

The High Pressure Addition of Aldehydes to Allylstannanes: a 'Diels–Alder Like' Transition State

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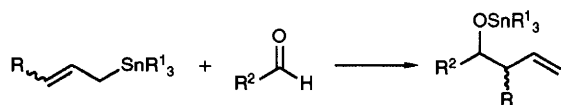
The activation volume for the addition of chloral to allyltributylstannane was found to be $-33.4 \pm 0.6 \text{ cm}^3 \text{ mol}^{-1}$, which is consistent with a concerted, cyclic transition state.

The addition of aldehydes to allylstannanes is a carbon–carbon bond forming reaction of considerable synthetic potential.¹ The product has useful functionality for further elaboration and variation of the mode of activation (*i.e.* heat,² high-pressure³ or the addition of a Lewis acid^{2,4}) and reaction conditions⁴ allows manipulation of the regio- and stereochemistry of addition. Further mechanistic studies, however, are necessary to elucidate fully the factors which determine this control.

We recently reported that high pressure is a mild, high yielding method for facilitating this transformation, which proceeds stereospecifically with *syn* approach of the aldehyde.⁵ This result is consistent with a six-membered cyclic transition state involving tin–oxygen coordination, as first proposed by Yamamoto *et al.*³ Additional important mechanistic information can be provided by quantifying the effect of pressure on the rate of aldehyde addition.⁶ High pressure organometallic chemistry in the liquid phase has received very little attention, despite the success of this technique as a synthetic method and mechanistic probe for many organic

reactions.⁶ We now report the activation volume for the addition of chloral to allyltributylstannane, the magnitude of which is consistent with the mechanism proposed and, in addition, suggests a concerted process.

Chloral adds to allylstannanes at elevated temperatures (100 °C, 20 h).⁷ To obtain pseudo first-order rate coefficients in a convenient time and at a convenient temperature (37.5 °C), reactions were performed in a large excess of allyltributylstannane (0.025 ml chloral in 4.0 ml of allylstannane). The disappearance of chloral was monitored at 320 nm and on completion, the identity of the product was confirmed by ¹³C NMR spectroscopy. For reactions at elevated pressures, the spectrophotometer cell was sealed with a silicon rubber cap to allow pressure equalization and placed in a thermostatted, high-pressure optical cell as previously described.⁸ Three to four experiments were performed at each pressure and each obeyed a first-order rate law to completion with standard



Scheme 1

Table 1 Addition of chloral to allyltributylstannane at 37.5 °C

<i>p</i> /bar	10 ⁴ <i>k</i> /s ⁻¹
1	7.31
200	9.68
400	12.2
600	16.3
800	21.5

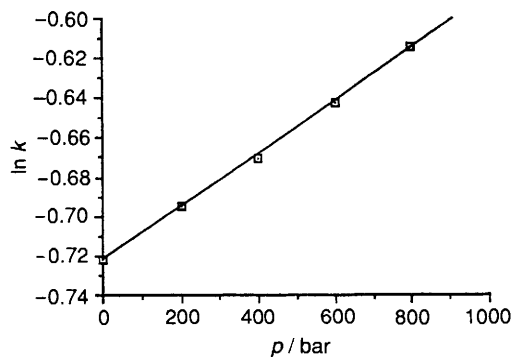


Fig. 1 Effect of pressure on chloral addition to allyltributylstannane

deviations better than 1% (Table 1). The plot of $\ln k$ against pressure (Fig. 1) was linear with a correlation coefficient of 0.999.

An activation volume of $-33.4 \pm 0.6 \text{ cm}^3 \text{ mol}^{-1}$ was calculated according to the equation $\Delta V^* = -RT \cdot d(\ln k)/dp$.⁶ This value lies within the range established for many examples of the Diels–Alder reaction ($-35 \pm 5 \text{ cm}^3 \text{ mol}^{-1}$) and is consistent with a single-step metallo–ene mechanism involving a tight transition state and well-developed bonding.⁶ This interpretation is supported by our previous observation of *syn* aldehyde addition.⁵

In practical terms, this large negative activation volume translates into a rate enhancement of approximately 10^3 at pressures between 10–20 kbar.⁶ We would expect that high pressure would be an ideal mechanistic probe and synthetic tool for a variety of similar organometallic reactions.

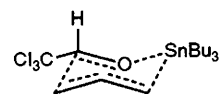


Fig. 2

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