene; **12** [24]; *Scheme 5*), accompanied by numerous by-products.

As a reaction mechanism for the reduction of thiocarbonyl compounds with LDA, we propose a hydride transfer *via* a six-membered transition state **A**, leading to the thiolate **B** and the imine **C** as a side-product (*Scheme 6*). This transition state resembles that of reactions of sterically demanding *Grignard* reagents with carbonyl compounds bearing bulky substituents, *i.e.*, **D** (*Scheme 6*) [25]. Also the $AlMe_3$-catalyzed asymmetric *Meerwein–Schmidt–Ponndorf–Verley* reduction of prochiral ketones with

Scheme 5



Scheme 6



^{i}PrOH in the presence of enantiomerically pure BINOL (= [1,1′-binaphthalene]-2,2′-diol) is rationalized by an analogous transition state [26].

3. Conclusions. – The unexpected hydride transfer of LDA proved to be a useful method for the reduction of 4,4-disubstituted 1,3-thiazole-5(4*H*)-thiones and non-enolizable thioketones leading to the corresponding thiols. This is the first observation of a reaction in which LDA acts as a hydride donor. Although the scope of the reaction is not fully explored, it is very useful in the series of thioketones. Especially important is the simple access to diaryl/hetaryl methanethiols, which are of great interest from the point of view of materials chemistry.

We thank the analytical sections of our institutes for spectra and analyses. Generous gift of a sample of di(ferrocenyl)thioketone by Dr. *Rafał Karpowicz* (University of Łódź) is acknowledged. *A. G.* and *H. H.* thank the *Swiss National Science Foundation* and *F. Hoffmann-La Roche AG*, Basel, for financial support, and *G. M.* and *M. J.* thank the *National Science Center* (Cracow, Poland) for generous support (Grant Maestro-3, Dec-2012/06/A/ST5/00219).

Experimental Part

1. *General*. The reactions with thioketones were generally performed under Ar in flame-dried flasks. Solvents and reagents were added by syringe. THF was dried with Na and benzophenone and freshly distilled before use. Other reagents were purchased and used as received without further purification. TLC: *Merck 60 F_{254}* SiO_2-coated Al-plates, 0.2 mm; detection of the substances on the TLC plates under UV light (λ 254 nm) or with $KMnO_4$ soln. Prep. TLC: *Merck 60 F_{254}* SiO_2-coated glass-plates, 2 mm. Column chromatography (CC): *Merck 60* SiO_2, 0.040–0.63 mm. M.p.: *Mettler-FP-5* or *MEL-TEMP II* (*Aldrich*) instrument; uncorrected. IR Spectra: *Perkin-Elmer-1600-FT-IR* or *FT-IR NEXUS* spectrophotometer; film or KBr pellets; cm^{-1}. ^{1}H- and ^{13}C-NMR Spectra: *Bruker-AC-300* and *Bruker-ARX-300* (300 and 75.5 MHz, resp.), or *Bruker AVIII 600* instrument (600 and 151 MHz, resp.), in $CDCl_3$; multiplicity of C-atoms from DEPT or 2D spectra (HMQC). MS: *Finnigan MAT-90* or *Finnigan SSQ-700* instrument (EI, 70 eV, or CI (NH_3 or isobutene)) or *Varian 500-MS LC Ion Trap* instrument (ESI-MS). Elemental analyses: *Vario EL* or a *Vario EL III* (*Elementar Analysensysteme GmbH*) instruments.

2. *Starting Materials.* All chemicals were commercially available (*Fluka*, *Aldrich*, and *Merck*). Lithium diisopropylamide (LDA) soln. (2.0M in THF) or (2.0M in THF/heptane/ethylbenzene) was purchased from *Fluka* and *Aldrich*, resp., and used as received. Solvents were purified as follows: hexane, distillation from CaH_2; AcOEt and CH_2Cl_2, distillation from K_2CO_3 and stored over molecular sieves (4 Å); THF (*purum*, *Fluka*) and Et_2O: dried over Na and dist.; toluene (p.a., *Merck*): stored over Na.

3. *Reactions of 1,3-Thiazole-5(4*H*)-thiones* **1** *with LDA. General Procedure 1* (*GP 1*). To a cooled soln. (−78°) of *4,4-dimethyl-2-phenyl-1,3-thiazole-5(4*H*)-thione* (**1a**) or *2-phenyl-3-thia-1-azaspiro[4.4]-non-1-en-4-thione* (**1b**) (1 mmol), resp. in THF (20 ml) was added a 2M LDA soln. in THF (0.8 ml, 1.6 mmol). The soln. decolorized after a few min, and the mixture was warmed to r.t. Then, a cooled (0°) aq. soln. of NH_4Cl was added, and the mixture was extracted with Et_2O (3×). The combined org. phase was dried ($MgSO_4$), the solvent was evaporated, and the residue was purified by prep. TLC (hexane/AcOEt).

