Unexpected *Ritter* Reaction During Acid-Promoted 1,3-Dithiol-2-one Formation

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A series of aryl-substituted 1,3-dithiol-2-ones was prepared by the *Bhattacharya–Hortmann* cyclization method. Unexpectedly, a *Ritter* reaction occurred during the acid-catalyzed cyclization at the cyano group of the aryl substituents and 1,3-dithiol-2-ones bearing a carboxy or a carboxamide group could be selectively obtained (see **1** and **2a** in *Scheme 1*). The formation of the acid or the amide functionality was temperature-dependent so that the one or the other group could be introduced selectively by modifying the reaction temperature.

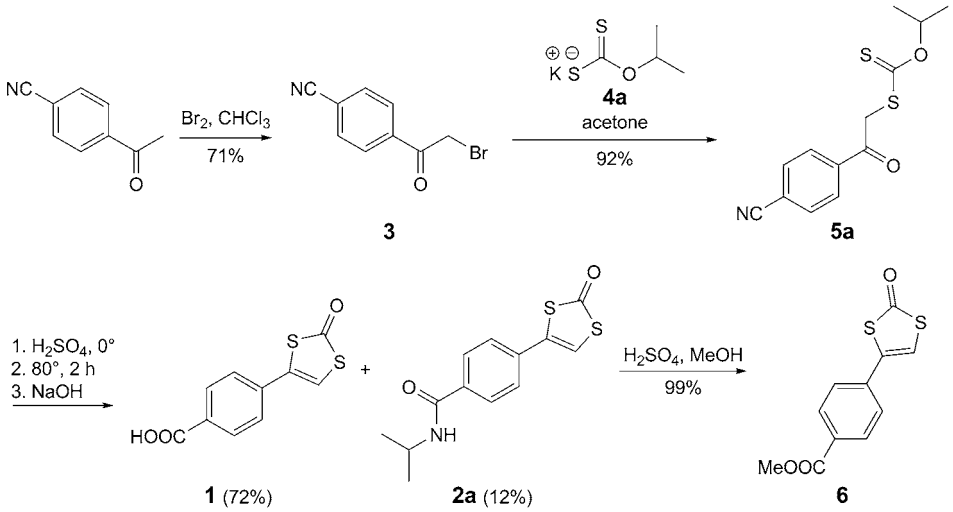
Introduction. – Herein, we report on the synthesis of a series of 5-aryl-substituted 1,3-dithiol-2-one derivatives. The proaromatic ring of the 1,3-dithiol-2-one moiety was generated by cyclization under acidic conditions by means of the *Bhattacharya–Hortmann* method [1]. Surprisingly, in the course of the synthesis of 4-(2-oxo-1,3-dithiol-4-yl)benzoic acid (**1**), an unexpected *Ritter* reaction occurred at the intermediate benzonitrile, competing with the hydrolysis of the nitrile group under acidic conditions and furnishing by-product **2a** by the transfer of an isopropyl group. Formation of amide **2a** was evidenced by NMR investigations. This group transfer was temperature-dependent, and the reaction conditions were optimized to selectively obtain 1,3-dithiol-2-ones derivatives **1** and **2a** (*Scheme 1*).

Results and Discussions. – The *Bhattacharya–Hortmann* synthesis of 1,3-dithiol-2-ones consists of a cyclization of *O*-alkyl dithiocarbonates in concentrated sulfuric acid. In the present study, *O*-isopropyl dithiocarbonate **5a** was prepared in 92% yield in one step by nucleophilic substitution of α-bromo-ketone **3** with potassium *O*-isopropyl carbonodithiotate (**4a**) [2] (*Scheme 1*).

The 4-(2-bromoacetyl)benzonitrile (**3**) was prepared in 71% yield by treatment of 4-acetylbenzonitrile in $CHCl_3$ with Br_2 (0.97 equiv.) overnight. Finally, **5a** was subjected to an acid-catalyzed ring closure in concentrated sulfuric acid at 80° for 2 h, wich provided **1** in 72% yield. The structure of acid **1** was confirmed by esterification with MeOH, producing ester **6**, reported previously [3].

Surprisingly, in the course of the synthesis of **1**, a by-product was formed in 12% yield and identified as being amide **2a**. Interestingly, the expected compound **1** could be

Scheme 1. *Synthetic Route Used for the Synthesis of 1,3-Dithiol-2-one Derivatives* **1** *and* **2a**



easily separated from its by-product by selective precipitation in acetone, acid **1** being the only one precipitating in this solvent. To determine the structure of by-product **2a**, NMR experiments were carried out in (D_6)DMSO. The ^{1}H-NMR spectra of **1** and **2a** in (D_6)DMSO (*Fig. 1*,*a* and *b*) only differed in the presence of two additional sets of signals for **2a**, assigned to an isopropyl group at δ(H) 1.16 (*d*) and 4.06 (*sept.*) and to an amide H-atom at δ(H) 8.28. The comparison of the ^{1}H-NMR spectra of **5a** and **2a** in $CDCl_3$ (*Fig. 2*,*a* and *b*) indicated that a transfer of the isopropyl group had occurred during cyclization. Indeed, the CH signal of the isopropyl group of **2** (δ(H) 4.28) was strongly upfield-shifted as compared to that of **5a** (δ(H) 5.69). A ^{1}H-NMR signal of **2a** was also detected at δ(H) 5.93. MS Analysis of **2a** allowed for the attribution of this additional H-atom to an NH group, the presence of an N-atom in **2a** being indicated by the isotope profile.

