Aliphatic Sulfonation, 16[+]

Sulfonation of Alkenes by Chlorosulfuric Acid, Acetyl Sulfate, and Trifluoroacetyl Sulfate

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An exploratory study has been made on the reaction of a number of non-branched alkenes in [D]chloroform as an aprotic solvent, using chlorosulfuric acid as reagent both in the presence and the absence of [D_8]1,4-dioxane as complexing agent. Reaction of cyclopentene (**1a**) with 1.1 mol-equiv. of chlorosulfuric acid in [D]chloroform in the presence of 2.2 mol-equiv. of [D_8]1,4-dioxane at 0 °C yielded quantitatively 1,2-cyclopentanesultone (**2a**). Under similar reaction conditions, the linear alkenes **1b**–**g** afforded the corresponding β-sultones **2b**–**g**. The $ClSO_3H$–dioxane complex acted as a sulfonating reagent with the alkenes to yield the corresponding β-sultones in a *syn* cycloaddition of SO_3 to the carbon–carbon double bond. In the absence of [D_8]1,4-dioxane the reaction of the linear alkenes **1a**–**1k** in [D]chloroform with chlorosulfuric acid at –40 °C led to the formation of the *sec*-alkyl chlorosulfates **5a–i**, which were formed after initial protonation of the alkene by the strongly acidic $ClSO_3H$. Cyclopentyl chlorosulfate (**5a**) in [D]chloroform at 0 °C was quantitatively converted into 1,2-cyclopentanesultone (**2a**). The *sec*-alkyl chlorosulfates **5b–i** at 0 °C gave rise to a mixture of the internal *trans*- and *cis*-β-sultones **2b**–**m**. Reaction of 1-octene (**1g**) with both acetyl sulfate (**6a**) and trifluoroacetyl sulfate (**6b**) as reagent in [D]chloroform at –20 °C directly afforded the products 1,2-octanesultone (**2g**), and the (*E*) and (*Z*) isomer of 2-octene-1-sulfonic acid (**4g**).

Introduction

As a sequel to our studies on the reaction of simple and monofunctionalized alkenes with sulfur trioxide,[1−5] we now report on the reaction of a series of olefins with chlorosulfuric acid and two related sulfuric acid derivatives, viz. acetyl sulfate and its trifluoro derivative. Sulfur trioxide reacts vigorously with alkenes to form β-sultones as the primary unstable products, which at room temperature eventually yield a complex mixture of alkenesulfonic acids and γ- and δ-sultones.[6,7] The very high reactivity of neat sulfur trioxide can be moderated by complexation with Lewis bases such as 1,4-dioxane and pyridine.[8,9] Another type of moderated sulfur trioxide donors are the complexes composed of SO_3 and protic species such as hydrochloric acid, acetic acid, and water.[10] Reagents of the latter group are very strong acids and may thus also act as proton donors. In fact, alkenes are protonated by sulfuric acid to give subsequently alkyl hydrogen sulfates in a reversible reaction.[11] Acetyl sulfate, i.e. the adduct of SO_3 and acetic acid, reacts with alkenes to afford the corresponding β-sultones in a stereospecific fashion.[12] In nonpolar solvents like chloroform alkenes are protonated by chlorosulfuric acid to give the corresponding chlorosulfonate esters.[13] However, the reaction of chlorosulfuric acid with 2-pentene in chloroform was reported to afford a mixture of 2-pentene-2-sulfonic acid and 2-pentene-3-sulfonic acid in a 4:1 ratio.[14] With diethyl ether as solvent the reaction of chlorosulfuric acid with alkenes proceeds differently,[13] since the chlorosulfuric acid adds to diethyl ether to form the corresponding oxonium complex.[15] Reaction of chlorosulfuric acid with an α-olefin in diethyl ether as solvent leads to the formation of 1- and 2-alkene-1-sulfonic acids in high yield via 2-chloroalkane-1-sulfonic acid as intermediate.[16]

We now report on a study of the reaction of chlorosulfuric acid with non-branched alkenes in chloroform as solvent both in the presence and the absence of dioxane at temperatures ranging from −40 to 25°C. In addition we have studied the reaction of 1-octene with both acetyl sulfate and trifluoroacetyl sulfate in $CDCl_3$ within the same temperature range. The objective of these exploratory studies was to obtain information as to the initial reaction products and their subsequent chemistry.

