Pergamon

Tetrahedron, Vol. 53, No. 7, pp. 2459-2474, 1997

0040-4020/97 $17.00 + 0.00

PII: S0040-4020(96)01184-2

C,C-Coupling with Sulfur-Stabilized Carbanions - 7.[1] Diastereoselectivity in the Addition of Electrophiles to the Carbanions of 2-(Alkylthio)thiolane 1-Oxides[2]

Jörg-Stephan Brunck[3], Barbara Deicke, Jürgen Voss*

Institut für Organische Chemie der Universität Hamburg, Martin-Luther-King-Platz 6, D-20146 Hamburg, Germany

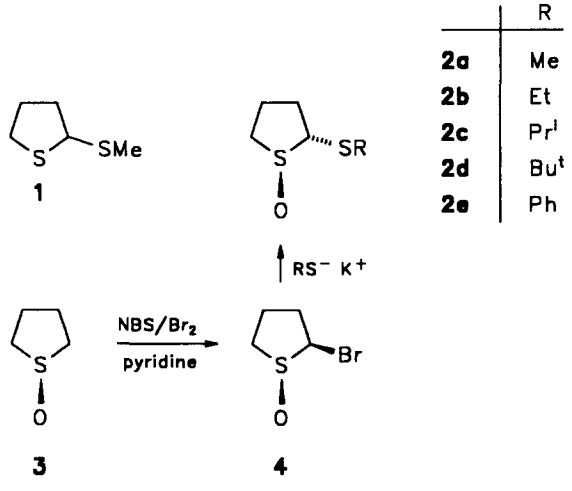
Abstract: Pure diastereoisomers of the 2-(alkylthio)thiolane 1-oxides **2** were prepared in a three-step synthesis. The carbanions of **2** were generated with different bases and treated with iodomethane and carbonyl compounds to form the methyl derivatives **6** and the carbinols **7**, respectively. The conformational stability (*α-diastereoselectivity*) of the carbanions as well as the asymmetric induction during the reaction with prochiral electrophiles (*β-diastereoselectivity*) was studied. A mechanism for the reaction with carbonyl compounds is proposed, which involves a six-membered cyclic transition state formed from the sulfoxide moiety and the metal cation. - Steric effects of the substrate and the electrophile are discussed. © 1997, Elsevier Science Ltd. All rights reserved.

In the course of the development of synthetic methods it was of special interest to find reagents that allow chemical conversion with the inverse reactivity to increase their synthetic potential. Among these „Umpoling" reagents[4] the 1,3-dithiane of Corey and Seebach[5] found widespread use in organic synthesis. Ogura and Tsuchihashi[6] demonstrated that methyl methylthiomethyl sulfoxide is a useful acylanion equivalent of formaldehyde that can be transformed to different substituted aldehydes and ketones. The possibility to synthesize cyclic ketones of various ring sizes is a major quality of this „Umpolung" reagent. Michael type additions of open-chain dithioacetal sulfoxides leading to 1,4-dicarbonyl compounds were reported by Schlessinger and coworkers.[7] The use of sulfoxide-stabilized carbanions in asymmetric synthesis was established by the work of Solladié.[8] In recent years Page[9] and Aggarwal[10] reported the use of 1,3-dithiane sulfoxide and 1,3-dithiane 1,3-dioxide in the diastereoselective addition of electrophiles. While sulfoxide-stabilized carbanions do usually show high stereoselectivity in the α-position, the β-stereoselectivity is often very poor.[10,11] The highest β-stereoselectivity is usually obtained for the addition of aromatic aldehydes to lithiated sulfoxides.[10,12,13]

Our interest in sulfur-stabilized carbanions started with the study of 2-(methylthio)thiolane (**1**).[14] However, the carbanion of **1** showed no remarkable asymmetric induction to prochiral centers on addition reactions with aldehydes. Since we attributed this lack of diastereoselectivity to an equilibrating carbanion we were looking for configurationally stable carbanions, which we found to be the dithioacetal sulfoxides **2**. In this report we present a study of the reactions of the dithioacetals **2** with electrophiles, which demonstrates the factors that effect diastereoselectivity during carbon-carbon bond formation. We will show that the sulfoxide moiety acts as a directing group for carbon-carbon bond formation of the carbanions of **2** with carbonyl compounds and how the exocyclic substituent effects β-diastereoselectivity at the addition of prochiral electrophiles. In this context we developed a transition-state model that is consistent with previously published X-ray crystallographic data of related complexes.[15]

RESULTS AND DISCUSSION

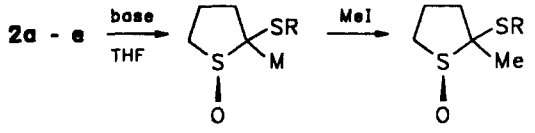
Preparation of Dithioacetal Sulfoxides **2a-e** (scheme 1). While the preparation of 2-(methylthio)thiolane sulfoxide (**2a**) has already been described in 1970[16] no further investigations have been performed on the reactivity of **2a** and related compounds. Starting from thiolane the dithioacetal sulfoxides **2a-e** were obtained in a three-step procedure with an overall yield of 33%, except for **2b** and **2c**, which were isolated in only 11% and 7%, respectively. The low yield step in this synthesis is the halogenation which gives **4** in only 40% yield. We found the best procedure for the preparation of **4** to be the bromination of **3**[17] with a 2:1 mixture of NBS/Br_2 in the presence of pyridine.[18] The dithioacetal sulfoxides **2** were prepared from **4** and the corresponding potassium alkanethiolates.[19] Whereas **2a**, **2c** and **2d** were isolated as single diastereoisomers, **2b** and **2e** gave diastereoisomeric mixtures with ratios of 4.5:1 and 1:1, respectively, which were separated by column chromatography.



	R
2a	Me
2b	Et
2c	Pr^i
2d	Bu^t
2e	Ph

Scheme 1

Alkylation of Dithioacetal Sufoxides **2a-e** (Scheme 2). The dithioacetal sulfoxide **2a** was deprotonated with Bu^nLi, LDA, Bu^nLi/tmeda, $KOBu^t$, and NaH in THF solution to yield the metallated products **5** (Scheme 2). The lithium bases allowed reaction temperatures below -30 °C to be applied, whereas deprotonation with $KOBu^t$ was performed at 0 °C. Iodomethane was added at -78 °C and the reaction mixture was allowed to warm up to room temp. within 3 h. The reaction with sodium hydride could only be achieved by simultaneous addition of the base and the electrophile to a THF solution of **2a** and heating to 45 °C. Interestingly, the reaction with sodium hydride, which was performed at elevated temperatures, gave 33% d.e., while the reactions with the other bases only gave 1:1 mixtures of diastereoisomers.



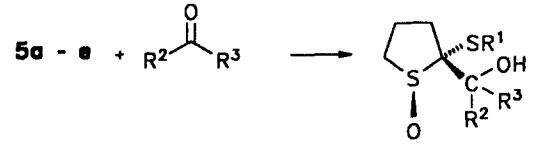
5a - e (M = Li, Na, K) **6a - e**

6a 47 – 98%, 0 – 33% d.e. (base = Bu^nLi, LDA, Bu^nLi/tmeda, Bu^tOK, NaH)
6b 97%, 5% d.e. (base = LDA)
6c 79%, 67% d.e. (base = LDA)
6d 40%, 80% d.e. (base = Bu^nLi)
6e 61%, 20% d.e. (base = LDA)

Scheme 2 (cf. Scheme 1 for the substituents R)

Increased diastereoisomeric excesses were observed for the alkylation products **6b** to **6e**. While **6b** was obtained in 5% d.e., **6c** gave 67% d.e. and **6d** 80% d.e. This increase in diastereoisomeric excess correlates with the increase of steric hindrance of the exocyclic substituent. In the same direction a decrease in reactivity can be observed, giving the most hindered alkylation product **6d** in only 40% yield.

Hydroxyalkylation of Dithioacetals **2a-e**. Whereas the alkylation reactions of alkyllithium compounds with iodomethane are supposed to proceed via an S_N2 attack at the electrophile,[20] we assume the hydroxyalkylation of the dithioacetals **2a-e** to follow a complexation mechanism. Therefore, we were interested in three aspects of this reaction, a) the conformational stability of the metallated dithioacetals **5a-e**, b) the asymmetric induction of the exocyclic substitutent of the dithioacetal at the carbonyl group of prochiral electrophiles, and c) the steric requirements of the attacking aldehyde itself.



