

Notes

Kinetics and Mechanism of the Thermolysis of 1,1-Dimethyl-1-germacyclohepta-2,4,6-triene

Kunio Mochida,^{*,†} Nao Matsuhisa,[†] Ryuji Sato,[‡] and Yasuhiro Nakadaira^{*,§}

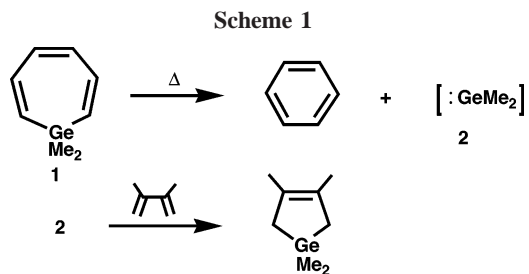
Department of Chemistry, Faculty of Science, Gakushuin University, 1-5-1 Mejiro, Toshima-ku, Tokyo 171-8588, Japan, Department of Chemistry, Faculty of Science, Tohoku University, Aoba-ku, Sendai 980-8578, Japan, and Department of Chemistry, The University of Electro-Communications, Chofu, Tokyo 182-8585, Japan

Received January 23, 2006

Summary: The thermolysis of 1,1-dimethyl-1-germacyclohepta-2,4,6-triene led to the formation of benzene and dimethylgermylene, as expected. The activation energy and thermodynamic data for the germylene extrusion reaction were determined to be $E_a = 21.2 \pm 0.1$ kcal/mol, $\Delta H^\ddagger = 20.5 \pm 0.1$ kcal/mol, and $\Delta S^\ddagger = -8.1 \pm 0.1$ cal/(mol K), respectively.

Introduction

Metallacycloheptatrienes containing group 14 elements,^{1–23} especially silacycloheptatrienes (silepins), have been studied extensively from various points of view:^{1–19} for example, the



possible cyclic (p-d) π conjugation,^{7,8,12,16–19} the general preparative methods for these metallacycles,^{16–19,21} and the thermal extrusion of the corresponding divalent species.^{16,17} Meanwhile, the appropriate synthetic routes to C-unsubstituted metallepins have been developed, and 1,1-dimethylgermacycloheptatriene, 1,1-dimethylgermacycloheptatriene, and 1,1-dibutylstannacycloheptatriene were prepared.^{16–18,21} Thus, a detailed analysis of their ¹H NMR spectra revealed that each of these metallacycles should adopt a boat geometry, which is not suitable for the cyclic (p-d) π conjugation.^{16–19,21} On the other hand, cyclic trienes such as 1,1-dimethylsilacycloheptatriene and 1,1-dibutylstannacycloheptatriene undergo thermolytic extrusion of the corresponding divalent species accompanied by the formation of benzene.^{16,17} We describe herein the first kinetics and mechanistic study of the thermolysis of 1,1-dimethylgermacycloheptatriene and discuss the relationship between the reactivity and the group 14 elements in these compounds.

Results and Discussion

At first 1,1-dimethylgermacycloheptatriene (**1**) was thermolyzed in toluene-*d*₈ containing 2,3-dimethylbuta-1,3-diene as a germylene trap^{24,25} in an evacuated sealed NMR tube at 80 °C (Scheme 1). The progress of the thermolysis was readily monitored by means of ¹H NMR spectral measurements, and the extrusion reaction was found to be complete within 30 min, judging from the change of signal intensities due to **1** and benzene formed. Formation of the trapped product 1,1,3,4-tetramethyl-1-germacyclopent-3-ene was evidenced by ¹H NMR and GC-MS spectral analyses of the thermolysate. Unidentified polymeric materials were also detected.

For kinetic measurements, the thermolysis of **1** was carried out similarly, but in the absence of a diene, in an evacuated