Results and Discussion

Sulfonation of Alkenes with Chlorosulfuric Acid in the Presence of Dioxane

Reaction of the alkenes **1a−g** with 1.1 mol-equiv. of chlorosulfuric acid and 2.2 mol-equiv. of [D_8]1,4-dioxane (further referred to as [D_8]dioxane or dioxane) were studied in [D]chloroform as solvent. In order to obtain information on the primary sulfonation products, the reactions were carried out at low temperatures. The composition of the homogeneous reaction mixtures were determined by ^{1}H- and ^{13}C-NMR spectroscopy. The ^{1}H- and ^{13}C-NMR assignments of the various sulfonation products are compiled in the Experimental Section.

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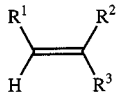
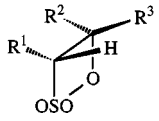


1

	R^1	R^2	R^3
a	CH_2-CH_2-CH_2		H
b	Me	H	Me
c	Me	Me	H
d	H	H	Et
e	*n*Pr	H	*n*Pr
f	*n*Pr	*n*Pr	H
g	H	H	*n*Hex
h	H	H	*n*Pr
i	Me	H	*n*Pr
j	Me	*n*Pr	H
k	Et	Et	H



2

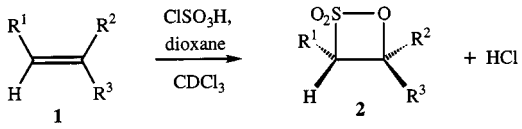
	R^1	R^2	R^3
a	CH_2-CH_2-CH_2		H
b	Me	H	Me
c	Me	Me	H
d	H	H	Et
e	*n*Pr	H	*n*Pr
f	*n*Pr	*n*Pr	H
g	H	H	*n*Hex
h	Me	H	Et
i	Me	Et	H
j	Me	H	*n*Pr
k	Me	*n*Pr	H
l	Me	H	*n*Pen
m	Me	*n*Pen	H

Addition of cyclopentene (**1a**) to a mixture of 1.1 mol-equiv. of chlorosulfuric acid in [D]chloroform as solvent in the presence of 2.2 mol-equiv. of [D_8]dioxane at 0°C gives 1,2-cyclopentanesultone (**2a**). At temperatures ≤ −20°C the rate of the β-sultone formation is very small, but after raising the temperature to 0°C it takes about 2 h to completely convert the cyclopentene into the β-sultone **2a**. The rate of reaction of cyclopentene with chlorosulfuric acid in the presence of [D_8]dioxane in [D]chloroform as solvent appears to be much smaller than that with the SO_3−dioxane complex, which reacts very rapidly with cyclopentene at temperatures as low as −40°C to afford the β-sultone **2a**[17]. This is in line with the p*K* values of the dissociation constants of the SO_3−dioxane complex (p*K* = 1.9) and chlorosulfuric acid (p*K* = 4.2) which were measured in a potentiometric study[18]. Apparently, the complex of chlorosulfuric acid with [D_8]dioxane[19] releases SO_3 slowly, which reacts with cyclopentene to afford the corresponding β-sultone **2a**. At room temperature the solution of 1,2-cyclopentanesultone in [D]chloroform in the presence of [D_8]dioxane is rather stable, the content of the β-sultone after 24 h still being > 90%.

Reaction of (*E*)-2-butene (**1b**) with 1.1 mol-equiv. of chlorosulfuric acid in [D]chloroform in the presence of 2.2 mol-equiv. of [D_8]dioxane for 2 h at room temperature affords solely *trans*-2,3-butanesultone (**2b**). Similarly, reaction of (*E*)-4-octene (**1e**) with 1.1 mol-equiv. of the chlorosulfuric acid−dioxane complex at room temperature for 2 h leads to the quantitative formation of *trans*-4,5-octanesultone (**2e**). Furthermore, reaction of both (*Z*)-2-butene (**1c**) and (*Z*)-4-octene (**1f**) with 1.1 mol-equiv. of chlorosulfuric acid in [D]chloroform in the presence of 2.2 mol-equiv. of [D_8]dioxane for 1.0 h at room temperature exclusively yields *cis*-2,3-butanesultone (**2c**) and *cis*-4,5-octanesultone (**2f**), respectively. The complex of chlorosulfuric acid and [D_8]dioxane thus reacts with the alkenes **1** by *syn* cycloaddition to afford the β-sultones **2**, as depicted in Scheme 1.