7a - n

Scheme 3 (cf. Table 1 for the substituents $R^1 - R^3$)

We chose the reaction of **2a-e** with acetone to test the configurational stability of the metallated dithioacetals **5a-e** (Scheme 3). Since in this reaction no additional asymmetric center is formed, the determination of the diastereoisomeric ratios should allow conclusions concerning the configurational stability of **5a-e**. The metallated species **5a-e** were generated by reaction of the corresponding dithioacetals **2a-e** with LDA or Bu^nLi in THF solution at -30 °C. The electrophiles were added after cooling to -78 °C and then the reaction mixture was allowed to warm up to room temperature within 3 h before quenching with methanol. In Table 1 the results of the hydroxyalkylation reactions are summarized. Entries 1, 7, 9, 15, and 17

Table 1. 1-Hydroxyalkylation of sulfoxide carbanions **5** (cf. Scheme 3)

Entry	Sulfoxide **2a - 2e**	Electrophile		Carbinol **7a - 7n**		
	R^1	R^2	R^3	yield [%]	7	d.e. [%]
1	Me	Me	Me	50	**a**	> 98
2	Me	Ph	H	76	**b**	40 - 98[a]
3	Me	$-(CH_2)_5-$		59	**c**	> 98
4	Me	Me	H	64	**d**	43
5	Me	Pr^i	H	85	**e**	33
6	Me	Bu^t	H	33	**f**	> 98
7	Et[b]	Me	Me	25	**g**	> 98
8	Et	Ph	H	46	**h**	49
9	Pr^i[b]	Me	Me	41	**i**	> 98
10	Pr^i	Ph	H	45	**j**	49
11	Pr^i	Me	H	68	**k**	31
12	Pr^i	Et	H	79	**l**	41
13	Pr^i	Pr^i	H	2	**m**	> 98
14	Pr^i	Bu^t	H	0		-
15	Bu^t	Me	Me	0		-
16	Bu^t	Ph	H	0		-
17	Ph	Me	Me	14	**n**	> 98
18	Ph	Ph	H	[c]		

a) Different bases (cf. Scheme 2). - b) $BF_3 \cdot Et_2O$ as catalyst. - c) Trace amount of complex product mixture.

describe the reactions of **5a-e** with acetone. While due to the low electrophilicity of acetone the yields are only moderate, the diastereoisomeric excesses are excellent (d.e. > 98%), i.e., only one diastereoisomer was observed. The *tert*-butyl derivative **2d** could not be reacted at all (entry 15), most probably due to the steric hindrance of the *tert*-butyl group of the exocyclic substituent. The same d.e. (>98%) was observed in the

reaction of **2a** with cyclohexanone (entry 3). Notably, a reaction of acetone with the carbanions of the ethylthio and the isopropylthio sulfoxides **2b** and **2c** occurred only in the presence of boron trifluoride etherate (entries 7 and 9), which is also indicative of the low electrophilic activity of acetone in attacking the metallated species **5**. However, these reactions confirm the configurational stability of **5a-e** in the hydroxylalkylation reaction, which is a necessary supposition for β-diastereoselectivity in the reaction with prochiral carbonyl compounds, such as aldehydes. Therefore, in a first attempt the metallated dithioacetals **5a-e** were treated with benzaldehyde under the same reaction conditions. As can be seen from entries 2, 8, and 10 the d.e. is 40 - 49%, whereas the *tert*-butyl derivative **2d** (entry 16) did not at all react. The reaction of **2e** with benzaldehyde (entry 18) resulted in a complex mixture of products that could not be separated into single compounds. Considering the configurational stability of the metallated dithioacetals **5**, the diastereoisomeric excess found for the benzaldehyde adducts **7b**, **7h**, and **7j** can be assigned to the asymmetric induction at the new chiral center generated from the prochiral carbonyl group. In this context two observations are noteworthy. a) The reaction of **2a** with benzaldehyde showed a remarkable base dependency. The d.e. of the reaction increased from 40% to 98%, when LDA was used instead of Bu^nLi/TMEDA. b) The increase of the steric hindrance of the exocyclic substituent (**2a**, **2b**, **2c**) is not sufficient to effect higher d.e. at the addition of benzaldehyde. However, the exocyclic substituent is necessary to induce β-diastereoselectivity during the new asymmetric center, as we were able to demonstrate by the reaction of thiolane sulfoxide (**3**) with benzaldehyde, which did not show any β-diastereoselectivity at all.[3,21]

Whereas marked β-diastereoselectivity is a known feature for the reaction of α-sulfinyl carbanions with aromatic aldehydes,[10,12,13] it is significantly lower with aliphatic aldehydes. We therefore investigated the reactions of **2a** and **2c** with different aliphatic aldehydes, also under the aspect of the steric requirements provided by the electrophile. The methylthio sulfoxide **2a** was successfully reacted with acetaldehyde, isobutyraldehyde, and pivalaldehyde (entries 4-6). Whereas the reaction with pivalaldehyde resulted in 98% d.e., only 33% and 43% d.e. were observed for the reaction of **2a** with isobutyraldehyde and acetaldehyde, respectively, demontrating that high steric hindrance of the electrophile results in high diastereoisomeric excess. The reactions of the isopropylthio sulfoxide **2c** with acetaldehyde, propionaldehyde, isobutyraldehyde, and pivalaldehyde (entries 11-14) reveal a straight increase in d.e. with increasing steric hindrance at the electrophile, which, on the other hand, inhibits any reaction of the pivalaldehyde (entry 14) and lowers the yield in case of the isobutyraldehyde (entry 13). However, chain-elongation (propanal) increased the d.e. by 10% (entry 12) as compared with acetaldehyde (entry 11).

MECHANISM

The d.e. in the alkylation reaction increases with the steric hindrance of the exocyclic substituent, giving 80% d.e. for the *tert*-butyl derivative **6d**. Mechanistically, the two diastereoisomers in this reaction represent the products from the backside attack and the Li-complexed side. However, as demonstrated by the hydroxyalkylation of **2** with acetone, the metallated species **5** shows excellent configurational stability (α-diastereoselectivity) during the attack of carbonyl compounds, yielding only one diastereoisomer in this

reaction. Therefore, the two different diastereoisomers obtained in the reaction of **2** with aldehydes must be assigned to the different configuration of the chiral center in β-position. β-Diastereoselectivity is observed in every successful addition of an aldehyde to **5**. Two effects have to be considered. a) Increasing steric hindrance of the exocyclic substituent of **2** increases the d.e. of the products **7**. Increasing steric hindrance of the aldehyde leads to increased d.e. of the products **7** as well. b) Overcrowded reactants suppress any reaction. The X-ray crystal structure analyses of two different addition products[15] show that the hydroxylalkylation reaction yielded the (*E*)-configurated products. We rationalize these results by a six-membered transition state, as outlined in the figure. In accordance with the X-ray crystal structures, the major diastereoisomer in the hydroxyalkylation reaction is formed from the transition state in which the bulkier substituent R^1 of the aldehyde occupies the equatorial position.

EXPERIMENTAL

Melting points were determined on an Electrothermal melting point apparatus and are corrected. NMR spectra were recorded on a Bruker AC 250 P or WM 400 (250 MHz or 400 MHz for ^1H and 62.9 MHz or 100.6 MHz for ^{13}C) using $CDCl_3$ as the solvent, unless otherwise noted. The chemical shifts are given as δ-values using TMS (δ = 0) or $CHCl_3$ (δ = 7.26) as internal standard for proton spectra and $CDCl_3$ (δ = 77.0) for carbon spectra. Infrared spectra (IR) were recorded on a Perkin Elmer FT-IR 1720x as KBr pellets or as liquid films on NaCl plates. Mass spectra were taken on a Varian CH7 by the electron impact (EI) method at 70 eV (direct inlet) or chemical ionization using ammonia. Silicagel 60 (E. Merck, 70 - 230 mesh) was used for column chromatography, precoated silica gel plates on alumina (E. Merck, 60 F_{254}) for tlc. All air sensitive reactions were conducted in flame dried glass ware under N_2 atmosphere. THF was distilled from Na/K benzophenone ketyl radical. Halogenated solvents were distilled and stored over 4Å molecular sieves. Acetone was dried over phosphorus pentoxide. Amines were dried over CaH_2. All carbonyl compounds were distilled prior to use.

Thiolane sulfoxide (**3**)[17] and *2-bromothiolane sulfoxide* (**4**)[18] were prepared as described in the literature.

General procedure for the preparation of the dithioacetal sulfoxides **2a-e**[19]: The mercaptan (17.8 mmol) was added to a solution of KOH (17.8 mmol) in ethanol (50 ml) and stirred for 1 h at 0 °C. A solution of 2-bromothiolane sulfoxide (**4**) (17.2 mmol) in ethanol (17 ml) was added and the resulting mixture was stirred for 1 h at 0 °C and 3 h at room temp. The white precipitate was filtered off, the solvent removed under reduced pressure and the residue dissolved in CH_2Cl_2. The organic layer was washed with water and brine, dried over Na_2SO_4 and concentrated *in vacuo*. The crude products of **2a** and **2d** were purified by distillation over a 25 cm Vigreux column at 0.01 Torr. **2b**, **2c**, and **2e** were purified by column chromatography on silica gel with ethyl acetate as eluent.

(E)-2-(Methylthio)thiolane 1-oxide (**2a**):[16] (89%): b.p. 81 °C/0.01 Torr. - ^{1}H NMR (250 MHz): δ = 1.92-2.04 (m, 1H), 2.09-2.26 (m, 1H), 2.28 (s, 3H, CH_3), 2.41-2.62 (m, 1H), 2.78-2.93 (m, 2H), 3.12 (dt, *J* = 13.8, 8.4 Hz, 1H), 3.97 (ddd, *J* = 8.2, 2.2, 1.2 Hz, 1H, 2-H). - ^{13}C NMR (62.9 MHz): δ = 16.58 (SCH_3), 25.13 (C-4), 31.95 (C-3), 52.08 (C-5), 72.34 (C-2). - IR (neat): ν = 2938, 1437, 1037 (S=O) cm^{-1}.

