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The Thermal Desulfination of Allylic Sulfonyl Halides

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Abstract: Allylic sulfonyl halides can be generated by halogenolysis of the corresponding triorganotin sulfinates. Allylic sulfonyl bromides and iodides undergo a first order, thermal desulfination with allylic rearrangement to yield the corresponding allylic halides. The desulfination of a cyclic allylic sulfonyl bromide is stereospecific, proceeding with γ-*syn* bromine migration.
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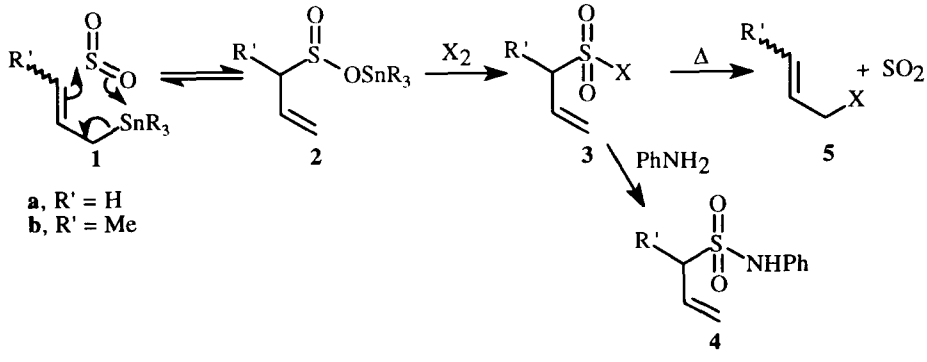
Organotin allylic sulfinates can be regio- and stereospecifically prepared by the metallo-ene addition of sulfur dioxide to allylic stannanes (Scheme 1, **1**→**2**).[1] We have recently reported that these relatively stable sulfinate derivatives are convenient precursors to the corresponding unstable, allylic sulfinic acids.[2] The latter can be generated *in situ* by acidolysis of the trialkyltin ester and subsequently undergo a spontaneous desulfination with allylic rearrangement. This reaction can be conveniently monitored (NMR or UV) and a detailed stereochemical and kinetic study[2c] provided evidence of a concerted, retro-ene mechanism involving a relatively compact, early transition state.

It occurred to us that cleavage of triorganostannane allylic sulfinates could be achieved with electrophiles other than proton, and that the resulting sulfinyl or sulfonyl intermediate may undergo an analogous rearrangement reaction. As a starting point to this study, we prepared tributylstannyl 2-propenesulfinate (**2a**, R = Bu) and examined the reaction of this substrate with chlorine, bromine and iodine (Scheme 1).



Scheme 1

Halogenolysis of **2a** (R = Bu) yielded allylic sulfonyl halides, **3a** (X = Cl, Br, I), which could be characterised by NMR and IR spectroscopy and isolated as the corresponding sulfonanilide, **4a**. 2-Propenesulfonyl chloride (**3a**, X = Cl) was quite stable, even on heating in chloroform (sealed tube) at 100 °C for 7 days. The corresponding bromide and iodide, however, underwent a thermal desulfination to yield

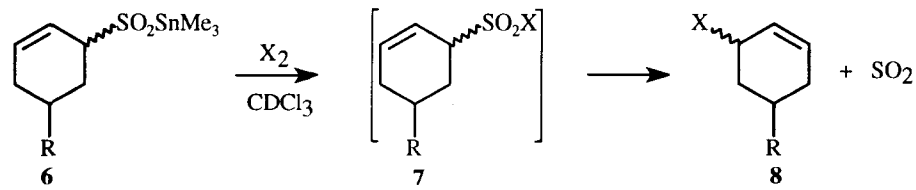
allylic halide, **5a** (Table 1). This decomposition could be conveniently monitored by ^{1}H NMR spectroscopy and, for iodide **3a**, also by UV spectrophotometry (λ_{max} = 320 nm). Desulfination obeyed a first - order rate law and the rate of reaction was dependent on the halide ($k_I >> k_{Br} >> k_{Cl}$) and, to a lesser extent, on the solvent (increasing with solvent polarity) but was unaffected by the presence or absence of light. These last two observations are consistent with an electrophilic, rather than a radical process.

Table 1. Rate constants for the thermal desulfination of **3a**.

X	solvent	T (°C)	k (s^{-1})
Cl	$CDCl_3$	100	n.r.[a]
Br	toluene - d_8	65	1.9 x 10^{-5}
Br	CD_3NO_2	65	8.5 x 10^{-5}
I	toluene - d_8	25	1.7 x 10^{-3}
I	CH_2Cl_2	28	3.2 x 10^{-3}
I	THF	28	5.3 x 10^{-3}

[a] No reaction after 7 days.

The desulfination of substituted allylic sulfonyl halides **3b** and **7a** (X = Br or I) were substantially faster. Reaction of tin sulfinate **2b** (R = Me) with bromine in dichloromethane yielded the sulfonyl bromide **3b**, which could be observed by ^{1}H NMR and isolated as the corresponding sulfonanilide, **4b**. Sulfonyl bromide **3b** underwent desulfination in $CDCl_3$ (-15 °C) exclusively with allylic rearrangement to yield 1-bromo-2-butene (**5b**, Z:E = 19:81). This reaction was too fast for an accurate rate constant to be determined by ^{1}H NMR spectroscopy, but was complete in less than five minutes. The corresponding reaction of cyclic allylic tin sulfinate **6a** (Scheme 2) with bromine in $CDCl_3$ (-15 °C) was too fast for the presumed intermediate **7a** to be detected in a ^{1}H NMR spectrum obtained within three minutes of bromine addition. Likewise, sulfonyl iodides **3b** and **7a** were not detected on iodinolysis of tin sulfinates **2b** (R = Me) and **6a** in $CDCl_3$ at -15 °C. Rather, sulfur dioxide was observed to bubble from these reactions immediately on iodine addition and the allylic iodides 2-iodo-2-butene (**5b**, Z:E = 38:62) and 1-iodo-2-cyclohexene (**8a**) together with iodotrimethylstannane were observed to be the exclusive products by ^{1}H and ^{13}C NMR spectroscopy.