General Procedure 2 (*GP 2*). To a cooled soln. (−78°) of **1a** or **1b** (1 mmol), resp., in THF (20 ml) was added a 2M LDA soln. in THF (0.8 ml, 1.6 mmol). After stirring for 15 min, MeI (0.06 ml, 1 mmol) was added, and stirring was continued at −78° for another 15 min. The mixture was poured into ice-water (100 ml) and extracted with Et_2O (3×). The combined org. phase was dried ($MgSO_4$), the solvent was evaporated, and the residue was purified by prep. TLC (hexane/AcOEt).

4,5-Dihydro-4,4-dimethyl-2-phenyl-1,3-thiazole-5-thiol (**4a**) [12]. *GP1*; prep. TLC (hexane/AcOEt 10:1). Yield: 154 mg (69%). Pale-yellow oil. IR (film): 2973*s*, 2929*m*, 2561*m* (br.), 1596*s*, 1576*s*, 1489*m*, 1447*s*, 1379*m*, 1360*m*, 1313*m*, 1259*s*, 1210*m*, 1174*s*, 949*s*, 847*m*, 823*m*, 765*s*, 690*s*, 614*s*. ^{1}H-NMR (300 MHz): 7.69–7.65 (*m*, 2 arom. H); 7.36–7.28 (*m*, 3 arom. H); 4.65 (*d*, *J* = 9.1, H–C(5)); 2.02 (*d*, *J* = 9.1, SH); 1.42, 1.37 (2*s*, 2 Me). ^{13}C-NMR (75 MHz): 163.5 (*s*, C=N); 133.1 (*s*, 1 arom. C); 131.2, 128.4, 128.1 (3*d*, 5 arom. CH); 80.2 (*s*, C(4)); 58.1 (*d*, C(5)); 26.3, 22.6 (2*q*, 2 Me). CI-MS: 226 (10), 225 (14), 224 (100, $[M+1]^+$).

4,5-Dihydro-4,4-dimethyl-5-(methylsulfanyl)-2-phenyl-1,3-thiazole (**9a**) [13]. *GP2*; prep. TLC (hexane/AcOEt 5:1). Yield: 161 mg (68%). Pale-yellow oil. IR (film): 3061*m*, 3027*m*, 2974*s*, 2918*s*, 2861*m*, 1596*s*, 1577*s*, 1489*s*, 1447*s*, 1380*m*, 1360*s*, 1313*m*, 1296*m*, 1260*s*, 1209*m*, 1175*s*, 1120*m*, 1074*m*, 1028*m*, 1001*m*, 949*s*, 854*m*, 832*s*, 765*s*, 690*s*, 677*s*, 642*m*, 614*s*. ^{1}H-NMR (300 MHz): 7.73–7.69 (*m*, 2 arom. H); 7.36–7.25 (*m*, 3 arom. H); 4.60 (*s*, H–C(5)); 2.06 (*s*, MeS); 1.50, 1.36 (2*s*, 2 Me). ^{13}C-NMR (75 MHz): 163.1 (*s*, C=N); 133.2 (*s*, 1 arom. C); 131.1, 128.4, 128.1 (3*d*, 5 arom. CH); 80.6 (*s*, C(4)); 67.5 (*d*, C(5)); 27.1, 23.4 (2*q*, 2 Me); 15.5 (*s*, MeS). EI-MS: 237 (12, M^+), 146 (9), 145 (100), 104 (31), 86 (53), 84 (94).

2-Phenyl-3-thia-1-azaspiro[4.4]non-1-ene-4-thiol (**4b**). *GP1*; prep. TLC (hexane/AcOEt 10:1). Yield: 156 mg (63%). Pale yellow oil. IR (film): 2976*s*, 2934*m*, 2560*m* (br.), 1594*s*, 1570*m*, 1489*m*, 1439*s*, 1360*m*, 1312*m*, 1210*m*, 1172*s*, 954*m*, 839*m*, 819*m*, 755*s*, 683*m*, 629*w*. ^{1}H-NMR (300 MHz): 7.83–7.78 (*m*, 2 arom. H); 7.47–7.29 (*m*, 3 arom. H); 4.79 (*d*, *J* = 8.4, H–C(5)); 2.19–2.10 (*m*, 2 H); 2.22 (*d*, *J* = 8.4, SH); 2.08–1.60 (*m*, 6 H). ^{13}C-NMR (75 MHz): 162.6 (*s*, C=N); 133.1 (*s*, 1 arom. C); 131.1, 128.4, 128.2 (3*d*, 5 arom. CH); 92.1 (*s*, C(4)); 57.6 (*d*, C(5)); 39.7, 36.6, 34.8, 24.5 (4*t*, 4 CH_2). EI-MS: 249 (6, M^+), 216 (30), 171 (100), 156 (9), 143 (8), 121 (22), 104 (59), 77 (31).

