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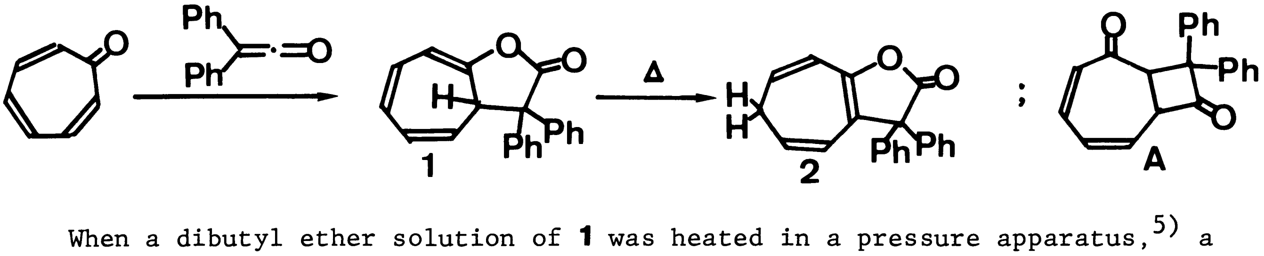
The Pressure Effect on the 1,5-Sigmatropic Hydrogen Shift of Tropylidene Derivative, 3,3-Diphenyl-3,3a-dihydrocyclohepta[b]furan-2-one

Shigeru SUGIYAMA* and Hitoshi TAKESHITA
Research Institute of Industrial Science, 86, Kyushu University,
Kasuga-koen, Kasuga, Fukuoka 816

The 1,5-sigmatropy of 3,3-diphenyl-3,3a-dihydrocyclohepta[b]furan-2-one was examined in dibutyl ether to 1600 bar at 130 °C. The rearrangement was slightly accelerated with pressure, and was different to the pressure effect of 1,5-sigmatropy of cyclopentadienes. The activation volume was in the range of the concerted process, but its transition state was as loose as those biradical-like.

The suprafacial 1,5-shifts have been a considerable interest and its mechanistic aspects were investigated by various means.1) According to the high-pressure kinetics, the range of the activation volumes ($\Delta V^{\neq}$) of 1,5-shift was found to be from +10 to -30 cm^3/mol,2) depending on the reaction mechanisms; a stepwise, biradical reaction is known to reveal positive $\Delta V^{\neq}$, but the concerted reaction shows negative $\Delta V^{\neq}$, of which the range is considerably varied by the tightness of the transition state. But, the systems ever studied were limited to the cyclopentadiene derivatives and 2-alkoxypyridine N-oxides; the migrating hydrogen and alkyl groups require only a short-distance flight. Thus, the kinetic analysis of the rearrangement for the cycloheptatrienes is worthwhile; their hydrogens must move longer distance than those of cyclopentadienes. Herein, we wish to report the pressure effect of the 1,5-sigmatropy of a cycloheptatriene, 3,3-diphenyl-3,3a-dihydrocyclohepta[b]furan-2-one (**1**),3) a (8+2)π cycloadduct of tropone to diphenylketene, to 3,3-diphenyl-3,6-dihydrocyclohepta[b]furan-2-one (**2**).

It has been mentioned that the conversion of **1** to **2** lacks a sensitivity towards solvent polarity and acidity.4) Therefore, this rearrangement is likely to proceed in non-ionic mechanism; i.e., a concerted 1,5-sigmatropy or biradical dissociation-recombination process. Now, we have carried out the thermolysis of **1** to **2** under various pressures at 130 °C.



When a dibutyl ether solution of **1** was heated in a pressure apparatus,5) a reaction occurred and its progress was monitored by high-pressure liquid chromatography (HPLC).6)

Table 1. Rate Constants (k) at 130 °C under Various Pressures

	Pressure/bar				
	1	400	800	1200	1600
10^6 k/s^{-1}	3.14±0.01	3.22±0.03	3.23±0.03	3.25±0.01	3.47±0.08

The results, summarized in Table 1, showed a slight rate acceleration with pressure; the $\Delta V^{\neq}=-RT(\partial \ln k/\partial P)_T$ was -2.2 cm^3/mol. Accordingly, the stepwise mechanism via a radical intermediate can be eliminated. The reaction volume (ΔV) was found to be +3.0 cm^3/mol at 60 °C from the densities of **1** and **2**. But, $\Delta V^{\neq}$ is relatively smaller than those of other concerted 1,5-sigmatropy, -4 to -30 cm^3/mol.[2] In the present case, the proton moves longer distance than that of the cyclopentadienes. Evidently, a transition state might be loose biradical-like. Such a loose biradical-like transition state was suggested for Cope rearrangement of bullvalene ($\Delta V^{\neq}=-0.5$ cm^3/mol),[2] though the figures of general 3,3-sigmatropy were found to be -5 to -18 cm^3/mol.[7]

Consequently, as far as the high-pressure kinetics concern, the 1,5-hydrogen shift of the tropylidenes is different from that of cyclopentadienes; its stronger biradical character must be attributable to the geometry of transition state, i.e., symmetry-allowed sigmatropic rearrangement requires the move of hydrogen to a distant position than the cyclopentadienes, and as results, they have revealed a smaller pressure effect than those of cyclopentadienes.

References

1) S. D. Kahn, W. J. Hehre, N. G. Rondan, and K. H. Houk, J. Am. Chem. Soc., 107, 8291 (1985).

2) W. J. le Noble, and M. R. Daka, J. Am. Chem. Soc., 100, 5961 (1978); E. M. Schulman, A. E. Merbach, M. Turin, R. Weddinger, and W. J. le Noble, ibid., 105, 3988 (1983).

3) Originally, the structure of **1** was considered to be a cyclobutanone derivative, **A**, on the basis of ^{1}H NMR and IR evidence (Ch. Jutz, I. Rommel, I. Lenngyel, and J. Feeney, Tetrahedron, 22, 1809 (1966)). And, the rearrangement of **A** to **2**, which should involve a 1,7-bond switch with geometrical change followed by 3,3-sigmatropy, was puzzled by kinetic analysis.[4] However, R. Gomper, A. Studeneer, and W. Elser (Tetrahedron Lett., 1968, 1019) revised the structure by chemical derivation. We are confident that, from the ^{13}C NMR spectrum, the structure **1** is correct; δ($CDCl_3$)=175.0 (lactonic carbonyl) and 120.2 being of the sp^2-carbon (which, according to a selective decoupling experiment, coupled to ^{1}H signal at δ=4.51).

4) A. S. Kende, Tetrahedron Lett., 1967, 2661.

5) In this study, the same apparatus was used as in the previous study (H. Takeshita, S. Sugiyama, and T. Hatsui, Bull. Chem. Soc. Jpn., 58, 2490 (1985)).

6) HPLC was measured with Nippon Waters' Model 244 Apparatus (Micropolasil, 7.8 mm (diameter) x 300 mm (length)).

7) K. R. Brower, J. Am. Chem. Soc., 83, 4370 (1961); G. Walling and M. Naiman, ibid., 84, 2628 (1962).

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