

Thermally Induced Ring Opening of Novel Group 14 Functionalized Vinylcyclopropenes

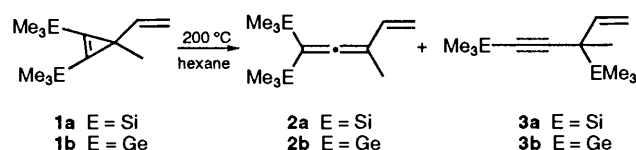
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Pyrolysis of 1,2-bis(Me₃E)-3-methyl-3-vinylcyclopropenes (E = Si, Ge) **1a** and **2a** at 200 °C is found to yield allene- and alkyne-type products in the ratios 5:1 and 2:1, respectively.

Thermal chemistry of cyclopropene derivatives has been a matter of considerable interest^{1,2} since the report of Wiberg and co-workers on the ring opening in the parent cyclopropene in 1960.³ In particular, the effect of substituents on the kinetics and product composition has been discussed in detail.^{1,2b-d} Recent reports on the exclusive formation of allenic-type products upon thermolysis of some 1,2-disubstituted cyclopropenes^{4,5} prompt us to communicate our preliminary results in related studies.

We describe here our finding that 1,2-bis(Me₃E)-3-methyl-3-vinylcyclopropenes (E = Si, Ge) **1a** and **b** undergo thermolytic ring opening to produce a mixture of novel organometallic functionalized allenic- (**2a** and **b**, respectively) and propylenic- (**3a** and **b**, respectively) type products (Scheme 1). This result represents an interesting contrast to the behaviour of hitherto studied 3-vinylcyclopropene derivatives in thermolysis.⁷



Scheme 1

In a typical experiment, a solution of the substrate (20.0 mmol) in dry hexane (3.5 cm³) was heated at 200 °C in a high pressure Schlenk tube until complete conversion of the starting material was achieved.† In each instance, GC analysis§ of the reaction products indicated the presence of two new compounds only, in ratios 5:1 and 2:1 for the thermolyses of **1a** and **b**, respectively. The products **2b** and **3b** were isolated from the reaction mixture and separated by TLC (hexane as eluent) and identified by their IR and NMR spectral data (Table 1). On the contrary, pyrolysis products of **1a** could not be separated despite many attempts involving preparative GC, column and TLC chromatography, and fractional distillation. Hence, they were assigned on the basis of the spectral properties of the raw pyrolysate (Table 1). Specifically, the IR spectrum of the latter displayed resonances at 1908 and 2145 cm⁻¹, characteristic for allenic⁸ and acetylenic⁸ functionalities, whereas the ¹³C NMR spectrum unequivocally revealed the presence of signals expected for the allenic carbon atoms⁹ (δ 213.28 and 87.30,

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‡ Full conversions of the starting compounds **1a** and **2a** were achieved in 9 d and 70 h, respectively.

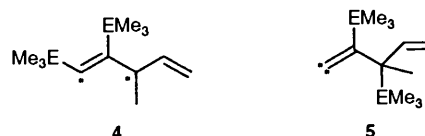
§ The product ratios show a small scatter but no systematic variation with reaction time, indicating that neither **2a** and **3a** nor **2b** and **3b** interconvert. Furthermore, an independent experiment has shown that **2a** does not undergo any other rearrangement when heated under the same conditions as **1a**.

Table 1 Characteristic IR, ¹H and ¹³C NMR data for **2a-3b**

Compound	Spectral data
2a	$\nu_{\max}(\text{film})/\text{cm}^{-1}$ 1908s (C=C=C), 1610m (C=C); $\delta_{\text{H}}(\text{CDCl}_3)$ 0.12 (18 H, s, SiMe ₃), 1.73 (3 H, s, CH ₃), 4.74–4.85 (2 H, m, =CH ₂), 6.28–6.37 (1 H, q, =CH); $\delta_{\text{C}}(\text{CDCl}_3)$ 0.14, 13.20, 87.30, 89.4, 107.30, 136.45, 213.28
3a	$\nu_{\max}(\text{film})/\text{cm}^{-1}$ 2145w (C=C), 1610m (C=C); $\delta_{\text{H}}(\text{CDCl}_3)$ 0.07 (9 H, s, SiMe ₃), 0.16 (9 H, s, SiMe ₃), 1.28 (3 H, s, CH ₃), 4.99–5.19 (2 H, m, =CH ₂), 5.67–5.76 (1 H, q, =CH); $\delta_{\text{C}}(\text{CDCl}_3)$ –4.68, 0.27, 20.40, 87.30, 110.43, 111.57, 139.86
2b	$\nu_{\max}(\text{film})/\text{cm}^{-1}$ 1909s (C=C=C), 1608m (C=C); $\delta_{\text{H}}(\text{CDCl}_3)$ 0.27 (18 H, s, GeMe ₃), 1.74 (3 H, s, CH ₃), 4.72–4.84 (2 H, m, =CH ₂), 6.31–6.40 (1 H, q, =CH); $\delta_{\text{C}}(\text{CDCl}_3)$ –0.24, 13.75, 87.93, 88.92, 107.01, 137.45, 207.50
3b	$\nu_{\max}(\text{film})/\text{cm}^{-1}$ 2130w (C=C), 1608m (C=C); $\delta_{\text{H}}(\text{CDCl}_3)$ 0.19 (9 H, s, GeMe ₃), 0.33 (9 H, s, GeMe ₃), 1.32 (3 H, s, CH ₃), 4.92–5.13 (2 H, m, =CH ₂), 5.71–5.80 (1 H, q, =CH); $\delta_{\text{C}}(\text{CDCl}_3)$ –4.92, 0.12, 21.06, 86.51, 109.08, 110.20, 140.67

respectively) as well as the signals at δ 110.43 and 87.30 characteristic of acetylenic carbons.⁹

Formation of both products may be envisaged to occur *via* [1,2]-EME₃ shifts from the common biradical **4**. It should be noted, however, that formation of propylene-type product might favour involvement of vinylidene-type intermediate **5**, as recently suggested by *ab initio* investigation of the C₃H₄ potential energy surface.¹⁰



It is interesting to note that **1b** rearranges more rapidly than its Si counterpart **1a**. Another point worth emphasizing is that substitution of GeMe₃ with SiMe₃ groups dramatically alters product ratio. It would be of considerable interest to establish whether the observed trend originates from the ground energy differences of the studied compounds, from the corresponding transition structure energy differences, or from a contribution from both.

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