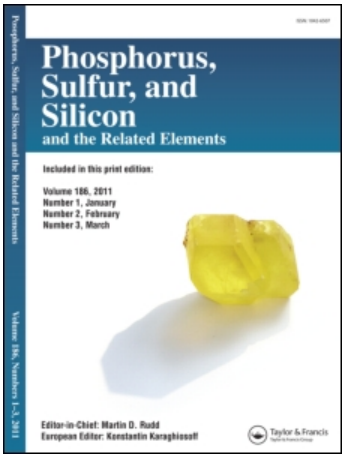

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THE THIO-ARBUZOV-REACTION. PART 9.[1] SYNTHESIS OF DISULFINATES AND DISULFOXIDES BY "DOUBLE" THIO-ARBUZOV-REACTIONS OF ALKOXYSULFANES WITH ω-ω'-BIS(BROMOMETHYL)-ARENES AND -ALKENES

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THE THIO-ARBUZOV-REACTION. PART 9.[1] SYNTHESIS OF DISULFINATES AND DISULFOXIDES BY "DOUBLE" THIO-ARBUZOV-REACTIONS OF ALKOXYSULFANES WITH ω,ω'-BIS(BROMOMETHYL)-ARENES AND -ALKENES

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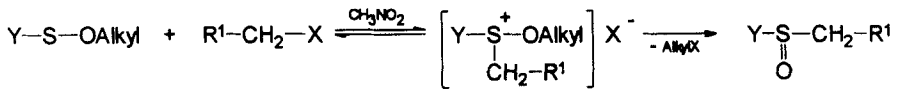
Thio-ARBUZOV-Reactions of dialkyl sulfoxylates and methyl benzenesulfenate, respectively, with several aromatic and aliphatic ω,ω'-bis(bromomethyl)arenes and -alkenes result in formation of new disulfinyl derivatives, i.e. disulfinates and disulfoxides. Eight new sulfinic esters and three new sulfoxides have been synthesized and characterized by their physical and spectroscopic data.

Key words: Thio-ARBUZOV-Reaction, dialkyl sulfoxylates, methyl benzenesulfenate, dielectrophiles, disulfinates, disulfoxides, ^{1}H- and ^{13}C-NMR data.

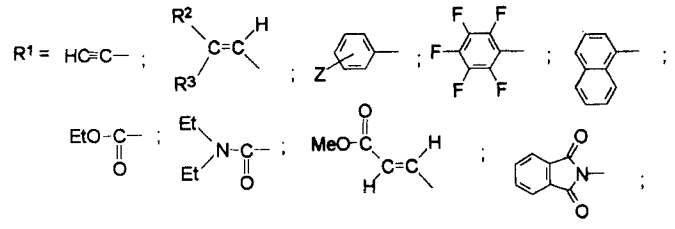
INTRODUCTION

Recently we have reported on the conversions of λ^2-alkoxysulfanes Y—S—OAlkyl into λ^4-sulfinyl derivatives which yielded a variety of unknown α-functionalized methanesulfinates.[1] These reactions, which start by an electrophilic attack of organic halides at the sulfur atom were named Thio-ARBUZOV-Reactions because of some similarities with the MICHAELIS-ARBUZOV-Reaction at λ^3-alkoxyphosphanes. It could be shown, that these transformations proceed via tricoordinated quasi sulfonium intermediates. These intermediate sulfur species are dealkylated in a second step accompanied by S=O bond formation. Thio-ARBUZOV-Reactions have been found to be facilitated by strong acceptor solvents like nitromethane[2,3]; Equation (1).