Treatment of 1-butene (**1d**) with 1.1 mol-equiv. of chlorosulfuric acid in the presence of 2.2 mol-equiv. of [D_8]dioxane in [D]chloroform as solvent at 0°C for 3.0 h leads to the formation of a mixture of 1,2-butanesultone (**2d**), 2-chloro-1-butanesulfonic acid (**3d**), and 2-butene-1-sulfonic acid (**4d**) in a molar ratio of 4:2:1. The 1,2-alkanesultones are much more reactive than the internal *cis*-β-sultones, whereas the latter are more reactive than the corresponding *trans*-β-sultones. It is therefore proposed that 2-chloro-1-butanesulfonic acid (**3d**) is formed by reaction of the 1,2-butanesultone (**2d**) with HCl, as shown in Scheme 2. The 2-butene-1-sulfonic acid [**4d**, (*E*)/(*Z*) = 1:1] is also thought to be a secondary product formed by thermal rearrangement of the 1,2-butanesultone (**2d**). Our conclusion that the 1,2-butanesultone (**2d**) is the primary product differs from an earlier report[16] that the primary product upon reaction of chlorosulfuric acid with α-olefins in the presence of diethyl ether would be the chlorinated alkanesulfonic acid **3**. The reaction of 1-octene (**1g**) with 1.1 mol-equiv. of the chlorosulfuric acid−dioxane complex in [D]chloroform at 0°C for 2.0 h similarly affords a mixture of 50% of 1,2-octanesultone (**2g**), 18% of 2-chloro-1-octanesulfonic acid (**3b**), 16% of a mixture of (*E*)- and (*Z*)-2-octene-1-sulfonic acid [**4b**, (*E*)/(*Z*) = 4:3], and 16% of the starting 1-octene.

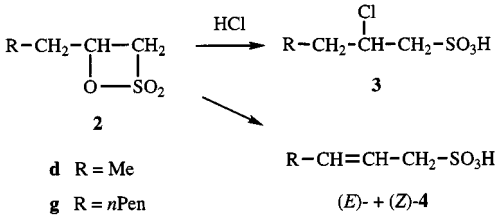
Thus, it appears that the primary reaction of alkenes with the chlorosulfuric acid−dioxane complex in [D]chloroform as solvent is the formation of the corresponding β-sultones. The rate of reaction of alkenes with the chlorosulfuric acid−dioxane complex is much slower than with the SO_3−dioxane complex; it is, however, of the same order of magnitude as upon using trimethylsilyl chlorosulfate[20,21] as reagent. The chlorosulfuric acid−dioxane complex is a sulfonating agent that slowly releases SO_3, which upon stereospecific cycloaddition to the alkenes affords the observed β-sultones.



1 2

	R^1	R^2	R^3
a	CH_2-CH_2-CH_2		H
b	Me	H	Me
c	Me	Me	H
d	H	H	Et
e	*n*Pr	H	*n*Pr
f	*n*Pr	*n*Pr	H
g	H	H	*n*Hex

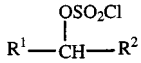
Scheme 1. Formation of β-sultones from the alkenes **1a–g** with chlorosulfuric acid and [D_8]dioxane in $CDCl_3$



Scheme 2. Conversion of the 1,2-alkanesultones **2** in the presence of HCl into the corresponding 1-alkane-2-chlorosulfonic acids **3**, and the (*E*)- and (*Z*)-2-alkene-1-sulfonic acids **4**

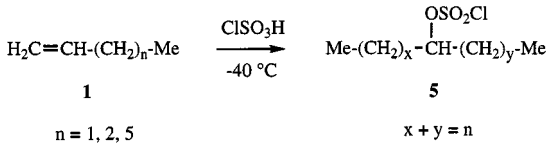
Reaction of Alkenes with Chlorosulfuric Acid in the Absence of Dioxane

