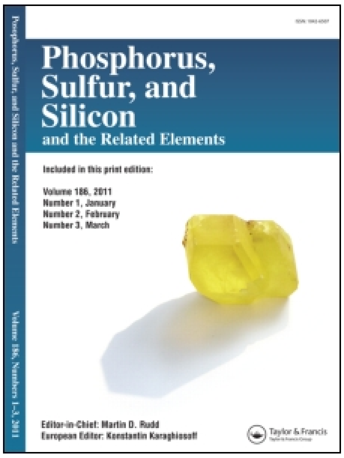

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Ruud M. Schonk[a]; Bert H. Bakker[a]; Hans Cerfontain[a]
[a] Laboratory of Organic Chemistry, University of Amsterdam Nieuwe Achtergracht 129, WS Amsterdam, The Netherlands

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REACTIONS OF ALKENES AND ω-PHENYLALKENES WITH SULFUR TRIOXIDE; SULFONATION AND FRIEDEL-CRAFTS TYPE OF CYCLIZATION

Ruud M. Schonk, Bert H. Bakker and Hans Cerfontain*
Laboratory of Organic Chemistry, University of Amsterdam
Nieuwe Achtergracht 129, 1018 WS Amsterdam, The Netherlands

Abstract Reaction of alkenes with SO_3 leads to the formation of β-sultones, carbyl sulfates, alkenesulfonic acids and γ-sultones, depending on the alkene structure and on the reaction conditions. The high selectivity for the cyclisation to 1,2,3,4-tetrahydronaphthalene sulfonic acid derivatives on reaction of well chosen ω-phenylalkenes with SO_3 infers the occurrence of a relatively fast equilibrium between ω-phenyl-m,n- and the ω-phenyl-n,m-alkanesultone intermediate.

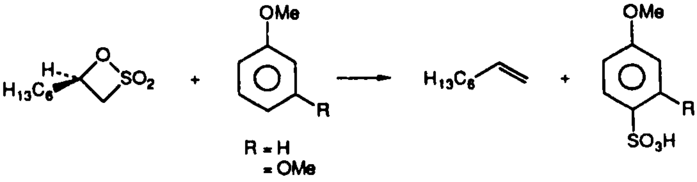
INTRODUCTION

The sulfonation of external and internal linear alkenes in organic solvents using various amounts of both SO_3 and $ClSO_3SiMe_3$ as reagent was studied recently.[1,2] On using one mol-equiv of SO_3 at -20°C the corresponding β-sultones are formed, the addition proceeding stereospecifically *via* a concerted *cis*-cycloaddition.[1] 1-Alkenes yield in addition in a primary process small amounts (10-20%) of the (*E*)- and (*Z*)-2-alkene-1-sulfonic acids. Upon reaction of the alkenes with an excess (≥ 2.0 mol-equiv) of SO_3 at 20°C the initially formed β-sultones are converted into the corresponding carbyl sulfates (*i.e.* sulfonate-sulfate anhydrides) *via* a stereospecific SO_3 insertion in the S-O bond of the β-sultone.[2]

The initial step of the sulfonation of linear alkenes by SO_3 to yield β-sultones is reversible. The equilibrium of this reaction lies far to the side of the β-sultone.[3] Reaction of a β-sultone with nucleophiles, such as water and methanol, leads in part to the reformation of the initial alkenes. This conversion proceeds by *retro*-sulfonation and trapping of the liberated SO_3 by the nucleophile. The loss of SO_3 from a β-sultone proceeds in a stereospecific *syn* elimination fashion. The sulfonation of linear olefins by SO_3 to yield β-sultones is thus a reversible process in which both the cycloaddition and the elimination of SO_3 proceed in a stereospecific *syn* fashion.