[†] Gakushuin University.[‡] Tohoku University.[§] The University of Electro-Communications.(1) Paquette, L. A. In *Nonbenzenoid Aromatics*; Snyder, J. P., Ed.; Academic Press: New York, 1970; Vol. I, p 249.(2) Birkofer, L.; Haddad, H. *Chem. Ber.* **1966**, *102*, 432.(3) Birkofer, L.; Haddad, H. *Chem. Ber.* **1972**, *105*, 2101.(4) Birkofer, L.; Haddad, H. *Chem. Ber.* **1977**, *110*, 3314.(5) Birkofer, L.; Haddad, H. *J. Organomet. Chem.* **1979**, *164*, C17.(6) Birkofer, L.; Haddad, H.; Zamarlik, H. *J. Organomet. Chem.* **1979**, *25*, C57.(7) Barton, T. J.; Volz, W. E.; Johnson, J. J. *Org. Chem.* **1971**, *36*, 3365.(8) Barton, T. J.; Kippenhan, R. C., Jr.; Nelson, A. J. *J. Am. Chem. Soc.* **1974**, *96*, 2272.(9) Corey, J. Y.; Deuber, M.; Bichmeir, B. *J. Organomet. Chem.* **1971**, *26*, 167.(10) Corey, J. Y.; Corey, E. R. *Tetrahedron Lett.* **1972**, 4669.(11) Corey, J. Y.; Farrell, R. L. *J. Organomet. Chem.* **1978**, *153*, 15.(12) Cartledge, F. K.; Mollers, P. D. *J. Organomet. Chem.* **1971**, *26*, 175.(13) Ishikawa, M.; Fuchikami, T.; Kumada, M. *Tetrahedron Lett.* **1976**, 1299.(14) Ishikawa, M.; Fuchikami, T.; Kumada, M. *J. Organomet. Chem.* **1978**, *162*, 223.(15) Andrianov, K. A.; Volkova, L. M.; Delazari, N. V.; Chumaeskii, N. A. *Khim. Geterotskil. Soedin.* **1967**, 435; *Chem. Abstr.* **1967**, *67*, 10869c.(16) Nakadaira, Y. In *Organosilicon and Bioorganosilicon Chemistry*; Sakurai, H., Ed.; Horwood: Chichester, U.K., 1985; Chapter 14, p 145.

(17) Sato, R. Doctoral Dissertation, Tohoku University, Sendai, Japan, 1985.

(18) Nakadaira, Y.; Sato, R.; Sakurai, H. *Organometallics* **1991**, *10*, 435.(19) Nishinaga, T.; Komatsu, K.; Sugita, N. *J. Org. Chem.* **1995**, *60*, 1309.(20) Corey, J. Y.; Dueber, M.; Malaidza, M. *J. Organomet. Chem.* **1972**, *36*, 49.(21) Nakadaira, Y.; Sato, R.; Sakurai, H. *J. Organomet. Chem.* **1992**, *441*, 411.(22) Leusink, A. J.; Noltes, J. G.; Budding, H. A.; van der Kerk, G. J. *M. Recl. Trav. Chim. Pays-Bas* **1964**, *83*, 1036.(23) Leusink, A. J.; Budding, H. A.; Noltes, J. G. *J. Organomet. Chem.* **1970**, *24*, 375.(24) Schriewer, M.; Neumann, W. P. *J. Am. Chem. Soc.* **1983**, *105*, 897.(25) Neumann, W. P.; Schriewer, M. *Tetrahedron Lett.* **1980**, *21*, 3273.

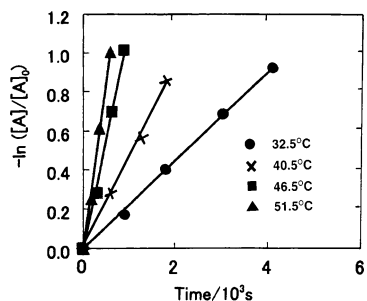


Figure 1. First-order plots for the thermolysis of **1**.

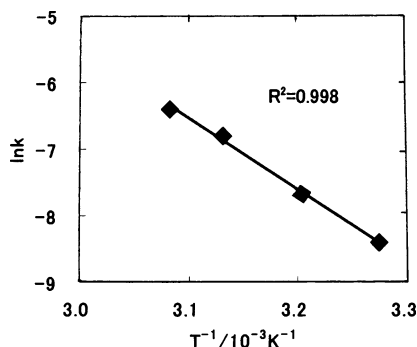


Figure 2. Arrhenius plot for the thermolysis of **1**.

sealed tube at four different temperatures, 32.5, 40.5, 46.5, and 51.5 °C, respectively. The ¹H NMR spectrum of each run showed only signals due to **1** and benzene around the olefinic proton region. The plots of $-\ln([A]/[A]_0)$ vs time gave straight lines (Figure 1), where $[A]$ and $[A]_0$ denote the concentration of **1** consumed and the initial concentration of **1**, respectively. The pyrolysis was observed to follow first-order kinetics: $10^4k/s = 2.23$ (32.3 °C), 4.90 (40.5 °C), 11.0 (46.5 °C), 16.7 (51.5 °C), where k is the rate constant.

