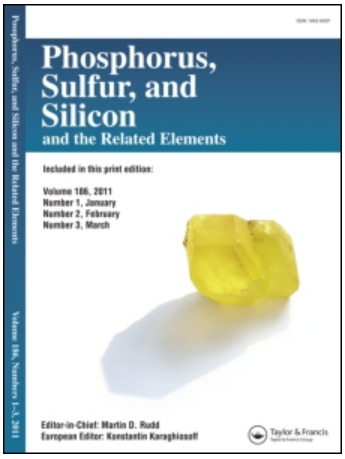

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THE THIO-ARBUZOV-REACTION. PART 7. UNSYMMETRIC SULFOXIDES PhS(O)CH_2R FROM METHYL BENZENESULFENATE AND BROMOALKANES RCH_2Br

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THE THIO-ARBUZOV-REACTION. PART 7.[1] UNSYMMETRIC SULFOXIDES $PhS(O)CH_2R$ FROM METHYL BENZENESULFENATE AND BROMOALKANES RCH_2Br

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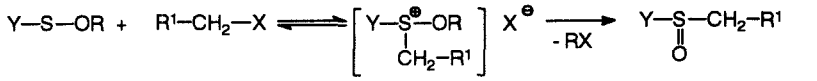
Alkylation reactions of methyl benzenesulfenate with bromoalkanes were studied and found to follow the Thio-ARBUZOV pathway.[1] The reaction concept was extended to the conversion of sulfenates into unsymmetric sulfoxides. Thus four new unsymmetric sulfoxides could be obtained and the synthesis of others already mentioned in the literature was improved.

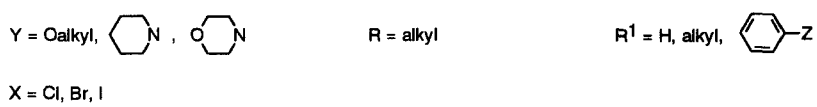
Key words: Thio-ARBUZOV-Reaction; methyl benzenesulfenate; bromoalkanes; unsymmetric sulfoxides; nitromethane; ^{19}F-NMR data.

INTRODUCTION

Divalent sulfur compounds of the general formula Y-S-Oalkyl can be alkylated by alkyl halides. The quasi-sulfonium intermediate formed in the first step contains a tri-coordinated sulfur atom which stabilizes by dealkylation and S=O bond formation[2]; Equation (1).



(1)



Because of the similarities with the well known MICHAELIS-ARBUZOV-Reaction in phosphorus chemistry this transformation of divalent sulfur species into tri-coordinated sulfinyl derivatives was named Thio-ARBUZOV-Reaction. This reaction represents a new synthetic route to sulfinic esters and sulfinamides starting from dialkyl sulfoxylates and aminosulfenates, respectively. Acceptor solvents like nitromethane or acetonitrile were shown to promote the reaction because of their influence on the polarity of the carbon-halogen bond. As the electrophilicity of the carbon atom is enhanced the attack at the sulfur lone pair is facilitated.[1]

Variation of R^1 is another opportunity to influence the electrophilic properties

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of the halogen bonded carbon atom. For that reason the reaction behaviour of a large number of alkyl halides R^1-CH_2-X towards dialkyl sulfoxylates was investigated.

Recently another type of sulfur compounds was involved into investigation of alkylation reactions. Using methyl benzenesulfenate we changed the nucleophilic

TABLE I

Substituted phenyl benzylsulfoxides $PhS(O)CH_2R^1$ **3–11**

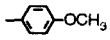
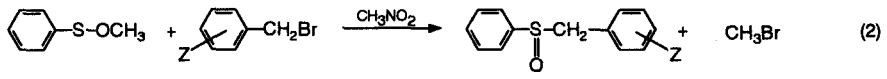
R^1	yield	compound	R^1	yield	compound
	79 %	**3**		55 %	**8**
	74 %	**4***		65 %	**9***
	65 %	**5**		46 %	**10***
	57 %	**6**		46 %	**11***
	69 %	**7**	* = new compound		

TABLE II

Analytical data of **3–11**

compound	m.p.[°C]	molecular formula	M[g/mol]	analysis (calcd.) found [%] C	H	N	S
3	123-124 (ref.[10] 125.5)	$C_{13}H_{12}OS$	216.30	(72.19) 72.24	(5.59) 5.75	- -	(14.82) 14.51
4*	144	$C_{13}H_{11}FOS$	234.29	(66.65) 66.73	(4.73) 4.83	- -	(13.68) 13.36
5	141 (subl.)	$C_{14}H_{11}F_3OS$	284.30	(59.15) 60.23	(3.90) 3.77	- -	(11.28) 11.40
6	158 (ref.[6] 161)	$C_{13}H_{11}NO_3S$	261.30	(59.76) 59.91	(4.24) 4.18	(5.36) 5.44	(12.27) 12.36
7	163-164 (ref.[8] 73-76)	$C_{14}H_{11}NOS$	241.31	(69.68) 70.09	(4.59) 4.58	(5.80) 5.86	(13.29) 13.66
8	131-132 (ref.[7] 129-130)	$C_{14}H_{14}O_2S$	246.32	(68.27) 68.40	(5.73) 5.90	- -	(13.02) 12.75
9*	85-86	$C_{14}H_{11}F_3OS$	284.30	(59.15) 58.90	(3.90) 4.04	- -	(11.28) 11.64
10*	89-90	$C_{13}H_{11}NO_3S$	261.30	(59.76) 60.17	(4.24) 4.35	(5.36) 5.30	(12.27) 12.10
11*	139-140	$C_{13}H_7F_5OS$	306.25	(50.99) 51.37	(2.30) 2.33	- -	(10.47) 10.39

properties of the sulfur atom and could obtain unsymmetric sulfoxides; Equation (2).



