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Intramolecular competition in Friedel–Crafts sulfocyclization of ω-(1-naphthyl)-*n*-alkenes and 1,7-diphenyl-3-heptene on reaction with sulfur trioxide [a]

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Abstract. Reactions of the ω-(1-naphthyl)-*n*-alkenes **1a–9a** and 1,7-diphenyl-3-heptene (**10**) (substrates which allow intramolecular competition in any occurring sulfocyclization) with sulfur trioxide were studied in the temperature range −60 to 25°C using dichloromethane as solvent and 1.5 mol equiv. of dioxane relative to the amount of SO_3 as reactivity moderator. 4-(1-Naphthyl)-1-butene reacts with SO_3, similar to a simple alkene, yielding at low temperature the β-sultone **1b**, which at 25°C in the presence of additional SO_3 is converted into the corresponding carbyl sulfate **1d**. Reaction of the ω-(1-naphthyl)-*n*-alkenes **2a–5a**, which have a $-(CH_2)_2-$ linkage between the 1-naphthyl (1-Np) and C=C moieties, with 1.1 equiv. of SO_3 at −60°C yields very rapidly, quantitatively and stereospecifically the 1,2,3,4-tetrahydro-1-alkyl-phenanthrene-2-sulfonic acids **2f–5f**. Reaction of the 3-(1-naphthyl)-1-phenyl-1-propenes **8a** and **9a**, having a $-CH_2-$ linkage between the 1-Np and C=C moieties, with 1.1 mol equiv. of sulfur trioxide at −60°C quantitatively yields the β-sultones **8c** and **9c**, which upon increasing the temperature, are converted into *trans*-3-phenylbenz[*g*]indane-2-sulfonic acid (**11**). Reaction of 1,7-diphenyl-3-heptene (**10**) with 1.1 equiv. of SO_3 leads to exclusive formation of 1,2,3,4-tetrahydro-1-(3-phenylpropyl)naphthalene-2-sulfonic acid (**13**). Using $ClSO_3SiMe_3$ instead of SO_3, the reaction proceeds less selectively and yields, in addition to **13**, 18% of 1,2,3,4-tetrahydro-1-(3-phenyl-1-sulfopropyl)naphthalene (**14**). Mechanisms for the formation of the various products are suggested and the observed selectivity in the sulfocyclizations are discussed.

Introduction

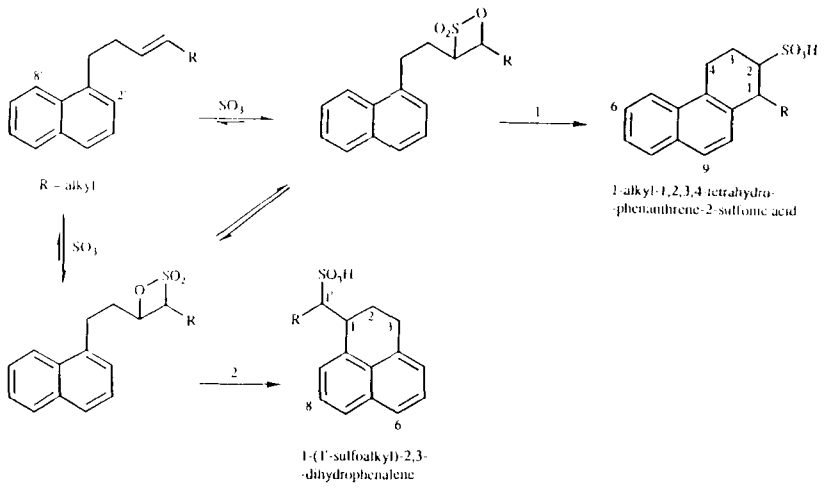
Reaction of ω-phenyl-*n*-alkenes with sulfur trioxide leads to sulfonation of the alkene moiety to yield quantitatively the corresponding β-sultones and carbyl sulfates (depending on the amount of SO_3 used). With substrates such as 5-phenyl-1-pentene, 6-phenyl-2-hexene and 5-phenyl-2-pentene, having a $-(CH_2)_3-$ or $-(CH_2)_2-$ linkage between the phenyl and the C=C moieties, sulfonation occurs, followed by a very fast Friedel–Crafts type of sulfocyclization with formation of a 1,2,3,4-tetrahydronaphthalene-derived sulfo product[2]. Further investigations have been reported on the scope and limitations of the Friedel–Crafts cyclization of ω-phenyl-*n*-alkenes with SO_3[3]. As an extension, we now report studies on intramolecular competition of sulfocyclization of a series of ω-(1-naphthyl)-*n*-alkenes and 1,7-diphenyl-3-heptene. ω-(1-Naphthyl)-*n*-alkenes containing a $-(CH_2)_2-$ bridge between the 1-naphthyl and C=C moieties allow intramolecular competition, as they have two different reactive naphthyl sites for the Friedel–Crafts cyclization, *viz.* the position 2 and 8, which would lead to the formation of 1,2,3,4-tetrahydro-1-alkylphenanthrene-2-sulfonic acid (route 1) and 2,3-dihydro-1-(sulfoalkyl)phenalene (route 2), respectively, as depicted in Scheme 1. Intramolecular competition of 1,7-diphenyl-3-heptene finds its origin in the difference in length of the two polymethylene linkages between the C=C moiety and the two phenyl groups.

Cycloalkylation with formation of a six-membered ring product has been observed on reaction of, *e.g.*, 4-(1-naphthyl)-1- and 4-(2-naphthyl)-1-butanols with a strong Lewis acid, the eventual tetrahydrophenanthrene products being formed via the initially produced carbenium ions[4]. With 4-(1-naphthyl)-1-butanol, the cyclization product is formed via two distinct pathways, *viz.*, by direct cycloaddition at the 2-position (for 84%), and by *ipso* attack at the 1-position of the naphthalene skeleton, and subsequent rearrangement of the resulting spiro type of σ complex to the same product (for 16%). 4-(2-Naphthyl)-1-butanol cyclizes exclusively by direct substitution at the 1-position[4].

