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Novel Tetramerization of 1-Trimethylsilyl-2-phenylcyclopropene

Gon-Ann Lee* and Chih-Yi Chang

Department of Chemistry, Fu Jen Catholic University, Hsinchuang, Taipei 24205, Taiwan, R.O.C.

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ABSTRACT: 1-Trimethylsilyl-2-phenylcyclopropene (**1**) was generated from bromo-lithium exchange of 1-bromo-2-phenylcyclopropene followed by treatment with trimethylsilylchloride. Compound **1** underwent ene dimerizations to give endo and exo dimers **5** and **6** which would dimerize by coupling reaction to yield a sole tetramer **4**.

Cyclopropene contains 27.7 Kcal/mol of olefinic strain energy and 55.2 Kcal/mol of strain energy[1] and undergoes ene dimerizations to form 3-cyclopropylcyclopropene, [2+2] dimerizations to form tricyclo[3.1.0.0^{2,4}]hexane, coupling dimerization to yield hexatriene, or rearrangement to vinyl carbene to release olefinic strain energy.[2] Baird reported that 1,2-substituted cyclopropene, 2-*tert*-butylcyclopropenecarboxylic acid, undergoes ene reactions to generate two stereodimers which were proposed to be formed from *endo* and *exo* transition structures[3] which were further studied by theoretical calculations.[4] Padwa reported that two 1,3,5-hexatrienes (cis and trans at central double bond) were isolated by heating 1-phenyl-2-carbomethoxy-3,3-dimethylcyclopropene and these two hexatriene could be readily interconverted by thermolysis.[5] However, Billups and Wiberg groups both claimed that only one 1,3,5-hexatriene was formed when 6-(bicyclo[4.1.0]hept-1-yl)bicyclo[4.1.0]hept-1(7)-ene underwent coupling dimerization reaction, and the configuration of the central double bond of this triene dimer was not known.[6] Therefore, to understand the mechanism for the formation of triene dimer of cyclopropene is of great interest.

Although 1-trimethylsilyl-2-phenylcyclopropene (**1**) was synthesized by carbometalation of 3-(trimethylsilyl)propargyl alcohol followed by iodinolysis, chlorination, and deiodochlorination, the chemistry of this compound was not studied yet.[7] We describe here a new synthesis and the stereochemistry of the dimerization and tetramerization of **1**. The immediate precursor of **1**, 1,1,2-tribromo-2-phenylcyclopropane (**2**),[8] was prepared by dibromocarbene addition of 1-bromo-1-phenylethene. Compound **2** was treated with 2.5 equiv of methyllithium at -40 °C and the mixture was stirred for 30 min before 1.5 equiv of trimethylsilyl chloride was added. The mixture was stirred at -40 °C for 30 min, and then allowed to warm to room temperature. Water was added, and the mixture was dried, concentrated, and chromatographed to give **1** (88 % isolated yield)[9] which was trapped by cyclopentadiene to give adduct **3** (Scheme I).[10] Compound **1** was generated and sealed in vacuum tube. After three weeks, the mixture was purified by recrystalization to give **4** (85 % isolated yield),[11] a tetramer of cyclopropene **1** and its structure was shown by single-crystal X-ray analysis (Figure I).

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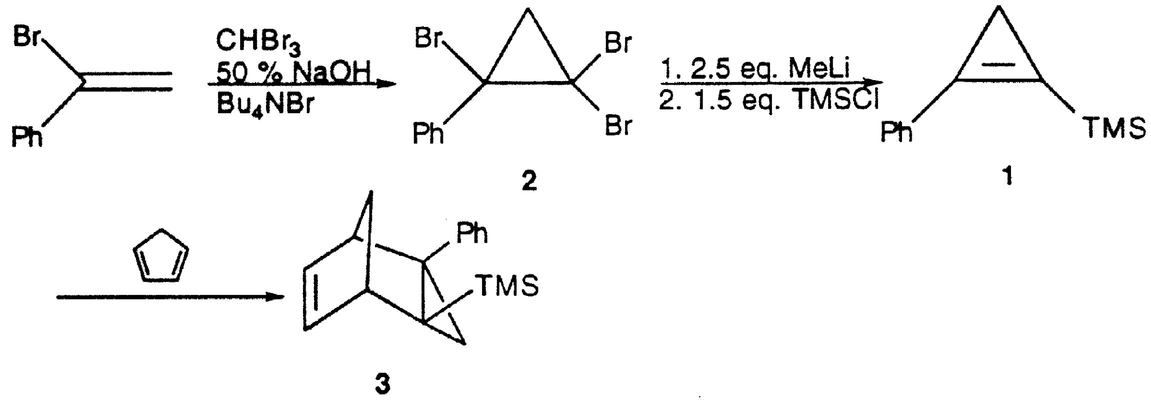
Scheme I