(2) (3-11)

Z = F, NO_2, CF_3, CH_3O, CN, H

RESULTS AND DISCUSSION

Methyl benzenesulfenate (**2**) was prepared by methanolysis of benzene sulfenylchloride in CCl_4 using triethylamine as HCl acceptor.[3] Chlorination of thiophenol in CCl_4 lead to benzene sulfenylchloride[4] (**1**).

The Thio-ARBUZOV-Reactions of methyl benzenesulfenate with various substitutet benzyl bromides proceed according Equation (2), the compounds obtained are collected in Table I. Four of the synthesized unsymmetric sulfoxides (marked with *) are not described in the literature yet, **5** was found to be one product of

TABLE III

Spectroscopic data of **4, 5, 9–11**

com-pound	IR [cm^{-1}] S=O	^{19}F-NMR[a] [ppm]	^{1}H-NMR[b] [ppm]	^{13}C-NMR[b] [ppm]
4*	1035	-114.1 - -113.5 [tt, ^{3}J(H,F)=14.2Hz ^{4}J(H,F)=6.8 Hz]	7.46-7.32 [m, 5H, Ph] 6.92-6.90 [m, 4H] 3.996/3.967 [2H, J_{AB}=12.8 Hz]	142.37, 131.18, 128.86, 124.30 [Ph] 162.70 [d, ^{1}J(C,F)=247.6 Hz] 131.98 [d, ^{3}J(C,F)=8.3 Hz] 124.75, 115.31 [d, ^{2}J(C,F)=21.8 Hz] 62.14 [-CH_2-] [c]
5	1035	-63.3 [s]	7.50-7.34 [m, 7H] 7.07 [d, 2H, J=8.1 Hz] 4.099/4.011 [2H, J_{AB}=12.7 Hz]	142.22, 131.39, 129.00, 124.22 [Ph] 133.00, 130.65, 130.50 [q, ^{2}J(C,F)=26.7 Hz] 125.20 [q, ^{3}J(C,F)=3.6 Hz] 123.93 [q, ^{1}J(C,F)=272.1 Hz] 62.45 [-CH_2-] [c]
9*	1035	-63.4 [s]	7.54-7.22 [m, 8H] 7.00 [s, 1H] 4.098/4.001 [2H, J_{AB}=12.8 Hz]	141.95, 131.41, 128.96, 124.20 [Ph] 133.82, 130.61 [q, ^{2}J(C,F)=32.3 Hz] 128.74, 126.95 [q, ^{3}J(C,F)=3.5 Hz] 124.92 [q, ^{3}J(C,F)=3.5 Hz] 123.70 [q, ^{1}J(C,F)=272.5 Hz] 62.33 [-CH_2-] [c]
10*	1040	-----	8.16-8.13 [m, 1H] 7.71-7.69 [m, 1H] 7.49-7.43 [m, 7H] 4.212/4.001 [2H, J_{AB}=12.9Hz]	141.70, 131.52, 129.04, 124.07 [Ph] 147.83, 136.43, 130.75, 129.08, 125.08, 123.03, 61.57 [-CH_2-] [c]
11*	1040	-140.8 - -140.2 [m, 2F] -153.3 - -152.7 [tt, 1F, ^{3}J(F,F)=21.4 Hz] -162.3 - -161.6 [m, 2F]	7.56-7.49 [m, 5H, Ph] 4.193/4.093 [2H, J_{AB}=13.0 Hz]	142.25, 131.70, 129.14, 124.16 [Ph] 50.26 [-CH_2-] [d]

a $CFCl_3$ as internal standard (solvent $CDCl_3$)
b TMS as internal standard
c solvent: $CDCl_3$
d solvent: DMSO-d_6

the hepatic microsomal metabolism of *p*-trifluoromethyl benzyl phenyl sulfide and **8** was isolated as one of the products obtained by electrochemical oxidation of *p*-methoxy benzyl phenyl sulfide in AcOH/$LiNO_3$ with only 12% yield. Thus the Thio-ARBUZOV-Reaction represents a new and easy way to racemic unsymmetric sulfoxides that can be obtained in good yields.

EXPERIMENTAL

All Thio-ARBUZOV-Reactions were carried out in dry nitromethane under anaerobic conditions. *General Procedure.* 15 mmol PhSOMe and 15 mmol of the benzyl bromide are dissolved in 12 ml nitromethane and stirred at 75°C for 8–10 hours. The reaction of methyl benzenesulfenate with *p*-$MeOC_6H_4CH_2Br$ was carried out at 35°C for 22 hours to avoid side reactions of the benzyl bromide. The reaction mixture is then allowed to cool to room temperature. In case of **3–8** the formed sulfoxides precipitate and can be filtered off; to complete isolation the solvent is removed and ether is added. **9**, **10** and **11** can be obtained after evaporation of the nitromethane and addition of dry hexane. The crystalline products are washed with cold ether or hexane and purified by recrystalization from ethanol.

Starting materials. All benzyl bromides with the exception of *p*-$MeOC_6H_4CH_2Br$ are commercially available. *p*-Methoxybenzylbromide was prepared by refluxing *p*-methylanisol and *N*-bromosuccinimide in dry CCl_4 with AIBN as radical starter according to Reference 5.

All sulfoxides were characterized by means of IR and NMR-spectroscopy. Analytical data for the new compounds **4**, **9–11** and of compound **5** are summarized in Tables II and III.

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