Results and discussion

Reactions of the ω-(1-naphthyl)-*n*-alkenes **1a–9a** and 1,7-diphenyl-3-heptene (**10**) with (in general 1.0 and 3.0 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[5] (method A, see Experimental). In order to

[a] Aliphatic sulfonation 12. For part 11, see ref. 1.

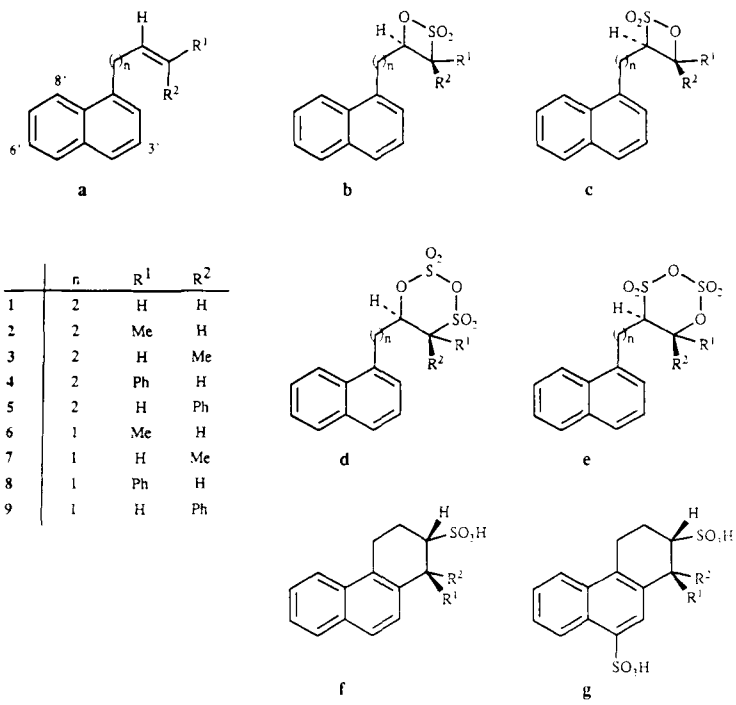


Scheme 1. Possible product formation of cycloalkylation of (E)-5-(1-naphthyl)-2-pentene (**2a**) *with* SO_3.

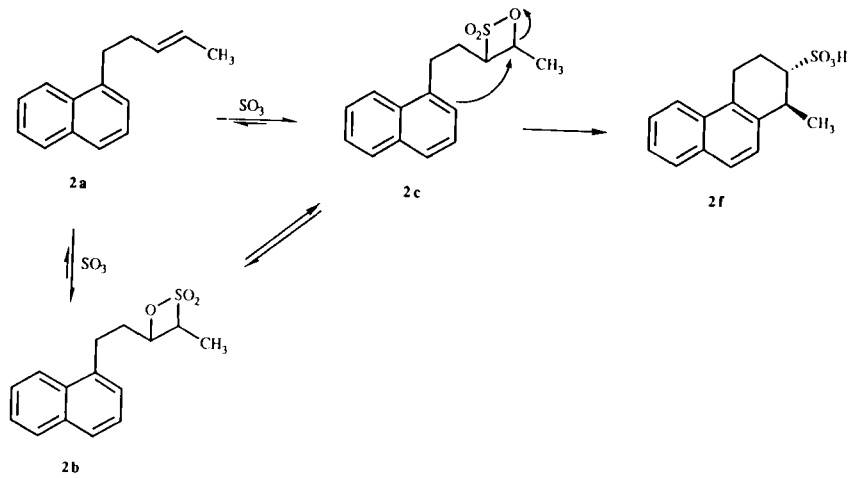
obtain information on the primary sulfonation products, the reactions were carried out at low temperatures, and the reaction mixtures were analyzed by ^{1}H NMR spectroscopy. The ^{1}H-NMR and some ^{13}C-NMR assignments of the ω-(1-naphthyl)-*n*-alkenes and their sulfo products are compiled in Tables I–II or in the Experimental section.

Reaction of 4-(1-naphthyl)-1-butene (**1a**) with 1.0 equiv. of SO_3 at −60°C leads to quantitative formation of β-sultone **1b**, which is stable at room temperature for at least 12 h. Addition of water and leaving the resulting heterogeneous mixture as such for 1 day, leads to quantitative desulfonation with reformation of 4-(1-naphthyl)-1-butene (**1a**). Upon using an excess of SO_3 (≥ 4.0 equiv.), we observed at 0°C slow conversion of the initial β-sultone **1b** into the carbyl sulfate **1d**. Allowing the reaction mixture to stand overnight led to subsequent aromatic sulfonation at the 4-position of the naphthalene ring to give **1d**-4-sulfonic acid. Exclusive sulfonation at the 4-position is in line with the results of *Lammertsma*[6], who observed that the sulfonation of 1-methylnaphthalene with SO_3 yields 1-methylnaphthalene-4-sulfonic acid as the sole product.

Reaction of a 3:1 mixture of (*E*)- (**2a**) and (*Z*)-5-(1-naphthyl)-2-pentene (**3a**), which have a $-(CH_2)_2-$ linkage between the 1-naphthyl and the C=C moieties, with 1.1 equiv. of SO_3 at low temperature leads to the quantitative formation of the *trans* and *cis* isomers of 1,2,3,4-tetrahydro-1-methylphenanthrene-2-sulfonic acid (**2f** and **3f**), respectively. This Friedel–Crafts type of cyclization is extremely fast: at −60°C, it is complete within 10 min. We propose that the formation of these products proceeds as shown for **2f** in Scheme 2. The initial β-sultone formation is followed by a S_N2 displacement of the naphthyl C(2) on the oxygen-carrying carbon of the side chain, similar to that established for the Friedel–Crafts cyclization of ω-phenyl-*n*-alkenes[2,3]. The *trans* to *cis* isomer ratio of the cyclization products is the same as the *E*/*Z* ratio of the starting pentenes **2a** and **3a**, indicating that (*i*) (not observed) β-sultones are the likely intermediates and (*ii*) cyclization proceeds stereospecifically with inversion at the oxygen-carrying carbon C(2). Thus, the present cyclization proceeds similar to that of the corresponding ω-phenyl-*n*-alkenes. Reaction of a 3:1 mixture of **2a** and **3a** with an excess of SO_3 (3.0 equiv.) leads to the rapid



	n	R^1	R^2
1	2	H	H
2	2	Me	H
3	2	H	Me
4	2	Ph	H
5	2	H	Ph
6	1	Me	H
7	1	H	Me
8	1	Ph	H
9	1	H	Ph

