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Reactivity and regioselectivity in the reaction of allylsilanes and some analogous all-carbon alkenes with sulfur trioxide [a,c]

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Abstract. Sulfonations of the 1-(trimethylsilyl)alk-2-enes **1a–12a**, the 1-(trimethylsilyl)-ω-phenylalk-2-enes **13a–18a**, the triisopropylsilylalk-2-enes **19a–21a**, 1-(trimethylsilyl)penta-2,4-diene (**22a**), and the allylsilane **23a** with sulfur trioxide were studied in the temperature range -60 to 25°C using dichloromethane-d_2 as solvent and 1.5 mol-equiv. of dioxane-d_8 relative to the amount of SO_3 as reactivity moderator. For comparison, the sulfonation of the all carbon analogues **24a–27a** were also studied. Reaction of the 1-(trialkylsilyl)alk-2-enes **1a–11a** and **13a–17a** with SO_3 at −60°C all afford the corresponding trialkylsilyl-alk-1-ene-3-sulfonate esters **c** within 20 min in yields of > 95%. 1-(Trimethylsilyl)-2-cycloheptylideneethane (**12a**) at −60°C gives a mixture of the trimethylsilyl sulfonate ester **12c** and the isomeric 1-(trimethylsilyl)-2-(1-cycloheptenyl)ethane-2-sulfonic acid (**12f**) in a molar ratio of 4:6. With 1-(trimethylsilyl)-2-(1,2,3,4-tetrahydro-1-naphthylidene)-ethane (**18a**) the exclusive product is 1-(trimethylsilyl)-2-(3,4-dihydro-1-naphthyl)ethane-2-sulfonic acid (**18f**). Direct NMR evidence for the formation of β-sultones as initial intermediates was observed in the sulfonation of the 1-(trimethylsilyl)-2-cycloalkylideneethanes **11a** and **12a**. Upon sulfonation of the 1-(triisopropylsilyl)-alk-2-enes **19a–21a** at −60°C the initial products are the β-sultone **20b-II** and the carbyl sulfates **19h-II** and **21h-II**, of which the relative yields depend on the amount of SO_3 employed. The SO_3 sulfonation of 1-(trimethylsilyl)penta-2,4-diene (**22a**) gives trimethylsilyl penta-1,3-diene-5-sulfonate (**22i**). The three homologous non-silicon containing 1-cycloalkylidenehexanes **24a–26a** at −60°C afford the respective 1-cycloalkylhexane-1,1′-sultones **24b-III–26b-III** which, at higher temperatures, isomerize to give the 1-(cycloalk-1′-enyl)hexane-1-sulfonic acids **24m–26m**. 1-Methylene-1,2,3,4-tetrahydronaphthalene (**27a**) reacts with SO_3 at −60°C to give (3,4-dihydro-1-naphthyl)methanesulfonic acid (**27o**). Treatment of the various products containing a trialkylsilyl sulfonate ester substituent with aqueous KOH gives quantitatively the corresponding potassium sulfonate salts.
Mechanisms for the formation of the various products are suggested and the observed selectivities are discussed.

Introduction [c,d]

As part of our studies on the sulfonation of simple alkenes with sulfur trioxide[2,3] and as a sequel to our studies on the reactions of monofunctionalized alkenes with that reagent[4–8], we now report on the reactions of allylsilane systems with SO_3. The objective of this exploratory study was to obtain information on the initial sulfonation products and their subsequent chemistry. The reactions were therefore studied at temperatures from -60 to 25°C to look for evidence of the existence of β-sultones, which have been shown to be the initial products in the reaction of simple alkenes with SO_3 at low temperatures[2,9,10]. Sulfonation of α-(trimethylsilyl)allenes[11] and α-[(trimethylsilyl)methyl]allenes[12] with trimethylsilyl chlorosulfonate or SO_3/dioxane as reagent leads to formation of propyne- and conjugated diene-systems, respectively. Reaction of conjugated dienes with SO_3 at low temperatures are known to give mono-unsaturated δ-sultones[13].

Results

Reactions of the allyltrimethylsilanes **1a–18a**, the allyltriisopropylsilanes **19a–21a**, 1-(trimethylsilyl)penta-2,4-diene (**22a**), and the cyclic allylic dimethylsilane **23a** with 1.0–3.0 mol-equiv. of SO_3 were studied in dichloromethane as solvent, using 1.5 mol-equiv. of dioxane (relative to the amount of SO_3) as reactivity moderator as the standard procedure (see Experimental section, method A). The sulfonation of **6a** was also effected using 1.2 mol-equiv. of trimethylsilyl chlorosulfonate as reagent[14] in dichloro-

[a] Aliphatic sulfonation 15. Preceding paper: see Ref. 1.
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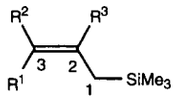
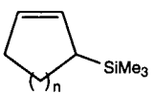
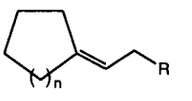
[c] Nomenclature. The numbering of the alkenyl carbon chain of the allylsilanes is such that the trialkylsilyl group is located at C(1). For reasons of consistency, the sulfo products have been numbered as the parent substrate.
[d] IUPAC nomenclature. β-sultone = 1,2-oxathietane 2,2-dioxide; γ-sultone = 1,2-oxathiolane 2,2-dioxide; δ-sultone = 1,2-oxathiane 2,2-dioxide; carbyl sulfate = cyclic sulfonate sulfate anhydride = 1,3,2,4-dioxadithiane 2,2,4,4-tetraoxide.



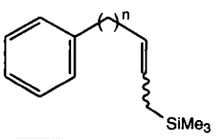
	R^1	R^2	R^3
1a	H	H	Me
(*E*)-**2a**	H	Me	H
(*Z*)-**2a**	Me	H	H
(*E*)-**3a**	H	1-Hex	H
(*Z*)-**3a**	1-Hex	H	H
(*E*)-**4a**	H	cHex	H
(*Z*)-**4a**	cHex	H	H
(*E*)-**5a**	H	cHex	Me
(*Z*)-**5a**	cHex	H	Me
6a	Me	Me	H



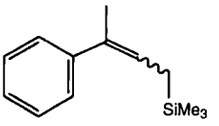
	n
7a	1
8a	2
9a	3



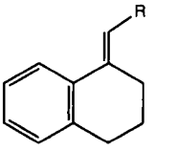
	n	R
10a	1	$SiMe_3$
11a	2	$SiMe_3$
12a	3	$SiMe_3$
24a	1	Bu
25a	2	Bu
26a	3	Bu



	n
13a	0
14a	1
15a	2
16a	3

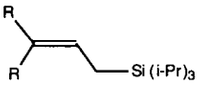


17a



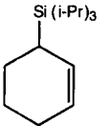
18a R = CH_2SiMe_3

27a R = H

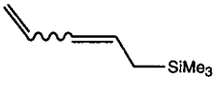


19a R = H

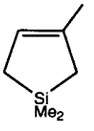
20a R = Me



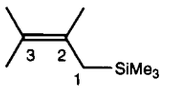
21a



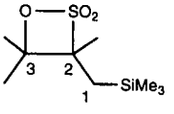
22a



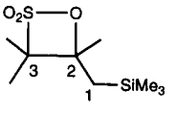
23a



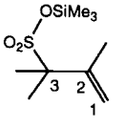
a



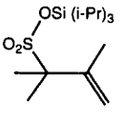
b-I (2,3)



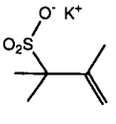
b-II (3,2)



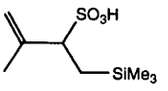
c



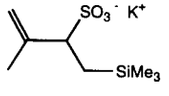
d



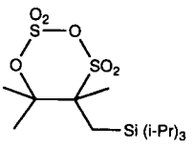
e



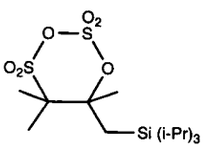
f



g



h-I



h-II

Figure 1. Basic structural elements of the allylsilanes and their sulfo products.

Table I Composition of the reaction mixtures of the 1-(trimethylsilyl)-2-cycloalkylideneethanes **11a** *and* **12a** *with 1.0 mol-equiv. of* SO_3 [a].

Temp. (°C)	Composition (%, ±3)					
	1-TMS-2-cyclohexylidene-ethane (**11a**)			1-TMS-2-cycloheptylidene-ethane (**12a**)		
	Substr.	β-Sultone **b-II** [b]	**c**	Substr.	β-Sultone **b-II** [b]	**e+g**
−60	53	40	7	< 3	> 97	< 3
−40	52	42	6		89	11
−20	50	38	12		67	33
0	38 [c]	< 3	62 [c]		5	95 [d]
25	< 3		> 97		< 3	> 97 [d]

[a] For the chemical behaviour of the homologous 1-(trimethylsilyl)-2-cyclopentylideneethane (**10a**), see Ref. 16. [b] As argued in the Discussion, the observed β-sultones formed from **11a** and **12a** are both of type **b-II**. [c] In between −20 and 0°C 3.0 mol-equiv. (0.72 mmol) of SO_3 was added to the reaction mixture. [d] The molar ratio **e**/**g** is 4/6.

methane as solvent. In addition, the SO_3 sulfonation of the alkenes **24a–27a**, which are the non-silicon containing analogues of the allyltrimethylsilanes **10a–12a** and **18a**, was studied for comparative purposes.

In order to obtain information on the primary sulfonation products, the reactions were carried out at low temperatures, using deuterated solvent and moderator, and examined by NMR spectroscopy. The ^{1}H- and ^{13}C-NMR assignments of the starting compounds and their sulfo products are given in the Experimental section. The basic structural elements of the allylsilanes and the various sulfo products are shown in Figure 1.

Sulfonation of the allyltrimethylsilanes **1a–9a** with 1.0–1.2 mol-equiv. of SO_3 at −60°C for 15–20 min gave the corresponding trimethylsilyl prop-1-ene-3-sulfonate esters **1c–9c**, respectively, in yields of > 95%. There is no evidence for any preceding β-sultone **b** as an intermediate. Even when a large excess of reactivity moderator was used the actually applied dioxane/SO_3 ratio being 10:1, the formation of the trimethylsilyl prop-1-ene-3-sulfonates **c** was found to be complete within 15 min. When 1-(trimethylsilyl)-3-methylbut-2-ene (**6a**) was sulfonated with 1.2 mol-equiv. of the far less reactive sulfonating reagent trimethylsilyl chlorosulfonate[14,15] in dichloromethane at −60°C the trimethylsilyl sulfonate ester **6c** was formed quantitatively within 20 min. When the temperature was increased from −60°C to room temperature the trimethylsilyl sulfonate esters **c** appeared to be thermally stable. Hydrolysis of these esters with an aqueous KOH solution yielded quantitatively the corresponding potassium sulfonate salts **e**.

On sulfonation with SO_3, the two 1-(trimethylsilyl)-2-cycloalkylideneethanes **11a** and **12a** behave differently from the allylsilanes **1a–9a** in that at −60°C there is direct ^{1}H-NMR evidence for the presence of the β-sultones **11b** and **12b** as the initially formed intermediates[16,17]. When the temperature is raised, **11b** rapidly gives the corresponding trimethylsilyl 1-vinylcyclohexane-1-sulfonate (**11c**), whereas **12b** yields a mixture of **12c** and 1-(trimethylsilyl)-2-cyclohept-1-enyl)ethane-2-sulfonic acid (**12f**) in a molar ratio of 4:6. This ratio was determined after conversion of the mixture of **12c** and **12f** at 25°C with aqueous KOH (see Experimental section, method B) into a mixture of the corresponding potassium salts **12e** and **12g**, and subsequent quantitative ^{1}H-NMR analysis using both DMSO-d_6 and D_2O as solvent. The compositions of the reaction mixtures obtained on reaction of the 1(-trimethylsilyl)-2-cycloalkylideneethanes **11a** and **12a** with SO_3 as a function of the reaction temperature, are given in Table I.