2-(Ethylthio)thiolane 1-oxide (**2b**): (30% of a 4.5:1 mixture of the *E/Z* - isomers). Diastereoisomer 1: R_f (EA) 0.27. - ^{1}H NMR (400 MHz, [D$_6$]DMSO): δ = 1.25 (t, *J* = 7.4 Hz, 3H, CH_3), 1.89-1.93 (m, 1H, 3-H), 1.98-2.10 (m, 1H, 4-H), 2.28-2.39 (m, 1H, 4-H), 2.64-2.78 (m, 1H, 3-H), 2.75 (q, *J* = 7.4 Hz, 2H, CH_2), 2.79 (dt, *J* = 7.4, 12.8 Hz, 1H, 5-H), 3.07 (dt, *J* = 8.3, 13.9 Hz, 1H, 5-H), 4.19 (ddd, *J* = 1.5, 3.9, 6.7 Hz, 1H, 2-H). - ^{13}C NMR (100.6 MHz, [D$_6$]DMSO): δ = 14.54 (CH_3), 24.89 (C-4), 26.46 (CH_2), 31.77 (C-3), 51.61 (C-5), 69.35 (C-2). - IR (neat): ν = 2963, 1451, 1034 (S=O) cm^{-1}. - MS (70 eV); *m/z* (%): 164 (7) [M$^+$], 103 (100) [$C_4H_7OS^+$], 87 (19) [$C_4H_7S^+$], 85 (20), 58 (48), 43 (46). - $C_6H_{12}OS_2$ (164.3): calcd. C 43.89, H 7.37, S 38.98; found C 42.89, H 7.52, S 36.92. Diastereoisomer 2: m.p. 34 °C; R_f(EA) 0.05. - ^{1}H NMR (400 MHz, [D$_6$]DMSO): δ = 1.22 (t, *J* = 7.4 Hz, 3H, CH_3), 1.88-2.01 (m, 2H, 3-H, 4-H), 2.14-2.24 (m, 1H, 4-H), 2.24-2.32 (m, 1H, 3-H), 2.64 (dq, *J* = 7.4, *J* = 13.6 Hz, 1H, CH_2), 2.69 (dq, *J* = 7.4 Hz, *J* = 12.9 Hz, 1H, CH_2), 2.77 (ddd, *J* =5.4, 8.2, 13.6 Hz, 1H, 5-H), 3.11 (ddd, *J* = 7.3, 8.6, 13.9 Hz, 1H, 5-H), 4.05 (dd, *J* = 6.9, 10.8 Hz, 1H, 2-H). - ^{13}C NMR (100.6 MHz, [D$_6$]DMSO): δ = 15.03 (CH_3), 23.56 (C-4), 25.86 (CH_2), 30.87 (C-3), 53.21 (C-5), 67.26 (C-2). IR (KBr): ν = 2967, 1452, 1028 (S=O) cm^{-1}. - MS (70 eV); *m/z* (%): 164 (8) [M$^+$], 103 (100) [$C_4H_7OS^+$], 87 (31) [$C_4H_7S^+$], 85 (39), 59 (59), 47 (20). - $C_6H_{12}OS_2$ (164.3): calcd. C 43.89, H 7.37,S 38.98; found C 43.89, H 7.70,S 36.20.

(E)-2-(Isopropylthio)thiolane 1-oxide (**2c**): (18%): b.p. 95-98 °C/0.1 Torr; R_f(EA) 0.30.- ^{1}H NMR (400 MHz, [D$_6$DMSO): δ = 1.25 (d, *J* = 6.7 Hz, 3H, CH_3), 1.32 (d, *J* = 6.6 Hz, 3H, CH_3), 1.86 (ddt, *J* = 13.5 Hz, *J* = 4.0 Hz, *J* = 6.6 Hz, 1H, 3-H), 1.98-2.08 (m, 1H, 4-H), 2.26-2.38 (m, 1H, 4-H), 2.69 (dt, *J* = 13.9 Hz, *J* = 7.1 Hz, 1H, 5-H), 2.69-2.76 (m, 1H, 3-H), 3.05 (dt, *J* = 13.9 Hz, *J* = 8.4 Hz, 1H, 5-H), 3.19 (sept, *J* = 6.7 Hz, 1H, $CH(CH_3)_2$), 4.20 (ddd, *J* = 1.3, 4.0, 6.8 Hz, 1H, 2-H). - ^{13}C NMR (62.9 MHz, [D$_6$]DMSO): δ = 23.19 (CH_3), 24.51 (C-4), 32.28 (C-3), 32.03 ($CH(CH_3)_2$, 51.51 (C-5), 68.80 (C-2). - IR (neat): ν = 2960, 1461, 1044 (S=O) cm^{-1}. - MS (70 eV); *m/z* (%): 178 (9) [M$^+$], 115 (31), 103 (100) [$C_4H_7OS^+$], 87 (21) [$C_4H_7S^+$], 85 (21), 73 (61), 55 (11). - $C_7H_{14}OS_2$ (178.3): calcd. C 47.15, H 7.91, S 35.96; found C 46.88, H 8.02, S 35.35. - HRMS $C_7H_{14}OS_2$: calcd. 178.0486; found 178.0496.

(E)-2-(tert-Butylthio)thiolane 1-oxide (**2d**): (89%): m.p. 33 °C. - ^{1}H NMR (250 MHz): δ = 1.42 (s, 9H, $C(CH_3)_3$), 1.97-2.20 (m, 2H), 2.35-2.55 (m, 1H), 2.74-2.88 (m, 1H), 2.90-3.13 (m, 2 H), 4.08-4.15 (m, 1H, 2-H). - ^{13}C NMR (62.9 MHz): δ = 24.57 (C-4), 31.15 ($C(CH_3)_3$, 33.14 (C-3), 44.84 ($C(CH_3)_3$, 51.61 (C-5), 67.37 (C-2). IR (neat): ν = 2962, 1462, 1042 (S=O) cm^{-1}. - MS (70 eV); *m/z* (%): 192 (10) [M$^+$], 136 (14), 87

(22) [$C_4H_7S^+$], 57 (100) [$C(CH_3)_3^+$]. - $C_8H_{16}OS_2$ (192.3): calcd. C 49.96, H 8.38, S 33.34; found C 48.46, H 8.38, S 32.22.

2-(Phenylthio)thiolane 1-oxide (**2e**): (83% of a 1:1 mixture of *E/Z* - isomers). Diastereoisomer 1. *Rf*(EA) 0.31. - ^{1}H NMR (250 MHz): δ = 2.03-2.32 (m, 2H), 2.45-2.64 (m, 1H), 2.81-3.00 (m, 2H), 3.08-3.21 (m, 1H), 4.40-4.46 (m, 1H, 2-H), 7.25-7.40 (m, 3H, Ar-H), 7.45-7.52 (m, 2H, Ar-H). - ^{13}C NMR (62.9 MHz): δ = 25.29 (C-4), 31.62 (C-3), 51.89 (C-5), 72.38 (C-2), 128.15 (C_{ar}), 129.40 (2*C_{ar}), 131.52 (2*C_{ar}), 132.82 (C_{ar}). Diastereoisomer 2: m.p. 97 °C; *Rf*(EA) 0.21. - ^{1}H NMR (250 MHz): δ = 1.90-2.12 (m, 1H), 2.21-2.53 (m, 3H), 2.85-3.19 (m, 2H), 4.07-4.17 (m, 1H, 2-H), 7.21-7.38 (m, 3H, Ar-H), 7.52-7.61 (m, 2H, Ar-H). - ^{13}C NMR (62.9 MHz): δ = 24.08 (C-4), 31.08 (C-3), 53.74 (C-5), 71.91 (C-2), 128.09 (C_{ar}), 129.25 (2*C_{ar}), 132.36 (2*C_{ar}), 133.48 (C_{ar}). - MS (70 eV); *m/z* (%): 212 (3) [M^+], 149 (29), 103 (100) [$C_4H_7OS^+$], 91 (19), 77 (16). - $C_{10}H_{12}OS_2$ (212.3): calcd. C 56.57, H 5.70, S 30.20; found C 56.55, H 5.74, S 30.15.

General procedure for the preparation of the products 6 and 7.

Method A. With Bu^{n}Li or KOBu^t: Sulfoxide **2a** (1 equiv.) was added at -78 °C under N_2 atmosphere to a solution of the base (1.1 equiv.) in THF and stirred for 1 h at -30 °C or 0 °C, respectively. After cooling to -78 °C, the electrophile (1 equiv.) was added and the mixture was allowed to warm up to room temp. within 3 h. The reaction mixture was quenched with methanol, the solvent removed under reduced pressure, and the residue was dissolved in CH_2Cl_2 and water. The aqueous layer was extracted with CH_2Cl_2 (3 times) and the combined organic extracts were were washed with brine, dried over Na_2SO_4, and concentrated under reduced pressure. The crude product was purified by column chromatography on silica gel.

Method B. With LDA or Bu^{n}Li/tmeda: The amine (1.1 equiv.) was dissolved in THF under N_2 atmosphere and cooled to -30 °C. n-BuLi (1.1 equiv.) and after 10 min the sulfoxide **2** (1 equiv.) were added. After stirring for 1 h at -30 °C, the solution was cooled to -78 °C and the electrophile (1 equiv.) was added and then the mixture was allowed to warm up to room temp. within 3 h. The mixture was quenched with methanol and treated as described above.

Method C. With NaH: A mixture of sodium hydride (1.1 equiv.), sulfoxide **2a** (1 equiv.), and the electrophile (1.1 equiv.) in THF was heated to 45 °C for 1.5 h. After cooling to room temp. the mixture was quenched with methanol and treated as described above.

If not described otherwise, method B was used and the crude products were purified by column chromatography on silica gel with ethyl acetate as eluent.

A typical batch size is: dithioacetal sulfoxide **2** (3.33 mmol), THF (30 ml), n-BuLi (1.6 M in hexane, 2.3 ml, 3.58 mmol), iodomethane (473 mg, 3.33 mmol).