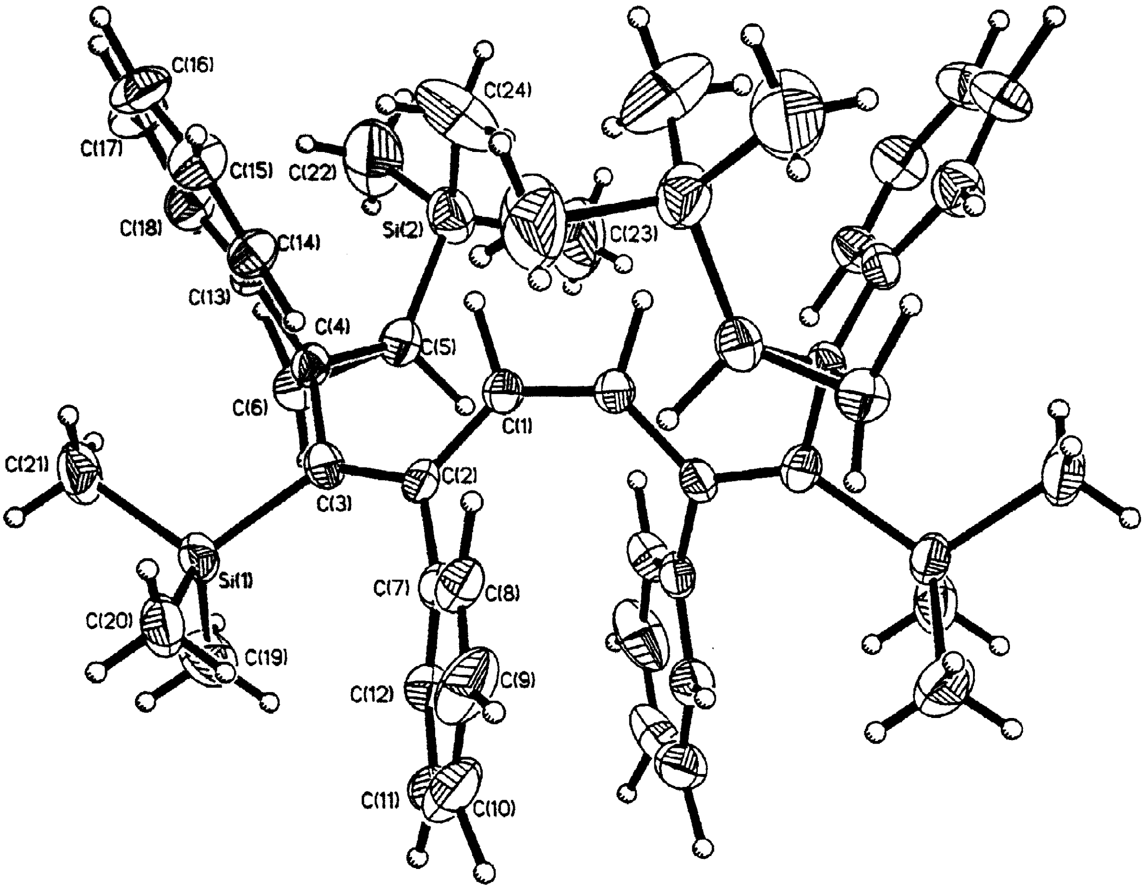
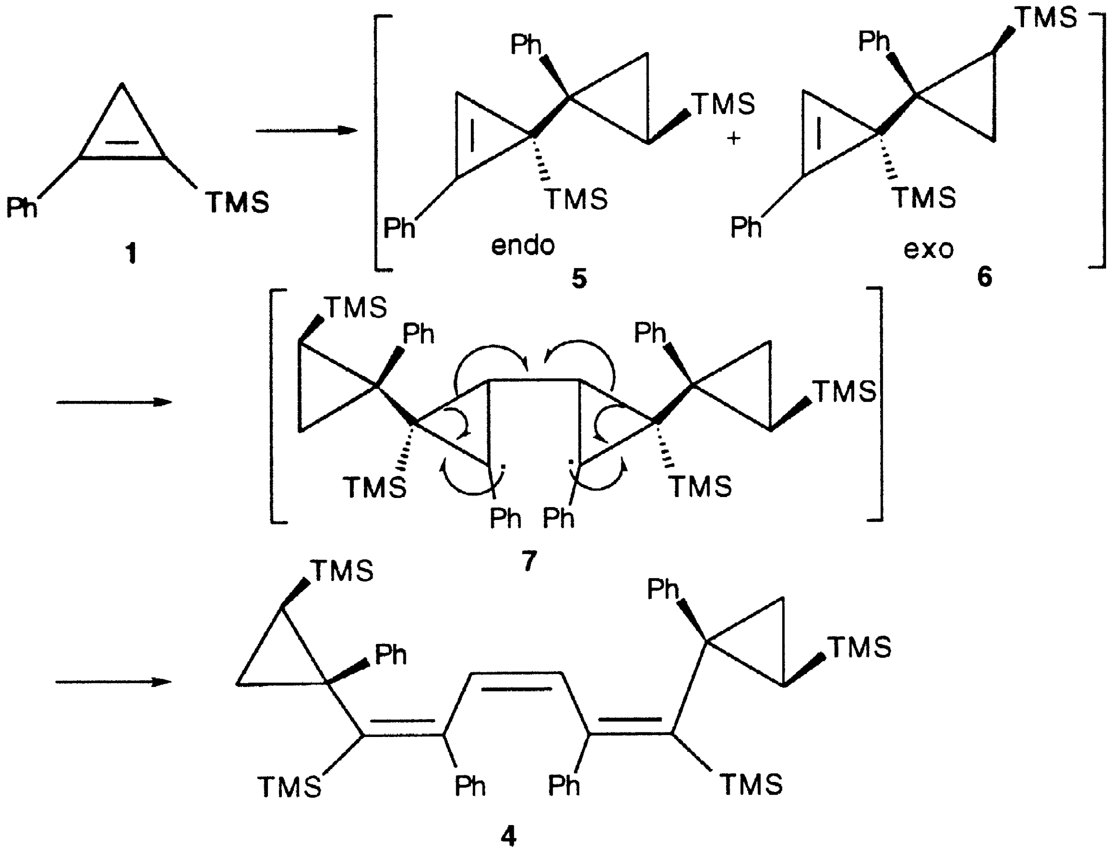


