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Reactions of styrene and derivatives with sulfur trioxide; characterization and chemistry of the initial products§

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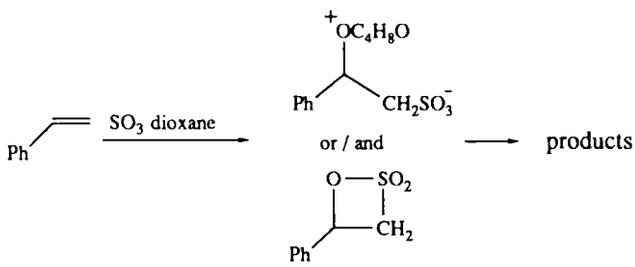
Abstract. The reactions of styrene derivatives **1a–14a** with sulfur trioxide were studied in the temperature range −60 to 25 °C using dichloromethane as solvent and 1.5 mol equiv. of dioxane as reactivity moderator. Reaction of styrene (**1a**) at low temperature yields the carbyl sulfate **1c** as the only observable intermediate in the ultimate formation of (*E*)-2-phenylethene-1-sulfonic acid (**1d**). The (phenyl) substituted styrenes **3a–5a** clearly demonstrate the presence of the β-sultones **3b–5b** as the sole initial products leading to the corresponding carbyl sulfates **3c–5c**. The initially formed β-sultone **b** in the reaction of styrene derivatives **3a–5a**, **9a** and **10a** with 1.0 mol equiv. of SO_3 disproportionates to yield equal amounts of the corresponding carbyl sulfate and the starting styrene. This is thought to indicate that there is an equilibrium between the β-sultone and the starting styrene. The group of the 1-methyl-substituted styrenes **11a–13a** are an exception to the generally observed eventual conversion of the initial intermediates into the 2-sulfonic acids **d**, since they give the corresponding 3-sulfonic acids **f**.
Mechanisms for the formation of the various products are proposed.

Introduction

As a sequel to our recent studies on the sulfonation of external and internal alkenes[1,2], we have set up a programme to study the reaction of phenyl-substituted alkenes with sulfur trioxide to determine the effect of the phenyl substituents on the formation of the β-sultone† and carbyl sulfate‡ and on their chemistry. In the present paper, we report on the reactions of the styrenes **1a–14a** with sulfur trioxide. The chemistry of non-conjugated phenylalkenes with SO_3 will be reported in a forthcoming paper[3].



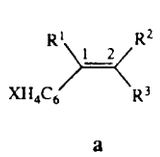
Scheme 1. Presumed initial products in the sulfonation of styrene[5,6].

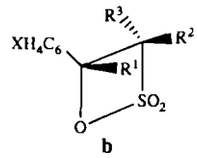
Sulfonation of styrene (**1a**) has been intensively studied by *Bordwell* and co-workers[5,6], but the presumed initial products, *i.e.*, the β-sultone **1b** or the isomeric zwitterionic intermediate (see Scheme 1), escaped detection. In 1954, *Bordwell* claimed to have isolated the relative unstable β-sultone[5], but *Zoller*[7] later suggested that the product isolated by *Bordwell* was instead the six-membered ring carbyl sulfate **1c**. The sulfonation of (*E*)-1-phenyl-1-propene (**9a**) and of 2-phenyl-1-propene (**11a**) with SO_3 has been studied at 17 °C in dioxane as solvent[8]. The former substrate led to the formation of *cis*- and *trans*-carbyl sulfate and 1-phenyl-1-propene-2-sulfonic acid in yields of 10, 48 and 2%, respectively, whereas the latter substrate gave 2-phenyl-2-propene-1-sulfonic acid (**11f**) and 2-phenyl-1-propene-1-(pyro)sulfonic acid in 92 and 8% yields, respectively. In this paper, we report on low-temperature experiments which gave direct evidence for the existence of the β-sultone as the initial sulfonation product of styrene and the various studied styrene derivatives, as well as on the further chemistry of the initial sulfonation products.

Results

The reactions of styrene derivatives **1a–14a** with (in general 1.0 or 2.0 mol equiv. of) SO_3 were studied mainly in dichloromethane as solvent, using 1.5 equiv. of dioxane (relative to the amount of SO_3) as a reactivity moderator[9], as the standard conditions (method A).
The reactions were carried out at low temperatures, and examined by ^{1}H NMR spectroscopy in order to obtain

§ Aliphatic sulfonation 7. For part 6, see ref. 4.
† IUPAC nomenclature: 1,2-oxathietane 2,2-dioxide.
‡ IUPAC nomenclature: cyclic sulfonate sulfate anhydride and 1,3,2,4-dioxadithiane 2,2,4,4-tetraoxide.


