

EVIDENCE OF VOLUME CONTRACTION IN THE TRANSITION STATE
OF THE DIELS ALDER REACTION¹⁾

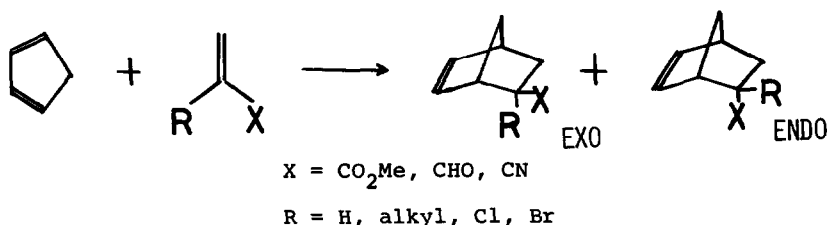
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In the Diels Alder reaction the adduct with the endo configuration is, in general, much preferred over the adduct having the exo configuration.²⁾ Woodward and Hoffmann have successfully interpreted this by the concept of secondary orbital interaction.³⁾ An important finding in this respect was reported by Grieger and Eckert.⁴⁾ The measurement of activation volumes of the particular Diels Alder reactions revealed that the volumes of the transition states were smaller than those of the adducts.

We wish to report some correlations between the extent of volume contraction and the strength of the secondary orbital interaction in the transition state by measuring the difference of activation volumes. The reactions of cyclopentadiene with some dienophiles in methylene chloride at 35°C were examined under atmospheric and high pressure. The reaction products were analyzed by g.l.c.⁵⁾



Pressure dependence of the exo:endo ratio is presented in Table. One can estimate the difference in activation volume between the exo and the endo transition states $\delta\Delta V^\ddagger = \Delta V^\ddagger_{(\text{exo})} - \Delta V^\ddagger_{(\text{endo})}$ ⁷⁾, from the following equation;

$$\left(\frac{\partial \ln \text{exo:endo}}{\partial p} \right)_T = - \frac{\delta \Delta V^\ddagger}{RT}$$

The correlation of $\log \text{exo:endo}$ with $\delta \Delta V^\ddagger$ demonstrates that the difference in the activation free energy between the exo and the endo transition states relates to $\delta \Delta V^\ddagger$ in two different types (case a and b in Fig.).

Table. Yield of the endo adduct under pressure and the value of $\delta \Delta V^\ddagger$

NO	R	X	Pressure (kg/cm ²)				$\delta \Delta V^\ddagger$ a) (cc/mole)
			1	1000	2000	3000	
1	H	CO ₂ Me	79.4% ^{b)}	79.7% ^{b)}	79.9% ^{b)}	79.9% ^{b)}	0.52
2	Dimethyl	maleate	75.3	75.9	76.3	76.6	0.82
3	H	CHO	74.9	75.1 ^{c)}	75.7	75.6	0.50
4	H	CN	60.3	60.5	60.8	61.1	0.22
5	CO ₂ Me	CO ₂ Me	50.0	50.0	50.0	50.0	0
6	Cl	CO ₂ Me	36.5	36.3	36.1	35.9	-0.21
7	Br	CO ₂ Me	38.8	38.2	37.9	37.5	-0.52
8	Me	CO ₂ Me	35.3	36.0	36.6	36.8	0.78
9	Et	CO ₂ Me	37.0	38.3	38.5	38.6	0.82
10	n-Bu	CO ₂ Me	30.6	31.3	31.8	32.1	0.83
11	Me	CN	13.8	14.1	14.7	-	0.75
12	Et	CN	9.95	10.3	10.6	-	0.99

a) The estimated error is at most 0.15 cc/mole.

b) Average of several experiments; maximum deviation is $\pm 0.2\%$.

c) The value under 500 kg/cm².