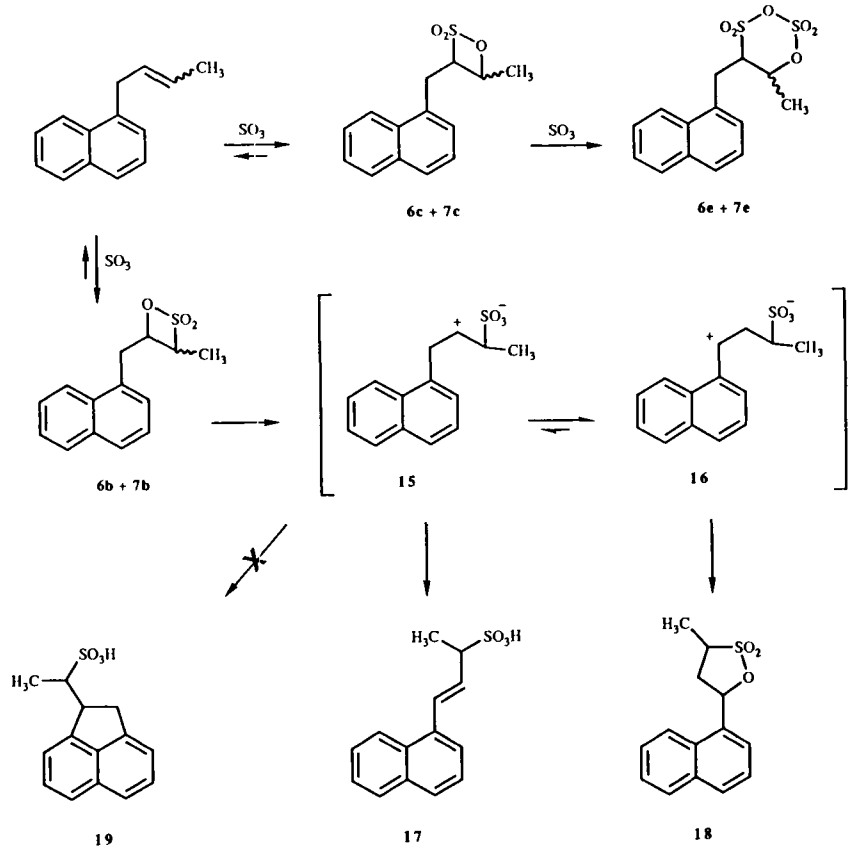


Scheme 2. Mechanism for cycloalkylation of (E)-5-(1-naphthyl)-2-pentene (**2a**) *with* SO_3.

formation of **2f** and **3f**, followed, at 25°C, by slow sulfonation of the naphthyl ring to yield *trans*- (**2g**) and *cis*-1,2,3,4-tetrahydro-1-methylphenanthrene-2,9-disulfonic acid (**3g**) in the same ratio as the starting *E*/*Z* ratio of the 2-pentenes **2a** and **3a**.

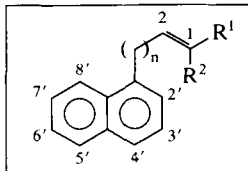
Similarly, reaction of a 1:1 mixture of (*E*)- (**4a**) and (*Z*)-4-(1-naphthyl)-1-phenyl-1-butene (**5a**) with 1.0 equiv. of SO_3 yields, quantitatively, the respective *trans* and *cis* isomers of 1,2,3,4-tetrahydro-1-phenylphenanthrene-2-sulfonic acid (**4f** and **5f**) in the same ratio as the starting *E*/*Z* ratio of the 4-(1-naphthyl)-1-phenyl-1-butenes (**4a** and **5a**). Upon using an excess of SO_3 ($\geq$ 2.0 equiv.) at 25°C, **4f** and **5f** are subsequently converted into *trans*- (**4g**) and *cis*-1,2,3,4-tetrahydro-1-phenylphenanthrene-2,9-disulfonic acid (**5g**), respectively. This slow sulfo-deprotonation at position 9 of the 1,2,3,4-tetrahydrophenanthrene skeleton is in line with the observations of *Lammertsma*[7], that reaction of 1,2-dimethylnaphthalene with SO_3 leads exclusively to the 4-sulfonic acid.

Sulfonation of a 2:1 mixture of (*E*)- (**6a**) and (*Z*)-4-(1-naphthyl)-2-butene (**7a**) with 1.0 equiv. of SO_3 at - 60°C leads to formation of the two isomeric 2,3- and 3,2-sultones **6b** + **7b** and **6c** + **7c** in the same ratio as the starting material. After raising the temperature to 25°C, both in the presence and absence of residual SO_3, the isomeric β-sultones are slowly converted into as yet unidentified products. We propose these additional products to be the corresponding *trans*- (**6e**) and *cis*-carbyl sulfate (**7e**), 4-(1-naphthyl)-3-butene-2-sulfonic acid (**17**) and 4-(1-naphthyl)-2,4-butanesultone (**18**) (see Scheme 3), resulting from the zwitter-ionic intermediates **15** and **16**. The formation of 1-(1-sulfoethyl)acenaphthene (**19**) can be excluded on the basis of the ^{1}H-NMR absorption signals (aromatic region).



Scheme 3. Reaction of (E)- (**6a**) *and (Z)-4-(1-naphthyl)-2-butene* (**7a**) *with* SO_3.

