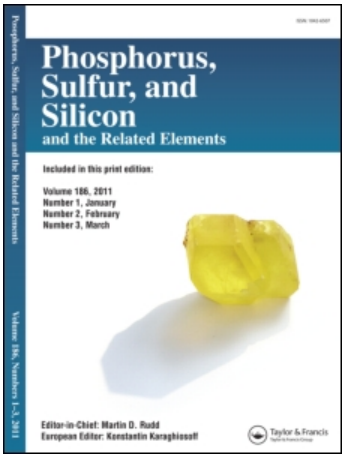

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THE THIO-ARBUZOV-REACTION. PART 8.[1] SYNTHESIS OF α-FUNCTIONALIZED METHANESULFINATES FROM DIALKYL SULFOXYLATES AND ALKYL BROMIDES R^1CH^2Br

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THE THIO-ARBUZOV-REACTION. PART 8.[1] SYNTHESIS OF α-FUNCTIONALIZED METHANESULFINATES FROM DIALKYL SULFOXYLATES AND ALKYL BROMIDES R^1CH_2Br

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Dedicated to Professor Kurt Issleib on the occasion of his 75th birthday.

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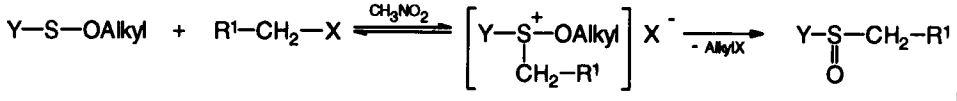
A variety of α-functionalized alkyl methanesulfinates could be obtained in good yields via Thio-ARBUZOV-Reactions of dialkyl sulfoxylates with different organic bromides. The new sulfinic esters have been characterized by their physical and spectroscopic data. Further experiments were carried out to study the influence of the substituent R^1 on the reactivity of the halide towards Thio-ARBUZOV transformations which led to some general conclusions concerning the demands on the electrophile.

Key words: Thio-ARBUZOV-Reaction, dialkyl sulfoxylates, organic bromides, α-functionalized alkyl methanesulfinates, ^{1}H- and ^{13}C-NMR data.

INTRODUCTION

Conversions of λ^2-alkoxysulfanes Y–S–OAlkyl into λ^4-sulfinyl derivatives caused by electrophilic attack of organic halides at the sulfur atom were named Thio-ARBUZOV-Reactions and thoroughly studied in our group during the last few years.[1-3] These transformations proceed via tri-coordinated quasi sulfonium intermediates followed by dealkylation and S=O bond formation and are facilitated by strong acceptor solvents like nitromethane; Equation (1).



(1)

Y = OAlkyl, Ph, >N R^1 = H, Alkyl, Ph, Allyl etc. X = Cl, Br, I

Thus the Thio-ARBUZOV-Reaction represents a facile synthetic route to sulfinic esters,[2] unsymmetric phenylsulfoxides[1] and sulfinamides[3] starting from dialkyl sulfoxylates, methyl benzenesulfenate and aminosulfenates, respectively.

We now report about the results of our systematic investigations on the reaction behaviour of a large number of modified halocarbons $R^1–CH_2–X$ towards dialkyl sulfoxylates. The electrophilicity of the halogen bonded carbon atom is strongly influenced by variation of R^1. The interaction of a large number of halocarbons

with dialkyl sulfoxylates was examined.[4] It appears that the number of suitable organic halides for a Thio-ARBUZOV-Reaction is considerably lower than in the MICHAELIS-ARBUZOV-Reaction. In the course of the experiments carried out with dialkyl sulfoxylates successful Thio-ARBUZOV transformations yielding sulfinic esters were only achieved with those organic halides containing a sp^2- or sp-hybridized carbon or nitrogen atom neighbouring the $-CH_2-X$ group.

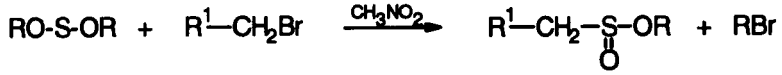
Even the introduction of strong electron withdrawing substituents R^1 like CF_3 or CN which were expected to enhance the electrophilic properties of the halogen bonded carbon atom did not lead to Thio-ARBUZOV-Reactions.

