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Functionally Substituted Vinyl Carbanions, 25[1]

Heteroatom Influence on Vinylic Deprotonation

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Direct lithiation of (*E*)-(phenylvinyl)phosphonate **2** with LDA takes place at 1-position; with electrophiles compounds **3** were obtained. The (*Z*)-1-(ethylsulfinyl)-2-(ethylthio)ethylene **7** delivers on reaction with methyllithium mainly the 1-lithiated species (*Z*)-**7A**. According to reactions with electrophiles, this functionally substituted vinyllithium species is configurationally labile. Depending on reaction temperature and time with electrophiles either (*Z*)- or (*E*)-products were obtained. Depending on substituents the 1,3-dithioles **10a–c** were lithiated either in 2- or 5-position; higher reaction temperature or prolonged reaction time leads to fragmentation of the lithiated species. The 1,3-dioxole **14b** gave only a product of vinylic lithiation.

Funktionell substituierte Vinyllithiumverbindungen, 25[1]

Heteroatom-Einfluß auf die vinylische Deprotonierung

Die direkte Lithiierung von (*E*)-(Phenylvinyl)phosphonat **2** mit LDA erfolgt an der 1-Stellung und liefert mit Elektrophilen die Verbindungen **3**. Das (*Z*)-1-(Ethylsulfinyl)-2-(ethylthio)-ethylen **7** gibt mit Methyllithium als Base ebenfalls bevorzugt 1-Lithiierung zu (*Z*)-**7A**. Nach den Reaktionen mit Elektrophilen ist die lithiierte Spezies jedoch nicht konfigurationsstabil. In Abhängigkeit von der Temperatur und der Zeit werden mit Elektrophilen (*Z*)- und (*E*)-Produkte erhalten. Die 1,3-Dithiole **10a–c** werden substituentenabhängig entweder an 2- oder 5-Stellung lithiiert; bei höheren Temperaturen oder verlängerter Reaktionszeit fragmentieren die lithiierten Spezies. Das 1,3-Dioxol **14b** liefert ein Produkt aus vinylischer Lithiierung.

The regioselectivity of the direct *C*-metalation of functionally substituted acrylates and derivatives is substituent dependent[2]. Inductive effects and intramolecular complexation play important roles in this regard. In addition, complexation may be responsible for big differences in the regioselectivity of kinetic versus thermodynamic hydrogen/metal exchange[3].

The positive influence of second row elements on the CH-acidity of sp^3-carbon atoms is well documented[4]. This influence on the direct lithiation of sp^2-carbon atoms is investigated in three different examples.

A. (*E*)-Phenylvinylphosphonate 2

(*Z*)- and (*E*)-cinnamonitrile were exclusively lithiated at the α-position[5]; however, (*E*)-cinnamic ester **1** gave with lithium diisopropylamide (LDA) in tetra-

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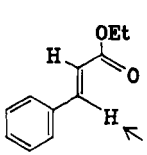
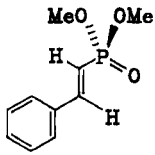
hydrofuran due to intramolecular complexation exclusively products from β-lithiation[6]. Therefore we have investigated the structurally analogues (*E*)-(phenylvinyl)-phosphonate **2**[7] under similar reaction conditions. *C*-Lithiated species were trapped with methan-[D]ol. According to ^{1}H NMR data the product **3a** showed only 1-deuteration. This finding was supported by reactions with propionaldehyde, benzaldehyde, trimethylsilyl chloride, and dimethyl disulfide as electrophiles. Only compounds **3b–e** were isolated as reaction products[8].

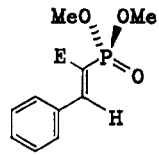
Scheme 1

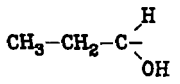
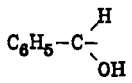