Addition of cyclopentene (**1a**) to 1.1 mol-equiv. of chlorosulfuric acid in [D]chloroform at −40°C leads immediately to the quantitative formation of cyclopentyl chlorosulfate (**5a**). Thus, chlorosulfuric acid in [D]chloroform without dioxane acts as a strong protic acid to give the chlorosulfate **5a** by initial protonation.[22,23] Addition of 1-butene (**1d**) to 1.1 mol-equiv. of $ClSO_3H$ in [D]chloroform at −40°C only leads to the formation of *sec*-butyl chlorosulfate (**5b**), the corresponding 1-butyl derivative not being present beyond the limit of detection by ^1H NMR. The same chlorosulfate **5b** was formed quantitatively when either (*E*)-2-butene (**1b**) was added to 1.1 mol-equiv. of chlorosulfuric acid in [D]chloroform at −40°C, or (*Z*)-2-butene (**1c**) was added to 1.1 mol-equiv. of chlorosulfuric acid in [D]chloroform at −60°C. Reaction of 1-pentene (**1h**) with 1.1 mol-equiv. of $ClSO_3H$ in [D]chloroform at −40°C affords a mixture of 2-pentyl chlorosulfate (**5c**) and 3-pentyl chlorosulfate (**5d**) in 80 and 20% yield, respectively. The ratio of the two chlorosulfates **5c** and **5d** remained the same upon keeping the solution at 0°C for 45 min. Concentrated sulfuric acid reacts similarly with linear alkenes to afford only the *sec*-alkyl hydrogen sulfates.[11] Reaction of (*Z*)-3-hexene (**1k**) with 1.1 mol-equiv. of $ClSO_3H$ in [D]chloroform at −40°C leads to a mixture of 46% of 2-hexyl chlorosulfate (**5e**) and 54% of 3-hexyl chlorosulfate (**5f**). A different ratio of the two chlorosulfates **5e** and **5f** was obtained upon reaction of 2-hexene [(*E*)/(*Z*) = 3:1] with 1.1 mol-equiv. of $ClSO_3H$ in [D]chloroform at −20°C, viz. 63% of **5e** and 37% of **5f**. Reaction of 1-octene (**1g**) with 1.1 mol-equiv. of $ClSO_3H$ in [D]chloroform at −40°C affords a mixture of 2-octyl chlorosulfate (**5g**), 3-octyl chlorosulfate (**5h**), and 4-octyl chlorosulfate (**5i**) in yields of 70, 18 and 12%, respectively. The composition of the three *sec*-octyl chlorosulfates does not change when the temperature is raised to 0°C and kept at that temperature for 50 min. On the other hand, treatment of (*E*)-4-octene (**1e**) or (*Z*)-4-octene (**1f**) with 1.1 mol-equiv. of $ClSO_3H$ in [D]chloroform at −40°C yields a mixture of 4-octyl chlorosulfate (**5i**) and 3-octyl chlorosulfate (**5h**) in a ratio of 4:1, with possibly in addition at most 3% of 2-octyl chlorosulfate (**5g**). The general scheme for the reaction of the linear α-alkenes with chlorosulfuric acid in [D]chloroform at −40°C is shown in Scheme 3. From the obtained results it appears that the addition of $ClSO_3H$ to linear alkenes in [D]chloroform as solvent only affords the internally substituted linear alkyl chlorosulfates, but not any 1-alkyl derivative. Remarkably, in the temperature range of −40 to 0°C the addition of chlorosulfuric acid to the linear alkenes does not yield the thermodynamically most stable mixture of *sec*-alkyl chlorosulfates, but the composition is mainly determined by the original position of the double bond in the alkene.