2-Methyl-2-(methylthio)thiolane 1-oxide (**6a**): (58% of a 1:1 mixture of *E/Z* - isomers). Diastereoisomer 1: *Rf*(EA) 0.10. - ^{1}H NMR (250 MHz): δ = 1.71 (s, 3H, CH_3), 2.01-2.13 (m, 2H), 2.16 (s, 3H, SCH_3), 2.33-

2.60 (m, 2H), 2.64-2.80 (m, 1H), 3.54-3.66 (m, 1H). - ^{13}C NMR (62.9 MHz): δ = 12.40 (CH_3), 18.49 (SCH_3), 24.98 (C-4), 39.45 (C-3), 54.04 (C-5), 72.85 (C-2). Diastereoisomer 2: *R*f(EA) 0.06. - ^{1}H NMR (250 MHz): δ = 1.48 (s, 3H, CH_3), 1.94-2.13 (m, 2H), 2.28 (s, 3H, SCH_3), 2.33-2.53 (m, 2H), 2.78-2.94 (m, 1H), 3.21-3.34 (m, 1H). - ^{13}C NMR (100.6 MHz): δ = 12.98 (CH_3), 21.35 (SCH_3), 23.55 (C-4), 37.45 (C-3), 52.60 (C-5), 73.67 (C-2). - IR (neat): ν = 2926, 1446, 1037 (S=O) cm^{-1}. - MS (70 eV); *m/z* (%): 164 (30) [M^+], 117 (69), 101 (100), 88 (14). - $C_6H_{12}OS_2$ (164.3): calcd. C 43.86, H 7.36, S 39.04; found C 41.31, H 7.57, S 32.50.

2-(Ethylthio)-2-methylthiolane 1-oxide (**6b**): (97% of a 1:1.1 mixture of *E/Z* - isomers). Diastereoisomer 1: *R*f(EA) 0.16. - ^{1}H NMR (400 MHz): δ = 1.24 (t, *J* = 7.6 Hz, 3H, CH_2CH_3), 1.73 (s, 3H, CH_3), 2.04-2.10 (m, 1H, 3-H), 2.11-2.17 (m, 1H, 4-H), 2.34-2.44 (m, 1H, 4-H), 2.45-2.53 (m, 1H, 3-H), 2.61-2.77 (m, 3H, CH_2, 5-H), 3.57-3.64 (m, 1H, 5-H). - ^{13}C NMR (62.9 MHz): δ = 14.51 (CH_2CH_3), 19.31 (CH_3), 23.64 (CH_2), 24.92 (C-4), 39.90 (C-3), 54.24 (C-5), 73.58 (C-2). - IR (neat): ν = 2970, 1425, 1032 (S=O) cm^{-1}. - MS (70 eV); *m/z* (%): 178 (11) [M^+], 160 (21) [M^+ - H_2O], 117 (71) [$C_5H_9OS^+$], 87 (26) [$C_4H_7S^+$], 59 (100), 45 (36). - $C_7H_{14}OS_2$ (178.3): calcd. C 47.15, H 7.91, S 35.96; found C 45.83, H 8.01, S 34.04. Diastereoisomer 2: *R*f(EA) 0.10. - ^{1}H NMR (400 MHz): δ = 1.28 (t, *J* = 7.6 Hz, 3H, CH_2CH_3), 1.48 (s, 3H, CH_3), 1.98-2.12 (m, 2H, 3-H, 4-H), 2.37-2.49 (m, 2H, 3-H, 4-H), 2.82 (q, *J* = 7.6 Hz, 2H, CH_2CH_3), 2.83-2.91 (m, 1H, 5-H), 3.23-3.30 (m, 1H, 5-H). - ^{13}C NMR (100.6 MHz): δ = 14.38 (CH_2CH_3), 21.75 (CH_3), 23.31 (C-4), 23.79 (CH_2), 37.93 (C-3), 52.73 (C-5), 74.54 (C-2). - MS (70 eV); *m/z* (%): 178 (10) [M^+], 160 (12) [M^+ - H_2O], 117 (51) [$C_5H_9OS^+$], 87 (22) [$C_4H_7S^+$], 59 (100), 45 (39). - HRMS $C_7H_{14}OS_2$: calcd. 178.0486; found 178.0489.

2-(Isopropylthio)-2-methylthiolane 1-oxide (**6c**): (79% of a 5:1 mixture of *E/Z* - isomers). Diastereoisomer 1: *R*f(EA) 0.42. - ^{1}H NMR (400 MHz): δ = 1.31 (d, *J* = 7.0 Hz, 3H, $CH(CH_3)_2$), 1.32 (d, *J* = 7.0 Hz, 3H, $CH(CH_3)_2$), 1.75 (s, 3H, CH_3), 2.03-2.44 (m, 2H, 3-H, 4-H), 2.33-2.44 (m, 1H, 4-H), 2.45-2.52 (m, 1H, 3-H), 2.68-2.77 (m, 1H, 5-H), 3.09-3.20 (sept, *J* = 7.0 Hz, 1H, $CH(CH_3)_2$), 3.55-3.62 (m, 1H, 5-H). - ^{13}C NMR (62.9 MHz): δ = 19.88 (2-CH_3), 24.80 (C-4), 25.07 (CH_3), 25.72 (CH_3), 34.66 ($CH(CH_3)_2$), 40.03 (C-3), 53.87 (C-5), 74.23 (C-2). - IR (neat): ν = 2959, 1453, 1036 (S=O) cm^{-1}. - MS (70 eV); *m/z* (%): 192 (18) [M^+], 174 (13) [M^+ - H_2O], 117 (99) [$C_5H_9OS^+$], 87 (100) [$C_4H_7S^+$], 75 (26) [$SCH(CH_3)_2^+$], 59 (57). - $C_8H_{16}OS_2$ (192.3): calcd. C 49.96, H 8.39, S 33.34; found C 49.86, H 8.45, S 33.15. Diastereoisomer 2: *R*f(EA) 0.28. - ^{1}H NMR (400 MHz): δ = 1.33 (d, *J* = 6.8 Hz, 3H, $CH(CH_3)_2$), 1.41 (d, *J* = 6.6 Hz, 3H, $CH(CH_3)_2$), 1.48 (s, 3H, CH_3), 1.96-2.05 (m, 2H), 2.08-2.16 (m, 2H), 2.39-2.43 (m, 1H), 2.79-2.93 (m, 1H), 3.22-3.33 (m, 1H, $CH(CH_3)_2$). - ^{13}C NMR (62.9 MHz): δ = 21.33 (2-CH_3), 22.86 (C-4), 24.16 (CH_3), 25.30

(CH_3), 34.18 ($CH(CH_3)_2$), 38.48 (C-3), 52.74 (C-5), 75.22 (C-2). - MS (70 eV); *m/z* (%): 174 (29) [$M^+ - H_2O$], 132 (18), 86 (25) [$C_4H_6S^+$], 45 (28), 43 (100) [$CH(CH_3)_2^+$].

2-(tert-Butylthio)-2-methylthiolane 1-oxide (**6d**): (40%): m.p. 55 °C; *R*f(EA) 0.13. - ^{1}H NMR (250 MHz): δ = 1.44 (s, 9H, $C(CH_3)_3$), 1.86 (s, 3H, CH_3), 1.97-2.15 (m, 2H), 2.26-2.51 (m, 2H), 2.66- 2.79 (m, 1H), 3.41-3.57 (m, 1H). - ^{13}C NMR (62.9 MHz): δ = 21.30 (CH_3), 24.55 (C-4), 33.02 ($C(CH_3)_3$), 41.90 (C-3), 47.23 ($C(CH_3)_3$), 53.48 (C-5), 75.46 (C-2). IR (KBr): ν = 2967, 1466, 1030 (S=O) cm^{-1}. - MS (70 eV); *m/z* (%): 206 (9) [M^+], 150 (29), 117 (82) [$M^+ - SC(CH_3)_3$], 87 (24), 57 (100). - $C_9H_{18}OS_2$ (206.4): calcd. C 52.38, H 8.79, S 31.08; found C 52.32, H 8.75, 31.06.

2-Methyl-2-(phenylthio)thiolane 1-oxide (**6e**): (61% of a 2:3 mixture of *E/Z* - isomers). Diastereoisomer 1: *R*f(EA) 0.19. - ^{1}H NMR (250 MHz): δ = 1.51 (s, 3H, CH_3), 2.10-2.28 (m, 2H), 2.39-2.67 (m, 2H), 2.72-2.88 (m, 1H), 3.61-3.78 (m, 1H), 7.30-7.45 (m, 3H, Ar-H), 7.51-7.59 (m, 2H, Ar-H). - ^{13}C NMR (100.6 MHz): δ = 21.69 (CH_3), 23.72 (C-4), 37.83 (C-3), 52.54 (C-5), 77.95 (C-2), 129.01 (2*C_{ar}), 129.48 (C_{ar}), 130.16 (C_{ar}), 137.02 (2*C_{ar}).- MS (70 eV); *m/z* (%): 226 (0.4) [M^+], 149 (6) 117 (54) [$M^+ - SC_6H_5$], 85 (100), 47 (11). - $C_{11}H_{14}OS_2$ (226.4): calcd. C 58.37, H 6.23, S 28.33; found C 57.96, H 6.21, S 27.12. Diastereoisomer 2: *R*f(EA) 0.16. - ^{1}H NMR (250 MHz): δ = 1.29 (s, 3H, CH_3), 1.99-2.12 (m, 2H), 2.38-2.51 (m, 2H), 2.81-2.99 (m, 1H), 3.17-3.30 (m, 1H), 7.30-7.41 (m, 3H, Ar-H), 7.66-7.75 (m, 2H, Ar-H). - ^{13}C NMR (100.6 MHz): δ = 19.66 (CH_3), 25.12 (C-4), 39.30 (C-3), 53.67 (C-5), 76.46 (C-2), 129.03 (2*Car), 129.09 (C_{ar}), 129.79 (C_{ar}), 137.16 (2*C_{ar}).