Reaction of the 1(-trimethylsilyl)-ω-phenylalk-2-enes **13a–16a** and 1-(trimethylsilyl)-3-phenylbut-2-ene (**17a**) with 1.0 mol-equiv. of SO_3 leads to the formation of the respective trimethylsilyl phenylalkene-3-sulfonate esters, **13c–17c**, which upon subsequent treatment with aqueous KOH give the corresponding potassium sulfonates **e**. The only product observed upon reaction of (*E*)-1(-trimethylsilyl)-2-(1,2,3,4-tetrahydro-1-naphthylidene)ethane (**18a**) with SO_3 at −60°C is 1-(trimethylsilyl)-2-(3,4-dihydro-1-naphthyl)ethane-2-sulfonic acid (**18f**), which was formed in a yield of > 95%.

1-(Triisopropylsilyl)prop-2-ene (**19a**) and 1-(triisopropylsilyl)cyclohex-2-ene (**21a**) react with SO_3 at −60°C to give the corresponding carbyl sulfates **19h-II** and **21h-II** and the triisopropylsilyl 1-(cyclo)alkene-3-sulfonate esters **19d** and **21d**. When the temperature is subsequently raised, the carbyl sulfates **19h-II** and **21h-II** still present are also converted into the silyl sulfonate esters **19d** and **21d** to give total yields of > 95% based on the starting substrate.

1-(Triisopropylsilyl)-3-methylbut-2-ene (**20a**) with 1.0 mol-equiv. of SO_3 at −60°C initially gives a β-sultone, probably **20b-II**, and subsequently the triisopropylsilyl sulfonate ester **20d**. The compositions of the reaction mixtures of **19a–21a** with SO_3 as a function of the reaction temperature are given in Table II. The triisopropylsilyl sulfonate esters **19d–21d** were easily converted with aqueous KOH into the corresponding potassium sulfonates **e**.

Sulfonation of 1-(trimethylsilyl)penta-2,4-diene (**22a**) with 1.0 mol-equiv. of SO_3 at −60°C gives trimethylsilyl penta-1,3-diene-5-sulfonate (**22i**), which on treatment with aqueous KOH affords the corresponding potassium sulfonate salt **22j**.

1,1,3-Trimethyl-1-silacyclopent-3-ene (**23a**) upon reaction with 1.1 mol-equiv. of SO_33 at −60°C gives mostly 2,5-dimethyl-5-silahex-1-ene-3,5-sultone (**23k**). There is no ^{1}H-NMR evidence for the presence of a β-sultone. Treatment of **23k** with aqueous KOH affords the disilyl ether **23l**. The present observations are in line with those re-

Table II Product formation on reaction of the 1-(triisopropylsilyl)alk-2-enes **19a–21a** *with* SO_3.

Substrate	SO_3 (mol-equiv., ±0.1)	Temp. (°C)	Reaction mixture composition (%, ±3)			
			Unconverted substrate **a**	β-Sultone **b-II**	Carbyl sulfate **h-II**	Silyl sulfonate ester **d**
19a	3.0	−60	< 3		88	12
		−40	–		89	11
		−20			67	33
		0			< 3	> 97
20a	1.0	−60	< 3	59		41
		−40	–	43		57
		−20		19		81
		0		12		88
		25		< 3		> 97
21a	1.2	−60	< 3		20	80
		−40	–		10	90
		−20			< 3	> 97

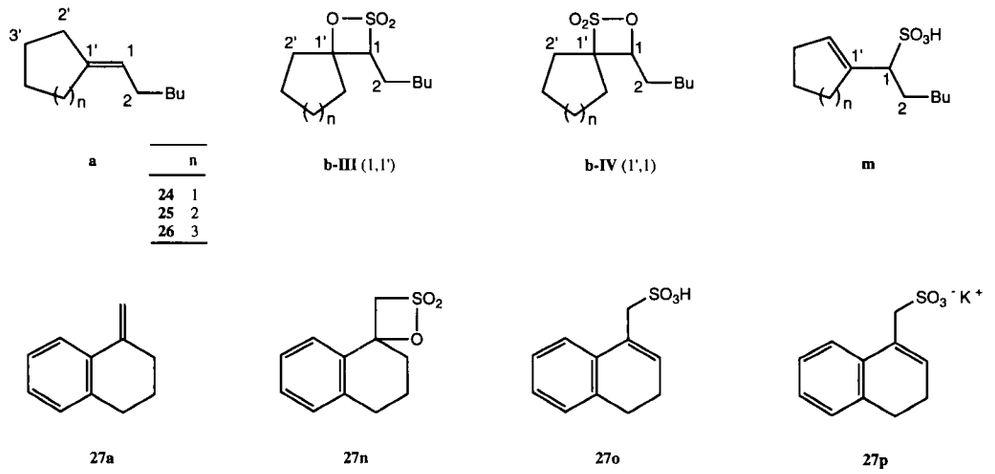
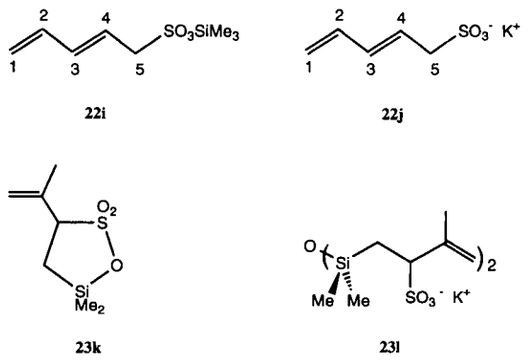


Figure 2. Structures of the non-silicon containing alkene analogues **24a–27a** *and their sulfo products.*



ported by *Calas* and coworkers, using trimethylsilyl chlorosulfonate as the sulfonating reagent[14].

On reaction with SO_3/dioxane in dichloromethane at −60°C the three non-silicon containing 1-cycloalkylidenehexanes **24a–26a** give the respective β-sultones **24b-III–26b-III** as primary products, as demonstrated by ^{1}H- and ^{13}C-NMR (see Figure 2)[18,20]. At higher temperatures the **III-b** type of β-sultones isomerize to give the 1-(cycloalk-1'-enyl)hexane-1-sulfonic acids **24m–26m**, respectively. The compositions of the reaction mixtures of **24a–26a** with 1.0 mol-equiv. of SO_3 as a function of the reaction temperature are given in Table III. 1-Methylene-1,2,3,4-tetrahydronaphthalene (**27a**) reacts with 1.0 mol-equiv. of SO_3 at −60°C to give (3,4-dihydro-1-naphthyl)methanesulfonic acid (**27o**) as the sole product, which with aqueous KOH affords the corresponding potassium sulfonate salt **27p**.

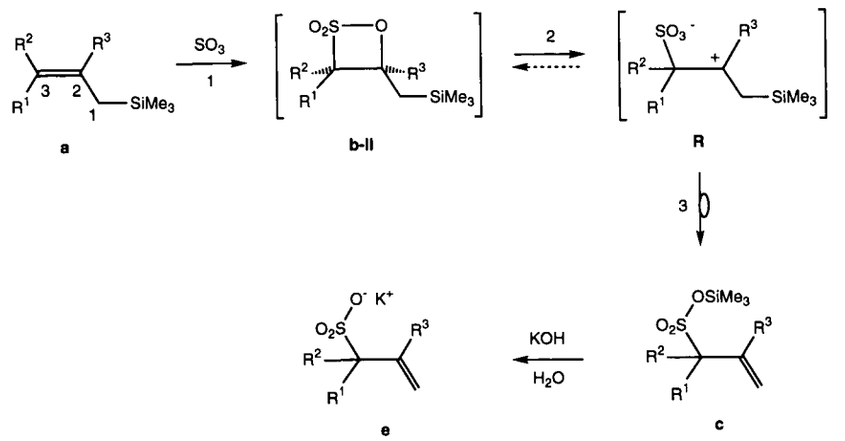
Discussion

Addition of SO_3 to alkenes leads to the formation of β-sultones as the initial products and proceeds stereospecifically via a concerted *cis* addition[2,4,21]. The regioselectivity of the β-sultone formation, which follows Markovnikov's rule, is also high, the addition of SO_3 to oct-1-ene[2], isobutene[10], and 2-methylbut-2-ene[10] giving exclusively octane-1,2-sultone,2-methylpropane-1,2-sultone and 3-methyl-butane-2,3-sultone, respectively. Studies using Catalin Stuart molecular models indicate that there is virtually no steric hindrance for the formation of 2,3-dimethylbutane-2,3-sultone from 2,3-dimethylbut-2-ene. The regioselectivity observed with the asymmetric alkenes, such as 2-methylbut-2-ene, is obviously determined by electronic effects in the transition state of the electrophilic addition of SO_3, in which the degree of bonding is stronger between S and C than that between O and C. The incipient positive charge at the latter carbon will then be stabilized by adiacent methyl(s), if present. With 1-(trialkylsilyl)alk-2-enes, such as 1-(trimethylsilyl) but-2-ene (**2a**), the situation is different. Now the silyl group at C(1) is capable of stabilizing the positive charge at C(2) by hyperconjugation involving the empty p_π orbital and the C(1)–Si bond[22]. This type of hyperconjugative stabilization is significantly greater than that due to hyperconjugation involving the empty p_π orbital and the C(1)–H and C(1)–C bonds[23].

Hydroboration of allylsilanes with both $BH_3 \cdot THF$ and 9-borabicyclo[3.3.1]nonane proceeds in a similar way as their SO_3 sulfonation in that there are no cationic intermediates formed and the BR_2 group is bonded to C(3) and the H to C(2)[24]. The in verse regioselectivity for both the sulfonation and hydroboration of allylsilanes, as compared with the corresponding alkenes, may be ascribed in

Table III Composition of the reaction mixtures of the 1-(cycloalkylidene)hexanes **24a–26a** *with 1.0 mol-equiv. of SO_3.*

Temp. (°C)	Composition (%, ±3)								
	1-Cyclopentylidene-hexane (**24a**)			1-Cyclohexylidene-hexane (**25a**)			1-Cycloheptylidene-hexane (**26a**)		
	Substr.	β-Sultone **b-III**	**m**	Substr.	β-Sultone **b-III**	**m**	Substr.	β-Sultone **b-III**	**m**
−60	< 3	76	24	70	30	< 3	95	5	< 3
−40				70	30	< 3			
−30	–	48	52				11	87	< 3
−20				< 3	50	50			
−10		< 3	> 97				< 3	< 3	> 97
0					< 3	> 97			