5

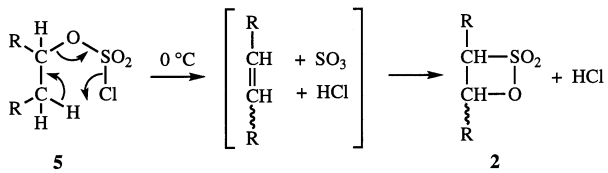
	R^1	R^2
a	CH_2-CH_2-CH_2-CH_2	
b	Me	Et
c	Me	*n*Pr
d	Et	Et
e	Me	*n*Bu
f	Et	*n*Pr
g	Me	*n*Hex
h	Et	*n*Pen
i	*n*Pr	*n*Bu



Scheme 3. Reaction of the α-olefins **1b**, **1g**, and **1h** with $ClSO_3H$ in $CDCl_3$ at −40°C

Although the chemistry of *prim*-alkyl chlorosulfates has been studied extensively, *sec*- and *tert*-alkyl derivatives are virtually unknown due to their high instability.[24] We have studied the fate of the unstable *sec*-alkyl chlorosulfates **5**, which were obtained upon reaction of the alkenes **1a–k** with chlorosulfuric acid at −40°C in [D]chloroform. Cyclopentyl chlorosulfate (**5a**), obtained by reaction of cyclopentene with $ClSO_3H$ at −40°C in [D]chloroform, is slowly

converted into 1,2-cyclopentanesultone (**2a**) upon raising the temperature to −10°C, the chlorosulfate **5a**/β-sultone **2a** ratio after 3 h being 2:8. Upon further raising the temperature to 0°C and keeping it there for 20 min the **5a**/**2a** ratio had decreased to 1:9. Leaving the β-sultone solution subsequently at room temperature overnight resulted mainly in decomposition, the remaining amount of the β-sultone **2a** being only 10%. Apparently, the stability of the 1,2-cyclopentanesultone (**2a**) in [D]chloroform is substantially higher in the presence than in the absence of [D_8]dioxane. Probably the [D_8]dioxane reduces the protic acidity of the reaction mixture, and thus the rate of decomposition of the β-sultone. Reaction of each of the three linear butenes **1b**, **1c** and **1d** with $ClSO_3H$ at −40°C in [D]chloroform yielded *sec*-butyl chlorosulfate (**5b**), which after 1 h at room temperature was gradually converted into a mixture of *trans*- (**2b**) and *cis*-2,3-butanesultone (**2c**) in a 3:2 ratio. Remarkably, only the internal β-sultones **2b** and **2c** were formed, but not 1,2-butanesultone (**1d**). Upon reaction of the 80:20 mixture of 2-pentyl (**5c**) and 3-pentyl chlorosulfate (**5d**, see before) in [D]chloroform at room temperature for 24 h, the resulting solution was found to contain 40% of *trans*-2,3-pentanesultone (**2h**), 12% of *cis*-2,3-pentanesultone (**2i**), ca. 8% of *trans*-3,2-pentanesultone, 20% of the starting 2-pentyl chlorosulfate (**5c**), and in addition small amounts of various decomposition products of the β-sultones. The 4:1 mixture of 4-octyl (**5i**) and 3-octyl chlorosulfate (**5h**) obtained from either (*E*)- or (*Z*)-4-octene (see before) was transformed after 10 min at room temperature into a mixture of 60% of the *trans* isomers of 3,4-, 4,3-, and 4,5-octanesultone, and 20% of a mixture of the corresponding *cis*-3,4-, -4,3-, and -4,5-octanesultone. The ^{1}H-NMR spectra of the *trans*-β-sultones show typical signals at δ = 4.15 and 4.32, whereas those of the corresponding *cis*-β-sultones appear at δ = 4.57 and 4.78. The reaction mixture consisting of 70% of 2-octyl chlorosulfate (**5g**), 18% of 3-octyl chlorosulfate (**5h**), and 12% of 4-octyl chlorosulfate (**5i**) in [D]chloroform (see before) afforded after 24 h at room temperature 30% of *trans*-2,3-octanesultone (**2l**) and 10% of *cis*-2,3-octanesultone (**2m**) as the main products, besides small amounts of the *trans*-3,4-, -4,5-, and -3,2-octanesultone. From the results presented it appears that the *sec*-alkyl chlorosulfates **5** are transformed into a mixture of internal *trans*- and *cis*-β-sultones. The proposed mechanism for this unexpected conversion is shown in Scheme 4. We presume that $ClSO_3H$ is eliminated from the *sec*-alkyl chlorosulfate in a cyclic process to afford a mixture of the (*E*) and (*Z*) isomers of the internal alkenes, together with SO_3 and HCl. Subsequent sulfonation of these alkenes by SO_3 then yields the corresponding β-sultones. From the preceding results it appears that in the absence of [D_8]dioxane the chlorosulfuric acid initially protonates the linear alkenes to afford *sec*-alkyl chlorosulfates, which are eventually converted into internal β-sultones.



