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NMR EVIDENCE FOR ß-SULTONES AS INITIAL PRODUCTS IN REACTIONS OF OLEFINS WITH SULPHUR TRIOXIDE

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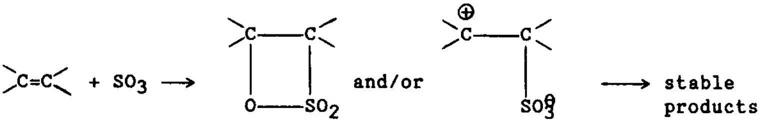
ABSTRACT

NMR evidence is provided to show that low temperature sulphonation of simple olefins of all structural types involves initial formation of ß-sultones, thus supporting the previously suggested concerted thermal $\pi 2_s + \pi 2_s$ cycloaddition mechanism.

INTRODUCTION

Sulphonation of olefins is currently a topic of major interest for detergent manufacture and it is, therefore, important to understand the reaction mechanisms as fully as possible. Reactions of olefins with sulphur trioxide (SO_3) give products which may be regarded as being derived from rearrangement of initially formed ß-sultones [1] or ß-zwitterions [2]$^{(1)}$, the α-carbon being defined as that bonded to sulphur:



[1] [2]

On the basis of relative rate studies for sulphonation of a range of mono-, di- and tri-alkyl substituted ethenes, it has been suggested that the initial reaction in olefin sulphonation is formation of the ß-sultone by a concerted thermal $\pi 2_s + \pi 2_s$ pathway$^{(2)}$. For linear monoalkyl and 1,2-dialkyl ethenes the existence of the corresponding ß-sultones in sulphonation is well established$^{(3-9)}$ and there is evidence to support our proposed pathway$^{(5,10)}$. However, for other olefin types, particularly those for which the cationic centre in the ß-zwitterion would be tertiary, there has so far been no evidence for ß-sultones and it has been widely assumed that the sulphonation reaction involves direct formation of the ß-zwitterion$^{(8)}$.

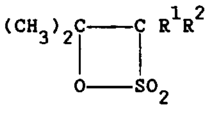
In view of the wider applications towards cycloaddition theory, we considered it a matter of some urgency to validate the thermal concerted $\pi 2_s + \pi 2_s$ mechanism by testing the prediction that ß-sultones should be formed from olefins of all structural types.

Here we present NMR evidence indicating that ß-sultones are formed initially in all cases, even those where the ß-zwitterion would appear to be particularly favoured.

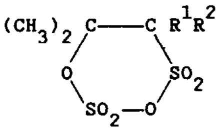
In these studies olefin sulphonation reactions were carried out by adding, via a syringe, SO_3 dissolved in the reaction solvent (usually $CDCl_3$ or CD_2Cl_2) to a cold solution of the olefin in the same solvent in an NMR tube. ^1H or ^{13}C NMR spectra, as appropriate, were recorded at pre-determined temperatures on a Bruker 360 MHz spectrometer. Chemical shifts were assigned by comparison with published $^1H^{(3,4)}$ and $^{13}C^{(6,7)}$ spectra of ß-sultones and pyrosultones derived from mono-alkyl and 1,2-dialkyl-ethenes.

Sulphonation of tetramethylethene

The NMR spectra of the reaction mixture at -63°C produced by a 1.8:1 mole ratio of SO_3: olefin show only the ß-sultone [3A] and ß-pyrosultone [4A] in approximately equal quantities and residual olefin.



[3]



[4]

$CH_2{:}C(CH_3).CR^1R^2.SO_3H$

[5]

For [3], [4] and [5]: A, $R^1=R^2=CH_3$; B, $R^1=CH_3$, $R^2=H$; C, $R^1=R^2=H$

The sample was held at 20°C for 5 minutes and then reanalysed at -63°C. Both ^1H and ^{13}C NMR spectra showed the disappearance of the ß-sultone with the appearance of the alkene sulphonic acid [5A] but no significant change in the ß-pyrosultone [4A] level. On storing at room temperature overnight, the reaction mixture gave a highly complex spectrum from which the ß-pyrosultone [4A] signals were no longer present, the major product being the alkene sulphonic acid [5A].

NMR: ß-sultone: $^1H(CD_2Cl_2)$ δ 1.56(s, ß-CH_3), 1.51(s, α-CH_3). $^{13}C(CD_2Cl_2)$ δ 23.76 (q, ß-CH_3), 19.56(q, α-CH_3), 81.2(s, α-C), 77.67(s, ß-C). ß-pyrosultone: $^1H(CD_2Cl_2)$ δ 1.77(s, ß-CH_3), 1.62(s, α-CH_3). $^{13}C(CD_2Cl_2)$ δ 96.5(s, ß-C), 65.6(s, α-C). Alkene sulphonic acid: $^1H(CD_2Cl_2)$ δ 1.9(s, ß-CH_3), 1.55(s, α-CH_3), 1.58(s, α-CH_3), 5.26(d, ß-CH_2). $^{13}C(CD_2Cl_2)$ δ 119(t, ß-CH_2), 140.4(s, ß-C)

Sulphonation of trimethylethene: The NMR spectra of the reaction mixture produced when SO_3 was added to trimethylethene (0.9:1 mole ratio of SO_3 to olefin) at -63°C showed the initial products to be the ß-sultone [3B] and the ß-pyrosultone [4B] in equal quantities with 48% of the original olefin remaining.