a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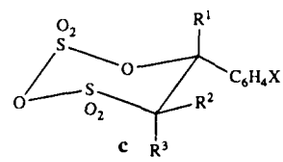
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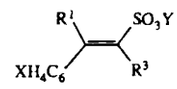
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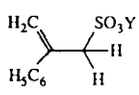
e Y=K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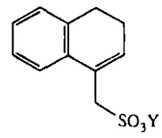
11g Y=K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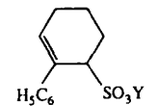
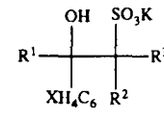

13f Y=H
13g Y=K


h

1 X=R¹=R²=R³=H
2 X=R¹=R²=H, R³=D
3 X=2-Cl, R¹=R²=R³=H
4 X=3-Cl, R¹=R²=R³=H
5 X=3-NO₂, R¹=R²=R³=H
6 X=4-Cl, R¹=R²=R³=H
7 X=2-Me, R¹=R²=R³=H
8 X=3-Me, R¹=R²=R³=H
9 X=R¹=R³=H, R²=Me
10 X=R¹=R²=H, R³=Me
11 X=R²=R³=H, R¹=Me
12 X+R¹=2'-(CH₂)₃-, R²=R³=H
13 X=R³=H, R¹+R²= -(CH₂)₄-
14 X=R¹=H, R²=R³=Me

information on the primary sulfonation products. ^{1}H and some ^{13}C NMR assignments of the styrene derivatives and their sulfo products are compiled in Tables I–III or in the Experimental Section.

The sulfonation of styrene (**1a**) with 2.0 equiv. of SO_3, at $-30°C$, leads to carbyl sulfate **1c** as the first observed product which, at room temperature, is slowly converted into (*E*)-2-phenylethene-1-sulfonic acid (**1d**). The formation of **1d** has been previously reported by *Bordwell*[5]. Reaction of styrene with 2.0 equiv. of SO_3 and subsequent alkaline work-up (method B) gave potassium (*E*)-2-phenylethene-1-sulfonate (**1e**) in high yield.

We have synthesized (*Z*)-β-deuteriostyrene (**2a**) in order to obtain information about the stereochemistry of the formation of the carbyl sulfate in the reaction of styrene with SO_3. The sulfonation of **2a** with 2.0 equiv. of SO_3 at $-60°C$ unfortunately also leads to the immediate formation of the carbyl sulfate **2c**, in which the orientation of the phenyl relative to the deuterium could not be established[10]. The carbyl sulfate **2c** is, at room temperature, eventually converted into the 1-alkenesulfonic acid **2d**.

Reaction of 2-chloro- (**3a**), 3-chloro- (**4a**) and 3-nitrostyrene (**5a**) with 1.0 equiv. of SO_3 at $-60°C$ yields a mixture of the styrene, the β-sultone (**b**) and the corresponding carbyl sulfate (**c**). After raising the temperature to $-20°C$, the β-sultone is converted into the carbyl sulfate with concomitant reformation of the styrene **3a**, **4a** and **5a** respectively. The compositions of the reaction mixtures of 3-chlorostyrene and 3-nitrostyrene with 1.0 and 0.5 equiv. of SO_3, respectively, are compiled in Table IV. Reaction of 3-nitrostyrene (**5a**) with 2.0 equiv. of SO_3 (method B) gave potassium 2-(3-nitrophenyl)-2-hydroxyethane-1-sulfonate (**5h**) in high yield (90%).

Reaction of 4-chlorostyrene (**6a**) with 1.0 equiv. of SO_3, at $-60°C$, leads to the formation of the carbyl sulfate **6c** and an unidentified product (after 10 min, the ratio of **6a**, **6c** and the unidentified product is 30:45:25). When the temperature is raised to $-20°C$, all the carbyl sulfate is converted into the (as yet) unidentified compound.

Sulfonation of 2-methyl- (**7a**) and 3-methylstyrene (**8a**) with 2.0 equiv. of SO_3 at $-60°C$ yields the corresponding carbyl sulfate. At room temperature, the carbyl sulfates are slowly converted into the 2-phenylethene-1-sulfonic acids **7d** and **8d**, respectively.

The reaction of (*E*)-1-phenyl-1-propene (**9a**) with 0.8 equiv. of SO_3, at $-60°C$, yields exclusively the carbyl sulfate **9c** (mixture of isomers, *cis*/*trans* = 1:10.4), via the *trans*-β-sultone **9b** as the intermediate[11]. The sulfonation of (*Z*)-1-phenyl-1-propene (**10a**) with 1.0 equiv. of SO_3 at $-30°C$ leads to complete conversion into the *cis*-β-sultone **10b**. The rapid β-sultone formation is followed by slower conversion into the corresponding carbyl sulfate **10c** (*cis*/*trans* = 1:7) with concomitant reformation of (*E*)- and (*Z*)-1-phenyl-1-propene in a ratio of 10:1. Reaction of (*Z*)-1-phenyl-1-propene with 2.0 equiv. of SO_3 yields, after initial formation of the *cis*-β-sultone, quantitatively the carbyl sulfate (mixture of isomers, *cis*/*trans* = 1:7).

