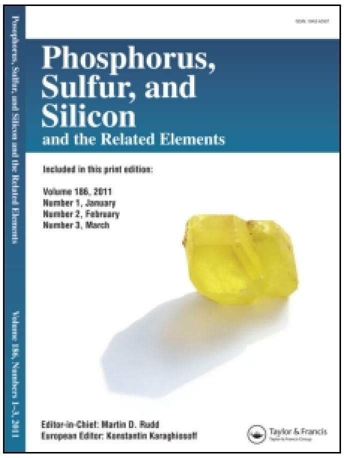

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SULFUR TRIOXIDE SULFONATION OF DIPHENYL ETHER, DIPHENYL SULFIDE, DIBENZO[*B, E*][1, 4]DIOXIN, AND XANTHENE

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Communication

SULFUR TRIOXIDE SULFONATION OF DIPHENYL ETHER, DIPHENYL SULFIDE, DIBENZO[*b*,*e*][1,4]DIOXIN, AND XANTHENE[1,2]

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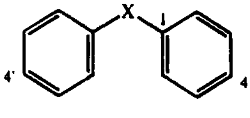
The sulfur trioxide sulfonation of diphenyl ether (**1**), diphenyl sulfide (**2**), and the related tricyclic dibenzo-[*b*,*e*][1,4]dioxin (**3**) and xanthene (**4**) has been studied. The substrates **1** and **2** both yield initially the 4-sulfonic acid derivative (4-S) and subsequently the 4,4′-S_2. In a large excess of 104.5 wt-% H_2SO_4 the further sulfonation of **1**-4,4′-S_2 gave the **1**-2,4,4′-S_3 and subsequently some **1**-2,4,2′,4′-S_4. Sulfonation of the dibenzodioxin **3** with 4.0 mol-equiv. of SO_3 gave the 2-S derivative, whereas with 12.0 mol-equiv. of SO_3 a mixture of the 2,7-S_2 and 2,8-S_2 was obtained in yields of 57 and 43%, respectively. Sulfonation of xanthene (**4**) with 4.0 mol-equiv. of SO_3 yielded the 2,7-S_2 derivative.

Key words: Sulfur trioxide sulfonation, diphenyl ether, diphenyl sulfide, dibenzo[*b*,*e*][1,4]dioxin, xanthene.

INTRODUCTION

As an extension of our studies on the sulfonation of alkoxy, di(alkyloxy), methylenedioxy, ethylenedioxy, and alkyleneoxy derivatives of benzene[4] and naphthalene,[5] we now report on the sulfonation of diphenyl ether (**1**), diphenyl sulfide (**2**), dibenzo[*b*,*e*][1,4]dioxin (**3**), and xanthene (**4**) mainly with sulfur trioxide as reagent.



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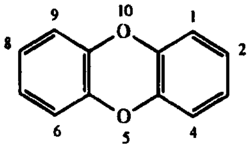
2 X = S



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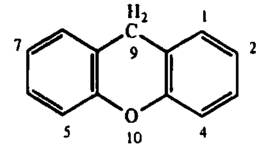

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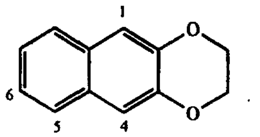

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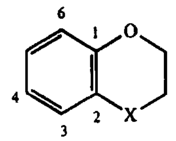


6 X = O
7 X = CH_2

The sulfonation of diphenyl ether (**1**) was studied extensively by Suter.[6] On using a mixture of 96 wt-% sulfuric acid and acetic anhydride as reagent at 100°C he isolated the 4-sulfonic acid derivative (4-S) in 93% yield, whereas with an excess of chlorosulfuric acid the 4,4′-disulfonyl chloride was obtained in a yield of 88%.[6] The reaction with 1.0 mol-equiv. of chlorosulfuric acid does not lead to selective monosulfonation of diphenyl ether.[7] The selective monosulfonation of diphenyl sulfide was effected using 0.8 mol-equiv. of SO_3 in liquid SO_2 at −50°C.[8]

RESULTS AND DISCUSSION

The sulfonation of diphenyl ether (**1**) and diphenyl sulfide (**2**) with SO_3 has been studied in nitromethane and dichloromethane as solvent, respectively. The results are given in Table I. The initial sulfonation occurs at the 4-position and the subsequent one at the 4′-position, yielding the 4,4′-S_2. The reactivity is smaller for the *ortho* than the *para* positions, mainly for electronic reasons, as was established from protodetritiation studies.[9]

Sulfonation of diphenyl ether (**1**) with a large excess of concentrated aqueous sulfuric acid—which served both as reagent and solvent—gave a mixture of the 4-S, 4,4′-S_2 and 2,4,4′-S_3 derivatives (see Table II). Upon using concentrated fuming sulfuric acid (104.5 wt-% H_2SO_4) eventually also some **1**-2,4,2′,4′-S_4 was formed.