In this paper we report about five groups of halocarbons which were found to react with dialkyl sulfoxylates yielding the expected Thio-ARBUZOV products. 18 new α-functionalized methanesulfinic esters were prepared by use of the following halogen components:

—3-bromo-1-propyne (propargyl bromide)
—substituted allyl bromides
—substituted benzyl bromides and 1-bromomethylnaphthalene
—derivatives of bromoacetic acid (bromoacetic esters, amides and methyl 4-bromocrotonate, i.e. a vinylogous bromoacetic ester)
—N-bromomethylphthalimide

RESULTS AND DISCUSSION

The Thio-ARBUZOV-Reactions proceed according to Equation (2), the obtained new sulfinates (**2–10**) are collected in Table I.



(2)

(1) **(2-10)**

Thus via Thio-ARBUZOV-Reactions a number of modified new sulfinates are easily available in good yields.

*2-Propyne-1-sulfinates (**2a–b**)*

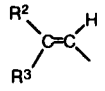
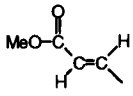
The reactions of propargyl bromide (3-bromo-1-propyne) with dialkyl sulfoxylates yield unsaturated sulfinic esters containing a C–C triple bond. In contrast to the analogous MICHAELIS-ARBUZOV-reaction[5] no isomerization of the propargyl group was observed. This is confirmed by the infrared and n.m.r. spectra of the sulfinates.

*Allylsulfinates (**3a–c**)*

The Thio-ARBUZOV-Reaction offers a comparatively simple route to substituted allylsulfinates (see Reference 6). For the isolated propyl 2-buten-1-sulfinate **3a** an E/Z-ratio of 5.33:1 was found by analysis of the integrals in the ^{1}H-n.m.r. spectrum.

TABLE I

α-functionalized alkyl methanesulfinates $R^1-CH_2-S(O)OR$ **2–10** (* = new compound)

R^1=	R =	yield	compd.	R^1=	R =	yield	compd.
HC≡C-	nPr	70 %	**2a***	EtO–C(=O)–	nPr	53 %	**7a**
	iPr	60 %	**2b***		iPr	47 %	**7b***
							
R^2 = Me; R^3 = H	nPr	85 %	**3a***		nPr	43 %	**8a***
R^2 = Me; R^3 = Me	nPr	71 %	**3b***		iPr	40 %	**8b***
R^2 = Ph; R^3 = H	iPr	91 %	**3c***				
							
Z = p-F_3C	nPr	44 %	**4a***		nPr	44 %	**9a***
Z = p-F	nPr	74 %	**4b***		iPr	51 %	**9b***
Z = p-MeO	nPr	90 %	**4c***				
Z = m-F_3C	nPr	85 %	**4d***				
	nPr	73 %	**5***		nPr	92 %	**10a***
					iPr	95 %	**10b***
	nPr	52 %	**6***				

In the case of propyl 3-phenyl-2-propen-1-sulfinate **3c** only the E-isomer was separated according to the ^1H ($^3J_{trans}$ = 15.9 Hz for the allylic protons) and ^{13}C n.m.r. data and the infrared absorption at 970 cm^{-1} [δ (C–H)-"out of plane"].

*Substituted Benzyl- and 1-Naphthylmethanesulfinates (**4a–6**)*

The number of new alkyl benzylsulfinates prepared via Thio-ARBUZOV-Reaction was extended by **4a–d** and **5** and the first alkyl 1-naphthylmethanesulfinate **6** could be isolated.

*Alkoxy- and N,N-Diethylaminocarbonylmethanesulfinates (**7–8**)*

The reaction of esters and amides of bromoacetic acid with dialkyl sulfoxylates yields methanesulfinates containing an α-alkoxycarbonyl or α-N,N-diethylaminocarbonyl substituent. The use of nitromethane as a solvent was shown to enhance the yield of **7a** (see Reference 7). The Thio-ARBUZOV-Reaction offers a direct way to sulfinates of the general formula $R^1O-C(O)-CH_2-S(O)-OR^2$ ($R^1 \neq R^2$) which are not available by the method described by DePree[8] and is an alternative route to Harpp and Back.[9]

4-Methoxycarbonyl-2-butene-1-sulfinates (**9a–b**)

Reacting methyl 4-bromocrotonate with dialkyl sulfoxylates the sulfinates **9a–b** could be isolated which represent red oils. Analysis of IR and n.m.r. spectra confirmed E-configuration for both products.

