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1-Chloro-3-trimethylsilylcyclopropene--A New Synthesis of 3,3'-Bicyclopropenyl

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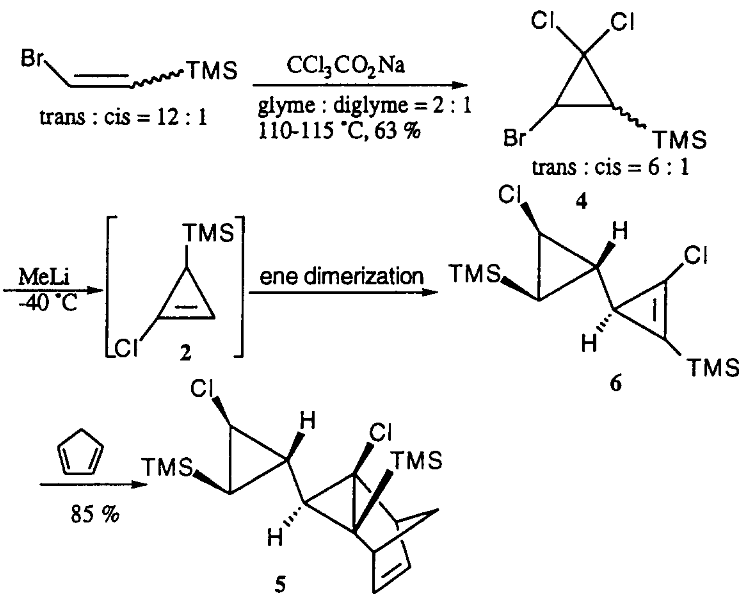
ABSTRACT: 3,3'-Bicyclopropenyl (**1**) was synthesized from a new isomer **3** of 1-chloro-2-(2-chloro-3-trimethylsilylcycloprop-1-yl)-3-trimethylsilylcyclopropanes, which was formed by ene dimerization of 1-chloro-3-trimethylsilylcyclopropene (**2**) followed by reduction with diimide. Compoumd **2** was generated by debromochlorination of 1-bromo-2,2-dichloro-3-trimethylsilylcyclopropane (**4**) which was synthesized by dichlorocarbene addition of β-bromovinyl trimethylsilane.

The valence isomers of benzene have attracted the attention of both theoretical and experimental chemists for well over a century.[1] The first derivative of the last-known isomer of benzene ($(CH)_6$), 3,3'-bicyclopropenyl (**1**), was prepared by Breslow and Gal by dimerization of triphenylcyclopropenyl radical in 1959,[2] but the parent compound was not synthesized until 1989 by Billups and Haley,[3,4] and the X-ray crystal structure of **1** was later determined in 1993.[5] Compound **1** has been prepared by treating the mixture of 1-chloro-2-(2-chloro-3-trimethylsilylcyclopropyl)-3-trimethylsilylcyclopropanes with tetra-*n*-butylammonium fluoride.[4] This mixture of cyclopropanes were generated by double monochlorocarbene additions to 1,4-bis(trimethylsilyl)buta-1,3-diene which was synthesized by coupling of β-bromovinyltrimethylsilanes.

Although ene dimerizations of cyclopropenes are well known,[6] the regioselectivity of these reations is rare.[7] Furthermore, the methods for designed synthesis of cyclopropenes have not been reported. We describe here the synthesis of 1-chloro-3-trimethylsilylcyclopropene (**2**), a new cyclopropene, and its use in a key step to prepare the immediate precursor of compound **1**, a sole new isomer **3**[8] of 1-chloro-2-(2-chloro-3-trimethylsilylcyclopropyl)-3-trimethylsilylcyclopropanes in high yield (92 %), which was not obtained by Billups' method, via ene dimerization. The starting material 1-bromo-2,2-dichloro-3-trimethylsilylcyclopropane (**4**)[9] (trans : cis = 6 : 1) was prepared by dichlorocarbene addition to β-bromovinyltrimethylsilane (trans : cis = 12 : 1). Compound **4** was treated with methyllithium at -40 °C and the mixture was stirred for one hour before cyclopentadiene was added. The structure of the Diel-Alder adduct **5**[10] which was formed from **6** (ene-dimer of **2**)[11] and cyclopentadiene, was determined by single-crystal X-ray analysis (Figure 1).