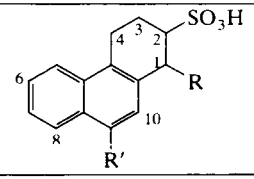
Table I *^{1}H NMR data of ω-(1-naphthyl)-n-alkenes* [a].



		^{1}H NMR ($CDCl_3$, δ, ppm) [b]											
		Naphthyl							Alkenyl				
	Substituents	CH(2')	CH(3')	CH(4')	CH(5')	CH(6')	CH(7')	CH(8')	CH(1)	CH(2)	CH_2(3)	CH_2(4)	R [c]
1a	$R^1 = R^2 = H$, $n = 2$	7.5–7.6 (m)	7.5–7.6 (m)	7.72 (d) 8.0	7.84 (dd) 4.6 2.3	7.5–7.6 (m)	7.5–7.6 (m)	8.02 (dd) 7.5 1.4	5.16 (m)	6.01 (m)	2.52 (dt) 7.9 6.8	3.15 (t) 8.3	5.16 (m)
2a	R^1 = Me, R^2 = H, $n = 2$	7.3–7.7 (m)	7.3–7.7 (m)	7.61 (d) 7.8	7.91 (dd) 4.6 2.3	7.3–7.7 (m)	7.3–7.7 (m)	8.11 (dd) 1.4 7.5	5.61 (m)	5.61 (m)	2.58 (m)	3.24 (t) 8.3	1.58 (d) 5.1
3a	R^1 = H, R^2 = Me, $n = 2$	7.3–7.7 (m)	7.3–7.7 (m)	7.61 (d) 7.8	7.91 (dd) 4.6 2.3	7.3–7.7 (m)	7.3–7.7 (m)	8.11 (dd) 1.4 7.5	5.61 (m)	5.61 (m)	2.58 (m)	3.24 (t) 8.3	1.76 (d) 4.9
4a	R^1 = Ph, R^2 = H, $n = 2$	7.2–7.6 (m)	7.2–7.6 (m)	7.81 (d) 11.5	7.94 (m)	7.2–7.6 (m)	7.2–7.6 (m)	8.19 (d) 9.0	6.55 (m)	6.55 (m)	2.78 (m)	3.34 (dd) 15.3 7.0	7.2–7.6 (m)
5a	R^1 = H, R^2 = Ph, $n = 2$	7.2–7.6 (m)	7.2–7.6 (m)	7.81 (d) 11.5	7.94 (m)	7.2–7.6 (m)	7.2–7.6 (m)	8.12 (dd) 8.4 1.5	6.55 (m)	5.90 (dt) 11.6 7.1	2.92 (m)	3.34 (dd) 15.3 7.0	7.2–7.6 (m)
6a	R^1 = Me, R^2 = H, $n = 1$	7.3–7.6 (m)	7.3–7.6 (m)	7.78 (d) 7.5	7.91 (dd) 5.7 2.2	7.3–7.6 (m)	7.3–7.6 (m)	8.09 (dd) 7.0 2.7	5.73 (m)	5.73 (m)	3.90 (d) 4.6	–	1.87 (d) 4.7
7a	R^1 = H, R^2 = Me, $n = 1$	7.3–7.6 (m)	7.3–7.6 (m)	7.78 (d) 7.5	7.91 (dd) 5.7 2.2	7.3–7.6 (m)	7.3–7.6 (m)	8.09 (dd) 7.0 2.7	5.73 (m)	5.73 (m)	3.80 (d) 4.8	–	1.74 (dd) 4.8 1.4
8a	R^1 = Ph, R^2 = H, $n = 1$	7.1–8.0 (m)							6.61 (m)	6.61 (m)	4.15 (m)	–	7.1–8.0 (m)
	R^1 = H, R^2 = Ph, $n = 1$	7.1–8.0 (m)							5.97 (m)	6.61 (m)	4.03 (d) 4.7	–	7.1–8.0 (m)

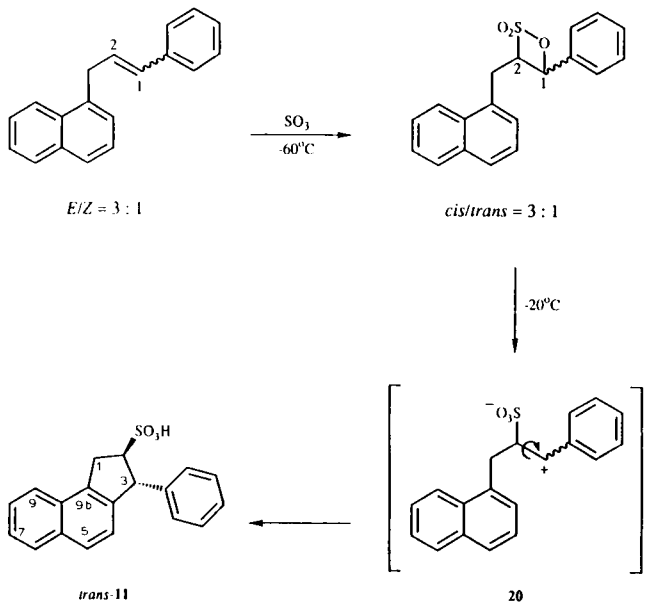
[a] The substrates are numbered starting at the double bond. [b] Underlined data represent coupling constants in Hz. [c] R stands for R^1 or R^2, as appropriate.

TABLE II ^1H *NMR data of substituted 1,2,3,4-tetrahydrophenanthrenes* [a].



