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<https://doi.org/10.15017/17202>

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出版情報 : 九州大学大学院総合理工学報告. 12 (3), pp.301-304, 1990-12-01. 九州大学大学院総合理工学研究科

バージョン :

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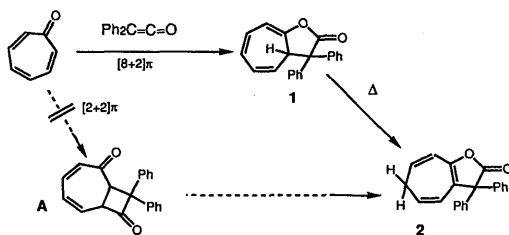
## The Effect of Pressure on Sigmatropic Rearrangements of Seven-Membered Conjugated Systems. [1, 5] Sigmatropy

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(Received August 28, 1990)

**Abstract:** The kinetic analysis of the [1,5] sigmatropy of 3,3-diphenyl-3,3a-dihydrocyclohepta[b]furan-2-one was carried out under various pressures (1 to 1600 bar). The activation volume of the [1,5] process of the cycloheptatriene was considerably less negative than that of either [1,5] sigmatropy of cyclopentadienes or [3,3] and [1,9] processes of tropones. This is due to an increase of a free radical character in the transition state in terms of a long-distance movement of the migrating groups.

Following our previous studies of high-pressure kinetic analysis of sigmatropic rearrangement of troponoids,<sup>1)</sup> we now extended the study to a [1,5] sigmatropy of tropylidene derivative, 3,3-diphenyl-3,3a-dihydrocyclohepta[b]furan-2-one (**1**) to 3,3-diphenyl-3,6-dihydrocyclohepta[b]furan-2-one (**2**).<sup>2)</sup> To our knowledge, there have been only two examples for kinetic studies of [1,5] sigmatropy, i.e., with cyclopentadiene derivatives<sup>3)</sup> and 2-alkoxy-pyridine *N*-oxide.<sup>4)</sup>



(Scheme 1)

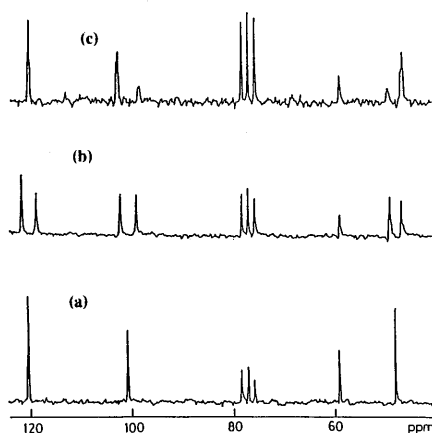
### Results and Discussion

Thermal rearrangement of the endo-hydrogen on the C-7 of cycloheptatriene (tropylidene) to C-4 position, i. e., [1,5] sigmatropy, is known for long time, and has been utilized in synthesis of tropne derivatives having various substituents. However, no high-pressure kinetic study seems to be carried out for the [1,5] sigmatropy in the field of the troponid. Generally, one must expect that the sigmatropy is mildly accelerated by pressure, because of its unimolecular concerted nature, and the activation volume is predicted to be ca.  $-10 \text{ cm}^3 \text{ mol}^{-1}$ . But, it is not clear that this can also be applicable in the seven-membered conjugated system. Recently, we have encountered an opportunity to investigate the problem. Once in a literature,<sup>2)</sup> a cycloaddition of diphenylketene to troponone was re-

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corded to form a [2+2] cycloadduct (**A**) which, according to the paper, isomerized to a compound (**2**). The mechanism of this rearrangement of **A** to **2**, which should involve 1,7-bond switch with geometrical change followed by [3,3] sigmatropy, was puzzled by kinetic analysis.<sup>5)</sup> Later on, this superficial "thermally-forbidden [1,7] sigmatropy" was correctly interpreted after the structure revision of **A** to an [8+2] cycloadduct (**1**).<sup>6)</sup> Our NMR experiments reconfirmed the structure of this cycloadduct **1**; i. e. the presence of a lactonic carbonyl carbon ( $\delta = 175.0$ ) was clear from the chemical shift, and an  $sp^2$ -carbon signal ( $\delta = 120.2$ ) coupled with the high-field-shifted proton signal ( $\delta = 4.51$ ), was proved by selective decoupling experiments to eliminate **A**, the alternative structure. As a result, the isomerization of **1** to **2** should be designated as the [1,5] sigmatropy. Therefore, we studied its high-pressure kinetic analysis. (**Fig. 1**)



