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The Synthesis of Potential Cyclopropenyl Anion Precursors: 3-Methyl-3-trimethylsilylcyclopropene and Its Dibenzoyl Derivative

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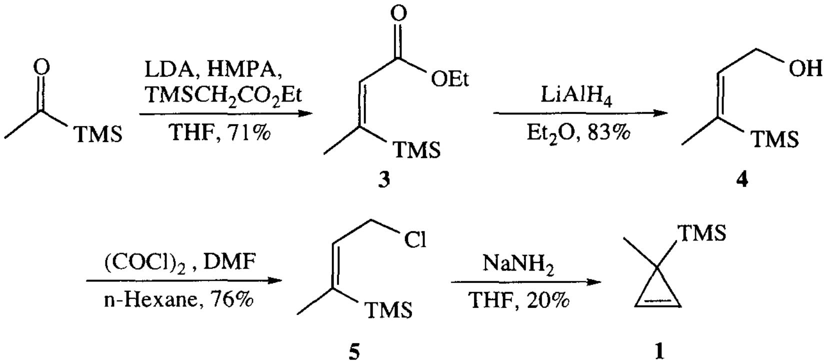
Abstract: 3-Methyl-3-trimethylsilylcyclopropene (1) was prepared by reacting (*Z*)-3-trimethylsilyl-2-butenyl chloride (5) with sodium amide. This compound (1) was converted to 1,2-dibenzoyl-3-methyl-3-trimethylsilylcyclopropene (2), a rare example of an isolable cyclopropene with two electron withdrawing groups at the vinyl position, and the thermal isomerization of 2 was probed. © 1997 Elsevier Science Ltd.

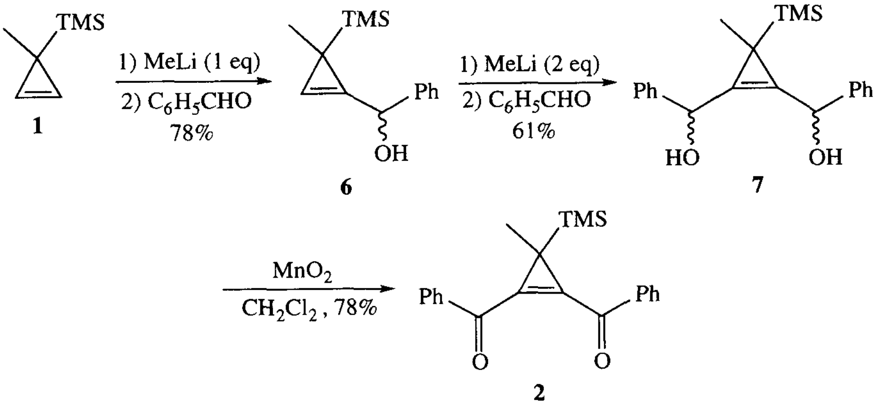
3-Trimethylsilylcyclopropene derivatives have been used to generate stable cyclopropenyl anions in the gas phase, and trappable intermediates consistent with the putative formation of cyclopropenyl anions in solution.[2] 3-Methyl-3-trimethylsilylcyclopropene (**1**) is of interest in this regard as it is expected to be thermally stable, and a good precursor for the preparation of cyclopropenes with two electron-withdrawing groups at the vinyl position. It also may be useful for obtaining thermodynamic data on methylcyclopropenyl anion via the DePuy kinetic method,[3] despite the fact that this ion is predicted to be less stable than it corresponding radical (i.e., it is unbound). In this report we describe the synthesis of **1**, its conversion to 1,2-dibenzoyl-3-methyl-3-trimethylsilylcyclopropene (**2**), and the thermal isomerization of **2**.

3-Methyl-3-trimethylsilylcyclopropene (**1**) was prepared as indicated in Scheme 1. Peterson olefination of acetyl trimethylsilane[4] with ethyl trimethylsilylacetate selectively afforded (*Z*)-ethyl-3-trimethylsilyl-2-butenate (**3**) in a 71% yield after distillation.[5] Reduction of this unsaturated ester with $LiAlH_4$ provided (*Z*)-3-trimethylsilyl-2-butenol (**4**), which was converted to its corresponding allylic chloride (**5**) with oxalyl chloride and *N,N*-dimethylformamide in a 63% overall yield for the two steps.[6] The high *Z* selectivity in the formation of **3** can be rationalized by examining the structure of the transition state and was confirmed by converting it to **4** and comparing this material with an independently synthesized sample.[7] The desired cyclopropene (**1**) was then obtained via an intramolecular cyclization upon reaction of **5** with sodium amide. This transformation is very sensitive to the reaction temperature, and under optimal conditions (45 °C), a 20% yield was achieved.[8] Alternative methods for the preparation of **1** including the base-induced elimination of 1-bromo-2-methyl-2-trimethylsilylcyclopropane (*tert*-BuOK/DMSO, LDA/THF, and *tert*-BuOK under heterogeneous conditions) and photolysis (350 nm or visible light) of 1-(trimethylsilyl)diazoethane with trimethylsilylacetylene were unsuccessful.[9]



