CHEMISTRY LETTERS, pp. 449-452, 1994.

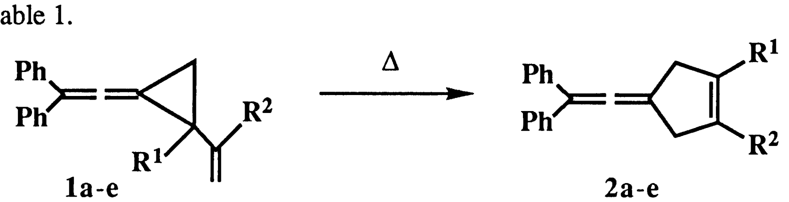
Thermal Rearrangement of 1-Alkenyl-2-(2',2'-diphenylethenylidene)cyclopropanes to 4-(2',2'-Diphenylethenylidene)cyclopent-1-enes

Kazuhiko MIZUNO,* Hikaru SUGITA, Tadashi KAMADA, and Yoshio OTSUJI*
Department of Applied Chemistry, College of Engineering, University of Osaka Prefecture, Sakai, Osaka 593

1-Alkenyl-2-(2',2'-diphenylethenylidene)cyclopropanes thermally rearranged to 4-(diphenylethenylidene)cyclopent-1-enes at relatively low temperature (≤ 373 K). Measurement of activation parameters revealed that the reactivity and mode of the reaction largely depend on structures of starting materials and products.

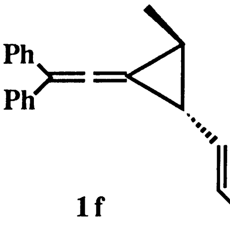
The vinylcyclopropane-cyclopentene rearrangement is a useful method for construction of five-membered ring systems.1) However, this reaction usually requires vigorous reaction conditions, such as heating at temperature above 450 K under inert atmosphere. In the course of our studies on the chemistry of vinylidenecyclopropanes, we have found that 1-alkenyl-2-(2',2'-diphenylethenylidene)cyclopropanes rearrange thermally at much lower temperatures (≤ 373 K) to give 4-(2',2'-diphenylethenylidene)cyclopent-1-enes in high yields.2, 3) We now report reactivity features of this rearrangement. Measurements of activation parameters revealed that the reactivity and mode of the reaction largely depended on structures of products and also of starting materials.

Heating 1-(2',2'-diphenylethenylidene)-2-vinylcyclopropane (**1a**) at 373 K under argon atmosphere for 15 min gave 4-(2',2'-diphenylethenylidene)cyclopent-1-ene (**2a**) in quantitative yield. The thermolysis of other ethenylidenecyclopropanes **1b-g** in a similar manner gave also the corresponding rearranged products **2b-g** in high yields, although the reactivity in this reaction depended on the structure of starting compounds. The results are summarized in Table 1.

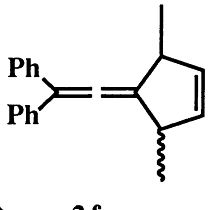


1a-e 2a-e

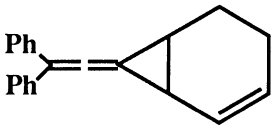
a: $R^1=R^2=H$, **b**: $R^1=H$, $R^2=Me$, **c**: $R^1=Me$, $R^2=H$,
d: $R^1=R^2=Me$, **e**: R^1-R^2=-$(CH_2)_4$-



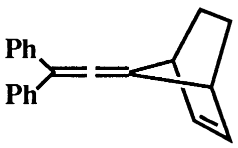
1f



2f



1g



2g

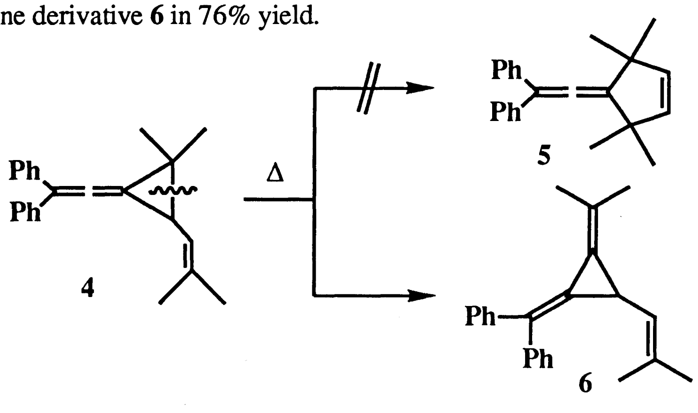
Table 1. Synthesis of Ethenylidenecyclopentenes

1	Reaction temp / K	Time / h	Product	Yield / %[a)]
1a	373	0.5	**2a**	>95
1b	373	0.5	**2b**	82
1c	373	0.5	**2c**	90 ± 5
1d	323	2	**2d**	88
1e	373	0.5	**2e**	92
1f	373	0.5	**2f**	62
1g	373	5	**2g**	69

a) Yields from ^{1}H NMR spectra. 1,4-Dimethoxybenzene was used as an internal standard.