Figure 2 shows the plot of $\ln k$ vs the reciprocal of the temperature (Arrhenius plot), which gives a straight line. From Arrhenius plots,²⁶ the activation energy of the germylene extrusion is estimated to be 21.2 ± 0.1 kcal/mol. Figure 3 shows the plot of $\ln(k/T)$ vs the reciprocal of the temperature (Eyring plot), which gives a straight line. On the basis of transition state theory,²⁶ the activation enthalpy (ΔH^\ddagger) and the activation entropy (ΔS^\ddagger) are calculated from the slope and intercept, respectively, which are given by

$$\ln(k/T) = (-\Delta H^\ddagger/R)T + \ln(k_B/h) + \Delta S^\ddagger/R$$

where T , R , k_B , and h are the absolute temperature, gas constant, Boltzmann's constant, and Planck's constant, respectively. From Figure 3, the values of ΔH^\ddagger and ΔS^\ddagger are determined to be 20.5 ± 0.1 kcal/mol and -8.1 ± 0.1 cal/(mol K), respectively. These are the first activation parameters obtained for the germylene extrusion reaction in the thermolysis of germepins.

These kinetic data indicate that **1** is the most thermally labile among metallepins containing group 14 elements (viz. $\Delta H^\ddagger = 25.9$ kcal/mol and $\Delta S^\ddagger = -7.3$ cal/(mol K) for the dimethylsilylene extrusion from 1,1-dimethylsilacycloheptatriene and $\Delta H^\ddagger = 25.2$ kcal/mol and $\Delta S^\ddagger = -6.7$ cal/(mol K) for the dibutylstannylene extrusion from 1,1-dibutylstannacycloheptatriene, respectively).^{16,17}

On pyrolysis some cycloheptatriene derivatives, such as tropone (cycloheptatrienone)²⁷ and tropone ethylene ketal,²⁸ were

(26) Atkins, P. W. In *Physical Chemistry*, 6th ed.; Oxford University Press: Oxford, U.K., 1980.

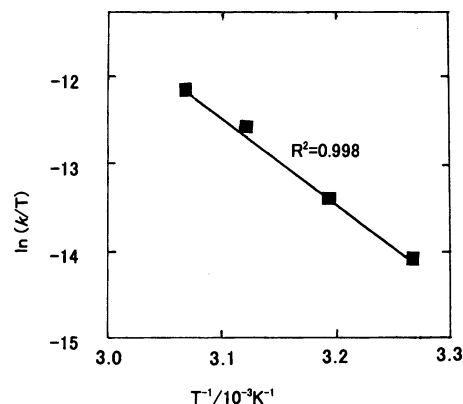
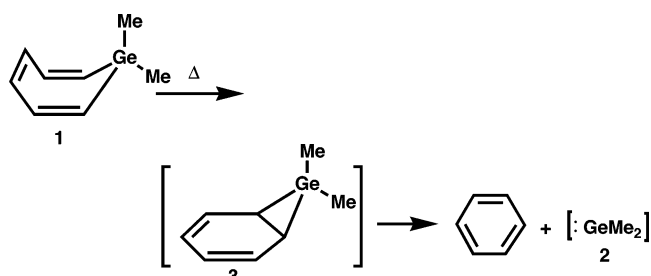


Figure 3. Eyring plot for the thermolysis of **1**.

Scheme 2



reported to give benzene in the same manner with activation parameters of $\Delta H^\ddagger = 52.6$ kcal/mol and $\Delta S^\ddagger = 2.8$ cal/(mol K) for tropone and $\Delta H^\ddagger = 30.8$ kcal/mol and $\Delta S^\ddagger = -7.2$ cal/(mol K) for tropone ethylene ketal. Since then, these kinetic data, particularly the negative value of ΔS^\ddagger for tropone ethylene ketal, have been explained by an extrusion reaction of this type proceeding in two steps via highly strained norcaradiene intermediates, which readily extrude the corresponding divalent fragments to give benzene. As in the cases of metallepins such as 1,1-dimethylsilacycloheptatriene and 1,1-dibutylstannacycloheptatriene, the large negative value of ΔS^\ddagger for **1** shows clearly that the transition state should be more rigid compared with the ground state, in which **1** adopts a rapidly inverting boat conformation.^{17,21} Therefore, the geometry in the transition state of the thermolysis of **1** is conceivably close to that of the germanorcaradiene **3** formed (Scheme 2), possibly from **1** in a thermally allowed disrotatory process.²⁹ A germacyclopropane is reported to be much more labile than a silacyclopropane^{30,31} but might be expected to be still more stable than a stannacyclopropane, because a Sn-C bond is weaker than a Ge-C bond.³²

These characteristic features of a cyclopropane containing a group 14 element imply that the silanorcaradiene may be more easily formed than the germanium analogue **3**, whereas **3** may be more thermally labile toward the extrusion. Actually, **1** is the most susceptible to thermolysis among the metallepins containing group 14 elements, as mentioned above, and this

(27) Amano, A.; Mukai, T.; Nakazawa, K.; Okayama, K. *Bull. Chem. Soc. Jpn.* **1976**, *49*, 1671.

