Synthesis of 3-aryl-3-trimethylsilylcyclopropenes and their dibenzoyl derivatives. Possible cyclopropenyl anion precursors?†

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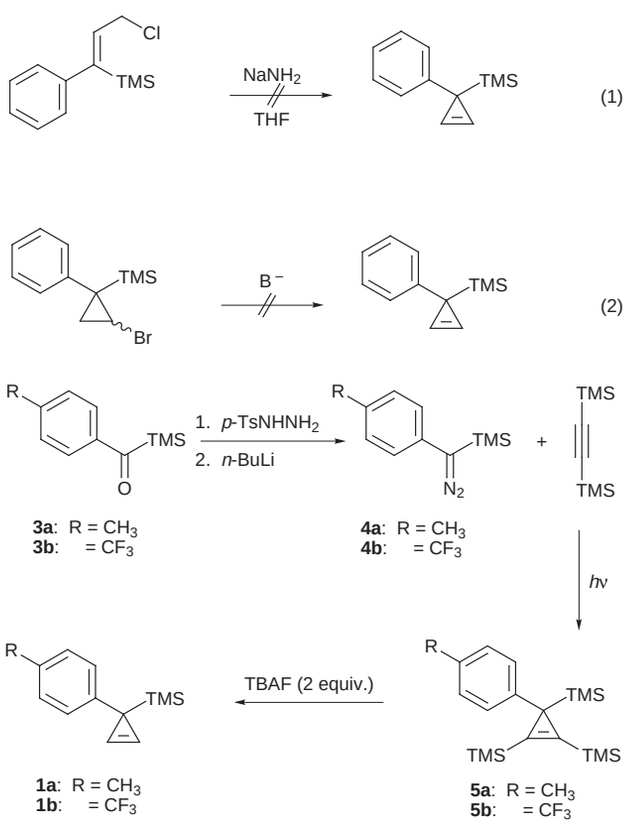
3-Aryl-3-trimethylsilylcyclopropenes (**1**) were synthesized by a four-step reaction sequence starting from known benzoyl trimethylsilanes. These cyclopropenes were thermalized on a gas chromatography column and the products were collected and identified. Their 1,2-dibenzoyl derivatives (**2**) were prepared in a two-step transformation beginning with 3-aryl-1,2,3-tris(trimethylsilyl)cyclopropenes (**5**), the ultimate intermediates in the syntheses of **1**. These compounds (**2**) are rare examples of isolable cyclopropenes with electron withdrawing groups at the vinyl positions. Fluoride-induced desilylation reactions of electron deficient cyclopropenes also are described and a carbon-centered electrophile has been successfully used to trap a putative cyclopropenyl anion.

Fluoride-induced desilylation reactions have been widely used to efficiently cleave silicon–centered groups, and can generate highly reactive species due to the strong silicon–fluorine bond.[1,2] Consequently, 3-trimethylsilylcyclopropene derivatives are attractive cyclopropenyl anion precursors for gas-phase and liquid-phase studies.[3] 3-Aryl-3-trimethylsilylcyclopropenes (**1**) are of interest in this regard as they should be thermally stable, the aryl group is a carbanion stabilizing substituent, and **1** should be a good substrate for adding additional stabilizing groups to the vinyl position. These cyclopropenes maybe also useful for obtaining thermodynamic data on arylcyclopropenyl anions in the gas phase *via* the DePuy kinetic method.[4] In this paper we describe the synthesis and thermolysis products of 3-(*p*-tolyl)-3-trimethylsilylcyclopropene (**1a**) and 3-(4-trifluoromethylphenyl)-3-trimethylsilylcyclopropene (**1b**), and the conversion of these compounds to their 1,2-dibenzoyl derivatives (**2**). The latter species represent rare examples of stable cyclopropenes with electron withdrawing (resonance stabilizing) groups at the vinyl positions. Some fluoride-induced trapping experiments also were briefly explored.