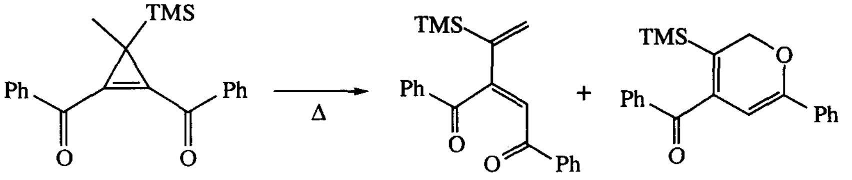
Scheme 1. Synthesis of 3-methyl-3-trimethylsilylcyclopropene (**1**).

Introduction of strong electron-withdrawing groups on to cyclopropene derivatives can lead to attractive precursors to stabilized cyclopropenyl anions. Cyclopropene **1** was converted to its dibenzoyl homolog **2** by taking advantage of the enhanced acidity of cyclopropenes at the vinyl position relative to typical alkenes. Deprotonation of **1** by methyllithium at -78 °C, followed by addition of benzaldehyde, gave **6** as a mixture of diastereomers in a 78% yield after chromatography. Two equivalents of MeLi at 0 °C were required to generate the vinyl anion of **6**, which was successfully trapped with benzaldehyde to afford a mixture of four diastereomeric diols (**7**).[10] Oxidation of this mixture with activated MnO_2 provides the desired enedione (**2**) in a 78% yield after flash column chromatography (silica gel, 100% hexane).[11]



Scheme 2. Synthesis of 1,2-dibenzoyl-3-methyl-3-trimethylsilylcyclopropene (**2**).

Enedione **2** is thermally unstable and slowly isomerizes at room temperature to afford **8** and **9** in a 4 – 5 : 1 ratio (eq 1).[12,13] The activation parameters for this rearrangement were obtained by NMR kinetics in

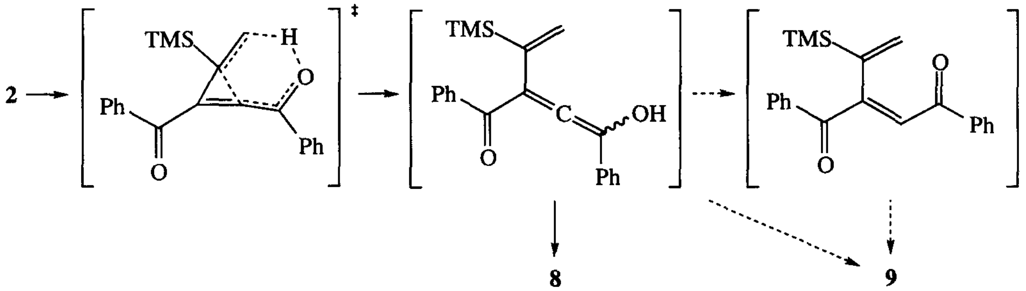


2 **8** **9**

~4–5 1

(1)

toluene–d_8 ($H^{\ddagger}$ = 18.4 ± 0.6 kcal/mol, $S^{\ddagger}$ = -24.7 ± 1.8 e.u.) and nitrobenzene–d_5 ($H^{\ddagger}$ = 18.9 ± 0.6 kcal/mol, $S^{\ddagger}$ = -22.8 ± 1.8 e.u.). These two solvents have very different dielectric constants (ε = 2.4 and 34.8 D, respectively) but the isomerization is accelerated in the more polar medium only by a factor of 1.4 at 100 °C. Given this insensitivity to the solvent polarity and the large negative entropies of activation, it seems likely that a concerted retro-ene reaction is operative (Scheme 3). This conclusion is supported by *ab initio* calculations (a low energy retro-ene transition structure was found at the MP2/6-31G(d,p) level for 3-methyl-1-formylcyclopropene, an analog of **2**) and the fact that 1,2-dibenzoyl-3-(4-methylphenyl)-3-trimethylsilylcyclopropene, a phenyl analog of **2** which cannot undergo the proposed retro-ene reaction, is considerably more stable than **2**.