N-Phthalimidomethanesulfinates (**10a–b**)

The first α-functionalized alkyl methanesulfinates containing a nitrogen atom neighbouring the CH_2–S(O) group were prepared in excellent yields by reaction of N-bromomethylphthalimide with the dialkyl sulfoxylates **1**. They represent white, crystalline compounds and are expected to be good precursors for further derivatization.

EXPERIMENTAL

All Thio-ARBUZOV-Reactions were carried out in dry nitromethane under anaerobic conditions.

TABLE II

Analytical data of **2–10**

compd.	m.p.[°C]/ b.p.[°C]	molecular formula	M[g/mol]	n_{20}	analysis (calcd.) found [%] C	H	N	S
2a	62 (2.7 mbar)	$C_6H_{10}O_2S$	146.21	1.4722	(49.29)	(6.89)	-	(21.93)
					48.98	6.91	-	21.94
2b	65 (4 mbar)	$C_6H_{10}O_2S$	146.21	1.4664	(49.29)	(6.89)	-	(21.93)
					49.03	6.81	-	21.87
3a	64-66 (0,7 mbar)	$C_7H_{14}O_2S$	162.25	1.4653	(51.82)	(8.70)	-	(19.76)
					51.59	8.89	-	19.49
3b	52-53 (0,07 mbar)	$C_8H_{16}O_2S$	176.27	1.4718	(54.51)	(9.15)	-	(18.19)
					53.45	9.09	-	18.12
3c	121-124 (0.02 mbar)	$C_8H_{16}O_2S$	224.32	1.5584	(64.25)	(7.19)	-	(14.29)
					63.42	6.98	-	14.09
4a	50 (m.p.)	$C_{11}H_{13}F_3O_2S$	266.28	-	(49.62)	(4.92)	-	(12.04)
					49.86	5.04	-	11.81
4b	118-119 (2.7 mbar)	$C_{10}H_{13}FO_2S$	216.27	1.5152	(55.54)	(6.06)	-	(14.82)
					55.74	6.05	-	14.48
4c	110-112 (0.01 mbar)	$C_{11}H_{16}O_3S$	228.31	1.5387	(57.87)	(7.06)	-	(14.04)
					57.86	7.12	-	13.66
4d	120 (0,007 mbar) [Kugelrohr]	$C_{11}H_{13}F_3O_2S$	266.28	1.4828	(49.62)	(4.92)	-	(12.04)
					49.08	4.92	-	11.94
5	75-76 (0.007 mbar)	$C_{10}H_9F_5O_2S$	288.23	1.4655	(41.67)	(3.15)	-	(11.12)
					41.39	3.14	-	11.52
6	141-143 (0.008 mbar)	$C_{14}H_{16}O_2S$	248.34	1.6025	(67.71)	(6.49)	-	(12.91)
					67.70	6.69	-	12.95
7a	75-78 (0.13 mbar)	$C_7H_{14}O_4S$	194.24	1.4484	(43.28)	(7.27)	-	(16.50)
					43.09	7.42	-	16.70
7b	85-87 (2 mbar)	$C_7H_{14}O_4S$	194.24	1.4500	(43.28)	(7.27)	-	(16.50)
					43.16	7.43	-	16.64
8a	100-104 (0.008 mbar)	$C_9H_{19}NO_3S$	221.31	1.4839	(48.84)	(8.65)	(6.33)	(14.49)
					48.23	8.53	6.53	14.78
8b	116-120 (0.007 mbar)	$C_9H_{19}NO_3S$	221.31	1.4839	(48.84)	(8.65)	(6.33)	(14.49)
					47.58	8.64	6.51	13.99
9a	100-101 (0.007 mbar)	$C_8H_{14}O_4S$	206.26	1.4896	(46.59)	(6.84)	-	(15.54)
					45.37	6.72	-	14.41
9b	100-103 (0.007 mbar)	$C_8H_{14}O_4S$	206.26	1.4902	(46.59)	(6.84)	-	(15.54)
					45.23	6.54	-	15.83
10a	69 (m.p.)	$C_{12}H_{13}NO_4S$	299.36	-	(53.92)	(4.90)	(5.24)	(11.99)
					54.04	4.85	5.28	11.83
10b	98-99 (m.p.)	$C_{12}H_{13}NO_4S$	299.36	-	(53.92)	(4.90)	(5.24)	(11.99)
					53.79	4.86	5.37	11.98