1



2



	E
3a	D
b	
c	
d	$(CH_3)_3Si$
e	CH_3S

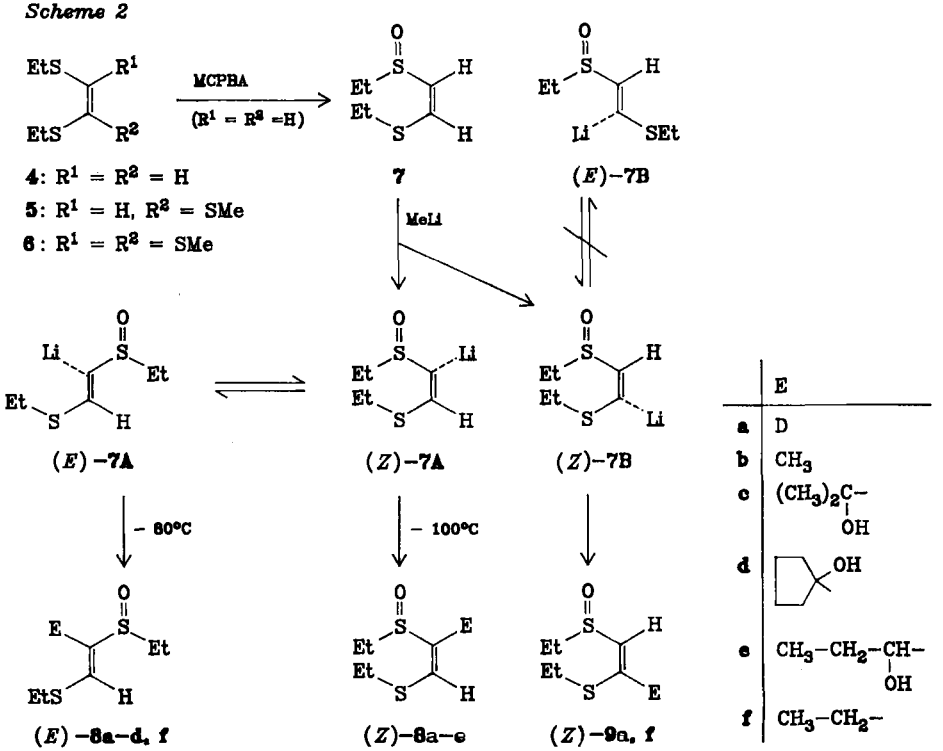
B. (*Z*)-1-(Ethylsulfinyl)-2-(ethylthio)ethylene 7

There are no examples known yet where in direct lithiation experiments β-alkylthio-substituted acrylates show different regioselectivity from the corresponding β-alkoxy-substituted acrylates. However, big differences in reactivity were observed[9]. As expected, alkylthio-substituted lithiated species are much more reactive. However, it is known that 1-alkoxy-2-(alkylthio)ethylene is lithiated at the carbon atom carrying the alkylthio group[10].

Oxidation of (*Z*)-1,2-bis(ethylthio)ethylene (**4**) with *m*-chloroperbenzoic acid (MCPBA) gave (*Z*)-1-(ethylsulfinyl)-2-(ethylthio)ethylene (**7**) as a structural analogue of β-(ethylthio)acrylate, which is lithiated exclusively in the β-position[9]. Lithiation of compound **7** with methyllithium (or *tert*-butyllithium[11]) is very much temperature and time dependent. At −120°C and a reaction time of 10 minutes the lithiated species (*Z*)-**7A** and (*Z*)-**7B** were generated in > 95:5 ratio according to deuteration to compounds (*Z*)-**8a** and (*Z*)-**9a**. The same result was obtained at −100°C and 1 minute reaction time. Longer reaction times or higher reaction temperature, for instance at −80°C and a reaction time of 15 minutes, led under inversion of configuration to equilibration and with methan-[D]ol the deuterated compounds (*E*)-**8a**, (*Z*)-**8a**, and (*Z*)-**9a** were formed in a 73:17:10 ratio. The same result was observed starting from (*E*)-1-(ethylsulfinyl)-2-(ethylthio)ethylene, which was obtained from compound **7** via this route. Therefore lithiation takes place in these compounds preferentially in 1-position. Deuterated compounds derived from the C-2 inverted species (*E*)-**7B** were not observed.

This result was also confirmed by reaction with other electrophiles. At −100°C and addition of the electrophiles methyl iodide, acetone, or cyclopentanone after 1 minute gave almost exclusively the *Z*-isomers (*Z*)-**8b–d** (> 95%); they were

Scheme 2



isolated as pure compounds. With propionaldehyde as electrophile the corresponding (*Z*)-**8e** adduct was obtained, which consisted of a 1:1-diastereoisomeric mixture[12], whose relative chirality was not assigned. At −80°C and addition of the electrophiles methyl iodide, acetone, or cyclopentanone after 15 minutes preferentially the (*E*)-isomers (*E*)-**8b**–**d** were formed (*E*:*Z* ≈ 4:1). A different result was obtained with the less reactive ethyl iodide as electrophile. At −100°C and at −80°C the adducts (*E*)-**8f** and (*Z*)-**9f** were isolated in a 4:1 ratio. The structures of these compounds were assigned on the basis of ^{1}H NMR chemical shifts of vinylic protons (Table 2).

