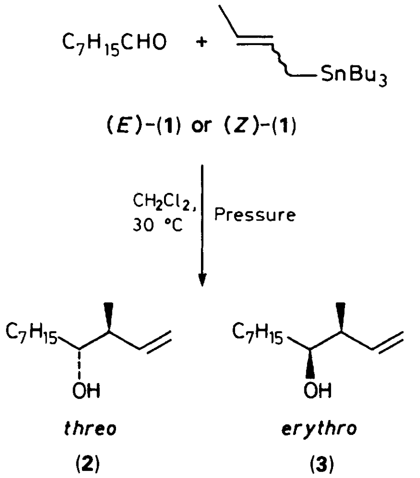
Intervention of the Boat Transition State in the Allylic Tin–Aldehyde Condensation at High Pressure

Yoshinori Yamamoto* and Ken-ichi Saito

Department of Chemistry, Faculty of Science, Tohoku University, Sendai 980, Japan

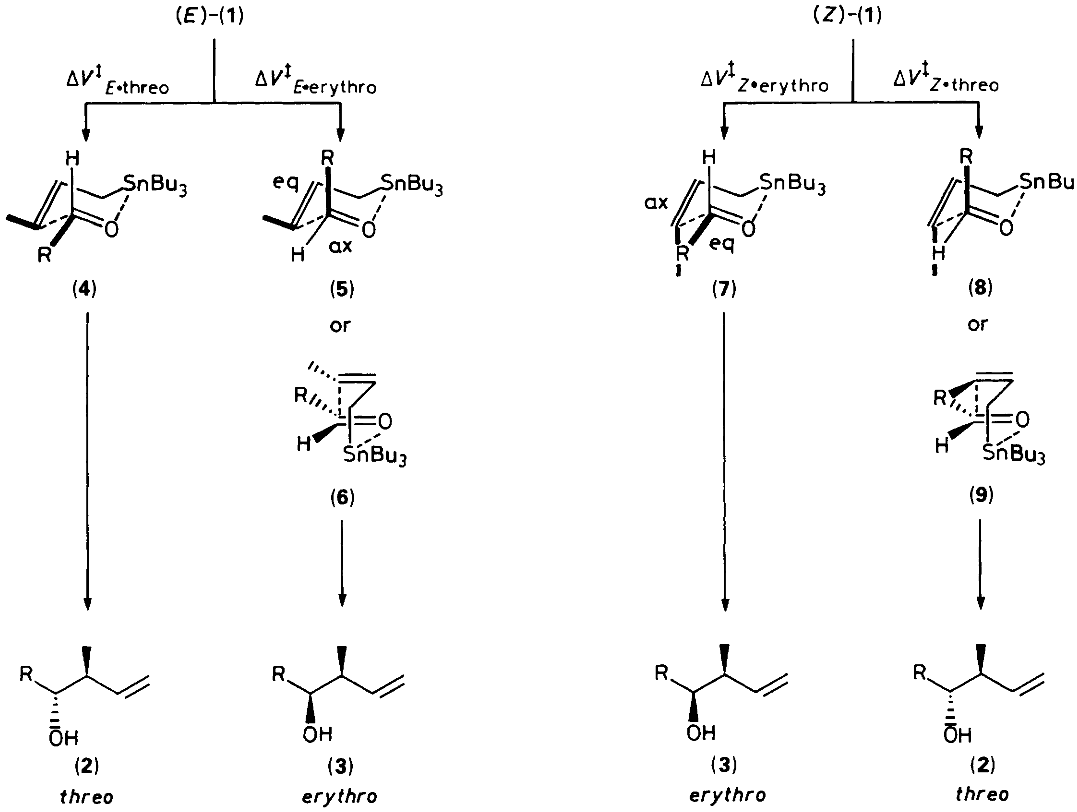
The volume data of the octanal–crotyltin condensation are obtained from the pressure dependence of the rate coefficient and of diastereoselectivity; analysis of $\Delta V^{\ddagger}$, $\Delta\Delta V^{\ddagger}$, and $V^{\ddagger}$ indicates the intervention of the boat transition state under high pressure condensation.

The allylic tin–aldehyde condensation reaction has been of much interest from both synthetic and mechanistic points of view.[1] The condensation takes place upon heating,[1] in the presence of Lewis acids,[1] or at high pressure.[2] The transition state geometries have been discussed only on the basis of the stereochemical outcome of the reactions. It is widely accepted that the Lewis acid-mediated reaction proceeds *via* an acylic transition state,[1,3] while in the absence of Lewis acids the condensation reaction[4] proceeds *via* a 6-membered chair transition state. We report for the first time that a boat transiton state is involved in the high pressure reaction of aliphatic aldehydes with crotyltin and demonstrate that discussions of the transition state geometry can be quantitative, based on the $\Delta V^{\ddagger}$ value, rather than qualitative, based on the stereochemical outcome.