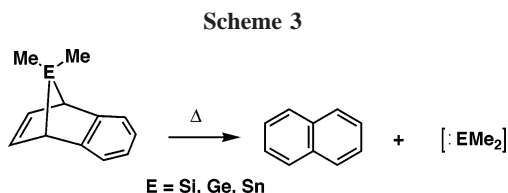
(28) Fukunaga, T.; Mukai, T.; Akasaki, Y.; Suzuki, R. *Tetrahedron Lett.* **1970**, 2975.

(29) Woodward, R. B.; Hoffmann, R. In *The Conservation of Orbital Symmetry*; Verlag Chemie: Weinheim, Germany, and Academic Press: New York, 1970.

(30) Homer, D. A.; Horner, R. S.; Grev, H.; Schaefer, H. F., III. *J. Am. Chem. Soc.* **1992**, *114*, 2093.

(31) Seyferth, D.; Massol, M.; Barrau, J.; Monteverdi, S. *J. Organomet. Chem.* **1980**, *185*, 307.

(32) Gilman, H.; Weyenberg, D. R. *J. Am. Chem. Soc.* **1968**, *90*, 3438.



fact shows that the transition state of the extrusion of **1**, a Me₂-Ge form, is located before the formation of **3** but that for the silenepin it follows the formation of the silanorcaradiene. Furthermore, the fact that **1** is thermally less stable than the corresponding stannepin may be interpreted by assuming the transition state for the extrusion of the stannylene also precedes the formation of the stannanorcaradiene or its equivalent. Since the Sn–C bond is longer than the Ge–C bond, the transition state for the formation of the stannanorcaradiene should be higher in energy than that for germanorcaradiene **3**.

It is worth noting that the thermal stability of 7-metallanorbornadiene derivatives is known to decrease in the order of silicon, germanium, and tin (Scheme 3).^{25,33,34} This may be ascribed reasonably to bond dissociation energies of the metal–carbon bonds involved.

Experimental Section

General Methods. ¹H and ¹³C NMR spectra were recorded on Varian Unity Inova 400 MHz and JEOL JNM-AL 300 MHz

(33) Sakurai, H.; Sakaba, H.; Nakadaira, Y. *J. Am. Chem. Soc.* **1982**, *104*, 6156.

(34) Grugel, C.; Neumann, W. P.; Schriewer, M. *Angew. Chem., Int. Ed. Engl.* **1979**, *18*, 543.

spectrometers. GC-MS spectra were measured with a JEOL JMS-DX 303 mass spectrometer. Gas chromatographic analyses were performed with a Shimadzu GC-8A instrument equipped with a 1 m 20% SE30 column.

Materials. Solvents were dried by refluxing over sodium benzophenone ketyl under a nitrogen atmosphere and were distilled just before use. 2,3-Dimethylbuta-1,3-diene was commercially available. 1,1-Dimethylgermacyclohepta-2,4,6-triene was prepared according to the reported procedure.²¹

Thermolysis of 1,1-Dimethylgermacyclohepta-2,4,6-triene (1). **1** (20 mg, 0.1 mmol) was thermolyzed in a toluene-*d*₈ solution containing 2,3-dimethylbuta-1,3-diene (41 mg, 0.5 mmol) in an evacuated sealed tube at 80 °C. The thermolysis was followed by the ¹H NMR spectrum of the thermolysate and was found to be complete within 30 min, affording benzene (0.1 mmol). Assignments of the ¹H NMR signals of the dimethylgermylene trapping product 1,1,3,4-tetramethyl-1-germacyclopent-3-ene were not attempted, because these NMR signals overlap with complex signals arising from unidentified polymeric materials produced, but in the GC-MS spectrum the molecular ion peak corresponding to the trapping product was clearly observed at *m/z* 186 (51%) calculated on the basis of ⁷⁴Ge.

Rate Constants of Thermolysis of 1,1-Dimethylgermacyclohepta-2,4,6-triene (1). A toluene-*d*₈ solution of **1** (10 mg, 0.05 mmol) was deoxygenated by argon bubbling and was thermolyzed at 32.5 ± 0.5, 40.5 ± 0.5, 46.5 ± 0.5, and 51.5 ± 0.5 °C, respectively. The progress of the reaction was monitored by means of ¹H NMR measurements.

OM0600689