Recl. Trav. Chim. Pays-Bas **111**, 389–401 (1992) 0165–0513/92/09389–13$3.75

Reactions of ω-phenylalkenes with sulfur trioxide; sulfonation and Friedel–Crafts type of cyclization[§]

Ruud M. Schonk, Bert H. Bakker and Hans Cerfontain*

Laboratory of Organic Chemistry, University of Amsterdam, Nieuwe Achtergracht 129, 1018 WS Amsterdam, The Netherlands
(Received March 9th, 1992)

Abstract. Reactions of ω-phenylalkenes **1a–31a** 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. ω-Phenylalkenes **1a–7a** react just like simple alkenes: at low temperature, they yield the (thermally unstable) β-sultones **1b–7b** and **4c–7c**, which at 25 °C are converted into the corresponding carbyl sulfates. Reactions of ω-phenylalkenes **8a–10a**, which have a $-(CH_2)_3-$ linkage between the Ph and the C=C moieties, with 1.1 equiv. of SO_3 at −60 °C yield very rapidly and quantitatively the 1-(1-sulfoalkyl)-1,2,3,4-tetrahydronaphthalenes **8f** and **9f** (= **10f**). Reaction of ω-phenylalkenes **11a** and **12a**, having a $-(CH_2)_2-$ linkage between Ph and C=C, with 1.1 mol equiv. of SO_3 at −60 °C leads to quantitative and stereospecific formation of 1-methyl-1,2,3,4-tetrahydronaphthalene-2-sulfonic acids **11h** and **12h**, respectively. The 5-(chlorophenyl)-2-pentenes **13a–16a** clearly demonstrate the presence of β-sultones **13b–16b** and **13c–16c** as the sole initial products leading to the Friedel–Crafts cyclization products **13h–16h**. Reaction of 1,3-diphenyl-1-propenes **26a** and **27a** with 1.5 equiv. of SO_3 at −60 °C quantitatively yields β-sultones **26c** and **27c**, which upon raising the temperature to −20 °C, are slowly converted into *trans*-1-phenylindane-2-sulfonic acid (**34**).
Attempted intermolecular Friedel–Crafts type of sulfoalkylation of arenes using β-sultones as reagent failed. Reaction of, for example, *trans*-4,5-octanesultone with anisole instead led only to transfer sulfodeprotonation, to yield (*E*)-4-octene and 4-methoxybenzenesulfonic acid.
Mechanisms for the formation of the various products are suggested.

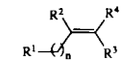
Introduction

As part of our studies on the sulfonation of α-olefins and internal alkenes, we are studying the reaction of monofunctionalized alkenes with sulfur trioxide. Our objective is to determine the effect of the 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 ω-phenylalkenes **1a–31a** with sulfur trioxide. The chemistry of conjugated phenylalkenes (styrenes) with SO_3 has been reported in a previous paper[1] and the chemistry of alkenoic acids and allenes will be reported in the near future.
The initial products of sulfonation of alkenes are thermally unstable β-sultones. The formation of these β-sultones proceeds in a stereospecific *syn* cycloaddition reaction, as shown for *Z* and *E* internal alkenes[2]. Sulfonation of alkenes with an excess of sulfur trioxide generally leads to carbyl sulfates. Carbyl sulfate formation is a two-step process; rapid formation of the β-sultone is followed by slow stereospecific conversion into carbyl sulfate. This may be explained in terms of insertion of SO_3 into the $O-SO_2$ bond of the β-sultone[3].

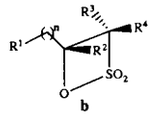
Treatment of phenyl-substituted alkenes and alkanols with strong Brønsted or Lewis acids may lead to cycloalkylation of the resulting carbenium ions[4]. The sulfuric acid sulfonation of ω-phenyl-1-alkanols has previously been reported[5]: reaction of 5-phenyl-1-pentanol and 6-phenyl-1-hexanol with 90% H_2SO_4 at 25 °C for 40 days yielded, after neutralization, mainly potassium 1-(m)ethyl-1,2,3,4-tetrahydronaphthalene-7-sulfonate together with a small amount of the corresponding 5-sulfonate salt. We have studied the reaction of ω-phenyl-1-alkanols with sulfur trioxide. Sulfonation of 5-phenyl-1-pentanol with 2.0 equiv. of SO_3 in dioxane or nitromethane as solvent, yielded 5-phenyl-1-pentyl hydrogen sulfate and 5-(4-sulfophenyl)-1-pentyl hydrogen sulfate, respectively, but no cycloalkylation product was formed[6].
Many examples of reactions of ω-phenylalkenes with Brønsted acids have been reported[4]. For instance, reaction of 3,3-dimethyl-4-phenyl-1-butene with concentrated H_2SO_4 gave a mixture of a trisubstituted indane and disubstituted tetraline in 60% yield[7]. In this paper, we report the scope and limitations of the reactions of ω-phenylalkenes with SO_3, which may act both as a sulfonating reagent and as a Lewis acid.

[§] Aliphatic sulfonation 9. For part 8, see ref. 21.

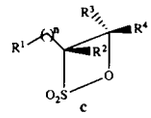
	R^1	R^2	R^3	R^4	n
1	C_6H_5	H	H	H	1
2	C_6H_5	H	H	H	2
3	C_6H_5	H	H	H	4
4	C_6H_5	H	H	CH_3	1
5	C_6H_5	H	CH_3	H	1
6	C_6H_5	H	H	CH_3	4
7	C_6H_5	H	CH_3	H	4
8	C_6H_5	H	H	H	3
9	C_6H_5	H	H	CH_3	3
10	C_6H_5	H	CH_3	H	3
11	C_6H_5	H	H	CH_3	2
12	C_6H_5	H	CH_3	H	2
13	4-ClC_6H_4	H	H	CH_3	2
14	4-ClC_6H_4	H	CH_3	H	2
15	2-ClC_6H_4	H	H	CH_3	2
16	2-ClC_6H_4	H	CH_3	H	2
17	2,4-$Cl_2C_6H_3$	H	H	CH_3	2
18	2,4-$Cl_2C_6H_3$	H	CH_3	H	2
19	2,6-$Cl_2C_6H_3$	H	H	CH_3	2
20	2,6-$Cl_2C_6H_3$	H	CH_3	H	2
21	C_6H_5	H	CH_3	CH_3	2
22	C_6H_5	H	C_2H_5	CH_3	2
23	C_6H_5	H	CH_3	C_2H_5	2
24	C_6H_5	CH_3	H	CH_3	2
25	C_6H_5	CH_3	CH_3	H	2
26	C_6H_5	H	H	C_6H_5	1
27	C_6H_5	H	C_6H_5	H	1
28	C_6H_5	H	H	C_6H_5	2
29	C_6H_5	H	C_6H_5	H	2
30	C_6H_5	H	H	C_6H_5	3
31	C_6H_5	H	C_6H_5	H	3



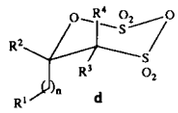
a



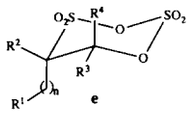
b



c

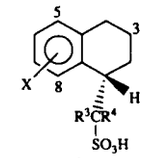


d



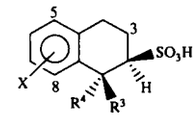
e

		R^3	R^4	X
8	f	H	H	H
8	g	H	H	7-SO_3H
9	f	H	CH_3	H

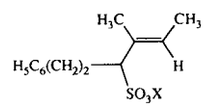


f, g

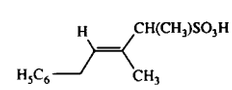
		R^3	R^4	X
11	h	H	CH_3	H
12	h	CH_3	H	H
11	i	H	CH_3	7-SO_3H
12	i	CH_3	H	7-SO_3H
13	h	H	CH_3	7-Cl
14	h	CH_3	H	7-Cl
15	h	H	CH_3	5-Cl
16	h	CH_3	H	5-Cl
21	h	CH_3	CH_3	H
28	h	H	C_6H_5	H
29	h	C_6H_5	H	H



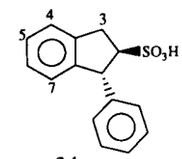
h, i



32k X = H
32l X = K



33k

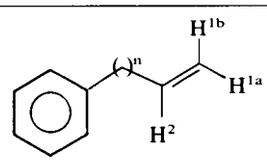


34

Results

Reactions of ω-phenylalkenes **1a–31a** with (in general, 1.0, 1.5 and 2.0 mol equiv. of) SO_3 were studied. The applied standard conditions were: dichloromethane as solvent and 1.5 mol equiv. of dioxane (relative to the amount of SO_3) as reactivity moderator[8] (method A, see Experimental). In order to obtain information on the primary sulfonation products, the reactions were carried out at low temperature, and the reaction mixtures were analyzed by ^1H NMR spectroscopy. The ^1H NMR and some ^{13}C NMR assignments of the ω-phenylalkenes and their sulfo products are compiled in Tables I–IX or in the experimental section.

Table I *^1H NMR data of ω-phenyl-1-alkenes.*

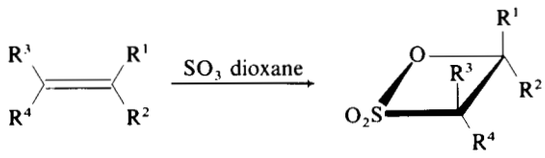


^1H NMR ($CDCl_3$, δ, ppm)[a]

Alkene	*n*	C^1H_2	C^2H	C^3H_2	C^4H_2	C^5H_2	C^6H_2	Ph
1a	1	5.16 (m)	6.10 (m)	3.49 (d) 3.4				7.32 (m)
2a	2	5.06 (m)	5.91 (m)	2.43 (qr) 6.7	2.77 (t) 7.2			7.26 (m)
3a	4	5.02 (m)	5.85 (m)	2.14 (qr) 7.1	1.49 (m)	1.70 (m)	2.67 (t) 7.3	7.25 (m)
8a	3	5.07 (m)	5.84 (m)	2.12 (qr) 7.4	1.74 (qn) 7.8	2.64 (t) 7.6		7.21 (m)

[a] Underlined data represent coupling constants in Hz.