TABLE III

Spectroscopic data

com-pound	IR [cm^{-1}]	^{1}H-NMR[b] δ [ppm]	^{13}C-NMR[b] δ [ppm]
2a	1135 (vs) ν(S=O) 3260 (s), 3300 (sh) ν(≡C-H) 2130 cm^{-1} (s) ν(-C≡C-)	4.06 [t, 2H, -O-CH_2] (^3J = 6.6 Hz); 3.60/3.52 [m, 2H, -CH_2-S(O)] (J_{AB} = 16.1 Hz, ^4J = 2.8 Hz) 2.41 [t, 1H, HC≡C] (^4J = 2.8 Hz); 1.75 [sext, 2H, -CH_2] (^3J = 7.3 Hz) 0.98 [t, 3H, -CH_3] (^3J = 7.4 Hz)	75.5 [HC≡CH-] 48.3 [-CH_2-S(O)] 72.6 [HC≡CH-] 23.3 [-CH_2-CH_3] 70.4 [-O-CH_2] 10.2 [-CH_3]
2b	1135 (vs) ν (S=O) 3260 (s), 3300 (sh) ν (≡C-H) 2130 (s) ν (-C≡C-)	4.56 [sept, 1H, -O-CH<] (^3J = 6.2 Hz); 3.57/3.50 [m, 2H, -CH_2-S(O)] (J_{AB} = 16.0 Hz, ^4J = 2.8 Hz) 2.38 [t, 1H, HC≡C] (^4J = 2.8 Hz); 1.41 [d, 3H, -CH_3] (^3J = 6.2 Hz) 1.36 [d, 3H, -CH_3] (^3J = 6.2 Hz)	75.2 [HC≡CH-] 48.8 [-CH_2-S(O)] 74.9 [-O-CH<] 23.7, 23.0 [-CH_3] 72.8 [HC≡CH-]
3a	1130 (vs) ν (S=O)	5.95-5.89 [m, 1H, -HC=CH-CH_2-] ($^3J_{cis}$=10.7Hz) (Z) 5.87-5.75 [m, 1H, -HC=CH-CH_2-] ($^3J_{trans}$=15.3Hz) (E); 5.51-5.40 [m, 1H, -HC=CH-CH_2-] 4.02/3.96 [m, 2H, -O-CH_2-CH_2-] (J_{AB}=10.1 Hz; ^3J = 6.6 Hz) 3.55-3.51 [m, 2H, -CH_2-S(O)] (Z); 3.49-3.35 [m, 2H, -CH_2-S(O)] (E) 2.09-1.67 [m, 5H, -CH_2-CH_3 and CH_3-CH=CH-]; 0.97 [t, 3H, -CH_2-CH_3] (^3J = 7.4 Hz) E/Z-ratio (calcd. from integral): 5.3 : 1	134.7 (E), 132.4 (Z) [-HC=CH-CH_2] 117.5 (E), 116.3 (Z) [-HC=CH-CH_2] 70.1 (Z), 70.0 (E) [-O-CH_2-] 60.8 (E), 55.6 (Z) [-CH_2-S(O)] 23.2 [-CH_2-CH_3] 9.8 [-CH_2-CH_3] 18.0 (E), 13.2 (Z) [-CH_3]
3b	1120 (s) ν (S=O)	5.25-5.19 [m, 1H, >C=CH-CH_2-] 4.02/3.96 [m, 2H, -O-CH_2-CH_2-] (J_{AB}=10.0 Hz; ^3J = 6.6 Hz) 3.54-3.40 [m, 2H, -CH_2-S(O)] 1.81 [s, 3H, H_3C-C=]; 1.73 [s, 3H, H_3C-C=] 1.72 [sext, 2H, -CH_2-CH_3] (^3J = 7.0 Hz); 0.97 [t, 3H, -CH_2-CH_3] (^3J = 7.4 Hz)	141.1 [$(H_3C)_2$-C=C] 25.7 [$(H_3C)_2$-C=C] 110.6 [>C=CH-CH_2-] 23.3 [-CH_2-CH_3] 70.0 [-O-CH_2-] 13.2 [$(H_3C)_2$-C=C] 57.1 [-CH_2-S(O)] 10.0 [-CH_2-CH_3]