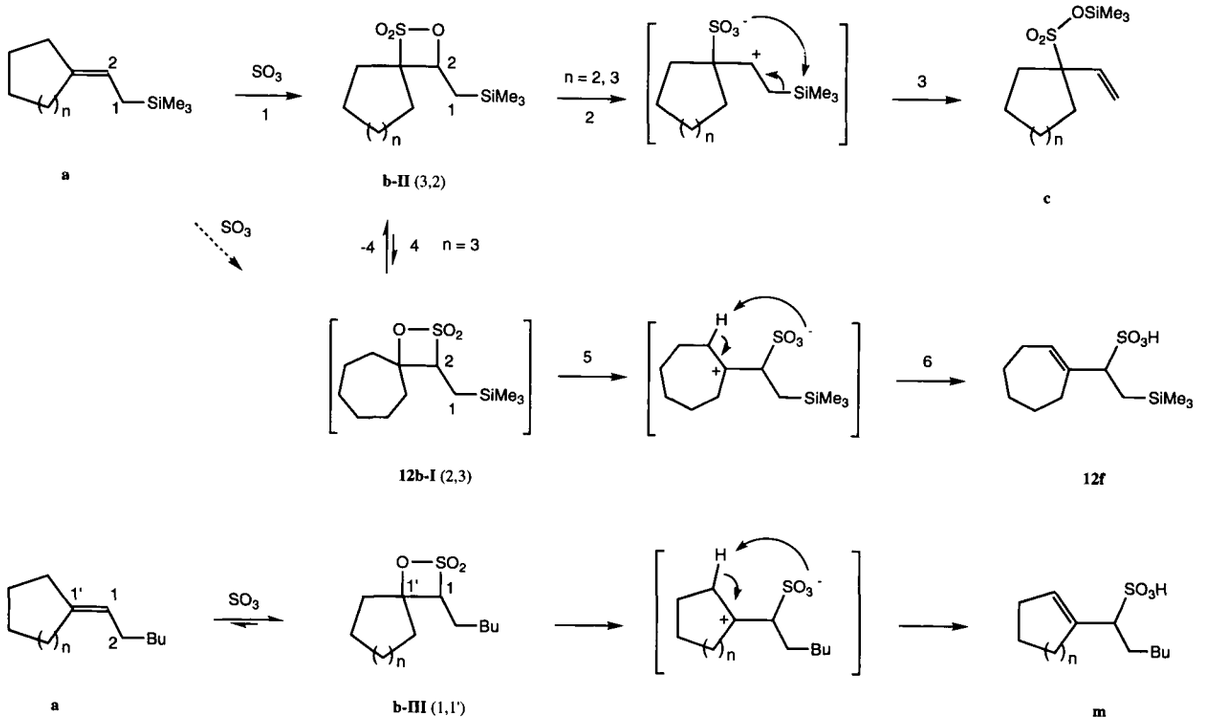


Scheme 1. Sulfonation of the 1-(trimethylsilyl)alk-2-enes **1a–9a** *with 1.1 mol-equiv. of SO_3 at low temperatures.*

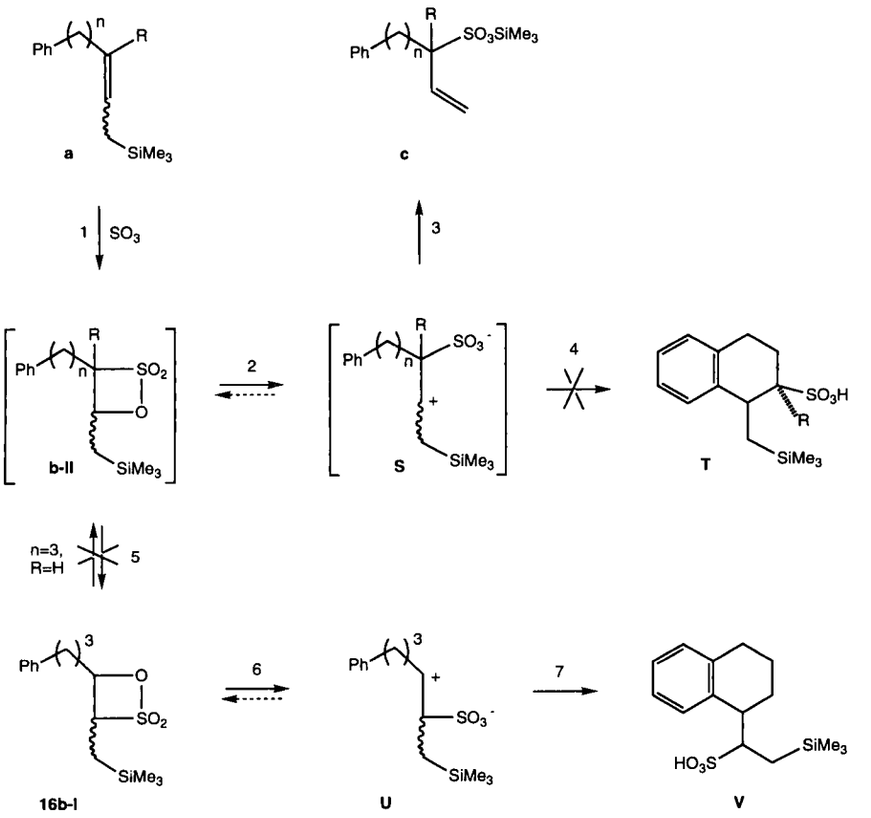
part to the ground state inverse polarization of the carbon-carbon double bond, which is reflected in the specific atomic coeffients of the HOMOs[25].

The sulfonation of the allylsilanes **1a–9a** with SO_3 proceeds rapidly. At −60°C the corresponding trimethylsilyl prop-1-ene-3-sulfonate esters **1c–9c** are formed within 20 min in high yields. Their formation is thought to proceed (see Scheme 1) via the initial formation of the β-sultones **b-II** (step 1; see before), which at −60°C are very rapidly and completely converted, via the dipolar intermediate **R** and a subsequent six-membered cyclic transition state, into the silyl sulfonate esters **c** (steps 2 and 3)[26]. Hydrolysis with aqueous KOH affords the potassium sulfonate salts. Sulfonation of 1-(trimethylsilyl)-2-cyclohexylideneethane (**11a**) and the homologous cycloheptylidene derivative **12a** at low temperature initially yield (see Scheme 2) the β-sultones **11b-II** and **12b-II** respectively (step 1). Upon raising the temperature, **11b-II** affords exclusively trimethylsilyl 1-vinylcyclohexane-1-sulfonate (**11c**) (steps 2 and 3), whereas **12b-II** gives a mixture of the silyl ester **12c** and 1-(trimethylsilyl)-2-(cyclohept-1′-enyl)ethane-2-sulfonic acid (**12f**) in a molar ratio of 4:6. The sulfonic acid product **12f** must result from β-sultone **12b-I** (steps 5 and 6) which, it is proposed, is formed predominantly by direct isomerization of **12b-II** (step 4). In fact, studies on the sulfocyclization of ω-phenylalkenes with SO_3 have shown that there is an extremely rapid interconversion between the initially formed isomeric *m,n*- and *n,m*-sultones which act as the intermediates undergoing intramolecular sulfocyclization[6,7]. Apparently, for the present isomeric β-sultones **12b-I** and **12b-II**, $k_4/k_{-4} \leqslant 0.04$. If one presumes the rate-limiting steps for the formation of **12c** and **12f** to be steps 2 and 5, respectively, the product ratio will be given by: $\mathbf{12c}/\mathbf{12f} = (k_2/k_4) \times k_5/(k_{-4} + k_5)$.

The series of 1-(trimethylsilyl)-ω-phenylalk-2-enes **13a–16a** was included in the present study in view of earlier observations that ω-phenylalkenes, which have a $-(CH_2)_3-$

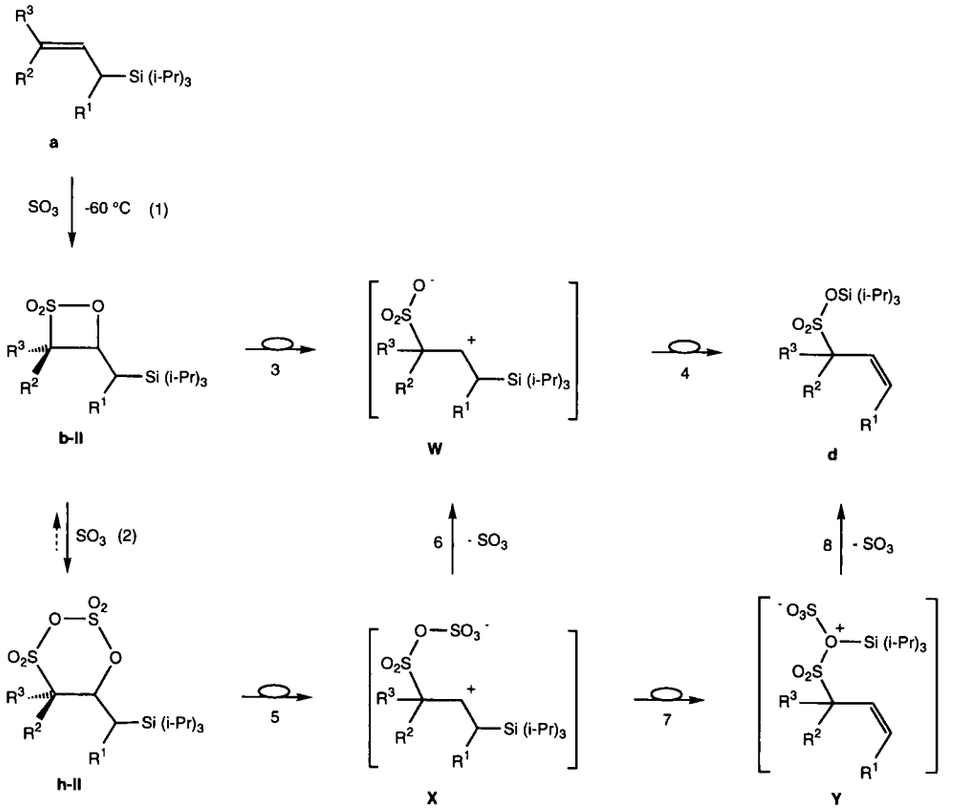


Scheme 2. Sulfonation of the 1-(trimethylsilyl)-2-cycloalkylideneethanes **11a** *and* **12a** *(n = 2 and 3) and 1-(cycloalkylidene)hexanes* **24a–26a** *(n = 1–3) with 1.1 mol-equiv. of SO_3 at −60°C.*



Scheme 3. Sulfonation of the 1-(trimethylsilyl)-ω-phenylalk-2-enes **13a–16a** *(R = H) and* **17a** *(n = 0, R = Me) with 1.1 mol-equiv. of SO_3 at -60°C.*

or $-(CH_2)_2-$ linkage between the phenyl and C = C moieties, undergo quantitative sulfocyclization on reaction with 1.1 mol-equiv. of SO_3 at −60°C within 10 min[6]. The former type of ω-phenylalkenes then affords 1-(1-sulfoalkyl)-1,2,3,4-tetrahydronaphthalenes, whereas the latter type leads to the stereospecific formation of *cis*-