The group transfer observed during the acid-catalyzed cyclization of the *O*-isopropyl dithiocarbonate **5a** result in **2a** can be assigned to a *Ritter* reaction [4] competing with the hydrolysis of the nitrile function (→**1**) under strongly acidic conditions. As proposed in *Scheme 2*, the nitrile group of **5a** can react with the activated isopropyloxonium ion formed during the cyclization to the 1,3-dithiol-2-one moiety. Nucleophilic attack of the cyano group followed by hydrolysis with water yields amide **2a**.

To prepare selectively **1** and **2a**, the influence of the reaction temperature on the two concomitant reactions was investigated. At room temperature, only amide **2a** was isolated after 2 h. By contrast, heating of the mixture at 85° for 2 h provided a mixture of **1** and **2a**, and heating at 90° provided only **1**. In the light of these observations, a series of *O*-alkyl dithiocarbonates **5b**–**5j**, prepared from primary, secondary, or tertiary alcohols, was investigated (*Scheme 3*). Unfortunately, all attempts to prepare *O*-alkyl dithiocarbonates **5b**–**5d** from the potassium or sodium *O*-alkyl carbonodithioates **4b**–

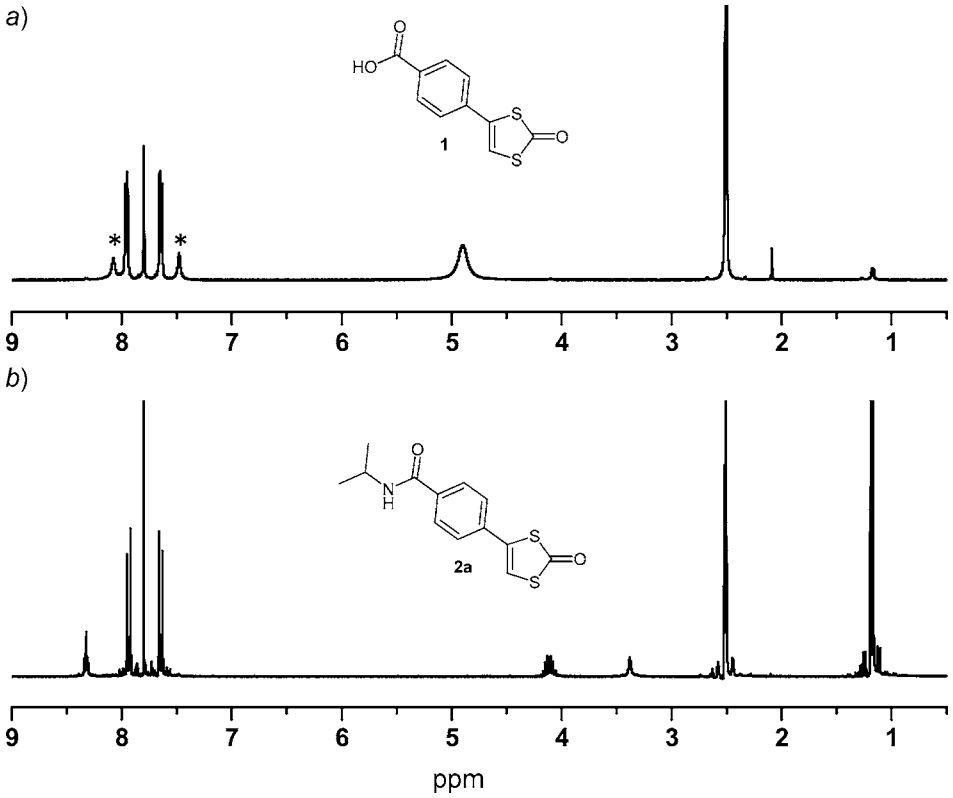


Fig. 1. *^{1}H-NMR Spectra* (400 MHz, (D_6)DMSO) *of* **1** *and* **2a**. * = Impurities.

4d prepared with tertiary alcohols failed, thus preventing the investigation the ransfer of groups issued from tertiary alcohols. As anticipated, cyclization of **5e**–**5g** (derived from secondary alcohols) at room temperature provided the corresponding amides **2e**–**2g** in yields of 71–84%. By contrast, no cyclization was achieved with **5h** and **5i**, only decomposition with evolution of fumes was observed upon addition of concentrated sulfuric acid. Therefore, more stable secondary cations are necessary to promote the *Ritter* reaction. Even the more stable benzylium cation derived from **5j** did not lead to the corresponding amide **2j**. Finally, synthesis of acid **1** starting from **5e**–**5g** was also verified. When carrying out the reaction at with **5e**–**5g** at 90° for 2 h, 1,3-dithiol-2-one derivative **1** was obtained as the unique reaction product in yields of 65–77%, whereas no acid was formed from **5h**–**5j**, since these *O*-alkyl dithiocarbonates decomposed already at room temperature in concentrated acid.