3c	1105 (vs), 1130 (vs), 1140 (sh) ν (S=O) 970 (m) δ (=C-H)[(C-H)-out-of-plane]	7.40-7.23 [m, 5H, Ph]; 6.65 [d, 1H, -HC=CH-CH_2-] ($^3J_{trans}$=15.9Hz) 6.20-6.09 [m, 1H, -HC=CH-CH_2-] ($^3J_{trans}$=15.9Hz, ^3J = 7.7 Hz) 4.49 [sept, 1H, -O-CH<] (^3J = 6.2 Hz); 3.67-3.54 [m, 2H, -CH_2-S(O)] 1.38 [d, 3H, -CH_3] (^3J = 6.2 Hz); 1.30 [d, 3H, -CH_3] (^3J = 6.2 Hz)	137.8, 128.5, 126.4, 136.1 [Ph] 128.0 [-HC=CH-CH_2] 61.8 [-CH_2-S(O)] 116.3 [-HC=CH-CH_2] 23.8, 23.1 [-CH_3] 74.3 [-O-CH<]
4a	1130 (vs), 1160 (sh) ν (S=O)	7.62 [d, 2H, p-F_3C-C_6H_4] (J_o = 8.1 Hz); 7.42 [d, 2H, p-F_3C-C_6H_4] (J_o = 8.1 Hz) 4.06/4.02 [m, 2H, -CH_2-S(O)] (J_{AB}=13 Hz); 4.02-3.86 [m, 2H, -O-CH_2-] (^3J = 6.6 Hz) 1.65 [sext, 2H, -CH_2-CH_3] (^3J = 7.1 Hz); 0.88 [t , 3H, -O-CH_2-CH_3] (^3J = 7.4 Hz)	130.9, 133.0 [p-F_3C-C_6H_4] 71.0 [-O-CH_2-] 130.5 [q, ^2J(C,F)=26.7 Hz] 63.6 [-CH_2-S(O)] 125.6 [q, ^3J(C,F)=3.7 Hz] 23.4 [-CH_2-CH_3] 124.0 [q, ^1J(C,F)=271.9 Hz] 10.1 [-CH_3]
4b	1120 (vs), 1140 (sh) ν (S=O)	7.29-7.19 [m, 2H, p-F-C_6H_4]; 7.08-6.97 [m, 2H, p-F-C_6H_4] 4.19-3.83 [m, 4H, -CH_2-S(O) and -O-CH_2-]; 1.62 [sext, 2H , -CH_2-CH_3] (^3J = 7.2 Hz) 0.87 [t, 3H, -O-CH_2-CH_3] (^3J = 7.4 Hz) q	162.8 [d, ^1J(C,F)=247.4 Hz] 71.1 [-O-CH_2-] 132.2 [d, ^3J(C,F)=7.6 Hz] 63.1 [-CH_2-S(O)] 124.6 [p-F-C_6H_4] 23.3 [-CH_2-CH_3] 115.7 [d, ^2J(C,F)=21.4 Hz] 10.1 [-CH_3]
4c	1120 (vs), 1140 (sh) ν (S=O)	7.18 [d, 2H, H_3C-O-C_6H_4] (J_o = 8.6 Hz); 6.84 [d, 2H, H_3C-O-C_6H_4] (J_o = 8.6 Hz) 3.98-3.80 [m, 4H, -CH_2-S(O) and -O-CH_2-]; 3.71 [s, 3H, H_3C-O-C_6H_4] 1.61 [sext, 2H, -CH_2-CH_3] (^3J = 7.0 Hz); 0.86 [t, 3H, -O-CH_2-CH_3] (^3J = 7.4 Hz)	159.6, 131.6, 121.0, 114.1 [H_3C-O-C_6H_4] 70.3 [-O-CH_2-] 55.0 [H_3C-O-] 63.4 [-CH_2-S(O)] 23.3 [-CH_2-CH_3] 10.1 [-CH_3]
4d	1130 (vs) ν (S=O)	7.61-7.58 [m, 2H, m-F_3C-C_6H_4]; 7.53-7.46 [m, 2H, m-F_3C-C_6H_4] 4.07/4.03 [m, 2H, -CH_2-S(O)] (J_{AB}=13.1Hz); 4.02-3.86 [m , 2H, -O-CH_2-] (^3J = 6.7 Hz) 1.65 [sext, 2H, -CH_2-CH_3] (^3J = 7.1 Hz); 0.86 [t, 3H, -O-CH_2-CH_3] (^3J = 7.4 Hz)	133.9 [m-F_3C-C_6H_4] 71.0 [-O-CH_2-] 131.0 [q, ^2J(C,F)=32.4 Hz] 63.6 [-CH_2-S(O)] 130.0, 129.2, 127.3, 125.0 [m-F_3C-C_6H_4] 123.9 [q, ^1J(C,F)=272.4 Hz] 23.3 [-CH_2-CH_3 10.0 [-CH_3]