It is important to note that the thermolysis of the stereochemically well-defined compound **1f** gave **2f** which was a cis- and trans-stereoisomeric mixture with respect of the 3,5-dimethyl substituents. This was suggested by the ^{1}H NMR spectrum of the reaction mixture. However, attempts to separate these two isomers in pure forms by chromatography were unsuccessful.

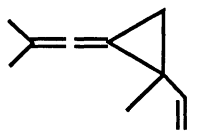
No rearrangement reaction occurred for 1-(2'-methylpropenylidene)-2-methyl-2-vinylcyclopropane (**3**) even at higher temperatures (>400 K). The thermolysis of the 3,3-dimethyl substituted compound **4** at 373 K for 4.5 h did not give the expected cyclopentene derivative **5**, but instead gave the 1,2-dimethylene-3-vinylcyclopropane derivative **6** in 76% yield.



4

5

6



3

The products were isolated by column chromatography on silica gel. Their structures were determined from the spectral data (^{1}H NMR, ^{13}C NMR, IR, and Mass spectra)[4)] and also by elemental analyses.

In order to obtain insight into mechanistic aspects of the above rearrangements, the reactions were carried out in C_6D_6 or perdeuterated toluene. The first order rate constants for the thermolysis of **1a-g** were determined by measuring the amounts of **2a-g** produced at several time intervals by ^{1}H NMR analyses of the reaction mixtures. The Arrhenius plots of the rate constants at varying temperatures gave straight lines, from which the activation enthalpies $\Delta H^{\neq}$ and the activation entropies $\Delta S^{\neq}$ at 363 K were calculated. The results are given in Table 2.

The $\Delta H^{\neq}$ values for the thermal rearrangement of vinylcyclopropanes to cyclopentenes are usually more than 150 kJ mol^{-1}. However, the $\Delta H^{\neq}$ values for the thermal rearrangement of **1a-g** to **2a-g** are in the range

Table 2. Activation Energies and Activation Entropies for the Pyrolysis of **1a-g** to **2a-g**

Substrate	$\tau_{1/2}$ / s at 363 K	$\Delta H^{\neq}$ / kJ mol^{-1}	$\Delta S^{\neq}_{363\ K}$ / kJ mol^{-1} K^{-1}
1a	301	116	22
1b	1227	122	27
1c	37	95	-19
1d	138	105	-2
1e	49	98	-13
1f	563	98	-33
1g	2123	132	30

of 95-132 kJ mol^{-1}. This indicates that the latter reaction occurs much more easily than the former reaction. Furthermore, a linear relationship (isokinetic relationship) was found between $\Delta H^{\neq}$ and $\Delta S^{\neq}$ values for the reaction of **1a-e** (Fig. 1). The plots for **1f** and **1g** exhibited an appreciable deviation from the above linear line. This result strongly suggests that the rearrangement of **1f** and **1g** shows a different mechanistic profile from that of **1a-e**.

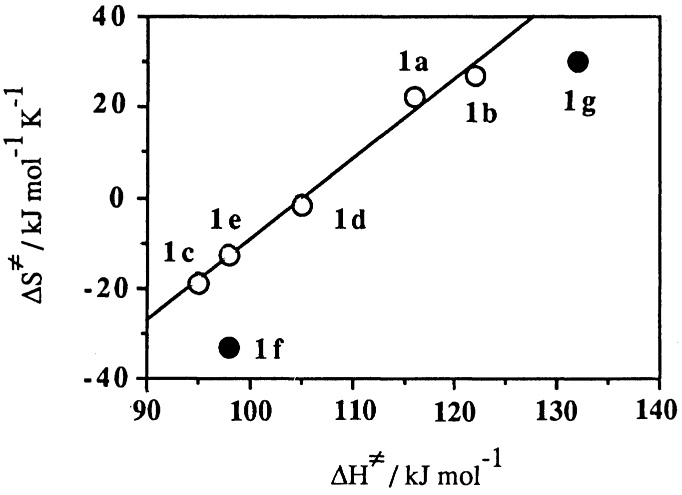
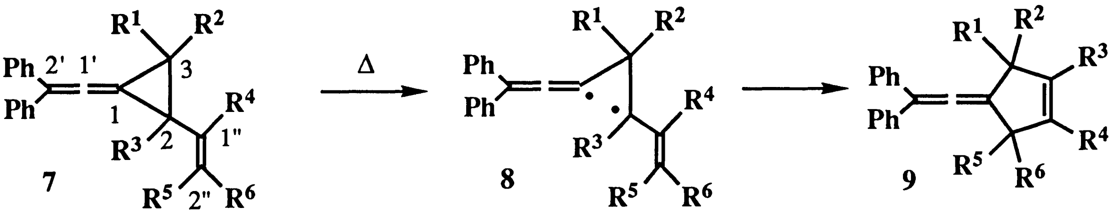


Fig. 1. Relationship between $\Delta H^{\neq}$ and $\Delta S^{\neq}$ at 363 K.