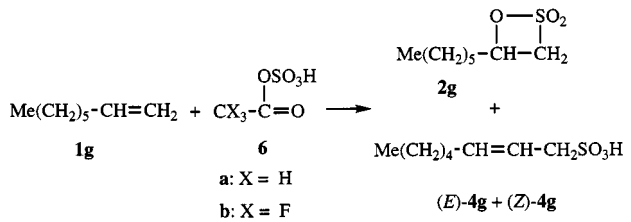
5 2

Scheme 4. Mechanism for the conversion of *sec*-alkyl chlorosulfates **5** into the β-sultones **2** in $CDCl_3$

Reaction of 1-Octene with Acetyl Sulfate and Trifluoroacetyl Sulfate

In the preceding section it was shown that chlorosulfuric acid, which is formally a complex of SO_3 and HCl, reacts as a strong acid with alkenes leading to the formation of *sec*-alkyl chlorosulfates. Both acetyl sulfate (**6a**) and its trifluoro derivative **6b** can also be considered as strongly acidic sulfonating reagents. Therefore we were interested to know whether the initial step of the acetyl sulfates **6a** and **6b** with an alkene would be protonation or sulfonation.

Reaction of 1-octene (**1g**) with 1.1 mol-equiv. of acetyl sulfate (**6a**), made up from equimolar amounts of acetic acid and SO_3, in [D]chloroform at −40°C for 10 min leads to the formation of 71% of 1,2-octanesultone (**2g**), 16% of a mixture of (*E*)- and (*Z*)-2-octene-1-sulfonic acid [**4g**, (*E*)/(*Z*) = 4:3), leaving 13% of unreacted 1-octene. After 10 min at 0°C, the remaining 1-octene had reacted to afford 81% of 1,2-octanesultone (**2g**) and 19% of a mixture of (*E*)- and (*Z*)-2-octene-1-sulfonic acid [**4g**, (*E*)/(*Z*) = 4:3). Reaction of 1-octene (**1g**) with 1.1 mol-equiv. of trifluoroacetyl sulfate (**6b**), made up from equimolar amounts of trifluoroacetic acid and SO_3, in [D]chloroform at −20°C for 10 min led to the formation of 63% of 1,2-octanesultone (**2g**) and 37% of a 3:2 mixture of (*E*)- and (*Z*)-2-octene-1-sulfonic acid (**4g**). Thus, 1-octene reacts with both acetyl sulfate and trifluoroacetyl sulfate to afford rapidly the sulfonation products 1,2-octanesultone (**2g**) and (*E*)- and (*Z*)-2-octene-1-sulfonic acid (**4g**) as depicted in Scheme 5. Although the acetyl sulfates **6a** and **6b** are strong acids there is no evidence for an initial protonation of the 1-octene, since the only observed procucts are the 1-sulfo compounds **2g** and **4g**. The sulfonating behaviour of both the acetyl sulfate (**6a**)[12] and trifluoroacetyl sulfate (**6b**) appears to be comparable with that of the chlorosulfuric acid−dioxane complex.



1g 6

Scheme 5. Reaction of 1-octene (**1g**) with acetyl sulfate (**6a**) and trifluoroacetyl sulfate (**6b**) in $CDCl_3$

Experimental Section

General: Materials: The high-purity alkene substrates, chlorosulfuric acid and trimethylsilyl chlorosulfate reagents, and [D]chloroform and [D_8]dioxane solvents were obtained commercially. Sulfo-

nation procedures and analysis: These were analogous to those described previously.[5,25,26] – ^{1}H- and ^{13}C NMR: Bruker AC-200 and WM-250 spectrometers. Of the various types of the homogeneous reaction mixtures the ^{1}H- and ^{13}C-NMR spectra were recorded applying APT (attached proton technique), COSY,[27] double resonance, and CH correlation,[28] as appropriate. The structural assignments of the components of the reaction mixtures were made on the basis of the observed ^{1}H-NMR chemical shifts, absorption ratios and coupling constants in combination with the ^{1}H-NMR-shielding parameters of the $-SO_2-O-$ and SO_3H substituents.[1,29] The product compositions of the various reaction mixtures were determined by multicomponent ^{1}H-NMR analysis on the basis of specific absorptions of the assigned components.[29]