Scheme 1

The pressure dependence of the rate coefficient k and of diastereoselectivity in the octanal–crotyltin condensation (Scheme 1) is summarized in Table 1. It was confirmed that the observed diastereoselectivity comes from kinetic control. The *threo* preference of the (Z)-isomer, the increase in *erythro* product from the (E)-isomer with increasing pressure, and the increase in the *threo* form from the (Z)-isomer at higher pressure clearly indicate the intervention of (**5**) or (**6**) in formation of the *erythro* product from the (E)-isomer, and of (**8**) or (**9**) in formation of the *threo* product from the (Z)-isomer (Scheme 1); these transition state geometries are more sterically crowded in comparison with (**4**) or (**7**) and thus



Scheme 2. Transition state geometry.

Table 1. Pressure effect on the rate and diastereoselectivity of the octanal–crotyltin condensation.[a]

Stannane	P /10^8Pa	k/kg mol^{-1} s^{-1}	ln k	*threo*/ *erythro*	ln (*threo*/*erytho*)
(*E*)	2.55	5.93×10^{-8}	−16.6	2.15/1	7.63×10^{-1}
(*E*/*Z* = 97/3)	3.92	2.28×10^{-7}	−15.5	1.80/1	5.90×10^{-1}
	6.37	4.44×10^{-7}	−14.6	1.57/1	4.51×10^{-1}
	7.65	6.21×10^{-7}	−14.3	1.51/1	4.09×10^{-1}
(*Z*)	2.55	9.74×10^{-8}	−15.8	1.16/1	1.58×10^{-1}
(*E*/*Z* = 5/95)	3.92	4.09×10^{-7}	−14.7	1.33/1	2.88×10^{-1}
	6.37	9.82×10^{-7}	−13.8	1.52/1	4.17×10^{-1}
	7.65	1.25×10^{-6}	−13.6	1.53/1	4.26×10^{-1}

[a] The concentration of substrates was 5.00×10^{-1} mol kg^{-1} (stannane : aldehyde = 1 : 1). The reaction progress and selectivity were followed by capillary g.l.c.

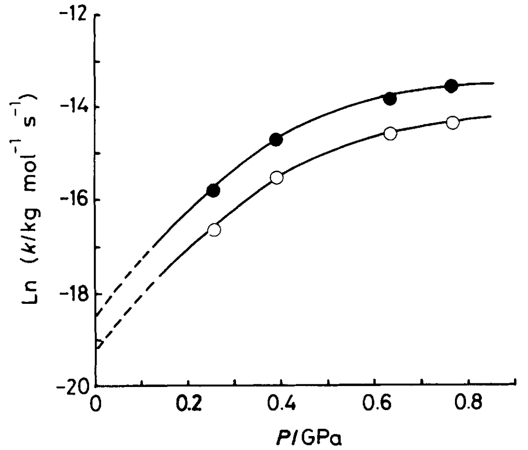


Figure 1. Pressure dependence of the rate coefficient, k. (*Z*)-Isomer (●), (*E*)-isomer (○).

must be favourable at high pressure. We will clarify the transition state geometry for formation of the *erythro* product from the (*E*)-isomer, (**5**) or (**6**), and the *threo* product from the (*Z*)-isomer, (**8**) or (**9**).

The ln k–P and ln (*threo*/*erythro*)–P plots are shown in Figures 1 and 2, respectively. From the ln k *vs.* P data,† the activation volume of the (*E*)-isomer was $\Delta V^{\ddagger}_{E} = -30.3 \pm 0.3$ cm^3 mol^{-1}, and that of the (*Z*)-isomer was $\Delta V^{\ddagger}_{Z} = -32.1 \pm 0.3$ cm^3 mol^{-1}. These values are very similar to those for ordinary intermolecular Diels–Alder reactions ($-\Delta V^{\ddagger} > 30$ cm^3 mol^{-1}).[5] The difference in activation volume between the reaction paths leading to (**2**) and (**3**) is obtained from equation (1).[6] From the slope of Figure 2, $\Delta\Delta V^{\ddagger}_{E} = 5.0 \pm 0.5$ cm^3 mol^{-1} and $\Delta\Delta V^{\ddagger}_{Z} = -4.3 \pm 0.5$ cm^3 mol^{-1}. Thus, the *threo*/*erythro* ratio at 1 atmosphere was found to be 3.24/1 for the (*E*)- and 1/1.23 for the (*Z*)-isomer. Since $\Delta V^{\ddagger}_{E}$ is a mean value of $\Delta V^{\ddagger}_{E\cdot threo}$ and $\Delta V^{\ddagger}_{E\cdot erythro}$, equation (2) can be deduced. Consequently, the individual $\Delta V^{\ddagger}$ values for each step in Scheme 2 were $\Delta V^{\ddagger}_{E\cdot threo} = -29.1 \pm 0.3$ cm^3 mol^{-1}, $\Delta V^{\ddagger}_{E\cdot erythro} = -34.1 \pm 0.3$ cm^3 mol^{-1}, $\Delta V^{\ddagger}_{Z\cdot threo} = -34.4 \pm 0.3$ cm^3 mol^{-1}, and $\Delta V^{\ddagger}_{Z\cdot erythro} = -30.1 \pm 0.3$ cm^3 mol^{-1}.