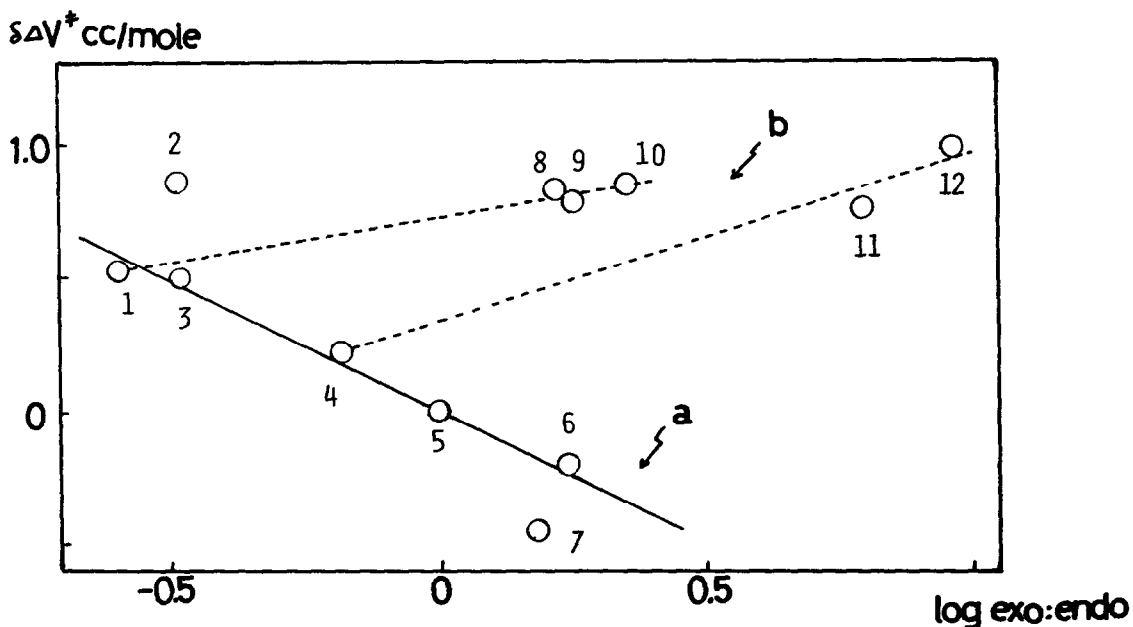


Fig. Correlation of log exo:endo with $\delta\Delta V^\ddagger$

(Numeral denotes dienophile number in Table)

In the case a, the lower the exo:endo ratio becomes, the larger the value of $\delta\Delta V^\ddagger$ is. While the Woodward-Hoffmann rule governs the stereochemistry of the concerted Diels Alder reactions, magnitude of substituent effect on the exo:endo ratio in these reactions is not predictable by this rule. However, the extent of stabilization due to the secondary orbital interaction in the endo transition state must be responsible for the exo:endo ratio. Therefore, the above mentioned trend in the case a is thought to indicate that the operation of the secondary orbital interaction is accompanied with a volume contraction in the transition state. A large volume contraction will be expected in a strongly endo-orienting Diels Alder reaction. In fact, this is the case in the reaction of maleic anhydride with isoprene etc. Volume contractions were estimated to be several cubic centimeters.⁴⁾

On the other hand, in the case b dienophiles employed yielded the exo adduct predominantly and the values of $\delta\Delta V^\ddagger$ were found to be larger than those in the case a. In this case, the methylene group of cyclopentadiene and the alkyl group of dienophile must be overcrowded in the endo transition state. This should result in an additional volume contraction⁸⁾ to exhibit more positive $\delta\Delta V^\ddagger$.¹⁰⁾

Contrarily, 2-chloro- and 2-bromoacrylates exhibited negative $\delta\Delta V^\ddagger$ in spite of their exo predominance. This unexpected observation suggests an existence of an attractive interaction between cyclopentadiene π - and halogen atom d-electrons. Steric repulsion between the halogen atom and the methylene group of cyclopentadiene can not account for the present result. Further investigations are in progress in our laboratory.

References and Footnotes

- 1) Organic Reaction under High Pressure IX.
- 2) J. Sauer, *Angew. Chem.*, 79, 76 (1967); J. G. Martin and R. K. Hill, *Chem. Rev.*, 61, 537 (1961).
- 3) R. B. Woodward and R. Hoffmann, "The Conservation of Orbital Symmetry" Verlag Chemie GmbH, Weinheim/Bergstr., Germany, p. 145 (1970).
- 4) R. A. Grieger and C. A. Eckert, *J. Amer. Chem. Soc.*, 92, 7149 (1970).
- 5) The separated products by a preparative g.l.c. gave satisfactory NMR spectra.⁶⁾
- 6) Y. Kobuke, T. Fueno and J. Furukawa, *J. Amer. Chem. Soc.*, 92, 6548 (1970).
- 7) $\Delta V^\ddagger < 0$, in the present case.
- 8) The presence of a steric hindrance in a reaction is characterized by a rate acceleration under pressure.⁹⁾
- 9) W. J. le Noble, *Progr. Phy. Org. Chem.*, 5, 312 (1967).
- 10) This additional volume contraction was estimated as about 0.3 cc/mole for the reaction of cyclopentadiene with methyl methacrylate.