(1)

Y = OAlkyl, Ph, >N X = Cl, Br, I



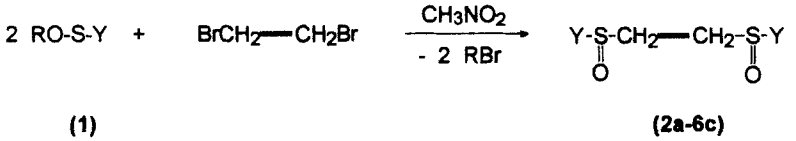
Thus the Thio-ARBUZOV-Reaction represents a facile synthetic route to sulfinic esters,[1,2] unsymmetric phenylsulfoxides[4] and sulfinamides[3,5] starting from dialkyl sulfoxylates, methyl benzenesulfenate and aminosulfenates, respectively. General demands on the structure of the electrophile are summarized in Reference 1, further details are given in Reference 6.

In this paper we report about Thio-ARBUZOV-Reactions of dialkyl sulfoxylates and methyl benzenesulfenate with ω,ω'-bis(bromomethyl)-arene and -alkene compounds which represent ω,ω'-dielectrophiles. These interactions lead to disubstitution of the halogen atoms by λ^4-sulfinyl units, see Equation (2). We could produce eleven new sulfinyl disubstituted species by use of the following halogen components:

—1,2-, 1,3- and 1,4-bis(bromomethyl)benzene
—2,2′-bis(bromomethyl)biphenyl
—1,4-dibromobut-2-ene

RESULTS AND DISCUSSION

The "double" Thio-ARBUZOV-Reactions proceed according to the given general Equation (2), the prepared new disulfinates and disulfoxides (**2–6**) are collected in Table I.



(2)

(1) **(2a-6c)**

Y = OR, Ph R = ^{n}Pr, ^{i}Pr, Me

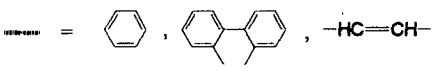
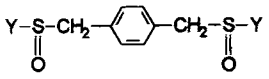
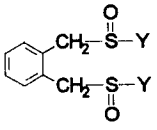
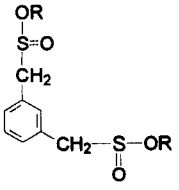
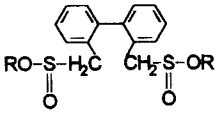
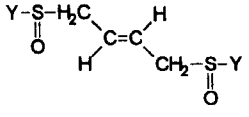


TABLE I

Disulfinates and disulfoxides **2–6**

structure	Y =	yield	compd.
	O^nPr	88 %	**2a**
	O^iPr	85 %	**2b**
	Ph	95 %	**2c**
	O^nPr	72 %	**3a**
	O^iPr	82 %	**3b**
	Ph	82 %	**3c**
	O^nPr	93 %	**4**
	O^nPr	57 %	**5**
	O^nPr	28 %	**6a**
	O^iPr	35 %	**6b**
	Ph	57 %	**6c**

Bis(alkoxysulfinylmethyl)benzenes (**2a,b**; **3a,b**; **4**)

Reactions of 1,2-, 1,3 and 1,4-bis(bromomethyl)benzenes with dialkyl sulfoxylates in CH_3NO_2 give disulfinic esters in excellent yields which represent either white, crystalline solids (**2a,b**) or yellowish oily liquids (**3a,b**; **4**) which are stable for several months without decomposition when kept refrigerated. The two chiral sulfur centres and hindered rotation in **3a,b** and **4** result in a doubling of the signals of the diastereotopic S-methylene protons (AB spin system) and also of the protons of the Oalkyl groups which represent $ABXYZ_3$ spin systems.

Bis(phenylsulfinylmethyl)benzenes (**2c**, **3c**)

White crystals of the corresponding disulfoxides are produced by Thio-ARBUZOV-Reactions of methyl benzenesulfenate with 1,2- and 1,4-bis(bromomethyl)benzenes.

Once again this procedure has proved to be a comparatively simple route to sulfoxides (see Reference 4).

2,2'-Bis(n-propoxysulfinylmethyl)biphenyl (**5**)

Starting from 2,2'-bis(bromomethyl)biphenyl we could obtain a viscous pale yellow oil by bulb to bulb distillation which represents the desired disulfinate **5** in 57% yield.

