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Reactions of Adamantylidenealkanes and Cyclopropylidenealkanes with Sulfur Trioxide[†]

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The reactions of adamantylidenealkanes $AdC{=}CR^3R^4$ (**1a**–**5a**) with sulfur trioxide in chloroform, dichloromethane, or dioxane have been studied by ^{1}H NMR spectroscopy over the temperature range −60 to 20 °C. When R^3 and R^4 = H, H and Me, or Me (**1a**, **2a**, **4a**), the reaction at low temperature yields a single β-sultone (**b**), whereas when R^3 and R^4 = Br (**3a**), two isomeric β-sultones (**3b**, **3c**) are formed in equal amounts. The reactants R^3, R^4 = H, H and Me, or Br also yield carbyl sulfates. The symmetric reactant R^3, R^4 = adamantylidene (**5a**) forms a β-sultone but no carbyl sulfate because of steric hindrance between the two adamantylidene groups. The β-sultone R^3, R^4 = H (**1b**) is converted in part into a cyclic dimer in the temperature range −30 to 10 °C. The primary sulfonation products of **1a** and **2a** are not stable above 0 °C and are converted into the corresponding alkenesulfonic acids. Reaction of cyclopropylidenealkanes $R^1R^2C{=}CC_2H_4$ (**8a**–**10a**) with sulfur trioxide gives substituted γ-sultones (**13**–**15**) rather than β-sultones.

Introduction

The reaction of simple alkenes with neat sulfur trioxide is extremely rapid. With a 1-alkene a complex mixture of 2-alkene-1-sulfonic acid and γ- and δ-sultones is obtained. These products result from the initially formed isomeric β-sultone[1,2] and the corresponding carbyl sulfate.[3] In order to obtain further information on the primary processes in the sulfonation of alkenes, we have studied the simple adamantylidenealkanes **1a**–**5a** (Chart I) in which the adamantylidene group may retard or prevent some of the commonly observed secondary reactions. In addition, the cyclopropylidenealkanes **8a**–**10a** have been studied because the strained cyclopropylidene moiety is prone to isomerize during electrophilic sulfonation.[4,5]

Results

The reactions of alkenes **1a**–**5a** and **8a**–**10a** with SO_3 (in general 1.0 equiv) have been studied mainly in dichloromethane in the absence and presence of dioxane (2.25 equiv relative to SO_3) as a reactivity moderator.

Adamantylidenealkanes. The compositions of the reaction mixtures obtained on reaction of the adamantylidenealkanes **1a**–**5a** with SO_3 are compiled in Table I. Reaction of methyleneadamantane (**1a**) with 1.0 and 2.0 equiv of SO_3 in CD_2Cl_2 at −60 °C yields as main products the β-sultone **1b** and the carbyl sulfate **1e** in ratios of 9:2 and ~1:1, respectively. At temperatures between −30 and 20 °C the ^{1}H NMR spectra show a broad singlet at 4.18 ppm, which is assigned to the cyclic dimer **1d**.[6] At room temperature the product is adamantylidenemethanesulfonic acid (**1g**). In the presence of dioxane as reactivity moderator at temperatures ≤10 °C, the sultone **1b** is the predominant product (80%), and no carbyl sulfate is formed.

Ethylideneadamantane (**2a**) with 1.0 equiv of SO_3 in CD_2Cl_2 at −40 °C similarly yields the β-sultone **2b** and the carbyl sulfate **2e** in a ratio of 3:1. As with **1a**, no carbyl sulfate is formed in the presence of dioxane-d_8 moderator. With both **1a** and **2a**, the presence of dioxane reduces the quantity of unidentified products.

Treatment of adamantylidenedibromomethane (**3a**) with 1.0 equiv of SO_3 in CH_2Cl_2 at 10 °C followed by quenching in water gave only recovered starting material. However, the ^{1}H NMR spectrum of the reaction mixture of **3a** with 0.8 equiv of SO_3 in CD_2Cl_2 has three [C(1)H + C(3)H] bridgehead peaks at 3.15 (starting material **3a**), 2.72, and 2.34 ppm, and a multiplet at 2.25–1.2 ppm from the other adamantylidene hydrogens, in a ratio of 35:32:30:~610. The 2.72 and 2.34 peaks are tentatively assigned to the β-sultones **3b** and **3c**, respectively.[10] On using 3.0 equiv of SO_3, **3a** has been fully converted, and there is a new triplet at 2.81 ppm (J = 5 Hz), in addition to the bridgehead peaks at 2.72 and 2.34 ppm. The intensity of the 2.34 ppm signal relative to the 2.72 ppm triplet (J = 5.5 Hz) is reduced by an amount corresponding to the intensity of the new peak at 2.81 ppm. Accordingly, the 2.81 ppm peak is assigned to the carbyl sulfate **3f**, the structure of which corresponds to that of the β-sultone with the bridgehead hydrogen peak at 2.34 ppm.

