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Sulfonation of 1- and 2-naphthol and their methanesulfonate esters with sulfur trioxide. The influence of initial sulfation on the sulfo-product composition [a,b]

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Abstract. The sulfonation of 1- and 2-naphthol with sulfur trioxide in $C^2H_3NO_2$ has been studied by using ^1H NMR. 1-Naphthol (**1**) yields, upon reaction with 1.0 mol-equiv of SO_3, a mixture of 2- and 4-sulfonic acids (2- and 4-S); upon increasing the reaction temperature, the relative amount of 2-S increases. Upon reaction with 4.0 mol-equiv of SO_3, the initially observed products are the hydrogen sulfate **1**-*O*,2,4-S_3 and some corresponding sulfonic anhydrides. After prolonged reaction times, some **1**-*O*-4,7-S_3 is formed.

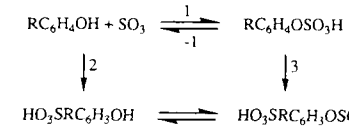
2-Naphthol (**3**), upon reaction with 1.0 mol-equiv of SO_3, yields a 85 : 15 mixture of 1-S and 8-S, whereas upon reaction with 2.0 mol-equiv of SO_3, a 8 : 14 : 78 mixture of the 5-S, 6-S and 8-S are formed. Sulfonation of **3**, either by (*i*) reaction with 1.2 and, subsequently, an additional 2.0 mol-equiv of SO_3, or (*ii*) by direct addition of 4.0 mol-equiv of SO_3, yields a mixture of the carbyl sulfates **5**-5-S and **5**-6-S and the hydrogen sulfate **3**-*O*,6,8-S_3, the relative yield depending on the method used.

The results are discussed in terms of initial formation of the corresponding naphthyl hydrogen sulfates and on the basis of a comparison with the reactions of 1- and 2-naphthyl methanesulfonates, the chosen model compounds for the hydrogen sulfates, with SO_3.

Introduction

In the reaction of phenols with sulfur trioxide, the initial reaction is electrophilic attack by SO_3 on the hydroxy oxygen, leading to the corresponding phenyl hydrogen sulfate in an equilibrium reaction (see Scheme 1, steps 1 and −1). Subsequently, ring sulfonation takes place, yielding a phenolsulfonic acid[1]. When using $\leqslant 1.0$ mol-equiv of SO_3, the phenol is the substrate species that is ring-sulfonated (sequence 1, −1, 2), whereas upon using a large excess of SO_3, it is the phenyl hydrogen sulfate that is sulfonated (sequence 1, 3). Depending on (the substituents present in) the substrate, this may lead to a variation in the sulfonic-acid product composition, as the hydroxy group is *ortho*/*para*-directing and activating, whereas the hydrogen sulfate group is also *para*-directing, but deactivating. In continuation of our present studies of mono- and disubstituted naphthalenes[2,3] we now report on SO_3 sulfonation of 1- and 2-naphthols (**1** and **3**, respectively).

The sulfonation of both 1- and 2-naphthols has been relatively well-studied[4–15]. However, most studies concern the specific synthesis of a single mono-, di- or trisulfonic acid by means of sulfuric acid[4–9] or chlorosulfonic acid[10–12] sulfonation under specified conditions. For **1**, the intended product was either **1**-4-sulfonic acid (**1**-4-S)[4,10], **1**-7-S^5 or **1**-2,4,7-S_3[6,11], whereas, with **3**, it was either **3**-1-S^{12}, **3**-6-S^7, **3**-3,6-S_2[8] or **3**-6,8-S_2[9]. The sulfonation of **1** with < 2.0 mol-equiv of H_2SO_4 in nitrotoluene yields a mixture of 2- and 4-S, the ratio of which increases upon increasing the reaction temperature[13]. The sulfation of **3** has been reported[14], as well as a kinetic study on the sulfuric acid sulfonation of **3**[15] leading to **3**-1-S, **3**-8-S and **3**-5-S as the initial products. None of these studies focussed on the reaction mechanism, in particular on the effect of any initial naphthyl hydrogen sulfate formation. Therefore, in addition to SO_3 sulfonation of **1** and **3**, we have now studied the reactions of the corresponding methanesulfonate esters **2** and **4** as model compounds for 1- and 2-naphthyl hydrogen sulfate, the intermediates that are anticipated to be initially formed in the reactions of **1** and **3** with SO_3. The methanesulfonate group (OSO_2CH_3) is considered to be a satisfactory, stable model for the hydrogen sulfate group (OSO_2OH)[16].