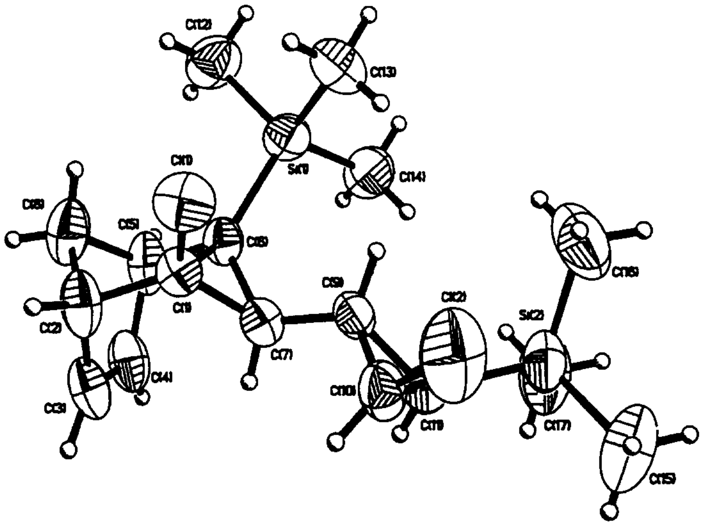
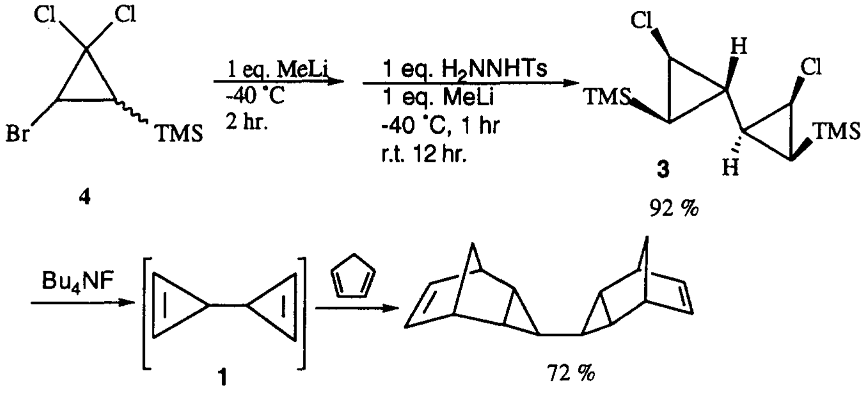


Figure 1. Crystal Structure of 6

The ene dimerization of compound **2**, in principle, can generate twenty-fure pairs of enantiomers of 3-cyclopropylcyclopropenes, but there is only one of them formed. There are three effects that influence the outcome. (1) The more stable alkene has the more highly substituted double bond; (2) As two cyclopropenes approach each other, two bulky trimethylsilyl groups are farther; (3) At the transition state, the interaction between chlorine atoms in two cyclopropenes is greater than that between two cyclopropene rings.

Compound **4** was treated with 1 equiv of methyllithium at -40 °C and the mixture was stirred for 2 hours and the product was reduced by diimide which was generated by reaction of 1 equiv of *p*-toluenesulfonhydrazide and another 1 equiv of methyllithium.[12] The mixture was stirred at -40 °C for 1 hour and room temperature for 12 hours, and only one product **3** was obtained. According to the ^{13}C NMR spectrum (containing 8 different carbons), this compound was formed from less hindered side of **6**.

The vacuum gas-solid reaction (VGSR)[13] procedure was employed to convert **3** to **1** with tetrabutylammonium fluoride at 25 °C and 20 mtorr and compound **1** was trapped with cyclopentadiene (72 % isolated yield).[4]



The chemistry of cyclopropenes **2** and **6** and elimination of **5** to generate fused 3,3'-bicyclopropenyl are under investigation.