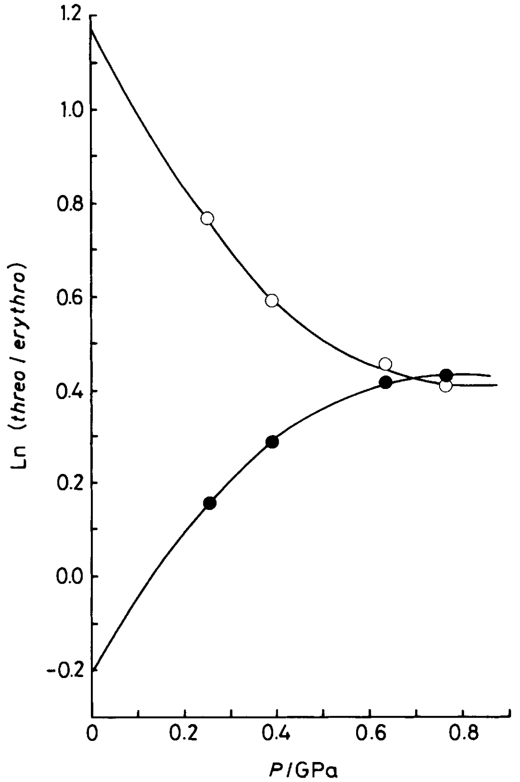


Figure 2. Pressure dependence of diastereoselectivity. (*Z*)-Isomer (●), (*E*)-isomer (○).

$$\begin{aligned}\Delta\Delta V^{\ddagger} &= \Delta V^{\ddagger}_{threo} - \Delta V^{\ddagger}_{erythro}\\ &= -RT[(\partial \ln k\, threo/k\; erythro)/\partial P]_{\mathrm{T}}\\ &= -RT[(\partial \ln threo/erythro)/\partial P]_{\mathrm{T}} \qquad (1)\end{aligned}$$

$$(3.24 \times \Delta V^{\ddagger}_{E\cdot threo} + \Delta V^{\ddagger}_{E\cdot erythro})/(3.24 + 1) = \Delta V^{\ddagger}_{E} \qquad (2)$$

$$\begin{aligned}V^{\ddagger}_{4} - \mathrm{V}^{\ddagger}_{7} &= (\Delta V^{\ddagger}_{E\cdot threo} + V^{\mathrm{R}}_{E}) - (\Delta V^{\ddagger}_{Z\cdot erythro} + V^{\mathrm{R}}_{Z})\\ &= (\Delta V^{\ddagger}_{E\cdot threo} - \Delta V^{\ddagger}_{Z\cdot erythro}) + (V^{\mathrm{R}}_{E} - V^{\mathrm{R}}_{Z}) \qquad (3)\end{aligned}$$

The volume difference between (**4**) (eq, eq) and (**7**) (eq, ax) (eq = equatorial, ax = axial) is obtained from equation (3), V^{R}_{E} and V^{R}_{Z}, the volumes of (*E*)-(**1**) and (*Z*)-(**1**), were found to be 3.276×10^2 and 3.255×10^2 cm^3 mol^{-1}. Therefore, $V^{\ddagger}_{4} - V^{\ddagger}_{7} = (-29.1 + 30.1) + 2.1 = 3.1 \pm 0.5$ cm^3 mol^{-1}. $V^{\ddagger}_{7}$ and $V^{\ddagger}_{5}$ must have a similar volume, since the former has the eq, ax geometry and the latter has the ax, eq geometry.‡ Consequently, it was anticipated that $V^{\ddagger}_{4} - V^{\ddagger}_{5}$ would be very close to 3.1 cm^3 mol^{-1}. However, the observed value for $V^{\ddagger}_{E\cdot threo} - V^{\ddagger}_{E\cdot erythro} = -29.1 + 34.1 = 5.0 \pm 0.5$ cm^3 mol^{-1}, which is fairly large compared to the expected value for (**5**), indicates intervention of (**6**), which has a smaller volume.[7]

Other aliphatic aldehydes, such as propanal; 2-ethylbutanal, 2-phenylpropanal, and pivalaldehyde exhibited a similar diastereoselectivity at high pressure: the *threo* adducts were formed predominantly regardless of the geometry of (**1**). The volume data for the 2-phenylpropanal condensation were obtained using the same procedure, and here also $V^{\ddagger}_{4}$ −

---

† The curve deviates from linearity at higher pressure owing to a pressure dependent decrease of activation volume.[5] Non-linear least-squares fit with quadratic equation.