Reaction of 2-phenyl-1-propene (α-methylstyrene) (**11a**) with 1.0 equiv. of SO_3 at $-20°C$ yields quantitatively 2-phenyl-2-propene-1-sulfonic acid (**11f**). The rate of formation of **11f** is relatively slow, but specific signals of the intermediate β-sultone and carbyl sulfate could not be found in the complicated ^{1}H NMR spectrum. Reaction of **11a** with 2.0 equiv. of SO_3 according to method B gave potassium 2-phenyl-2-propene-1-sulfonate (**11g**).

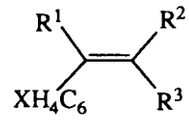
The reactions of 1-methylene-1,2,3,4-tetrahydronaphthalene (**12a**) and 1-phenyl-1-cyclohexene (**13a**) with 1.0 equiv. of SO_3 are similar to the reaction of 2-phenyl-1-propene, and give quantitatively (3,4-dihydronaphthalenyl)methanesulfonic acid (**12f**) and 2-phenyl-2-cyclohexene-1-sulfonic acid (**13f**), respectively. The weak ^{1}H NMR signal at 4.64 ppm ($-60°C$) is assigned to the β-sultone **13b** which is the intermediate in the formation of **13f**. Quenching of the reaction mixture of **12a** with water and subsequent neutralization with an aqueous KOH solution gave potassium (3,4-dihydronaphthalenyl)methanesulfonate (**12g**).

Sulfonation of 2-methyl-1-phenyl-1-propene (**14a**) with 2.0 equiv. of SO_3 at $-60°C$ leads to direct formation of the β-sultone **14b**. This β-sultone is quite stable at this temperature, but leads to a complex mixture of products at temperatures above 0°C.

Discussion

The sulfonation of styrene (**1a**) with 2.0 equiv. of SO_3 eventually gives a quantitative yield of (*E*)-2-phenylethene-1-sulfonic acid (**1d**) via the carbyl sulfate **1c**. The formation

Table I ^1H *NMR data of styrenes (phenylethenes).*

	 a			^1H NMR ($CDCl_3$, δ, ppm)[a]		
X	R^1	R^2	R^3	R^1	R^2	R^3
H	H	H	H	6.85 (dd) (10.9) (17.7)	5.35 (dd) (0.9) (10.9)	5.89 (dd) (0.9) (17.7)
3-NO_2	H	H	H	6.91 (dd) (10.9) (17.6)	5.52 (d) (10.9)	6.05 (d) (17.6)
3-Cl	H	H	H	6.68 (dd) (10.9) (17.6)	5.32 (d) (10.9)	5.78 (d) (17.6)
3-Me	H	H	H	6.75 (dd) (10.9) (17.6)	5.28 (d) (10.9)	5.97 (d) (17.6)
2-Cl	H	H	H	7.12 (dd) (11.0) (17.5)	5.39 (dd) (1.0) (11.0)	5.75 (dd) (1.0) (17.5)
2-Me	H	H	H	6.98 (dd) (10.9) (17.5)	5.32 (dd) (1.3) (10.9)	5.66 (dd) (1.3) (17.5)
4-Cl	H	H	H	6.69 (dd) (10.9) (17.7)	5.29 (dd) (0.6) (10.9)	5.74 (dd) (0.6) (17.7)
H	H	H	Me	6.51 (dd) (1.8) (11.6)	5.89 (dq) (8.8) (11.6)	1.97 (dd) (1.8) (8.8)
H	H	Me	H	6.43 (m)	1.94 (d) (5.1)	6.43 (m)
H	Me	H	H	2.25 (s)	5.51 (br)	5.21 (br)
H	H	Me	Me	6.29 (s)	1.88 (s)	1.92 (s)
H	H	H	D	6.72 (dt) (2.6) (10.9)	5.24 (d) (10.9)	–
$-(CH_2)_3-$		H	H	2.56 (t)[b] 1.92 (q) 2.86 (t)[c]	5.48 (br)	4.96 (br)
H	$-(CH_2)_4-$		H	2.24 (br) 1.76 (m)[d]	2.45 (br)	6.16 (br)

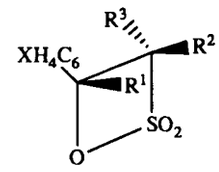
[a] Coupling constants in Hz within parentheses. [b,c] Allylic and benzylic methylene respectively. [d] $-CH_2-(C\underline{H}_2)_2-CH_2-$.

of **1d** has been reported previously by *Bordwell*[5,6]. He suspected that β-sultones or the isomeric zwitterionic intermediates (some doubtful evidence[5] indicates initial β-sultone formation) were the initial products in the formation of the alkenesulfonic acid (Scheme 1).