Acknowledgments

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8. m.p. 76-77 °C; ^{1}H NMR (CDCl$_3$): δ 3.50 (1H, dd, *J* = 6.8 , 6.6 Hz), 3.19 (1H, dd, *J* = 8.4, 3.0 Hz), 1.26 (1H, ddd, *J* = 9.3, 8.4, 3.0 Hz), 0.66 (1H, ddd, *J* = 11.4, 9.3, 6.8 Hz), 0.23-0.15 (2H, m), 0.21 (9H, s), 0.16 (9H, s); ^{13}C NMR (CDCl$_3$): δ 39.57 (CH), 39.01 (CH), 26.72 (CH), 23.63 (CH), 14.83 (CH), 12.71 (CH), 0.89 (CH$_3$), -0.32 (CH$_3$).
9. b.p. 48-52 °C/ 0.4 torr; *trans*-form ^{1}H NMR (CDCl$_3$): δ 3.42 (1H, d, *J* = 8.6 Hz), 1.01 (1H, d, *J* = 8.6 Hz), 0.19 (3H, s); ^{13}C NMR (CDCl$_3$): δ 63.25 (C), 33.04 (CH), 32.37 (CH), -1.47 (CH$_3$); *cis*-form ^{1}H NMR (CDCl$_3$): δ 3.84 (1H, d, *J* = 11.1 Hz), 1.29 (1H, d, *J* = 11.1 Hz), 0.25 (3H, s); ^{13}C NMR (CDCl$_3$): δ 63.25 (C), 35.43 (CH), 29.70 (CH), -0.13 (CH$_3$).
10. m.p. 78-79 °C; ^{1}H NMR (CDCl$_3$): δ 6.02-5.98 (1H, m), 5.64-5.61 (1H, m), 3.08 (1H, dd, *J* = 8.3, 2.8 Hz), 2.97-2.94 (1H, m), 2.94-2.89 (1H, m), 1.99 (1H, dt, *J* = 7.2, 1.6 Hz), 1.66-1.62 (1H,m), 1.37 (1H, ddd, *J* = 9.4, 8.3, 2.8 Hz), 0.37 (1H, d, *J* = 9.4 Hz),, 0.21 (9H, s), 0.16 (9H, s); ^{13}C NMR (CDCl$_3$): δ 132.91 (CH), 132.80 (CH), 62.08 (C), 59.85 (CH$_2$), 54.72 (CH), 40.26 (CH), 24.60 (CH), 19.10 (C), 15.43 (CH),0.32 (CH$_3$), -0.18 (CH$_3$). X-ray analysis: $C_{17}H_{28}Cl_2Si_2$, M_r = 359.47, colorless crystals, crystal size 0.5x0.5x0.3 mm, orthorhombic, Pbca, *a* = 14.452 (2) Å, *b* = 12.334 (3) Å, *c* = 22.834 (3) Å, V = 4070.0 (9) Å^3, Z = 8, d = 1.173 g cm^{-3}, absorption coefficient 0.430 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; 3.00 to 60.00°/min. in ω, scan range (ω) 0.45°, background measurement: stationary crystal and stationary counter at beginning and end of scan, each for 0.5 % of total scan time, index ranges $-1 \le h \le 17$, $-1 \le k \le 14$, $-27 \le l \le 1$, reflection collected 4481, independent reflections 3580 (R_{int} = 8.26 %), observed reflections 1793 ($F > 4.0\ \sigma(F)$), Min. / Max. transmission 0.4101 / 0.4479, refinement method Full-Matrix Least-Squares, quantity minimized $\Sigma w(F_0-F_c)^2$, hydrogen atoms Riding model, fix isotropic U, weighting scheme $w^{-1} = \sigma^2(F) + 0.0010\ F^2$, number of parameters refined 190, final R indiced (obs. data) R = 5.78 %, wR = 6.54 %, goodness-of fit 1.24, data-to-parameter ratio 9.4 : 1, largest difference peak 0.29 eÅ-3, largest difference hole -0.34 eÅ.
11. ^{1}H NMR (CDCl$_3$): δ 3.06 (1H, dd, *J* = 8.4, 3.3 Hz), 2.19 (1H, d, *J* = 3.4 Hz), 1.30 (1H, dt, *J* = 8.4, 3.4 Hz), 0.20 (9H, s), 0.08 (9H, s), -0.18 (1H, t, *J* = 8.4 Hz).
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