1,4-Bis(alkoxysulfinyl)but-2-ene (**6a,b**)

The first "double" Thio-ARBUZOV-Reaction carried out starting from an aliphatic dielectrophile was the synthesis of 1,4-bis(sulfinylmethyl)but-2-ene by interaction of 1,4-dibromobut-2-ene with dialkyl sulfoxylates. The resulting sulfinates were separated by bulb to bulb distillation.

According to infrared [γ(C—H)-"out of plane" at 980 cm^{-1}] and nmr spectroscopic data both compounds show E-configuration.

1,4-Bis(phenylsulfinyl)but-2-ene (**6c**)

The reaction of methyl benzenesulfenate with 1,4-dibromobut-2-ene lead to **6c** in 57% yield. The isolated disulfoxide contains both the E and Z isomer in an 2:1 ratio which was estimated from the integrals in the ^1H nmr spectrum.

TABLE II

Analytical data of **2–6**

compd.	m.p.[°C]/ b.p.[°C]	molecular formula	M[g/mol]	n_{20}	analysis (calcd.) found [%] C	H	S
2a	75-77	$C_{14}H_{22}O_4S_2$	318.44	-	(52.80) 52.60	(6.96) 7.16	(20.14) 20.76
2b	75	$C_{14}H_{22}O_4S_2$	318.44	-	(52.80) 51.62	(6.96) 6.88	(20.14) 20.70
2c	231-232	$C_{20}H_{18}O_2S_2$	354.48	-	(67.77) 68.15	(5.12) 5.15	(18.09) 17.73
3a	225 (0,007 mbar)	$C_{14}H_{22}O_4S_2$	318.44	1.5451	(52.80) 52.88	(6.96) 7.03	(20.14) 20.15
3b	180 (0,006 mbar)	$C_{14}H_{22}O_4S_2$	318.44	1.5385	(52.80) 52.44	(6.96) 7.13	(20.14) 20.14
3c	119-120	$C_{20}H_{18}O_2S_2$	354.48	-	(67.77) 66.98	(5.12) 4.94	(18.09) 17.88
4	230 (0.006 mbar)	$C_{14}H_{22}O_4S_2$	318.44	1.5434	(52.80) 51.54	(6.96) 6.98	(20.14) 19.64
5	195 (0.006 mbar)	$C_{20}H_{26}O_4S_2$	394.54	-	(60.89) 58.64	(6.64) 6.05	(16.25) 15.81
6a	140-150 (0.007 mbar)	$C_{10}H_{20}O_4S_2$	268.39	1.5045	(44.75) 43.91	(7.51) 7.57	(23.89) 23.67
6b	47-48	$C_{10}H_{20}O_4S_2$	268.39	-	(44.75) 44.93	(7.51) 7.28	(23.89) 23.66
6c	97-98	$C_{16}H_{16}O_2S_2$	304.42	-	(63.13) 62.83	(5.30) 5.18	(21.06) 20.76