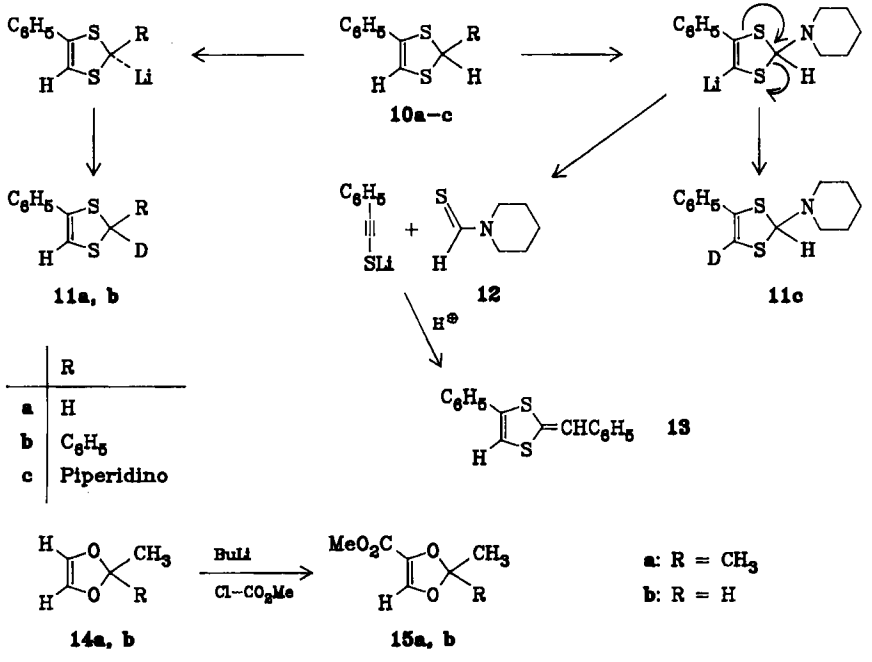
C. 1,3-Dithioles 10a–c and 1,3-Dioxoles 14a, b

Lithiation of bis(ethylthio)ethylene (**4**) at low temperatures and reaction with electrophiles can be carried out without difficulty[13]. For instance with dimethyl disulfide as electrophile the tris(alkylthio)ethylene **5** was obtained. Subsequent lithiation and dimethyl disulfide treatment gave the tetrakis(alkylthio)ethylene **6** in good yield[14] (Scheme 2).

Combination of the bis(alkylthio)ethylene moiety with the dithioacetal moiety, which is important in nucleophilic acylation reactions[4], leads to the 1,3-dithiole system **10**. The competition between direct vinylic and dithioacetal lithiation was investigated in the derivatives **10a**–**c**[15]. With the 2-unsubstituted dithiole **10a**

and the 2-phenyl-substituted dithiole **10b** at −120°C and LDA as a base exclusively lithiation in 2-position was deduced from deuteration with methan-[D]ol resulting in compounds **11a, b**[16]. Surprisingly, the 2-piperidino-substituted dithiole **10c** led with *tert*-butyllithium at −100°C to lithiation in 5-position (**10c**:**11c** = 60:40). Extending the reaction time to 4 hours gave 75% 5-deuterated product **11c**. In addition fragmentation of the lithiated intermediate was observed, which became the main reaction (60−70%) at −80°C and 1 hour reaction time. According to Scheme 3 (thioformyl)piperidine **12**[17] and via dimerisation the alkylidenedithiole **13**[18] were products. Both compounds were assigned by independent syntheses.

Scheme 3



Lithiation of the vinylic position in compound **10c** demonstrated that first row elements with a negative inductive effect may not support sp^3 carbanion formation due to destabilizing effects of interacting lone pair orbitals[19]. Therefore it was of interest to investigate the direct lithiation of the 1,3-dioxole system **14**. At −80°C and with *tert*-butyllithium as a base the 2,2-dimethyl derivative **14a**[20] behaved like the *cis*-enediol ether[21] and gave clean vinylic lithiation leading with methyl chloroformate to the ester **15a**[22]. The same result was obtained with 2-methyl-1,3-dioxole (**14b**)[20], which gave the ester **15b**. Lithiation in 2-position of compound **14b** is not only hampered by unfavorable lone pair orbital interactions of oxygen-1, carbon-2, and oxygen-3 in the carbanionic species but also by generation of a heterocyclic 8π-electron system[19].

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Experimental Part

Melting points are uncorrected, they were determined according to Tottoli on dried samples in open capillaries. – ^{1}H NMR spectra were recorded in $CDCl_3$ (Me_4Si, 0.00 ppm) with a Bruker CP 80 CW) and a Bruker WM 250 Cryospec. – R_F values refer to TLC performed on silica gel (Merck) with the solvent systems noted. – Column chromatography was performed under normal pressure with silica gel (Merck, 70–325 mesh) and under medium pressure with silica gel (Merck "LiChroprep" Si 60, 40–60 μm) with the solvent systems noted. – Lithiation experiments were carried out under a nitrogen atmosphere with dry and oxygen free tetrahydrofuran as solvent.

Dimethyl (E)-(2-Phenylvinyl)phosphonate (**2**): This compound was obtained by literature procedure[7].