	Substituents	^1H NMR (δ, ppm) [b]										
		R	CH(1)	CH(2)	CH_2(3)	CH_2(4)	CH(5)	CH(6)	CH(7)	CH(8)	CH(9)	CH(10)
2f/3f	R = Me, R′ = H *trans / cis*	1.47 (d) 6.7 (*trans*) 1.52 (d) 7.0 (*cis*)	3.61 (m)	3.12 (m)	2.2–2.5 (m)	3.41 (m) 3.56 (m)	7.88 (d) 7.8	7.48 (m)	7.48 (m)	7.79 (d) 7.9	7.66 (d) 8.5	7.26 (d) 8.6
2g/3g	R = Me, R′ = SO_3H *trans / cis*	1.18 (d) 6.8 (*trans*)	3.25 (m)	2.91 (m)	1.7–2.5 (m)	2.22 (m) 2.58 (m)	7.45 (m)	7.14 (m)	7.14 (m)	8.53 (d) 8.6	–	7.79 (s)
4f/5f	R = Ph, R′ = H *trans / cis*	6.9–7.5 (m)	4.82 (d) 4.3 (*trans*) 4.87 (d) 4.4 (*cis*)	3.8–3.6 (m)	2.40 (m)	3.7–3.2 (m)	8.05 (d) 8.3	7.56 (m)	7.56 (m)	7.79 (d) 7.4	7.56 m	7.00 (d) 8.2
4g/5g	R = Ph, R′ = SO_3H *trans / cis*	7.0–7.3 (m)	4.90 (m)	3.67 (m)	2.45 (m)	3.2–3.8 (m)	7.78 (d) 7.4	7.69 (m)	7.69 (m)	8.61 (m)	–	8.17 (m)

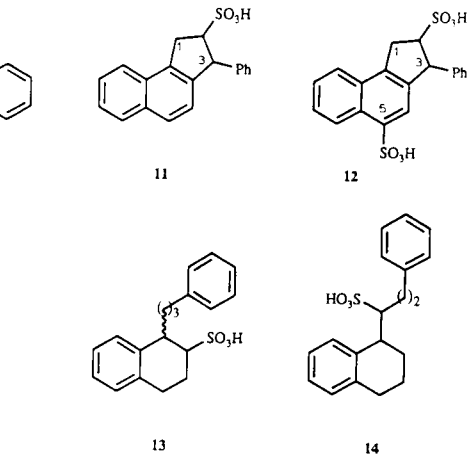
[a] In some cases, because of overlap, the specific ^1H NMR signals of the *cis*- and *trans*-isomers could not be assigned. [b] Underlined data represent coupling constants.



Scheme 4. Mechanism for cycloalkylation of (E)- (**8a**) *and (Z)-3-(1-naphthyl)-1-phenyl-1-propene* (**9a**) *with SO_3.*

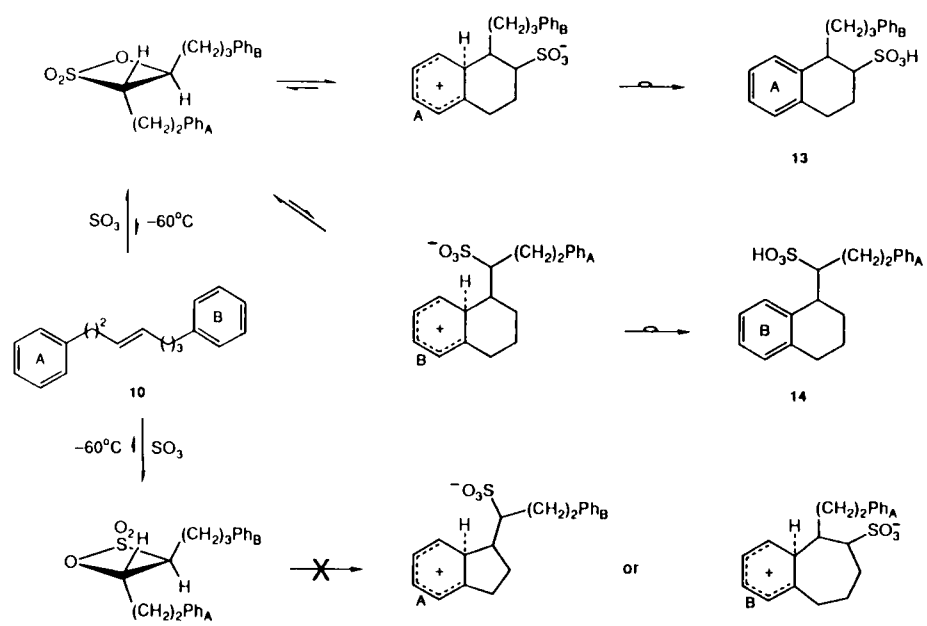
Reaction of a 3 : 1 mixture of (*E*)- (**8a**) and (*Z*)-3-(1-naphthyl)-1-phenyl-1-propene (**9a**) with 1.1 equiv. of SO_3 at −60°C leads to the stereospecific formation of *trans*- and *cis*-2,1-sultones **8c** and **9c**, respectively. The *cis*/*trans* ratio of the 2,1-sultones is the same as the *E*/*Z* ratio of the starting ω-(1-naphthyl)alkenes **8a** and **9a**. After raising the temperature to −40°C, only the *trans*-sultone **8c** is rapidly converted into the five-membered ring cyclization product *trans*-3-phenylbenz[*g*]indane-2-sulfonic acid (**11**)[8]. However, upon raising the temperature to 0°C, the *cis*-sultone **9c** is also slowly converted into the same cyclization product **11**. Thus, for this type of substrate, cycloalkylation is *not* stereospecific, and sulfocyclization is, therefore, proposed to proceed (see Scheme 4) via the conjugatively stabilized benzylic sulfonate dipolar intermediate **20**, as was suggested for the cyclization of a mixture of (*E*)- and (*Z*)-1,3-diphenyl-1-propenes[3,9].

Upon using instead 3.0 equiv. of SO_3, the formation of *trans*-**11** at 0°C is followed by relatively slow sulfonation of its naphthyl ring at the 4-position, providing *trans*-3-phenylbenz[*g*]indane-2,5-disulfonic acid (**12**) in quantitative yield.