After storage overnight at -23°C the β-sultone [3B] had isomerised to form the alkene-sulponic acid [5B] but the β-pyrosultone was still present and its level remained stable over a further 6 hours at room temperature.

NMR: β-sultone: $^{1}H(CD_2Cl_2)$ δ 4.55(q, α-H). $^{13}C(CD_2Cl_2)$ δ 76.5(s, β-C), 73.0(d, α-C). β-pyrosultone: $^{1}H(CD_2Cl_2)$ δ 1.65(d, α-CH_3), 1.7(s, β-CH_3), 1.8(s, β-CH_3), 3.80(q, α-H). $^{13}C(CD_2Cl_2)$ δ 94.0(s, β-C), 60.5(d, α-C). Alkenesulphonic acid: $^{1}H(CD_2Cl_2)$ δ 1.55(d, α-CH_3), 1.87(s, β-CH_3), 3.91(q, α-H), 5.2(d, β-CH_2). $^{13}C(CD_2Cl_2)$ δ 62.5(d, α-c), 119.0(t, β-CH_2), 136.6(s, β-C)

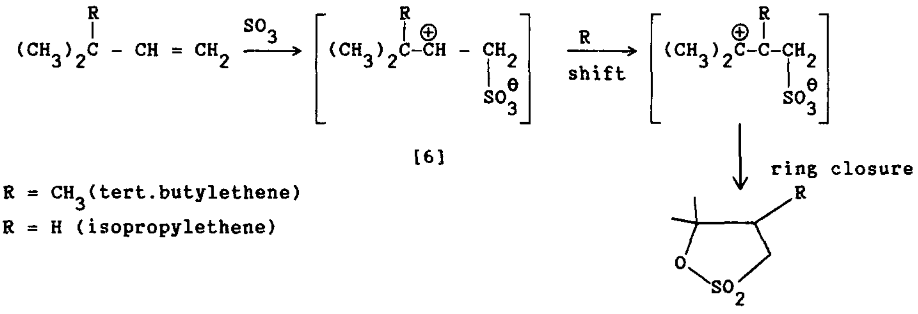
Sulphonation of Isobutene:

In the ^{13}C NMR spectrum of isobutene, the two methyl groups are equivalent. However after addition of SO_3, in the spectrum of the reaction mixture at -63°C which showed the tertiary β-sultone [3C] to be the major product, the two methyls of the β-sultone are found at different chemical shifts and hence are non-equivalent. This can only be the case if the β-sultone ring is non-planar and this is further evidence to support that of Nagayama et al.(5) for the non-planarity of β-sultone rings. Also in the low temperature spectrum, there is evidence for the β-pyrosultone [4C]. On warming at room temperature for 30 minutes, the β-sultone no longer remains and appears to have isomerised to the corresponding alkene sulphonic acid [5C]. The β-pyrosultone however appears to be stable under such conditions.

NMR: β-sultone: $^{13}C(CD_2Cl_2)$ δ 26.8(q, β-CH_3), 28.2(q, β-CH_3), 68.0(t, α-C), 72.8(s, β-C). β-pyrosultone: $^{13}C(CD_2Cl_2)$ δ 21.5(q, β-CH_3), 25.9(q, β-CH_3), 49.8(t, α-C), 89.5(s, β-C). Alkene sulphonic acid: $^{13}C(CD_2Cl_2)$ δ 28.4(q, β-CH_3), 58.2(t, α-C), 121.0(t, β-CH_2), 131.5(s, β-C).

Sulphonation of Tertiarybutylethene and Isopropylethene:

The major products formed in the sulphonation of tert.butylethene(11,12) and isopropylethene(12) have been reported as being the γ-sultones [7]



[6]

[7]

R = CH_3(tert.butylethene)
R = H (isopropylethene)

The formation of [7] has been rationalised in terms of a methide ($R=CH_3$) or hydride (R=H) shift on the ß-zwitterions [6], followed by ring closure.

The proton NMR spectra of the reaction mixtures obtained by addition of SO_3 to the olefins at low temperature showed the corresponding ß-sultones to be the major products.

For the tert.butylethene case (temperature -50°), the γ-sultone [7] was also present at a low level and a considerable amount of olefin remained unreacted. In the case of isopropylethene (temperature -63°), the ß- and γ-sultones were present in approximately equimolar amounts and very little olefin remained. On warming to 20°C, the reaction mixtures gave spectra in which the ß-sultones and the unreacted olefins were no longer present and the γ-sultones [7] were the major products.

<u>NMR</u>: tertiary butylethene, ß-sultone: $^1H(CD_2Cl_2, -50°C)$ δ 0.9 (s, tert.butyl),
δ 4.25 (m,1α-H & ß-H), 4.42 (m,α-H)
isopropylethene, ß-sultone $^1H(CD_2Cl_2, -63°C)$ δ 0.87 & 0.98 (two d, two CH_3s)
2.05 (m,-C<u>H</u>Me_2), 4.30 & 4.63 (two m, two α-H & one ß-H)

CONCLUSION

Our findings provide the first direct evidence for the existence of tertiary-ß-sultones and demonstrate that the initial reaction of SO_3 with olefins of all structural types produces ß-sultones. This evidence strongly supports the thermal $\pi 2_s + \pi 2_s$ concerted cycloaddition mechanism previously suggested(2).

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