Dimethyl (E)-(1-Deuterio-2-phenylvinyl)phosphonate (**3a**), *General Procedure for the Synthesis of Compounds* **3b–e**: A solution of 0.60 g (2.82 mmol) **2** in 20 ml of dry tetrahydrofuran was added to a cooled (−100°C) solution of 3.1 mmol of lithium diisopropylamide in 20 ml of dry tetrahydrofuran [prepared from 315 mg (3.1 mmol) of diisopropylamine and 2 ml of a 1.55 M *tert*-butyllithium solution in *n*-hexane]. After 45 min at −100°C 2 ml of methan-[D]ol was added and the reaction mixture kept for another 5 min at −100°C. After addition of water ether extraction was carried out. The organic layer was washed once with water, dried over anhydrous sodium sulfate, and the solvent evaporated. The residue was distilled; b. p. 129°C/2 Torr. Yield 550 mg (90%); according to the ^{1}H NMR data this material was more than 95% deuterated at 1-position. – TLC [silica gel; $CHCl_3$/ether, 1:1]: R_F = 0.31 (R_F of compound **2**: 0.31).

Compounds **3b–e** were obtained by addition of 3 mmol of the electrophiles after 15 min at −100°C. The reaction mixtures were kept 1 h at −100°C, then left to arrive 0°C, and worked up as described above. The resulting products were chromatographed on silica gel with $CHCl_3$/MeOH, 19:1 (**3b**); $CHCl_3$/ether, 1:1 (**3c**, **3d**), 2:1 (**3e**). For yields, analytical and ^{1}H NMR data see Tables 1 and 2.

(Z)-1,2-Bis(ethylthio)ethylene (**4**) was obtained by modification of a literature procedure[23]: To a solution of 20 g (0.36 mol) of KOH, 60 ml of ethanol and 15 ml (0.2 mol) of ethanethiol was added 9.6 g (0.1 mol) of (*Z*)-1,2-dichloroethylene under a nitrogen atmosphere. For initiation of the reaction the mixture was heated up to 60–70°C, then refluxed for 30 min, cooled to room temperature, and poured on water. The product was extracted with ether, the organic layer dried over anhydrous sodium sulfate, and the solvent evaporated. The residue was distilled; b. p. 99–102°C/11 Torr (lit.[23] 100–102°C/11 Torr). Yield 11.2 g (76%). – ^{1}H NMR ($CDCl_3$, 80 MHz): δ = 6.07 (s, 2H, –CH=), 2.75 (q, 4H, $2CH_2$), 1.35 (t, 6H, $2CH_3$).

(Z)-1,2-Bis(ethylthio)-1-(methylthio)ethylene (**5**): To a solution of 0.59 g (4.0 mmol) of **4** in 30 ml of dry tetrahydrofuran was added at −80°C 5 ml (8.0 mmol) of *tert*-butyllithium (1.6 M solution in *n*-hexane). After 10 min 0.75 g (8.0 mmol) of dimethyl disulfide was added to the yellow reaction mixture. After 1 h at −80°C the reaction mixture was left to arrive room temperature, then it was extracted with chloroform/water. The organic layer was dried over potassium carbonate and the solvent evaporated. The residue was distilled, b. p. 58°C/

Table 1. Physical data and elemental analyses of compounds **3b–e**, (*Z*)-**8b–e**, (*E*)-**8b–d,f**, (*Z*)-**9f**