Table II ^1H *NMR data of β-sultone products of ω-phenyl-1-alkenes.*

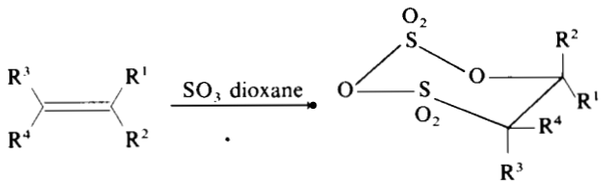


^{1}H NMR (CD_2Cl_2, δ, ppm)[a]

β-Sultone	R^1	R^2	R^3	R^4	R^1	R^2	R^3	R^4
1b	Ph-CH_2	H	H	H	7.32 (m) 3.22 (m)	4.77 (q) 6.36	4.31 (dd) 5.70 12.84	4.62 (dd) 7.49 12.84
2b	Ph-$(CH_2)_2$	H	H	H	7.20 (m) 2.75 (m) 2.20 (m)	4.54 (m)	4.17 (dd) 5.09 12.06	4.61 (dd) 7.62 12.06
3b	Ph-$(CH_2)_4$	H	H	H	7.19 (m) 2.61 (t) 1.64 (q) 1.44 (m) 1.90 (m)	4.56 (m)	4.22 (dd) 5.48 12.48	4.68 (dd) 7.65 12.48
4b	Ph-$(CH_2)_3$	H	H	H	7.16 (m) – [b]	4.57 (m)	4.23 (dd) 5.1 12.38	4.68 (dd) 7.66 12.38

[a] Underlined data represent coupling constants in Hz. [b] This β-sultone is a minor product and so exact absorptions could not be detected.

Table III ^1H *NMR data of carbyl sulfate products of ω-phenyl-1-alkenes.*



^{1}H NMR (CD_2Cl_2, δ, ppm)[a]

Carbyl sulfate	R^1	R^2	R^3	R^4	R^1	R^2	R^3	R^4
1d	Ph-CH_2	H	H	H	7.39 (m) 3.26 (m)	5.30 (m)	3.55 (dd) 11.4 14.5	3.79 (dd) 1.8 14.5
2d	Ph-$(CH_2)_2$	H	H	H	7.29 (m) 2.84 (m) 2.26 (m)	5.10 (m)	3.60 (dd) 11.1 14.6	3.76 (dd) 2.1 14.6
3d	Ph-$(CH_2)_4$	H	H	H	7.20 (m) 2.65 (t) 2.01 (m) 1.89 (m)	5.14 (m)	3.60 (dd) 11.3 14.46	3.78 (dd) 1.86 14.46
8d	Ph-$(CH_2)_3$	H	H	H	– [b]	– [b]	– [b]	– [b]

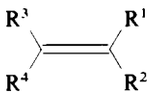
[a] Underlined data represent coupling constants in Hz. [b] Carbyl sulfate not detected.

*Formation of β-sultones and carbyl sulfates**

Sulfonation of ω-phenyl-1-alkenes **1a–3a** with 2.0 equiv. of SO_3, at −60°C leads to the formation of thermally unstable β-sultones **1b–3b** which at 20°C are subsequently converted slowly into the corresponding carbyl sulfates **1d–3d**. Using 4.0 equiv. of SO_3, the formation of 6-(ω-phenylalkyl)-1,3,2,4-dioxadithiane 2,2,4,4,-tetraoxides **1d–3d** is followed by relatively slow sulfonation of the phenyl group at the *para* position, providing the corresponding ω[(4-sulfophenyl)alkyl]-1,3,2,4-dioxadithiane 2,2,4,4,-tetraoxides.

* IUPAC names: β-sultone = 1,2-oxathiane 2,2-dioxide; in *m,n*-sultone, *m* refers to position of SO_2.
Carbyl sulfate = 1,3,2,4-dioxadithiane 2,2,4,4,-tetraoxide.

Table IV ^1H *NMR data of 5-phenyl-2-pentene derivatives*[a].



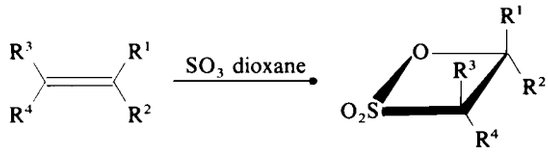
$R^4 = (CH_2)_2R^5$

^1H NMR ($CDCl_3$, δ, ppm)

Alkene	Substituents	R[c]	C^1H	C^2H	C^3H_2	C^4H_2	R^5
9a	R^1 = Me $R^2 = R^3$ = H $R^5 = C_6H_5$	1.70 (dd) 3.3 1.2	------- 5.53 (m) -------		2.36 (m)	2.72 (t) 7.0	7.25 (m)
10a	$R^1 = R^3$ = H R^2 = Me $R^5 = C_6H_5$	1.67 (dd) 5.0 0.9	------- 5.56 (m) -------		2.48 (m)	2.78 (t) 7.2	7.36 (m)
14a	$R^1 = R^3$ = H R^2 = Me $R^5 = 4'\text{-}ClC_6H_4$	1.55 (d) 5.8	------- 5.43 (m) -------		2.33 (m)	2.64 (t) 7.5	7.12 (d) 7.24 (d)
16a	$R^1 = R^3$ = H R^2 = Me $R^5 = 2'\text{-}ClC_6H_4$	1.59 (d) 4.9	------- 5.53 (m) -------		2.41 (m)	2.81 (t) 7.2	7.21 (m, 3H) 7.36 (dd, 1H)
18a	$R^1 = R^3$ = H R^2 = Me $R^5 = 2',4'\text{-}Cl_2C_6H_3$	1.55 (dd) 5.6 0.9	------- 5.46 (m) -------		2.35 (m)	2.75 (t) 7.0	7.15 (m, 2H) 7.36 (s, 1H)
20a	$R^1 = R^3$ = H R^2 = Me $R^5 = 2',6'\text{-}Cl_2C_6H_3$	1.61 (d) 4.9	------- 5.53 (m) -------		2.45 (m)	2.98 (t) 7.8	7.05 (dt, 1H) 7.26 (d, 2H)
21a	$R^1 = R^2$ = Me R^3 = H $R^5 = C_6H_5$	1.59 (s) 1.72 (s)	–	5.24 (m)	2.32 (m)	2.66 (t) 6.0	7.23 (m)
25a	R^1 = H $R^2 = R^3$ = Me (*E*/*Z*) $R^5 = C_6H_5$	1.52 1.73	5.23 (m)	–	2.33 (m)	2.70 (m)	7.26 (m)

[a] The substrates are numbered starting at the double bond. [b] Underlined data represent coupling constants in Hz. [c] R stands for R^1 and/or R^2, as appropriate.

Table V ^1H *NMR data of β-sultone products of 5-phenyl-2-pentene derivatives.*

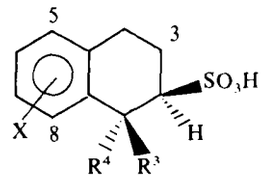


^1H NMR (CD_2Cl_2, δ, ppm)[a]

β-Sultone	R^1	R^2	R^3	R^4	R^1	R^2	R^3	R^4
21c	Me	Me	$Ph(CH_2)_2$	H	1.63 (s)	1.51 (s)	–[b]	4.41 (dd) 4.5 11.0
22c	Me	Et	H	$Ph(CH_2)_2$	1.59 (s)	–[b]	4.36 (dd) 4.9 9.5	–[b]
23c	Me	Et	$Ph(CH_2)_2$	H	1.50 (s)	–[b]	–[b]	4.40 (dd) 4.9 10.9
24b	$Ph(CH_2)_2$	Me	H	Me	–[b]	1.56 (s)	4.85 (q) 7.3	1.47 (d) 7.3
25b	$Ph(CH_2)_2$	Me	Me	H	–[b]	1.56 (s)	1.42 (d) 7.5	4.65 (q) 7.5

[a] Underlined numbers represent coupling constants in Hz. [b] This signal could not be detected.

Table VI ^1H *NMR data of tetraline derivatives.*



Tetraline	Substrate	^1H NMR (δ, ppm)[a]						Solvent[b]
		R^3	R^4	C^2H	C^3H_2	C^4H_2	CH (Ar)	
11h	R^3 = X = H R^4 = Me.	3.32 (m)	1.42 (d) 7.2	3.12 (m)	2.08 (m)	2.79 (m)	7.04 (m)	D_2O
11i	R^3 = H, X = SO_3K R^4 = Me	3.46 (m)	1.46 (d) 7.2	3.46 (m)	2.30 (m)	3.03 (m)	7.77 (m) 7.34 (d)	D_2O
12h	R^4 = X = H R^3 = Me	1.27 (d) 6.8	3.32 (m)	3.12 (m)	2.08 (m)	2.79 (m)	7.04 (m)	D_2O
12i	R^4 = H, X = SO_3K R^3 = Me	1.40 (d) 6.8	------- 3.46 (m) -------		2.30 (m)	3.03 (m)	7.77 (m) 7.34 (d)	D_2O
13h	R^3 = H, X = Cl R^4 = Me	3.47 (m)	1.45 (d) 7.1	3.47 (m)	2.23 (m)	2.89 (m)	7.08 (m)	CD_2Cl_2
14h	R^4 = H, X = Cl R^3 = Me	1.37 (d) 6.9	------ 3.49–3.45 ------		2.23 (m)	2.89 (m)	7.08 (m)	CD_2Cl_2
15h	X = R^3 = H R^5 = Cl, R^4 = Me	3.48 (m)	1.48 (d) 7.2	3.48 (m)	2.25 (m)	± 2.9 (br)	7.15 (m)	CD_2Cl_2
16h	R^4 = X = H R^5 = Cl, R^3 = Me	1.37 (d) 6.9	------- 3.48 (m) -------		2.25 (m)	± 2.9 (br)	7.15 (m)	CD_2Cl_2
21h	R^3 = R^4 = Me X = H	1.54 (s)	1.67 (s)	3.32 (dd) 11.1 2.7	2.45 (m) 2.16 (m)	2.92 (m)	7.28 (br)	CD_2Cl_2
28h	R^3 = X = H R^4 = Ph	4.67 (d) 5.5	7.19 (m)	3.68 (m)	2.28 (m)	3.03 (m)	7.19 (m)	CD_2Cl_2
29h	R^4 = X = H R^3 = Ph	7.19 (m)	4.78 (d) 4.6	3.68 (m)	2.28 (m)	3.03 (m)	7.19 (m)	CD_2Cl_2

[a] Underlined data represent coupling constants in Hz. [b] Spectra in D_2O as solvent refer to the corresponding potassium sulfonate.