‡ Strictly speaking, this argument should be advanced on R = Me. However, as mentioned later, the effect of R upon the volume data seems to be small.

$V^{\ddagger}_{E\text{-}erythro} = 5.0 \pm 0.5$ cm^3 mol^{-1}. The high pressure reaction of benzaldehyde with (*E*)-(**1**) or (*Z*)-(**1**) gave the *threo* or *erythro* forms, respectively, and thus proceeded through a 6-membered chair transition state,[2] where $V^{\ddagger}_4 - V^{\ddagger}_7$ (R = Ph) again was found to be 3.1 ± 0.5 cm^3 mol^{-1}. Accordingly, the volume differences between (**4**) and (**7**), or between (**4**) and (**6**), are not so much influenced by the substituent R.§ In conclusion, the above mentioned analytical procedure based on volume data helps clarify transition state geometry and may be applied to other systems such as aldol and Claisen condensation reactions.

Received, 2nd June 1989; Com. 9/02303H

References

1 For reviews see (a) M. Pereyre, J.-P. Quintard, and A. Rahm. 'Tin in Organic Synthesis,' Butterworths, London, 1987; (b) V. G. Kumar Das and C. K. Chu, in 'The Chemistry of the Metal Carbon Bond,' eds. F. R. Hartley and S. Patai, Wiley, New York, 1985, vol. 3, p. 1; (c) Y. Yamamoto, *Acc. Chem. Rev.*, 1987, **20**, 243; (d) Y. Yamamoto, *Aldrichim. Acta*, 1987, **20**, 45.

2 Y. Yamamoto, H. Yatagai, Y. Ishihara, N. Maeda, and K. Maruyama, *Tetrahedron*, 1984, **40**, 2239.

3 S. E. Denmark, B. R. Henke, and E. J. Weber, *J. Am. Chem. Soc.*, 1987, **109**, 2512; S. E. Denmark, E. J. Weber, T. M. Wilson, and T. M. Willson, *Tetrahedron*, 1989, **45**, 1053.

4 Y. Yamamoto and K. Maruyama, *Heterocycles*, 1982, **18**, 357; R. W. Hoffmann, *Angew. Chem., Int. Ed. Engl.*, 1982, **21**, 555.

5 T. Asano and W. J. Le Noble, *Chem. Rev.*, 1978, **78**, 407; R. van Eldik, T. Asano, and W. J. Le Noble, *ibid.*, 1989, **89**, 549; K. Matsumoto and A. Sera, *Synthesis*, 1985, 999; N. S. Isaacs and A. V. George, *Chem. Britain*, 1987, 47; W. G. Dauben, J. M. Gerdes, and G. C. Look, *Synthesis*, 1986, 532.

6 L. F. Tietze, T. Hübsch, E. Voss, M. Buback and W. Tost, *J. Am. Chem. Soc.*, 1988, **110**, 4065.

7 The volume difference between eq, eq-1,2-dimethylcyclohexane and its ax, ax-conformer is 6 cm^3 mol^{-1} (eq, eq > ax, ax): D. J. Gardiner, N. A. Walker, and M. P. Dare-Edwards, *Spectrochim. Acta, Part A*, 1987, **43**, 21. The volume data mentioned in the text gave $V^{\ddagger}_4$ (eq, eq.) − $V^{\ddagger}_{Z\text{-}threo}$ (ax, ax) = 7.4 ± 0.5 cm^3 mol^{-1}. The expected value for $V^{\ddagger}_7 - V^{\ddagger}_8$ is not available. However, the observed value (7.4 cm^3 mol^{-1}) is larger than 6 cm^3 mol^{-1} for $V^{\ddagger}_{\mathrm{DMC}}$ (eq, eq) − $V^{\ddagger}_{\mathrm{DMC}}$ (ax, ax) (DMC = 1,2-dimethylcyclohexane).

---

§ The present results clearly show the intervention of a non-chair form at high pressure. However, this does not necessarily mean that a boat form is the only option. Other flexible cyclohexane analogues such as the twist-boat are possible.