Compound	Yield [%]	R_F (Solvent System)	M.p. [°C]	Molecular Formula	Elemental Analyses	C	H	S
Dimethyl (*E*)-[1-(1-hydroxypropyl)-2-phenylvinyl]phosphonate (**3b**)	66	0.54 ($CHCl_3$/MeOH, 19:1)	54–55	$C_{13}H_{19}O_4P$ (270.2)	Calc.	57.78	7.09	
					Found	57.47	7.02	
Dimethyl (*E*)-[1-(α-hydroxybenzyl)-2-phenylvinyl]phosphonate (**3c**)	71	0.22 ($CHCl_3$/ether, 1:1)	104	$C_{17}H_{19}O_4P$ (318.3)	Calc.	64.14	6.01	
					Found	63.90	6.19	
Dimethyl (*E*)-[2-phenyl-1-(trimethylsilyl)vinyl]-phosphonate (**3d**)	49	0.33 ($CHCl_3$/ether, 1:1)	oil	$C_{13}H_{21}O_3PSi$ (284.4)	Calc.	54.91	7.44	
					Found	54.55	7.49	
Dimethyl (*Z*)-[1-(methylthio)-2-phenylvinyl]-phosphonate (**3e**)	55	0.38 ($CHCl_3$/ether, 2:1)	oil	$C_{11}H_{15}O_3PS$ (258.3)	Calc.	51.16	5.85	
					Found	51.21	6.06	
(*Z*)-2-(Ethylsulfinyl)-1-(ethylthio)-1-propene [(*Z*)-**8b**]	90	($CHCl_3$/MeOH, 99:1) 0.19	oil	$C_7H_{14}O_2S$ (178.3)	Calc.	47.15	7.92	35.96
					Found	47.20	7.85	35.66
(*E*)- ... [(*E*)-**8b**]	72	0.15	oil		Found	46.97	7.92	35.80
(*Z*)-2-(Ethylsulfinyl)-1-(ethylthio)-3-methyl-1-buten-3-ol [(*Z*)-**8c**]	90	($CHCl_3$/MeOH, 99:1) 0.16	oil	$C_9H_{18}O_2S_2$ (222.4)	Calc.	48.61	8.16	28.84
					Found	48.79	8.21	29.01
(*E*) ... [(*E*)-**8c**]	70	0.12	oil		Found	48.80	8.17	28.68
(*Z*)-1-(Ethylsulfinyl)-2-(ethylthio)-1-(1-hydroxycyclopentyl)ethylene [(*Z*)-**8d**]	76	($CHCl_3$/MeOH, 99:1) 0.16	oil	$C_{11}H_{20}O_2S_2$ (248.4)	Calc.	53.19	8.12	
					Found	52.86	8.07	
(*E*)- ... [(*E*)-**8d**]	65	0.13	oil		Found	52.91	8.01	
(*Z*)-2-(Ethylsulfinyl)-1-(ethylthio)-1-penten-3-ol [(*Z*)-**8e**]:		($CHCl_3$/MeOH, 99:1)		$C_9H_{18}O_2S_2$ (222.4)	Calc.	48.61	8.16	28.84
1. Diastereoisomer:	43	0.15	oil		Found	48.81	8.00	28.98
2. Diastereoisomer:	43	0.12	oil		Found	48.80	8.06	28.84
(*E*)-2-(Ethylsulfinyl)-1-(ethylthio)-1-butene [(*E*)-**8f**]	73	($CHCl_3$/MeOH, 99:1) 0.23		$C_8H_{16}OS_2$ (192.3)	Calc.	49.96	8.38	33.34
					Found	49.81	8.28	32.61
(*Z*)-1-(Ethylsulfinyl)-2-(ethylthio)-1-butene [(*Z*)-**9f**]	19	0.19	oil		Found	49.75	8.34	[a]

[a] Not determined.

Table 2. ^{1}H NMR data of compounds **2**, **3a–e**, **7**, (*Z*)-**8a–e**, (*E*)-**8a–d,f**, **9a,f**, and **10a–c**