Reaction of 2-adamantylidenepropane (**4a**) with 1.0 equiv of SO_3 in CD_2Cl_2 at −60 °C leads to the formation of one β-sultone (80%) and ≃5% of a compound with a ^{1}H NMR absorption pattern at 5.02–5.05 ppm. This absorption suggests a methylene group by analogy with a similar absorption of 2,3-dimethyl-1-butene-3-sulfonic acid (**12**) from reaction of 2,3-dimethyl-2-butene with SO_3,[2] and is assigned to 2-isopropenyl-2-adamantanesulfonic acid (**11**). The ratio of the β-sultone to the alkenesulfonic acid (13 ± 2) is independent of reaction temperature from −60 to 20 °C. If the sultone had structure **4c**, the ratio β-sultone/**11** should decrease with increasing reaction temperature because **4c** should rearrange to form more **11**.[1,2] The observed constancy of this ratio implies that the β-sultone has structure **4b**. Furthermore, the presence of **11** at −60 °C after a short reaction time (≤15 min) and the constancy of the **4b**/**11** ratio indicate that **11** is formed directly from the reactants, most likely by an ene reaction.[11]

[†] Aliphatic Sulfonation. 3. For part 2, see ref 3.

(1) Bakker, B. H.; Cerfontain, H. *Tetrahedron Lett.* **1987**, *28*, 1699.

(2) Roberts, D. W.; Jackson, P. S.; Saul, C. D.; Clemett, C. J. *Tetrahedron Lett.* **1987**, *28*, 3383.

(3) Bakker, B. H.; Cerfontain, H. *Tetrahedron Lett.* **1987**, *28*, 1703.

(4) de Boer, Th. J. *Chimia* **1977**, *81*, 483.

(5) Shabarov, Y. S.; Levina, R. Y.; Potapov, V. K. *J. Org. Chem. USSR* **1962**, *32*, 3129.

(6) The formation of a cyclic dimer **d** was also observed on reaction of styrene[7] and tetrafluoroethene[8] with SO_3 and on reaction of 1-propanol with sulfuryl chloride.[9]

(7) Bordwell, F. G.; Peterson, M. L.; Rondestvedt, C. S., Jr. *J. Am. Chem. Soc.* **1954**, *76*, 3945.

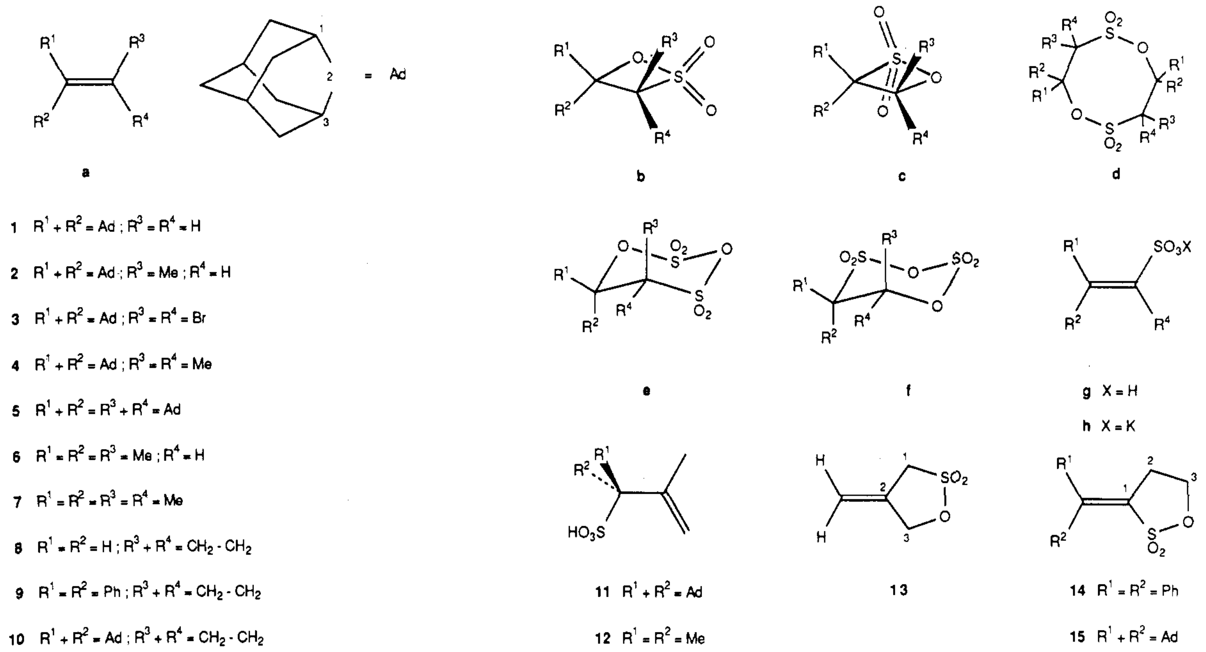
(8) Knunyants, I. L.; Sokolski, G. A. *Angew. Chem.* **1972**, *11*, 623.