Sulfonation of dibenzo[*b*,*e*][1,4]dioxin (**3**) with 4.0 mol-equiv. of SO_3 in dichloromethane-d_2 as solvent, using in total 5.0 mol-equiv. of dioxane-d_8 as a reactivity moderator, at 0°C leads to the formation of the 2-S derivative as the only product in a yield of 5%.[10] This substitution pattern is similar to that of the related 1,2-(ethylenedioxy)benzene (**6**), which upon monosulfonation yields only the **6**-4-

TABLE I

Sulfonation of diphenyl ether (**1**) and diphenyl sulfide (**2**) with SO_3

Substrate	SO_3 (mol-equiv.)	Solvent[a]	Temp. (°C)	React. time (h)	Product mixture composition (%, ± 2)[b] substr.[c]	4-S	$(4\text{-}SO_2)_2O$	4,4′-S_2
1	1.0	N	0	3.0	n.d.	74		26
	2.0	N	0	3.0	n.d.	85		15
	3.0	N	0	3.0	n.d.	18		82
	4.0	N	0	3.0	n.d.	-		>98
	16.0	N	0	3.0	n.d.			>98
2	4.0	CD_2Cl_2	-30	1.5	>98			
			-15	3.0	98	2		
			0	4.5	96	4		
			25	6.0	23[d]	63[d]	4[d]	10[d]
			25	25.0	-	-		>98

[a] N stands for nitromethane. [b] For the reactions of **1** and **2** with SO_3, S stands for SO_3^- and SO_3H, respectively. [c] n.d. stands for not determined. [d] Molar composition!

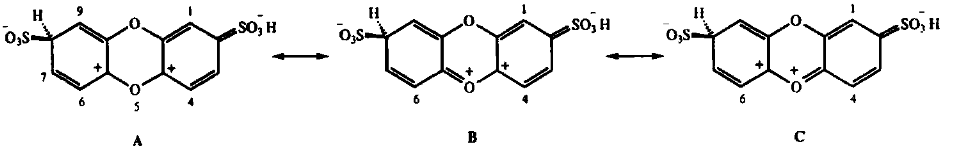
TABLE II

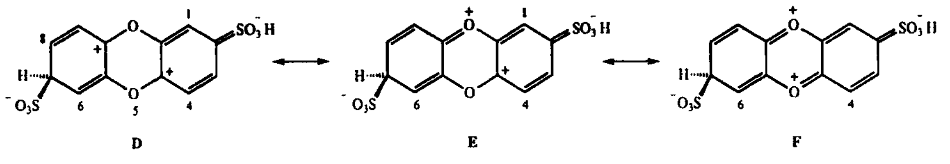
Sulfonation of diphenyl ether (**1**) in sulfuric acid at 25°C

H_2SO_4 (wt-%, ±0.5)	Reaction time (h)	Reaction mixture composition (%, ± 2)[a]			
		4-S	4,4'-S_2	2,4,4'-S_3	2,2',4,4'-S_4
86.9	0.5	22	78		
98.5	0.5	16	61	23	
104.5	0.7	-	45	55	
	19.5		32	65	3
	93		26	68	6
	620		14	75	11

[a] S stands for SO_3H.

S.[4] Sulfonation of **3** with 12.0 mol-equiv. of SO_3 in nitromethane at 25°C gives a mixture of the 2,7- and 2,8-S_2 derivatives in yields of 57 and 43%, respectively. The somewhat lower content of the 2,8-S_2 isomer is ascribed to a somewhat higher energy content of the corresponding σ-complex leading to **3**-2,8-S_2, due to repulsive charge interaction[11] between O(5) and the adjacent C(4a) and C(5a), as is evident from the mesomeric structures **A–C**. As appears from a comparison of the mesomeric structures **D–F** with **A–C** the repulsive charge interaction will be substantially less for the σ-complex leading to the 2,7-S_2 than to the 2,8-S_2.





Sulfonation of xanthene (**4**) with 4.0 mol-equiv. of SO_3 and 4.8 mol-equiv. of dioxane in dichloromethane as solvent at 25°C, followed by working up with water and subsequent neutralization yields dipotassium **3**-2,7-disulfonate as the only water soluble product. This substitution pattern is similar to that of the related chromane (**7**), the monosulfonation of which yields only the 4-S derivative.[4] For both xanthene and chromane, the mesomeric stabilization of the various sulfonation σ-complexes by the oxygen thus appears to outweigh that by the benzylic CH_2 group.