Sulfonation of a 1:2.1 mixture of (*E*)- (**4a**) and (*Z*)--4-phenyl-2-butenes (**5a**) with 2.0 equiv. of SO_3 at −60°C gave immediately a complex mixture of *trans*- and *cis*-2,3--sultones (**4b** + **5b**) and isomeric 3,2-sultones (**4c** + **5c**). Similar results were found for the reaction of a 1:4 mixture of (*E*)- (**6a**) and (*Z*)-7-phenyl-2-heptene (**7a**). For both (**4a** + **5a**) and (**6a** + **7a**), the 2,3-sultone/3,2-sultone ratio = 4:1, the *trans*/*cis* ratio of the sultones is the same as the starting *E*/*Z* ratio of ω-phenyl-2-alkenes **4a–7a**. After raising the temperature to 20°C, the sultones are converted slowly into their corresponding carbyl sulfates.

Friedel–Crafts type of cycloalkylation reactions

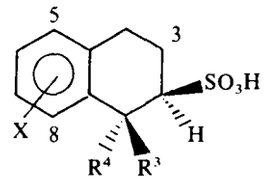
Reaction of 5-phenyl-1-pentene (**8a**) with 1.1 equiv. of SO_3 at −60°C yields rapidly and quantitatively 1-(sulfomethyl)--1,2,3,4-tetrahydronaphthalene (**8f**). Initial products, such as the β-sultone or its carbyl sulfate, could not be detected, even at −60°C. Reaction of **8a** with ≥2 equiv. of SO_3 at −60°C leads to the rapid formation of **8f**, followed, at room temperature, by slow sulfonation at the phenyl ring to yield 1-(sulfomethyl)-1,2,3,4-tetrahydronaphthalene-7-sulfonic acid (**8g**). Reaction of **8a** with 1.2 equiv. of SO_3 according to method B (see Experimental) gave potassium 1-(sulfomethyl)-1,2,3,4-tetrahydronaphthalene in 93% yield.

Reaction of (*E*)- (**9a**) and (*Z*)-6-phenyl-2-hexene (**10a**) with 1.2 equiv. of SO_3, at low temperature, leads to the exclusive formation of 1-(1-sulfoethyl)-1,2,3,4-tetrahydronaphtalene (**9f**). This Friedel–Crafts type of cyclization is extremely fast: at −60°C, it is complete within 10 min.

Sulfonation of mixtures of different ratios of (*E*)- (**11a**) and (*Z*)-5-phenyl-2-pentene (**12a**) (1.0:3.0, 1.0:1.0 and 4.6:1.0) with 2.0 equiv. of SO_3 leads to a similar intramolecular Friedel–Crafts alkylation, to yield quantitatively the *trans* and *cis* isomers of 1-methyl-1,2,3,4-tetrahydronaphthalene--2-sulfonic acid (**11h** and **12h**)[9] in the same ratio as the starting *E*/*Z* ratio of the 2-pentenes **11a** and **12a**. Reaction of a mixture of **11a** and **12a** with an excess (≥4 equiv.) of SO_3 according to method B gave a mixture of the *trans* and *cis* isomers of dipotassium 1-methyl-1,2,3,4-tetrahydronaphthalene-2,7-disulfonate (**11i** and **12i**).

Reaction of a 1:3 mixture of (*E*)- (**13a**) and (*Z*)-5-(4-chlorophenyl)-2-pentenes (**14a**) and a 1:2.8 mixture of (*E*)- (**15a**) and (*Z*)-5-(2-chlorophenyl)-2-pentenes (**16a**) with 1.0 equiv.

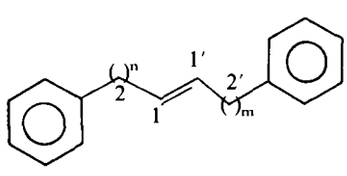
Table VII ^{13}C *NMR data of tetraline derivatives.*



Tetraline	Substrate	R^b	^{13}C NMR (δ, ppm) C(1)	C(2)	C(3)	C(4)	C(5–8)	Solvent[a]
11h	R^3 = X = H R^4 = Me	25.2	32.1	63.2	22.0	26.4	± 126	D_2O
12h	R^4 = X = H R^3 = Me	19.3	34.0	61.2	18.9	28.5	± 126	D_2O
13h	R^3 = H, X = Cl R^4 = Me	26.4	35.6	63.4	24.4	27.7	± 130	D_2O
14h	R^4 = H, X = Cl R^3 = Me	20.2	36.1	61.3	20.8	29.7	± 132	D_2O
21h	R^3 = R^4 = Me X = H	25.6 30.8	38.2	69.8	23.0	29.6	± 127	CD_2Cl_2
28h	R^3 = X = H R^4 = Ph	–	44.6	62.3	19.0	28.2	–	CD_2Cl_2
29h	R^4 = X = H R^3 = Ph	–	45.1	64.7	22.2	26.8	–	CD_2Cl_2

[a] Spectra in D_2O as solvent refer to the corresponding potassium sulfonate. [b] R stands for R^3 and/or R^4, as appropriate.

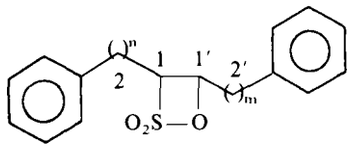
Table VIII ^1H *NMR data of 1,ω-diphenylalkenes.*



Alkene		2 × Ph	^1H NMR ($CDCl_3$, δ, ppm)[a] H^4	H^3	H^2	H^1	$H^{1'}$
26a, **27a**	*n* = 1 *m* = 0	7.35 (m)			3.57 (d) 3.72 (d)	6.50 (m)	
28a, **29a**	*n* = 2 *m* = 0	7.39 (m)		2.92 (t) 8.1	2.65 (m) 2.77 (m)	6.50 (m)	
30a, **31a**	*n* = 3 *m* = 0	7.27 (m)	2.68 (m)	1.81 (m)	2.30 (m)	6.41 (m)	

[a] Underlined data represent coupling constants in Hz.

Table IX CHO and CHS ^1H NMR data of β-sultone products of 1,ω-diphenylalkenes.



^1H NMR (CD_2Cl_2, δ, ppm)[a]

β-Sultone	Config.		H$^{1'}$	H^1
26a	*trans*	*n* = 1 *m* = 0	5.25 (d) 6.3	4.94 (q) 6.4
27a	*cis*		5.72 (d) 8.5	5.41 (m)
29a	*cis*	*n* = 2 *m* = 0	5.63 (d) 8.4	5.08 (m)
30a	*trans*	*n* = 3 *m* = 0	5.10 (d) 6.2	4.71 (q) 6.9
31a	*cis*		5.67 (d) 8.4	5.11 (m)

[a] Underlined data represent coupling constants in Hz.

Table X 2,3- and 3,2-sultone ratios on sulfonation of 2-alkenes and ω-phenyl-2-alkenes[a] with SO_3 in dichloromethane at −60°C.

Alkene[b]		β-Sultone composition at −60°C (%)	
		2,3 (**b**)	3,2 (**c**)
(*E*)-2-hexene[6]		82	18
(*Z*)-2-hexene[6]		80	20
(*E*)-2-octene[23]		80	20
(*E*)-7-phenyl-2-heptene	(**6a**)	79	21
(*Z*)-7-phenyl-2-heptene	(**7a**)	80	20
(*E*)-5-(2-chlorophenyl)-2-pentene	(**13a**)	36	64
(*Z*)-5-(2-chlorophenyl)-2-pentene	(**14a**)	38	62
(*E*)-5-(4-chlorophenyl)-2-pentene	(**15a**)	37	63
(*Z*)-5-(4-chlorophenyl)-2-pentene	(**16a**)	39	61
(*E*)-5-(2,4-dichlorophenyl)-2-pentene	(**17a**)	41	59
(*Z*)-5-(2,4-dichlorophenyl)-2-pentene	(**18a**)	40	60
(*E*)-5-(2,6-dichlorophenyl)-2-pentene	(**19a**)	39	61
(*Z*)-5-(2,6-dichlorophenyl)-2-pentene	(**20a**)	39	61
(*E*)-4-phenyl-2-butene	(**4a**)	83	17
(*Z*)-4-phenyl-2-butene	(**5a**)	81	19
(*E*)-3-phenyl-2-propene[1,a]		≥98	≤2
(*Z*)-3-phenyl-2-propene[1,a]		≥98	≤2

[a] For reasons of convenience the 1-phenyl-1-propenes are numbered as being a ω-phenyl-2-alkene. [b] The 6-phenyl-2-hexenes (**9a** and **10a**) and 5-phenyl-2-pentenes (**11a** and **12a**) at −60°C cyclize too rapidly to determine the ratio of the intermediary 2,3- and 3,2-sultones.

of SO_3 yields at low temperature (−60°C) a mixture of the *trans*- and *cis*-2,3-sultones (**13b** + **14b** and **15b** + **16b**), the *trans*- and *cis*-3,2-sultones (**13c** + **14c** and **15c** + **16c**) and the Friedel–Crafts cyclization products 1-methyl-7-chloro--1,2,3,4-tetrahydronaphthalene-2-sulfonic acids (**13h** + **14h**) and 1-methyl-5-chloro-1,2,3,4-tetrahydronaphthalene-2-sulfonic acids (**15h** + **16h**), respectively. For both the reaction of **13a** + **14a** and **15a** + **16a**, the 2,3-sultone/3,2-sultone ratio is 2:3 (see Table X). The *trans* and *cis* isomers of the sultones and of the cyclization products are in the same ratios as the starting *E*/*Z* ratios of the starting materials **13a–16a**. After raising the temperature to 20°C, the sultones were converted rapidly into the substituted tetralines **13h** + **14h** and **15h** + **16h**, respectively. Sulfonation of a mixture of (*E*)- (**17a**) and (*Z*)-5-(2,4-dichlorophenyl)-2-pentene (**18a**) and of a mixture of (*E*)- (**19a**) and (*Z*)-5--(2,6-dichlorophenyl)-2-pentene (**20a**) with 1.0 equiv. of SO_3 at −60°C leads to complete conversion into the 2,3- and 3,2-sultones, again in a ratio of 2:3. Reaction of the mixtures of geometric isomers **17a** + **18a** and **19a** + **20a** with ≥2.0 equiv. of SO_3 leads, after the initial fast formation of β-sultones, to subsequent slow conversion into the corresponding carbyl sulfates **17d–20d** and **17e–20e**; in fact, the conversion of the β-sultones after 5 days at room temperature is only 60%. Reaction of an isomeric mixture of 5-(4-chlorophenyl)-2-pentenes (**13a** and **14a**) with 0.9 equiv. of SO_3 at −60°C gave a 8.5:0.5:1.0 mixture of the substituted tetralines (**13h** and **14h**), β-sultones [2,3-sultones (**13b** and **14b**) and 3,2-sultones (**13c** an **14c**)] and starting compound. After raising the temperature to 25°C, the composition of the reaction mixture remained the same; only after 12 h at room temperature were all the various sultones present converted into tetralines **13h** and **14h**. However, upon injection of 0.2 equiv. of SO_3 into the reaction mixture formed at −60°C, the β-sultone products and the unconverted substrate were rapidly converted into substituted tetralines **13h** and **14h**.