(9) Markgraf, J. H.; Hess, B. A., Jr.; Nichols, C. W.; King, R. W. *J. Org. Chem.* **1964**, *29*, 1499.

(10) The assignment of the 2.34 ppm bridgehead absorption to the β-sultone **3c** is based on its relatively large upfield shift as compared with the corresponding alkene **3a** (Δδ = −0.81 ppm), the differences in chemical shifts between the bridgehead of the other types of β-sultones and the corresponding alkenes being significantly smaller, viz. −0.29 ppm for **1b**, 0.25 and 0.34 for **2b**, −0.43 for **3b**, and −0.44 for **4b**.

0022-3263/89/1954-1680$01.50/0

Chart I



1 $R^1 + R^2 = Ad$; $R^3 = R^4 = H$
2 $R^1 + R^2 = Ad$; $R^3 = Me$; $R^4 = H$
3 $R^1 + R^2 = Ad$; $R^3 = R^4 = Br$
4 $R^1 + R^2 = Ad$; $R^3 = R^4 = Me$
5 $R^1 + R^2 = R^3 + R^4 = Ad$
6 $R^1 = R^2 = R^3 = Me$; $R^4 = H$
7 $R^1 = R^2 = R^3 = R^4 = Me$
8 $R^1 = R^2 = H$; $R^3 + R^4 = CH_2-CH_2$
9 $R^1 = R^2 = Ph$; $R^3 + R^4 = CH_2-CH_2$
10 $R^1 + R^2 = Ad$; $R^3 + R^4 = CH_2-CH_2$

Table I. Product Formation in the Sulfonation of the Adamantylidenealkanes 1a–5a

						reaction mixture composition (mol %)								
							sultones			carbyl sulfate		alkene-sulfonic (11)		
alkene	SO$_3$ equiv, ±0.2	solvent	2.25 equiv of dioxane-d_8	temp, °C	method[a]	substrate **a**	**b**	**c**	dimer **d**	**e**	**f**	acid **g**	K salt **h**	unidentified products
1a	1.0	CH_2Cl_2	–	10	A								90	
	1.0	$CDCl_3$	–	10	B	–	9		1–2	6		46		37
				20[b]								68		32
	1.0	CD_2Cl_2	–	–60	B	7	46			10				37
				–40		4	51		1	11		1		32
				–20		≤1	29		15	14		9		33
				0			11		22	14		24		29
				20			0.5		–	0.5		72		27
	2.0	CD_2Cl_2	–	–60	B	1	28			24				47
				–20		–	27–29		≤2	22		7		42
				0			11		7	18		22		43
				20			0.5		1	7		63		28
	1.0	CD_2Cl_2	+	–30	C	15	83							2
				30		6	42					48		4
				20[c]		2	<1					91		6
2a	1.0	CH_2Cl_2	–	10	A								74	
	1.0	CD_2Cl_2	–	–40	B	–	35			13				52
				20			32			5		23		40
				20[c]			*e*			*e*		34		43
	1.0	CD_2Cl_2	+	–30	B	17	71							12
				20[c]		14	30					40		16
				20[b]		21	–					76		5
3a	1.0	CH_2Cl_2	–	10	A	≥97								
	0.8	CD_2Cl_2	–	–60	B	37	31	29			1			3
				20		35	31	30			+			4
	3.0	CD_2Cl_2	–	–60	B	–	50	34			16			–
				–20			45	36			17			2
4a	1.0	CD_2Cl_2	–	–60	B	2	77						6	15
				0		–	52						4	44
				20			37						3	60
	1.0	CD_2Cl_2	+	–30	C		84							16
				20			79							21
5a	1.0	CH_2Cl_2	–	10	A	≥97								
	1.0	CD_2Cl_2	–	–60	B	7	82							11 (11[f])
				0		28	62							10 (8[f])
				20[d]		24	61							15 (7[f])
	1.0	CD_2Cl_2	+	–30	C	7	91							2
				20		20	76							4

[a] See the Experimental Section. [b–d] Determined after ca. 72, 24, and 48 h, respectively. [e] The sum of **2b** and **2e** is 23%. [f] Content of species with ^1H NMR absorption of the four bridgehead hydrogens at 3.08 ppm, compare ref 17.