Scheme 3. A proposed mechanism for the thermal isomerization of **2**.

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8. The following spectroscopic data were obtained for **1**: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.23 (q, 2 H, J = 0.6 Hz), 1.04 (t, 3 H, J = 0.6 Hz), -0.09 (s, 9 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 117.2 (d), 25.2 (q), 8.3 (s), -2.7 (q); IR (neat) 2955, 2853, 1637, 1448, 1248, 1058, 987, 889, 835, 751 cm^{-1}; HRMS (CI, isobutane as ionizing gas) calcd for $C_7H_{14}Si$ (M^+) 126.0864, found $C_7H_{14}Si$ (M^+) 126.0869.
9. A small amount of **1** (~5%) was observed in the heterogeneous elimination reaction, but the major product is 2-(trimethylsilyl)methylenecyclopropane.
10. An attempt to convert **1** directly into **7** using slightly more than 2 eq of MeLi and PhCHO only led to **6**.
11. The following spectroscopic data were obtained for **2**: ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.11 (dm, 4 H, J = 7.8 Hz), 7.61 (tt, 2 H, J = 7.2 Hz and 1.2 Hz), 7.49 (tm, 4 H, J = 7.8 Hz), 1.61 (s, 3 H), 0.09 (s, 9 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 185.7 (s), 136.3 (s), 134.2 (d), 131.3 (s), 129.3 (d), 128.9 (d), 29.3 (s), 22.6 (q), -2.22 (q); IR (neat) 3070, 2954, 2856, 1783, 1640, 1597, 1580, 1314, 1259, 1084, 1023, 901, 840 cm^{-1}; HRMS (CI, isobutane as ionizing gas) calcd for $C_{21}H_{23}O_2Si([M + H]^+)$ 335.1467, found $C_{21}H_{23}O_2Si([M + H]^+)$ 335.1461.
12. The isomerization products were characterized as follows. The major product (**8**): ^{1}H NMR ($CDCl_3$) δ 7.90 (m, 4 H), 7.56 ~ 7.43 (m, 6 H), 7.24 (s, 1 H), 6.59 (d, 1 H, J = 1.5 Hz), 6.03 (d, 1 H, J = 1.5 Hz), 0.36 (s, 9 H); ^{13}C NMR ($CDCl_3$) δ 197.8 (s), 188.4 (s), 159.4 (s), 147.2 (s), 137.4 (s), 136.0 (s), 135.4 (t), 133.2 (d), 133.1 (d), 128.7 (d), 128.6 (d), 128.5 (d), 128.4 (d), 122.0 (d), -0.42 (q); IR (KBr) 3062, 3029, 2954, 2932, 2872, 1674, 1661, 1598, 1580, 1448, 1359, 1262, 1222, 1177, 1021, 955, 862, 843 cm^{-1}; HRMS (EI) calcd for $C_{21}H_{22}O_2Si$ (M^+) 334.1389, found $C_{21}H_{22}O_2Si$ (M^+) 334.1387. The minor product (**9**): ^{1}H NMR ($CDCl_3$) δ 7.96 (dt, 2 H, J = 7.2 and 1.2 Hz), 7.60 (m, 3 H), 7.47 (m, 3 H), 7.34 (m, 2 H), 6.06 (s, 1 H), 4.88 (s, 2 H), 0.07 (s, 9 H); ^{13}C NMR ($CDCl_3$) δ 197.8 (s), 154.7 (s), 144.8 (s), 136.4 (s), 133.5 (d), 133.3 (s), 129.9 (d), 129.5 (d), 128.6 (d), 128.4 (d), 127.9 (s), 125.3 (d), 100.2 (d), 68.8 (t), -0.91 (q); IR (neat) 3032, 3005, 2962, 2922, 2854, 1727, 1649, 1580, 1449, 1384, 1260, 1075, 1026, 844 cm^{-1}; HRMS (EI) calcd for $C_{21}H_{22}O_2Si$ (M^+) 334.1389, found $C_{21}H_{22}O_2Si$ (M^+) 334.1388.
13. The neat compound (**2**) slowly decomposes to several products including **8** and **9** at -12 °C.

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