From these different results, it can be concluded that at room temperature, the kinetic of hydrolysis of the nitrile group of **5a** and **5e**–**5g** is extremely slow and allows the nucleophilic attack at the carbocation issued from the 1,3-dithiol-2-one cyclization. When elevating the temperature, the kinetic of hydrolysis is enhanced and hydrolysis of the nitrile competes with the *Ritter* reaction, furnishing a mixture of both the acid **1** and

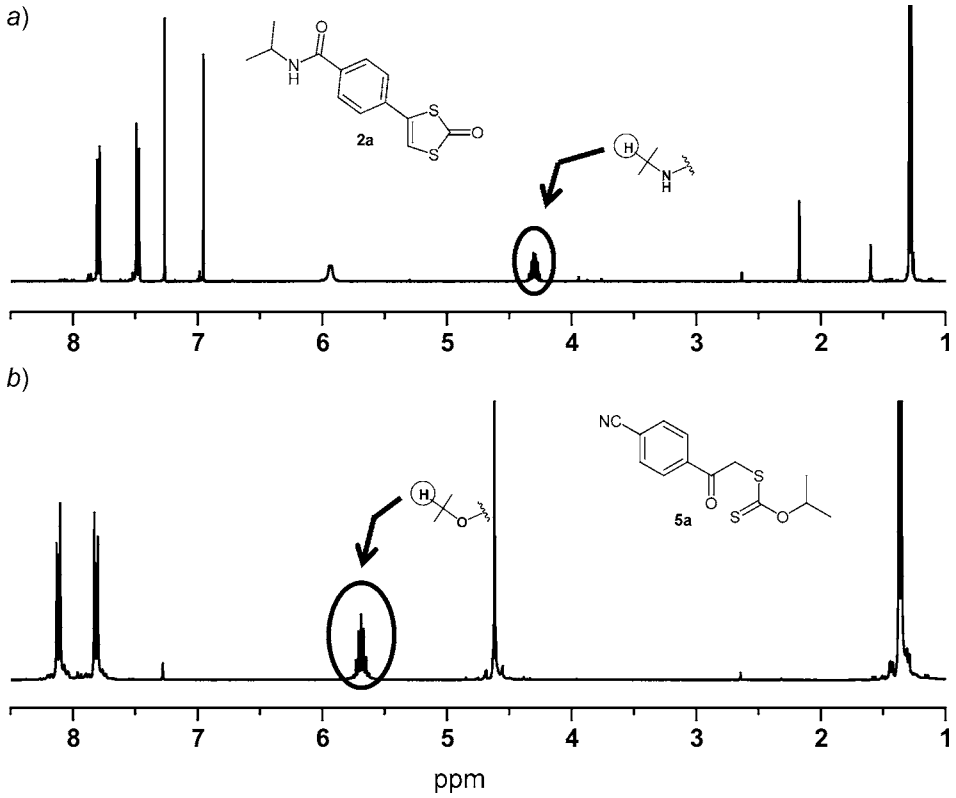


Fig. 2. *^{1}H-NMR Spectra* (400 MHz, $CDCl_3$) *of* **2a** *and* **5a**

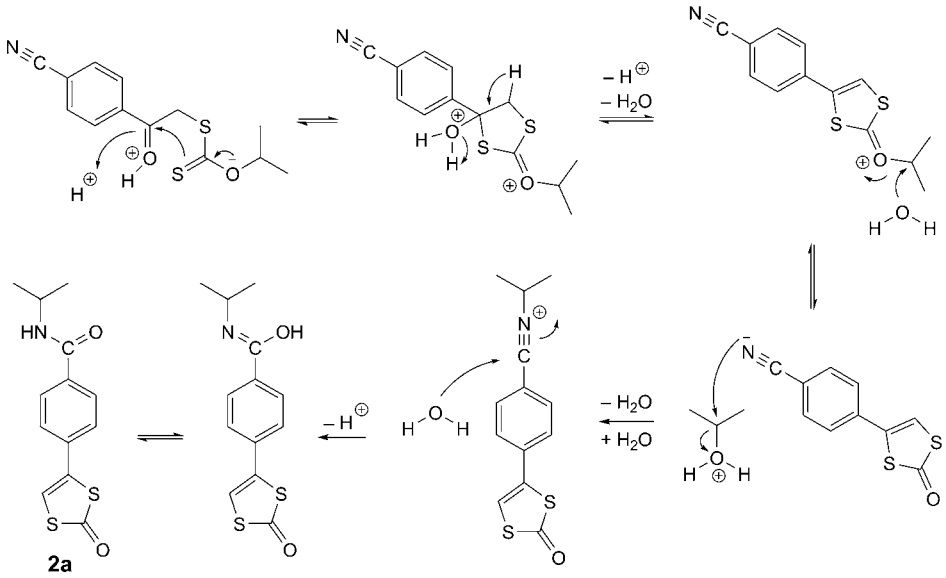
the amide **2a** and **2e** – **2g**, respectively. Finally, at a temperature $> 90°$, hydrolysis of the nitrile is extremely fast and **1** is immediately formed.