We have not been able to demonstrate the presence of a β-sultone (or zwitterionic intermediate) in the reaction of styrene with SO_3, even at −30°C. Apparently, the subsequent sulfonation of the β-sultone **1b** to the carbyl sulfate is too fast. The reaction of styrene with 1.0 equiv. of SO_3 and a five-fold excess of dioxane gives relatively slowly the carbyl sulfate; even at −60°C, no β-sultone was detected. The rate of conversion of the β-sultone is apparently large relative to the rate of its formation. In 1954, *Bordwell*[5] presumed that he had isolated the intermediate β-sultone by addition of pentane to the sulfonation solution. On the basis of both our work and that of *Zoller*[7,12] it is very difficult to believe that the product isolated by *Bordwell* was the β-sultone **1b**, since the reaction was carried out at 0°C, at which temperature the conversion of the β-sultone into the carbyl sulfate is fast relative to the preceding β-sultone formation. *Zoller*[7] has suggested that the isolated intermediate was instead the carbyl sulfate, a proposal which is in line with our present results.

The introduction of a chloro or nitro[13] (*i.e.*, an electron-withdrawing) substituent into the *meta* or *ortho* position of the phenyl group may prove the presence of a β-sultone as initial product of the sulfonation of a styrene. In fact, the main product of the reaction of 3-chloro- (**4a**) and 3-nitrostyrene (**5a**) at low temperature is the β-sultone **b** (see Table IV). If the temperature is raised, the β-sultone is converted into the corresponding carbyl sulfate with concomitant reformation of the styrene. Obviously, either an equilibrium between the β-sultone and its styrene precursor occurs or there is a direct disproportionation reaction between two β-sultone molecules; this latter reaction is

Table II ^{1}*H NMR data of β-sultones (1,2-oxathietane 2,2-dioxides).*

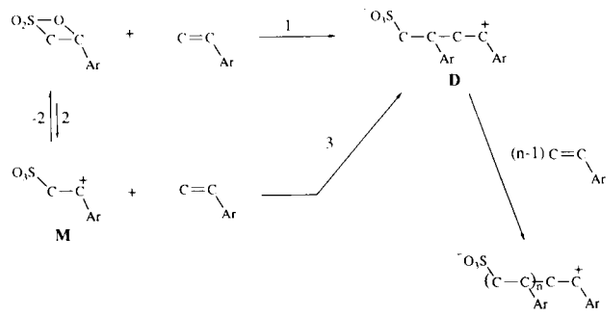
	 b			^{1}H NMR (CD_2Cl_2, δ, ppm)[a]		
X	R^1	R^2	R^3	R^1	R^2	R^3
H	H	H	H	–[b]	–[b]	–[b]
3-NO_2	H	H	H	5.70 (dd) (5.9) (8.1)	4.64 (dd) (5.9) (13.3)	5.20 (dd) (8.1) (13.3)
3-Cl	H	H	H	5.55 (dd) (6.0) (8.0)	4.63 (dd) (6.0) (13.5)	5.13 (dd) (8.0) (13.5)
2-Cl	H	H	H	5.80 (dd) (5.7) (8.1)	4.85 (dd) (5.7) (13.3)	5.45 (dd) (8.1) (13.3)
H	H	Me	H	5.05 (d) (6.4)	1.72 (d) (7.0)	4.79 (q) (7.0)
H	H	H	Me	5.69 (d) (8.4)	5.26 (q) (7.8)	1.11 (d) (7.4)
H	H	Me	Me	5.67 (s)	1.80 (s)	1.42 (s)

[a] Coupling constants in Hz within parentheses. [b] No β-sultone could be detected.

thought to be unlikely. The introduction of a methyl (*i.e.*, an electron-donating) group into the *ortho* or *meta* position of the phenyl ring, as in **7a** and **8a**, has no pertinent effect either on the rate of formation of the sultone or the carbyl sulfate.

The reactions of styrenes with Cl, OMe or OH in the *para* position differ from that of the *meta*- and *ortho*-substituted styrenes in that the ^{1}H NMR spectra are highly complex and contain mainly broad signals indicative of the formation of polymers, and that no specific signals of a β-sultone and/or the corresponding carbyl sulfate were found. The polymerization is thought to proceed (see Scheme 2) via the dimeric benzylic-sulfonate dipolar species **D** which is formed by nucleophilic substitution of the styrene on the β-sultone (step 1), or/and by initial heterolysis of the β-sultone to the monomeric benzylic-sulfonate dipolar species **M** (step 2) and subsequent nucleophilic addition of a styryl molecule thereon (step 3).