TABLE III

Spectroscopic data

com-pound	IR [cm^{-1}]	^{1}H-NMR[a] δ [ppm]	^{13}C-NMR[a] δ [ppm]	
2a	1125 (vs), 1150 (s) ν (S=O)	7.31 [s, 4H, C_6H_4]; 4.04/3.97 [m, 4H, $-CH_2$-S(O)] (J_{AB} = 13.0 Hz)	130.9 [C-H (Ph)]	64.0 [$-CH_2$-S(O)]
		3.95-3.85 [m, 4H, -O-CH_2] (ABXYZ$_3$-system); 1.65 [sext, 4H, $-CH_2$] (^{3}J = 7.1 Hz)	129.1 [C_q (Ph)]	23.4 [$-CH_2$-CH_3]
		0.89 [t, 6H, $-CH_3$] (^{3}J = 7.4 Hz)	70.6 [-O-CH_2]	10.1 [$-CH_3$]
2b	1120 (vs), 1145 (s) ν (S=O)	7.30 [s, 4H, C_6H_4]; 4.39 [sept, 2H, -O-CH<] (^{3}J = 6.2 Hz)	130.8 [C-H (Ph)	64.3 [$-CH_2$-S(O)]
		4.00/3.96 [m, 4H, $-CH_2$-S(O)] (J_{AB} = 13.0 Hz); 1.34 [d, 6H, $-CH_3$] (^{3}J = 6.2 Hz)	129.2 [C_q (Ph)]	23.7, 22.9 [$-CH_3$]
		1.13 [d, 6H, $-CH_3$] (^{3}J = 6.2 Hz)	74.6 [-O-CH<]	
2c	1020 (m), 1040 (s) ν (S=O)	7.51-7.36 [m, 10H, Ph]; 6.87 [s, 4H, C_6H_4]	142.6, 131.3, 128.9, 124.3 [Ph]	
		4.06-3.96 [m, 4H, $-CH_2$-S(O)]	130.4 [C-H (Ph)]	63.0 [$-CH_2$-S(O)]
			129.2 [C_q (Ph)]	
3a	1105 (sh), 1130 (s) ν (S=O)	7.29 [s, 4H, C_6H_4]; 4.24-4.12 [m, 4H, $-CH_2$-S(O)] (2 AB-systems)	132.2, 128.4 [C-H (Ph)]	61.14, 61.08 [$-CH_2$-S(O)]
		4.00-3.80 [m, 4H, -O-CH_2] (2 ABXYZ$_3$-systems); 1.65 [2 sext, 4H, $-CH_2$]	128.9 [C_q (Ph)]	23.2 [$-CH_2$-CH_3]
		0.82 [2 t, 6H, $-CH_3$] (^{3}J = 7.4 Hz)	70.8 [-O-CH_2]	8.9 [$-CH_3$]
3b	1105 (m), 1130 (vs) ν (S=O)	7.32 [s, 4H, C_6H_4]; 4.42-4.34 [m, 2H, -O-CH<]	132.0, 128.2 [C-H (Ph)	61.37, 61.27 [$-CH_2$-S(O)]
		4.27-4.14 [m, 4H, $-CH_2$-S(O)] (2 AB-systems); 1.32 [2 d, 6H, $-CH_3$] (^{3}J = 6.2 Hz)	128.9 [C_q (Ph)]	23.4, 22.6 [$-CH_3$]
		1.11 [2 d, 6H, $-CH_3$] (^{3}J = 6.2 Hz)	74.5 [-O-CH<]	
3c	1025 (m), 1040 (s) ν (S=O)	7.50-7.35 [m, 10H, Ph]; 7.19-7.13 [m, 2H, C_6H_4]	142.7, 131.3, 129.0, 124.2 [Ph]	
		6.90-6.85 [m, 2H, C_6H_4]; 4.10-3.93 [m, 4H, $-CH_2$-S(O)]	132.0, 128.4 [C-H (Ph)]	60.4 [$-CH_2$-S(O)]
			129.7 [C_q (Ph)]	
4	1105 (sh), 1130 (vs) ν (S=O)	7.24-7.13 [m, 4H, C_6H_4]; 3.97-3.86 [m, 4H, $-CH_2$-S(O)] (AB-system)	132.4, 130.3, 129.6, 129.1 [C-H (Ph)]	
		3.84-3.76 [m, 4H, -O-CH_2]; 1.55 [sext, 4H, $-CH_2$] (^{3}J = 7.2 Hz)	128.8 [C_q (Ph)]	23.3 [$-CH_2$-CH_3]
		0.79 [t, 6H, $-CH_3$] (^{3}J = 7.3 Hz)	70.6 [-O-CH_2]	10.1 [$-CH_3$]
			63.95, 63.90 [$-CH_2$-S(O)]	
5	1115 (sh), 1140 (vs) ν (S=O)	7.56-7.21 [m, 8H, biphenyl]; 3.97-3.67 [m, 8H, $-CH_2$-S(O) and -O-CH_2]	141.2, 139.8, 131.6, 130.7, 130.4, 129.4 [biphenyl]	
		1.67-1.53 [m, 4H, $-CH_2$]; 0.86-0.80 [m, 6H, $-CH_3$]	128.9, 128.3, 128.1, 128.0, 127.6, 127.5 [biphenyl]	
			70.8, 70.4 [-O-CH_2]	23.2 [$-CH_2$-CH_3]
			62.1, 61.9 [$-CH_2$-S(O)]	10.0 [$-CH_3$]
6a	1130 (s) ν (S=O)	5.73-5.71 [m, 2H, -CH=]; 3.98-3.84 [m, 4H, -O-CH_2-]	125.7 [-CH=]	23.2 [$-CH_2$-CH_3]
	980 (vs) δ [(C-H)-out of plane]	3.50-3.39 [m, 4H, $-CH_2$-S(O)]; 1.64 [sext, 4H, $-CH_2$-CH_3] (^{3}J = 7.1 Hz)	70.4 [-O-CH_2-]	10.0 [$-CH_3$]
		0.88 [t, 6H, $-CH_3$] (^{3}J = 7.4 Hz)	60.5 [$-CH_2$-S(O)]	
6b	1115 (s), 1130 (sh), 1140 (sh) ν (S=O)	5.80-5.74 [m, 2H, -CH=]; 4.49 [sept, 2H, -O-CH<] (^{3}J = 6.2 Hz)	126.0 [-CH=]	23.8 [$-CH_3$]
	980 (vs) δ [(C-H)-out of plane]	3.55-3.41 [m, 4H, $-CH_2$-S(O)]; 1.38 [d, 6H, $-CH_3$] (^{3}J = 6.2 Hz)	74.3 [-O-CH<]	23.1 [$-CH_3$]
		1.32 [d, 6H, $-CH_3$] (^{3}J = 6.2 Hz)	61.0 [$-CH_2$-S(O)]	
6c	1020 (w), 1040 (vs) ν (S=O)	7.64-7.45 [m, 10H, Ph]	142.6, 131.2, 129.1, 124.2 [Ph]	
	970 (m) δ [(C-H)-out of plane]	5.48-5.44 [m, 2H, -CH=]; 5.42-5.34 [m, 2H, -CH=] (integral ratio 1:2)	126.4, 126.3 [-CH=]	
		3.56-3.37 [m, 4H, $-CH_2$-S(O)]	59.83, 59.66 [$-CH_2$-S(O)]	