Conclusions. – A competition between a *Ritter* reaction and the normal hydrolysis of a cyano group under acidic conditions occurred during the synthesis of **1** from benzonitrile derivative **5a**. Interestingly, adjustment of the reaction temperature allowed for the selective preparation of acid **1** or amide **2a**. This unexpected *Ritter* reaction opens the way towards carboxamide-substituted and highly soluble 1,3-dithiol-2-one derivatives and tetrathiafulvalenes as solubilizing alkyl chains can be easily introduced by this method.

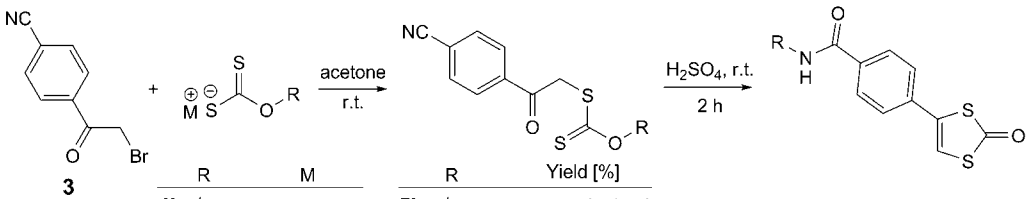
Experimental Part

General. All starting materials and solvents were purchased from *Aldrich* and *Alfa Aesar* and used as supplied commercially. Potassium *O*-isopropyl carbonodithioate (**4a**) [2], potassium *O*-ethyl carbonodithioate (**4h**) [5], and potassium *O*-butyl carbonodithioate (**4i**) [6] were prepared according to the literature procedures. All reactions were performed under Ar, unless otherwise stated. ^{1}H- and ^{13}C-NMR Spectra: *Bruker-Avance-400* spectrometer, at 400 (^{1}H) and 100 MHz (^{13}C) and r.t. in 5 mm o.d. tubes; δ in

Scheme 2. *Proposed Mechanism for the Formation of* **2a**



Scheme 3. *Syntheses of 1,3-Dithiol-2-one Derivatives Starting from Various Dithiocarbonates*



	R	M
4b	^{t}Bu	K
4c	$EtMe_2C$	Na
4d	$PhMe_2C$	Na
4e	EtMeCH	K
4f	Pr_2CH	Na
4g	Cyclohexyl	K or Na
4h	Et	K
4i	Bu	K
4j	$PhCH_2$	Na

	R	Yield [%]
5b	^{t}Bu	not obtained
5c	$EtMe_2C$	not obtained
5d	$PhMe_2C$	not obtained
5e	EtMeCH	84
5f	Pr_2CH	80
5g	Cyclohexyl	71
5h	Et	93
5i	Bu	89
5j	$PhCH_2$	74

	R	Yield [%]
2e	EtMeCH	77
2f	Pr_2CH	70
2g	Cyclohexyl	65
2h	Et	not formed
2i	Bu	not formed
2j	$PhCH_2$	not formed

ppm rel. to the solvent peaks of $CDCl_3$ (δ(H) 7.26; δ(C) 77.0), *J* in Hz. HR-ESI-MS: performed at the Spectropole of Aix-Marseille University (Marseille); *QStar-Elite* mass spectrometer (*Applied Biosystems Sciex*); in *m*/*z*.

4-(2-Oxo-1,3-dithiol-4-yl)benzoic Acid (**1**). To conc. (98%) H_2SO_4 (5 ml) was added at 0° **5a** (0.5 g, 1.8 mmol). The mixture was heated at 90° for 2 h under air. After cooling, the soln. was poured on ice and the resulting precipitate filtered and then dissolved in acetone or $CHCl_3$. This soln. was dried ($MgSO_4$) and concentrated to half the volume. The precipitate was filtered off and dried under vacuum: 0.4 g (88%) of **1**. Light beige powder. ^{1}H-NMR ($CDCl_3$): 6.96 (*s*, 1 H); 7.48 (*d*, *J* = 8.4, 2 H); 7.80 (*d*, *J* = 8.4, 2 H). ^{1}H-NMR ((D_6)DMSO): 7.48–7.65 (*m*, 2 H); 7.80 (*s*, 1 H); 7.93–8.07 (*m*, 2 H). ^{13}C-NMR

((D$_6$)DMSO): 116.0; 125.9; 128.4; 132.3; 134.3; 134.4; 166.9; 193.4. HR-ESI-MS: 238.9828 ($C_{10}H_7O_3S_2^+$, $[M+H]^+$; calc. 238.9831).