The differences in behaviour of 2- and 4-chlorostyrene are unexpected. It may be ascribed (see Scheme 2) to the higher nucleophilicity of 4- compared to 2-chlorostyrene in the initial polymerization step 1, and/or to the higher rate of the

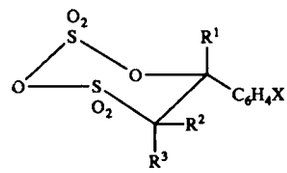


Scheme 2. β-Sultone-catalyzed polymerization of styrene.

heterolysis step 2 for 4- compared to 2-chlorostyrene, leading for 4-chlorostyrene to a very low concentration of β-sultone, which is, in fact, below the limits of ^{1}H NMR detection.

Sulfonation of the (*E*)- and (*Z*)-1-phenyl-1-propenes (**9a** and **10a**) with 2.0 equiv. of sulfur trioxide leads to the formation of the corresponding *trans*- and *cis*-2,1-sultones **9b** and **10b**, respectively, which are converted into the corresponding carbyl sulfates **9c** and **10c**. With (*E*)-1-phenyl-1-propene (**9a**), at –30°C, the conversion of the initial *trans*-β-sultone into the *trans*-carbyl sulfate is fast relative to the formation of the *trans*-β-sultone. The stereospecific formation of the *trans*-carbyl sulfate is in line with the stereospecific formation of the carbyl sulfates from aliphatic external and internal alkenes[1], which are formed by insertion of SO_3 into the $O-SO_2$ bond of the β-sultone. Reaction of (*Z*)-1-phenyl-1-propene (**10a**) with 2.0 equiv. of sulfur trioxide at –30°C quantitatively yields the *cis*-β-sultone **10b**. The stereospecific formation of the β-sultones [(*E*) → *trans* and (*Z*) → *cis*] is in line with the stereospecific formation of β-sultones formed from aliphatic external and internal alkenes[2,14,15]. The further conversion of the *cis*-β-sultone **10b** into the corresponding carbyl sulfate is slow, relative to that observed for the *trans*-β-sultone **9b** in the sulfonation of (*E*)-1-phenyl-1-propene. The main eventual product upon starting with the (*Z*)-styrene derivative **10a** is the *trans*-carbyl sulfate, which is remarkable in view of the (*Z*) → *cis* and (*E*) → *trans* stereoselectivity observed for the carbyl sulfate formation from the β-sultones of simple aliphatic external and internal alkenes[1]. The reaction of (*Z*)-1-phenyl-1-propene (**10a**) with 1.0 equiv. of SO_3 at –30°C also leads to complete formation of the *cis*-β-sultone **10b**, which is converted mainly into the corresponding *trans*-carbyl sulfate **9c** with concomitant reformation of mainly (*E*)-1-phenyl-1-propene (**9a**). The proposed mechanism for the sulfonation of the 1-phenyl-1-propenes is depicted in Scheme 3. The benzylic sulfonate and the benzylic pyrosulfonate dipolar intermediates **A** and **B** are

Table III ^1H *NMR data of the carbyl sulfate products.*

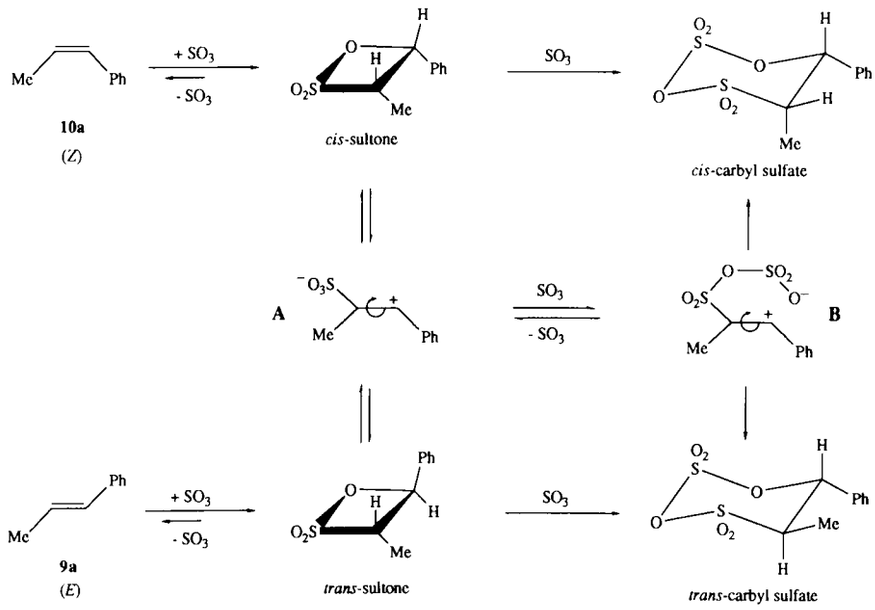
	 c			^1H NMR (CD_2Cl_2, δ, ppm)[a]		
X	R^1	R^2	R^3	R^1	R^2	R^3
H	H	H	H	6.12 (dd) (8.9) (4.5)	4.02 (m)	
3-NO_2	H	H	H	6.26 (dd) (2.3) (11.2)	4.13 (dd) (2.3) (14.6)	4.01 (dd) (11.2) (14.6)
3-Cl	H	H	H	6.10 (dd) (2.5) (10.9)	4.07 (m)	
3-Me	H	H	H	6.08 (dd) (5.5) (8.0)	4.00 (m)	
2-Cl	H	H	H	6.45 (dd) (1.4) (11.6)	4.21 (dd) (1.4) (14.6)	3.89 (dd) (11.6) (14.6)
2-Me	H	H	H	6.27 (dd) (3.4) (9.8)	4.08 (m)	
4-Cl	H	H	H	6.10 (dd) (3.5) (9.6)	4.08 (m)	
H	H	Me	H	5.79 (d) (10.7)	1.32 (d) (7.1)	4.06 (m)
H	H	H	Me	6.14 (d) (2.7)	3.43 (dt) (7.1) (2.7)	1.21 (d) (7.1)
H	H	H	D	6.10 (br)	4.08 (br)	–