TABLE III (*Continued*)

5	1130 (vs), 1150 (vs) ν (S=O)	4.14/4.09 [m, 2H, -CH_2-S(O)] (J_{AB}=13.3Hz); 4.07-3.93 [m, 2H, -O-CH_2-] 1.69 [sext, 2H, -CH_2-CH_3] (^3J = 7.2 Hz); 0.93 [t, 3H, -O-CH_2-CH_3] (^3J = 7.4 Hz)	147.2 (m), 143.9 (m), 142.7 (m), 139.2 (m) [C_6F_5-] 136.0 (m), 104.0 (m) [C_6F_5-]; 70.8 [-O-CH_2-] 50.3 [-CH_2-S(O)]; 23.2 [-CH_2-CH_3]; 9.8 [-CH_3]
6	1130 (vs), 1145 (sh) ν (S=O)	8.04-7.38 [m, 7H, naphthyl]; 4.48/4.41 [m, 2H, naphthyl-CH_2-S(O)] (J_{AB} = 13.3 Hz) 3.95/3.78 [m, 2H, -O-CH_2-CH_2-] (J_{AB}=10.0 Hz; ^3J = 6.9 Hz) 1.51 [sext, 2H, -CH_2-CH_3] (^3J = 7.3 Hz); 0.75 [t , 3H, -CH_2-CH_3] ^3J = 7.4 Hz)	133.6, 132.0, 129.4, 128.9, 128.6 [naphthyl] 126.4, 125.8, 125,4, 125,2, 123,4 [naphthyl] 70.7 [-O-CH_2-] 62.0 [-CH_2-S(O)] 23.2 [-CH_2-CH_3] 9.8 [-CH_3]
7a	1110 (s), 1150 (vs) ν (S=O) 1745 (vs) ν (C=O)	4.24 [q, 2H, -O-CH_2-CH_3] (^3J = 7.1 Hz); 4.09-4.01 [m, 2H, -O-CH_2-CH_2-] (^3J = 6.6 Hz) 3.75 [s, 2H, -C(O)-CH_2-S(O)]; 1.73 [sext, 2H, -CH_2-CH_2-] (^3J = 7.0 Hz) 1.31 [t, 3H, -O-CH_2-CH_3] ^3J = 7.1 Hz); 0.98 [t, 3H, -CH_2-CH_3] (^3J = 7.3 Hz)	164.1 [-C(O)-] 61.6 [-O-CH_2-CH_3] 70.1 [-O-CH_2-CH_2-] 23.1 [-CH_2-CH_3] 62.0 [-CH_2-S(O)]; 13.9 [-O-CH_2-CH_3]; 9.9 [-CH_3]
7b	1115 (s), 1150 (vs) ν (S=O) 1740 (vs) ν (C=O)	4.54 [sept, 1H, -O-CH<] (^3J = 6.2 Hz); 4.23 [q, 2H, -O-CH_2-CH_3] (^3J = 7.1 Hz) 3.72 [s, 2H, -C(O)-CH_2-S(O)]; 1.39 [d, 3H, -CH_3] (^3J = 6.2 Hz) 1.32 [d, 3H, -CH_3] (^3J = 6.2 Hz); 1.30 [t, 3H, -CH_2-CH_3] (^3J = 7.1 Hz)	164.2 [-C(O)-] 61.5 [-O-CH_2-CH_3] 74.7 [-O-CH<] 23.5, 22.8 [-CH_3] 62.4 [-CH_2-S(O)] 13.9 [-O-CH_2-CH_3]
8a	1110 (s), 1140 (vs) ν (S=O) 1635 (vs) ν (C=O)	4.08/4.01 [m, 2H, -O-CH_2-] (J_{AB} = 10.0 Hz, ^3J = 6.5 Hz) 3.89/3.83 [m, 2H, -C(O)-CH_2-S(O)] (J_{AB} = 14.0 Hz); 3.48-3.35 [m, 4H, N<(CH_2-CH_3)$_2$] 1.73 [sext, 2H, -O-CH_2-CH_2-] (^3J = 7.0 Hz); 1.23 [t, 3H, -N<(CH_2-CH_3)$_2$] (^3J = 7.2 Hz) 1.15 [t, 3H, -N<(CH_2-CH_3)$_2$] (^3J = 7.2 Hz); 0.96 [t, 3H, -CH_2-CH_3] (^3J = 7.4 Hz)	163.4 [-C(O)-] 23.5 [-CH_2-CH_2-CH_3] 71.2 [-O-CH_2-CH_2-] 14.5, 13.0 -N<(CH_2-CH_3)$_2$ 62.5 [-CH_2-S(O)] 10.2 [-CH_3] 42.8, 40.5 [-N<(CH_2-CH_3)$_2$]