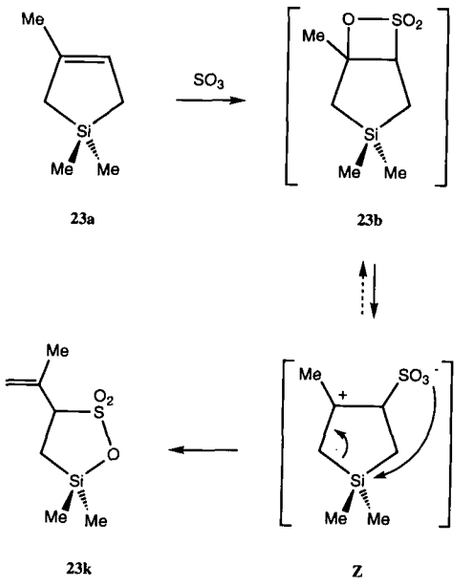
Scheme 4. Reaction of the 1-(triisopropylsilyl)alk-2-enes **19a** *($R^1 = R^2 = R^3 = H$),* **20a** *($R^1 = H$; $R^2 = R^3 = Me$) and* **21a** *[$R^1 + R^2 = -(CH_2)_3-$; $R^3 = H$] with 1.1 mol-equiv. of SO_3, initially at −60°C and subsequently at higher temperatures up to room temperature.*

and *trans*-1-methyl-1,2,3,4-tetrahydronaphthalene-2-sulfonic acids[6]. The sulfonation of the 1(-trimethylsilyl)-ω-phenylalk-2-enes **13a–17a** with 1.1 mol-equiv. of SO_3 at −60°C is also very rapid and leads exclusively to the corresponding trimethylsilyl ω-phenylalk-1-ene-3-sulfonate esters **13c–17c**. The formation of the silyl esters may be explained (see Scheme 3) in terms of the formation of the (not observed) β-sultones **13b-II–17b-II** and their conversion, via the dipolar intermediates **S**, into the silyl sulfonate esters **c**. The absence of the sulfocyclization products **T** and **V** is notable. For $n = 2$, the intramolecular trimethylsilyl transfer (step 3) is apparently much faster than the formation of the cyclization product **T** (step 4). The absence of product **V** indicates that $k_2 \gg k_5$, and that the β-sultone equilibrium **16b-II** ⇌ **16b-I** lies strongly towards **16b-II**. For the two styrene-type of allylsilanes **13a** and **17a** the absence of products resulting from the **b-*T*** type of β-sultone is remarkable, since products derived from this type of β-sultone have been observed in the SO_3 sulfonation of various styrenes. For instance, 1-phenylethene and (*E*)-1-phenyprop-1-ene at −60°C give the corresponding carbyl sulfates **h-L**, apparently resulting from the **b-I**-type of β-sultones as intermediates, which at 0°C afford the corresponding (*E*)-1-phenylalkene-2-sulfonic acids[4,27]. Likewise, 2-phenylprop-1-ene[4] gives 2-phenyl-prop-2-ene-1-sulfonic acid, and 1-phenylcyclohexene[4] the corresponding 2-phenylcyclohex-1-ene-3-sulfonic acid[28]. As to the transition states of formation of the two possible β-sultones from the 1-(trimethylsilyl)-3-phenylalk-2-enes **13a** and **17a**, the C–Si hyperconjugative stabilization is apparently stronger than the direct conjugative stabilization by the phenyl group, the latter type of conjugation probably being hampered by steric inhibition. The formation of 1-(trimethylsilyl)-2-(3,4-dihydro-1-naphthyl)ethane-2-sulfonic acid (**18f**) as the only product from 1-trimethylsilyl-2-(1,2,3,4-tetrahydro-1-naphthylidene)ethane (**18a**) is also noteworthy. Obviously product **18f** is formed from β-sultone **18b-I**; the strain that would result from the formation of the tricyclic β-sultone **18b-II** is thought to prevent its actual formation[29].

From the structures of the final products obtained on sulfonation of the 1-(trialkylsilyl)alk-2-enes **1a–11a** and **13a–17a**, it appears that the preceding β-sultones must have been the corresponding 1-(trimethylsilyl)alkane-3,2-sultones **b-II**. However, the formation of the products **12f** and **18f** upon sulfonation of **12a** and **18a** indicates that the preceding β-sultones must have been of type **b-I**.

On reaction of the 1-(triisopropylsilyl)alk-2-enes **19a–21a** with 1.0 mol-equiv. of SO_3 the eventual products are the corresponding triisopropylsilyl alk-1-ene-3-sulfonate esters **19d–21d**, obtained in yields of > 95%. With **20a** at −60°C the initially observed product is the β-sultone **20b-II**, whereas the initial products of **19a** and **21a** are the carbyl sulfates **19h-II** and **21h-II**, respectively (see Table III). The formation of the various products is thought to proceed (see Scheme 4) by the intial addition of SO_3 to the 1-(triisopropylsilyl)alk-2-enes to give the β-sultone **b-II** (as was observed with **20a**), from which either the carbyl sulfate **h-II** is formed by step 2 (as observed with **19a** and **21a**), or the triisopropylsilyl sulfonate ester **d** by steps 3 and 4 via the dipolar intermediate **W**. The conversion of the carbyl sulfates **19h-II** and **21h-II** at higher temperatures into the corresponding silyl sulfonate esters **d** is thought to proceed by the sequences of steps 5, 6, and 4, and/or 5, 7, and 8.

The observed difference in the low temperature sulfonation of 1-(triisopropyl)-3-methylbut-2-ene (**20a**) and its 1-trimethylsilyl homologue **6a** is noteworthy in that there is clear ^{1}H-NMR evidence for the presence of the β-sultone **20b-II** with the former substrate, whereas with the latter there is no direct evidence for the intermediacy of either of the two corresponding β-sultones. Apparently, the rate of isomerization of β-sultone **20b-II** into the triisopropyl sulfonate ester **20c** is much smaller than that of β-sultone **6b-II**, due to the much larger steric requirements of the triisopropylsilyl, compared with the trimethylsilyl group. This makes the intramolecular migration of the former group much slower than that of the latter.



Scheme 5. Sulfonation of the unsaturated silane **23a** *with 1.1 mol-equiv. of SO_3 at −60°C.*

Sulfonation of 1-(trimethylsilyl)penta-2,4-diene (**22a**) with 1.0 mol-equiv. of SO_3 at −60°C gives quantitatively trimethylsilyl penta-1,3-diene-5-sulfonate (**22i**). There is no NMR evidence for the presence of 1-(trimethylsil-yl) pent-3-ene-5,2-sultone. However, this compound cannot be excluded as an intermediate in view of the behaviour of penta-1,3-diene. Reaction of this conjugated diene with 1.0 mol-equiv. of SO_3 at −60°C yields quantitatively the corresponding pent-3-ene-5,2-sultone, which on raising the temperature to 25°C rearranges slowly to give 1,3-pentadiene-5-sulfonic acid on raising the temperature to 25°C[13]. Reaction of 1,1,3-trimethyl-1-silacyclopent-3-ene (**23a**) with 1.1 mol-equiv. of SO_3 at −60°C gives 2,5-dimethyl-5-silahex-1-ene-3,5-sultone (**23k**) as the main product. Given the symmetrical position of the silicon and the asymmetrical position of the 3-Me both relative to the C = C moiety in the five-membered ring, the presumed β-sultone formed initially will have structure **23b** (see Scheme 5). Heterolysis of its C–O bond will afford the dipolar intermediate **Z**, which isomerizes via a five-membered bicyclic transition state to yield the γ-sultone **23k**. Reaction of the non-silicon containing 1-(cycloalkylidene)hexanes **24a–26a** with 1.1 mol-equiv. of SO_3 at −60°C gives as primary products, observed by NMR, only the 1-cycloalkylhexane-1,1′-sultones **24b-III–26b-III** (see Figure 2). At higher temperatures the β-sultones isomerize to give the 1-(cycloalk-1′-enyl)hexane-1-sulfonic acids **24m–26m**. 1-Methylene-1,2,3,4-tetrahydronaphthalene (**27a**) reacts at −60°C to give (3,4-dihydro-1-naphthyl)methanesulfonic acid (**27o**), probably (see Figure 2) via β-sultone **27n** as intermediate, although the presence of this sultone could not be confirmed.

Experimental

The ^{1}H- and ^{1}^{3}C-NMR spectra were recorded on Bruker AC-200 and WM-250 spectrometers. The IR spectra were obtained using a Perkin-Elmer 1310 spectrophotometer.

Materials

The compounds **1a–3a** and **5a–7a** were a gift from the group of Dr. *H. Hiemstra*. 1-(Trimethylsilyl)penta-2,4-diene (**22a**) was obtained from ABCR GmbH and Co. (Karlsruhe, Deutschland), and used without further purification.

The allylsilanes **4a** and **10a–18a** were prepared from the appropriate corresponding carbonyl compound, applying the Wittig-type reaction developed by *Seyferth* and coworkers[30,31]. The cyclic allylsilanes **8a** and **9a**, and the 1-(tri-isopropylsilyl)(cyclo)alk-2-enes **19a–21a** were prepared by allylic bromination of the corresponding (cyclo)alkenes with *N*-bromosuccinimide[32,33] and conversion of the resulting 3-bromo(cyclo)alkenes with metallic magnesium and trimethylsilyl chloride[34] (as for **8a** and **9a**) or with magnesium and triisopropylsilyl trifluoromethylsulfonate (as for **19a–21a**). The silane **23a** was prepared as described[35]. The alkenes **24a–27a** were prepared from the corresponding carbonyl compounds by a Wittig reaction, using the appropriate alkyltriphenylphosphonium bromide[36].

Sulfonation procedures

Method A (standard procedure). Liquid sulfur trioxide (10 μl, 0.24 mmol) was injected into a stirred solution of 30 μl of dioxane-d_8 (0.36 mmol) in 1.0 ml of dichloromethane-d_2, cooled at −78°C under an argon atmosphere. The desired amount of substrate (usually1.0 mol-equiv.) was then injected into the stirred solution. The reaction mixture was subsequently 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 appropiate time intervals during which the NMR tube was re-cooled at −70°C. The total procedure took, in general, 4–6 h.

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 substrate was injected and the resulting mixture stirred for 1 h under Ar. The reaction mixture was warmed to 0°C, poured into 10 ml of water and the resulting mixture neutralized to pH 7 with aqueous KOH. The dichloromethane was removed by rotary evaporation and the remaining water and dioxane were removed by freeze-drying. The remaining potassium sulfonate mixture was dissolved in DMSO-d_6 or D_2O and subjected to NMR analysis.

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 of the isolated potassium sulfonates in D_2O on the basis of the observed chemical shifts, absorption area ratios and coupling constants in combination with the substituent shielding parameters[37]. ^{1}H- and ^{13}C-NMR spectral data of the various products obtained, occasionally applying the APT technique, are compiled 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[38].

Spectroscopic data of substrates and products

The NMR spectra of the substrates were recorded using $CDCl_3$ as solvent and those of the products in CD_2Cl_2, *i.e.* the reaction solvent, with exception of the potassium sulfonate products, which were recorded either in D_2O as solvent or, as with the potassium sulfonate salts **12e** and **12g**, in DMSO-d_6. The chemical shifts, δ, are given in ppm. The IR spectra of the various compounds were recorded using $CHCl_3$ as solvent; the IR absorption data are given in cm^{-1}.

Starting materials. 1-(Trimethylsilyl)-2-methylprop-2-ene (**1a**). ^{1}H-NMR ($CDCl_3$): 0.03 [s, 9H; $Si(CH_3)_3$]; 1.5–1.6 (m, 2H; CH_2Si); 1.6–1.8 (m, 3H; CH_3); 4.4–4.5 (m, 1H; $=CH^aH^b$); 4.58 (m, 1H; $=CH^aH^b$).

1-(Trimethylsilyl)-2-butene (**2a**, $E/Z = 90/10$). ^{1}H-NMR ($CDCl_3$): 0.00 [s, 9H; $Si(CH_3)_3$]; 1.47 (d, 2H, *J* 6.7 Hz; *E*-CH_2Si); 1.49 (d, 2H, *J* 7.0 Hz; *Z*-CH_2Si); 1.65 (d, 3H, *J* 5.3 Hz; CH_3); 5.15–5.50 (m, 2H; CH = CH).

1-(Trimethylsilyl)non-2-ene (**3a**, $E/Z = 83/17$). ^{1}H-NMR ($CDCl_3$): 0.00 [s, 9H; $Si(CH_3)_3$]; 0.8–0.9 (m, 3H; CH_3); 1.3–1.6 [br s, 8H; $(CH_2)_4$]; 1.39 (d, 2H, *J* 7.7 Hz; *Z*-CH_2Si); 1.47 (d, 2H, *J* 7.9 Hz; *E*-CH_2Si); 1.9–2.0 (m, 2H; $=CCH_2$); 5.2–5.4 (m, 2H; CH = CH).