The (characteristic) ^1H NMR data of the 2,3- and 3,2-sultones, resulting from **13a–20a**[10], are listed in Table XI.

5-Phenyl-2-pentenes. Reaction of 5-phenyl-2-methyl-2-pentene (**21a**) with 1.0 equiv. of SO_3 at low temperature (−60°C) yields quantitatively 3,2-sultone **21c**. This rapid sultone formation is followed, at 0°C, by slow conversion into 1,1-dimethyl-1,2,3,4-tetrahydronaphthalene-2-sulfonic acid (**21h**). The ^{13}C NMR data of **21c** are given in the Experimental. Reaction of **21a** with 1.0 equiv. of SO_3 according to method B gave the potassium salt of **21h**.

Sulfonation of a 1.3:1 mixture of (*Z*)- (**22a**) and (*E*)-6-phenyl-3-methyl-3-hexene (**23a**) with 1.0 equiv. of SO_3, at −60°C also leads to the complete formation of a 1.3:1 mixture of the *cis*- and *trans*-4,3-sultones **22c** and **23c**, which are then both slowly converted into (*E*)-6-phenyl--3-methyl-2-hexene-4-sulfonic acid (**32k**). A similar reaction occurs with a 1:1 mixture of (*E*)- (**24a**) and (*Z*)-5-phenyl--3-methyl-2-pentene (**25a**). After rapid formation (at −60°C) of *cis*- and *trans*-2,3-sultones **24b** and **25b**, slow

Table XI ^1H NMR data of 2,3- and 3,2-sultones of **13a–20a**.

Sultone (**13–20**)	Configuration	H^2 (δ, (±0.05) ppm)	H^3 (δ, (±0.05) ppm)
2,3-sultone (**13b**, **15b**, **17b**, **19b**)	*trans*	4.47 (m)	4.14 (m)
(**14b**, **16b**, **18b**, **20b**)	*cis*	4.95 (q)[a]	4.59 (m)
3,2-sultone (**13c**, **15c**, **17c**, **19c**)	*trans*	4.34 (m)	4.34 (m)
(**14c**, **16c**, **18c**, **20c**)	*cis*	4.79 (m)	4.79 (m)

[a] *J* 7.64 Hz.

conversion (at 0°C) into only (*E*)-5-phenyl-3-methyl--3-pentene-2-sulfonic acid (**33k**) took place. Reaction of **22a** and **23a** with 2.0 equiv. of SO_3 and subsequent alkaline work-up gave only potassium (*E*)-6-phenyl-3-methyl--2-hexene-4-sulfonate (**32l**) in high yield (90%).

1,ω-Diphenylalkenes. Reaction of a 1 : 1 mixture of (*E*)- (**26a**) and (*Z*)-1,3-diphenyl-1-propene (**27a**) with 1.0 equiv. of SO_3 at −60°C leads to formation of a 1 : 1 mixture of the 2,1-sultones **26c** and **27c**. The *trans*-2,1-sultone **26c** is at −20°C slowly converted into *trans*-carbyl sulfate **26e**, whereas *cis*-2,1-sultone **27c** is at 0°C slowly converted into 1-phenylindane-2-sulfonic acid (**34**) (one isomer only[11]). At room temperature, *trans*-carbyl sulfate **26e** is also eventually converted into disubstituted indane **34**.

Reaction of a mixture of isomers (*E*)- (**28a**) and (*Z*)--1,4-diphenyl-1-butene (**29a**) in a ratio of 2.5 : 1 with 1.5 equiv. of SO_3 at −60°C leads to the stereospecific formation of *trans*- and *cis*-2,1-sultones **28c** and **29c** (*trans*/*cis* 2.5 : 1), compounds which are relatively rapidly converted into a mixture of *trans*- (**28h**) and *cis*-1-phenyl-1,2,3,4-tetrahydronaphthalene-2-sulfonic acid (**29h**) in the same isomeric ratio as the starting material. Sulfonation of a 1.7 : 1 mixture of (*E*)- (**30a**) and (*Z*)-1,5-diphenyl-1-pentene (**31a**) with 2.0 equiv. of SO_3 leads at −60°C to the rapid formation of *trans*- (**30c**) and *cis*-2,1-sultones (**31c**), respectively, in a 1.7 : 1 ratio. After raising the temperature to −20°C, the 2,1-sultones are both slowly converted into *trans*-carbyl sulfate **30e**[12].

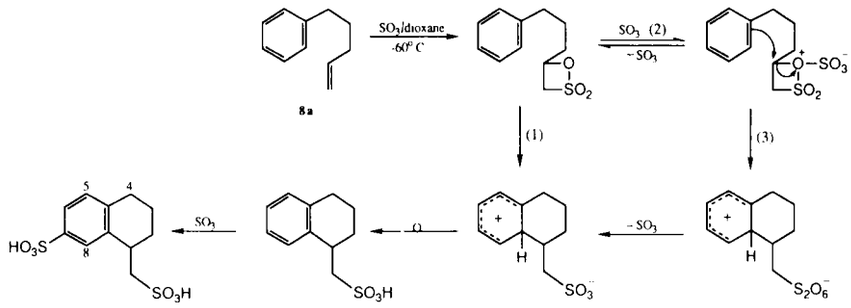
Attempts to effect intermolecular Friedel–Crafts type of alkylation

Reaction of *cis*-4-octene with 1.0 equiv. of SO_3 in chloroform at −40°C leads to quantitative formation of the 4,5-sultone[13]. After raising the temperature to 20°C and adding 1.2 mol equiv. of methoxybenzene, the reaction mixture was found to contain (*Z*)-4-octene, *cis*-4,5-octanesultone, 1-methoxybenzene and 1-methoxybenzene-4-sulfonic acid[13] as the only components, illustrating transfer-sulfonation of the arene by the β-sultone. Similar reactions were carried out with 1-octene and *trans*-4-octene in order to establish the effect of the β-sultone structure (see Table XII). The results clearly demonstrate the difference in transfer sulfonation in the order 1,2- > *cis*-4,5- > *trans*-4,5--octanesultone. We have also varied the arene and have compared toluene, anisole and 1,3-dimethoxybenzene in their reactions with *cis*-4,5-octanesultone in chloroform (see Table XII). Toluene with *cis*-4,5-octanesultone does not lead to transfer sulfonation. The experimental data of the transfer sulfonation of anisole and 1,3-dimethoxybenzene are compiled in Table XII. In order to test whether the intermolecular Friedel–Crafts alkylation can be induced by

Table XII Reaction of arenes with β-sultones[13] *in 0.50 ml of* CD_2Cl_2 *and 0.36 mmol dioxane-*d_8 *at 22°C.*

Substrate	Reagent	Reaction time (min)	Reaction mixture composition (mmol)			
			Arene	β-Sultone	Arene-4--sulfonic acid	Alkene[a]
toluene	*cis*-4,5-octanesultone	0	0.290	0.182	0	0.058
		120	0.290	0.182	0	0.058
		1430	0.290	0.182	0	0.058
anisole	*cis*-4,5-octanesultone	0	0.290	0.168	0	0.072
		110	0.271	0.149	0.019	0.091
		220	0.261	0.139	0.029	0.101
		355	0.247	0.125	0.043	0.115
		1425	0.184	0.062	0.106	0.178
1,3-dimethoxybenzene	*cis*-4,5-octanesultone	0	0.290	0.162	0	0.078
		90	0.258	0.130	0.032	0.110
		215	0.226	0.098	0.064	0.142
		345	0.195	0.067	0.095	0.173
		1415	0.128	0	0.162	0.240
anisole	*trans*-4,5-octanesultone	0	0.290	0.189	0	0.051
		95	0.277	0.176	0.013	0.064
		215	0.273	0.172	0.017	0.068
		335	0.267	0.166	0.023	0.074
		1425	0.223	0.122	0.067	0.118
anisole	1,2-octanesultone[b]	0	0.290	0.143	0	0.061
		110	0.263	0.116	0.027	0.088
		230	0.235	0.088	0.055	0.116
		400	0.207	0.060	0.083	0.144
		1430	0.157	0	0.143	0.204
anisole	*cis*-4,5-octanesultone + 0.072 mmol SO_3 (at *t* 10 min)	0	0.290	0.194	0	0.046
		110	0.167	0.194	0.113	0.046
		235	0.148	0.175	0.142	0.065
		355	0.129	0.156	0.161	0.084
		1400	0.146	0.073	0.244	0.167
toluene	*cis*-4,5-octanesultone + 0.072 mmol SO_3 (at *t* 10 min)	0	0.290	0.184	0	0.056
		105	0.290	0.240	0	0

[a] The *cis*- and *trans*-4,5-octanesultone yield (*Z*)- and (*E*)-4-octene, respectively. [b] At −60°C in addition to the 1,2-octanesultone, 15% of β,γ-unsaturated sulfonic acid was formed, probably by a direct "ene" type of reaction, the amount of which remained constant at 22°C for 1430 min[23].