EXPERIMENTAL

The substrates **1**, **2** and **4** were obtained commercially, whereas **3** was a gift from Dr. P. Mulder (University of Leiden). The ^1H NMR spectra were obtained using a Varian XL-100 and Bruker AC-200, WM-250 and ARX-400 instruments. With sulfuric acid as solvent the chemical shifts were measured relative

TABLE III

^{1}H NMR data of the sulfoproducts of diphenyl ether (1) and diphenyl sulfide (2)

Compound[a]	Solvent[b]	δ (ppm, ± 0.02)[c]							
		2	3	4	5	6	2'	3'	4'
1	CD_2Cl_2	7.01	7.35	7.11					
1-4-S	CD_2Cl_2	7.04	7.84	-			7.09	7.43	7.26
	D_2O	6.90	7.58				6.90	7.27	7.12
	86.9-SA	7.24	7.95				7.42	7.68	7.10
	98.5-SA	7.34	8.04				7.50	7.72	7.22
1-4,4'-S_2	CD_2Cl_2	7.18	7.93	-					-
	D_2O	6.97	7.63						
	86.9-SA	7.18	7.95						
	98.5-SA	7.32	8.04						
	104.5-SA	7.32	8.04						
1-2,4,4'-S_3	D_2O	-	8.39	-	7.99	7.18	7.30	7.93	-
	98.5-SA		8.63		8.27	7.27	7.48	8.14	
	104.5-SA		8.63		8.28	7.27	7.50	8.15	
1-2,2',4,4'-S_4	104.5-SA	-	8.68	-	8.41	7.55	-		-
2	CD_2Cl_2	<----	7.30 - 7.43	---->					
2-4-S	CD_2Cl_2	7.26	7.74	-			<----	7.43 - 7.57	---->
(2-4-SO_2)$_2$O	CD_2Cl_2	7.19	7.67	-			<----	7.30 - 7.43	---->
2-4,4'-S_2	CD_2Cl_2	7.4 - 7.6	7.86	-					-

---

[a] For D_2O as solvent S stands for SO_3^-, and for both CD_2Cl_2 and sulfuric acid (SA) as solvent it stands for SO_3H. [b] SA stands for wt-% sulfuric acid. [c] All $^3J_{H,H}$'s and $^4J_{H,H}$'s were found to be 7.5 - 8.0 and 1.5 - 2.0 Hz, respectively.

TABLE IV

^{1}H NMR data of dibenzo[*b*,*e*][1,4]dioxin (**3**), xanthene (**4**) and their sulfo products[a,b]

Compound	Solvent	δ (ppm, ± 0.010)[c]							
		1	2	3	4	6	7	8	9
3	CD_2Cl_2	← - - - 6.827 - 6.912 (m) - - - →							
3-2-S	CD_2Cl_2	7.344 (d)	-	7.409 (dd)	6.492 (d)	← - - - 6.88 - 6.95 (m) - - - →			
3-2,7-S_2	D_2O	7.226 (d)	-	7.347 (dd)	6.849 (d)		-		
3-2,8-S_2	D_2O	7.214 (d)	-	7.359 (dd)	6.900 (d)			-	
4[d]	CD_2Cl_2	7.15-7.22 (m)	7.00-7.07 (m)	7.15-7.22 (m)	7.00-7.07 (m)				4.037(s)
4-2,7-S_2	D_2O	7.356 (d)	-	7.441 (d,d)	6.734 (d)		-		3.57 (s)

[a] It should be realized that the skeleton numbering of **3** and **4** is different. [b] S stands for SO_3H when the solvent is CD_2Cl_2 and for SO_3^- when the solvent is D_2O. [c] The $^3J_{H,H}$ and $^4J_{H,H}$ coupling constants are ≈ 8.5 and ≈ 2.2 Hz, respectively. [d] The assignment of H(1) - H(4) of xanthene (**4**) were made on the basis of a long range $^3J_{C,H}$ correlation spectrum, using the ARX 400 NMR spectrometer.

to a 1% HDO solution in D_2O as external reference (concentric capillary), and subsequently converted to virtual internal TMS as reference. For the other solvents the chemical shifts are relative to (virtual) internal TMS as reference.

The sulfonation procedures with concentrated sulfuric acid as reagent and solvent, and with SO_3 in dichloromethane and in nitromethane as solvent were similar as described before.[4,5] The structural assignments of the sulfo products were made on the basis of the observed ^1H NMR chemical shifts, the absorption area ratios and coupling constants, in combination with the shielding parameters of the SO_3^- and SO_3H substituents.[12] The assignments of **3**-2,7-S_2 and **3**-2,8-S_2 are based on the following reasoning. The -M effect of the 7-sulfo group of **3**-2,7-S_2 leads to an electron charge deficiency at O(10), which will induce a somewhat smaller electron deficiency at C(1). Likewise, the conjugative effect of the 8-sulfo group of **3**-2,8-S_2 leads to an electron deficiency at O(5), which induces a smaller electron deficiency at C(4). The ^1H NMR doublet (J = 8.5 Hz) absorptions at 6.900 and 6.849 ppm are therefore assigned to the 4-H of the 2,8-S_2 and 2,7-S_2 derivatives, respectively.

The various ^1H NMR assignments are presented in Tables III and IV. The compositions of the sulfonation reaction mixtures and the sulfonated product mixtures were determined by multicomponent ^1H NMR analysis on the basis of specific absorptions of the various components.[12]

ACKNOWLEDGEMENT

The authors wish to thank Dr. P. Mulder (University of Leiden) for a gift of dibenzo[*b*,*e*][1,4]dioxin.

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