With **4a**, the decomposition of the initial sulfonation product is significantly less in the presence than in the absence of dioxane.

Treatment of adamantylideneadamantane (**5a**) with 1.0 equiv of SO_3 in CH_2Cl_2 at 10 °C followed by quenching in water gave only recovered starting material. Reaction of **5a** with 1.0 equiv of SO_3 in CD_2Cl_2 with or without dioxane-d_8 leads to the β-sultone **5b**, characterized by its low-field singlets at 2.61 and 2.52 ppm, assigned to 1- and 3-H and 1′- and 3′-H, respectively. With increasing temperature the content of the starting alkene increases at the expense of the sultone, which may indicate that the formation of **5b** from **5a** is reversible.[12,16] There is no evidence for the formation of a carbyl sulfate from **5a**. Studies with Catalin Stuart molecular models revealed that β-sultone **5b** can be constructed but that carbyl sulfate **5e** cannot because of prohibitive steric hindrance between the two adamantylidene moieties.

There is no evidence for the formation of a carbyl sulfate of type **f** from the asymmetric adamantylidenealkanes **1a**, **2a**, and **4a**.

Alkylidenecyclopropanes. Reaction of methylenecyclopropane (**8a**) with 1.0 equiv of SO_3 in CD_2Cl_2 in the presence of 1.1 equiv of dioxane-d_8 at −50 °C yields more than 97% of 2-methylene-1,3-propanesultone (**13**), which is stable at 20 °C for at least 4 days. The same product is formed on using 1.0 equiv of SO_3 in dioxane-d_8 as solvent at 17 °C. (Diphenylmethylene)cyclopropane (**9a**) with 0.9 equiv of SO_3 in dioxane-d_8 at 17 °C afford on the other hand 1-(diphenylmethylene)-1,3-propanesultone (**14**) as the only product.

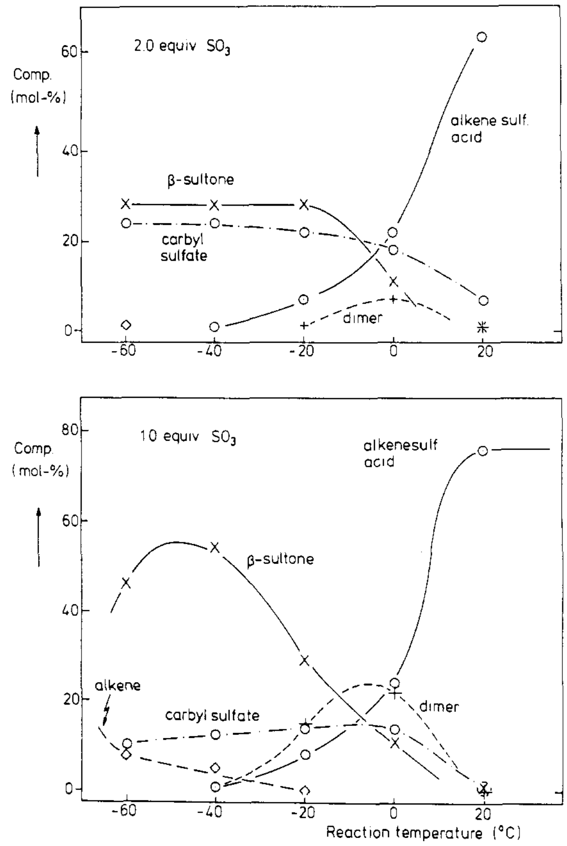
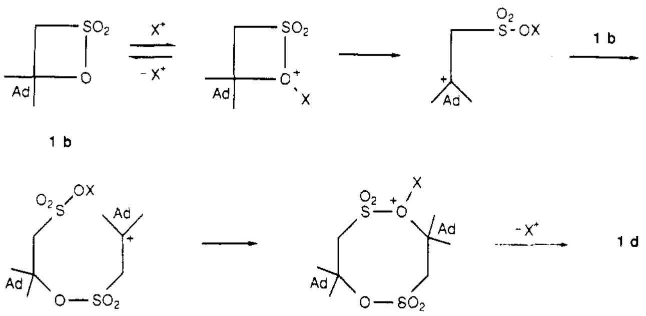


Figure 1. Dependence of the molar product composition on reaction temperature for the reaction of **1a** with SO_3. (◇ - - - ◇) **1a**; (×——×) **1b**; (+ - - - - - - +) **1d**; (○-·-·-○) **1e**; (⊙——⊙) **1g**.