We recently reported the synthesis of 3-methyl-3-trimethylsilylcyclopropene[5] and attempted to adapt this strategy to the preparation of 3-phenyl-3-trimethylsilylcyclopropene. The key cyclization step involving the reaction of (*Z*)-3-chloro-1-phenyl-1-trimethylsilylpropene with sodium amide, however, failed to produce the desired compound (eqn. 1). An alternative method, the base-induced elimination of hydrogen bromide from 1-bromo-2-phenyl-2-trimethylsilylcyclopropane with *t*-BuOK–DMSO, LDA–THF or *t*-BuOK under heterogeneous conditions also was unsuccessful (eqn. 2).[6]

The successful synthesis of 3-(*p*-tolyl)-3-trimethylsilylcyclopropene (**1a**) and 3-(4-trifluoromethylphenyl)-3-trimethylsilylcyclopropene (**1b**) was carried out as shown in Scheme 1. Conversion of the known aryl trimethylsilyl ketones (**3**)[7] to their diazo compounds (**4**) was accomplished *via* their toluene-*p*-sulfonyl hydrazones in overall yields of 65 and 74%.[8,9] Photolysis of the aryl (trimethylsilyl)diazomethanes in a large excess of bis(trimethylsilyl)acetylene led to the 3-aryl-1,2,3-tris(trimethylsilyl)cyclopropenes (**5**) in 56 and 65% yields. Since the vinyl hydrogens in a cyclopropene are much more acidic than the allylic ones (pK_a ~29 *vs.* 61),[10] treatment of **5** with 2 equivalents of tetra-*n*-butylammonium fluoride (TBAF) selectively desilylated the trimethylsilyl groups at the vinyl positions to afford the target compounds in 75 and 70% yields.[11]



Scheme 1

In the purification of **1a** and **1b** by preparative gas chromatography, isomerization and dimerization occurred on a SE-30 column at 160 °C. The resulting products were found to be 3-(trimethylsilyl)indene derivatives (**6**) and tricyclo[3.1.0.0^{2,4}]hexane dimers (**7**) based upon spectroscopic analysis (^{1}H and ^{13}C NMR as well as HRMS). Isomerization of cyclopropenes into

† ^{1}H NMR spectra are available as supplementary data available from BLDSC (SUPPL. NO. 57535, pp. 15) or the RSC Library. See Instructions for Authors available *via* the RSC web page (http:www.rsc.org/authors).

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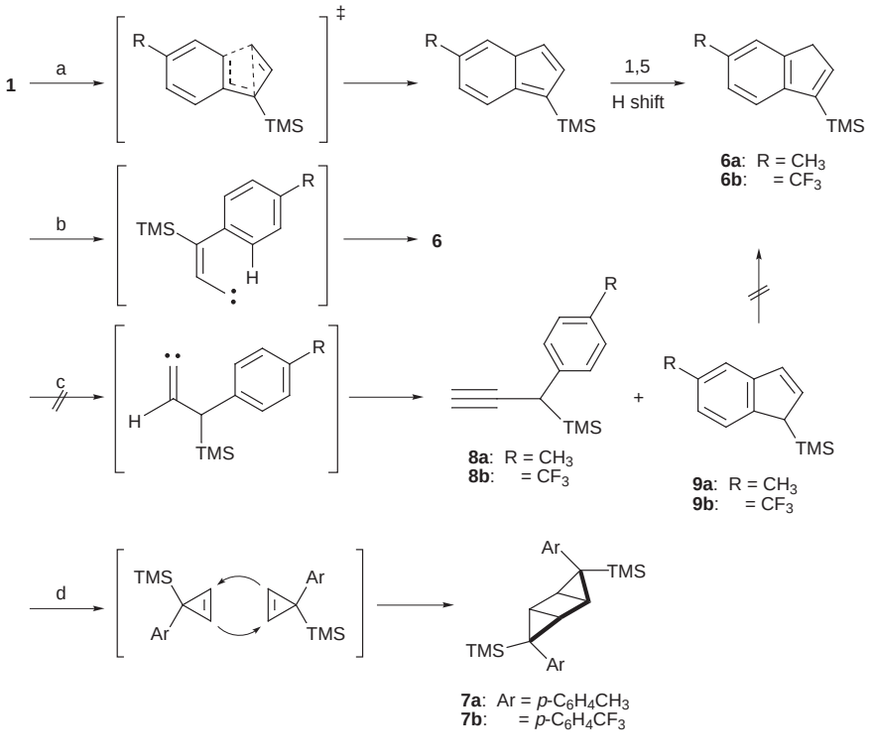
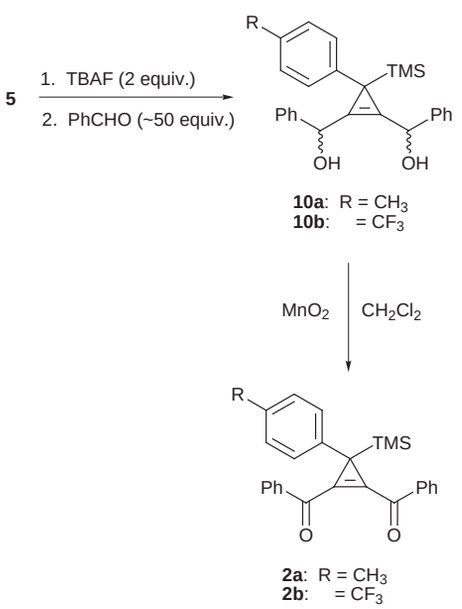