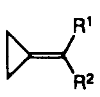
RESULTS

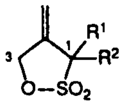
Transfer sulfonation of reactive aromatic compounds, like anisole and 1,3-dimethoxybenzene, can be effected with β-sultones. The sulfonation of anisole has been effected by 1.0 equiv of 1,2-octanesultone, *cis*-4,5-octanesultone and *trans*-4,5-octanesultone at 20°C for 20 h, the yields of the corresponding alkenes (which are equal to the yield of anisole-4-sulfonic acid) being 78, 46 and 43% respectively. The rate of transfer sulfonation of anisole and 1,3-dimethoxybenzene by 1.0 equiv of *trans*-4,5-octane-sultone is the same, indicating that the loss of SO_3 is the rate limiting step.Transfer of SO_3 from a β-sultone to another non-branched alkene does also occur:

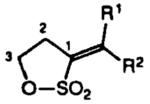


trans-3,4-hexanesultone + cyclopentene ⇄ (*E*)-3-hexene + 1,2-cyclopentanesultone

The formation of 1,2-cyclopentanesultone again proceeds most likely by *retro*-sulfonation of the 3,4-hexanesultone and subsequent sulfonation of the cyclopentene by the liberated SO_3.[3]



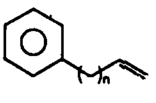




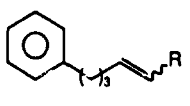
1	$R^1 = R^2 = H$	**5**	
2	$R^1 + R^2 = CH_2-CH_2$	**6**	
3	$R^1 = R^2 = Ph$		**7**
4	$R^1 + R^2$ = 2,2 - adamantylidene		**8**

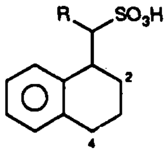
The sulfonation of the cyclopropylidenealkanes **1**[4] and **2** with 1 equiv of SO_3 yields 2-methylene-1,3-propanesultone (**5**) and its 1,1-ethano derivative (**6**) respectively. (Diphenylmethylene)cyclopropane (**3**)[4] and adamantylidenecyclopropane (**4**)[4] on the contrary yield the 1-alkylidene-1,3-propanesultones **7** and **8**, respectively. The formation of these γ-sultones is very rapid, even at -60°C; in fact, we were unable to obtain any ^1H NMR evidence for the intermediacy of the corresponding β-sultones.

Reaction of the ω-phenyl-1-alkenes **9** - **11** with ≥ 1.1 equiv of SO_3 at -20°C yields exclusively the corresponding 1,2-sultones which in the presence of an excess of SO_3 at room temperature yield the corresponding carbyl sulfates. With styrene (**12**) the initial β-sultone is not observed as such, since the conversion of the β-sultone into the carbyl sulfate is relatively fast. In fact, the degree of conversion of the β-sultone into the corresponding carbyl sulfate was found to increase in the order 1,2-octane- ≃ 6-phenyl-1,2-hexane- < 4-phenyl-1,2-butane- << 3-phenyl-1,2- propane- << 2-phenyl-1,2-ethane-sultone.



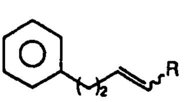
9 n = 1
10 n = 2
11 n = 4
12 n = 0

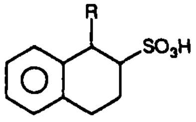




13	R = H	**15**
14	R = Me	**16**
	R = $(CH_2)_2Ph$	**17**

Reaction of the 5-phenyl-1-pentenes **13** and **14** [which have a $-(CH_2)_3-$ linkage between the Ph and the C=C] with 1.1 equiv of SO_3 at -30°C yields very rapidly and quantitatively the 1-sulfomethyl-1,2,3,4-tetrahydronaphthalenes **15** and **16** respectively. No β-sultone or carbyl sulfate could be observed as intermediate, not even at -60°C. Reaction of **18** [which has a $-(CH_2)_2-$ linkage between the Ph and C=C] with 1.1 equiv of SO_3 leads to the formation of 1-methyl-1,2,3,4-tetrahydronaphthalene-2-sulfonic acid (**21**) in quantitative yield. This cyclization proceeds stereospecifically, as appeared from experiments starting with (*E*)/(*Z*) mixtures of 0.33, 1.0 and 4.6 which afforded the *cis*- and *trans*-isomers of **21** in the same ratios. Of the two possible cyclization products which may result on reaction of 1,7-diphenyl-3-heptene (**20**) [having both a $-(CH_2)_2-$ and a $-(CH_2)_3-$ linkage between the C=C and the phenyls] with 1.1 equiv of SO_3 at -50°C, only **23** is obtained quantitatively. With $ClSO_3SiMe_3$, the reaction proceeds less selectively, the yield of **23** being 82% with 18% of probably **17**.