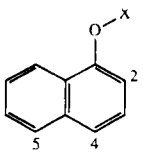


Scheme 1. Mechanism of sulfonation of RC_6H_4OH with SO_3.

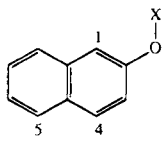
[a] Aromatic sulfonation part 118. For part 117, See Ref. 3.

[b] For reasons of convenience, all sulfo products have been numbered as for the corresponding substrates.

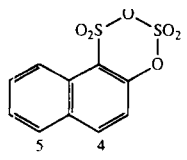
In the context of a study of the sulfonation of 1,6-oxido[10]annulene *, we have already reported the SO_3 sulfonation of the isomeric 1-naphthol[17], showing a large dependence of product composition on reaction conditions.



1 X = H
2 X = SO_2CH_3



3 X = H
4 X = SO_2CH_3



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Results and discussion

The sulfonation of 1- (**1**) and 2-naphthol (**3**) and their respective methanesulfonate esters (**2**) and (**4**), with sulfur trioxide in nitromethane-d_3 has been studied using ^1H NMR. The results of these studies are collected in Tables I–IV.

* IUPAC name: 11-oxabicyclo[4.4.1]undeca-1,3,5,7,9-pentaene.

Table II Reaction of 1-naphthol (1) with 1.0 mol-equiv of SO_3 in CH_3NO_2 for 60 min.

Reaction temp. (°C)	Sulfo product composition (%, ± 2) [a]	
	2-S	4-S
−20	< 1	> 99 [b]
0 [c]	15	85
20 [d]	33	67
40 [d]	70	30

[a] S stands for SO_3. [b] The yield of **1**-4-S is *ca.* 10%. [c] Taken from Ref. 17; substrate conversion ⩾ 99%. [d] The amount of unconverted substrate has not been determined.

Sulfonation of 1-naphthol (1) and 1-naphthyl methanesulfonate (2)

The initial sulfonation of 1-naphthol with SO_3 in nitromethane yields both the 2-sulfonic acid (2-S) and 4-S (Table 1). This is to be expected, as the hydroxy group is

Table I Reaction of 1-naphthol (1) and its methanesulfonate ester (2) with SO_3 in $C^2H_3NO_2$ at ambient temperature.

Naphthalene substituent	SO_3 mol-eq. (±0.1)	Reaction time (min)	Product-mixture composition (%, ± 2) [a,b]								
			Substr [c]	2-S	4-S	(2-4-SO_2)$_2$O	2,4-S_2	4,7-S_2	*O*,2,4-S_3	*O*,4,7-S_3	X [c]
1-OH	1.0	10	31	20	49						
		125	25	24	51						
		1620	24	48	28						
		6000 [d]	nd	78	22						
	4.0	45 [c]							58		42
		100							82		18
		4400							81	–	19
		8855							77	3	20
		46000 [d]					54	21	25	–	–
1-OSO_2CH_3	1.0	10	26		74						
	3.0	10			70	30					
		1455			66	24		7			
		8805			83			17			

[a] S stands for SO_3H when $C^2H_3NO_2$ is the solvent, and for SO_3 when using ^2H_2O. [b] All compositions are molar compositions. [c] nd stands for not determined (see Experimental). [d] Product mixture obtained after alkaline aqueous work-up of the above-mentioned reaction mixture. [e] Other products are present, which are tentatively assigned to be intermolecular sulfonic anhydrides of **1**-*O*,2,4-S_3, based on four relatively high field triplets of H(6) and H(7) at δ 7.52, 7.68, 7.93 and 8.06 ppm.

Table III Reactions of 2-naphthol (3) with SO_3 in $C^2H_3NO_2$ at ambient temperature.