Scheme 1. Mechanisms for cycloalkylation of 5-phenyl-1-pentene (**8a**) *with* SO_3.

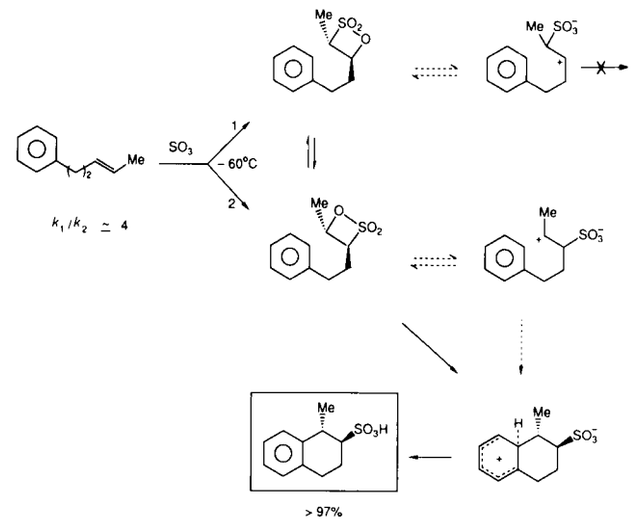
SO_3 catalysis, as was observed for the cycloalkylation of the 5-(4-chlorophenyl)-2-pentenes **13a** and **14a**, we added 0.3 equiv. of SO_3 directly after mixing *cis*-4,5-octanesultone with 1.2 equiv. of anisole at 22°C. This led only to the very rapid formation of 0.3 equiv. of anisole-4-sulfonic acid and did not lead to any Friedel–Crafts alkylation. Mixing of *cis*-4,5-octanesultone with 1.2 equiv. of toluene and addition of 0.3 equiv. of SO_3 led to the sulfonation of the remaining (*Z*)-4-octene (*cf.*, Table XII) and not to the sulfonation of toluene. Attempts at intermolecular Friedel–Crafts alkylation of 1,3-xylene with *trans*-4,5-octanesultone as reagent, using 2.1 mol equiv. of aluminum chloride as a catalyst[22], did not lead to any alkylated product.

Discussion

Reaction of ω-phenyl-1-alkenes **1a–3a** with sulfur trioxide at −60°C yields quantitatively β-sultones **1b–3b**[15]. At 25°C, these β-sultones in the presence of a residual of SO_3 are converted into their corresponding carbyl sulfates **1d–3d**. With the ω-phenylalkenes, there is intramolecular competition between the C=C and phenyl moieties for reaction with SO_3. With 1.0 equiv. of SO_3, no sulfo-deprotonation of the phenyl group is observed beyond the limits of ^{1}H NMR detection which is 2%. Applying the relationship of the relative substrate conversion for two competitive *intra*molecular reactions as a function of time, as reported by *Ingold*[16], to each of the three ω-phenylalkenes **1a–3a**, it follows that $k_{olefine}/k_{phenyl} \geq 100$. This is in line with the value of 130 reported by *Takei* et al.[17] for the intermolecular competition of 1-hexadecene and dodecylbenzene. With respect to the relative reactivity of the β-sultone and phenyl group towards SO_3, we also did not observe sulfo-deprotonation of the phenyl group beyond the limits of ^{1}H NMR detection.

Reaction of 5-phenyl-1-pentene (**8a**), which has a $-(CH_2)_3-$ linkage between the Ph and the C=C, with 1.1 equiv. of SO_3 at −60°C yields very rapidly and quantitatively 1-(sulfomethyl)-1,2,3,4-tetrahydronaphthalene (**8f**). We propose that the formation of **8f** proceeds as shown in Scheme 1. Initial β-sultone formation is followed by S_N2 displacement of the phenyl C(2′) on the oxygen-carrying carbon. Although we have not been able to demonstrate the presence, even at −60°C, of a β-sultone or carbyl sulfate as intermediate in this sulfocyclization reaction, we propose the existence of a β-sultone because of the results found for reactions of the (monochlorophenyl)alkenes with SO_3 (see later). Sulfonation of 5-phenyl-1-pentene (**8a**) with an excess of sulfur trioxide (>2 equiv.) at −60°C leads to cycloalkylation, which is followed at 20°C by sulfonation of the phenyl ring of the resulting tetraline **8f** to yield 1-(sulfomethyl)-1,2,3,4-tetrahydronaphthalene-7-sulfonic acid (see Scheme 1). Exclusive sulfonation at position 7 is in line with the results of *Schaasberg–Nienhuis*[18], who observed that the rate constants for the sulfonation of ω-phenyl-1-alkenesulfonic acids with sulfuric acid at the *para* position increase strongly with increasing length of the intermediate polymethylene chain[19]. Reaction of the 5-phenyl-2-hexenes (**9a** + **10a**), which also have a $-(CH_2)_3-$ linkage between the Ph and the C=C, with 1.1 equiv. of SO_3 at −60°C yields very rapidly and quantitatively 1-(1-sulfoethyl)-1,2,3,4-tetrahydronaphthalene (**9f**).

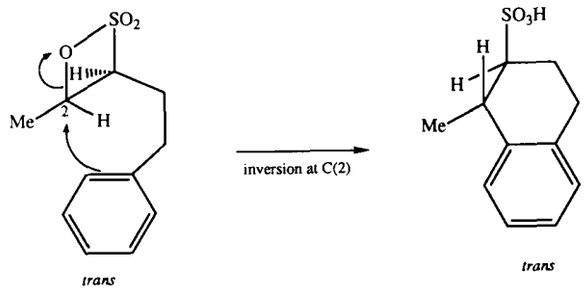
Reaction of (*E*)- (**11a**) and (*Z*)-5-phenyl-2-pentenes (**12a**), which have a $-(CH_2)_2-$ linkage between the Ph and C=C, with 1.1 equiv. of SO_3 at −60°C leads to the quantitative formation of **11h** and **12h**, respectively. For a series of experiments with varying ratios of (*E*)- and (*Z*)-5-phenyl-2-pentene (1:3, 1:1 and 4.6:1), sulfocyclization was in each experiment found to lead to the same ratio of the resulting *trans* and *cis* isomers as that of the starting (*E*) and (*Z*) isomers, indicating (i) that β-sultones are the likely intermediates and (ii) that cyclization proceeds stereospecifically (see Scheme 2).



Scheme 2. Cycloalkylation of (E)*-5-phenyl-2-pentene* (**11a**).

According to the results on the sulfonation of (*E*)-2-octene obtained by *Bakker*[20] and on those of (*E*)- (**6a**) and (*Z*)-7-phenyl-2-heptene (**7a**), one would expect that, with both the 5-phenyl-2-pentenes (**11a** and **12a**) and the 6-phenyl-2-hexenes (**9a** and **10a**), a mixture of 2,3- and 3,2-sultones will be formed in a ratio of 4:1 (*cf.*, Table X). The formation of only one final cyclization carbon skeleton (≥97%), *viz.*, 1-methyl-1,2,3,4-tetrahydronaphthalene-2-sulfonic acids (**11h** and **12h**) and 1-(1-sulfoethyl)-1,2,3,4-tetra-

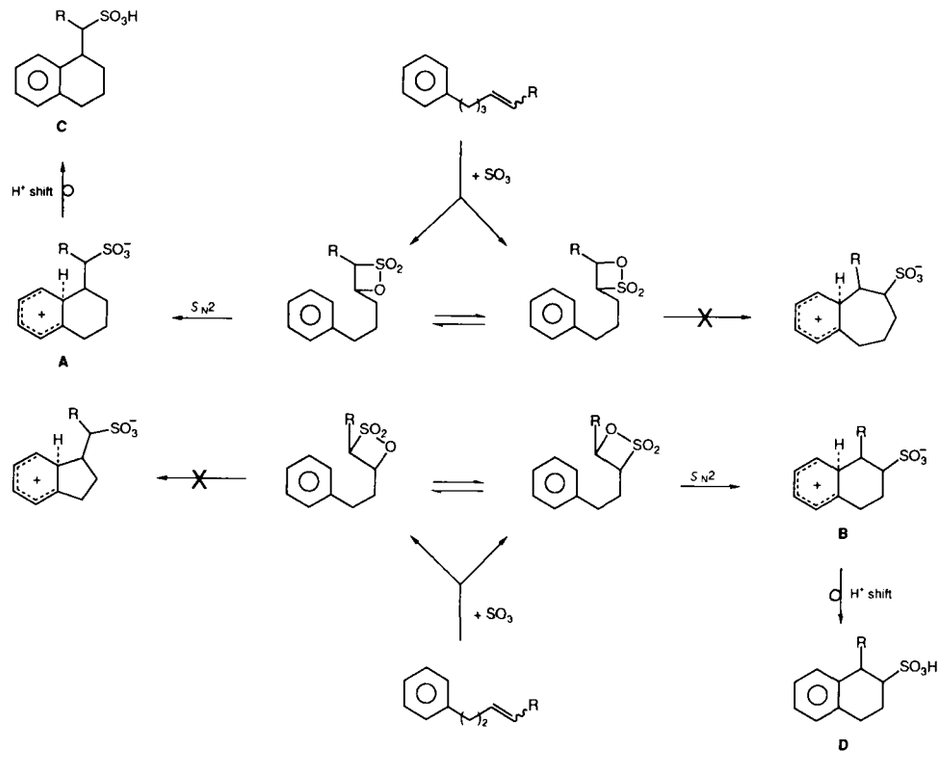
hydronaphthalene (**9f**), respectively, is, therefore, unexpected. Apparently, an equilibrium must exist between the isomeric *m,n*- and *n,m*-sultones of which the interconverting steps have to be very fast, even at −60°C, which may proceed by a direct or indirect interconversion via the starting phenylalkene and sulfur trioxide (see later). The present results clearly show that the reaction is stereospecific and proceeds with inversion at C(2). Therefore, we describe the sulfocyclization as an S_N2 reaction at C(2), as depicted in Scheme 3. This assignment is in line with the