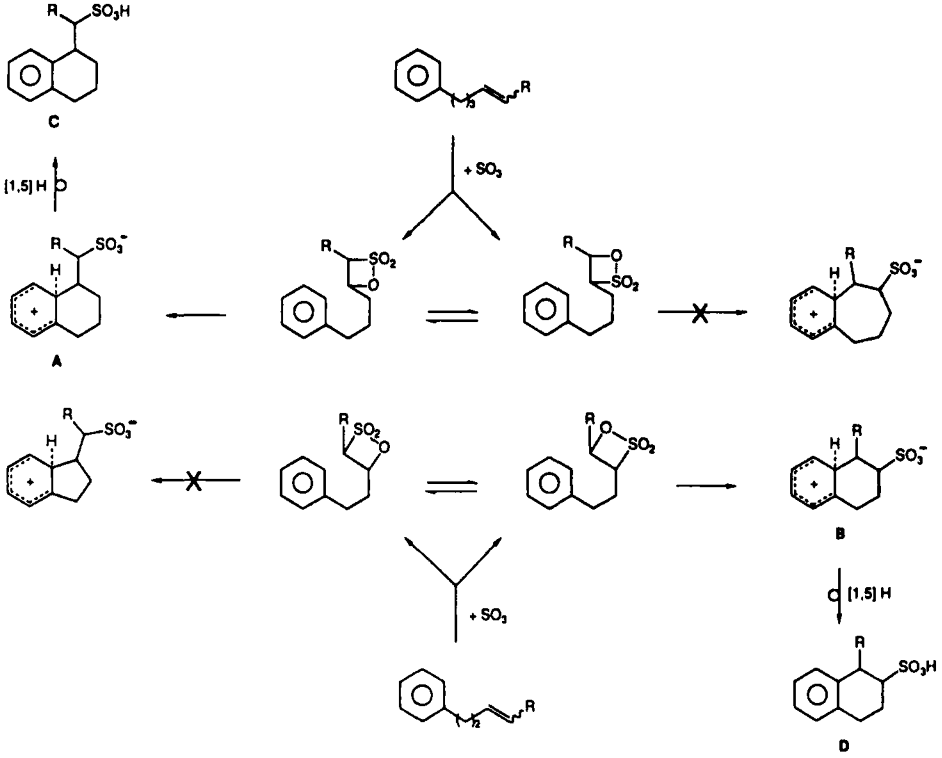




18	R = Me	**21**
19	R = Ph	**22**
20	R = $(CH_2)_3Ph$	**23**

The quantitative formation of the six-membered ring cyclization products **16** and **21** - **23** upon reaction of the respective phenylalkenes **14** and **18** - **20** with SO_3

at ≤ -30°C infers that there exists a very fast equilibrium between the isomeric m,n- and n,m-sultones (see Scheme 1), which are the presumed precursors of the specific σ-complexes **A** and **B** leading to the two respective types of cyclization products **C** and **D**. Using 5-(2-chlorophenyl)-2-pentene as starting substrate it was shown that the formation of the cyclization product **D** from the preceding β-sultone is catalyzed by SO_3.



SCHEME 1 Mechanism of formation of the cyclization products **C** and **D** upon reaction of $Ph(CH_2)_nCH{=}CHR$ (n = 2, 3) with SO_3.

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