1-(Trimethylsilyl)-3-cyclohexylprop-2-ene (**4a**, $E/Z = 83/17$). ^{1}H-NMR ($CDCl_3$): 0.01 [s, 9H; $Si(CH_3)_3$]; 1.0–1.3 (m, 6H; $[CH_2(CH_2)_3CH_2]$; 1.38 (d, 2H, *J* 7.2 Hz; *Z*-CH_2Si); 1.46 (dd, 2H, *J* 0.9 and 8.3 Hz; *E*-CH_2Si); 1.6–1.7 (m, 4H; CH_2CHCH_2); 2.1–2.2 (m, 1H; $CHCH_2$); 5.0–5.3 (m, 2H; CH = CH).

1-(Trimethylsilyl)-3-cyclohexyl-2-methylprop-2-ene (**5a**, $E/Z = 65/35$). ^{1}H-NMR ($CDCl_3$): 0.02 [s, 9H; $Si(CH_3)_3$]; 0.8–1.4 (m, 6H; $[CH_2(CH_2)_3CH_2]$; 1.44 (s, 2H; *Z*-CH_2Si); 1.51 (s, 2H; *E*-CH_2Si); 1.5–1.7 [m, 7H; CH_3 and $=CH(CH_2)_2$]; 2.0–2.9 (m, 1H; $CHCH=$); 4.82 (d, 1H, *J* 10.0 Hz; =CH).

1-(Trimethylsilyl)-3-methylbut-2-ene (**6a**). ^{1}H-NMR ($CDCl_3$): 0.01 [s, 9H; $Si(CH_3)_3$]; 1.38 (d, 2H, *J* 8.5 Hz; CH_2Si); 1.57 (s, 3H; $=C\text{-}C^aH_3$); 1.70 (s, 3H; $=C\text{-}C^bH_3$); 5.16 (t, 1H, *J* 8.47 Hz; =CH).

1-(Trimethylsilyl)cyclopent-2-ene (**7a**). ^{1}H-NMR ($CDCl_3$): 0.02 [s, 9H; $Si(CH_3)_3$]; 1.7–2.2 (m, 3H; CH(d2CH); 2.3–2.4 (m, 2H; $CHCH_2$); 5.6–5.7 (m, 2H; CH = CH).

1-Trimethylsilylcyclohex-2-ene (**8a**). ^{1}H-NMR ($CDCl_3$): 0.02 [s, 9H; $Si(CH_3)_3$]; 1.47 (br s, 3H; CH_2CHSi); 1.7–1.8 (m, 2H; $CHCH_2CH_2$); 1.96 (br s, 2H; $CHCH_2CH_2$); 5.62 (s, 2H; CH = CH). IR: 2995 (s, C-H); 1630 (w, C = C); 1245 and 828 (s; Si-C).

1-(Trimethylsilyl)cyclohept-2-ene (**9a**). ^{1}H-NMR ($CDCl_3$): 0.01 [s, 9H; $Si(CH_3)_3$]; 0.8–0.9 (m, 1H, CHSi), 1.0–1.8 [m, 6H; $CH(CH_2)_3$], 2.1–2.2 (m, 2H, $=CHCH_2CH_2$); 5.6–5.7 (m, 2H; CH = CH). IR: 2995 (w, C-H); 1630 (w, C = C), 1245 and 828 (s, Si-C).

1-(Trimethylsilyl)-2-cyclopentylideneethane (**10a**). ^{1}H-NMR ($CDCl_3$): 0.00 [s, 9H, $Si(CH_3)_3$], 1.36 (d, 2H, *J* 8.4 Hz, CH_2Si); 1.5–1.7 [m, 4H, $=CCH_2(CH_2)_2$]; 2.1–2.3 [m, 4H; $=C(CH_2)_2$]; 5.27 (br t, 1H, *J* 8.6 Hz; =CH). IR: 2950 (s, C-H); 1620 (w, C = C), 1242 and 850 (s, Si-C).

1-(Trimethylsilyl)-2-cyclohexylideneethane (**11a**). ^{1}H-NMR ($CDCl_3$): −0.01 [s, 9H; $Si(CH_3)_3$], 1.40 (d, 2H, *J* 8.6 Hz, CH_2Si), 1.53 (br s, 6H, $CH_2(CH_2)_3CH_2$]; 2.0–2.1 [m, 4H; $=C(CH_2)_2$]; 5.09 (t, *J* 8.6 Hz; =CH). IR: 2950 (s, C-H); 1655 (w, C = C); 1240 and 850 (s, Si-C).

1-(Trimethylsilyl)-2-cycloheptylideneethane (**12a**). ^{1}H-NMR ($CDCl_3$): 0.00 [s, 9H; $Si(CH_3)_3$]; 1.37 (d, 2H, *J* 8.5 Hz; CH_2Si); 1.51 [br s, 8H; $CH_2(CH_2)_4CH_2$]; 2.19 [br s, 4H; $=C(CH_2)_2$]; 5.17 (t, 1H, *J* 8.5 Hz; =CH). IR: 2940 (s, C-H); 2840 (m, C-H); 1655 (w, C = C); 1240 and 855 (s, Si-C).

1-(Trimethylsilyl)-3-phenylprop-2-ene (**13a**, $E/Z = 86/14$). ^{1}H-NMR ($CDCl_3$): 0.04 [s, 9H; $Si(CH_3)_3$]; 1.65 (d, 2H, *J* 6.7 Hz; *E*-CH_2Si); 1.84 (d, 2H, *J* 10.5 Hz; *Z*-CH_2Si; 6.23 (m, 2H; CH = CH); 7.2–7.4 (m, 5H; C_6H_5). IR: 3080 and 3050 (w, C_6H_5); 2950 (m, C-H); 1590 (w, C = C); 1240 and 855 (s, Si-C).

1-(Trimethylsilyl)-4-phenylbut-2-ene (**14a**, $E/Z = 90/10$). ^{1}H-NMR ($CDCl_3$): 0.08 [s, 9H; $Si(CH_3)_3$]; 1.52 (m, 2H; *Z*-CH_2Si); 1.63 (d, 2H, *J* 7.5 Hz; *E*-CH_2Si); 3.39 (m, 2H; CH_2Ph); 5.53 (m, 2H; CH = CH); 7.15–7.35 (m, 5H; C_6H_5). IR: 3060 and 3000 (w, C_6H_5); 2950 (m, C-H); 1595 (w, C = C); 1240 and 855 (s, Si-C).

1-(Trimethylsilyl)-5-phenylpent-2-ene (**15a**, $E/Z = 82/18$). ^{1}H-NMR ($CDCl_3$): 0.04 [s, 9H; $Si(CH_3)_3$]; 1.43 (d, 2H; *J* 7.4 Hz; *Z*-CH_2Si); 1.49 (d, 2H, *J* 9.8 Hz; *E*-CH_2Si); 2.3–2.4 (m, 2H; $=CCH_2$); 2.70 (t, 2H, *J* 8.3 Hz; CH_2Ph); 5.3–5.5 (m, 2H; CH = CH); 7.15–7.35 (m, 5H; C_6H_5). IR: 3060 and 3000 (w, C_6H_5); 2945 (s, C-H); 2850 (m, C-H); 1595 (w, C = C); 1240 and 850 (s, Si-C).

1-(Trimethylsilyl)-6-phenylhex-2-ene (**16a**, $E/Z = 81/19$). ^{1}-NMR ($CDCl_3$): 0.01 [s, 9H; $Si(CH_3)_3$]; 1.43 (d, 2H; *J* 8.0 Hz; *Z*-CH_2Si); 1.46 (d, 2H, *J* 8.2 Hz: *E*-CH_2Si); 1.69 (qui, 2H, *J* 7.5 Hz; $CH_2CH_2CH_2$); 2.0–2.1 (m, 2H; $=CCH_2$); 2.64 (t, 2H, *J* 7.7 Hz; CH_2Ph); 5.3–5.5 (m, 2H; CH = CH); 7.15–7.35 (m, 5H; C_6H_5). IR: 3060 and 2995 (w, C_6H_5); 2920 (s, C-H), 2850 (m, C-H); 1595 (w, C = C); 1240 and 855 (s, Si-C).

1-(Trimethylsilyl)-3-phenylbut-2-ene (**17a**, $E/Z = 88/12$). ^{H}-NMR ($CDCl_3$): 0.06 [s, 9H; $Si(CH_3)_3$]; 1.43 (d, 2H, *J* 8.5 Hz; *Z*-CH_2Si); 1.67 (d, 2H, *J* 8.5 Hz; *E*-CH_2Si); 1.99 (s, 3H, CH_3), 5.89 (t, 1H, *J* 8.5 Hz; =CH); 7.2–7.4 (m, 5H; C_6H_5). IR: 3080 and 3050 (w, C_6H_5), 2550 (m, C-H); 1240 and 850 (s, Si-C).

(*E*)-1-(Trimethylsilyl)-2-(1,2,3,4-tetrahydro-1-naphthylidene)ethane (**18a**). ^{1}H-NMR ($CDCl_3$): 0.05 [s, 9H; $Si(CH_3)_3$]; 1.66 (d, 2H, *J* 8.9 Hz; CH_2Si); 1.7–1.9 (m, 2H; $CH_2CH_2CH_2$), 2.4–2.5 (m, 2H; $=CCH_2$); 2.78 (t, 2H, *J* 6.2 Hz; benzylic CH_2); 6.13 (t, 1H, *J* 8.9 Hz; =CH); 7.1–7.3 (m, 3H; H_{arom}); 7.53 (d, 1H, *J* 6.0 Hz; H_{atom}).

1-(Triisopropylsilyl)prop-2-ene (**19a**). ^{1}H-NMR ($CDCl_3$). 0.8–1.2 [m, 21H, $Si(CH(CH_3)_2)_3$]; 1.64 (d, 2H, *J* 8.1 Hz; CH_2Si); 4.81 (d, 1H, *J* 10.0 Hz; $CH = CH^aH^b$); 4.91 (d, 1H, *J* 17.0 Hz; $CH = CH^aH^b$); 5.8–5.9 (m, 1H; $CH_2 = CH$). IR: 2940 and 2860 (s, C-H); 1640 (m, C = C)); 880 (s, Si-C).

1-(Triisopropylsilyl)-3-methylbut-2-ene (**20a**). ^{1}H-NMR ($CDCl_3$): 1.60 (s, 3H; CH_3); 1.69 (s, 3H; CH_3) 1.97 (t, 2H, *J* 7.5 Hz; CH_2Si); 5.13 (t, 2H, *J* 7.5 Hz; =CH). IR: 2940 and 2860 (s, C-H); 880 (s, Si-C).

1-(Triisopropylsilyl)cyclohex-2-ene (**21a**). ^{1}H-NMR ($CDCl_3$): 1.0–1.2 [m, 21H; $Si(CH(CH_3)_2)_3$]; 1.8–2.0 [m, 7H; $(CH_2)_3CHSi$]; 5.5–5.6 (m, 1H; $=CHCH_2$); 5.73 (dd, 1H *J* 10.3 Hz; $=CHCHSi$).

1-(Trimethylsilyl)penta-2,4-diene (**22a**, $E/Z = 86/14$). ^{1}H-NMR ($CDCl_3$): 0.01 [s, 9H; $Si(CH_3)_3$]; 1.54 (d, 2H, *J* 7.9 Hz; *E*-CH_2Si); 1.66 (d, 2H, *J* 9.1 Hz; *Z*-CH_2Si); 4.86 (d, 1H, *J* 10.0 Hz; $=CH^aH^b$); 5.00 (d, 1H, *J* 16.9 Hz; $=CH^aH^b$); 5.7–5.8 (m, 1H; $=CHCH_2$); 5.93

(dd, 1H, *J* 10.1 and 15.2 Hz; CH = C*H*CH =); 6.30 (ddd, 1H, *J* 10.0, 10.1 and 16.9 Hz; CH_2 = C*H*).

