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# SULFONATION OF ALKENES WITH SULFUR TRIOXIDE; REVERSIBLE STEREOSPECIFIC β-SULTONE FORMATION†

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*Abstract:* The small differences in the rate coefficients of β-sultone formation between the internal and the terminal double bond in the octenes **2a-c** and (*Z*)-1,10-nonadecadiene are evidence for a concerted cycloaddition of sulfur trioxide. The formation of β-sultone **1d** is accompanied by 15% of 2-octene-1-sulfonic acid, formed in a primary side-reaction. The sulfonation of the octenes **2a-d** to their β-sultones **1a-d** is reversible. Desulfonation of the β-sultones **1a-d** by water to the olefins **2a-d** proceeds in a stereospecific *syn* fashion.

Sulfonation of linear olefins by sulfur trioxide is a complicated process which eventually leads to mixtures of mainly alkenesulfonic acids and γ- and δ-sultones.[2] The inital products of sulfonation reactions are thermally unstable β-sultones.[3] The formation of these β-sultones proceeds in a stereospecific *syn* cycloaddition reaction as was shown for *Z* and *E* internal olefins[4,5] and a stereospecifically deuterated α-olefin.[6] Such a stereospecific β-sultone formation is best explained by a $[2_s+2_s]$ synchronous cycloaddition mechanism.[7] Further information with regard to the mechanism may be obtained from the relative sulfonation rates of internal and α-olefins.

## Relative rate of β-sultone formation for internal and terminal linear olefins

The relative sulfonation rates of alkenes have been the subject of several investigations. Roberts *et al.*[7] have determined the sulfonation rates of a variety of linear and branched alkenes by measuring the amounts of unreacted starting material and found only small rate differences. On the other hand, Canselier *et al.*[8] reported on the basis of the amounts of the sulfo products obtained after alkaline hydrolysis that internal olefins react more slowly than α-olefins by a factor of 9. Also Roberts[9] noticed that it is difficult to sulfonate internal olefins to completion under conditions where α-olefins readily do so. The sulfonation of alkenes proceeds however in two steps; the first one is the formation of β-sultones, which is followed by their thermal rearrangement to β-alkenesulfonic acids and γ-sultones.

We have determined the relative rate of formation of the primary sulfonation product, the β-sultone, for 1-octene and

Table I Relative rate coefficients of β-sultone formation[a]

| alkenes | $SO_3$-dioxane | $ClSO_3Si(CH_3)_3$ |
|---|---|---|
| (*Z*)-4-octene / (*E*)-4-octene | 2.1 ± 0.2 | 1.8 ± 0.2 |
| (*Z*)-4-octene / 1-octene | 1.7 ± 0.2 | 1.4 ± 0.2 |
| (*E*)-4-octene / 1-octene | 0.9 ± 0.1 | 0.8 ± 0.1 |
| (*Z*)-1,10-nonadecadiene | 1.2 ± 0.2[b] | 1.3 ± 0.2[b] |

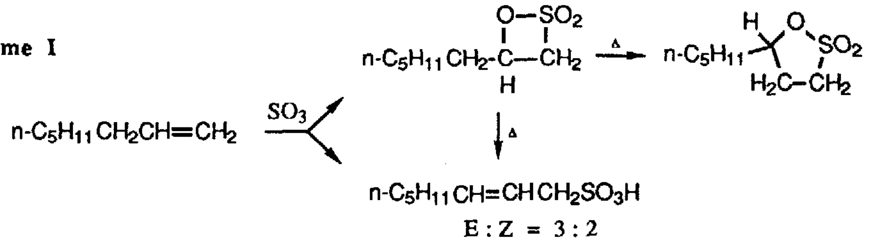
[a] The rate coefficient ratio was calculated from the amounts of the two β-sultones formed and applying the equation of Ingold (see ref. 8, p. 111). [b] Ratio of the conversion of the internal and the terminal double bond.