Compound	^{1}H NMR ($CDCl_3$, δ; internal TMS) Coupling Constants (Hz)
2	7.70 (dd, 1H, $C_6H_5-CH=$; J = 18 Hz, J = 24 Hz), 7.80–7.40 (m, 5H, C_6H_5), 6.35 (dd, 1H, $=CH-P$; $J = J$ = 18 Hz), 3.82 (d, 6H, $2OCH_3$)
3a	7.85–7.40 (m, 6H, C_6H_5, $-CH=$), 3.82 (d, 6H, $2OCH_3$; J = 11.0 Hz)
3b	7.44–7.30 (m, 6H, C_6H_5, $-CH=$), 4.73–4.50 (m, 1H, C*H*OH), 3.83 (d, 3H, OCH_3; J = 11.5 Hz), 3.81 (d, 3H, OCH_3; J = 11.5 Hz), 3.27 (d, 1H, OH; J = 10.4 Hz), 2.03–1.85, 1.79–1.64 (2 m, 2H, CH_2CH_3), 0.97 (t, 3H, CH_2CH_3; J = 7.3 Hz)
3c	7.98–7.40 (m, 11H, $2C_6H_5$, $-CH=$), 6.18 (dd, 1H, C*H*OH; J = 11 Hz, J = 32 Hz), 4.48 (d, 1H, OH; J = 10.4 Hz); 3.81 (d, 3H, OCH_3; J = 11.5 Hz), 3.48 (d, 3H, OCH_3; J = 11.5 Hz)
3d	8.60 (d, 1H, $-CH=$; J = 33 Hz), 7.70–7.30 (m, 10H, $2C_6H_5$), 3.87 (d, 6H, $2OCH_3$; J = 11.5 Hz), 0.07 (s, 9H, $Si(CH_3)_3$)
3e	7.75 (d, 1H, $-CH=$; J = 22 Hz), 7.95–7.25 (m, 5H, C_6H_5), 3.80 (d, 6H, $2OCH_3$; J = 11.5 Hz), 2.35 (s, 3H, SCH_3)
7	6.82 (d, 1H, $=CH-SEt$; J = 9 Hz), 6.12 (d, 1H, $=CH-SO-$; J = 9 Hz), 2.97–2.63 (m, 4H, $2CH_2$), 1.40, 1.33 (2 t, 6H, $2CH_3$; J = 6.7 Hz)
(*Z*)-**8a**	6.85 (br, 1H, $=CH-SEt$), 2.94–2.62 (m, 4H, $2CH_2$), 1.40, 1.33 (2 t, 6H, $2CH_3$; J = 6.7 Hz)
(*E*)-**8a**	7.06 (t, 1H, $=CH-SEt$; J = 2 Hz), 2.97–2.60 (m, 4H, $2CH_2$), 1.35, 1.28 (2 t, 6H, $2CH_3$; J = 6.7 Hz)
(*Z*)-**9a**[a]	6.12 (sbr, 1H, $=CH-SO-$), 2.97–2.63 (m, 4H, $2CH_2$), 1.40, 1.33 (2 t, 6H, $2CH_3$; J = 6.7 Hz)
(*Z*)-**8b**	6.50 (s, 1H, $=CH-SEt$), 3.00–2.51 (m, 4H, $2CH_2$), 2.01 (s, 3H, $=C-CH_3$), 1.32, 1.24 (2 t, 6H, $2CH_3$; J = 6.7 Hz)
(*E*)-**8b**	6.77 (s, 1H, $=CH-SEt$), 2.95–2.32 (m, 4H, $2CH_2$), 1.82 (s, 3H, $=C-CH_3$), 1.32, 1.13 (2 t, 6H, $2CH_3$; J = 6.7 Hz)
(*Z*)-**8c**	6.51 (s, 1H, $=CH-SEt$), 5.15 (s, 1H, OH), 3.47–2.60 (m, 4H, $2CH_2$), 1.55–1.20 (m, 12H, $4CH_3$)
(*E*)-**8c**	6.56 (s, 1H, $=CH-SEt$), 4.12 (s, 1H, OH), 3.34–2.50 (m, 4H, $2CH_2$), 1.57–1.07 (m, 12H, $4CH_3$)
(*Z*)-**8d**	6.57 (s, 1H, $=CH-SEt$), 4.67 (s, 1H, OH), 3.45–2.62 (m, 4H, $2CH_2$), 2.37–1.21 (m, 14H, $2CH_3$, $4CH_2$)
(*E*)-**8d**	6.67 (s, 1H, $=CH-SEt$), 3.67 (sbr, 1H, OH), 3.28–2.62 (m, 4H, $2CH_2$), 2.62–1.11 (m, 14H, $2CH_3$, $4CH_2$)
(*Z*)-**8e**	1. Diastereoisomer: 6.66 (s, 1H, $=CH-SEt$), 4.47 (t, 1H, C*H*OH; J = 7 Hz), 3.63 (sbr, 1H, OH), 3.16–2.61 (m, 4H, $2CH_2$), 1.95–0.88 (m, 11H, CH_2, $3CH_3$) 2. Diastereoisomer: 6.72 (s, 1H, $=CH-SEt$), 4.52 (t, 1H, C*H*OH; J = 7 Hz), 3.71 (sbr, 1H, OH), 3.28–2.63 (m, 4H, $2CH_2$), 1.95–0.87 (m, 11H, CH_2, $3CH_3$)
(*E*)-**8f**	6.76 (s, 1H, $=CH-SEt$), 2.97–2.00 (m, 6H, $3CH_2$), 1.42–1.02 (3 t, 9H, $3CH_3$)
(*Z*)-**9f**	5.73 (s, 1H, $=CH-SO-$), 3.02–2.32 (m, 6H, $3CH_2$), 1.42–1.09 (3 t, 9H, $3CH_3$)
10a	7.44–7.20 (m, 5H, C_6H_5), 6.28 (s, 1H, 5-H), 4.50 (s, 2H, CH_2)
10b	7.65–7.25 (m, 10H, $2C_6H_5$), 6.30 (s, 1H, 5-H), 6.08 (s, 1H, 2-H)
10c	7.60–7.20 (m, 5H, C_6H_5), 6.44 (s, 1H, 5-H)[b], 6.28 (s, 1H, 2-H)[b], 2.70–2.45 (m, 4H, $2CH_2$), 1.70–1.25 (m, 6H, $3CH_2$)

[a] This compound was obtained in a 73:17:10 ratio of compounds (*Z*)-**8a**, (*E*)-**8a**, and (*Z*)-**9a**; for details see chapter B. — [b] This assignment (ref.[15]) was independently proven by unequivocal deuteration experiments.

10^{-3} Torr. Yield 0.66 g (85%). – ^{1}H NMR (80 MHz, $CDCl_3$): δ = 6.60 (s, 1H, –CH=), 2.92–2.64 (m, 4H, $2CH_2$), 2.29 (s, 3H, SCH_3), 1.36–1.16 (m, 6H, $2CH_2CH_3$).