SO_3 mol-eq (±0.1)	Reaction time (min)	Product mixture composition (%, ± 2) [a,b]												
		Substr [c]	**3**							**3**-*O*-S			**5**		
			1-S	5-S	6-S	8-S	1,5-S_2	1,6-S_2	6,8-S_2	5-S	8-S	6,8-S_2	–	5-S	6-S
1.0	10	–	85			15									
2.0	245	29		6	10	55									
	1375 [d]	29		6	8	57									
				8	14	78									
1.2	4		82							3	15				
1.2 + 2.0 [e]	93		–							4	16		62		18
	270									–	17		46	4	34
	4230							35			5	14	9	3	34
	7260 [d]							56			–	20	–	4	20
							5	75	20						
4.0	5									7	51		34		8
	20									7	47		32		14
	215									–	41	6	24	6	23
	2760							10			20	28	13	6	23
	7080							25			7	40	5	5	18
	10080 [d]							32			5	45	–	6	12
							9	46	44						

[a–d] See the corresponding superscripts in Table I. [e] After 90 min, 2.0 mol-equiv of SO_3 were added to the reaction mixture; the times given are total reaction times.

Table IV Reactions of 2-naphthyl methanesulfonate (4) with SO_3 in $C^2H_3NO_2$ at ambient temperature.

SO_3 (mol-eq) (±0.1)	Reaction time (min)	Product mixture composition (%, ±2) [a,b]			
		Substrate [c]	5-S	6-S	8-S
1.0	10	43	8	6	43
	95	42	8	6	44
	33000	42	9	6	43
	[d]		13	11	76
3.0	10	7	7	7	68
	175	6	10	7	70

[a-d] See the corresponding superscripts of Table I.

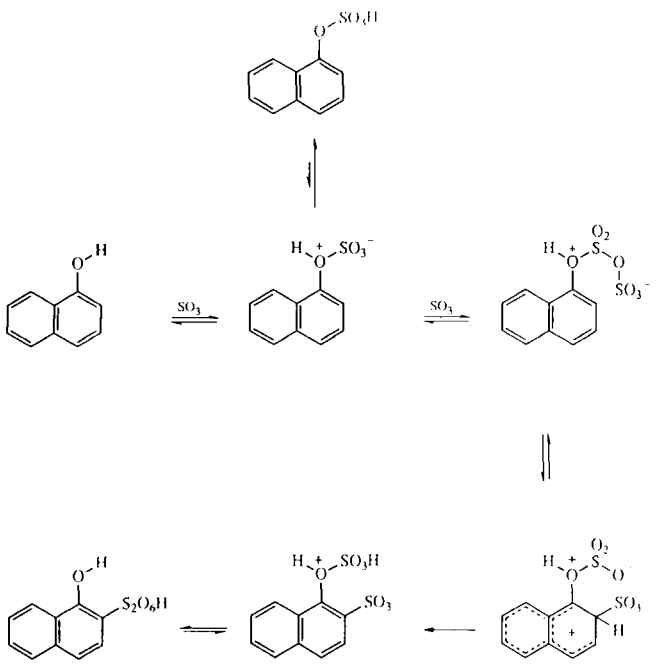
ortho/para-directing, and the inductive electron release by the hydroxy group will be more pronounced in the ring to which it is attached than in the other ring[18]. Interestingly, the 2-S/4-S ratio increases from < 0.01 at −20°C to 2.33 at 40°C (see Table II). This can be ascribed to a difference in the substrate species that is sulfonated, the ArOH/$ArOSO_3H$ equilibrium ratio increasing with increasing temperature[20]. The absence of any 2-S at −20°C can be ascribed to steric factors from the hydrogen sulfate group. The exclusive formation of 4-S in the sulfonation of 1-naphthyl methanesulfonate (**2**) is also indicative of this steric factor, as the methanesulfonate group is comparable in size with the hydrogen sulfate group. At higher temperatures, it is the naphthol that is sulfonated, leading to a mixture of 2- and 4-S. Furthermore, at higher temperatures, **1**-2-S may (in part) be formed by isomerization of **1**-4-S, further increasing the ratio 2-S/4-S. This is, in fact, observed after prolonged reaction times at 20°C (see Table I) and may also be the case in the H_2SO_4 sulfonation of **1** in nitrotoluene as solvent[13].