Figure I. The structure of tetramer **4**.

According to the single-crystal X-ray analysis, the tetramer was formed from two diastereomers **5** and **6** which were ene dimers of cyclopropene **1**. These two ene dimers **5** and **6** were proposed to be formed from *endo* and *exo* tranistion structures. There are two effects that influence the outcome. (1) The double bond conjugated to phenyl group is more stable than that bonded to silyl group; (2) The carbocation on the carbon-2 is more stable than that on canbon-1 in compound **1**. The dimerization of ene dimers would presumably involve a 1,4-diyl intermediate **7** that could undergo cyclopropyl rings cleavage to give the triene tetramer **4** (Scheme II). In principle, initial bond formation would occur to generate three types of intermediates - two phenylcyclopropyl **7**, a phenylcyclopropyl and a cyclopropyl, and two cyclopropyl biradicals. Because the intermediate **7** is the most stable biradical, the coupling of ene dimers generated tetramer **4** as a sole adduct. To the best of our knowledge, none of cyclopropene derivatives undergo ene dimerization followed by coupling reaction to give tetramers exclusive of bicyclo[4.1.0]hept-1(6)-ene and bicyclo[4.1.0]hept-1(7)-ene.[6] Compound **1** is the first simple cyclopropene derivative that can form this type tetramer.

The chemistry of cyclopropenes **5** and **6** and triene tetramer **4** is under investigation.