NMR-Spectroscopic Data of the Sulfo Products

1,2-Cyclopentanesultone (2a):[12] ^{1}H NMR ($CDCl_3$): δ = 4.97 (m, 1 H), 4.91 (m, 1 H), 1.50−2.50 (m, 6 H).

***trans*-2,3-Butanesultone (2b):**[30] ^{1}H NMR ($CDCl_3$): δ = 4.33 (m, 1 H, CHS), 4.21 (m, 1 H, CHO), 1.59 (d, *J* = 7.3, 3 H, 1-Me), 1.57 (d, *J* = 7.3, 3 H, 4-Me).

***cis*-2,3-Butanesultone (2c):**[30] ^{1}H NMR ($CDCl_3$): δ = 4.88 (m, 1 H, CHS), 4.76 (m, 1 H, CHO), 1.50 (d, *J* = 7.2, 3 H, 1-Me), 1.48 (d, *J* = 6.3, 3 H, 4-Me).

1,2-Butanesultone (2d):[12] ^{1}H NMR ($CDCl_3$): δ = 4.54 (dd, *J* = 12.3, 7.5, 1 H, CHS), 4.40 (m, 1 H, CHO), 4.11 (dd, *J* = 12.3, 5.5, 1 H, CHS), 1.90 (m, 2 H), 0.94 (t, *J* = 7.3, Me).

***trans*-2,3-Pentanesultone (2h):** ^{1}H NMR ($CDCl_3$): δ = 4.34 (m, 1 H, CHS), 3.98 (m, 1 H, CHO), 1.89 (m, 2 H), 1.57 (d, *J* = 7.1, 3 H, 1-Me), 0.96 (t, *J* = 7.4, 3 H, 5-Me).

***cis*-2,3-Pentanesultone (2i):** ^{1}H NMR ($CDCl_3$): δ = 4.85 (m, 1 H, CHS), 4.45 (m, 1 H, CHO), 1.65 (m, 2 H), 1.43 (d, *J* = 6.6, 3 H, 1-Me), 0.98 (t, *J* = 7.4, 3 H, 5-Me).

***trans*-4,5-Octanesultone (2e):**[1] ^{13}C NMR ($CDCl_3$): δ = 77.7 (CHS), 72.5 (CHO), 36.5 (C-6, CH_2), 30.4 (C-3, CH_2), 19.9 (CH_2), 18.1 (CH_2), 13.5 (CH_3), 13.4 (CH_3).

***cis*-4,5-Octanesultone (2f):**[1] ^{13}C NMR ($CDCl_3$): δ = 75.0 (CHS), 70.0 (CHO), 31.7 (C-6, CH_2), 26.3 (C-3, CH_2), 20.6 (CH_2), 18.3 (CH_2), 13.5 (CH_3), 13.4 (CH_3).

1,2-Octanesultone (2g):[1] ^{13}C NMR ($CDCl_3$): δ = 64.2 (CH_2S), 65.6 (CHO), 34.9 (CH_2), 31.4 (CH_2), 28.5 (CH_2), 24.5 (CH_2), 22.4 (CH_2), 14.0 (CH_3).

***trans*-2,3-Hexanesultone (2j):** ^{1}H NMR ($CDCl_3$): δ = 4.45 (m, 1 H, CHS), 4.13 (m, 1 H, CHO), 1.88 (m, 2 H), 1.64 (d, *J* = 7.1, Me), 1.43 (m, 2 H), 0.96 (t, *J* = 7.3, Me).