Remarkably, the ratio of **1**-2-S/**1**-4-S is significantly higher when using a mixture of dioxane and dichloromethane (1:5, v/v) than when using dioxane or nitromethane as solvent (1.8, 0.24 and 0.18, respectively[17]). The SO_3 sulfonation of anisole and phenol in dichloromethane, contrary to that in only dioxane or nitromethane, yields a substantial amount of *ortho* sulfonic acid[21]. This phenomenon can therefore be ascribed to enhanced *intra*molecular *ortho* sulfonation via SO_3 complexation on the C(sp^2)-bonded oxygen[21], as depicted in Scheme 2 for 1-naphthol. This mechanism will be more favored in the absence of a SO_3-complexing solvent. Thus, on increasing the amount of dioxane, the amount of SO_3 complexation at the substrate oxygen will decrease, leading to a decrease in the relative degree of sulfonation at position 2.

Table V ^{1}H-NMR data of 1- and 2-naphthol, their methanesulfonate esters and their SO_3 sulfonation products.

Compound [a]		Solvent [b]	δ (ppm, ±0.03) [c,d,e]							
			1	2	3	4	5	6	7	8
1-OH		N		6.99	7.42	7.53	7.93	7.59	7.59	8.28
		W		7.00	7.42	7.53	7.93	7.59	7.59	8.19
	-2-S	N			7.73	7.62	8.00	7.84	7.74	8.45
		W			7.66	7.41	7.88	7.59	7.59	8.32
	-4-S	N		7.06	8.20		8.59	7.84	7.74	8.45
		W		6.66	7.93		8.48	7.90	7.59	8.32
	-2,4-S_2	W			8.37		8.44	7.72	7.55	8.44
	-4,7-S_2	W			8.43		8.53	7.99		8.85
1-OS	-2,4-S_2	N			8.80		8.84	8.26	8.15	8.71
		W			8.56		8.69	7.91	7.80	8.73
	-4,7-S_2	N						8.41		9.16
1-OSO_2CH_3		N	3.44	7.63	7.62	7.97	8.04	7.75	7.68	8.30
	-4-S	N	3.52	7.76	8.40		8.72	7.96	7.89	8.43
	-4,7-S_2	N	3.60	7.90	8.56		8.90	8.28		8.92
(1-OSO_2CH_3-4-SO_2)$_2$O		N	3.53	7.53	8.08		8.19	7.46	7.71	8.18
2-OH		N	7.29		7.22	7.87	7.87	7.40	7.52	7.79
		W	7.28		7.20	7.88	7.88	7.40	7.51	7.79
	-1-S	N			7.27	8.17	7.99	7.59	7.77	8.48
		W			7.17	7.97	7.90	7.46	7.66	8.49
	-5-S	N				8.55		8.13	7.62	
		W				8.49				
	-6-S	N					8.48			
		W					8.22			
	-8-S	N	7.95		7.36	8.04	8.20	7.52	8.26	
		W	7.84		7.21	7.91	8.00	7.35	8.05	
	-1,5-S_2	W			7.35	8.20		8.06	7.72	8.75
	-1,6-S_2	N			7.45	8.32	8.55		8.13	
		W			7.21	8.00	8.30		7.95	8.62
	-6,8-S_2	W	7.85		7.26	8.04	8.35 [f]		8.39 [f]	
5		N			7.70	8.58	8.27	7.91	8.03	8.44
	-5-S	N			7.94	9.25				8.80
	-6-S	N			7.89	8.78	8.88		8.41	8.68
2-OS	-5-S	N				8.78		8.40		8.28
	-8-S	N	8.62		7.76	8.28	8.39 [g]	7.80	8.42 [g]	
	-6,8-S_2	N	8.70		7.95	8.48	8.96		8.72	
2-OSO_2CH_3		N	7.92	3.35	7.55	8.09	8.06 [h]	7.65	7.70	8.06 [h]
	-5-S	N		3.39		8.78		8.40		8.28
		W	7.73			8.74				
	-6-S	N	7.92	3.40	7.64		8.65		7.94	
		W	7.73				8.42			
	-8-S	N	8.56	3.41	7.74	8.29	8.41 [i]	7.81	8.44 [i]	
		W	8.50	3.41	7.39	7.85	7.85	7.48	8.12	

[a] S stands for SO_3H when $C^2H_3NO_2$ is the solvent and for SO_3^- when using ^2H_2O. [b] N and W stand for $C^2H_3NO_2$ and ^2H_2O, respectively. [c] All δ values are relative to internal TMS. [d] All $^3J_{H,H}$'s and $^4J_{H,H}$'s were found to be 7.5–9.5 and 1.5–2.5 Hz, respectively. [e] Due to the large overlap, not all signals could be assigned. [f,g] The assignment may be reversed. [h] Center of unresolved multiplet. [i] The assignment may be reversed.