(E)-2-(1-Hydroxy-1-methylethyl)-2-(methylthio)thiolane 1-oxide (**7a**): (50%): m.p. 50 °C; *R*f(EA) 0.28. - ^{1}H NMR (250 MHz): δ = 1.37 (s, 3H, CH3), 1.74 (s, 3H, CH3), 2.01-2.14 (m, 2H), 2.16 (s, 3H, SCH_3), 2.50-2.67 (m, 1H), 2.82-2.95 (m, 1H), 3.20-3.36 (m, 1H), 3.60-3.73 (m, 1H), 4.80 (br.s, 1H, OH). - ^{13}C NMR (100.6 MHz): δ = 14.77 (SCH_3), 25.99 (C-4), 27.98 (CH_3), 28.98 (CH_3), 30.88 (C-3), 54.57 (C-5), 78.22 (C-OH), 81.90 (C-2). - IR (KBr): ν = 3368 (OH), 2977, 1412, 1032 (S=O) cm^{-1}. - MS (70 eV); *m/z* (%): 208 (2) [M^+], 190 (9), 133 (100), 85 (65), 47 (22). - $C_8H_{16}O_2S_2$ (208.3): calcd. C 46.12, H 7.74, S 30.78; found C 46.98, H 7.59, S 30.72.

2-(1-Hydroxy-1-phenylmethyl)-2-(methylthio)thiolane 1-oxide (**7b**): (76% of a mixture of the *E/Z* - isomers). Diastereoisomer 1: m.p. 147 °C. - ^{1}H NMR (250 MHz): δ = 1.78-2.05 (m, 2H), 2.21 (s, 3H, SCH_3), 2.21-2.42 (m, 3H), 2.63-2.80 (m, 1H), 3.45 (d, *J* = 2.0 Hz, 1H, CHOH), 5.10 (d, *J* = 2.0 Hz, 1H, OH), 7.30-7.38 (m, 3H, Ar-H), 7.43-7.50 (m, 2H, Ar-H). - ^{13}C NMR (62.9 MHz): δ = 13.26 (SCH_3), 24.87 (C-4), 33.87 (C-3), 52.28 (C-5), 74.57 (CHOH), 85.43 (C-2), 128.04 (2*C_{ar}), 128.25 (2*C_{ar}), 128.82 (C_{ar}), 137.81 (C_{ar}). - IR (KBr): ν = 3201 (OH), 1439, 1041 (S=O) cm^{-1}. - MS (70 eV); *m/z* (%): 256 (1) [M^+], 209 (40) [M^+ -

SCH_3], 191 (42), 105 (100) [$C_7H_5O^+$], 85 (31). - $C_{12}H_{16}O_2S_2$ (256.4): calcd. C 56.22, H 6.29, S 25.01; found C 56.64, H 6.48, S 24.75. Diastereoisomer 2: m.p. 75 °C. - ^{1}H NMR (250 MHz): δ = 1.70-1.82 (m, 1H), 1.86 (s, 3H, SCH_3), 2.01-2.18 (m, 1H), 2.45-2.61 (m, 1H), 2.78-2.90 (m, 1H), 3.23-3.37 (m, 1H), 3.70-3.81 (m, 1H), 5.32 (d, *J* = 1.4 Hz, 1H, C*H*OH), 5.52 (br. s, 1H, OH), 7.30-7.42 (m, 3H, Ar-H), 7.48-7.55 (m, 2H, Ar-H). - ^{13}C NMR (62.9 MHz): δ = 12.28 (SCH_3), 25.20 (C-4), 29.55 (C-3), 55.60 (C-5), 75.73 (CHOH), 77.75 (C-2), 127.69 (2*C_{ar}), 128.04 (2*C_{ar}), 128.36 (C_{ar}), 138.80 (C_{ar}).

(E)-2-(1-Hydroxycyclohexyl)-2-(methylthio)thiolane 1-oxide (**7c**): (59%): m.p. 72 °C; *R*f(EA) 0.32. - ^{1}H NMR (250 MHz): δ = 1.52-1.81 (m, 10H), 1.98-2.11 (m, 2H), 2.14 (s, 3H, SCH_3), 2.52-2.63 (m, 1H), 2.78-2.90 (m, 1H), 3.22-3.37 (m, 1H), 3.59-3.72 (m, 1H), 4.41 (br. s, 1H, OH). - ^{13}C NMR (62.9 MHz): δ = 14.44 (SCH_3), 20.94, 21.75, 25.39, 25.56, 29.07, 34.00, 34.87, 53.76, 78.92, 82.53. - IR (neat): ν = 3368 (OH), 2932, 1447, 1029 (S=O) cm^{-1}. - MS (70 eV); *m/z* (%): 248 (6) [M^+], 183 (45), 151 (29), 133 (100) [$C_5H_9S_2^+$], 87 (20), 47 (10). - $C_{11}H_{20}O_2S_2$ (248.4): calcd. C 53.19, H 8.12, S 25.82; found C 53.71, H 8.05, 25.74.

2-(1-Hydroxyethyl)-2-(methylthio)thiolane 1-oxide (**7d**): (64% of a 5:2 mixture of diastereoisomers). Diastereoisomer 1: m.p. 81 °C. - ^{1}H NMR (250 MHz): δ = 1.39 (d, *J* = 7.5 Hz, 3H, CH_3), 2.02- 2.27 (m, 3H), 2.33 (s, 3H, SCH_3), 2.39-2.54 (m, 1H), 2.95-3.04 (m, 3H, 5-H, OH), 4.11-4.22 (m, 1H, C*H*OH). - ^{13}C NMR (62.9 MHz): δ = 13.00 (SCH_3), 18.81 (CH_3), 24.89 (C-4), 34.12 (C-3), 52.79 (C-5), 69.33 (CHOH), 85.20 (C-2). - IR (neat): ν = 3307 (OH), 2927, 1439, 1035 (S=O) cm^{-1}. - MS (70 eV); *m/z* (%): 194 (1) [M^+], 176 (16) [M^+ - H_2O], 147 (100) [M^+ - SCH_3], 113 (24), 87 (53), 47 (48). - $C_7H_{14}O_2S_2$ (194.3): calcd. C 43.27, H 7.26, S 33.00; found C 43.28, H 7.36, S 33.23. Diastereoisomer 2: m.p. 50 °C. - ^{1}H NMR (400 MHz): δ = 1.39 (d, *J* = 6.4 Hz, 3H, CH_3), 1.57-1.72 (m, 1H), 2.17 (s, 3H, SCH_3), 2.17-2.29 (m, 1H), 2.47-2.66 (m, 1H), 2.79-2.93 (m, 1H), 2.96-3.09 (m, 1H), 3.37-3.50 (m, 1H), 4.67 (q, *J* = 6.4 Hz, 1H, C*H*CH_3), 4.75 (br. s, 1H, OH). - ^{13}C NMR (100.6 MHz): δ = 12.17 (SCH_3), 18.21 (CH_3), 25.60 (C-4), 30.59 (C-3), 53.11 (C-5), 67.73 (CHOH), 76.35 (C-2).

2-(1-Hydroxy-2-methylpropyl)-2-(methylthio)thiolane 1-oxide (**7e**): (85% of a 2:1 mixture of diastereoisomers). Diastereoisomer 1: *R*f(EA) 0.71. - ^{1}H NMR (250 MHz): δ = 0.99 (d, *J* = 7.1 Hz, 3H, $CH(CH_3)_2$), 1.14 (d, *J* = 7.1 Hz, 3H, $CH(CH_3)_2$), 1.66-1.78 (m, 1H), 2.18 (s, 3H, SCH_3), 2.20-2.29 (m, 1H), 2.32-2.65 (m, 2H), 2.71-2.85 (m, 1H), 3.00-3.19 (m, 1H), 3.34-3.48 (m, 1H), 4.20-4.25 (m, 1H), 4.34-4.39 (m, 1H). - ^{13}C NMR (62.9 MHz): δ = 12.99 (SCH_3), 15.73 (CH_3), 21.74 (CH_3), 27.07 (C-4), 29.71 ($CH(CH_3)_2$), 32.21 (C-3), 52.47 (C-5), 74.51 (CHOH), 78.04 (C-2). Diastereoisomer 2: m.p. 97 °C; *R*f(EA) 0.24. - ^{1}H NMR (250 MHz): δ = 1.04 (d, *J* = 4.2 Hz, 3H, $CH(CH_3)_2$), 1.19 (d, *J* = 4.2 Hz, 3H, $CH(CH_3)_2$), 1.85-1.96 (m, 1H), 2.03-2.16 (m, 1H), 2.20-2.45 (m, 2H), 2.48 (s, 3H, SCH_3), 2.50-2.63 (m, 1H), 2.70-2.84

(m, 1H), 3.41-3.54 (m, 1H), 3.70 (d, J = 7.5 Hz, 1H), 3.89-3.96 (m,1H). - ^{13}C NMR (62.9 MHz): δ = 14.62 (SCH_3), 18.79 (CH_3), 21.47 (CH_3), 26.66 (C-4), 31.64 $CH(CH_3)_2$), 36.05 (C-3), 51.25 (C-5), 79.53 (CHOH), 82.49 (C-2). - IR (KBr): ν = 3284 (OH), 2928, 1465, 1022 (S=O) cm^{-1}. - MS (70 eV); *m/z* (%): 222 (1) [M^+], 189 (13), 175 (38) [M^+ - SCH_3], 133 (100) [$C_5H_9S_2^+$], 87 (67), 61 (43), 47 (43). - $C_9H_{18}O_2S_2$ (222.4): calcd. C 48.61, H 8.16, S 28.84; found C 49.14, H 7.93, S 28.68.