Scheme 3. S_N2 *cycloalkylation of* trans-*5-phenyl-3,2-pentanesultone.*

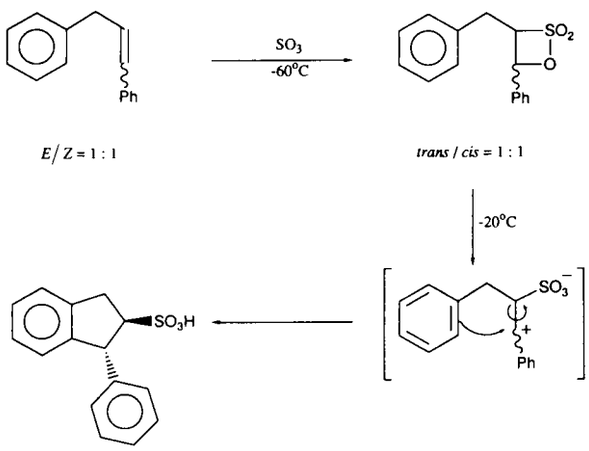
mechanism for the hydrolysis of aliphatic β-sultones which proceeds with inversion under neutral and acidic reaction conditions[21]. S_N2 type of reactions of *trans*- (**9b**) and *cis*--6-phenyl-2,3-hexanesultone (**10b**) and *trans*- (**11c**) and *cis*--5-phenyl-3,2-pentanesultone (**12c**) lead (see Scheme 4) to σ-complexes **A** and **B**, respectively. The final cyclization products **C** and **D** are subsequently formed by proton transfer in a six-membered cyclic transition state. We never observed formation of an indane skeleton for sulfur trioxide cycloalkylation of simple ω-phenylalkenes as observed by *Colonge*[7] using sulfuric as reagent.

A method to demonstrate the presence of β-sultones, as precursor for cycloalkylation, is to introduce one or two deactivating chloro substituents in the phenyl ring which will reduce nucleophilicity of the phenyl group and thus lower the rate of the Friedel–Crafts type of cyclizaton. In fact reaction of 5-(4-chlorophenyl)-2-pentenes (**13a** and **14a**) and 5-(2-chlorophenyl)-2-pentenes (**15a** and **16a**) with SO_3 at −60°C gave a mixture of 2,3- and 3,2-sultone in ratio 2:3. However, subsequent Friedel–Crafts reaction is still quite fast at that temperature. The reaction of 5-(2,4--dichlorophenyl)-2-pentene (**17a** and **18a**) and 5-(2,6--dichlorophenyl)-2-pentene (**19a** and **20a**) with SO_3 at −60°C, also gave a mixture of 2,3- and 3,2-sultones in a ratio 2:3. With these substrates, the β-sultone does not undergo Friedel–Crafts cyclization to form the substituted tetraline, because the 6-position of the phenyl group is not sufficiently reactive (as with **17a** and **18a**), or it is blocked by chlorine (as with **19a** and **20a**). Reaction of both (**17a** + **18a**) and (**19a** + **20a**) with excess of sulfur trioxide (≥2 equiv.) leads, after rapid formation at −60°C of the two *m,n*- and *n,m*-alkanesultones, to formation of the corresponding carbyl sulfates. This reaction is very slow at 25°C: after 5 days, only 60% of the β-sultones were converted. The ratio of unconverted β-sultones remains 2:3, illustrating that rate coefficients for SO_3 insertion into the $O-SO_2$ bond are approximately equal for the two β-sultones.
Reaction of 1,4-diphenyl-1-butenes (**28a** and **29a**) with 1.5 equiv. of SO_3 at −60°C leads, analogously to that of the geometric isomers of 5-phenyl-2-pentene (**11a** and **12a**), to quantitative formation of 1-phenyl-1,2,3,4-tetrahydronaphthalene-2-sulfonic acids (**28h** and **29h**). This sulfocyclization proceeds stereospecifically and is very fast even at −60°C. Reaction of 1,3-diphenyl-1-propenes (**26a** and **27a**) with 1.5 equiv. of SO_3 at −60°C quantitatively yields the *trans*- and *cis*-2,1-sultones, respectively, which upon raising the temperature to −20°C are slowly converted into 1-phenylindan-2-sulfonic acid (**34**). Starting with a 1:1 mixture of (*E*)- and (*Z*)-1,3-diphenyl-1-propene, only one isomer of **34**



Scheme 4. General mechanism for cycloalkylation of ω-phenylalkenes.

is formed, which is probably the *trans* isomer for steric reasons, illustrating that the cycloalkylation is not stereospecific. It is, therefore, proposed that the sulfocyclization proceeds via the conjugatively stabilized benzylic sulfonate dipolar intermediate (see Scheme 5).



Scheme 5. Mechanisms for cycloalkylation of (E)- (**26a**) *and (Z)-1,3-diphenyl-1-propene* (**27a**) *with* SO_3.

Such a dipolar intermediate is also important in the sulfonation of a 1.7 : 1 mixture of (*E*)- (**30a**) and (*Z*)-1,5-diphenyl--1-pentene (**31a**) with 2.0 equiv. of SO_3. At −60 °C, stereospecific formation of β-sultones **30c** and **31c** took place, followed by non-stereospecific conversion, via the dipolar intermediate, into the *trans*-carbyl sulfate **30e**. It thus appears that benzylic sulfonate dipolar species[1] are essential intermediates in the reduction, or even the total loss of stereospecificity in the Friedel–Crafts cyclization upon sulfonation of 1,3- and 1,5-diphenyl-1-alkenes with SO_3 at temperatures above −20 °C.

*Inter*molecular Friedel–Crafts alkylation of arenes by sultones was reported by *Truce* and *Hoerger*[22], who showed that 1,4-butanesultone readily reacts with aromatic compounds in the presence of aluminum chloride as catalyst to give good yields of 4-aryl-1-butanesulfonates. For the dependence of the rate of cycloalkylation of 5-(4-chlorophenyl)-2-pentene (**13a**) on the SO_3 concentration, it appears that the tetralinesulfonic acid formation is catalyzed by SO_3 (see Scheme 1, steps 2 + 3).

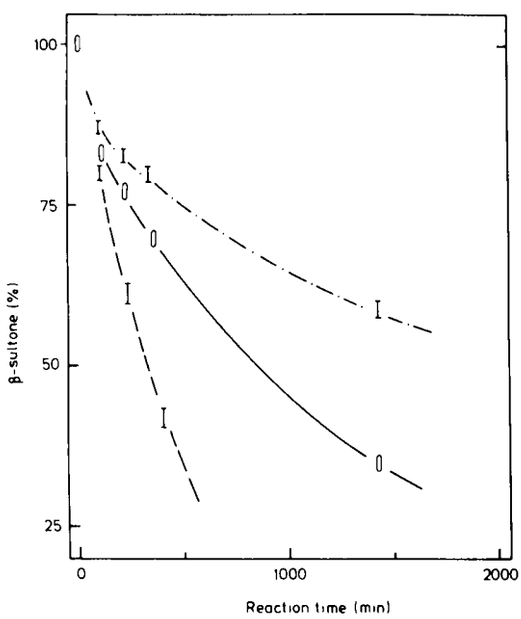


Figure 1. Transfer sulfonation of anisole by 1,2- (----), cis*-4,5- (————) and* trans*-4,5-octanesultone (· – · – ·).*

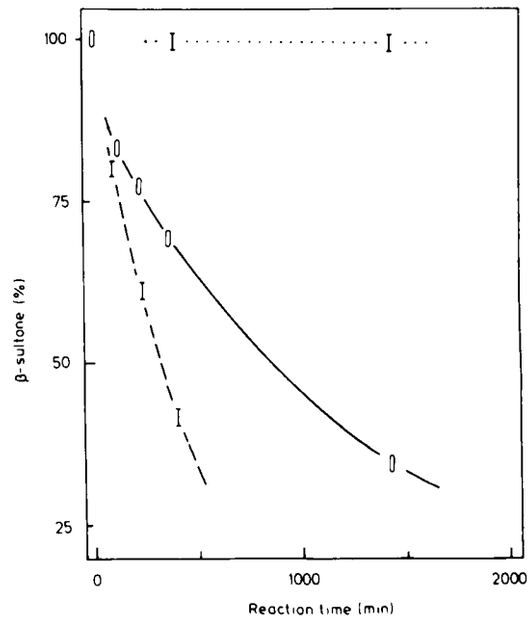


Figure 2. Transfer sulfonation of toluene (· · · · · · · ·), anisole (————) and 1,3-dimethoxybenzene (– – –) by cis*-4,5--octanesultone.*

Attempts to effect intermolecular Friedel–Crafts alkylation with β-sultones as reagents did not give the desired alkylation of the aromatic compound, but instead led to transfer of SO_3 from the β-sultones to the aromatic compounds (*cf.*, Table XII). Typical conversion curves are shown in Figures 1 and 2. Transfer sulfonation is thought to proceed by reactions (1) and (2). From steady-state treatment of the SO_3 concentration, one arrives for the rate of sulfonation of arene and for the rate of β-sultone conversion at equations (3) and (4), respectively. The rate of transfer sulfonation depends both on the rate of desulfonation of the β-sultone and the reactivity of the arene relative to that of the (reformed) alkene.

$$\text{β-sultone} \underset{-1}{\overset{1}{\rightleftharpoons}} \text{alkene} + SO_3 \qquad (1)$$

$$ArH + SO_3 \xrightarrow{2} ArSO_3H \qquad (2)$$

$$\frac{d[ArSO_3H]}{dt} = \frac{k_1 \cdot k_2 \cdot [ArH] \cdot [\text{β-sultone}]}{k_{-1} \cdot [\text{alkene}] + k_2 \cdot [ArH]} \qquad (3)$$

$$-\frac{d[\text{β-sultone}]}{dt} = k_1 \cdot [\text{β-sultone}] \cdot \left(1 - \frac{1}{1 + k_2 \cdot [ArH]/(k_{-1} \cdot [\text{alkene}])}\right) \qquad (4)$$

Transfer sulfonation of linear olefins by β-sultones has previously been reported[23]: *trans*-3,4-hexanesultone with 1.0 equiv. of cyclopentene at 25 °C for 20 h led to the formation of 1,2-cyclopentanesultone and (*E*)-3-hexene (both at a yield of 35%). The existence of a very fast equilibrium between the isomeric *m,n*- and *n,m*-sultones in the sulfocyclization at −60 °C (see before) cannot be explained by the relatively very slow desulfonation of the β-sultone and

subsequent resulfonation, as observed in the above-mentioned transfer sulfonations at 25 °C. The free energy of activation is apparently very much higher for the dissociation of the β-sultone into alkene and SO_3 than that for the interconversion of the two isomeric β-sultones. Therefore, we propose that the very fast *m,n*-sultone ⇄ *n,m*-sultone interconversion proceeds via a π-complex intermediate between SO_3 and the C=C bond of the alkene.