Scheme 2. Mechanism for the intramolecular sulfonation of 1-naphthol via its hydrogen pyrosulfate.

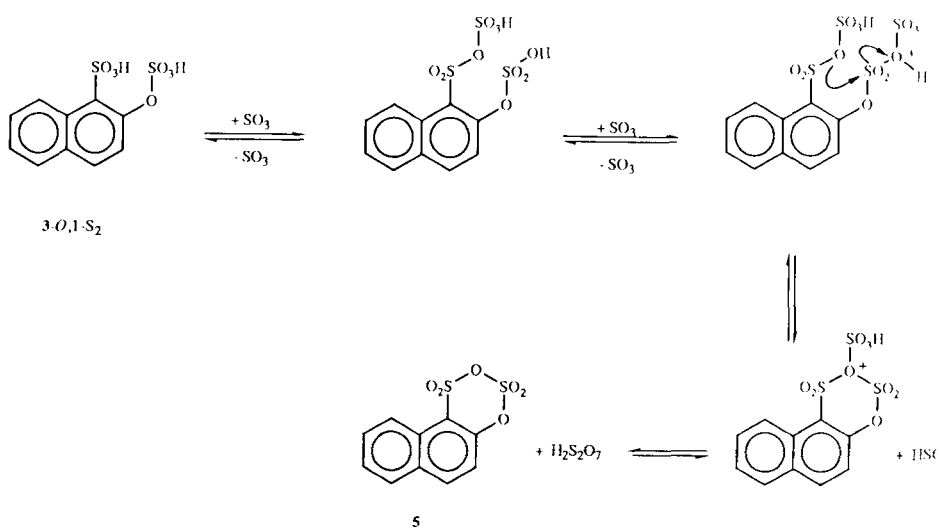
Reaction of **1** with 4.0 mol-equiv of SO_3 in nitromethane leads to the formation of **1**-*O*,2,4-S_3 and the corresponding intermolecular sulfonic anhydrides. The very slow subsequent rearrangement of **1**-*O*,2,4-S_3 into the thermodynamically more stable **1**-*O*,4,7-S_3 is due to relief of steric strain between the 1-OSO_3H and the 2-SO_3H groups. The sulfonation of **2** with an excess of SO_3 shows that sulfonation at a carbon adjacent to the OSO_2CH_3 group, does not take place, the only disulfonic acid product being **2**-4,7-S_2. On the basis of these two observations, we propose that the final product of the sulfonation of **1** is formed by initial disulfonation of 1-naphthol and subsequent sulfation.

Sulfonation of 2-naphthol (3) and 2-naphthyl methanesulfonate (4)

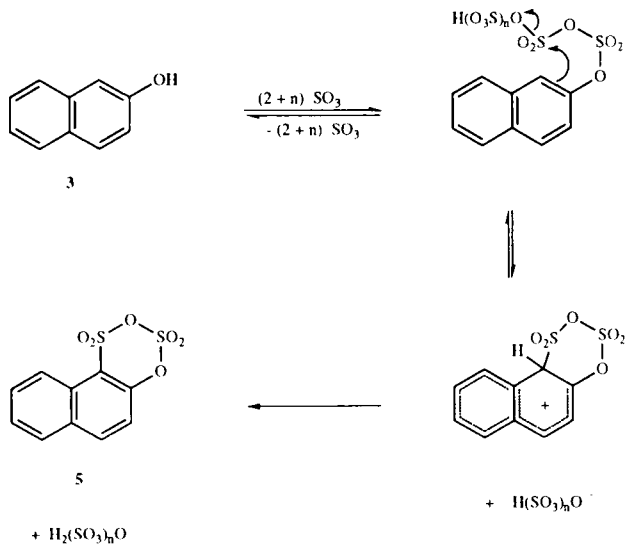
Upon sulfonation of **3** with 1.0 mol-equiv of SO_3, **3**-1-S is the main product (Table III), whereas, remarkably, on using 2.0 mol-equiv of SO_3, a mixture of **3**-5-S, **3**-6-S and **3**-8-S in a ratio of 8:14:78 is formed. Sulfonation of 2-naphthyl methanesulfonate (**4**), the chosen model compound for 2-naphthyl hydrogen sulfate (**3**-*O*-S), yields a mixture of **4**-5-S, **4**-6-S and **4**-8-S in a ratio of 13:11:76 (Table IV). These observations clearly indicate that the sulfonation of **3** with 1.0 mol-equiv of SO_3 occurs (mainly) via 2-naphthol, of which the most reactive position is C(1)[22], whereas that when using 2.0 mol-equiv of SO_3, occurs mainly via the hydrogen sulfate. The formation of the 5-sulfonic acid is ascribed to the "naphthalene α-effect", which is a pertinent factor in the sulfonation of deactivated naphthalenes[23].