***cis*-2,3-Hexanesultone (2k):** ^{1}H NMR ($CDCl_3$): δ = 4.97 (m, 1 H, CHS), 4.64 (m, 1 H, CHO).

***trans*-2,3-Octanesultone (2l):** ^{1}H NMR ($CDCl_3$): δ = 4.38 (m, 1 H, CHS), 4.07 (m, 1 H, CHO), 1.87 (m, 2 H), 1.60 (d, *J* = 7.2, Me), 1.2−1.5 (m, 6 H), 0.86 (Me). – ^{13}C NMR ($CDCl_3$): δ = 72.8 (CHS), 74.0 (CHO), 34.1 (CH_2), 31.0 (CH_2), 24.2 (CH_2), 22.3 (CH_2), 13.9 (C-8, CH_3), 13.4 (C-1, CH_3).

***cis*-2,3-Octanesultone (2m):** ^{1}H NMR ($CDCl_3$): δ = 4.88 (m, 1 H, CHS), 4.57 (m, 1 H, CHO), 1.80 (m, 2 H), 1.53 (d, *J* = 7.4, Me), 1.30 (m, 6 H), 0.87 (Me). – ^{13}C NMR ($CDCl_3$): δ = 69.8 (CHS), 70.4 (CHO), 31.1 (CH_2), 29.6 (CH_2), 24.7 (CH_2), 22.3 (CH_2), 9.2 (C-1, CH_3), 13.8 (C-8, CH_3).

Cyclopentyl Chlorosulfate (5a): ^{1}H NMR ($CDCl_3$): δ = 5.46 (m, 1 H), 2.11 (m, 2 H), 1.97 (m, 2 H), 1.77 (m, 4 H).

2-Butyl Chlorosulfate (5b): ^{1}H NMR ($CDCl_3$): δ = 5.04 (m, 1 H), 1.83 (m, 2 H), 1.54 (d, *J* = 6.3 Hz, 3 H, 1-Me), 1.01 (t, *J* = 7.4 Hz, 3 H, 4-Me). – ^{13}C NMR ($CDCl_3$): δ = 19.7 (C-1), 90.8 (C-2), 29.1 (C-3), 9.4 (C-4).

2-Pentyl Chlorosulfate (5c): ^{1}H NMR ($CDCl_3$): δ = 5.02 (m, 1 H), 1.80 (m, 2 H), 1.47 (d, *J* = 6.3 Hz, 3 H, 1-Me), 1.42 (m, 2 H), 0.91 (t, *J* = 7.2 Hz, 3 H, 5-Me).

3-Pentyl Chlorosulfate (5d): ^{1}H NMR ($CDCl_3$): δ = 4.84 (m, 1 H), 1.65 (m, 4 H), 0.96 (t, *J* = 7.4 Hz, 6 H).

2-Hexyl Chlorosulfate (5e): ^{1}H NMR ($CDCl_3$): δ = 5.06 (m, 1 H), 1.80 (m, 2 H), 1.53 (d, *J* = 6.2 Hz, 3 H, 1-Me), 1.35 (m, 4 H), 0.89 (3 H, 6-Me).

3-Hexyl Chlorosulfate (5f): ^{1}H NMR ($CDCl_3$): δ = 4.95 (m, 1 H), 1.80 (m, 4 H), 1.40 (m, 2 H), 0.99 (t, *J* = 7.4 Hz, 3 H, 1-Me), 0.94 (t, *J* = 7.1 Hz, 3 H, 6-Me).

2-Octyl Chlorosulfate (5g): ^{1}H NMR ($CDCl_3$): δ = 5.08 (m, 1 H), 1.76 (m, 2 H), 1.54 (d, *J* = 6.3 Hz, 3 H, 1-Me), 1.25−1.35 (m, 8 H), 0.84 (3 H, 8-Me).

3-Octyl Chlorosulfate (5h): ^{1}H NMR ($CDCl_3$): δ = 4.98 (m, 1 H), 1.80 (m, 4 H), 1.35 (m, 6 H), 0.99 (t, *J* = 7.3 Hz, 3 H, 1-Me), 0.85 (3 H, 8-Me).

4-Octyl Chlorosulfate (5i): ^{1}H NMR ($CDCl_3$): δ = 4.98 (m, 1 H), 1.80 (m, 4 H), 1.35 (m, 6 H), 0.94 (m, 6 H).

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