Reaction of 1,7-diphenyl-3-heptene[10] (**10**) with 1.1 equiv. of SO_3 in the presence of 1.6 mol equiv. of dioxane at −60°C gave regioselectively and exclusively 1,2,3,4-tetrahydro-1-(3-phenylpropyl)naphthalene-2-sulfonic acid (**13**)[11] in a yield of > 97%. Based on the results of 5-phenyl-2-pentene and 6-phenyl-2-hexene, we presume that the reaction proceeds via the corresponding β-sultones and thus stereospecifically. On using the less reactive sulfonating reagent $ClSO_3SiMe_3$[12] at −20°C, the cyclization leads to **13** for 82% and to the alternative cyclization product 1,2,3,4-tetrahydro-1-(3-phenyl-1-sulfopropyl)naphthalene (**14**) for 18%. The presence of **14** is based on ^{1}H-NMR absorptions of equal intensity at δ 3.77 (m) and 3.80 (m)[13] for CH(1) and CH–SO_3H, respectively. The loss of selectivity is due to the lower sulfonating reactivity of $ClSO_3SiMe_3$ which, therefore, requires a higher reaction temperature (−20°C), leading to lower selectivity in the subsequent sulfocyclization. The quantitative formation of **13** on using SO_3 at −60°C may be explained in terms of a lower energy content of **13** as compared to **14**[14].

Notably, the absence of formation of any 2,3-dihydro-1-(1-sulfoalkyl)phenalene (see Scheme 1) on reaction of the ω-(1-naphthyl)-*n*-alkenes **2a–5a** with SO_3 and of any 1-(1-sulfoalkyl)acenaphthene (*e.g.* **19**, see Scheme 3) on reaction of ω-(1-naphthyl)-*n*-alkenes **6a** and **7a** with SO_3, illustrates that the cycloalkylation of ω-(1-naphthyl)-*n*-al-



Scheme 5. Mechanism for the cycloalkylation of 1,7-diphenyl-3-heptene (**10**) *with SO_3 and $ClSO_3SiMe_3$.*

kenes occurs specifically at the adjacent naphthyl C(2) and not at the *peri* carbon. *Lammertsma* et al.[7] reported however that the *peri* position has a lower localization energy and is, therefore, more reactive. The exclusive sulfocyclization at the 2-position which gave the 1,2,3,4-tetrahydrophenanthrene derivative **2f** instead of the 2,3-dihydrophenalene (see Scheme 1) or acenaphthene derivative **19** may be explained in terms of the lower degree of strain in the resulting six-membered ring upon forming the 1,2,3,4-tetrahydrophenanthrene skeleton, compared to the newly formed six- and five-membered rings upon forming the 2,3-dihydrophenalene and the acenaphthene skeletons, respectively. In fact, this is clearly apparent from a study with space-filling Catalin Stuart molecular models. The formation of the five-membered ring cyclization product with 3-(1-naphthyl)-1-phenyl-1-propenes (**8a** and **9a**) differs from those of the non-phenyl-containing ω-(1-naphthyl)-*n*-alkenes **2a–5a** in that there is now only one β-sultone formed, *viz.* the 2,1-sultone, and that the positive charge of the corresponding dipolar intermediate **20** is conjugatively stabilized by the adjacent phenyl group (see Scheme 4). From molecular model studies, it appears that cyclization at the *peri* position, which would give rise to a six-membered ring product, is sterically very unfavorable, rendering more attractive the sterically less hindered cyclization at C(2) with formation of the five-membered ring product **11**.

Both the exclusive formation of **13** on reaction of 1,7-diphenyl-3-heptene (**10**) with SO_3, and of a 4:1 mixture of **13** and **14**, on using $ClSO_3SiMe_3$ as sulfonating reagent, as well as the exclusive formation of 1,2,3,4-tetrahydro-1-alkylphenanthrene-2-sulfonic acids (**2f–5f**) from the ω-(1-naphthyl)-*n*-alkenes (**2a–5a**), indicate that a very rapid equilibrium must exist between the initially formed isomeric *m,n*- and *n,m*-sultones, as was proposed to explain the highly regioselectivity in the sulfocyclization of simple ω-phenyl-*n*-alkenes[3] and simple alkenoic acids[15].

Experimental

The ^{1}H 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 and the IR spectra on a Perkin–Elmer 1310 instrument.

Materials

The ω-(1-naphthyl)alkenes **1a–5a** were prepared in three steps from 1-naphthalenecarbaldehyde, which on reaction with cyanoacetic acid was converted into (*E*)-3-(1-naphthyl)propenenitrile, as reported by *Stokker* et al.[16]. Subsequent hydrogenation of the propenenitrile using 10% Pd/C as catalyst gave the corresponding naphthylpropanenitrile. Reduction of this nitrile by diisobutylaluminum hydride then gave the corresponding 4-naphthylbutanal. Wittig reaction of this butanal[17], using the appropriate alkyltriphenylphosphonium bromide as reagent[18], finally yielded the required ω-(1-naphthyl)alkene substrates **1a–5a**. The ω-(1-naphthyl)alkenes **6a–9a** were prepared in two steps from 2-(1-naphthyl)ethanol, starting by oxidation, as reported by *Swern* et al.[19], followed by Wittig reaction of the resulting aldehyde, using the appropriate alkyltriphenylphosphonium bromide as reagent[18]. 1,7-Diphenyl-3-heptene (**10**) was prepared in two steps from 4-phenyl-1-butanol, starting by oxidation, as reported by *Corey* and *Suggs*[20], followed by Wittig reaction of the resulting aldehyde, using (3-phenylpropyl)triphenylphosphonium bromide[17]. The ^{1}H-NMR and ^{13}C-NMR data of the substrates are listed in Table I or later.

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. 45 μl of, *e.g.*, 4-(1-naphthyl)-2-butene (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-(1-naphthyl)-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 Ar atmosphere, and the mixture stirred for 1 h. The reaction mixture was warmed to 0°C and poured into 10 ml of water and then 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 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 from the isolated potassium sulfonates in D_2O as solvent on the basis of the observed chemical shifts, absorption area ratios and coupling constants in combination with substituent shielding parameters[21]. The ^{1}H- and ^{13}C-NMR spectral data of the various products, which were obtained with the special aid of NOE and APT techniques if required, are compiled in Tables I and II, and in this section. The compositions of the reaction mixtures, as well as the [*E*]/[*Z*] ratios of the starting compounds, were determined by multicomponent ^{1}H NMR analysis on the basis of specific absorptions of the assigned components[22].