1,1,3-Trimethyl-1-silacyclopent-3-ene (**23a**). ^{1}H-NMR ($CDCl_3$): 0.17 [s, 6H; $Si(CH_3)_2$]; 1.2–1.3 (m, 2H; =CHCH_2); 1.28 [s, 2H; =C(CH_3)-CH_2]; 1.76 (s, 3H; =CCH_3); 5.4–5.5 (m, 1H; =CH). IR: 2950 (s, C-H); 2870 (m, C-H); 1625 (w, C = C); 1245 and 835 (s, Si-C).

1-Cyclopentylidenehexane (**24a**). ^{1}H-NMR ($CDCl_3$): 0.87 (t, 3H, *J* 6.7 Hz; CH_3); 1.28 [br s, 6H; (CH_2)$_3$$CH_3$]; 1.5–1.7 [m, 4H; =C$CH_2$($CH_2$)$_2$]; 1.9–2.0 (m, 2H; =CHC$H_2$); 2.1–2.3 [m, 4H; =C($CH_2$)$_2$]; 5.2–2.3 (m, 1 H; =CH).

1-Cyclohexylidenehexane (**25a**). ^{1}H-NMR ($CDCl_3$): 0.72–0.88 (m, 3H; CH_3); 1.17 [br s, 6H; (CH_2)$_3$$CH_3$]; 1.42 [br s, 6H; =C$CH_2$($CH_2$)$_3$]; 1.8–1.9 (m, 2H; =CHC$H_2$); 1.9–2.1 [m, 4H; =C($CH_2$)$_2$]; 4.99 (t, 1H, *J* 7.3 Hz; =CH). IR: 2920 and 2840 (s, C-H); 1660 (w, C = C).

1-Cycloheptylidenehexane (**26a**). ^{1}H-NMR ($CDCl_3$): 0.83–0.95 (m, 3H; CH_3); 1.29 [br s, 6H; (CH_2)$_3$$CH_3$]; 1.45–1.6 [m, 8H, =C$CH_2$($CH_2$)$_4$]; 1.9–2.0 (m, 2H, =CHC$H_2$); 2.1–2.3 [m, 4H; =C($CH_2$)$_2$]; 5.13 (t, 1H, *J* 7.0 Hz; =CH). IR: 2920 and 2840 (s, C-H), 1640 (w, C = C).

1-Methylene-1,2,3,4-tetrahydronaphthalene (**27a**). ^{1}H-NMR ($CDCl_3$): 1.89 (m, 2H; CH_2C$H_2$$CH_2$); 2.54 (t, 2H, *J* 6.0 Hz; =CCH_2); 2.86 (t, 2H, *J* 6.3 Hz; benzylic CH_2); 4.96 [s, 1H, =CH(*E*)]; 5.48 [s, 1H; =CH(*Z*)]; 7.1–7.2 (m, 3H; H_{arom}); 7.6–7.7 (m, 1H; H_{arom}). ^{13}C-NMR: 23.7, C(3); 30.3, C(2); 33.1, C(4); 107.7, =CH_2, 124.0, 125.7, 127.4, 129.0, C(5)–C(8), 134.6, 137.2, 143.3, C(1), C(4a), C(8a). IR: 3080 and 3060 (w, C-H_{arom}), 2930 (m, C-H); 2860 (w, C-H), 1620 (w, C = C).

Sulfo products. Trimethylsilyl 2-methyl-1-propene-3-sulfonate (**1c**). ^{1}H-NMR (CD_2Cl_2): 0.33 [s, 9H; $Si(CH_3)_3$]; 1.88 (s, 3H; CH_3); 3.73 (s, 2H; CH_2); 5.02 (s, 1H; =CH^aH^b); 5.15 (s, 1H; =CH^aH^b).

Potassium 2-methylprop-1-ene-3-sulfonate (**1e**). ^{1}H-NMR (D_2O): 1.97 (s, 3H; CH_3); 3.71 (s, 2H; CH_2); 5.11 (s, 1H; =CH^aH^b); 5.18 (s, 1H; =CH^aH^b). ^{13}C-NMR: 23.6, CH_3; 60.9, CH_2; 119.9, *C*H_2 = C; 138.8, CH_2=*C*.

Trimethylsiiyl but-1-ene-3-sulfonate (**2c**). ^{1}H-NMR (CD_2Cl_2): 0.36 [s, 9H; $Si(CH_3)_3$]; 1.48 (m, 3H; CH_3); 3.7 (q, 1H, *J* 7.2 Hz; $CHSO_3$); 5.3–5.4 (m, 2H; =CH_2); 5.8–5.9 (m, 1H; =CH).

Potassium but-1-ene-3-sulfonate (**2e**). ^{1}H-NMR (D_2O): 1.50 (d, 3H, *J* 6.9 Hz; CH_3); 3.73 (q, 1H, *J* 7.2 Hz; $CHSO_3^-$); 5.43 (d, 1H, *J* 10.3 Hz; =CH^aH^b); 5.46 (d, 1H, *J* 17.2 Hz; =CH^aH^b); 6.08 (m, 1H; =CH).

Trimethylsilyl non-1-ene-3-sulfonate (**3c**). ^{1}H-NMR (CD_2Cl_2): 0.35 [s, 9H; $Si(CH_3)_3$]1; 0.85 (s, 3H; CH_3); 1.25 [s, 8H; CH_3(CH_2)$_4$]; 1.66 (m, 1H; C$H^aH^b$$CSO_3$); 1.9–2.1 (m, 1H; C$H^aH^b$$CSO_3$); 3.4–3.6 (m, 1H; $CHSO_3$); 5.3–5.4 (m, 2H; =CH_2); 5.6–5.7 (m, 1H; =CH).

Trimethylsilyl 3-cyclohexylprop-1-ene-3-sulfonate (**4c**). ^{1}H-NMR (CD_2Cl_2): 0.33 [s, 9H; $Si(CH_3)_3$]; 1.0–1.3 [m, 6H; CH_2(CH_2)$_3$$CH_2$]; 1.6–1.7 (m, 3H; C$H^aH^bCHCH_2$); 1.93 (d, 1H, *J* 12.3 Hz; CH^aH^bCH); 2.0–2.1 (m, 1H, *J* 3.6 Hz; C*H*CH_2); 3.40 (dd, 1H, *J* 3.6 and 10.2 Hz; $CHSO_3$); 5.29 (d, 1H, *J* 16.6 Hz; =CH^aH^b); 5.42 (d, 1H, *J* 9.9 Hz; =CH^aH^b); 5.75–5.85 (m, 1H; =CH).

Potassium 3-cyclohexylprop-1-ene-3-sulfonate (**4e**). ^{1}H-NMR (D_2O): 1.0–1.3 [m, 6H; CH_2(CH_2)$_3$$CH_2$]; 1.69 (br t, 3H; C$H^aH^bCHCH_2$); 1.9–2.0 (m, 2H; C$H^aH^b$C*H*$CH_2$), 3.31 (dd, 1H, *J* 3.8 and 10.1 Hz; $CHSO_3^-$); 5.29 (d, 1H, *J* 16.9 Hz; =CH^aH^b); 5.35 (d, 1H, *J* 10.2 Hz; =CH^aH^b); 5.85 (ddd, 1H, *J* 10.1, 10.2 and 16.9 Hz; =CH).

Trimethylsilyl 3-cyclohexyl-2-methylprop-1-ene-3-sulfonate (**5c**). ^{1}H-NMR (CD_2Cl_2): 0.36 [s, 9H; $Si(CH_3)_3$]; 0.9–1.4 [m, 6H, CH_2(CH_2)$_3$$CH_2$]; 1.6–1.8 [(m, 4H; CHCH(CH_2)$_2$]; 1.72 (s, 3H; CH_3); 2.18 (br d, 1H; C*H*$CHSO_3$); 3.41 (d, 1H, *J* 9.5 Hz, $CHSO_3$); 5.00 (s, 1H; =CH^aH^b); 5.09 (s, 1H; =CH^aH^b). ^{13}C-NMR: 0.1, $Si(CH_3)_3$; 19.9, =CCH_3; 25.9, 3×CH_2; 31.1, CH_2; 31.1, CH_2; 36.8, CH; 76.4, CS; 118.3, =CH_2; 139.8, =C.

Potassium 3-cyclohexyl-2-methylprop-1-ene-3-sulfonate (**5e**). ^{1}H-NMR (D_2O): 0.8–1.3 [m, 6H; CH_2(CH_2)$_3$$CH_2$]; 1.6–2.0 (m, 4H; C$H_2CHCH_2$); 1.79 (s, 3H; CH_3); 2.14 (br d, 1H; CH); 3.32 (d, 1H, *J* 9.9 Hz; $CHSO_3^-$); 4.95 (s, 1H; =CH^aH^b); 5.02 (s, 1H; =CH^aH^b).

Trimethylsilyl 3-methylbut-1-ene-3-sulfonate (**6c**). ^{1}H-NMR (CD_2Cl_2): 0.31 [s, 9H; $Si(CH_3)$3]; 1.43 (s, 3H; CH_3); 1.46 (s, 3H; CH_3); 5.3–5.4 (m, 2H; =CH_2); 5.9–6.1 (m, 1H; =CH). ^{13}C-NMR: 0.5, SiC_3; 22.2, 2×CH_3; 62.8, CSO_3; 118.2, =CH_2; 137.5, =CH.

Potassium 3-methylbut-1-ene-3-sulfonate (**6e**). ^{1}H-NMR (D_2O): 1.49 (s, 6H; 2×CH_3); 5.36 (d, 1H, *J* 10.7; =CH^aH^b); 5.40 (d, 1H, *J* 17.5; =CH^aH^b); 6.16 (dd, 1H, *J* 10.7 and 17.5 Hz; =CH).

Potassium cyclopent-1-ene-3-sulfonate (**7e**). ^{1}H-NMR (D_2O): 2.28 (m, 2H; C$H_2$$CHSO_3^-$); 2.5–2.6 (m, 2H; =C$CH_2$); 4.1–4.2 (m, 1H; $CHSO_3^-$); 5.8–5.9 (m, 1H; =C*H*CH_2); 6.2–6.3 (m, 1H; =C*H*$CHSO_3^-$).

Trimethylsilyl cyclohex-1-ene-3-sulfonate (**8c**). ^{1}H-NMR (CD_2Cl_2): 0.38 [s, 9H; $Si(CH_3)_3$]; 1.5–1.8 (m, 2H; CH_2C$H_2$$CH_2$); 1.8–2.1 (m, 4H; C$H_2$$CH_2CH_2$); 3.65–3.8 (m, 1H; $CHSO_3$); 5.7–5.9 (m, 1H; =C*H*CH_2); 6.0–6.1 (m, 1H; =C*H*$CHSO_3$).

Potassium cyclohex-1-ene-3-sulfonate (**8e**). ^{1}H-NMR (D_2O): 1.5–1.7 (m, 1H; C$H^aH^b$$CHSO_3^-$); 1.8–2.0 (m, 2H; =CHC$H_2CH_2$); 2.0–2.15 (m, 3H; =CHC$H_2$ and C$H^aH^b$$CHSO_3^-$); 3.6–3.7 (m, 1H; $CHSO_3^-$); 5.8–5.9 (m, 1H; =C*H*CH_2); 6.12 (dd, 1H, *J* 2.1 and 10.3 Hz; =C*H*$CHSO_3^-$).