**Fig. 1** The  $^{13}\text{C}$  NMR Spectra of **1**. a) Complete Decoupled Spectra; b) Off-Resonance Spectra; c) Selective Decoupling Spectra (Irradiated with Radio Frequency of  $\delta = 4.44$  in  $^1\text{H}$  NMR)

The rate constants ( $k$ ) for this [1,5] shift in dibutyl ether at  $130^\circ\text{C}$  under various pressures are listed in **Table 1**. This rearrangement was slightly accelerated with pressure. The activation volume ( $\Delta V^\ddagger$ ) was evaluated with eq. 1 by using a linear function of logarithm of the reaction rates ( $\ln k$ ) vs. pressure ( $P$ ).

$$\Delta V^\ddagger = -RT \left( \frac{\partial \ln k}{\partial P} \right)_T \quad (\text{eq. 1})$$

The eq. 1 gave  $\Delta V^\ddagger$  values of  $-2.2 \pm 0.9 \text{ cm}^3 \text{ mol}^{-1}$ . It has been mentioned that this rearrangement showed a very small solvent effect in respects of polarity and acidity.<sup>5)</sup> Certainly, this rearrangement is not ionic, but a [1,5] sigmatropy or biradical dissociation-recombination process. According to a knowledge of the high-pressure kinetics, the range of  $\Delta V^\ddagger$  of [1,5] shifts was  $+10$  to  $-30 \text{ cm}^3 \text{ mol}^{-1}$ ,<sup>3,4)</sup> depending on the reaction mechanism;  $\Delta V^\ddagger$  of a stepwise, biradical reaction is known to be positive, but that of the concerted reaction is negative, being reflected from the tightness of the transition state. Consequently, the stepwise mechanism via a radical intermediate is eliminated for the isomerization of **1** to

**2**, and this must fall in a category of the [1,5] sigmatropy.

For a [1,5] sigmatropy, the  $\Delta V^\ddagger$  value obtained for **1** to **2** is relatively smaller than those of typical [1,5] sigmatropy ( $-6.7$  to  $-18.2$   $\text{cm}^3 \text{mol}^{-1}$ )<sup>1,7,8)</sup> and [1,9] sigmatropy ( $-10.1$  to  $-11.1$   $\text{cm}^3 \text{mol}^{-1}$ ).<sup>1)</sup> Generally, the different figures for  $\Delta V^\ddagger$  were explained in terms of a change of the polarities between the transition and ground states. However, as the isomerization of **1** to **2** was not affected from the solvent polarity,<sup>6)</sup> we should consider the alternative explanation for this difference. This is, geometry of the transition state. The previously studied sigmatropies except the Cope rearrangement of bullvalene fall into the same category, i. e., migrating groups or atoms all moved only a short distance. In such cases, the transition state should be tight. In the [1,5] sigmatropy of **1**, however, the migrating hydrogen has to move a longer distance across the boat-formed cycloheptatriene ring. As the result, the transition state must become relatively loose due to a biradical character.