Scheme I. Formation of the Cyclic Dimer 1d from the β-Sultone 1b



The ¹H NMR spectrum of the reaction mixture from cyclopropylideneadamantane (**10a**) with 1.0 equiv of SO_3 in dioxane-d_8 at 17 °C indicated the presence of 1-adamantylidene-1,3-propanesultone (**15**, 60%) in addition to 15% unreacted substrate. With 1.0 equiv of SO_3 and 2.25 equiv of dioxane-d_8 in CD_2Cl_2 at −30 to 10 °C, the yield of **15** is substantially lower (≃20%), and in the absence of dioxane it is even less (≃10%).

Discussion

Adamantylidenealkanes. Reaction of an asymmetric alkene **a** with SO_3 may lead in principle to two different β-sultones **b** and **c**. However, **1a** and **2a** form only **1b** and **2b**, respectively, in line with observations by Roberts et al.[2] on isobutene and 2-methyl-2-butene. This result indicates that the electrophilic sulfur atom reacts preferentially with the slightly more nucleophilic carbon of the double bond. Because of the stereospecificity in the formation of β-sultones from terminal[1] and internal[1,26] simple

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(11) Hoffmann, H. M. R. *Angew. Chem.* **1969**, *8*, 597.

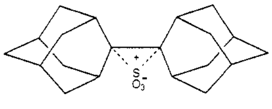
(12) A related equilibrium phenomenon is observed with phenyl hydrogen sulfates, which are formed in more than 99.9% yield on reaction of equimolar amounts of a phenol and SO_3 at temperatures ≤ −20 °C. At higher temperatures the equilibrium is shifted slightly to the side of the phenol and SO_3, which then engage in irreversible carbon sulfonation to yield phenol-4-sulfonic acid.[13-15]

(13) Cerfontain, H.; Koeberg-Telder, A.; Lambrechts, H. J. A.; de Wit, P. *J. Org. Chem.* **1984**, *49*, 4917.

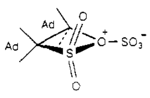
(14) Cerfontain, H.; Coenjaarts, N. J.; Koeberg-Telder, A., accepted for publication in *Recl. Trav. Chim. Pays-Bas*.

(15) De Wit, P. Thesis (in English), University of Amsterdam, 1988, Chapters 4–7.

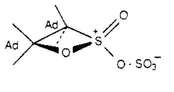
(16) The ¹H NMR spectra of the reaction mixtures of **5a** with 1.0 equiv of SO_3 in CD_2Cl_2 in the *absence* of dioxane-d_8 at −60 to 0 °C also exhibit a broadened singlet at 3.08 ppm, the relative intensity of which decreases with increasing temperature. This signal is absent in the presence of 2.25 equiv of dioxane-d_8. It may therefore tentatively be assigned a priori to the 1,1′,3,3′-hydrogens of the dipolar π-complex **16** formed between SO_3 and the difficultly accessible double bond of **5a**[17,19] or to those hydrogens of the Lewis complexes **17** and **18**, formed by reaction of SO_3 with one of the oxygen atoms of the sultone **5b**. Of these three structures only **16** complies with the observation of only one (broadened) singlet for the four bridgehead hydrogens 1, 1′, 3, and 3′.