Starting materials

4-(1-Naphthyl)-1-butene (**1a**). ^{13}C NMR ($CDCl_3$, δ, ppm): 32.5 ($\underline{C}H_2CH=CH_2$), 34.9 ($\underline{C}H_2C_{10}H_7$), 115.0 (CH=$\underline{C}H_2$), 123.8 (Np C7), 125.4, 125.6, 125.8, 126.0, 126.7 (Np C2, C3, C4, C5, C6), 128.8 (Np C8), 131.9 (Np C8a), 134.0 (Np C4a), 138.0 (Np C1), 138.3 ($\underline{C}H=CH_2$). IR ($CHCl_3$, cm^{-1}): 3060 (s), 3000 (m), 2930 (s), 2860 (m), 1630 (m), 1590 (m), 1510 (m), 1460 (m), 1430 (m), 1390 (m), 960 (s), 910 (s). MS (EI) *m/z*: 182 (M, 32), 141 (100), 115 (12). Accurate mass calculated for $C_{14}H_{14}$: 182.1095; found: 12.1083.

(E)-5-(1-Naphthyl)-2-pentene (**2a**). ^{13}C NMR ($CDCl_3$, δ, ppm): 12.7 (CH_3), 28.1 ($\underline{C}H_2CH=C$), 33.2 ($\underline{C}H_2$-Np), 123.7, 124.5, 125.3, 125.7, 125.9, 126.6, 128.7, 129.8 (Np C2, C3, C4, C5, C6, C7, C8, $\underline{C}H=\underline{C}H$), 131.9 (Np C8a), 133.9 (Np C4a), 138.1 (Np C1). MS (EI) *m/z*: 196 (M, 25), 141 (100), 115 (14). Accurate mass calculated for $C_{15}H_{16}$: 196.1252; found: 196.1261.

(Z)-5-(1-Naphthyl)-2-pentene (**3a**). ^{13}C NMR ($CDCl_3$, δ, ppm): 17.9 (CH_3), 32.9 ($\underline{C}H_2CH=C$), 33.7 ($\underline{C}H_2$-Np), 123.8, 124.5, 125.5, 125.6, 125.8, 126.4, 128.7, 129.8, 130.8 (Np C2, C3, C4, C5, C6, C7, C8, $\underline{C}H=\underline{C}H$), 131.9 (Np C8a), 133.9 (Np C4a), 138.2 (Np C1). MS (EI) *m/z*: 196 (M, 25), 141 (100), 115 (14). Accurate mass calculated for $C_{15}H_{16}$: 169.1252; found: 169.1261.

(E)- and (Z)-5-(1-Naphthyl)-2-pentene (**2a** *and* **3a**). IR ($CHCl_3$, cm^{-1}): 3010 (m), 2940 (m), 1590 (m), 1510 (m), 1390 (m), 790 (s), 770 (s).

(E)- and (Z)-4-(1-Naphthyl)-1-phenyl-1-butene (**4a** *and* **5a**). IR ($CHCl_3$, cm^{-1}): 3050 (m), 3000 (m), 2930 (s), 2860 (m), 1630 (m), 1590 (m), 1510 (m), 1460 (m), 1430 (m), 1390 (m), 990 (m), 910 (s). MS (EI) *m/z*: 258 (M, 22), 167 (7), 141 (100), 115 (14), 91 (8). Accurate mass calculated for $C_{20}H_{18}$: 258.1409; found: 258.1431.

1,7-Diphenyl-3-heptene (**10**)[8]. ^{1}H NMR ($CDCl_3$, δ, ppm): 1.64 (m, CH_2), 2.04 (m, CH_2), 2.35 (m, CH_2), 2.60 (t, *J* 7.7 Hz, $C\underline{H}_2Ph$), 2.68 (t, *J* 7.1 Hz, $C\underline{H}_2Ph$), 5.45 (m, CH=CH), 7.28 (m, 10H, 2×Ph).

Sulfo products

4-(1-Naphthyl)-1,2-butanesultone (**1b**). ^{1}H NMR (CD_2Cl_2, δ, ppm): 2.2–2.5 (m, $C\underline{H}_2CHO$), 3.14 (m, $C\underline{H}^aH^b$-Np), 3.34 (m, $CH^a\underline{H}^b$-Np), 4.14 (dd, *J* 16.0, 8.8 Hz, $C\underline{H}^cH^dSO_2$), 4.59 (m, $CH^c\underline{H}^dSO_2$, $C\underline{H}O$), 7.2–7.7 (m, Np H2, H3, H6, H7), 7.8 (d, *J* 7.6 Hz, Np H4), 7.88 (dd, *J* 7.5, 1.9 Hz, Np H5), 8.00 (d, *J* 7.9 Hz, Np H8).

6-[2-(1-Naphthyl)ethyl]-1,3,2,4-dioxadithiane 2,2,4,4-tetraoxide (carbyl sulfate **1d**). ^{1}H NMR (CD_2Cl_2, δ, ppm): 2.34 (m, C$\underline{H}_2$CHO), 3.25 (m, CH^{a}H^b-Np), 3.46 (m, CH$^a\underline{H}^b$-Np), 3.60 (dd, *J* 11.7, 7.8 Hz, C$\underline{H}^c$H^{d}SO$_2$), 3.78 (dd, *J* 11.9, 2.0 Hz, CH$^c\underline{H}^d$SO$_2$), 5.16 (m, CHO), 7.2–7.7 (m, Np H2, H3, H6, H7), 7.79 (d, *J* 7.6 Hz, Np H4), 7.87 (dd, *J* 7.5, 1.9 Hz, Np H5), 8.00 (d, *J* 7.9 Hz, Np H8).