Scheme 2

indenes is a well-known transformation which can be effected by acid, heat or irradiation.[12] This pathway is analogous to the vinylcyclopropane–cyclopentene rearrangement and may occur *via* a concerted reaction (Scheme 2, pathway a).[13] The intermediacy of a vinylcarbene in a thermal process has been established in at least one case,[14] so a stepwise process (pathway b) is also quite possible. Strong evidence for vinylidenes in the thermolysis of cyclopropenes has been reported as well.[15] Apparently, this intermediate is not formed in this case to any appreciable extent (pathway c) since it would be expected to lead to 3-aryl-3-(trimethylsilyl)propynes (**8**) and 1-(trimethylsilyl)indenes (**9**), neither of which was obtained. A control experiment also indicated that **9** (R = H)[16] does not isomerize to **6** (R = H) on the GC column at 160 °C.

A [2 + 2] cyclization (pathway d in Scheme 2) leads to the other thermolysis product (**7**). This type of dimerization is known to be thermodynamically favorable because the cycloaddition across the cyclopropene double bonds reduces the ring strain of the system by about 26 kcal mol^{-1}.[17] Zeolites, Lewis acids and transition metal complexes can effectively catalyze this process which presumably occurs in a stepwise manner.[18] The NMR spectra of **7** indicate that they have magnetically equivalent aryl and trimethylsilyl groups. This is insufficient information to assign the stereochemistry of the product, but since every tricyclo[3.1.0.$0^{2,4}$]hexane derivative whose structure has been determined to date is *anti* (undoubtedly, because the *syn* isomer is much more strained),[19] we infer that **7** is *anti* as well. As for the arrangement of the aryl and trimethylsilyl substituents, the latter group is larger and should occupy both equatorial (*exo*) positions. This assignment is in accord with an X-ray crystal structure of 3-ethoxycarbonyl-3-trimethylsilylcyclopropene dimer in which the trimethylsilyl groups occupy the *exo* positions.[20]

Introduction of strong electron withdrawing groups on to cyclopropene derivatives potentially can lead to stabilized cyclopropenyl anion precursors.[21] In this regard, both 1,2,3-tris(trimethylsilyl)cyclopropenes (**5**) are of interest as they can be converted into their 1,2-dibenzoyl derivatives.[22] This was accomplished by reacting cyclopropenes **5a** and **5b** with TBAF in the presence of a large excess (~50 equiv.) of benzaldehyde in anhydrous THF (Scheme 3). The resulting diols (**10**) were

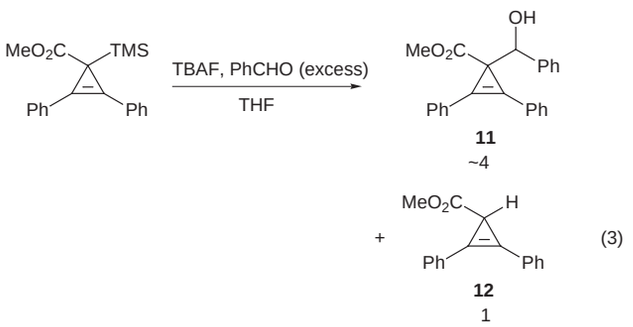


Scheme 3

formed as a mixture of four diastereomers in 42 and 44% yields. Subsequent oxidation with activated manganese dioxide cleanly provided the desired dibenzoyl cyclopropenes (**2**) in yields of 65 and 82%. 1,2-Dibenzoyl-3-methyl-3-trimethylsilylcyclopropene recently was shown to undergo a concerted retro-ene reaction ($\Delta H^{\ddagger} = 18.4 \pm 0.6$ kcal mol^{-1}, $\Delta S^{\ddagger} = -24.7 \pm 1.8$ e.u. in toluene),[5] and readily isomerized ($t_{1/2} \sim 3$ h) at 70 °C. In contrast, the aryl analogues **2a** and **2b** can not rearrange *via* this pathway, and only slowly decompose to unidentified products at 125 °C in xylene. These compounds are rare examples of room temperature stable cyclopropenes which have two resonance stabilizing substituents at the vinyl positions.