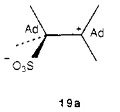
16



17

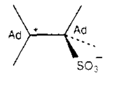


18



19a

⇌

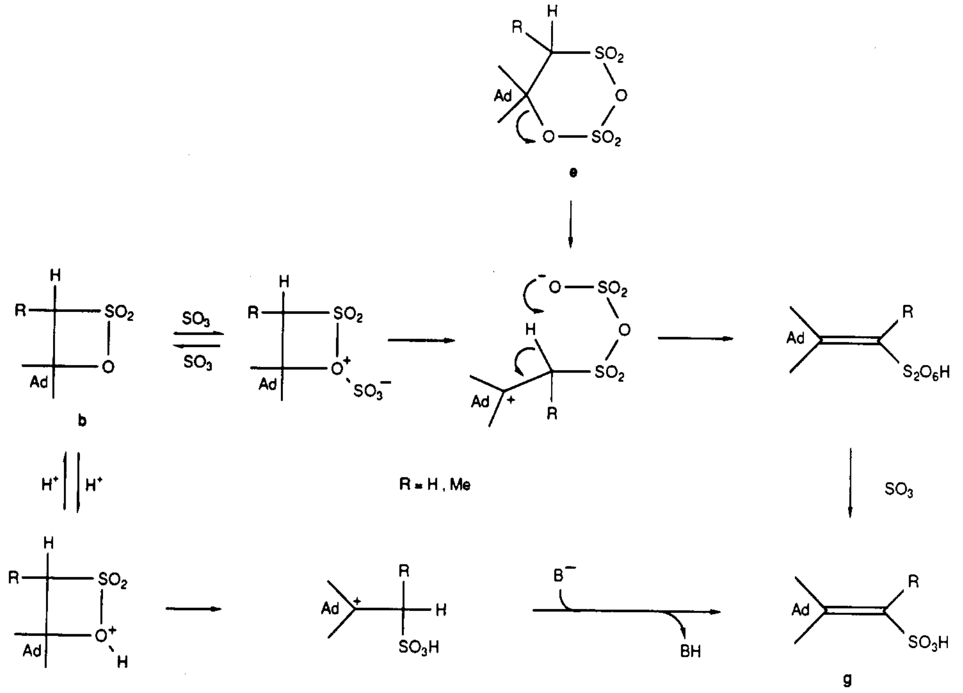


19b

However, the singlet absorption may also be explained in terms of the equilibrium **19a** ⇌ **19b** of which the reaction rates then have to be rapid relative to the ¹H NMR time scale, a phenomenon that was in fact observed for the SO_3 transfer from methanepyrosulfonic acid to methanesulfonic acid.[25]

(17) The possibility of a π-complex intermediate along the reaction path leading to a β-sultone from simple alkenes was considered recently.[18]

Scheme II. Conversion of β-Sultone b and Carbyl Sulfate e into Alkenesulfonic Acid g

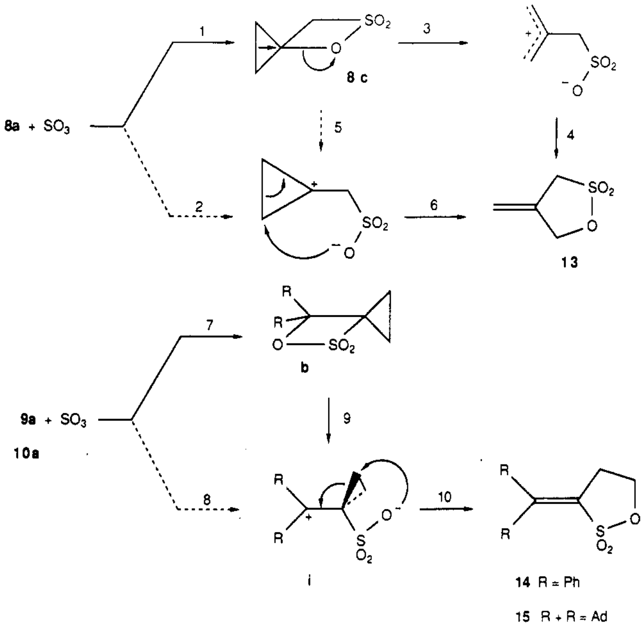


alkenes, and the relatively small rate differences in the sulfonation of alkenes,[18] it has been concluded that β-sultone formation proceeds via a concerted cis cycloaddition.[1,18] In the transition state of this addition the β carbon of the incipient β-sultone bears a relatively small positive charge. From **3a** the two β-sultones **3b** and **3c** are formed in equal amounts, indicating a balance between steric and electronic effects.

The adamantylidenealkanes **1a**–**3a** form both sultones and carbyl sulfates, and the proportion of the latter increases when >1 equiv of SO_3 is used (Table I). A carbyl sulfate is formed from the corresponding β-sultone by stereospecific insertion of SO_3.[3] An eight-membered cyclic dimer (**1d**) is formed from **1a** at temperatures ≥ −20 °C, the amount being substantially greater when using 1.0 rather than 2.0 equiv of SO_3. From the dependence of product composition on reaction temperature in the absence of dioxane (Figure 1), it appears that the dimer **1d** is formed predominantly, if not exclusively, from the β-sultone **1b**. Although there are several possible mechanisms for the formation of **1d**, the fact that none is formed in the presence of dioxane (Table I) indicates that the acid-catalyzed mechanism shown in Scheme I is the most likely one.

At temperatures > 0 °C, the primary sulfonation products **b**, **d**, and **e** from **1a** and **2a** are not stable, and the reaction products are **1g** and **2g**, respectively. As appears from Figure 1, the rate of conversion into alkenesulfonic acid is greater for the β-sultone **1b** than for the carbyl sulfate **1e**, probably owing to relief of ring strain in the β-sultone. The conversion of the β-sultones **b** and the carbyl sulfates **e** into the alkenesulfonic acids **1g** and **2g** may be explained in terms of the mechanisms **b** → **g** and **e** → **g** (Scheme II).

Scheme III. Formation of Methylene-1,3-propanesultones from the Cyclopropylidenealkanes 8a–10a



Alkylidenecyclopropanes. The reaction of methylenecyclopropane (**8a**) with 1.0 equiv of SO_3 at −50 °C for a short time (≃20 min) produced no β-sultone or carbyl sulfate[27] but only the rearranged product 2-methylene-

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(18) Roberts, D. W.; Williams, D. L.; Bethell, D. *J. Chem. Soc., Perkin Trans. 1* **1985**, 389.