Potassium cyclohept-1-ene-3-sulfonate (**9e**). ^{1}H-NMR (D_2O): 1.70 [m, 4H; CH_2(CH_2)$_2$$CH_2$]; 2.1–2.2 [m, 4H; C$H_2$($CH_2$)$_2CH_2$]; 3.7–3.8 (m, 1H; $CHSO_3^-$); 5.91 (dd, 1H, *J* 3.2 and 11.0 Hz; =C*H*CH_2); 6.0–6.1 (m, 1H; =C*H*$CHSO_3^-$).

β-Sultone **10b-II**. ^{1}H-NMR: 4.72 (m, 1H; CHO?).

Trimethylsilyl 1-vinylcyclopentane-1-sulfonate (**10c**). ^{1}H-NMR (CD_2Cl_2): 0.40 [s, 9H; $Si(CH_3)_3$]; 1.6–2.4 [m, 8H; $(CH_2)_4$]; 5.3–5.5 (m, 2H; CH = CH_2); 5.9–6.1 (m, 1H; C*H* = CH_2).

Potassium 1-vinylcyclopentane-1-sulfonate (**10e**). ^{1}H-NMR (D_2O): 1.6–1.8 [m, 4H, CH_2(CH_2)$_2$$CH_2$], 1.9–2.0 (m, 2H; C^a$H_2$$CSO_3^-$), 2.05–2.2 (m, 2H, C^b$H_2$$CSO_3^-$); 5.33 (d, 1H, *J* 10.7 Hz; =CH^aH^b); 5.37 (d, 1H, *J* 17.5 Hz; =CH^aH^b); 6.08 (dd, 1H, *J* 10.7 and 17.5 Hz; =CH).

β-Sultone **11b-II**. ^{1}H-NMR (CD_2Cl_2). 4.31 (dd, 1H, *J* 4.2 and 11 Hz; CHO). ^{13}C-NMR 77.7, CHO; 83.2, CSO_2. Assignment by ATP.

Trimethylsilyl 1-vinylcyclohexane-1-sulfonate (**11c**). ^{1}H-NMR (CD_2Cl_2): 0.35 [s, 9H; $Si(CH_3)_3$]; 1.55–1.7 [m, 6H; CH_2(CH_2)$_3$$CH_2$]; 1.8–2.1 [m, 4H; C$H_2$($CH_2$)$_3CH_2$]; 4.83 (d, 1H, *J* 10.6 Hz; =CH^aH^b); 4.98 (dd, 1H, *J* 19.0 Hz; =CH^aH^b); 5.5–5.6 (m, 1H; C*H* = CH_2).

β-Sultone **12b-II**. ^{1}H-NMR (CD_2Cl_2): 4.37 (dd, 1H, *J* 32 and 13.1 Hz; CHO).

Potassium 1-vinylcycloheptane-1-sulfonate (**12e**). ^{1}H-NMR (DMSO-d_6): 1.2–1.8 [m, 8H; CH_2(CH_2)$_4$$CH_2$]; 2.0–2.3 [m, 4H; C$H_2$($CH_2$)$_4CH_2$]; 4.9–5.05 (m, 2H; C$H_2$ = CH); 5.78 (dd, 1H, *J* 10.8 and 17.6 Hz; CH_2 = CH). (D_2O): 1.4–2.4 [m, 12H; $(CH_2)_6$]; 5.3–5.5 (m, 2H; CH_2 = CH); 5.9–6.0 (m, 1H; CH_2 = C*H*).

Potassium 1-(trimethylsilyl)-2-(cyclohept-1′-enyl)ethane-2-sulfonate (**12g**). ^{1}H-NMR (DMSO-d_6): −0.01 [s, 9H; $Si(CH_3)_3$]; 0.93 (dd, 1H, *J* 12.3 and 14.8 Hz; CH^aH^bSi); 1.15 (dd, 1H, *J* 2.9 and 14.8 Hz; CH^aH^bSi); 1.2–1.8 [m, 6H; =CHCH_2(CH_2)$_3$]; 2.0–2.1 (m 4H; CH_2C = CHCH_2); 2.99 (dd, 1H, *J* 2.9 and 12.3 Hz; $CHSO_3^-$); 5.5–5.6 (m, 1H; =CH). (D_2O): 0.07 [s, 9H; $Si(CH_3)_3$]; 0.9–1.0 (m, 1H; CH^aH^bSi); 1.22 (m, 1H; CH^aH^bSi); 1.3–2.4 [m, 10H; $(CH_2)_5$]; 3.5–3.6 (m, 1H; $CHSO_3^-$); 5.9–6.0 (m, 1H; =CH).

Trimethylsilyl 3-phenylprop-1-ene-3-sulfonate (**13c**). ^{1}H-NMR: 0.22 [s, 9H; $Si(CH_3)_3$]; 4.81 (d, 1H, *J* 8.9 Hz; $CHSO_3$); 5.4–5.5 (m, 2H; =CH_2); 6.2–6.4 (m, 1H; =CH); 7.2–7.4 (m, 5H; C_6H_5).

Potassium 3-phenylprop-1-ene-3-sulfonate (**13e**). ^{1}H-NMR (D_2O): 4.29 (d, 1H, *J* 8.3 Hz; $CHSO_3^-$); 5.00 (d, 1H, *J* 18.0 Hz; j = CH^aH^b); 5.07 (d, 1H, *J* 10.8 Hz; =CH^aH^b); 6.1–6.3 (m, 1H; CH_2 = C*H*); 7.1–7.4 (m, 5H; C_6H_5). ^{13}C-NMR: 73.2, CS; 123.6, =CH_2; 131.0, 131.6, 131.8, 135.7, =CH and $[C(2)–C(6)]_{Ph}$; 138.8, $C(1)_{Ph}$.

Trimethylsilyl 4-phenylbut-1-ene-3-sulfonate (**14c**). ^{1}H-NMR (CD_2Cl_2): 0.39 (s, 9H; $Si(CH_3)_3$]; 2.93 (dd, 1H, *J* 11.3 and 13.6 Hz, PhCH^aH^b); 3.46 (dd, 1H, *J* 3.5 and 13.6 Hz; PhH^aH^b), 3.81 (td, 1H, *J* 3.3 and 10.4 Hz; $CHSO_3$); 5.4–5.6 (m, 2H; =CH_2); 5.7–5.8 (m, 1H; =CH); 7.15–7.35 (m, 5H, C_6H_5).

Trimethylsilyl 5-phenylpent-1-ene-3-sulfonate (**15c**). ^{1}H-NMR (CD_2Cl_2). 0.32 [s, 9H; $Si(CH_3)_3$]; 2.2–2.4 (m, 2H; CH_2), 2.5–2.6 (m, 1H, CH^aH^b), 2.7–2.8 (m, 1H; CH^aH^b), 3.45 (td, 1H, *J* 2.9 and 10.3 Hz; $CHSO_3$); 5.4–5.6 (m, 2H; =CH_2); 5.6–5.7 (m, 1H, =CH); 7.2–7.4 (m, 5H; C_6H_5).

Trimethylsilyl 6-phenylhex-1-ene-3-sulfonate (**16c**). ^{1}H-NMR (CD_2Cl_2): 0.32 [s, 9H, $Si(CH_3)_3$]; 1.51 (m, 3H; CH^aH^bCH_2CH$_2$), 2.0–2.1 (m, 1H; CH^aH^b); 2.5–2.6 (m, 2H; CH_2Ph); 3.51 (td, 1H, *J* 2.8 and 10.3 Hz; $CHSO_3$); 5.3–5.5 (m, 2H; =CH_2); 5.5–5.6 (m, 1H; =CH); 7.2–7.4 (m, 5H; C_6H_5).

Potassium 6-phenyhex-1-ene-3-sulfonate (**16e**). ^{1}H-NMR (D_2O): 1.55–1.75 (m, 3H; CH_2CH_2CH$_2$ and C$H^aH^b$$CHSO_3^-$); 1.9–2.0 (m, 1H; C$H^aH^b$$CHSO_3^-$); 2.6–2.7 (m, 2H; C$H_2$Ph); 3.40 [td, 1H, *J* 3.2(d) and 9.5(t) Hz; $CHSO_3^-$); 5.34 (d, 1H, *J* 17.6 Hz; =CH^aH^b); 5.36 (d, 1H, *J* 9.0 Hz; =CH^aH^b); 5.7–5.8 (m, 1H; =CH): 7.2–7.4 (m, 5H; C_6H_5).

Trimethylsilyl 3-phenylbut-1-ene-3-sulfonate (**17c**). ^{1}H-NMR (CD_2Cl_2): 0.41 [s, 9H; $Si(CH_3)_3$]; 1.98 (s, 3H; CH_3); 5.3–5.8 (m, 2H; =CH_2); 6.6–6.7 (m, 1H; =CH); 7.2–7.7 (m, 5H; C_6H_5).

Potassium 3-phenylbut-1-ene-3-sulfonate (**17e**). ^{1}H-NMR (D_2O): 1.89 (s, 3H; CH_3); 5.39 (d, 1H, *J* 17.4 Hz; =CH^aH^b); 5.46 (d, 1H, *J* 10.9 Hz; =CH^aH^b); 6.70 (dd, 1H; *J* 10.9 and 17.4 Hz, =CH); 7.2–7.5 (m, 4H; C_6H_4); 7.69 [d, 1H, *J* 8.2 Hz; CH(2)$_{Ph}$]. ^{13}C-NMR: 23.2, CH_3; 69.7, CSO_3^-; 120.1, =CH_2; 130.6, 131.0, =CH and $C_{meta\text{-}\ and\ para\text{-}Ph}$; 141.5, $C_{ortho\text{-}Ph}$; 142.6, $C(1)_{Ph}$.

1-(Trimethylsilyl)-2-(3,4-dihydro-1-naphthyl)ethane-2-sulfonic acid (**18f**). ^{1}H-NMR (CD_2Cl_2): 0.12 [s, 9H; $Si(CH_3)_3$]; 1.4–1.5 (m, 2H; CH_2Si); 2.3–2.4 (m, 2H; =CCH_2); 2.77 [t, 2H, *J* 7.9 Hz; CH_2(benzylic)]; 4.40 (dd, 1H, *J* 6.5 and 11.7 Hz; C*H*SO_3H); 6.41 (t, 1H, *J* 4.7 Hz; =CH); 7.1–7.3 (m, 3H; H_{arom}); 7.3–7.4 (m, 1H; H_{arom}). The given assignments were aided by double resonance experiments. Upon irradiation at 2.36 ppm, the triplets at 2.77 and 6.41 ppm

reduce to singlets, while irradiation at 4.40 ppm reduces the multiplet at 1.43 ppm to a singlet. At −60°C the signals of CH_2Si and $CHSO_3H$ are 1.43 (d, 2H, *J* 7.9 Hz) and 4.37 (t, 1H, *J* 7.9 Hz), respectively.

Triisopropylsilyl prop-1-ene-3-sulfonate (**19d**). ^{1}H-NMR (CD_2Cl_2): 0.9–1.2 [m, 21H; $Si(CH(CH_3)_2)_3$]; 3.82 (d, 2H, *J* 7.2 Hz; CH_2SO_3); 5.4–5.5 (m, 2H; $=CH_2$); 5.90 (m, 1H; =CH). ^{13}C-NMR: 17.3, $Si[CH(CH_3)_2]_3$; 56.91, CSO_3; 123.58, $=CH_2$; 126.18, =CH.

Potassium 1-propene-3-sulfonate (**19e**). ^{1}H-NMR (D_2O): 3.65 (d, 2H, *J* 7.2 Hz; $CH_2SO_3^-$); 5.5–5.6 (m, 2H; CH_2); 5.9–6.0 (m, 1H; =CH). ^{13}C-NMR: 58.3, CSO_3^-; 124.9, $=CH_2$; 130.5, =CH.