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

EXPERIMENTAL

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

General Procedure

30 mmol alkoxysulfane RO—S—Y (12.5% excess) and 13.33 mmol of the "dibromide" are dissolved in 20 mL of nitromethane (45 mL in case of **2c** to avoid coprecipitation of the starting dibromide with the product) and stirred at 60–65°C for 10–12 hours. The reaction mixtures are then allowed to cool down to room temperature and the solvent is removed in vacuo. In cases of **2a–c**, **3c** and **6b,c** the formed sulfinates precipitate after addition of *n*-hexane and can be filtered off. The crystalline products are washed with cold *n*-hexane, **2c** and **3c** are purified by recrystallization from ethanol.

All other disulfinic esters can be obtained by fractionate bulb to bulb distillation in a very good vacuum and represent pale yellow oily liquids.

Starting materials: Dialkyl sulfoxylates RO—S—OR (R = ^{n}Pr, ^{i}Pr) were prepared according to THOMPSON by alcoholysis of sulfur dichloride in CH_2Cl_2 at −78°C using triethylamine as HCl acceptor.[7]

Methyl benzenesulfenate was produced by methanolysis of benzene sulfenylchloride in CCl_4 with triethylamine as HCl acceptor.[8] Chlorination of thiophenol in CCl_4 lead to the benzene sulfenylchloride.[9]

All dibromides are commercially available. 1,2-bis(bromomethyl)benzene (ALDRICH) was twice recrystallized prior to use to remove traces of HBr which would have caused decomposition of the alkoxysulfanes.

All analytical and spectroscopic data for **2–6** are summarized in Tables II and III.

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