8b	1105 (s), 1140 (vs) ν (S=O) 1640 (vs) ν (C=O)	4.34 [sept, 1H, -O-CH<] (^3J = 6.2 Hz); 3.70/3.62 [m, 2H, -C(O)-CH_2-S(O)] (J_{AB} = 13.9 Hz) 3.34-3.12 [m, 4H, N<(CH_2-CH_3)$_2$]; 1.21 [d, 3H, -CH_3] (^3J = 6.2 Hz) 1.13 [d, 3H, -CH_3] (^3J = 6.2 Hz); 1.05 [t, 3H, -N<(CH_2-CH_3)$_2$] (^3J = 7.2 Hz) 0.97 [t, 3H, -N<(CH_2-CH_3)$_2$] (^3J = 7.1 Hz)	163.0 [-C(O)-] 42.4, 40.1 [-N<(CH_2-CH_3)$_2$] 74.5 [-O-CH<] 23.4, 22.7 [<(CH_3)$_2$] 62.3 [-CH_2-S(O)] 14.1, 12.6 [-N<(CH_2-CH_3)$_2$]
9a	1130 (s), 1145 (vs) ν (S=O) 1725 (vs) ν (C=O) 980 (m) δ (=C-H)[(C-H)-out-of-plane]	6.94-6.83 [m (2t), 1H, =CH-CH_2-] ($^3J_{trans}$ = 15.6 Hz, ^3J = 7.9 Hz); 6.10 [d, 1H, -C(O)-CH=] ($^3J_{trans}$ = 15.6 Hz); 4.09-3.95 [m, 2H, -O-CH_2-] 3.75 [s, 3H, -O-CH_3]; 3.64 [dd, 2H, -C(O)-CH_2-S(O)] (^3J = 7.9 Hz, ^4J = 1.1 Hz) 1.73 [sext, 2H, -O-CH_2-CH_2-] (^3J = 7.1 Hz); 0.97 [t, 3H, -CH_2-CH_3] (^3J = 7.3 Hz)	165.1 [-C(O)-] 59.5 [-CH_2-S(O)] 134.2 [-C(O)-CH=] 51.2 [-O-CH_3] 127.6 [=CH-CH_2-] 23.0 [-CH_2-CH_2-CH_3] 70.2 [-O-CH_2-CH_2-] 9.7 [-CH_3]
9b	1125 (s), 1145 (vs) ν (S=O) 1725 (vs) ν (C=O) 980 (m) δ (=C-H)[(C-H)-out-of-plane]	6.81-6.70 [m (2t), 1H, =CH-CH_2-] ($^3J_{trans}$ = 15.7 Hz, ^3J = 7.9 Hz) 5.96 [d, 1H, -C(O)-CH=] ($^3J_{trans}$ = 15.7 Hz); 4.39 [sept, 1H, -O-CH<] (^3J = 6.2 Hz) 3.64 [s, 3H, -O-CH_3]; 3.48 [d, 2H, -C(O)-CH_2-S(O)] (^3J = 7.9 Hz) 1.27 [d, 3H, -CH_3] (^3J = 6.2 Hz); 1.20 [d, 3H, -CH_3] (^3J = 6.2 Hz)	165.4 [-C(O)-] 60.1 [-CH_2-S(O)] 134.5 [-C(O)-CH=] 51.5 -O-CH_3] 127.8 [=CH-CH_2-] 23.6, 22.9 [-CH_3] 74.5 [-O-CH<]
10a	1155 (vs) ν (S=O) 1820 (vs) ν (C=O)	7.95-7.87 [m, 2H, Ph]; 7.82-7.75 [m, 2H, Ph]; 4.75/4.66 [m, 2H, N-CH_2-S(O)] (J_{AB} = 13.0 Hz) 4.07 [m, 2H, -O-CH_2-]; 1.71 [sext, 2H, -CH_2-CH_3] (^3J = 7.2 Hz) 0.93 [t, 3H, -CH_3] (^3J = 7.4 Hz)	166.7 [-C(O)-] 58.5 [-CH_2-S(O)] 134.5, 131.5, 123.8 [Ph] 23.3 [-CH_2-CH_3] 70.3 [-O-CH_2-] 10.0 [-CH_3]
10b	1155 (vs) ν (S=O) 1825 (vs) ν (C=O)	7.95-7.89 [m, 2H, Ph]; 7.81-7.75 [m, 2H, Ph]; 4.70/4.68 [m , 2H, N-CH_2-S(O)] (J_{AB} = 12.9 Hz) 4.54 [sept, 1H, -O-CH<] (^3J = 6.2 Hz); 1.39 [d, 3H, -CH_3] (^3J = 6.2 Hz) 1.27 [d, 3H, -CH_3] (^3J = 6.2 Hz)	166.8 [-C(O)-] 59.4 [-CH_2-S(O)] 134.5, 131.6, 123.9 [Ph] 23.8, 23.2 [-CH_3] 75.6 [-O-CH<]