As shown in Table XI, the ratios of the 2,3- and 3,2-sultones for the 5-(monochlorophenyl)- (**13a–16a**) and 5-(dichlorophenyl)-2-pentenes (**17a–20a**), *viz.*, of 4 : 6, differ significantly from the ratios of 8 : 2 observed for the aliphatic alkenes, the two 7-phenyl-2-heptenes (**6a** and **7a**) and the two 4-phenyl-2-butenes (**4a** and **5a**). This deviating β-sultone ratio for **13a–20a** (and possibly for **11a** and **12a**) may be explained in terms of anchimeric assistance by the phenyl group in the formation of the 3,2-sultones.

With respect to the synthetic scope of Friedel–Crafts cyclization, sulfocyclization (β-sultone initiated cyclization) of the phenylalkenes is more attractive than Brønsted-acid-catalyzed cyclization of phenylalkenes in view of the formation of only one product, usually formed in quantitative yield. In contrast, proton-acid-catalyzed (*e.g.*, trifluoroacetic acid[24]) cycloalkylation of arylalkenes generally yields, in addition, a variety of side products, due to hydride shifts in the initially formed carbenium type intermediates, among others.

Experimental

The ^{1}H NMR and ^{13}C NMR spectra were recorded on Bruker WM-250 and AC-200 instruments; mass spectra were recorded on Varian MAT-711 and ZAB-2HF double-focussing mass spectrometers.

Materials

ω-Phenylalkenes **2a–10a** and **21a–31a** were prepared in two steps from the corresponding primary alcohols, starting by oxidation, as reported by *Corey* and *Suggs*[25], followed by Wittig reaction of the resulting aldehydes, using the appropriate alkyltriphenylphosphonium bromide[26].

(*E*)- and (*Z*)-5-phenyl-2-pentene (**11a** and **12a**) were synthesized by alkylation of 4-phenyl-1-butyne with methyl iodide, as described by *Brandsma*[27], followed by hydrogenation of the resulting 5-phenyl-2-pentyne. **11a** was hydrogenized using P-2 Nickel as catalyst[28] and **12a** using lithium aluminum hydride[29].

5-[(Di)chlorophenyl]-2-pentenes **13a–20a** were each prepared via a three-step synthesis starting from the corresponding 3-[(di)chlorophenyl]propenoic acids. Reduction of these compounds, according to the method reported by *Nystrom* et al.[30], led to the corresponding aryl-1-alkanols, which upon oxidation as described by *Swern* et al.[31] gave the corresponding ω-arylalkanals. A Wittig reaction of these aldehydes with ethyltriphenylphosphonium bromide[26] finally yielded the corresponding 5-[(di)chlorophenyl]-2-pentenes.

3-Phenyl-1-propene (**1a**) was obtained commercially and used without further purification.

The ^{1}H NMR data of the substrates are listed in Table I, IV and VIII and later in the text.

Sulfonation procedures and analysis

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. 20 µl of, *e.g.*, 5-phenyl-2-pentene (0.24 mmol) was 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 up to room temperature, after appropriate time intervals in which the NMR tube was kept at −70 °C. The complete procedure took (in total) 4–6 h, unless stated otherwise.

Method B. 1.0 or 0.5 mmol of *e.g.* 5-phenyl-2-pentene was injected to a stirred solution of 1.0 mmol of SO_3, 1.5 mmol of dioxane and 10 ml of dichloromethane, cooled at −30 °C under an Ar atmosphere and the mixture stirred for 1 h. The reaction mixture was warmed to 0 °C and then poured into 10 ml of water and neutralized to pH 7 with an aqueous solution of KOH. Dichloromethane was removed by rotary evaporation and, then the remaining water and dioxane were removed by freeze drying. The remaining potassium sulfonates were dissolved in D_2O or DMSO-d_6 and subjected to NMR analysis.

The structural assignments of the products were made from the ^{1}H NMR spectra of the reaction mixture solutions, using deuterated solvents or from the isolated potassium sulfonates in D_2O [or DMSO-d_6] as solvent on the basis of the observed chemical shifts, absorption area ratios and coupling constants in combination with substituent shielding parameters[32]. The ^{1}H and ^{13}C NMR spectral data of the various products are compiled in Tables II and III, and in 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[33].

Starting material

4-Phenyl-2-butene (E/Z *1 : 2.1*) (**4a** *and* **5a**). ^{1}H NMR (CD_3NO_2, δ, ppm): 1.67 (m, 3H, CH_3), 3.41 (m, 2H, CH_2), 5.63 (m, 2H, CH=CH), 7.27 (m, 5H, C_6H_5).

7-Phenyl-2-heptene (E/Z *1 : 1.4*) (**6a** *and* **7a**). ^{1}H NMR (CD_2Cl_2, δ, ppm): 1.40 (m, 2H, $CHCH_2C\underline{H}_2$), 1.61 (m, 5H, $C\underline{H}_3$, $C_6H_5CH_2C\underline{H}_2$), 2.06 (m, $CHC\underline{H}_2$), 2.62 (m, 2H, $C_6H_5C\underline{H}_2$), 5.42 (m, 2H, CH=CH, 7.22 (m, 5H, C_6H_5).

6-Phenyl-2-hexene (E/Z[34]) (**9a** *and* **10a**). ^{1}H NMR (CD_2Cl_2, δ, ppm): 1.60 (d, *J* 4.9 Hz, 3H, CH_3), 1.66 (m, 2H, $CHC\underline{H}_2$), 2.10 (m, 2H, $CH_2C\underline{H}_2CH_2$), 2.64 (t, *J* 7.5 Hz, 2H, $C_6H_5C\underline{H}_2$), 5.46 (m, 2H, HC=CH), 7.24 (m, 5H, C_6H_5).

Products

6-Phenyl-1,2-hexanesultone (**3c**). ^{13}C NMR (CD_2Cl_2, δ, ppm): 24.8 ($\underline{C}H_2CH_2CHO$), 31.5 ($\underline{C}H_2CH_2Ph$), 35.3 ($\underline{C}H_2CHO$), 36.0 ($\underline{C}H_2Ph$), 64.8 (CH_2SO_2), 66.2 (CHO), 126.2, 128.7, 128.8, 142.5 (aromatic C).

5-Phenyl-2-methyl-3,2-pentanesultone (**21c**). ^{13}C NMR (CD_2Cl_2, δ, ppm): 22.3 ($\underline{C}H_3CO$), 27.6 ($\underline{C}H_2CHS$), 28.7 ($\underline{C}H_3CO$), 33.0 ($\underline{C}H_2CH_2CHS$), 77.0 (CO), 78.4 ($\underline{C}HSO_2$), 126.6, 128.5, 128.7, 139.5 (aromatic C).

6-Phenyl-3-methyl-4,3-hexanesultone (cis/trans *1.3 : 1*) (**22c** *and* **23c**). ^{13}C NMR (CD_2Cl_2, δ, ppm): 7.9/8.6 ($\underline{C}H_3CH_2$), 19.9/25.2 ($\underline{C}H_3CO$), 27.3/34.9 ($CH_3\underline{C}H_2$), 28.2/28.4 ($\underline{C}H_2CS$), 33.5/33.6 ($C\underline{C}H_2CH_2$), 77.2/79.4 ($\underline{C}HSO_2$)), 80.0 (CO), 127.0, 128.9, 129.0, 129.1, 139.6 (aromatic C).

Potassium 1-(sulfomethyl)-1,2,3,4-tetrahydronaphthalene (**8f**). ^{1}H NMR (D_2O, δ, ppm): 1.79 (m, 2H, $CH_2C\underline{H}_2CH_2$), 2.02 (m, 2H, $CH_2C\underline{H}_2CH$), 3.20 (m, 4H, $C\underline{H}_2SO_3K$, $CC\underline{H}_2CH_2$), 3.39 (m, 1H, $C\underline{H}CH_2SO_3K$), 7.22 (m, 4H, aromatic H). ^{13}C NMR (D_2O, δ, ppm): 18.8 ($CH_2\underline{C}H_2CH_2$), 26.7 ($CH_2\underline{C}H_2CH$), 29.2 ($\underline{C}HCH_2SO_3K$), 33.9 ($C\underline{C}H_2$), 58.4 (CH_2SO_3K), 126.2, 126.7 (aromatic C). MS (FAB$^+$) *m/z*: 421 [(M + K)$^+$, 67], 383 (40), 303 (100), 253 (35), 147 (51), 91 (24). (FAB$^-$) *m/z*: 343 [(M − K)$^-$, 100], 225 (54), 80 (34).

1-Sulfomethyl-1,2,3,4-tetrahydronaphthalene-7-sulfonic acid (**8g**). ^{1}H NMR (CD_2Cl_2, δ, ppm): 1.86 (m, 2H, $CH_2C\underline{H}_2CH_2$), 2.06 (m, 2H, $CH_2C\underline{H}_2CH$), 2.85 (m, 2H, $CC\underline{H}_2CH_2$), 3.42 (m, 2H, $C\underline{H}_2SO_3H$), 3.56 (m, 1H, $C\underline{H}CH_2SO_3H$), 7.27 (d, *J* 8.1 Hz, 1H, $CH_2CC\underline{H}$), 7.64 (dd, *J* 2.0, 8.0 Hz, 1H, $CHC\underline{H}CSO_3H$), 7.77 (d, *J* 1.5 Hz, 1H, $CC\underline{H}CSO_3H$).