(*Z*)- and (*E*)-4-octene in intermolecular competition experiments. Equimolar amounts of two olefins (0.12 mmol each) were sulfonated with 0.08 mmol of $SO_3$ complexed with 0.10 mmol of dioxane-$d_8$ and with 0.08 mmol of trimethylsilyl chlorosulfonate[10] at -20 to 0°C and the amounts of the two β-sultones formed were determined on the basis of their specific absorptions in the $^1H$ NMR spectrum[6] of the reaction mixture. The relative rate coefficients in Table I show that the difference in rate of β-sultone formation for internal and terminal alkenes is relatively small. The internal Z double bond is somewhat more reactive than the terminal one, whereas the *E* double bond is slightly less so. The largest rate difference is found between (*Z*)- and (*E*)-4-octene. The same observation was made for the *intramolecular* competition using (*Z*)-1,10-nonadecadiene.[11] The small rate differences are in favor of a synchronous cycloaddition mechanism and are hard to explain when zwitter ions are considered as intermediates.[7]

## Primary formation of 2-alkenesulfonic acid from 1-alkenes and sulfur trioxide

During our study of the reaction of sulfur trioxide complexed with dioxane with 1-octene at low temperature (below -10°C) using $^1H$ NMR we noticed that the formation of 1,2-octanesultone was accompanied by the formation of small amounts (15%) of a compound with typical absorptions at δ 5.85, 5.48, 3.91 and 3.82 ppm, which were assigned to 2-octene-1-sulfonic acid[12] present as a mixture of *E*- and Z-isomer in a ratio of 3 to 2. These alkenesulfonic acids can in principle be formed by thermal rearrangement of 1,2-sultones, but it is known[13] that this isomerization is slow at temperatures below 0°C.

**Scheme I**

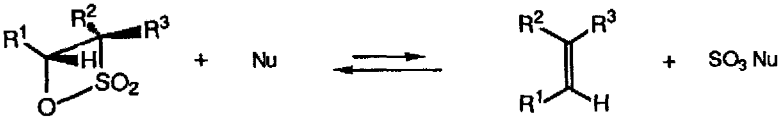


Using the mildly sulfonating agent $ClSO_3SiMe_3$ at 0°C, we observed that the amounts of 2-octene-1-sulfonic acid[14] (E/Z = 3:2) and β-sultone increased simultaneously in a constant ratio of 1 to 5.5. Both the β-sultone and the 2-octene-1-sulfonic acid are thus produced directly from the α-olefin in the sulfonation process as shown in Scheme I. From kinetic calculations on the thermal rearrangement of 1,2-sultones, Canselier *et al.*[13] also concluded that a small portion of the 2-alkenesulfonic acid did not originate from the corresponding β-sultone. They proposed a common zwitter ionic intermediate for the formation of both the β-sultone and the 2-alkenesulfonic acid. We assume instead that alkenes react with $SO_3$ to give simultaneously [2+2] cycloadditions and ene-type reaction products such as β-alkenesulfonic acids, similarly as in singlet oxygenation reactions of olefins.

On reaction of (*E*)- and (*Z*)-4-octene with $SO_3$ at 0°C the formation of 3-octene-4-sulfonic acids is far less pronounced (<5%) and for these internal alkenes it remains therefore doubtful whether the primary ene reaction occurs.