In order to further examine the influence of the amount of SO_3 used on the product distribution, 2-naphthol was disulfonated in two different ways, *viz.*, (*i*) by monosulfonation with 1.2 mol-equiv of SO_3 and subsequent addition of 2.0 mol-equiv of SO_3, and (*ii*) by sulfonation with 4.0 mol-equiv of SO_3. The addition of 2.0 mol-equiv to the reaction mixture obtained on reaction with 1.2 mol-equiv of SO_3, containing mainly **3**-1-S, leads to the immediate formation of 1,2-naphthalene carbyl sulfate **5** (IUPAC name: naphthol[1,2-*e*][1,3,2,4]dioxadithiin 2,2,4,4-tetraoxide). A mechanism for this conversion is given in Scheme 3; the driving force for the rearrangement is the relief of steric strain between the 1-sulfonic acid group and the 2-hydrogen sulfate group in **3**-*O*,1-S_2. The absence of **3**-*O*,1-S_2 and the presence of **5** is concluded from a comparison of the ^1H chemical shifts, as calculated on the basis of the additivity of substituent shifts for **3**-*O*,1-S_2, and those observed. The chemical shift of H(8) of **5** is upfield relative to that of H(8) in **3**-1-S. This is not to be expected for **3**-*O*,1-S_2, as the combined 1-SO_3H and 2-OSO_3H groups have a large down-field substituent shift effect on H(8) as a result of *peri* interaction. This *peri* interaction is diminished by the formation of the carbyl sulfate ring. Further sulfonation of **5** occurs on C(6). After very prolonged reaction times, **3**-1,6-S_2 is observed, illustrating proto-desulfation. The **5**-5-S and **3**-*O*,6,8-S_3 formed originate from the **3**-*O*,5-S_2 and **3**-*O*,8-S_2 initially formed, respectively. Aqueous alkaline work-up yields a mixture of the corresponding dipotassium 2-naphtholdisulfonates.

The major product upon direct addition of 4.0 mol-equiv of SO_3 to a solution of **3** is **3**-*O*,8-S_2. The formation of 34% of **5** in addition to **3**-*O*,5-S_2 and **3**-*O*,8-S_2 is in contrast to sulfonation with 2.0 mol-equiv of SO_3 [in which case, no sulfonation occurs at C(1)]. Its immediate formation is ascribed to the intramolecular sulfonation route shown in Scheme 4, which requires a large excess of reagent to be present in the initial stage of the reaction. This type of mechanism was recently also postulated for



Scheme 3. Mechanism for the conversion of 3-O,1-S_2 into 5.



Scheme 4. Mechanism for the intramolecular conversion of 3 into 5; $n \geq 2$.

the formation of the intramolecular 4,15-disulfonic anhydride of [2.2]paracyclophane from the 4-sulfonic acid[24].

From the constancy of the total amounts of various types of products, it can be derived that (*i*) **3**-*O*,8-S_2 yields **3**-*O*,6,8-S_3 (**3**-*O*,8-S_2 + **3**-*O*,6,8-S_3 = 47%), (*ii*) **5** yields **5**-6-S (**5** + **5**-6-S = 47%) and (*iii*) **3**-*O*,5-S_2 yields **5**-5-S (**3**-*O*,5-S_2 + **5**-5-S = 6%); thus, all these secondary products are directly derived from one of the initial products.