[a] solvent: $CDCl_3$; TMS as internal standard

General Procedure: 30 mmol $(RO)_2S$ (10% excess in case of **10a, b**) and 30 mmol of the bromide are dissolved in 15 ml nitromethane and stirred at 65–70°C for 8–10 hours. The reaction with $p\text{-}MeOC_6H_4CH_2Br$ must be carried out at 35°C for 22 hours to avoid side reactions of the benzyl bromide. The reaction mixtures are then allowed to cool down to room temperature and the solvent is removed in vacuum. In case of **4a, 10a** and **10b** the formed sulfinates precipitate after addition of n-pentane and can be filtered off. The crystalline products are washed with cold n-pentane, **4a** is purified by recrystallization from ethanol. All other sulfinic esters can be obtained after fractionated vacuum distillation and represent pale yellow or red (**9a–b**) liquids or oils with unpleasant onion like odours.

Starting Materials: Dialkyl sulfoxylates RO–S–OR (R = ^{n}Pr, ^{i}Pr) (**1**) were prepared according to Thompson by alcoholysis of sulfur dichloride in CH_2Cl_2 at −78°C using triethylamine as HCl acceptor.[10]

All alkyl bromides with exception of $p\text{-}MeOC_6H_4CH_2Br$ and $Et_2N\text{-}C(O)\text{-}CH_2Br$ are commercially available. p-Methoxybenzylbromide was prepared by refluxing p-methylanisol and N-bromosuccinimide in dry CCl_4 and AIBN as radical starter according to Reference 11; N,N-diethyl-α-bromoacetamide was obtained from bromoacetyl bromide and diethylamine in 1,2-dichloroethane.[12]

All analytical and spectroscopic data for **2–10** are summarized in Tables II and III.

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