[a] Coupling constants in Hz within parentheses.

essential; these species are lower in energy than the corresponding simple alkyl sulfonate type of dipolar species, which lack the benzylic cationic stabilization. The rate of formation of the dipolar intermediate **A** is greater for the *cis*- than the *trans*-sultone as result of a larger relief of strain, the energy content of the *cis* isomer being greater, due to the eclipsed orientation of the Me and Ph groups. Similarly, the rate coefficient will be smaller for the conversion of the dipolar species **A** into the *cis*- than the *trans*-β-sultone. Therefore, the carbyl sulfate which is the eventual product on starting both with (*E*)- and (*Z*)--1-phenyl-1-propene will have mainly the *trans*-configuration. We cannot decide from the present results whether (and if so, to what extent) the conversion of the dipolar inter-

Table IV Composition of reaction mixture on reaction of 3-chloro- (**4a**) *and 3-nitrostyrene* (**5a**) *with* SO_3.

Substrate	SO_3 (equiv.)	Temperature (°C)	Composition (%)			
			a	**b**	**c**	Unidentified product(s)
4a	1.0	−60	36.4	34.0	29.6	–
		−40	38.9	22.2	38.9	–
		−20	44.6	9.6	45.8	–
		0	53.5	–	46.5	–
		25	–	–	10.0	90
5a	0.5	−20	70.1	23.7	6.2	
		0	56.4	34.0	9.6	
		25	76.5	–	23.5	



Scheme 3. Mechanism for the sulfonation of (E)- and (Z)-1-phenyl-1-propene.

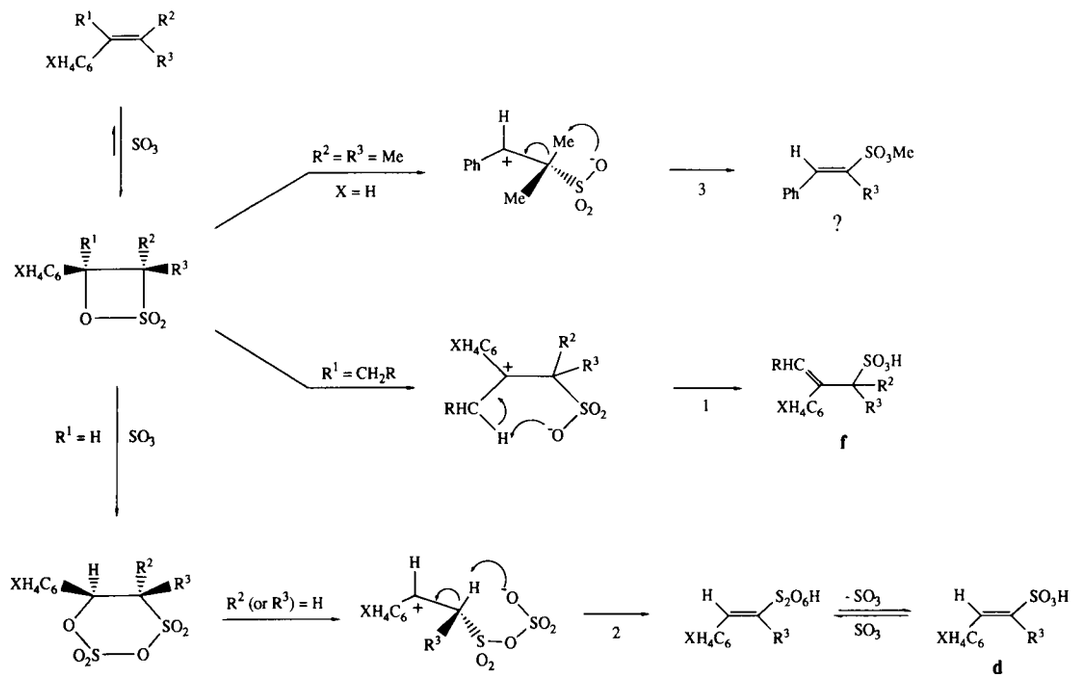
mediate **A** into the two carbyl sulfate isomers proceeds via the dipolar intermediate **B**.