Scheme II



Acknowledgments

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8. m.p. 83.5-84.5 °C; ^{1}H NMR ($CDCl_3$): δ 7.31-7.49 (5H, m), 2.52 (1H, d, *J* = 9.3 Hz), 2.26 (1H, d, *J* = 9.3 Hz); ^{13}C NMR ($CDCl_3$): δ 140.14 (C), 129.23 (CH), 129.01 (CH), 128.85 (CH), 43.01 (C), 37.24 (CH_2), 31.88 (C).
9. ^{1}H NMR ($CDCl_3$): δ 7.32-7.63 (5H, m), 1.13 (2H, s), 0.32 (9H, s); ^{13}C NMR ($CDCl_3$): δ 131.61 (C), 131.11 (C), 129.49 (CH), 128.68 (CH), 128.63 (CH), 111.15 (C), 5.82 (CH_2), -1.17 (CH_3).
10. m.p. 59.8-61.0 °C; ^{1}H NMR ($CDCl_3$): δ 7.16-7.36 (5H, m), 6.03 (1H, dd, *J* = 3.3, 5.3 Hz), 5.80 (1H, dd, *J* = 3.1, 5.3 Hz), 2.90 (1H, m), 2.77 (1H, m), 2.26 (1H, dt, J = 2.3, 4.2 Hz), 1.75 (1H, dt, *J* = 2.3, 4.2 Hz), 1.17 (1H, dd, *J* = 2.9, 5.0 Hz), 0.76 (1H, d, *J* = 5.0 Hz), -0.20 (9H, s); ^{13}C NMR ($CDCl_3$): δ 144.11 (C), 132.34 (CH), 132.10 (CH), 128.76 (CH), 128.02 (CH), 125.78 (CH), 62.30 (CH_2), 52.09 (CH), 45.88 (CH), 34.62 C), 23.82 (CH_2), 17.60 (C), -1.82 (CH_3).
11. m.p. 232-234 °C; ^{1}H NMR ($CDCl_3$): δ 7.01-7.21 (20H, m), 6.78 (2H, s), 1.67 (2H, dd, *J* = 4.2, 8.3 Hz), 1.17 (2H, dd, *J* = 4.2, 11.2 Hz), 0.81 (2H, dd, *J* = 8.3, 11.2 Hz), -0.12 (18H, s), -0.52 (18H, s); ^{13}C NMR ($CDCl_3$): δ 152.49 (C), 151.92 (C), 143.09 (C), 142.46 (C), 134.85 (CH), 129.87 (CH), 127.75 (CH), 127.25 (CH), 126.54 (CH), 126.41 (CH), 125.51 (CH), 34.38 (C), 21.47 (CH), 17.16 (CH_2), 2.04 (CH_3), -0.24 (CH_3); X-ray analysis: $C_{48}H_{64}Si_4$, M_r = 753.4, colorless crystals, crystal size 0.6x0.5x0.2 mm, monoclinic, C2/c, *a* = 22.562 (3) Å, *b* = 10.691 (2) Å, *c* = 19.935 (3) Å, β = 99.850 (0)°, V = 4737.4 (12) Å^3, Z = 4, d = 1.056 g cm^{-3}, absorption coefficient 0.155 mm^{-1}, Siemens R3m/V, Siemens SHELXTL PLUS (PC Version), λ = 0.71073 Å, 2θ = 7.0-45.0°, scan type ω, scan speed variable; 6.00 to 50.00°/min. in ω, scan range (ω) 0.50°, background measurement: stationary crystal and stationary counter at beginning and end of scan, each for 0.5 % of total scan time, index ranges $-1 \le h \le 26$, $-1 \le k \le 12$, $-23 \le l \le 23$, reflection collected 5049, independent reflections 4171 (R_{int} = 35.72 %), observed reflections 2079 (F > 4.0 σ (F)), Min. / Max. transmission 0.5785 / 0.5986, refinement method Full-Matrix Least-Squares, quantity minimized $\Sigma w(F_0-F_c)^2$, hydrogen atoms Riding model, fix isotropic U, weighting scheme $w^{-1} = \sigma^2$ (F) + 0.0008 F^2, number of parameters refined 235, final R indiced (obs. data) R = 7.75 %, wR = 9.52 %, goodness-of fit 1.90, data-to-parameter ratio 8.8 : 1, largest difference peak 0.34 eÅ-3, largest difference hole -0.33 eÅ.