4-(Methylsulfanyl)-2-phenyl-3-thia-1-azaspiro[4.4]non-1-ene (**9b**). *GP2*; prep. TLC (hexane/AcOEt 5:1). Yield: 212 mg (80%). Colorless oil. IR (film): 3061*m*, 3026*m*, 2959*s*, 2870*s*, 1596*s*, 1577*s*, 1489*s*, 1447*s*, 1313*s*, 1256*s*, 1176*m*, 1157*m*, 1074*m*, 1050*m*, 1021*m*, 993*s*, 942*s*, 832*s*, 766*s*, 690*s*, 611*s*. ^{1}H-NMR (300 MHz): 7.74–7.71 (*m*, 2 arom. H); 7.34–7.24 (*m*, 3 arom. H); 4.61 (*s*, H–C(5)); 2.27–2.22 (*m*, 1 H); 2.20–2.06 (*m*, 1 H); 1.97 (*s*, MeS); 1.95–1.59 (*m*, 6 H). ^{13}C-NMR (75 MHz): 162.7 (*s*, C=N); 133.3 (*s*, 1 arom. C); 130.9, 128.4, 128.1 (3*d*, 5 arom. CH); 91.7 (*s*, C(4)); 66.0 (*d*, C(5)); 39.3, 34.1, 24.9, 23.9 (4*t*, 4 CH_2); 14.0 (*s*, MeS). EI-MS: 263 (10, M^+), 216 (10), 174 (12), 171 (100), 170 (20), 120 (9), 104 (39).

4. *Reactions of Thioketones* **10** *with LDA. General Procedure 3* (*GP 3*). A soln. of thioketone (2.0 mmol) in dry THF (3.0–5.0 ml) was added dropwise to a soln. of LDA (2.0M in THF/heptane/ethylbenzene, 1.25 ml, 2.5 mmol) at −78° and stirred at this temp. for 10 min. Then, excess MeI (0.45 ml) was added, and the resulting mixture was stirred another 10 min. After addition of H_2O (15 ml), the mixture was extracted with Et_2O (3 × 10 ml), the combined org. layers were dried ($MgSO_4$), filtered, and the solvents were removed *in vacuo*. Crude products were purified by flash chromatography (FCC, SiO_2).

Adamant-2-yl Methyl Sulfide (=*2-(Methylsulfanyl)tricyclo[3.3.1.1^{3,7}]decane*; **11a**) [16]. *GP 3*; FCC (petroleum ether (PE)/CH_2Cl_2 6:1). Yield: 154 mg (42%). Colorless oil. IR (film): 3010–2850, 1450, 1100, 965. ^{1}H-NMR (600 MHz): 2.97 (br. *s*, 1 H); 2.17–2.13 (*m*, 2 H); 2.08 (*s*, MeS); 1.73–2.01 (*m*, 10 H); 1.51–1.56 (*m*, 2 H). ^{13}C-NMR (151 MHz): 55.0 (*d*, CH(2)); 38.7, 37.8 (2*t*); 32.5 (*d*); 31.9 (*t*); 27.8, 27.6 (2*d*); 14.9 (*q*, MeS). ESI-MS: 183 (100, $[M+1]^+$), 135 (63, $[M-\text{MeS}]^+$).

endo-*Pentacyclo[5.4.0.0^{2,6}.0^{3,10}.0^{5,9}]undec-8-yl Methyl Sulfide* (=*Methyl (5*S*)-Octahydro-1*H*-2,4,1-(ethane[1,1,2]triyl)cyclobuta[*cd*]pentalen-5-yl Sulfide*; **11b**). *GP 3*; FCC (PE/CH_2Cl_2 4:1). Yield: 179 mg (47%). Colorless oil. IR (film): 2970–2830, 1455, 1285. ^{1}H-NMR (600 MHz): 2.73–2.70, 2.59–2.56, 2.55–2.53 (3*m*, 5 H, 2:2:1); 2.43–2.33, 2.26–2.20 (2*m*, 5 H, 2:3); 2.10 (*s*, MeS); 1.70, 1.19 (2*d*, *J* = 10.4, 1 H each); 1.05–1.01 (*m*, 1 H). ^{13}C-NMR (151 MHz): 50.0, 47.0, 46.2, 46.0, 42.4, 42.0, 41.7, 39.3, 36.2 (9*d*); 34.4, 28.2 (2*t*); 17.5 (*q*, MeS). ESI-MS: 193 (100, $[M+1]^+$). Anal. calc. for $C_{12}H_{16}S$ (192.32): C 74.94, H 8.39; found: C 74.95, H 8.29.