The reaction of styrene derivatives **1a**, **6a** and **7a** with sulfur trioxide yields the 1-alkenesulfonic acids **1d**, **6d** and **7d**, respectively. The α-alkyl-substituted styrenes **11a–13a** react extremely rapidly with SO_3 to yield quantitatively the corresponding 2-alkenesulfonic acids **11f–13f**. The proposed mechanisms for the formation of the two types of alkenesulfonic acids are given in Scheme 4.

Reaction of 2-methyl-1-phenyl-1-propene (**14a**) with 1.0 and 2.0 equiv. of SO_3 at −60 °C quantitatively yields the β-sultone **14b**. The reaction is regiospecific. The sulfur is bound to the tertiary C(2) atom. With simple aliphatic alkenes, the SO_2 moiety is bound to the least substituted carbon atom. Apparently, the effect of the phenyl group is dominant. The β-sultone **14b** is remarkably stable even at 0 °C; it is, in fact, the most stable of the presently obtained β-sultones. The origin of its higher stability is the fact (see Scheme 4) that reaction steps 1 and 2 (in which a proton transfer from carbon to one of the respective sulfonate and pyrosulfonate oxygens are the essential steps) cannot occur, and that the possible alternative Me^+ shift to one of the sulfonate oxygens (step 3) will not occur, or only very slowly.

Experimental

The ^1H- and ^{13}C-NMR spectra were recorded on Bruker AC-200 and WM-250 instruments.



Scheme 4. Mechanism for the formation of unsaturated sulfonic acids in the sulfonation of styrenes.

Materials

1-Methylene-1,2,3,4-tetrahydronaphthalene (**12a**) was synthesized by a simple Wittig reaction of α-tetralone and methyltriphenylphosphonium bromide, using the method described by *Maercker*[17]. (*Z*)-β-Deuteriostyrene (**2a**) was prepared by reduction of 1-phenylacetylene-2-*d*[18], as reported by *Baldwin* et al.[19], at a yield of 20% with an isotopic purity of 97%, determined by ^{1}H NMR. The other styrene derivatives were obtained commercially and used without further purification. The ^{1}H NMR data of the substrates are listed in Table I.

Sulfonation procedures

Method A (standard procedure). Liquid sulfur trioxide (10 µl, 0.24 mmol) was injected into a stirred solution of 32 µl of dioxane-d_8 (0.36 mmol) in 0.5 ml of CD_2Cl_2, cooled at −70 °C under an Ar atmosphere. 25 µl of the styrene (0.24 mmol) were then injected into the stirred solution. The reaction mixture was transferred under Ar into a cooled NMR tube and ^{1}H NMR spectra were taken at chosen temperatures (ranging from −60 °C to room temperature), after appropriate time intervals in which the NMR tube was restored at −70 °C. The complete procedure involved a total time span of 4–6 h unless stated otherwise.

Method B. To a stirred mixture of 1.0 mmol of SO_3, 1.5 mmol of dioxane and 10 ml of dichloromethane at −30 °C, 1.0 or 0.5 mmol of the styrene was injected and the mixture was stirred for 1 h under an Ar atmosphere. The reaction mixture was warmed to 0 °C and poured into 10 ml of water and neutralized to pH 7 with aqueous KOH. The dichloromethane was removed by rotary evaporation and the remaining water and dioxane by freeze-drying. The remaining potassium sulfonate was dissolved in D_2O or DMSO-d_6 and subjected to NMR analysis.

NMR analysis

The structural assignments of the products were made using ^{1}H NMR spectra of the reaction mixture solutions in deuterated solvents or of the isolated potassium sulfonates in D_2O (or DMSO-d_6), on the basis of the observed chemical shifts, absorption area ratios and coupling constants in combination with substituent shielding parameters[20]. The ^{1}H- and ^{13}C-NMR spectral data of the various products are compiled in Tables II and III, and this section. The compositions of the reaction mixtures were determined by multicomponent ^{1}H NMR analysis on the basis of specific absorptions of the assigned components[21].