Unfortunately, the TBAF mediated desilylation of **2** in the presence of a large excess of benzaldehyde did not afford the desired alcohols. Unidentified products were obtained instead, presumably, because **2** undergoes a facile Michael addition. If one uses poorer Michael acceptors at the vinyl positions as in

1,2,3-triphenyl-3-trimethylsilylcyclopropene, no reaction occurs at room temperature and only protonolysis is observed under forcing conditions.[3a,6] In order to successfully trap a putative cyclopropenyl anion with benzaldehyde a delicate balance must be struck between stabilizing the incipient negative charge and activating the cyclopropene double bond to nucleophilic attack. 3-Methoxycarbonyl-3-trimethylsilylcyclopropene[20] is not reactive enough, but its 1,2-diphenyl derivative gives a good yield (78%) of the addition product (**11**, eqn. 3) along with a



(3)

small amount of the protodesilylated material (**12**) in a ratio of *ca*. 4 : 1. These results suggest that it will be difficult to generate a stable cyclopropenyl anion *via* a TBAF-induced desilylation. More aggressive (and anhydrous) sources of fluoride, however, are worth exploring. Studies along these lines are underway and will be reported in due course.

Experimental

General methods

All glassware was soaked in a base bath (KOH–isopropyl alcohol) for at least 12 h, washed with water and either oven dried or flame dried prior to use. Solvents and reagents were dried and purified using standard non-acidic methods. Boiling points given for materials distilled under argon or nitrogen are uncorrected for differences in atmospheric pressure.

Nuclear magnetic resonance (NMR) spectra were recorded with a Varian VXR-300, Unity 500, or Bruker AC300 spectrometer and are reported in ppm (δ). Infrared spectra were obtained with a Mattson Instruments Polaris FT-IR spectrometer and are reported in wavenumbers (cm^{-1}). High resolution mass spectra were recorded on a Finnigan MAT 95 mass spectrometer or a Finnigan 2001-DD FTMS. Preparative gas chromatography was carried out on a Varian 700 Aerograph chromatograph with helium as the carrier gas.

p-Tolyl trimethylsilyl ketone tosylhydrazone[9]

4-Methylbenzoyltrimethylsilane (**3a**, 14.0 g, 0.073 mol)[7] in 10 mL of methanol was added to a suspension of toluene-*p*-sulfonyl hydrazide (13.5 g, 0.073 mol) in 25 mL of methanol. The mixture was stirred for 1 h at 45 °C and then cooled to −10 °C. The solid product was filtered and washed with a small amount of cold methanol to give 25.6 g (97%) of the hydrazone as a white solid: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.75 (d, 2 H, J = 8.1 Hz), 7.65 (br s, 1 H), 7.28 (d, 2 H, J = 8.1 Hz), 7.17 (d, 2 H, J = 8.1 Hz), 6.72 (d, 2 H, J = 8.1 Hz), 2.41 (s, 3 H), 2.31 (s, 3 H), 0.07 (s, 9 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 168.8 (s), 143.9 (s), 138.7 (s), 135.5 (s), 131.4 (s), 130.2 (d), 129.4 (d), 127.9 (d), 125.8 (d), 21.6 (q), 21.2 (q), −2.3 (q); IR (KBr) 3195, 3064, 3044, 2964, 1915, 1669, 1598, 1497, 1402, 1330, 1158, 1094, 850, 813, 684 cm^{-1}.