Diphenylmethyl Methyl Sulfide (**11c**) [20]. *GP 3*; FCC (PE/CH_2Cl_2 3:1). Yield: 224 mg (52%). Colorless solid. M.p. 29–31° ([20]: 30–31°). IR (KBr): 3095–2825, 1490, 1450, 1420, 1080. ^{1}H-NMR (600 MHz): 7.46–7.42, 7.36–7.31, 7.27–7.22 (3*m*, 10 arom. H, 4:4:2); 5.08 (*s*, 1 H); 2.01 (*s*, MeS). ^{13}C-NMR (151 MHz): 141.3 (*s*, 2 arom. C); 128.5, 128.3, 127.1 (3*d*, 10 arom. CH); 56.1 (*d*, CH)); 15.8 (*q*, MeS). ESI-MS: 215 (4, $[M+1]^+$), 167 (100, $[M-\text{MeS}]^+$).

*10,11-Dihydro-5*H*-dibenzo[*a,d*]cyclohepten-5-yl Methyl Sulfide* (=*Dibenzosuber-5-yl Methyl Sulfide*) (**11d**). *GP 3*; FCC (PE/CH_2Cl_2 3:1). Yield: 197 mg (41%). Colorless solid. M.p. 72–73°. IR (KBr): 3060–2830, 1490, 1445, 1425. ^{1}H-NMR (600 MHz): 7.25–7.12 (*m*, 8 arom. H); 4.93 (*s*, 1 H); 3.85–3.78, 2.96–2.89 (2*m*, 2 H each, CH_2CH_2); 1.99 (*s*, MeS). ^{13}C-NMR (151 MHz): 140.7, 137.4 (2*s*, 2 arom. C); 130.9, 130.6, 127.7, 125.8 (4*d*, 8 arom. CH); 58.5 (*d*, CH)); 33.0 (*t*, CH_2CH_2); 16.8 (*q*, MeS). ESI-MS: 193 (100, $[M-\text{MeS}]^+$). Anal. calc. for $C_{16}H_{16}S$ (240.37): C 79.95, H 6.71; found: C 80.03, H 6.66.

Methyl Phenyl(thiophen-2-yl)methyl Sulfide (=*2-[(Methylsulfanyl)(phenyl)methyl]thiophene*; **11e**). *GP 3*; FCC (PE/CH_2Cl_2 4:1). Yield: 39 mg (9%). Pale-orange oil. IR (film): 3100–2825, 1600, 1495, 1450, 1435, 1230. ^{1}H-NMR (600 MHz): 7.46 (br. *d*, *J* = 7.7, 2 H, Ph); 7.36–7.32 (*m*, 2 H, Ph); 7.29–7.25 (*m*, 1 H, Ph); 7.22 (br. *dd*, *J* = 5.0, 0.9, 1 H); 6.96–6.91 (*m*, 2 H); 5.25 (*s*, CH–S); 2.05 (*s*, MeS). ^{13}C-NMR (151 MHz): 145.9, 141.1 (2*s*, 2 arom. C); 128.6, 128.1, 127.6 (3*d*, 5 CH, Ph); 126.6, 125.7, 125.1 (3*d*, 3 CH); 51.2 (*d*, CH–S); 16.0 (*q*, MeS). ESI-MS: 221 (27, $[M+1]^+$), 173 (100, $[M-\text{MeS}]^+$). Anal. calc. for $C_{12}H_{12}S_2$ (220.36): C 65.41, H 5.49; found: C 65.41, H 5.63.

Di(ferrocenyl)methyl Methyl Sulfide (**11f**). According to *GP 3*, di(ferrocenyl)thioketone (77 mg, 0.186 mmol) was reacted with LDA (0.30 ml, 0.60 mmol) and MeI (171 mg, 0.75 µl, 1.2 mmol). FCC (PE/CH_2Cl_2 3:1) afforded **11f** (30 mg, 37%). Orange solid. M.p. 107–108°. IR (KBr): 3120–2855, 1635, 1410, 1105, 1000. ^{1}H-NMR (600 MHz): 4.46 (*s*, 1 H); 4.26, 4.16, 4.13 (3 br. *s*, 18 H, 2:4:12); 1.88 (*s*, MeS). ^{13}C-NMR (151 MHz): 91.4 (*s*, 2 arom. C); 69.0 (*d*, 10 arom. CH); 68.0, 67.8, 67.09, 67.07 (4 *d*, 8 arom. CH); 45.3 (*d*, CH); 15.8 (*q*, MeS). ESI-MS: 430 (26, M^+), 383 (100, $[M-\text{MeS}]^+$). HR-EI-MS: 430.0150 (M^+, $C_{22}H_{22}Fe_2S^+$; calc. 430.0141).

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