Carbyl sulfate **19h-II**. ^{1}H-NMR (CD_2Cl_2): 3.66 (dd, 1H, *J* 1.0 and 15.0 Hz; $CH^aH^bSO_2$); 3.92 (dd, 1H, *J* 1.0 and 15.0 Hz; $CH^aH^bSO_2$); 5.25 (dt, 1H, *J* 4.3 and 10.9 Hz, CHO).

β-Sultone **20b-II** (3,2). ^{1}H-NMR (CD_2Cl_2): 4.39 (dd, 1H, *J* 1.8 and 12.8 Hz, CHO).

Triisopropylsilyl 3-methylbut-1-ene-3-sulfonate (**20d**). ^{1}H-NMR (CD_2Cl_2): 0.9–1.1 [m, 21H, $Si(CH(CH_3)_2)_3$] 1.43 (s, 6H; $2\times CH_3$); 5.36 (d, 1H, *J* 10.8 Hz; $CH=CH^aH^b$); 5.39 (d, 1H, *J* 17.2 Hz; $CH=CH^aH^b$); 6.09 (dd, 1H, *J* 10.7 and 17.3 Hz; $CH_2=CH$).

Potassium 3-methylbut-1-ene-3-sulfonate (**20e**). ^{1}H-NMR (D_2O): 1.42 (s, 6H; $2\times CH_3$); 5.29 (d, 1H, *J* 10.3 Hz; $CH=CH^aH^b$); 5.34 (d, 1H, *J* 16.6 Hz; $CH=CH^aH^b$); 6.09 (dd, 1H, *J* 10.3 and 16.6 Hz; $CH_2=CH$). ^{13}C-NMR: 24.7, CH_3; 63.1, CSO_3^-; 119.1, $=CH_2$; 141.9, =CH.

Triisopropylsilyl cyclohex-1-ene-3-sulfonate (**21d**). ^{1}H-NMR (CD_2Cl_2): 0.8–1.1 [m, 21H; $Si(CH(CH_3)_2)_3$]; 1.6–2.1 (m, 6H; $CH_2CH_2CH_2$); 3.7–3.8 (m, 1H; $CHSO_3$); 5.7–5.9 (m, 1H; $=CHCH_2$); 6.0–6.1 (m, 1H; $=CHCSO_3$). ^{13}C-NMR: 17.3, CH_3; 19.9, 23.9, 24.6, $3\times CH_2$; 58.9, CSO_3; 119.8, $=CHCH_2$; 134.4, $=CHCSO_3$.

Potassium cyclohex-1-ene-3-sulfonate (**21e**). ^{1}H-NMR (D_2O): 1.5–2.1 (m, 6H; $CH_2CH_2CH_2$); 3.65–3.75 (m, 1H; $CHSO_3^-$); 5.7–5.85 (m, 1H; $=CHCH_2$); 6.05–6.12 (dd, 1H, *J* 2.2 and 9.9 Hz; $=CHCSO_3^-$).

Carbyl sulfate **21h-II**. ^{1}H-NMR (CD_2Cl_2): 3.44 (br s, 1H; $CHSO_2$); 5.15–5.25 (m, 1H; CHO).

Trimethylsilyl penta-1,3-diene-5-sulfonate (**22i**). ^{1}H-NMR (CD_2Cl_2): 0.38 [s, 9H; $Si(CH_3)_3$]; 3.79 (d, 2H, *J* 7.3 Hz; CH_2SO_3); 5.22 (d, 1H, *J* 9.5 Hz; $CH=CH^aH^b$); 5.32 (d, 1H *J* 16.3 Hz; $CH=CH^aH^b$); 5.7–5.8 (m, 1H; $=CHCH_2$); 6.3–6.4 (m, 2H; =CH-CH=). ^{13}C-NMR: 0.63, $Si(CH_3)_3$; 56.0, CH_2; 120.26, C(4); 120.44, C(1); 135.9, C(2); 139.5, C(3).

Potassium penta-1,3-diene-5-sulfonate (**22j**). ^{1}H-NMR (D_2O): 3.68 (d, 2H, *J* 7.5 Hz; CH_2SO_2); 5.21 (d, 1H, *J* 9.5 Hz; $CH=CH^aH^b$); 5.34 (d, 1H, *J* 16.5 Hz; $CH=CH^aH^b$); 5.8–5.9 (m, 1H; $=CHCH_2$); 6.4–6.5 (m, 2H; =CHCH=).

2,5-Dimethyl-5-silahex-1-ene-3,5-sultone (**23k**). ^{1}H-NMR (CD_2Cl_2): 0.48 (s, 3H; $C^aH_3SiC^bH_3$); 0.53 (s, 3H; $C^aH_3SiC^bH_3$); 1.44 (d, 1H, *J* 7.2 Hz; $SiCH^aH^b$); 1.63 (d, 1H, *J* 12.4 Hz; $SiCH^aH^b$), 1.95 (s, 3H, CH_3), 3.93 (dd, 1H, *J* 7.3 and 12.4 Hz; $CHSO_2$), 5.2–5.3 (m, 2H, $=CH_2$).

Dipotassium bis(2,5-dimethyl-3-sulfo-5-silahex-1-en-5-yl) ether (**23l**). ^{1}H-NMR (D_2O): 0.15 [s, 6H; Si(CH$_3$)2]; 1.25–1.35 (m, 2H, $SiCH_2$), 1.85 (s, 3H; $=CCH_3$); 3.64 (dd, 1H, *J* 24.5 and 11.5 Hz; $CHSO_3^-$); 5.10 (s, 2H; $C=CH_2$). ^{13}C-NMR: 1.7, CH_3; 1.9, CH_3; 20.0, $SiCH_2$; 22.0, $=CCCH_3$; 67.2, $CHSO_3^-$; 120.3, $=CH_2$; 143.9, $C=CH_2$.

1-Cyclopentylhexane-1,1′-sultone (β-sultone **24b-III**, see Figure 2). ^{1}H-NMR (CD_2Cl_2): 4.64 (dd, 1H, *J* 4.9 and 11.1 Hz; $CHSO_2$).

1-(Cyclopent-1′-enyl)hexane-1-sulfonic acid (**24m**). ^{1}H-NMR (CD_2Cl_2): 0.89 (t, 3H, *J* 6.2 Hz; CH_3); 1.30 [br s, 6H; $(CH_2)_3CH_3$]; 1.9–2.1 (m, 4H; $=CHCH_2CH_2$ and CH_2CHSO_3H); 2.3–2.5 (m, 4H; $CiH_2CH=CCH2$); 3.84 (dd, 1H, *J* 3.7 and 11.2 Hz; $CHSO_3H$); 5.85 (s, 1H; =CH).

1-Cyclohexylhexane-1,1′-sultone (β-sultone **25b-III**, see Figure 2). ^{1}H-NMR (CD_2Cl_2): 4.23 (dd, 1H, *J* 5.1 and 10.7 Hz; $CHSO_2$).

1-(Cyclohex-1′-enyl)hexane-1-sulfonic acid (**25m**). ^{1}H-NMR (D_2O): 0.87 (t, 3H, *J* 6.4 Hz; CH_3); 1.2–1.35 [m, 6H; $(CH_2)_3CH_3$]; 1.55–1.7 [m, 4H; $=CCH_2(CH_2)_2$]; 1.9–2.0 (m, 2H; CH_2CHSO_3H); 2.0–2.2 (m, 4H; $CH_2CH=CCH_2$); 3.54 (dd, 1H, *J* 4.2 and 11.0 Hz; $CHSO_3H$); 5.85 (s, 1H; =CH).

1-Cycloheptylhexane-1,1′-sultone (β-sultone **26b-III**, see Figure 2). ^{1}H-NMR (CD_2Cl_2): 4.30 (dd 1H, *J* 4.5 and 11.2 Hz; $CHSO_2$). ^{13}C-NMR: 80.8 ($CHSO_2$); 82.6 (CO). Assignment by ATP.

1-(Cyclohept-1′-enyl)hexane-1-sulfonic acid (**26m**). ^{1}H-NMR (CD_2Cl_2): 0.8–1.0 [m, 5H; CH_3 and $=CH(CH_2)_2CH_2$]; 1.30 [br s, 6H; $(CH_2)_3CH_3$]; 1.45–1.6 (m, 4H; $=CCH_2CH_2CH_2CH_2$); 1.7–1.8 (m, 2H; CH_2CHSO_3H); 2.15–2.3 (m, 4H; $CH_2CH=CCH_2$); 3.56 (dd, 1H, *J* 3.9 and 11.1 Hz; $CHSO_3H$); 5.94 (t, 1H, *J* 6.5 Hz; =CH).

(3,4-Dihydro-1-naphthyl)methanesulfonic acid (**27o**). ^{1}H-NMR (CD_2Cl_2): 2.3–2.45 (m, 2H, $=CHCH_2$); 2.81 (t, 2H, *J* 8.1 Hz; CH_2Ph); 4.24 (s, 2H; CH_2SO_3H); 6.30 (t, 1H, *J* 4.6 Hz; =CH); 7.1–7.3 [m, 3H; H(5)–H(7)]; 7.37 [d, 1H, 7.0 Hz; H(8)].

Potassium (3,4-dihydro-1-naphthyl)methanesulfonate (**27p**). ^{1}H-NMR (D_2O): 2.2–2.4 (m, 2H, $=CHCH_2$); 2.76 (t, 2H, *J* 8.0 Hz; CH_2Ph); 4.07 (s, 2H; $CH_2SO_3^-$); 6.24 (t, 1H, *J* 4.6 Hz; =CH); 7.1–7.3 [m, 3H; $H(5)–H(7)_{Ar}$]; 7.42 [d, 1H, 7.0 Hz; $H(8)_{Ar}$]. ^{13}C-NMR: 25.2, $=CCH_2$; 30.0, C(4); 56.6, CSO_3^-; 126.2, $=CHCH_2$; 129.1, 130.1, 130.4, C(6)–C(8), 130.4, C(4), 136.1, 139.6, C(4a) and C(8a), 136.2, C(5).

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16 On reaction of the homologue 1-(trimethylsilyl)-2-cyclopentylideneethane (**10a**) with SO_3 at -60°C there is initially a ^{1}H-NMR multiplet absorption of low intensity at 4.72 ppm, which is tentatively assigned to a β-sultone **10b**. After heating the reaction mixture to room temperature the trimethylsilyl sulfonate ester **10c** was obtained as the only product, suggesting that the preceding β-sultone is of type **b-II**.
17 For the further assignment of the type of β-sultone that is formed on reaction of the various trialkylallylsilanes with SO_3, *viz.* **b-I** or **b-II**, see the Discussion.
18 The observed β-sultones formed on reaction of **24a–26a** with 1.1 mol-equiv. of SO_3 at -60°C are assigned to the **b-III** type by analogy with the chemical behaviour of 2-methylbut-2-ene and methylenecyclohexane of which the primary products are 3-methylbutane-2,3-sultone[10] and 1-methylcyclo-hexane-1′,1-sultone (IUPAC: 1-oxa-2-thiaspiro[3,5]nonane 2,2-dioxide)[19].
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26 MINDO/3 calculations on 3-methylbut-2-enylsilane applying geometrical optimalization have shown the dihedral angle Si–C(1), C(2)–C(3) to be 110°, due to hyperconjugative stabilization as

result of overlap between the empty p_π orbital and the Si–C(1) bond[22]. Studies with Catalin Stuart molecular models show that the approach of SO_3 to the carbon-carbon π bond from the upper side of the plane through the but-2-enyl carbons, *i.e.* the side at which the silyl group is located, will encounter some steric hindrance, while SO_3 attack from the opposite side of the plane through the but-2-enyl skeleton does not encounter any steric hindrance.

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