N-*(1-Methylethyl)-4-(2-oxo-1,3-dithiol-4-yl)benzamide* (**2a**). To conc. (98%) H_2SO_4 soln. (10 ml) was added at r.t. **5a** (0.5 g, 1.8 mmol). The mixture was stirred at r.t. for 2 h under air atmosphere. The soln. was poured on ice and extracted with $CHCl_3$, the extract dried ($MgSO_4$) and concentrated, the residue suspended in pentane, and the beige solid filtered off and dried under vacuum: 0.4 g (82 %) of **2a**. ^{1}H-NMR ((D$_6$)DMSO): 1.16 (*d*, *J* = 6.4, 6 H); 4.06 (*sept.*, *J* = 6.4, 1 H); 7.63 (*d*, *J* = 8.5, 2 H); 7.78 (*s*, 1 H); 7.89 (*d*, *J* = 8.5, 2 H); 8.31 (*d*, *J* = 7.7, 1 H). ^{1}H-NMR ($CDCl_3$): 1.28 (*d*, *J* = 6.6, 6 H); 4.28 (*sept.*, *J* = 6.6, 1 H); 6.11 (*d*, *J* = 7.2, 1 H); 6.96 (*s*, 1 H); 7.46 (*d*, *J* = 6.6, 2 H); 7.80 (*d*, *J* = 6.6, 2 H). ^{13}C-NMR ($CDCl_3$): 23.6; 42.9; 114.1; 127.1; 128.6; 134.6; 135.9; 136.1; 166.4; 192.7. HR-ESI-MS: 302.0279 ($C_{13}H_{13}NNaO_2S_2^+$, $[M+Na]^+$; calc. 302.0280).

N-*(1-Methylpropyl)-4-(2-oxo-1,3-dithiol-4-yl)benzamide* (**2e**). As described for **2a**, from **5e**: **2e** (77%). ^{1}H-NMR ($CDCl_3$): 0.97 (*t*, *J* = 7.4, 3 H); 1.24 (*d*, *J* = 6.6, 3 H); 1.54 – 1.64 (*m*, 2 H); 4.07 – 4.15 (*m*, 1 H); 6.07 (*d*, *J* = 8.0, NH); 6.95 (*s*, 1 H); 7.45 (*d*, *J* = 8.5, 2 H); 7.80 (*d*, *J* = 8.5, 2 H). ^{13}C-NMR ($CDCl_3$): 10.4; 20.5; 29.7; 47.3; 113.4; 126.3; 127.8; 133.9; 135.1; 135.5; 165.8; 193.3. HR-ESI-MS: 316.0438 ($C_{14}H_{15}NNaO_2S_2^+$, $[M+Na]^+$; calc. 316.0436).

4-(2-Oxo-1,3-dithiol-4-yl)-N-*(1-propylbutyl)benzamide* (**2f**). As described for **2a**, from **5f**: **2f** (70%). ^{1}H-NMR ($CDCl_3$): 0.88 (*t*, *J* = 7.4, 6 H); 1.32 – 1.43 (*m*, 4 H); 1.51 – 1.76 (*m*, 4 H); 4.01 – 4.06 (*m*, 1 H); 7.65 (*d*, *J* = 8.2, 2 H); 7.96 (*d*, *J* = 8.2, 2 H). ^{13}C-NMR ($CDCl_3$): 13.9; 22.1; 28.0; 52.2; 115.8; 127.5; 128.1; 132.4; 134.5; 138.8; 167.0; 197.7. HR-ESI-MS: 358.0911 ($C_{17}H_{21}NNaO_2S_2^+$, $[M+Na]^+$; calc. 358.0906).

N-*Cyclohexyl-4-(2-oxo-1,3-dithiol-4-yl)benzamide* (**2g**). As described for **2a**, from **5g**: **2g** (65%). ^{1}H-NMR ((D$_6$)DMSO): 1.10 – 1.42 (*m*, 4 H); 1.59 – 1.82 (*m*, 6 H); 3.73 – 3.79 (*m*, 1 H); 6.64 (br. *s*, NH); 6.87 (*s*, 1 H); 7.62 (*d*, *J* = 8.5, 2 H); 7.92 (*d*, *J* = 8.5, 2 H). ^{13}C-NMR ((D$_6$)DMSO): 24.9; 30.4; 34.3; 48.5; 115.8; 124.9; 125.7; 128.2; 134.0; 135.9; 164.4; 191.9. HR-ESI-MS: 342.0598 ($C_{16}H_{17}NNaO_2S_2^+$, $[M+Na]^+$; calc. 342.0593).

4-(2-Bromoacetyl)benzonitrile (**3**). To 4-acetylbenzonitrile (2 g, 13.8 mmol) in $CHCl_3$ (25 ml) was slowly added at r.t. Br_2 (0.67 ml, 2.10 g, 13.4 mmol) in $CHCl_3$ (25 ml) within roughly 2 h. The mixture was stirred at r.t. overnight. The solvent was evaporated and the residue purified by CC (SiO_2, pentane/CH_2Cl_2 1:1: **3** (2.1 g, 71%). Light beige solid. NMR Data: consistent with those reported previously [4]. ^{1}H-NMR ($CDCl_3$): 4.44 (*s*, 2 H); 7.81 (*d*, *J* = 6.6, 2 H); 8.08 (*s*, *J* = 6.6, 2 H). ^{13}C-NMR ($CDCl_3$): 31.2; 117.8; 118.5; 130.2; 133.5; 137.7; 191.0.

Potassium O-*(1,1-Dimethylethyl) Carbonodithioate* (**4b**). Commercially available potassium *tert*-butoxide (10.7 g, 95 mmol) was suspended in dry THF (150 ml) and cooled in an ice bath. CS_2 (5.8 ml, 95 mmol) was then slowly added to the soln., resulting in almost a solid light beige piece. The crystals were filtered off and washed with Et_2O (3 × 100 ml): **4l** (14.1 g, 79%), which was used without any further purification. ^{1}H-NMR ((D$_6$)DMSO): 1.55 (*s*, 9 H). ^{13}C-NMR ((D$_6$)DMSO): 28.4; 81.7; 229.6. HR-ESI-MS: 187.9730 ($C_4H_6KOS_2^-$, M^-; calc. 187.9732).