The present results suggest that formation of naphthyl hydrogen sulfate is more effective with 2- than with 1-naphthol, as the change in product distribution upon increasing the amount of SO_3 reagent is more dramatic with the former than the latter substrate. In fact, the resemblance of the sulfonation pattern of 2-naphthol with 2.0 mol-equiv of SO_3 with that of the corresponding 2-naphthyl methanesulfonate is striking, whereas there is a large difference between the sulfonation of 1-naphthol and the corresponding methanesulfonate on reaction with 4.0 mol-equiv of SO_3, the former yielding its 2,4-S_2 derivative and the latter the 4,7-S_2. One reason may be the *peri* strain encountered by the 1-OSO_3H group, rendering the 1-OSO_3H group relatively unstable, an effect that is absent with the 2-OSO_3H group. Secondly, it has been calculated[25] that the electron density of the oxygen is somewhat higher with 2- than with 1-naphthol, which may infer that the degree of *O*-sulfonation may be greater for 2-naphthol. Furthermore, sulfonation "*ortho*" and "*peri*" to the OSO_2CH_3 group does not occur, primarily for steric reasons.

It is apparent from the present study that the relative amount of SO_3 used has a large influence on the type of product(s) obtained. Thus, synthesis of **3**-8-S is most conveniently performed by reaction of **3** with 2.0 mol-equiv of SO_3. **3**-6,8-S_2 can then be obtained by adding additional SO_3 to the reaction mixture containing mainly **3**-8-S. Reaction of **3** with 1.0 mol-equiv of SO_3 mainly yields **3**-1-S, from which **3**-1,6-S_2 can be obtained by adding 2.0 mol-equiv of SO_3. **1**-4-S is best obtained by reaction of **1** at −20°C with 1.0 mol-equiv of SO_3 for prolonged reaction times.

Experimental

1- And 2-naphthol were obtained commercially and used as such. The methanesulfonates were synthesized from the corresponding naphthol following a published procedure[26]. The NMR spectra were recorded on Bruker AC-200 and WM-250 spectrometers.

Sulfonation procedures

Method A. A solution of the desired amount of SO_3 in 7.0 ml of nitromethane was added to a homogeneous solution of 1.0 mmol of substrate in 7.0 ml of nitromethane at the desired temperature in an argon atmosphere. After the appropriate reaction time, 1.0 ml of ^1H_2O was added and the mixture heated to 40°C to hydrolyze (most of) the anhydrides. The aqueous layer was isolated and extracted at room temperature three times with 1–2 ml of CH_2Cl_2 to remove any unconverted substrate and remaining nitromethane. The residual CH_2Cl_2 was removed by bubbling N_2 through the aqueous solution for 30 min. The aqueous layer was subsequently neutralized with 10% aqueous potassium hydroxide and the water removed by freeze drying. Subsequently, a ^{1}H-NMR spectrum of the resulting potassium sulfonate salt mixture, dissolved in ^2H_2O, was recorded for product assignment and quantitative analysis.

Method B. A solution of the desired amount of SO_3 in 0.5 ml of $C^2H_3NO_2$ was added to a solution of 0.10 mmol of substrate in 0.5 ml of $C^2H_3NO_2$ at 0°C under argon. A sample of the resulting homogeneous reaction mixture was then transferred into an NMR tube and, subsequently, ^{1}H-NMR spectra were recorded at ambient temperature (20–22°C), allowing appropriate time intervals. The reaction mixtures thus obtained were worked up with H_2O and, subsequently, treated as described in method A.

Structural assignments of the sulfo products of the SO_3 sulfonations were made on the basis of the observed ^{1}H-NMR chemical shifts, absorption-area ratios and coupling constants in combination with the shielding parameters of the OH, OSO_2CH_3, OSO_3H, SO_3^-, SO_3H^2 and $(-SO_2)_2O^3$ substituents. The assignments are compiled in Table V. The compositions of the sulfonation reaction mixtures and the sulfonated product mixtures were determined by multicomponent ^{1}H-NMR analysis on the basis of the specific absorptions of the various components[27].

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