$C_7H_{14}S_3$ (194.4) Calc. C 43.25 H 7.26 S 49.49 Found C 43.39 H 7.31 S 49.70

(Z)-1,2-Bis(ethylthio)-1,2-bis(methylthio)ethylene (**6**): To a solution of 0.56 g (2.88 mmol) of **5** in 30 ml of dry tetrahydrofuran was added at –70°C 2 ml (3.2 mmol) of *tert*-butyllithium (1.6 M solution in *n*-hexane). After 30 min 0.5 ml (5.5 mmol) of dimethyl disulfide was added to the reaction mixture. After 1 h at –70°C the reaction mixture was left to arrive room temperature (1 h), then it was extracted with ether/water. The organic layer was dried over potassium carbonate and the solvent evaporated. The residue was chromatographed on silica gel [petroleum ether (40–60°C)/chloroform, 9:1]; yield 0.52 g (75%). – TLC [silica gel; petroleum ether (40–60°C)/chloroform, 9:1]: R_F = 0.17. – ^{1}H NMR (80 MHz, $CDCl_3$): δ = 2.87 (q, 4H, $2CH_2$; J = 7 Hz), 2.39 (s, 6H, $2SCH_3$), 1.25 (t, 6H, $2CH_2CH_3$).

$C_8H_{16}S_4$ (240.5) Calc. C 39.96 H 6.71 S 53.33 Found C 39.96 H 6.64 S 53.39

(Z)-1-(Ethylsulfinyl)-2-(ethylthio)ethylene (**7**): To a solution of 4.44 g (0.03 mol) of **4** in 200 ml of dry dichloromethane was added at 0°C a solution of 5.70 g (0.03 mol) of *m*-chloroperbenzoic acid in 200 ml of dry dichloromethane. After 12 h the reaction mixture was treated three times with a saturated sodium hydrogencarbonate solution in water (80 ml). The organic layer was dried over magnesium sulfate and the solvent evaporated. The residue was distilled; b.p. 96°C/10^{-3} Torr. Yield 4.7 g (96%). – ^{1}H NMR data: see Table 2.

$C_6H_{12}OS_2$ (164.3) Calc. C 43.87 H 7.36 Found C 43.79 H 7.38

(Z)-1-Deuterio-, (E)-1-Deuterio-, and (Z)-2-Deuterio-1-(ethylsulfinyl)-2-(ethylthio)ethylene [(*Z*)-**8a**, (*E*)-**8a**, and (*Z*)-**9a**]. *General Procedure for the Synthesis of Compounds* (*Z*)-**8b–d,f**, (*E*)-**8b–e**, (*Z*)-**9f**: To a solution of 0.67 g (4.08 mmol) of **7** in 30 ml of dry tetrahydrofuran was added under nitrogen at –120°C 3 ml (4.8 mmol) of methyllithium (1.6 M solution in ether). After t_1 = 10 min at T = –120°C 2 ml methan-[D]ol was added and the reaction mixture was kept for t_2 = 5 min at –120°C. Then it was extracted with chloroform/water. The organic layer was dried over potassium carbonate and the organic solvent evaporated. The residue was distilled; b.p. 96°C/10^{-3} Torr. Yield 0.65 g (97%). According to the ^{1}H NMR data this material was quantitatively deuterated. It consisted of > 95% of pure (*Z*)-**8a** with a very minor contamination of (*Z*)-**9a**.

Applying the same procedure with t_1 = 1 min, T = –100°C, t_2 = 5 min gave practically identical results. With t_1 = 15 min, T = –80°C, t_2 = 5 min a 73:17:10-mixture of (*E*)-**8a**, (*Z*)-**8a**, and (*Z*)-**9a** was obtained. Compounds (*Z*)-**8b–e** were obtained by addition of 5 mmol of the electrophile: after t_1 = 1 min at T = –100°C. The reaction mixtures were kept for t_2 = 1 h at T = –100°C, then left to arrive 0°C, and worked up as described above. The resulting products (> 19:1 mixtures of (*Z*)-**8b–e**:(*Z*)-**9a–e**) were purified by chromatography on silica gel with $CHCl_3$/MeOH, 99:1. (*Z*)-**8e** consisted of a 1:1-mixture of two diastereoisomers, which were separated (Table 1). Compounds (*E*)-**8b–d** were obtained by addition of 5 mmol of the electrophile after t_1 = 15 min at T = 80°C. The reaction mixtures were kept for t_2 = 1 h at T = –80°C, then left to arrive 0°C, and worked up as described above. The resulting products were 4:1 mixtures of (*E*)-**8b–d**:(*Z*)-**8b–d**, which were separated by chromatography on silica gel with $CHCl_3$/MeOH, 99:1.

Addition of 5 mmol of ethyl iodide as electrophile at t_1 = 1 min, T = –100°C, t_2 = 1 h or t_1 = 15 min, T = –80°C, t_2 = 1 h resulted in 4:1 mixtures of compounds (*E*)-**8f** and (*Z*)-**9f**, which were separated (Table 1).

For yields, analytical and ^{1}H NMR data of these compounds see Tables 1 and 2.

4-Phenyl-1,3-dithiole (**10a**) *and 4-Phenyl-2-piperidino-1,3-dithiole* (**10c**) were obtained via literature procedures[15].