6 **7** **8**

a, R = H
b, R = CH_3

Scheme 2

The stereochemistry of desulfination was investigated using diastereomeric mixtures of trimethylstannyl 5-methylcyclohex-2-enesulfinate, **6b** (Table 2). Brominolysis of two different diastereomeric mixtures of **6b** in $CDCl_3$ at 25 °C yielded identical ratios of the corresponding allylic bromides, **8b** (entries 1 and 2). When the same reactions were performed at -50 °C (entries 3 and 4), however,

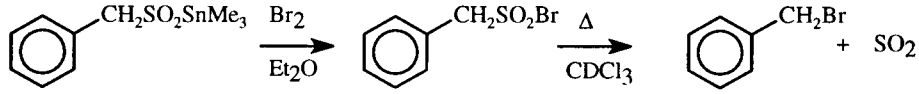
brominolysis and subsequent desulfination proceeded stereospecifically with overall retention of configuration. These reactions were allowed to warm to room temperature and ^{13}C NMR analysis revealed isomerisation to the equilibrium diastereomeric ratio observed previously. Iodinolysis of two different diastereomeric mixtures of **6b** yielded identical ratios of the corresponding allylic iodides, even when performed at low temperatures (entries 5 to 8).

Table 2. The stereochemistry of halogenolysis and desulfination of **6b**.

entry	X	T (°C)	**6b** (*trans* :*cis*)[a]	**8b** (*trans* :*cis*)[a]
1	Br	25	44:56	76:24
2	Br	25	71:29	76:24
3	Br	-50	44:56	44:56
4	Br	-50	71:29	72:28
5	I	-50	44:56	84:16
6	I	-50	71:29	84:16
7	I	-78[b]	44:56	84:16
8	I	-78[b]	71:29	84:16

[a] Determined by ^1H and ^{13}C NMR spectroscopy. [b] Performed in toluene-d_8.

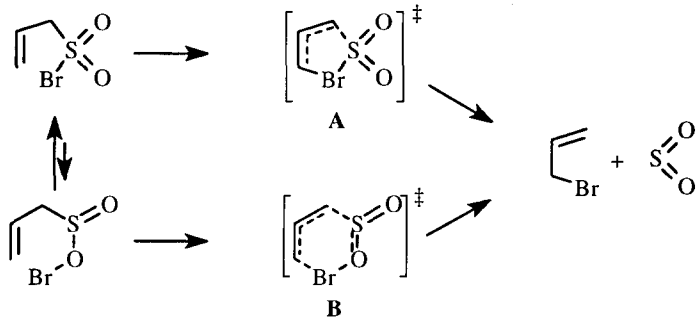
Brominolysis of trimethylstannyl benzylsulfinate (**9**) yielded the corresponding benzylsulfonyl bromide (**10**) which underwent a very slow desulfination to yield benzyl bromide, **11** (Scheme 3). This latter reaction required heating at 80 °C for 5 days and resulted in approximately 50% conversion with some decomposition.



9 **10** **11**

Scheme 3

The free radical desulfination of methyl- and ethylsulfonyl bromide occurs in the gas phase above 200 °C[3] and it seems reasonable that the desulfination of **10** could occur via the same mechanism under less vigorous conditions. The desulfination of **10** is, however, considerably slower than the corresponding process **3a**→**5a** (X = Br) and if both reactions involved rate determining heterolytic cleavage of the carbon - sulfur bond, then a reversal in this order of reactivity would be expected. It is also unlikely that a step-wise desulfination of allylic sulfonyl bromides would proceed with the exclusive γ-*syn* bromine migration which was observed. Rather, the above data for allylic sulfonyl bromides are consistent with a concerted process involving some charge development in the transition state as evidenced by the modest solvent effect (Table 1). Two possible cyclic transition states, **A** and **B** (Scheme 4), can reasonably be invoked. While there is no evidence for the allylic sulfinyl hypobromite leading to transition state **B**, such a transition state would mirror that for the corresponding retro-ene desulfination of allylic sulfinic acids.[2] There is also some evidence that the thermal extrusion of sulfur dioxide from sulfolene derivatives might proceed via a prior sulfone - sulfinate lactone isomerisation.[4]



Scheme 4

Desulfination of the corresponding allylic sulfonyl iodides was first order and, again, proceeded faster in polar solvents. The conversion **3b**→**5b** (X = I) suggests allylic rearrangement, although **5b** is also the thermodynamically favoured regioisomer and allylic isomerisation is likely to be facile. The *syn* stereospecificity observed for bromine migration was not observed for the corresponding iodine migration, possibly due to a rapid isomerisation of the initial product to an equilibrium mixture of E and Z **8b**, even at low temperatures. A step-wise desulfination via a symmetrical intermediate cannot, therefore, be excluded.

In concluding we note that the reaction of allylic stannanes with sulfur dioxide is reversible. Heating **2a** at 120 °C for four hours under vacuum (0.5 mm Hg) resulted in a 60% conversion to **1a**. Tin sulfinate **6a** also underwent desulfination to approximately the same extent under these conditions. Microscopic reversibility suggests that these reactions should proceed via a concerted "retro-metallo-ene" transition state, analogous to **B**.

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