It is true that an importance of tightness in geometry of transition state has been pointed out for the Cope rearrangement of bullvalene, whose  $\Delta V^\ddagger$  was  $-0.5$   $\text{cm}^3 \text{mol}^{-1}$ .<sup>2)</sup> It was suggested that the transition state of Cope rearrangement was rather loose biradical-type.<sup>3)</sup>

One must suspect that this small negative  $\Delta V^\ddagger$  may be arisen from the small change of the entropy between the initial and transition states. It seems to be reasonable that the activation entropy ( $\Delta S^\ddagger$ ) of the shift of hydrogen is small. But, as reported in the thermal Z-E isomerization of azobenzenes,<sup>9)</sup>  $\Delta V^\ddagger$  dose not always correlate to  $\Delta S^\ddagger$ . Furthermore,  $\Delta V^\ddagger$  for the [1,5] sigmatropy of hydrogen migration in 5-(trimethylsilyl) cyclopentadiene has been reported to be  $-26.5$   $\text{cm}^3 \text{mol}^{-1}$ .<sup>3)</sup> Up to date,  $\Delta S^\ddagger$  for the [1,5]

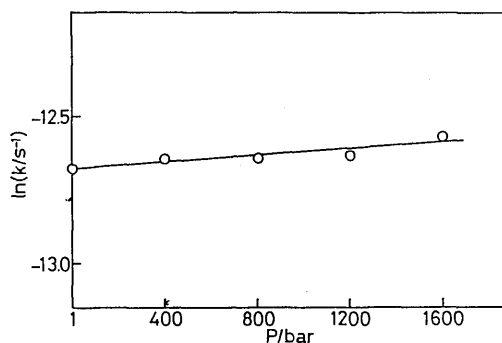


Fig. 2 The Pressure Dependence of  $\ln k$  for the Isomerization of **1** to **2** in Dibutyl Ether at 130°C.

Table 1 The First-Order Rate Constants for the Reaction of **1** to **2** under Various Pressures at 130°C.

Solvent	Pressure/bar				
	1	400	800	1200	1600
Butyl ether	$3.14 \pm 0.01$	$3.22 \pm 0.03$	$3.23 \pm 0.03$	$3.25 \pm 0.01$	$3.47 \pm 0.08$

sigmatropy of the hydrogen migration in cyclopentadiene were reported to be  $-14$  to  $-65$  J mol<sup>-1</sup> K<sup>-1</sup> (mean value,  $-34$  J mol<sup>-1</sup> K<sup>-1</sup>)<sup>10</sup> and were not too small. These facts overcome the above question.

In conclusion, the  $\Delta V^\ddagger$  values for the sigmatropy showed to be dependent on the migrating distance of the moving groups or atoms. And the high-pressure kinetics can provide a reliable information concerning either the concerted nature of the thermal process or the differentiation of the electrocyclic modes of the process involved, in general.<sup>11)</sup>

## Experimental

**Materials** Dibutyl ether was carefully purified by distillation under N<sub>2</sub> atmosphere (bp 142°C). Compounds **1** and **2** were prepared by the reported procedures<sup>2)</sup> and analytically-pure samples (in respects of elemental analysis and high-pressure liquid chromatography) were obtained by recrystallizations, and/or chromatography:

**1:** mp 109-110°C (from EtOH) (lit.<sup>2)</sup> 108-109°C); <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$  = 3.62 (1H, dt,  $J$  = 4, 1.5 Hz), 4.51 (1H, ddd,  $J$  = 10, 4 0.5 Hz), 5.88-6.12 (2H, m), 6.28-6.55 (2H, m), and 7.0-7.6 (10H, m). <sup>13</sup>CNMR (CDCl<sub>3</sub>)  $\delta$  = 48.4, 59.3, 100.6, 120.2, 126.4, 127.6 (2C), 127.8, 128.3, 128.9 (4C), 129.2 (4C), 139.1, 141.1, 143.0 and 175.0.

**2:** mp 161-162°C (from EtOH) (lit.<sup>2)</sup> 158.5-159.5°C).

**Kinetic Measurements.** The apparatus for kinetic runs was the same as used in our previous studies.<sup>12)</sup> The reaction temperatures were controlled within  $\pm 0.5^\circ\text{C}$ . The progress of the reactions was monitored by high-pressure liquid chromatography [Nippon Waters Model 244 Apparatus] by increase of product formations and decrease of the starting materials.

The authors thank The Ministry of Education, Science and Culture for a Grant-in Aid for Scientific Research to S. S. (No. 6174094 and 63740293).

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