1d-*4-sulfonic acid.* ^{1}H NMR (CD_2Cl_2, δ, ppm): 2.34 (m, C$\underline{H}_2$CHO), 3.25 (m, CH^{a}H^b-Np), 3.46 (m, CH$^a\underline{H}^b$-Np), 3.60 (dd, *J* 11.7, 7.8 Hz, C$\underline{H}^c$H^{d}SO$_2$), 3.78 (dd, *J* 11.9, 2.0 Hz, CH$^c\underline{H}^d$SO$_2$), 5.16 (m, CHO), 7.30–8.00 (m, Np H2, H6, H7, H8), 8.18 (d, *J* 7.6 Hz, Np H3), 8.70 (dd, *J* 7.8, 2.1 Hz, Np H5).

trans-1,2,3,4-Tetrahydro-1-methylphenanthrene-2-sulfonic acid (**2f**). ^{13}C NMR (CD_2Cl_2, δ, ppm): 18.9 (CH_3), 19.0 ($\underline{C}H_2$CHS), 25.8 ($\underline{C}H_2$-Np), 34.8 ($\underline{C}HCH_3$), 61.0 (CHS), 123.4 [CH(5)], 125.8, 126.6, 127.1, 127.7, 128.8 (C6, C7, C8, C9, C10), 129.3, 132.1, 132.4, 137.9 (C4a, C5a, C8a, C1a).

cis-1,2,3,4-Tetrahydro-1-methylphenanthrene-2-sulfonic acid (**3f**). ^{13}C NMR (CD_2Cl_2, δ, ppm): 25.0 (CH_3), 21.2 ($\underline{C}H_2$CHS), 22.7 ($\underline{C}H_2$-Np), 34.2 ($\underline{C}HCH_3$), 62.7 (CHS), 123.4 (C5), 125.7, 126.6, 126.8, 127.6, 128.7 (C6, C7, C8, C9, C10), 130.4, 132.0, 132.2, 135.8 (C4a, C5a, C8a, C1a).

trans-1,2,3,4-Tetrahydro-1-phenylphenanthrene-2-sulfonic acid (**4f**). ^{13}C NMR (CD_2Cl_2, δ, ppm): 21.1 ($\underline{C}H_2$CHS), 23.0 ($\underline{C}H_2$-Np), 45.4 ($\underline{C}$H-Ph), 66.7 (CHS), 123.6–145.1 (aromatic C).

cis-1,2,3,4-Tetrahydro-1-phenylphenanthrene-2-sulfonic acid (**5f**). ^{13}C NMR (CD_2Cl_2, δ, ppm): 19.1 ($\underline{C}H_2$CHS), 25.6 ($\underline{C}H_2$-Np), 45.8 ($\underline{C}$H-Ph), 64.1 (CHS), 123.6–145.1 (aromatic C).

trans-3-(1-Naphthyl)-1-phenyl-2,1-propanesultone (**8c**). ^{1}H NMR (CD_2Cl_2, δ, ppm): 3.82 (m, CH$^a\underline{H}^b$-Np), 3.98 (m, CH$^a\underline{H}^b$-Np), 5.15 (q, *J* 6.4 Hz, CHSO$_2$), 5.36 (d, *J* 6.4 Hz, CHO), 7.0–8.0 (m, 12H, Np + Ph).

cis-3-(1-Naphthyl)-1-phenyl-2,1-propanesultone (**9c**). ^{1}H NMR (CD_2Cl_2, δ, ppm): 3.11 (dd, *J* 15.5, 4.8 Hz, CH$^a\underline{H}^b$-Np), 3.33 (dd, *J* 15.4, 10.7 Hz, CH$^a\underline{H}^b$-Np), 5.60 (m, CHSO$_2$), 5.79 (d, *J* 8.5 Hz, CHO), 7.0–8.0 (m, 12H, Np + Ph).

trans-3-Phenylbenz[g]indane-2-sulfonic acid (*trans*-**11**). ^{1}H NMR (CD_2Cl_2, δ, ppm): 3.56 (m, CH_2), 3.92 (m, CHSO$_3$H), 5.10 (d, *J* 3.1 Hz, C$\underline{H}$-Ph), 6.9–8.0 (m, 11H, Np + Ph). ^{13}C NMR (CD_2Cl_2, δ, ppm): 28.0 (CH_2), 46.7 ($\underline{C}$H-Ph), 62.4 (CHS), 123–145 (aromatic C).

trans-3-Phenylbenz[g]indane-2,5-disulfonic acid (*trans*-**12**). ^{1}H NMR (CD_2Cl_2, δ, ppm): 3.56 (m, CH_2), 3.92 (m, CHSO$_3$H), 5.10 (d, *J* 3.1 Hz, C$\underline{H}$-Ph), 6.9–8.7 (m, 10H, Np + Ph). ^{13}C NMR (CD_2Cl_2, δ, ppm): 27.7 (CH_2), 46.3 ($\underline{C}$H-Ph), 62.4 (CHS), 123–145 (aromatic C).

1,2,3,4-Tetrahydro-1-(3-phenylpropyl)naphthalene-2-sulfonic acid (**13**). ^{1}H NMR (CD_2Cl_2, δ, ppm): 1.66 [m, 4H, ($\underline{C}H_2$)$_2$CH$_2$Ph], 2.12 (m, 1H, CH$\underline{H}^a$H^b), 2.34 (m, 2H, CH_2), 2.66 (m, 3H, CH$^a\underline{H}^b$, CH_2), 2.98 (m, 2H, CH_2), 3.32 (m, 1H, CHSO$_3$H), 3.50 (m, 1H, CHCHSO$_3$H), 7.25 (m, 10H, 2 × Ph). ^{13}C NMR (CD_2Cl_2, δ, ppm): 19.6 (CH_2), 27.4 (CH_2), 30.1 (CH_2), 30.9 (CH_2), 36.5 (CH_2), 40.0 ($\underline{C}$HCHSO$_3$H), 62.5 (CHSO$_3$H), 125–130 [9 × CH(aromatic)], 134.7, 139.0, 142.9 [C(aromatic)].

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