Potassium (E)-2-phenylethene-1-sulfonate (**1e**). ^{1}H NMR (DMSO-d_6, δ, ppm): 6.86 (d, *J* 15.8 Hz, 1H, PhCH), 6.95 (d, *J* 15.8 Hz, 1H, CHS), 7.45 (m, 5H, C_6H_5). ^{13}C NMR (DMSO-d_6, δ, ppm): 127.0 (Ph C2, C6), 128.3 (CHS), 128.7 (Ph C3), 130.2 (Ph C4), 134.5 (CHPh), 135.2 (Ph C1).

Potassium 2-hydroxy-2-(3-nitrophenyl)ethane-1-sulfonate (**5h**). ^{1}H NMR (D_2O, δ, ppm): 3.26 (dd, *J* 14.3 and 6.9 Hz, 1H, CH^aS), 3.46 (dd, *J* 14.3 and 6.3 Hz, 1H, CH^bS), 5.56 (t, *J* 6.6 Hz, 1H, CHO), 7.44 (t, *J* 8.0 Hz, 1H, Ph H5), 7.67 (d, *J* 7.7 Hz, 1H, Ph H6), 8.08 (dd, *J* 8.3 and 1.0 Hz, 1H, Ph H4), 8.14 (d, *J* 1.0 Hz, 1H, Ph H2). ^{13}C NMR (D_2O, δ, ppm): 58.9 (CH_2S), 79.1 (CHOH), 124.9, 126.5, 132.6, 136.6, 143.3, 150.6 (Ph C).

3,3-Dimethyl-4-phenyl-1,2-oxathietane 2,2-dioxide (**14b**). ^{1}H NMR, see Table II. ^{13}C NMR (CD_2Cl_2, δ, ppm): 23.7 (CH_3), 29.5 (CH_3), 79.7 (CS), 83.6 (CO), 128.4 (Ph C1), 129.3 (Ph C2, C6), 129.6 (Ph C3, C5), 130.2 (Ph C4).

(E)-2-(o-Tolyl)ethene-1-sulfonic acid (**7d**). ^{1}H NMR (CD_2Cl_2, δ, ppm): 2.44 (s, 3H, CH_3), 6.88 (d, *J* 15.4 Hz, 1H, PhCH), 7.90 (d, *J* 15.4 Hz, 1H, CHS), 7.54 (d, *J* 9.0 Hz, 1H, Ph H6), 7.28 (m, 3H, Ph H3, H4, H5).

(E)-2-(m-Tolyl)ethene-1-sulfonic acid (**8d**). ^{1}H NMR (CD_2Cl_2, δ, ppm): 2.38 (s, 3H, CH_3), 6.92 (d, *J* 15.5 Hz, 1H, PhCH), 7.56 (d, *J* 15.5 Hz, 1H, CHS), 7.32 (m, 4H, C_6H_4).

2-Phenyl-2-propene-1-sulfonic acid (**11f**). ^{1}H NMR (CD_2Cl_2, δ, ppm): 4.67 (d, *J* 1.6 Hz, 2H, CH_2S), 7.09 (t, *J* 1.6 Hz, 1H, $=CH^a$), 7.53 (m, 6H, $=CH^b$, C_6H_5).

Potassium (3,4-dihydro-1-naphthalenyl)methanesulfonate (**12g**). ^{1}H NMR (D_2O, δ, ppm): 2.30 (m, 2H, Np H3), 2.76 (t, *J* 8.0 Hz, 2H, Np H4), 4.07 (s, 2H, CH_2S), 6.24 (t, *J* 4.6 Hz, Np H2), 7.22 (m, 3H, Np H5–H7), 7.42 (d, *J* 7.0 Hz, 1H, Np H8). ^{13}C NMR (D_2O, δ, ppm): 25.7 (Np C3), 30.0 (Np C4), 56.6 (CH_2S), 126.1 (Np C2), 130.4 (Np C1), 129.1, 130.1, 130.4 (Np C5–C8), 136.1, 139.6 (Np C4a, C8a).

2-Phenyl-2-cyclohexene-1-sulfonic acid (**13f**). 1H NMR (CD_2Cl_2, δ, ppm): 1.75 (m, 1H, Cy $H6^a$), 2.05 (m, 2H, Cy H5), 2.34 (m, 2H, Cy H4), 2.60 (m, 1H, Cy $H6^b$), 4.44 (br, 1H, Cy H1), 6.30 (t, *J* 3.9 Hz, 1H, Cy H3), 7.33 (m, 5H, Ph). ^{13}C NMR (CD_2Cl_2, δ, ppm): 16.6 (Cy C5), 24.5 (Cy C6), 25.5 (Cy C4), 58.3 (Cy C1), 126.1 (Ph C2, C6), 127.1 (Ph C4), 128.2 (Ph C3, C5), 130.5 (Cy C2), 134.9 (Cy C3), 141.2 (Ph C1).

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