Sodium O-*(1,1-Dimethylpropyl) Carbonodithioate* (**4c**). To 2-methylbutan-2-ol (60 ml) and dry THF (30 ml) was added Na (2.3 g, 100 mmol). The reflux was maintained overnight for complete consumption of Na. The soln. was cooled in an ice bath, CS_2 (5.8 ml, 95 mmol) was slowly added to the resulting orange soln., and stirring was maintained overnight. During that time, a precipitate formed, which was filtered off, washed with pentane, and dried under vacuum: **4c** (11.5 g, 65%), which was used without any further purification. ^{1}H-NMR ((D$_6$)DMSO): 0.92 (*t*, *J* = 7.3, 3 H); 1.20 (*s*, 6 H); 1.51 (*q*, *J* = 7.3, 2 H). ^{13}C-NMR ((D$_6$)DMSO): 8.4; 26.0; 32.7; 64.9; 229.2. HR-ESI-MS: 163.0253 ($C_6H_{11}NaOS_2^-$, M^-; calc. 163.0257).

Sodium O-*(1-Methyl-1-phenylethyl) Carbonodithioate* (**4d**). To 2-phenylpropan-2-ol (30 ml) and dry THF (50 ml) was added Na (2.3 g, 100 mmol). The reflux was maintained overnight for complete consumption of Na. After cooling in an ice bath, CS_2 (5.8 ml, 95 mmol) was slowly added to the resulting orange soln., and stirring at r.t. was continued overnight (no precipitate formed). The soln. was concentrated to the third of its initial volume, and a precipitate appeared which was filtered off, washed with cold pentane, and dried under vacuum: **4d** (10.7 g, 48%), which was used without any further purification. ^{1}H-NMR ((D$_6$)DMSO): 1.52 (*s*, 6 H); 7.24 – 7.26 (*m*, 1 H); 7.35 (*t*, *J* = 7.3, 2 H); 7.49 (*d*, *J* = 7.5, 2 H). ^{13}C-NMR ((D$_6$)DMSO): 28.3; 65.7; 127.6; 127.9; 129.2; 137.2; 229.1. HR-ESI-MS: 211.0256 ($C_{10}H_{11}NaOS_2^-$, M^-; calc. 211.0257).

Potassium O-(*1-Methylpropyl*) *Carbonodithioate* (**4e**). KOH (10.5 g, 190 mmol) was added to (70 g) butan-2-ol, and the mixture was heated under reflux for 1 h. After cooling in an ice bath, CS_2 (11.5 ml, 190 mmol) was slowly added to the resulting wine-red soln., resulting in almost a solid piece. The crystals were filtered off and washed with Et_2O (3×100 ml): **4e** (27.2 g, 76%), which was used without any further purification. ^{1}H-NMR ((D_6)DMSO): 0.82 (*t*, *J* = 7.4, 3 H); 1.12 (*d*, *J* = 6.2, 3 H); 1.40–1.64 (*m*, 2 H); 5.33 (*q*, *J* = 6.2, 1 H). ^{13}C-NMR ((D_6)DMSO): 9.9; 19.2; 28.4; 77.0; 230.2. HR-ESI-MS: 149.0105 ($C_5H_9KOS_2^-$, M^-; calc. 149.0100).

Sodium O-*(1-Propylbutyl) Carbonodithioate* (**4f**). To heptan-4-ol (10 ml, 70 mmol) in dry THF (100 ml) was added NaH (95% dry; 1.69 g, 70 mmol). The mixture was stirred at r.t. for 30 min. After cooling to 0°, CS_2 (4.3 ml, 70 mmol) was slowly added to the resulting orange soln., and the mixture was stirred at r.t. overnight. THF was then evaporated, a minimum of Et_2O added, followed by pentane which precipitated the salt. It was filtered off, washed several times with Et_2O, and dried under vacuum: **4f** (12.6 g, 84%). ^{1}H-NMR ((D_6)DMSO): 0.84 (*t*, *J* = 7.1, 6 H); 1.24–1.29 (*m*, 4 H); 1.34–1.48 (*m*, 4 H); 5.46 (*m*, 1 H). ^{13}C-NMR ((D_6)DMSO): 14.1; 18.2; 36.0; 78.7; 229.6. HR-ESI-MS: 191.0576 ($C_8H_{15}NaOS_2^-$; M^-; calc. 191.0570).