## Elimination of sulfur trioxide from β-sultones

β-Sultones are highly reactive species[15] which isomerize thermally to alkenesulfonic acids and 5- and 6-membered ring sultones. As strained cyclic sulfonate esters, they are also prone to substitution reactions under mild conditions even with weak nucleophiles.[16] In the course of our investigations on reactions of β-sultones with nucleophiles we noticed that the usual substitution reaction leading to β-substituted alkanesulfonic acids was accompanied by formation of starting material, the original alkenes. We have investigated this elimination reaction in detail for *cis*- and *trans*-4,5-octanesultone and for 1,2-octanesultone. In order to get high levels of elimination products we used water under acidic conditions at low concentrations in a heterogeneous dichloromethane-water mixture in order to trap the liberated sulfur trioxide in the water layer as sulfuric acid. Solutions of the β-sultones **1a-c** (0.5 M) in $CH_2Cl_2$ were prepared by reaction of 27 mmol of $SO_3$ and 30 mmol of dioxane in 50 ml of dichloromethane with 24 mmol of alkene at -20°C under an argon atmosphere. Then water (10 ml) was added and the heterogeneous mixture was stirred vigorously for 5 days at room temperature. After neutralization, the $CH_2Cl_2$ layer was analyzed for alkenes with GLC.[17] Freeze-drying of the aqueous layer afforded the β-hydroxyoctanesulfonates.[4,18] The yields of alkene **2**, given in Table II, show that the internal β-sultones, particularly *trans*-4,5-octanesultone **1a**, eliminate $SO_3$ to a high extent. Essentially the same results were obtained when the reactions were performed on a small scale and monitored with $^1H$ NMR using deuterated solvents to establish that the starting olefins had been fully converted into their β-sultones at low temperature prior to the start of the elimination reaction. The transfer of $SO_3$ from *trans*-β-sultone **1a** to water is slow in spite of the high eventual yield. After one day only 40% of β-sultone **1a** had been converted and the complete β-sultone conversion, yielding 86% of the alkene **2a**, takes 5 days. In contrast, 1,2-sultone **1c** reacts quickly to give mainly 2-hydroxy-1-octanesulfonic acid and only 28% of the elimination product **2c** in one day. The rate of desulfonation of these two β-sultones is apparently of the same order of magnitude, just as is the case for the rate of formation of the β-sultones from the alkenes (Table I). The eventual high yield of desulfonation product for *trans*-β-sultone **1a** is thus mainly caused by its thermal stability[5] and its low reactivity towards substitution. Large amounts of desulfonation product are thus to be expected for unreactive β-sultones. In fact, for the stable fluorinated β-sultones[19] and for some adamantylidene substituted β-sultones[1] such transfer reactions of $SO_3$ were also observed.



**1a-d** **2a-d**

Table II. Desulfonation of β-sultones by water

| β-sultone **1** | $R^1$ | $R^2$ | $R^3$ | yield alkene **2** (%) |
|---|---|---|---|---|
| **a** | n-$C_3H_7$ | H | n-$C_3H_7$ | 86 |
| **b** | n-$C_3H_7$ | n-$C_3H_7$ | H | 62 |
| **c** | n-$C_6H_{13}$ | H | H | 28 |
| **d** | n-$C_6H_{13}$ | H | D | n.d. |

On treatment of a 0.5 molar solution of β-sultone **1a** in $CDCl_3$ with $CD_3OD$ we observed with $^1H$ NMR a similar desulfonation and substitution reaction to the alkene and 5-methoxy-4-octanesulfonic acid respectively. The ratio of substitution *versus* desulfonation product depends on the methanol concentration and decreases from 1.5 *via* 0.50 to 0.10 on using 25, 10 and 3.0 equiv of methanol respectively. The desulfonation of β-sultone **1a** is definitely less dependent on the methanol concentration than the bimolecular substitution reaction. We therefore suggest that the desulfonation of β-sultones proceeds by *retro*-sulfonation and subsequent trapping of the liberated $SO_3$ by the nucleophile.

Transfer of $SO_3$ from β-sultones derived from linear olefins to other alkenes is usually slower than their isomerizations and will also depend on the mutual reactivity of the alkenes. We have observed transfer of $SO_3$ when 0.24 mmol of *trans*-3,4-hexanesultone[5] was treated with one equiv of cyclopentene in 0.5 ml of $CDCl_3$ at room temperature. The formation of *cis*-1,2-cyclopentanesultone[5] was measured with $^1H$ NMR by the appearance of its typical low field absorptions centered at δ 4.99 (m, 2H) ppm. In a slow reaction, after one day, 35% of cyclopentene was converted into its β-sultone with concomittant formation of an equal amount of 3-hexene.

The elimination of sulfur trioxide from the β-sultones by water is *stereospecific*. The reactions of *trans*- and *cis*-4,5-octanesultone afforded (*E*)- and (*Z*)-4-octene, respectively, each in more than 95% purity as established by GLC.[17] In a similar elimination reaction of *trans*-1-D-1,2-octanesultone **1d**,[6] which was monitored with $^1H$ NMR, only (*E*)-1-D-1-octene (**2d**) was formed. The sulfonation of linear olefins by sulfur trioxide to yield β-sultones is thus a *reversible* process in which both the cycloaddition and elimination of sulfur trioxide proceed in a stereospecific *syn* fashion. The equilibrium of the reaction, however, lies very far to the side of the β-sultone. It should be noted that an analogous stereospecific *syn* elimination of sulfur dioxide has been reported in the mechanism of the formation of olefins from β-hydroxy sulfinamides.[20]

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† Aliphatic sulfonation Part 4. For Part 3, see ref. 1.

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