Thermal Decomposition of Allylic Sulfinic Acids: Confirmation of a Retro-ene Mechanism

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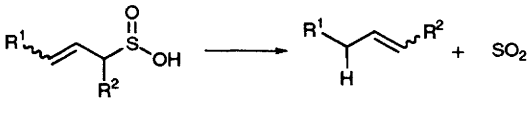
The acidolysis of trialkyltin allylic sulfinates yields the corresponding sulfinic acids which undergo a first-order thermal decomposition with γ-*syn* substitution as predicted for a retro-ene mechanism.

The thermal decomposition of allylic sulfinic acids is a synthetically useful procedure for the allylic transposition of double bonds (Scheme 1).[1–7]

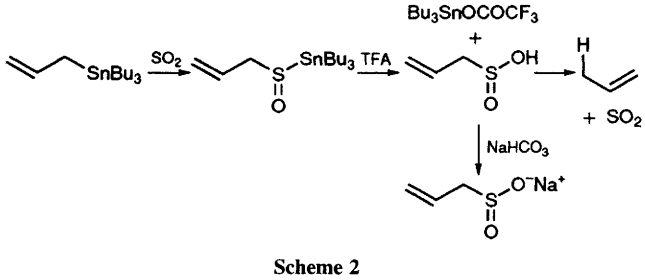
Desulfination is usually facile at room temperature[1] and the allylic sulfinic acid is not isolated, but formed as a transient intermediate in, for example, the isomerization of alkenes with sulfur dioxide[3] or the oxidation of allylic thiols.[4] The regio- and stereo-chemical information which has been reported[1–7] can be rationalized by a cyclic retro-ene mechanism, but further kinetic and stereochemical evidence is necessary to confirm this proposition. The instability of the substrates makes this task difficult using published synthetic procedures. We now report that allylic sulfinic acids can be prepared regio- and stereo-specifically from allylic stannanes and the kinetics of decomposition conveniently followed by NMR spectroscopy.

The reaction of allylic stannanes with sulfur dioxide in chloroform is rapid and quantitative at room temperature and yields the corresponding tin allylsulfinate regio- and stereo-specifically with γ-*syn* substitution.[8] Acidolysis of tributyltin allylsulfinate with trifluoroacetic acid (TFA, 1 equiv.) in chloroform immediately yields tributyltin trifluoroacetate and allylsulfinic acid which can be observed decomposing to propene (by NMR spectroscopy) or isoalted as the sodium salt (86% isolated yield) on quenching with aqueous sodium bicarbonate (1 equiv.) (Scheme 2). The sodium, lithium and potassium salts also can be made almost quantitatively by reacting the tin sulfinate with an ethanolic solution of the corresponding alkali metal hydroxide for the 3 h at room temp.

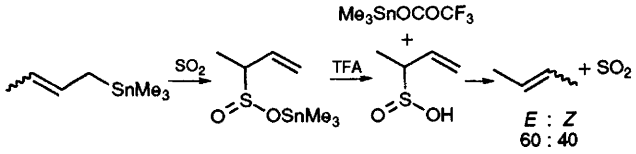
The decomposition to propene and sulfur dioxide can be accurately monitored by ^{1}H NMR spectroscopy. Using 0.9 equiv. of TFA in toluene, decomposition is first order with $k_{297\,K} = 5.5 \times 10^{-4}\ s^{-1}$, $\Delta H^{\ddagger} = 48 \pm 4\ kJ\ mol^{-1}$ and $\Delta S^{\ddagger} = -146 \pm 17\ J\ K^{-1}\ mol^{-1}$. The rate of reaction is constant for different proportions of TFA up to one equivalent. At proportions even slightly greater than one equivalent, the rate of reaction is too fast to measure accurately by NMR spectroscopy. With 1.1 equiv. of TFA at 298 K the reaction was complete within 4 min.



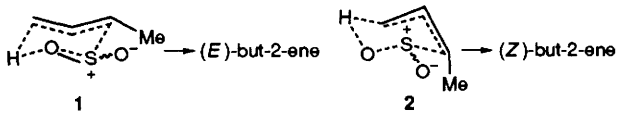
Scheme 1



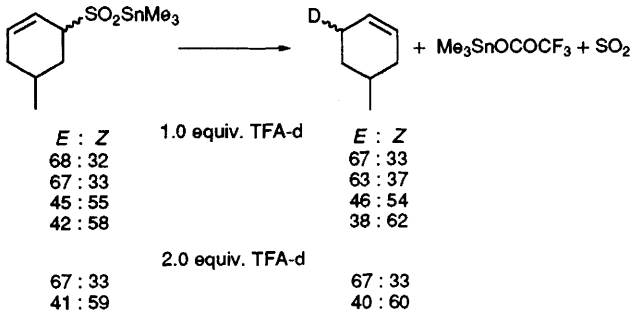
Scheme 2



Scheme 3



Scheme 4

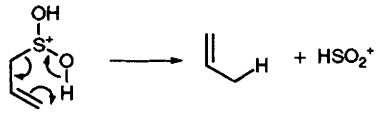


Scheme 5 TFA-d = CF_3CO_2D

The reaction of trimethyltin but-3-enyl-2-sulfinate (prepared from but-2-enyltrimethylstannane and sulfur dioxide) with 1.0 equiv. of TFA in chloroform at room temp. was regiospecific yielding but-2-ene ($E:Z$ = 1.5) (Scheme 3).

The modest excess of the *E* isomer can be rationalized by a concerted cyclic mechanism in which transition state **1** is of slightly lower energy than transition state **2** (Scheme 4).

More conclusive stereochemical information was obtained by employing a conformationally defined cyclic system. Different isomeric ratios of *Z* and *E* trimethyltin 5-methylcyclohex-2-enylsulfinate were reacted with 1.0 and 2.0 equiv. of TFA-d in chloroform or dichloromethane at room temp. (Scheme 5). The relative proportions of *Z* and *E* 5-deuterio-3-methylcyclohexene were determined by integration of the ^2H NMR spectrum of the corresponding dibromides.[9] Desulfination was stereospecific at both concentrations of TFA-d (within experimental error) with *syn* deuterium substitution.



Scheme 6

These observations of first-order desulfination and γ-*syn* substitution confirm a retro-ene mechanism for the thermal decomposition of allylic sulfinic acids. The relatively large negative value of $\Delta S^{\ddagger}$ is consistent with a concerted process. Interestingly, acidolysis with greater than one equivalent of TFA is also stereospecific but occurs at a much greater rate. This result can be rationalized by the retro-ene desulfination of a protonated sulfinic acid intermediate (Scheme 6).

We have demonstrated that allylic sulfinic acids (and the corresponding alkali metal salts) can be conveniently prepared from allylic stannanes. From a synthetic perspective it is also interesting to note that direct acidolysis of allylic stannanes proceeds with predominantly γ-*anti* substitution[9] whereas the sequence **1** sulfur dioxide insertion, **2** acidolysis results in overall α-*syn* substitution.

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