Potassium O-*Cyclohexyl Carbonodithioate* (**4g**, M = K). To cyclohexanol (20 ml) was added KOH (5.3 g, 94.8 mmol). The mixture was refluxed for 1 h. After cooling in an ice bath, THF (100 ml) was added. Then, CS_2 (2.9 ml, 95 mmol) was slowly added to the resulting wine-red soln. in which a light brown precipitate formed. The mixture was stirred overnight at r.t. The orange solid was filtered off and washed with Et_2O (3×10 ml): **4g** (M = K; 13.8 g, 68%). ^{1}H-NMR ($CDCl_3$): 1.22–1.85 (*m*, 10 H); 5.21 (br. *s*, 1 H). ^{13}C-NMR ($CDCl_3$): 23.9; 25.2; 38.6; 39.2; 39.7; 77.5; 229.2. HR-ESI-MS: 175.0255 ($C_7H_{11}KOS_2^-$, M^-; calc. 175.0257).

Sodium O-*Cyclohexyl Carbonodithioate* (**4g**, M = Na). Cyclohexanol (10 g, 100 mmol) was suspended in dry THF (100 ml) and NaH (95%, dry; 2.4 g, 100 mmol) was added at 0° to the soln. Stirring was maintained for 30 min, and CS_2 (6 ml, 100 mmol) was slowly added. The soln. was stirred at r.t. overnight. Addition of pentane precipitated a brown solid which was filtered off, washed several times with pentane and dried under vacuum: **4g** (M = Na; 17.8 g, 90%). ^{1}H-NMR ($CDCl_3$): 1.22–1.85 (*m*, 10 H); 5.21 (br. *s*, 1 H). ^{13}C-NMR ($CDCl_3$): 25.2; 38.6; 39.2; 77.5; 229.2. ESI-MS: 175.0273 ($C_7H_{11}NaOS_2^-$, M^-; calc. 175.0257).

Sodium O-*(Phenylmethyl) Carbonodithioate* (**4j**). To a soln. of benzyl alcohol (10 g) and dry THF (100 ml) cooled to 0°, NaH (95 %, dry; 2.22 g, 92 mmol) was added. After 30 min at r.t., the soln. was cooled to 0°, and CS_2 (7 ml, 116 mmol) was added. The soln. was stirred at r.t. overnight, and addition of pentane, precipitated a white solid which was filtered off, washed several times with pentane and dried under air: **4j** (14.1 g, 74%). ^{1}H-NMR ((D_6)DMSO): 5.35 (*s*, 2 H); 7.29–7.35 (*m*, 5 H). ^{13}C-NMR ((D_6)DMSO): 71.9; 127.1; 127.8; 128.0; 138.2; 229.4. HR-ESI-MS: 182.9948 ($C_8H_7NaOS_2^-$, M^-; calc. 182.9944).

S-*[2-(4-Cyanophenyl)-2-oxoethyl]* O-*(1-Methylethyl) Carbonodithioate* (**5a**). Potassium *O*-isopropyl dithiocarbonate (**4a**; 2.5 g, 14.3 mmol) was added under stirring to a soln. of **3** (3.2 g, 14.3 mmol) in acetone (30 ml). The mixture was stirred at r.t. overnight, then the solvent evaporated, and the residue suspended in EtOH, filtered, and dried under vacuum: **5a** (3.7 g, 92%). ^{1}H-NMR ($CDCl_3$): 1.36 (*d*, *J* = 6.4, 6 H); 4.62 (*s*, 2 H); 5.69 (*sept.*, *J* = 6.4, 1 H); 7.81 (*d*, *J* = 8.6, 2 H); 8.12 (*d*, *J* = 8.6, 2 H). ^{13}C-NMR ($CDCl_3$): 21.1; 42.9; 79.2; 116.7; 117.6; 128.5; 132.5; 138.7; 191.4; 211.8. HR-ESI-MS: 280.0455 ($C_{13}H_{14}NO_2S_2^+$, $[M+H]^+$; calc. 280.0460).

S-*[2-(4-Cyanophenyl)-2-oxoethyl]* O-*(1-Methylpropyl) Carbonodithioate* (**5e**). As described for **5a**, from **4e**: **5e** (84%). ^{1}H-NMR ($CDCl_3$): 0.93 (*t*, *J* = 7.4, 3 H); 1.34 (*d*, *J* = 6.3, 3 H); 1.62–1.83 (*m*, 2 H); 4.62 (*s*, 2 H); 5.54–5.61 (*m*, 1 H); 7.82 (*d*, *J* = 8.5, 2 H); 8.11 (*d*, *J* = 8.5, 2 H). ^{13}C-NMR ($CDCl_3$): 9.5; 18.6; 28.4; 43.1; 84.0; 116.9; 117.8; 128.9; 132.6; 138.9; 191.6; 212.3. HR-ESI-MS: 294.0619 ($C_{14}H_{16}NO_2S_2^+$, $[M+H]^+$; calc. 294.0617).

S-*[2-(4-Cyanophenyl)-2-oxoethyl]* O-*(1-Propylbutyl) Carbonodithioate* (**5f**). As described for **5a**, from **4f**: **5f** (80%). ^{1}H-NMR ($CDCl_3$): 0.88 (*t*, *J* = 7.4, 6 H); 1.32–1.43 (*m*, 4 H); 1.51–1.76 (*m*, 4 H); 4.62 (*s*, 2 H); 5.54 (*qt*, *J* = 7.0, 1 H); 7.81 (*d*, *J* = 8.5, 2 H); 8.12 (*d*, *J* = 8.5, 2 H). ^{13}C-NMR ($CDCl_3$): 13.9; 25.0; 29.2; 67.8; 69.8; 116.6; 117.6; 132.1; 132.5; 139.3; 191.6; 211.9. HR-ESI-MS: 336.1088 ($C_{17}H_{22}NO_2S_2^+$, $[M+H]^+$; calc. 336.1086).