2,4-Diphenyl-1,3-dithiole (**10b**): To a solution of 0.92 g (2.6 mmol) of 2,4-diphenyl-1,3-dithiolium perchlorate[24] in 50 ml of ethanol was added at 0°C 0.3 g (7.93 mmol) of sodium borohydride. After 30 min at 0°C the reaction mixture was stirred for 2 h at room temperature. The solvent was evaporated and the residue treated with water. The crystals were filtered off and recrystallized from ethanol/water, 4:1; yield 0.56 g (85%) colourless crystals; m.p. 70°C. – ^{1}H NMR data: see Table 2.

$C_{15}H_{12}S_2$ (256.4) Calc. C 70.27 H 4.72 S 25.01 Found C 69.52 H 4.86 S 25.17

2-Deuterio-4-phenyl- and 2-Deuterio-2,4-diphenyl-1,3-dithiole (**11a** and **11b**): A solution of 0.24 g (1.36 mmol) of **10a** in 20 ml of dry tetrahydrofuran was added to a cooled (−120°C) solution of 1.6 mmol of lithium diisopropylamide in 20 ml of dry tetrahydrofuran [prepared from 162 mg (1.6 mmol) of diisopropylamine and 1 ml of a 1.6 M *tert*-butyllithium solution in *n*-hexane]. After 30 min at −120°C 1 ml of methan-[D]ol was added and the reaction mixture kept for 15 min at −120°C. Then it was extracted with chloroform/water. The organic layer was dried over potassium carbonate and the organic solvent evaporated. The material obtained (0.22 g) consisted of a 4:1 mixture of **11a**:**10a** (^{1}H NMR assignment).

With the same procedure from 0.35 g (1.36 mmol) of **10b** a 1:1 mixture of **11b**:**10b** was obtained (^{1}H NMR assignment).

5-Deuterio-4-phenyl-2-piperidino-1,3-dithiole (**11c**) *and Fragmentation:* To a solution of 526 mg (2.0 mmol) of **10c** in 30 ml of dry tetrahydrofuran was added under nitrogen at $T = -100$°C 1.3 ml (2.30 mmol) of *tert*-butyllithium (1.76 M solution in *n*-hexane). After $t_1 = 1$ h at $T = -100$°C 2 ml of methan-[D]ol were added and the reaction mixture was kept for $t_2 = 5$ min at $T = -100$°C. Then it was extracted with chloroform/water. The organic layer was dried over sodium sulfate and the organic solvent evaporated. The residue obtained was recrystallized from ethanol/water, 4:1. Yield 0.46 g (87%) of 6:4 of **10c**:**11c** (^{1}H NMR assignment).

Applying the same procedure with $t_1 = 4$ h, $T = -100$°C, $t_2 = 5$ min gave 1:6:1 of **10c**:**11c**: fragmentation according to Scheme 3.

With $t_1 = 1$ h, $T = -80$°C and $t_2 = 5$ min 170 mg (32%) of **11c** were isolated. When the mother liquor was treated with *n*-hexane 2-benzylidene-4-phenyl-1,3-dithiole (**13**) was obtained, which was compared with identical material[18]. *N*-(Thioformyl)piperidine (**12**) remained in the residue of the mother liquor. It was assigned by ^{1}H NMR and comparison with authentical material[17].

2,2-Dimethyl-1,3-dioxole (**14a**) and *2-Methyl-1,3-dioxole* (**14b**) were obtained by literature procedures[20].

Methyl 2,2-Dimethyl-1,3-dioxole-4-carboxylate (**15a**) *and Methyl 2-Methyl-1,3-dioxole-4-carboxylate* (**15b**). *General Procedure:* To a solution of 8.16 mmol of **14a** or **14b** in 30 ml of dry tetrahydrofuran was added under nitrogen at −80°C 9.6 mmol of *tert*-butyllithium (1.6 M solution in *n*-hexane). After 1 h 10 mmol of methyl chloroformate was added and the reaction mixture kept for 1 h at −80°C and then left to arrive room temperature. Then it was extracted with ether/water, the organic layer was dried over potassium carbonate and the organic solvent evaporated. The residue was distilled by bulb to bulb distillation. **15a**: see ref.[22]. **15b**: b.p. 120–125°C/12 Torr, yield 0.80 g (68%). – ^{1}H NMR (80 MHz, $CDCl_3$):

δ = 7.15 (s, 1H, 5-H), 6.19 (q, 1H, 2-H; J = 5 Hz), 3.81 (s, 3H, OCH_3), 1.62 (d, 3H, CH_3; J = 5 Hz). – IR (KBr): ν_{CO} = 1730 cm^{-1}. – MS (70 eV): m/z = 144 (M^+), 129 ($M^+ - CH_3$), 113 ($M^+ - OCH_3$).

Because of decomposition a correct elemental analysis could not be obtained for **15b**.

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