(E)-2-(1-Hydroxy-2,2-dimethylpropyl)-2-(methylthio)thiolane 1-oxide (**7f**): (33%): m.p. 176 °C. - ^{1}H NMR (400 MHz): δ = 1.17 (s, 9H, $C(CH_3)_3$), 2.03-2.09 (m, 1H), 2.23-2.41 (m, 2H), 2.42 (s, 3H, SCH_3), 2.51-2.60 (m, 1H), 2.61-2.70 (m, 1H), 3.52-3.59 (m, 1H), 3.60-4.00 (br. s, 1H, OH), 3.91 (s, 1H, C*H*OH). - ^{13}C NMR (100.6 MHz): δ = 14.01 (SCH_3), 26.96 (C-4), 27.12 ($C(CH_3)_3$), 35.66 (C-3), 36.45 ($C(CH_3)_3$), 49.50 (C-5), 80.26 (CHOH), 82.72 (C-2). - IR (KBr): ν = 3306 (OH), 2954, 1471, 1030 (S=O) cm^{-1}. - MS (70 eV); *m/z* (%): 236 (1) [M^+], 179 (2) [M^+ - C_4H_9], 133 (66), 87 (15), 57 (100) [$C_4H_9^+$], 47 (10). - $C_{10}H_{20}O_2S_2$ (236.4): calcd. C 50.81, H 8.53, S 27.13; found C 50.94, H 8.46, S 27.98.

(E)-2-(Ethylthio)-2-(1-hydroxy-1-methylethyl)thiolane 1-oxide (**7g**): Acetone with 10% boron trifluoride etherate was used as electrophile. (25%): m.p 45 °C; R_f(EA) 0.47. - ^{1}H NMR (400 MHz): δ = 1.22 (t, J = 7.6 Hz, 3H, CH_2CH_3), 1.36 (s, 3H, CH_3), 1.72 (s, 3H, CH_3), 2.03-2.10 (m,1H, 3-H), 2.11-2.19 (m, 1H, 4-H), 2.55-2.66 (m, 2H, 4-H, CH_2), 2.67-2.76 (m, 1H, CH_2), 2.81-2.91 (m, 1H, 5-H), 3.23-3.31 (m, 1H, 3-H), 3.62-3.70 (m,1H, 5-H), 54.80 (br. s, 1H, OH). - ^{13}C NMR (62.9 MHz): δ = 14.04 (CH_2CH_3), 25.35 (CH_2), 25.69 (C-4), 27.66 (CH_3), 28.62 (CH_3), 31.30 (C-3), 54.03 (C-5), 77.69 (C-2), 82.47 (COH). - IR (KBr): ν = 3277 (OH), 2966, 1457, 1027 (S=O) cm^{-1}. - MS (70 eV); *m/z* (%): 222 (1) [M^+], 147 (100) [$C_6H_{11}S_2^+$], 103 (24) [$C_4H_7OS^+$], 85 (70), 59 (70), 47 (21). - $C_9H_{18}O_2S_2$ (222.4): calcd. C 48.61, H 8.16, S 28.84; found C 48.61, H 8.13, S 28.62.

2-(Ethylthio)-2-(1-hydroxy-1-phenylmethyl)thiolane 1-oxide (**7h**): (46% of a 2.9:1 mixture of diastereoisomers): Diastereoisomer 1: m.p. 75 °C; R_f(EA) 0.62. - ^{1}H NMR (400 MHz): δ = 1.06 (t, J = 7.4 Hz, 3H, CH_2CH_3), 1.73-1.79 (m, 1H, 3-H), 2.05-2.23 (m, 2H, 4-H, CH_2), 2.46-2.56 (m, 2H, 4H, CH_2), 2.79-2.87 (m, 1H, 5-H), 3.25-3.33 (m, 1H, 3-H), 3.72-3.79 (m, 1H, 5-H), 5.34 (d, J = 1.5 Hz, 1H, C*H*OH), 5.51 (br. s, 1H, OH), 7.31-7.38 (m, 3H, Ar-H), 7.50-7.52 (m, 2H, Ar-H). - ^{13}C NMR (62.9 MHz): δ = 13.60 (CH_3), 23.35 (C-4), 25.19 (CH_2), 29.83 (C-3), 55.57 (C-5), 76.12 (CHOH), 78.74 (C-2), 127.69 (2*C_{ar}), 127.94 (C_{ar}, 128.31 (C_{ar}), 138.92 (C_{ar}). - IR (KBr): ν = 3275 (OH), 2928, 1450, 1027 (S=O) cm^{-1}. - MS (70 eV); *m/z* (%): 270 (1) [M^+], 209 (27), 147 (100) [$C_6H_{11}S_2^+$], 105 (97) [$C_7H_5O^+$], 87 (20) [$C_4H_7S^+$], 77 (94), 45 (32). - $C_{13}H_{18}O_2S_2$ (270.4): calcd. C 57.74, H 6.71, S 23.71; found C 57.49, H 6.76, S 22.88. Diastereoisomer 2: m.p. 160 °C; R_f(EA) 0.30. - ^{1}H NMR (400 MHz): δ = 1.13 (t, J = 7.4 Hz, 3H, CH_2CH_3), 1.49-1.55 (m, 1H, 3-H), 2.08-2.20 (m, 1H, CH_2), 2.39-2.48 (m, 1H, CH_2), 2.53-2.61 (m, 1H, 3-H), 2.64-2.72 (m, 1H, 4-H), 2.76-2.91

(m, 2H, 4-H, 5-H), 3.64-3.71 (m, 1H, 5-H), 4.02 (d, J = 5.6 Hz, 1H, C*H*OH), 5.31 (d, J = 5.6 Hz, 1H, OH), 7.31-7.40 (m, 3H, Ar-H), 7.52-7.55 (m, 2H, Ar-H). - ^{13}C NMR (62.9 MHz): δ = 14.65 (CH_3), 24.82 (C-4), 25.52 (CH_2), 34.90 (C-3), 53.46 (C-5), 75.36 (CHOH), 83.38 (C-2), 127.90 (C_{ar}), 127.96 (C_{ar}), 128.16 (C_{ar}), 139.91 (C_{ar}). - IR (KBr): ν = 3250 (OH), 2966, 1489, 1019 (S=O) cm^{-1}. - MS (70 eV); *m/z* (%): 270 (1) [M^+], 209 (28), 163 (10) [$C_6H_{11}OS_2^+$], 147 (60) [$C_6H_{11}S_2^+$], 105 (100) [$C_7H_5O^+$], 87 (20), 79 (92). - $C_{13}H_{18}O_2S_2$ (270.4): calcd. C 57.74, H 6.71, S 23.71; found C 57.48, H 6.78, S 23.13.

(E)-2-(1-Hydroxy-1-methylethyl)-2-(isopropylthio)thiolane 1-oxide (**7i**): Acetone with 10% boron trifluoride etherate was used as electrophile. (41%): m.p. 39 °C; R_f(EA) 0.53. - ^{1}H NMR (400 MHz): δ = 1.30 (d, J = 7.1 Hz, 3H, CH(C*H*3)2), 1.35 (d, J = 6.6 Hz, 3H, CH(C*H*3)2), 1.37 (s, 3H, CH3), 1.71 (s, 3H, CH3), 1.98-2.05 (m, 1H, 3-H), 2.22-2.33 (m, 1H, 4-H), 2.62-2.73 (m, 1H, 4-H), 2.90-2.97 (m, 1H, 5-H), 3.10 (sept, J = 6.9 Hz, 1H, C*H*(CH3)2), 3.26-3.35 (m, 1H, 3-H), 3.51-3.60 (m, 1H, 5-H), 4.90 (br. s, 1H, OH). - ^{13}C NMR (100.6 MHz): δ = 24.95 (CH(*C*H3)2), 26.08 (C-4), 26.96 (CH(*C*H3)2), 27.80 (CH3), 28.62 (CH3), 31.62 (C-3), 36.44 *C*H(CH3)2), 52.85 (C-5), 77.60 (C-2), 83.86 (COH). - IR (KBr): ν = 3369 (OH), 2972, 1460, 1030 (S=O) cm^{-1}. - MS (70 eV); *m/z* (%): 236 (1) [M^+], 160 (62), 118 (100), 87 (20), 71 (68), 47 (14). - $C_{10}H_{20}O_2S_2$ (236.4): calcd. C 50.81, H 8.53, S 27.13; found C 50.04, H 8.52, S 27.19.