S-*[2-(4-Cyanophenyl)-2-oxoethyl]* O-*Cyclohexyl Carbonodithioate* (**5g**). As described for **5a**, from **4g** (M = Na or K): **5g** (71%). ^{1}H-NMR ($CDCl_3$): 1.28–1.44 (*m*, 4 H); 1.52–1.60 (*m*, 2 H); 1.70–1.76 (*m*, 2 H); 1.95–2.00 (*m*, 2 H); 4.62 (*s*, 2 H); 5.47–5.52 (*m*, 2 H); 7.82 (*d*, *J* = 8.5, 2 H); 8.12 (*m*, *J* = 8.5, 2 H). ^{13}C-NMR ($CDCl_3$): 23.3; 24.9; 30.6; 42.9; 83.7; 116.6; 117.6; 128.7; 132.4; 138.7; 191.4; 211.6. HR-ESI-MS: 320.0777 ($C_{16}H_{17}NO_2S_2^+$, $[M+H]^+$; calc. 320.0773).

S-*[2-(4-Cyanophenyl)-2-oxoethyl]* O-*Ethyl Carbonodithioate* (**5h**). As described for **5a**, from **4h**: **5h** (93%). ^{1}H-NMR ($CDCl_3$): 1.26 (*t*, *J* = 7.1, 3 H); 4.56 (*q*, *J* = 7.1, 2 H); 4.90 (*s*, 2 H); 8.06 (*d*, *J* = 8.5, 2 H); 8.19 (*d*, *J* = 8.5, 2 H). ^{13}C-NMR ($CDCl_3$): 14.0; 42.9; 70.7; 115.5; 118.0; 128.9; 132.9; 138.9; 192.1; 212.9. HR-ESI-MS: 266.0307 ($C_{12}H_{12}NO_2S_2^+$, $[M+H]^+$; calc. 266.0304).

O-*Butyl* S-*[2-(4-Cyanophenyl)-2-oxoethyl]* *Carbonodithioate* (**5i**). As described for **5a**, from **4i**: **5i** (89%). ^{1}H-NMR ($CDCl_3$): 0.94 (*t*, *J* = 7.3, 3 H); 1.38–1.46 (*m*, 2 H); 1.74–1.87 (*m*, 2 H); 3.74 (*t*, *J* = 6.4, 2 H); 4.58 (*t*, *J* = 6.6, 2 H); 4.64 (*s*, 2 H); 7.82 (*d*, *J* = 8.5, 2 H); 8.11 (*d*, *J* = 8.5, 2 H). ^{13}C-NMR ($CDCl_3$): 13.6; 19.1; 30.2; 43.4; 75.1; 116.9; 117.7; 128.9; 132.7; 138.9; 191.4; 213.0. HR-ESI-MS: 294.0616 ($C_{14}H_{16}NO_2S_2^+$, $[M+H]^+$; calc. 294.0617).

S-*[2-(4-Cyanophenyl)-2-oxoethyl]* O-*(Phenylmethyl) Carbonodithioate* (**5j**). As described for **5a**, from **4j**: **5j** (74%). ^{1}H-NMR ($CDCl_3$): 4.60 (*s*, 2 H); 5.55 (*s*, 2 H); 7.30–7.36 (*m*, 5 H); 7.74 (*d*, *J* = 8.5, 2 H); 8.03 (*d*, *J* = 8.5, 2 H). ^{13}C-NMR ($CDCl_3$): 43.1; 76.0; 116.6; 117.6; 128.4; 128.5; 128.56; 128.6; 132.4; 133.8; 138.6; 191.2; 212.2. ESI-MS: 328.0462 ($C_{17}H_{14}NO_2S_2^+$, $[M+H]^+$; calc. 328.0460).

Methyl 4-(2-Oxo-1,3-dithiol-4-yl)benzoate (**6**). Acid **1** (1 g, 4.2 mmol) was suspended in MeOH, and conc. (98%) H_2SO_4 soln. (cat. amount) was added. The mixture was refluxed overnight. After cooling, the MeOH was evaporated, H_2O was added, the aq. phase extracted with CH_2Cl_2, the extract washed several times with a dil. aq. K_2CO_3 soln., dried ($MgSO_4$) and concentrated, and the residue subjected to CC (SiO_2, CH_2Cl_2): **6** (quant.). White solid. ^{1}H-NMR ($CDCl_3$): 3.92 (*s*, MeO); 7.00 (*s*, 1 H); 7.50 (*d*, *J* = 8.4, 2 H); 8.08 (*d*, *J* = 8.4, 2 H). ^{13}C-NMR ($CDCl_3$): 52.4; 114.0; 126.2; 127.5; 130.5; 133.8; 136.6; 166.2; 191.7. ESI-MS: 270.0245 ($C_{11}H_{12}NO_3S_2^+$, $[M+NH_4]^+$; calc. 270.0253).

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Received June 20, 2012