(19) Stable adamantylideneadamantane chloronium,[20-22] brominium-,[22-24] and iodonium ion[22] salts were described previously.

(20) Wieringa, J. H.; Strating, J.; Wijnberg, H. *Tetrahedron Lett.* **1970**, 4579.

(21) Nugent, W. A. *J. Org. Chem.* **1980**, *45*, 4533.

(22) Olah, G. A.; Schilling, P.; Westerman, P. W.; Liu, H. C. *J. Am. Chem. Soc.* **1974**, *96*, 3581.

(23) Strating, J.; Wieringa, J. H.; Wijnberg, H. *J. Chem. Soc., Chem. Commun.* **1969**, 907.

(24) Slebocka-Tilk, H.; Ball, R. G.; Brown, R. S. *J. Am. Chem. Soc.* **1985**, *107*, 4504.

(25) Robinson, E. A.; Silberberg, V. *Can. J. Chem.* **1966**, *44*, 1437.

(26) Nagayama, M.; Okumura, O.; Noda, S.; Mori, A. *Bull. Chem. Soc. Jpn.* **1974**, *74*, 2158.

(27) The absence of any high-field cyclopropane absorption and the strictly 1:1 area ratio of the quasi-quintet absorptions at 3.93 and 4.93 ppm of **13** rule out the presence of any spirosultone **8c** or the corresponding carbyl sulfate **8f**.

1,3-propanesultone (**13**). It is possible that the initial product may be the spirosultone **8c** (Scheme III), which isomerizes rapidly to **13** at −50 °C. This isomerization may proceed by way of steps 3 and 4. Step 5 is less likely than step 3: solvolyses of cyclopropyl derivatives with good leaving groups usually involve simultaneous fission of the cyclopropyl C(2)–C(3) bond, with the developing electron deficiency on C(1) being filled by the electrons of the C(2)–C(3) bond moving into the back lobe of the C–O bond.[28] Although considered less likely, it is possible that **13** is formed from **8a** stepwise by electrophilic addition of SO_3 to the terminal C(sp^2), forming the dipolar cyclopropeniumsulfonate intermediate followed by ring closure (steps 2 and 5).

The attack of SO_3 on the double bonds of (diphenylmethylene)cyclopropane (**9a**) and adamantylidenecyclopropane (**10a**) is opposite to that of **8a**, since the position of the methylene group in **14** and **15** differs from that in **13**. Again the formation of **14** and **15** may proceed by initial formation of the β-sultone **b** and subsequent isomerization by the sequence 9 and 10.

Experimental Section

Materials. Substrates **1a** and **2a** were synthesized by a Wittig reaction of 2-adamantanone with the required alkyltriphenylphosphonium bromide[29] in yields of 51 and 83%, respectively. The synthesis of **4a** by this method failed. Adamantylidenedibromomethane (**3a**) was prepared by reaction of dibromomethylene triphenylphosphorane—generated in situ from tetrabromomethane and triphenylphosphine—with 2-adamantanone in 14% yield, following the method of Posner.[30] Methylation of **3a** with $Me_2Cu(I)Li$[30] afforded **4a** in 61% yield. **1a**: mp 136 °C; IR ($CHCl_3$, cm^{-1}) 3070 (m), 2920 (s), 2850 (s), 1645 (m), 1450 (m), 885 (m). **2a**: IR ($CHCl_3$, cm^{-1}) 3050 (w), 2920 (s), 2850 (s), 1670 (w), 1645 (m), 1445 (s), 1385 (m). **3a**: mp 85.0–87.5 °C; IR ($CHCl_3$, cm^{-1}) 2910 (s), 2840 (s), 1445 (m), 1095 (m), 950 (m), 905 (s), 885 (w), 850 (w). **4a**: mp 40–41 °C; IR ($CHCl_3$, cm^{-1}) 2910 (s), 2850 (s), 1695 (s), 1670 (w), 1445 (m), 1050 (w), 870 (w). The melting point, ^{1}H NMR, and IR data of **1a**–**4a** are similar to the reported data.[31–33] The other alkenes were gifts from Dr. A. Hofland (**10a**[34]), Dr. K. Hummelen (**5a**[24]), and Dr. W. J. van Tunen (**8a**[35] and **9a**[29]).

Sulfonation Procedures and Analysis. A. To a solution of 1.0 mmol of the alkene in 5.0 mL of dichloromethane was slowly added under nitogen at 10 °C while stirring a solution of 1.0 mmol of SO_3 in 5.0 mL of dichloromethane, and the resulting mixture was stirred for another 30 min. Then the reaction mixture was poured into 10 mL of water and neutralized with an aqueous solution of $KHCO_3$. The dichloromethane was removed by rotaevaporation and the remaining water by freeze-drying. The remaining potassium sulfonates were dissolved in D_2O and subjected to NMR analysis.