2-(1-Hydroxy-1-phenylmethyl)-2-(isopropylthio)thiolane 1-oxide (**7j**): (45% of a 2.9:1 mixture of diastereoisomers). Diastereoisomer 1: m.p. 107 °C; R_f(EA) 0.81. - ^{1}H NMR (400 MHz): δ = 1.12 (d, J = 6.6 Hz, 3H, CH(C*H*$_3$)$_2$), 1.15 (d, J = 6.6 Hz, 3H, CH(C*H*$_3$)$_2$), 1.83-1.91 (m, 1H, 3-H), 2.12-2.22 (m, 1H, 4-H), 2.47-2.58 (m, 1H, 4-H), 2.73-2.88 (m, 2H, 5-H, C*H*(CH$_3$)$_2$), 3.36-3.44 (m, 1H, 3-H), 3.70-3.77 (m, 1H, 5-H), 5.30-5.40 (br. s, 1H, OH), 5.55 (s, 1H, C*H*OH), 7.32-7.36 (m, 3H, Ar-H), 7.50-7.52 (m, 2H, Ar-H). - ^{13}C NMR (62.9 MHz): δ = 24.93 (CH$_3$), 25.28 (C-4), 25.99 (CH$_3$), 30.60 (C-3), 34.84 (*C*H(CH$_3$)$_2$), 54.76 (C-5), 76.73 (CHOH), 80.04 (C-2), 127.97 (C_{ar}, 128.10 (C_{ar}), 128.26 (C_{ar}), 139.25 (C_{ar}). - IR (KBr): ν = 3320 (OH), 2967, 1453, 1029 (S=O) cm^{-1}. - MS (70 eV); *m/z* (%): 284 (1) [M^+], 209 (26) [$C_{11}H_{13}O_2S^+$], 161 (70), 105 (100), 87 (30), 77 (71). - $C_{14}H_{20}O_2S_2$ (284.5): calcd. C 59.12, H 7.09, S 22.54; found C 59.36, H 7.08, S 22.76. Diasteroisomer 2: m.p. 154 °C; R_f(EA) 0.43. - ^{1}H NMR (400 MHz): δ = 1.24 (d, J = 7.0 Hz, 3H, CH(C*H*$_3$)$_2$), 1.32 (d, J = 7.0 Hz, 3H, CH(C*H*$_3$)$_2$), 1.44-1.52 (m, 1H, 3-H), 2.14-2.25 (m, 1H, 4-H), 2.38-2.48 (m, 1H, 4-H), 2.55-2.63 (m, 1H, 3-H), 2.77-2.85 (m, 1H, 5-H), 3.60-3.74 (m, 2H, 5-H, C*H*(CH$_3$)$_2$), 3.89 (d, J = 5.0 Hz, 1H, C*H*OH), 5.36 (d, J = 5.0 Hz, 1H, OH), 7.28-7.37 (m, 3H, Ar-H), 7.52-7.55 (m, 2H, Ar-H). - ^{13}C NMR (100.6 MHz): δ = 24.81 (CH$_3$), 25.44 (C-4), 27.60 (CH$_3$), 35.91 (C-3), 36.18 (*C*H(CH$_3$)$_2$), 52.80 (C-4), 75.44 (CHOH), 84.44 (C-2), 127.90 (C_{ar}), 128.13 (C_{ar}), 128.18 (C_{ar}), 140.02 (C_{ar}). - IR (KBr): ν = 3268 (OH), 3033, 2967, 1450, 1020 (S=O) cm^{-1}. - MS (CI, NH_3): *m/z* (%): 285 (5) [M^+ + 1], 210 (9) [$C_{11}H_{14}O_2S^+$],

161 (100) [$C_7H_{13}S_2^+$], 87 (19). - $C_{14}H_{20}O_2S_2$ (284.5): calcd. C 59.12, H 7.09, S 22.54; found C 59.26, H 7.10, S 22.50.

2-(1-Hydroxyethyl)-2-(isopropylthio)thiolane 1-oxide (**7k**): (68% of a 1.9:1 mixture of diastereoisomers): Diastereoisomer 1: *Rf*(EA) 0.61. - ^{1}H NMR (400 MHz): δ = 1.33 (d, *J* = 6.6 Hz, 6H, CH(C*H*$_3$)$_2$), 1.42 (d, *J* = 6.4 Hz, 3H, C*H*$_3$CHOH), 1.64-1.71 (m, 1H, 3-H), 2.13-2.19 (m, 1H, 4-H), 2.49-2.59 (m, 1H, 4-H), 2.88-2.90 (m, 1H, 5-H), 3.00-3.08 (m, 1H, 3-H), 3.19-3.29 (sept, *J* = 6.6 Hz, 1H, C*H*(CH$_3$)$_2$), 3.49-3.56 (m, 1H, 5-H), 4.75 (q, *J* = 6.4 Hz, 1H, CH$_3$C*H*OH), 4.94-5.05 (br. s, 1H, OH). - ^{13}C NMR (100.6 MHz): δ = 19.46 (*C*H$_3$CHOH), 25.12 (CH$_3$), 25.74 (C-4), 25.88 (CH$_3$), 31.86 (C-3), 35.20 (*C*H(CH$_3$)$_2$), 53.85 (C-5), 69.34 (CHOH), 79.00 (C-2). - IR (neat): ν = 3371 (OH), 2973, 1443, 1034 (S=O) cm^{-1}. - MS (70 eV); *m/z* (%): 222 (1) [M^+], 161 (53), 147 (100) [$C_6H_{11}O_2S^+$], 103 (28), 87 (65), 59 (43), 47 (21). $C_9H_{18}O_2S_2$ (222.4): calcd. C 48.61, H 8.16, S 28.84; found C 48.67, H 8.36, S 28.73. Diastereoisomer 2: *Rf*(EA) 0.30. - ^{1}H NMR (400 MHz): δ = 1.32 (d, 3H, CH(C*H*$_3$)$_2$, J = 6.4 Hz, 1.34 (d, *J* = 6.8 Hz, 3H, CH(C*H*$_3$)$_2$), 1.45 (d, *J* = 6.6 Hz, 3H, C*H*$_3$CHOH), 1.74-1.81 (m, 1H, 3-H), 2.19-2.27 (m, 1H, 4-H), 2.34-2.41 (m, 1H, 3-H), 2.42-2.53 (m, 1H, 4-H), 2.80-2.86 (m, 1H, 5-H), 3.52-3.60 (m, 1H, 5-H), 3.60-3.70 (br. s, 1H, OH), 3.80 (sept, *J* = 6.8 Hz, 1H, C*H*(CH$_3$)$_2$), 4.44 (q, *J* = 6.6 Hz, 1H, C*H*OH). - ^{13}C NMR (100.6 MHz): δ = 19.16 (*C*H$_3$CHOH), 25.03 (CH$_3$), 25.76 (C-4), 26.96 (CH$_3$), 35.60 (*C*H(CH$_3$)$_2$), 35.90 (C-3), 52.38 (C-5), 70.26 (CHOH), 84.57 (C-2). - MS (70 eV); *m/z* (%): 161 (51), 119 (72), 87 (5), 43 (100).

2-(1-Hydroxypropyl)-2-(isopropylthio)thiolane 1-oxide (**7l**): (79% of a 2.4:1 mixture of diastereoisomers): Diastereoisomer 1: m.p. 50 °C; *Rf*(EA) 0.73. - ^{1}H NMR (400 MHz): δ = 1.08 (t, *J* = 7.0 Hz, 3H, CH$_2$C*H*$_3$), 1.31 (d, *J* = 7.0 Hz, 3H, CH(C*H*$_3$)$_2$), 1.33 (d, *J* = 7.0 Hz, 3H, CH(C*H*$_3$)$_2$), 1.35-1.47 (m, 1H, 4-H), 1.62-1.69 (m, 1H, 3-H), 2.02-2.10 (m, 2H, C*H*$_2$CH$_3$), 2.47-2.57 (m, 1H, 4-H), 2.79-2.85 (m, 1H, 5-H), 2.98-3.05 (m, 1H, 3-H), 3.22 (sept, *J* = 7.0 Hz, 1H, C*H*(CH$_3$)$_2$), 3.42-3.56 (m, 1H, 5-H), 4.38 (d, *J* = 10.4 Hz, 1H, C*H*OH), 4.95 (br. s, 1H, OH). - ^{13}C NMR (100.6 MHz): δ = 10.53 (*C*H$_3$CH$_2$), 25.20 (CH$_3$), 25.79 (CH$_3$), 25.91 (CH$_3$*C*H$_2$), 25.93 (C-4), 32.38 (C-3), 35.21 (*C*H(CH$_3$)$_2$), 53.84 (C-5), 74.54 (CHOH), 82.11 (C-2). IR (KBr): ν = 3338 (OH), 2976, 1461, 1026 (S=O) cm^{-1}. - MS (70 eV); *m/z* (%): 236 (6) [M^+], 161 (100) [$C_7H_{13}O_2S^+$], 103 (32), 87 (53), 59 (24), 47 (12). - $C_{10}H_{20}O_2S_2$ (236.4): calcd. C 50.81, H 8.53, S 27.12; found C 51.20, H 8.39, S 26.48. Diastereoisomer 2: m.p. 115 °C; *Rf*(EA) 0.26. - ^{1}H NMR (400 MHz): δ = 1.11 (t, *J* = 7.2 Hz, 3H, CH$_2$C*H*$_3$), 1.31 (d, *J* = 7.0 Hz, 3H, CH(C*H*$_3$)$_2$), 1.33 (d, *J* = 7.0 Hz, 3H, CH(C*H*$_3$)$_2$), 1.58-1.67 (m, 1H, 4-H), 1.80-1-95 (m, 2H, 3-H, 4-H), 2.17-2.28 (m, 1H, C*H*$_2$CH$_3$), 2.37-2.44 (m, 1H, 3-H), 2.47-2.57 (m, 1H, C*H*$_2$CH$_3$), 2.78-2.84 (m, 1H, 5-H), 3.39 (d, *J* = 6.0 Hz, 1H, OH), 3.49-3.57 (m, 1H, 5-H), 3.79 (sept, *J* = 7.0 Hz, 1H, C*H*(CH$_3$)$_2$), 4.07-4.12 (m, 1H, C*H*OH). - ^{13}C NMR (100.6 MHz): δ = 10.91 (*C*H$_3$CH$_2$), 24.95 (CH$_3$), 25.91 (CH$_3$*C*H$_2$), 26.12 (C-4), 26.91 (CH$_3$), 35.62 (*C*H(CH$_3$)$_2$), 35.89 (C-3), 52.06 (C-5), 76.28

(CHOH), 84.25 (C-2). - IR (KBr): ν = 3294 (OH), 2972, 1456, 1014 (S=O) cm^{-1}. - MS (70 eV); *m/z* (%): 236 (4) [M^+], 193 (13), 161 (100) [$C_7H_{13}O_2S^+$], 103 (34), 87 (60), 59 (29), 47 (14). - $C_{10}H_{20}O_2S_2$ (236.4): calcd. C 50.81, H 8.53, S 27.12; found C 51.05, H 8.47, S 26.61.