Dipotassium 1-(sulfomethyl)-1,2,3,4-tetrahydronaphthalene-7-sulfonate. ^{13}C NMR (D_2O, δ, ppm): 20.2 ($CH\underline{C}H_2CH_2$), 28.7 ($CH_2\underline{C}H_2CH_2$), 30.7 ($C\underline{C}H_2CH_2$), 36.5 ($\underline{C}HCH_2SO_3K$), 59.2 (CH_2SO_3K), 125.1, 127.8, 131.9 (CH(Ar)), 141.6, 142.1, 143.5 (C(Ar)).

Potassium 1-(1-sulfoethyl)-1,2,3,4-tetrahydronaphthalene (**9f**). ^{1}H NMR (D_2O, δ, ppm): 1.11 (d, *J* 6.9 Hz, 3H, $C\underline{H}_3CHSO_3K$), 1.5–2.5 (m, 4H, $CHC\underline{H}_2C\underline{H}_2$), 2.74 (m, 2H, $CC\underline{H}_2CH_2$), 3.67 (m,

2H, CHCHSO$_3$K), 7.26 (m, 4H, aromatic H). MS (FD) *m/z*: 317 [(M + K)$^+$, 100]; the isotopic pattern of **9f** is in agreement with the molecular structure.

(E)-6-Phenyl-3-methyl-2-hexene-4-sulfonic acid (**32k**). ^{1}H NMR (CD_2Cl_2, δ, ppm): 1.74 (d, *J* 7.2 Hz, 3H, $CH_3CH=C$), 1.78 (d, *J* 1.0 Hz, 3H, $CH_3C=CHCH_3$), 2.00–2.75 [br, 4H, $(CH_2)_2CHSO_3H$], 3.55 (dd, *J* 4.0, 11.1 Hz, 1H, $CHSO_3H$), 5.65 (dq, *J* 1.0, 7.2 Hz, 1H, $CH_3CH=C$), 7.20 (m, 5H, C_6H_5).

Potassium (E)-6-phenyl-3-methyl-2-hexene-4-sulfonate (**32l**). ^{13}C NMR (D_2O, δ, ppm): 15.3 (1C, $H_3CCH=C$), 16.0 (1C, $H_3CC=CH$), 32.1 (CH_2CHSO_3K), 35.6 ($C_6H_5CH_2$), 72.0 ($CHSO_3K$), 128.6 ($CH=C$), 130.2 [4′-C(Ph)], 131.08, 131.1[2′-, 3′-, 5′-, 6′-C(Ph)], 132.7 [1′-C(Ph)], 144.2 ($C=C(CH_3)CH$).

(E)-5-Phenyl-3-methyl-3-pentene-2-sulfonic acid (**33k**). ^{1}H NMR (CD_2Cl_2, δ, ppm): 1.60 (d, *J* 7.1 Hz,.3H, CH_3CHSO_3H), 1.88 (s, 3H, $CH=CCH_3$), 3.47 (d, *J* 7.2 Hz, 2H, CH_2CH), 3.97 (q, *J* 7.1 Hz, 1H, $CHSO_3H$), 5.84 (m, 1H, $HC=CCH_3$), 7.27 (m, 5H, C_6H_5).

1-Phenylindane-2-sulfonic acid (**34**). ^{1}H NMR (CD_2Cl_2, δ, ppm): 3.55 (m, 2H, CH_2), 4.00 (m, 1H, $CHSO_3H$), 4.87 (d, *J* 6.6 Hz, CHC_6H_5), 6.90 (d, *J* 7.2 Hz, 1H, 7-H), 7.31 (m, 8H, aromatic H). ^{13}C NMR (CD_2Cl_2, δ, ppm): 34.96 (CH_2), 53.9 (CHC_6H_5), 68.9 ($CHSO_3H$), 124.7, 125.5, 127.6, 127.8, 128.0, 128.7, 129.1 (aromatic C), 140.0 (3a-C), 143.4 (7a-C), 144.2 (8-C). MS (FAB$^+$) *m/z*: 351 [(M + K)$^+$, 50], 301 (30), 213 (98), 177 (90). Accurate mass calculated for $C_{15}H_{13}O_3SK_2$: 318.9445; found: 318.9445.

Potassium 1-phenyl-1,2,3,4-tetrahydronaphthalene-2-sulfonic acid (**28h**). MS (FD) *m/z*: 365 [(M + K)$^+$, 100], the isotopic pattern of **28h** is in agreement with the molecular structure.

Acknowledgements

The authors wish to thank Dr. *J. Stapersma* for valuable discussions, Mrs. *H. van der Laan–Ctvrteckova* for recording the low-temperature NMR spectra and Drs. *J. B. Kramer* for performing some experiments.

References and notes

1 *R. M. Schonk, B. H. Bakker* and *H. Cerfontain*, Recl. Trav. Chim. Pays-Bas **111**, 49 (1992).
2 *M. Nagayama, O. Okumura, S. Noda, H. Mandai* and *A. Mori*, Bull. Chem. Soc. Japan **47**, 2158 (1974).
3 *B. H. Bakker* and *H. Cerfontain*, Tetrahedron Lett. **28**, 1703 (1987).
4 *R. Taylor*, "Electrophilic Aromatic Substitution", Wiley & Sons, Chichester, 1990, p. 209–213, and references cited therein.
5 *A. Koeberg-Telder* and *H. Cerfontain*, J. Chem. Soc. Perkin II 1776 (1976).
6 *R. M. Schonk*, unpublished results.
7 *J. Colonge* and *P. Garnier*, Bull. Soc. Chim. France **15**, 436 (1948).
8 *C. M. Suter, P. B. Evans* and *J. M. Kiefer*, J. Am. Chem. Soc. **60**, 538 (1938).
9 The exact configuration cannot be assigned on the basis of ^{1}H NMR spectroscopy due to the small difference in the coupling constants (*J* 4.6 and 5.5 Hz for **11h** and **12h**, respectively). We expect that the sulfocyclization must proceed with inversion at C(2), so that **11h** and **12h** will have the *trans* and *cis* configurations, respectively (see Scheme 3).
10 The four specific ^{1}H NMR absorption peaks of the *cis*- and *trans*-β-sultone ring hydrogens of the 2,3- and 3,2-sultones resulting from **13a–20a** are within each of the four groups, within 0.05 ppm.
11 This isomer, in all likelihood, has the *trans* configuration[12], although this could not be established using ^{1}H NMR spectroscopy.
12 Sulfonation of (*Z*)-1-phenyl-1-propene with SO_3 leads to the formation of the *trans*-carbyl sulfate in view of the importance of the resonance-stabilized benzylic-sulfonate dipolar species in the product formation[1].
13 *B. H. Bakker* and *H. Cerfontain*, Tetrahedron Lett. **28**, 1699 (1987).
14 *H. D. Goossens, H. J. A. Lambrechts, H. Cerfontain* and *P. de Wit*, Recl. Trav. Chim. Pays-Bas **107**, 426 (1988).
15 No β,γ-unsaturated sulfonic acid was formed at −60 °C, which indicates that the "ene" reaction, observed with aliphatic alkenes[23], does not take place during sulfonation of ω-phenyl-1-alkenes.
16 *V. M. Castro*, Ph.D. Thesis (in French), Institute National Polytechnique de Toulouse, France, 1986.
17 *K. Takei, K. Tsuto, S. Miyamoto* and *J. Wakatsuki*, J. Am. Oil. Chem. Soc. **62**, 314 (1985).
18 *H. Cerfontain* and *Z. R. H. Schaasberg–Nienhuis*, J. Chem. Soc. Perkin Trans. II 180 (1973).
19 The rate coefficients for sulfodeprotonation at positions 6 and 7 of 1-(sulfomethyl)-1,2,3,4-tetrahydronaphthalene (**8f**) were calculated using the sulfonation rate coefficients for 2-phenyl-1-ethanesulfonic acid (2P1ESA) and 5-phenyl-1-pentanesulfonic acid (5P1PSA) at the *para* positions[18] of $k_7/k_6 \sim k_{2P1ESA}/k_{5P1PSA} = 53$.
20 *B. H. Bakker* and *H. Cerfontain*, 2nd Congres Mondial des Agents de Surface (1988), Vol. II, p. 32.
21 *B. H. Bakker, R. M. Schonk* and *H. Cerfontain*, Recl. Trav. Chim. Pays-Bas **111**, 138 (1992).
22 *W. E. Truce* and *F. D. Hoerger*, J. Am. Chem. Soc. **76**, 5357 (1954).
23 *B. H. Bakker* and *H. Cerfontain*, Tetrahedron Lett. **30**, 5451 (1989).
24 *T. J. Mason* and *R. O. C. Norman*, J. Chem. Soc. Perkin Trans. II 1840 (1973).
25 *E. J. Corey* and *J. W. Suggs*, Tetrahedron Lett. **16**, 2647 (1975).
26 *A. Maercker*, in "Organic Reactions", Vol. 14, *A. C. Cope*, ed., Wiley & Sons, New York, 1965, p. 270–490, and references cited therein.
27 *L. Brandsma*, "Preparative Acetylenic Chemistry", Elsevier, Amsterdam, 2nd ed., 1988, p. 39, and references cited therein.
28 *C. A. Brown* and *V. K. Ahujal*, J. Org. Chem. **38**, 2226 (1973).
29 *H. Hiemstra, M. H. A. M. Sno, R. J. Vijn* and *W. N. Speckamp*, J. Org. Chem **50**, 4014 (1985).
30 *R. F. Nystrom* and *W. G. Brown*, J. Am. Chem. Soc. **69**, 2549 (1947).
31 *A. J. Mansura, Shui-Ling Huang* and *D. Swern*, J. Org. Chem. **43**, 2482 (1978).
32 *M. Hesse, H. Meier* and *B. Zeeh*, "Spectroscopische Methoden in der organischen Chemie", George Thieme Verlag, Stuttgart, 2nd ed., 1984, p. 176.
33 *H. Cerfontain, A. Koeberg-Telder, C. Kruk* and *C. Ris*, Anal. Chem. **46**, 72 (1974).
34 The *E*/*Z* ratio could not be established on the basis of ^{1}H NMR spectroscopy due to overlap of the specific absorption signals.