B. A solution of 0.20 mmol of the alkene in 0.6 mL of CD_2Cl_2 or $CDCl_3$, which was cooled to −70 °C under an argon atmosphere, was injected with 0.8–3.0 equiv of SO_3, and the resulting solution was siphoned into an NMR tube, which was cooled at −70 °C. NMR spectra were taken at chosen temperatures after appropriate time intervals over a total reaction time of 4–6 h unless stated otherwise.

C. To 0.20 mmol of the alkene contained in an NMR tube at −70 °C was added under argon a solution of 0.50–3.0 equiv of SO_3 and the desired amount of dioxane-d_8 (2.25 equiv relative to SO_3) in 0.6 mL of CD_2Cl_2, the resulting mixture was homogenized using a spacemill, and NMR spectra were recorded as described under **B**.

D. To a solution of 1.0 mL of dioxane-d_8 and 21 μL (0.50 mmol) of SO_3 was added at 17 °C under nitrogen 0.50 mmol of (diphenylmethylene)cyclopropane (**9a**) or adamantylidenecyclopropane (**10a**), and the mixture was stirred at 17 °C for 1 h. The solution was then transferred into an NMR tube, and an NMR spectrum was recorded. The reaction mixture obtained from **10a** was subsequently quenched with water, the solution was neutralized with an aqueous $KHCO_3$ solution, and the solvents were removed by rotaevaporation and freeze-drying. The residue was extracted with chloroform or dichloromethane, the solvent was removed by rotaevaporation, and the residue was subjected to ^{1}H NMR and mass spectrometric analyses.

The structural assignments of the products were made from the ^{1}H NMR spectra of the reaction mixture solutions with deuterated solvents or from the isolated potassium sulfonates in D_2O on the basis of the observed chemical shifts, absorption area ratios, and coupling constants in combination with substituent shielding parameters[36] and in part on the basis of a comparison with the ^{1}H NMR data of related sulfo products.[1–3,37] 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]

Reaction of adamantylidenecyclopropane (**10a**) with SO_3 in dioxane-d_8 led to 1-adamantylidene-1,3-propanesultone (**15**) as the only product in the reaction mixture that has been assigned by ^{1}H NMR analysis. After the reaction was quenched with D_2O and $KHCO_3$, $CDCl_3$ was added. ^{1}H NMR analysis showed the presence of **15** in the $CDCl_3$ solution; the D_2O solution did not reveal any NMR absorption. **15**: MS *m/z* 254 ($M^{\bullet +}$, 100), 198 (6), 190 (6), 188 (8), 160 (10), 145 (8), 131 (11), 117 (22); high-resolution mass spectrum, *m/z* 254.097 59, calcd for $C_{13}H_{18}O_3S$ 254.097 66; IR ($CHCl_3$, cm^{-1}) 3000 (w), 2920 (s), 2850 (m), 1662 (w) (C=C), 1333 (s) + 1169 (s) ($O{-}SO_2$).

The ^{1}H NMR spectra were recorded on Bruker WM-250 and AC-200 and Varian XL-100 spectrometers, the mass spectra on Varian MAT-711 and ZAB-2HF double-focusing mass spectrometers, and the IR spectra on a Perkin-Elmer 1310 instrument.

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Registry No. **1a**, 875-72-9; **1b**, 118868-89-6; **1d**, 118868-90-9; **1e**, 118868-91-0; **1g**, 118868-92-1; **1h**, 118868-97-6; **2a**, 13376-16-4; **2b**, 118868-93-2; **2e**, 118868-94-3; **3a**, 38773-13-6; **3b**, 118868-95-4; **3c**, 118868-96-5; **3f**, 118890-27-0; **4a**, 20441-18-3; **4b**, 118868-98-7; **5a**, 30541-56-1; **5b**, 118868-99-8; **8a**, 6142-73-0; **9a**, 7632-57-7; **10a**, 99298-53-0; **11**, 118868-85-2; **13**, 118868-86-3; **14**, 118868-87-4; **15**, 118868-88-5; SO_3, 7446-11-9.

Supplementary Material Available: ^{1}H and ^{13}C NMR spectral data of **1a**–**5a** and **8a**–**10a** and their sulfonation products in CD_2Cl_2, $CDCl_3$, dioxane-d_8, and D_2O, fast atom bombardment negative and positive ion mass spectral data of **1h** and **2h**, and the product yields of **15** as a function of the sulfonation conditions (5 pages). Ordering information is given on any current masthead page.

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