(E)-2-(1-Hydroxy-2-methylpropyl)-2-(isopropylthio)thiolane 1-oxide (**7m**): (2%): m.p. 134 °C; *R*f(EA) 0.30. - ^{1}H NMR (400 MHz): δ = 1.02 (d, *J* = 6.8 Hz, 3H, CH(C*H*$_3$)$_2$), 1.18 (d, *J* = 6.8 Hz, 3H, CH(C*H*$_3$)$_2$), 1.29 (d, *J* = 6.8 Hz, 3H, CH(C*H*$_3$)$_2$), 1.34 (d, *J* = 6.8 Hz, 3H, CH(C*H*$_3$)$_2$), 1.91-1.97 (m, 1H, 3-H), 2.16 (sept, *J* = 6.8 Hz, 1H, C*H*(CH$_3$)$_2$), 2.21-2.35 (m, 1H, 4-H), 2.44-2.60 (m, 2H, 3-H, 4-H), 2.73-2.80 (m, 1H, 5-H), 3.48-3.54 (m, 1H, 5-H), 3.56 (d, *J* = 6.0 Hz, 1H, OH), 3.88 (sept, *J* = 6.8 Hz, 1H, C*H*(CH$_3$)$_2$), 3.99 (m, 1H, C*H*OH). - ^{13}C NMR (100.6 MHz): δ = 19.04 (CH$_2$*C*H$_3$), 21.18 (CH$_3$), 24.76 (CH$_3$), 26.38 (C-4), 27.37 (CH$_3$), 31.55 (*C*H(CH$_3$)$_2$), 35.37 (S*C*H(CH$_3$)$_2$), 36.26 (C-3), 50.86 (C-5), 79.58 (CHOH), 84.72 (C-2). - IR (KBr): ν = 3309 (OH), 2981, 1452, 1022 (S=O) cm^{-1}. - MS (70 eV); *m/z* (%): 250 (7) [M^+], 175 (62) [$C_8H_{15}O_2S^+$], 103 (69), 87 (98), 71 (100), 47 (16). - $C_{11}H_{22}O_2S_2$ (250.4): calcd. C 52.76, H 8.86, S 25.61; found C 52.54, H 8.83, S 24.57.

(E)-2-(1-Hydroxy-1-methylethyl)-2-(phenylthio)thiolane 1-oxide (**7n**): (14%): m.p. 55 °C; *R*f(EA/CCl_4) 0.22. - ^{1}H NMR (250 MHz): δ = 1.50 (s, 3H, CH$_3$), 1.62 (s, 3H, CH$_3$), 1.69-1.88 (m, 1H), 1.91-2.06 (m, 1H), 2.40-2.60 (m, 1H), 2.86-3.01 (m, 1H), 3.19-3.35 (m, 2H), 5.01 (s, 1H, OH), 7.32-7.58 (m, 5H, Ar-H). - ^{13}C NMR (62.9 MHz): δ = 25.82 (C-4), 27.96 (CH$_3$), 28.64 (CH$_3$), 31.14 (C-3), 51.92 (C-5), 77.17 (COH), 86.60 (C-2), 129.42 (2*C$_{ar}$), 129.91 (C$_{ar}$), 130.19 (C$_{ar}$), 136.88 (2*C$_{ar}$). - IR (neat): ν = 3371 (OH), 3058, 2961, 1440, 1004 (S=O) cm^{-1}. - MS (70 eV); *m/z* (%): 227 (8) [M^+ - C_2H_3O], 195 (100) [M^+ - $C_3H_7O_2$], 129 (99), 85 (86), 77 (53), 47 (11).

ACKNOWLEGDEMENTS

Support of our work by the *Deutsche Forschungsgemeinschaft* and the *Fonds der Chemischen Industrie* is gratefully acknowledged.

REFERENCES

1. Part 6: Birk, C.; Voss, J. *Tetrahedron* **1996**, *52*, 12745-12760.
2. Presented in parts at the *16th International Symposium on the Organic Chemistry of Sulfur*, Merseburg, Germany, **1994**; Brunck, J.-S.; Voss, J. *Phosphorus, Sulfur, Silicon* **1994**, *95*, 403-404.
3. Brunck, J.-S. *Dissertation*, University of Hamburg, **1993**.
4. Seebach, D. *Angew. Chem.* **1969**, *81*, 690-700; *Angew. Chem. Int. Ed. Engl.* **1969**, *8*, 639-649.
5. Corey, E.J.; Seebach, D. *Angew. Chem.* **1965**, *77*, 1134-1135; *Angew. Chem. Int. Ed. Engl.* **1965**, *4*, 1075-1076, 1077.

For a more recent review see: Page, P.C.B.; van Niel, M.B.; Prodger, J.C. *Tetrahedron* **1989**, *45*, 7643-7677.

6. 6a. Ogura, K.; Yamashita, M.; Suzuki, M.; Furukawa, S.; Tsuchihashi, G. *Bull. Chem. Soc. Jpn.* **1984**, *54*, 1637-1642. 6b. Ogura, K.; Tsuchihashi, G. *Tetrahedron Lett.* **1971**, 3151-3154.
7. Herrmann, J.L.; Richman,J.E.; Schlessinger, R.H. *Tetrahedron Lett.* **1973**, 3271-3274, 3275-3278.
8. 8a. Solladié, G. *Synthesis* **1981**, 185-196; 8b: Solladié, G.; Colobert, F.; Ruiz, P.; Hamdouchi, C.; Carreno, M.C.; Ruano, J.L.G. *Tetrahedron Lett.* **1991**, *32*, 3695-3698; 8c. For a review on sulfoxide-stabilized carbanions see: Walker, A.J. *Tetrahedron Asymm.* **1992**, *3*, 961-998.
9. 9a. Page, P.C.B.; Allin, S.M.; Collington, E.W.; Carr, R.A.E. *Tetrahedron Lett.* **1994**, *35*, 2607-2608; 9b. Page, P.C.B.; Slawin, A.M.Z.; Westwood, D.; Williams, D.J. *J. Chem. Soc., Perkin Trans. 1* **1989**, 185-187.
10. 10a. Aggarwal, V.K.; Franklin, R.; Maddock, J.; Evans, G.R.; Thomas, A.; Mahon, M.F.; Molloy, K.C. Rice, M.J. *J. Org. Chem.* **1995**, *60*, 2174-2182; 10b. Aggarwal, V.K.; Davies, I.W.; Franklin, R.; Maddock, J.; Mahon, M.F.; Molloy, K.C. *J. Chem. Soc., Perkin Trans. 1* **1994**, 2363-2368.
11. 11a. Pyne, S.G.; Boche, G. *J. Org. Chem.* **1989**, *54*, 2663-2667; 11b. Satoh, T.; Onda, K., Yamakawa, K. *Tetrahedron Lett.* **1990**, *31*, 3567-3570.
12. Sakuraba, H.; Ushiki, S. *Tetrahedron Lett.* **1990**, *31*, 5349-5352.
13. 13a. Delogu, G.; De Lucchi, O.; Maglioli, P.; Valle, G. *J. Org. Chem.* **1991**, *56*, 4467-4473. 13b. De Lucchi, O. *Phosphorus Sulfur Silicon* **1993**, *74*, 195-213.
14. Böge, A.; Brunck, J.-S.; Schwär, G.; Voss, J. *Chem. Ber.* **1992**, *125*, 1641-1646.
15. 15a. Brunck, J.-S.; Voss, J.; Olbrich, F.; Viebrock, H. *Acta Crystallogr. Sect. C* **1993**, *49*, 934-936; 15b. Brunck, J.-S.; Voss, J.; Viebrock, H.; Olbrich, F. *Acta Crystallogr. Sect. C.* **1994**, *50*, 1370-1372.
16. Ogura, K.; Tsuchihashi, G. *Chem. Commun.* **1970**, 1689-1690.
17. Tarbell, D.S.; Weaver, C. *J. Am. Chem. Soc.* **1941**, *63*, 2939-2942.
18. Iriuchijima, S.; Tsuchihashi, G. *Synthesis* **1970**, 588-589.
19. Parham, W.E.; Heberling, J. *J. Am. Chem. Soc.* **1955**, *77*, 1175-1177.
20. Oae, S.; Uchida, Y. in *The Chemistry of Sulfones and Sulfoxides* (Eds.: Patai, S.; Rappoport, Z.; Stirling, C.J.M.), Wiley, New York, **1988**, chapter 12.
21. A detailed study of the reactions of the α-sulfinyl carbanions of **3** and their transformations will be published separately.

(*Received in Germany* 5 *November* 1996; *accepted* 19 *December* 1996)