The mechanistic features of the rearrangement of **1a-g** to **2a-g** may be summarized as follows: (1) The thermolysis of **1a-g** proceeds via a biradical intermediate **8** rather than via a concerted 1,3-sigmatropic shift at the ethenylidene carbon from C_2 to C_2'' (Scheme 1). Note that according to the Woodward-Hoffmann rules, the thermally allowed concerted process for this reaction is a sterically difficult antarafacial mode of migration. (2) Driving forces for the facile generation of the biradical would be: 1) the stabilization of the radical center C_1 in **8** by an allylic resonance over the C_1-C_1'-C_2' moiety, 2) the stabilization of the radical center C_2 in **8** by an allylic resonance over the C_2-C_1''-C_2'' moiety, and 3) the destabilization of the starting compound **7** by a severe steric strain within the cyclopropane ring.

The result of Fig. 1 may be accounted for in terms of transition state structures of the reactions. For the



Scheme 1.

rearrangement of **1a-e** to **2a-e**, the products are not so much sterically hindered. Hence, the enthalpy changes for these reactions would be largely negative. While, for the rearrangements of **1f-g** to **2f-g**, the products are highly strained by a 1,3-diaxial interaction between the 3,5-dialkyl substituents of cyclopentene ring. In these cases, the enthalpy changes would be less negative, compared with the former cases. The Hammond postulate predicts that the former reactions (more exothermic) have an early transition state, while the latter reactions (less exothermic) have a late transition state. The late transition state will have a more product-like, rigid structure. Less favorable (more negative) $\Delta S^{\neq}$ values are therefore expected for the reactions of **1f-g** to **2f-g**, compared with those for the reactions of **1a-e** to **2a-e**. This hypothesis is supported by the result of Fig. 1.

The lower reactivity for **3** appears to be ascribed to a greater dissociation energy of the C_1-C_2 bond: the resonance stabilization of the allylic C_1-C_1'-C_2' radical for **3** is smaller than those for **1a-f**. In the case of **4**, the C_2-C_3 bond dissociates to give **6**. A marked tendency for the C_2-C_3 bond dissociation in **4** comes from the stabilization of a 1,3-biradical centered at C_2 and C_3 atoms: Note that the C_3 radical center is stabilized by two methyl groups in addition to an allylic resonance over the C_3-C_1-C_1' moiety. Furthermore, the instability of **5** due to the steric repulsion among four methyl groups at C_3 and C_2'' would prevent the formation of this molecule. The above results indicate that the reactivity of the thermolysis of vinylidenecyclopropanes is strongly affected by the substituents attached on the cyclopropane ring. The detailed mechanistic studies of the rearrangement reactions are now in progress.

References

1) T. Hudlicky, T. M. Kutchan, and S. M. Naqvi, *Org. React.*, **33**, 247 (1985) and references sited therein.

2) H. Sugita, K. Mizuno, T. Mori, K. Isagawa, and Y. Otsuji, *Angew. Chem., Int. Ed. Engl.*, **30**, 984 (1991).

3) Previously, we have reported the 1,2- and 1,4-addition of alkenylidenecarbenes to 1,3-dienes. In these reactions, the formation of 1,4-adducts was explained by the direct 1,4-addition of alkenylidenecarbenes to 1,3-dienes. However, the possibility of the thermal isomerization from 1,2-adducts to 1,4-adducts still remains for this reaction.$^{2)}$

4) Spectral data of **2g**: ^{1}H NMR ($CDCl_3$, 270 MHz): δ=1.23 (m, 2H), 1.96 (m, 2H), 3.47 (m, 2H), 6.21 (s, 2H), 7.17-7.38 (m, 10H); ^{13}C NMR ($CDCl_3$, 67 MHz): δ=25.5, 46.0, 111.7, 119.4, 126.9, 128.2, 128.3, 128.4, 128.7, 134.8, 137.9, 138.2, 185.5; IR (neat) 1990 cm^{-1}; UV$_{max}$ (cyclohexane) 277 nm (ε 14000); HRMS Found 270.1338. Calcd for $C_{21}H_{18}$ (M^+) 270.1408. **6**: ^{1}H NMR ($CDCl_3$, 270 MHz): δ=1.54 (s, 3H), 1.73 (s, 3H), 1.83 (s, 3H), 1.89 (s, 3H), 2.87 (m, 1H, J=8.9 Hz), 4.80 (m, 1H, J=8.9 Hz), 7.16-7.48 (m, 10H); ^{13}C NMR ($CDCl_3$, 67 MHz): δ=18.3, 23.2, 23.5, 23.6, 25.7, 115.1, 125.0, 125.9, 126.8, 127.1, 127.6, 127.9, 128.0, 128.1, 128.3, 130.1, 131.6, 140.3, 142.0; IR (neat) 1601 cm^{-1}; UV$_{max}$ (cyclohexane) 312 nm (ε 29700); HRMS Found 300.1807. Calcd for $C_{23}H_{24}$ (M^+) 300.1878.

(Received November 12, 1993)