(*p*-Tolyl)trimethylsilyldiazomethane 4a[9]

The requisite hydrazone (25.0 g, 0.069 mol) in 500 mL of anhydrous THF was cooled to 0 °C and then 27.6 mL of 2.5 M *n*-BuLi (0.069 mol) was slowly added. The reaction mixture was filtered after being stirred in the dark at room temperature for 2 days. Ether was added to the filtrate which was then washed with water and dried over anhydrous magnesium sulfate ($MgSO_4$). Evaporation of the solvent gave a red oil which provided 9.1 g (67%) of the diazo compound after vacuum distillation: bp 58–61 °C (0.2 mm); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.12 (dm, 2 H, J = 8.2 Hz), 6.93 (dt, 2 H, J = 8.4 and 1.8 Hz), 2.33 (s, 3 H), 0.36 (s, 9 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 132.9 (s), 130.0 (s), 129.8 (s), 129.7 (d), 122.9 (d), 20.9 (q), −0.93 (q); IR (neat) 3023, 2959, 2928, 2038, 1610, 1565, 1509, 1284, 1253, 1176, 941, 843, 808 cm^{-1}; HRMS-EI M^+ Calcd for $C_{11}H_{16}N_2Si$ 204.1083, Found 204.1085; $(M - N_2)^+$ Calcd for $C_{11}H_{16}Si$ 176.1022, Found 176.1016.

4-Trifluoromethylphenyl trimethylsilyl ketone tosylhydrazone[8,9]

The procedure for the synthesis of *p*-tolyl trimethylsilyl ketone tosylhydrazone was followed. In this case, 3.75 g (0.02 mol) of toluene-*p*-sulfonyl hydrazide in 10 mL of methanol and 5.1 g (0.02 mol) of [4-(trifluoromethyl)benzoyl]trimethylsilane in 6 mL of methanol were used, and the reaction mixture was stirred for 1.5 h at 45 °C before being cooled to −10 °C. An 87% yield (7.2 g) of the desired hydrazone was achieved: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.76 (d, 2 H, J = 8.09 Hz), 7.65 (d, 2 H, J = 8.2 Hz), 7.31 (d, 2 H, J = 8.01 Hz), 7.00 (d, 2 H, J = 8.08 Hz), 3.4 (s, 1 H), 2.44 (s, 3 H), 0.09 (s, 9 H); ^{19}F NMR (282 MHz, $CDCl_3$, $CFCl_3$ = δ 0.00) δ −63.3 (s); ^{13}C NMR (75 MHz, $CDCl_3$) δ 166.6 (s), 144.2 (s), 138.5 (s), 135.3 (s), 130.8 (s; q, $^2J_{C-F}$ = 32.6 Hz), 129.5 (d), 127.9 (d), 126.6 (d), 126.5 (d; q, $^3J_{C-F}$ = 3.0 Hz), 123.6 (s; q, $^1J_{C-F}$ = 272.2 Hz), 21.6 (q), −2.5 (q); IR (KBr) 3188, 3065, 2955, 2894, 1616, 1406, 1384, 1328, 1252, 1160, 1126, 1068, 870, 848, 680 cm^{-1}.

(4-Trifluoromethylphenyl)trimethylsilyldiazomethane 4b[8,9]

An LDA solution (0.0156 mol in 40 mL of anhydrous THF) was prepared at −10 °C by reacting 6.24 mL of 2.5 M *n*-BuLi with 2.3 mL of diisopropylamine. The resulting solution was transferred to an addition funnel and was added dropwise under nitrogen at −78 °C to 6.5 g (0.0156 mol) of the appropriate hydrazone in 100 mL of anhydrous THF. After 3 h the mixture was allowed to warm to room temperature and the solvent was removed under reduced pressure. The solid residue was heated to 100 °C at a pressure of 0.2 mm and 3.4 g (85%) of the diazomethane was obtained as a red oil: bp 60–62 °C (0.2 mm); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.52 (d, 2 H, J = 8.4 Hz), 7.08 (d, 2 H, J = 8.4 Hz), 0.38 (s, 9 H); ^{19}F NMR (282 MHz, $CDCl_3$, $CFCl_3$ = δ 0.00) δ −62.53 (s); ^{13}C NMR (75 MHz, $CDCl_3$) δ 138.6 (s), 125.8 (d; q, $^3J_{C-F}$ = 3.6 Hz), 125.0 (s; q, $^2J_{C-F}$ = 32.5 Hz), 124.4 (s; q, $^1J_{C-F}$ = 271 Hz), 122.5 (d), 120.9 (s), −1.06 (q); IR (neat) 2964, 2049, 1612, 1515, 1414, 1331, 1284, 1256, 1165, 1119, 1070, 1012, 941, 842, 756 cm^{-1}; HRMS-EI M^+ Calcd for $C_{11}H_{13}F_3N_2Si$ 258.0800, Found 258.0807, $(M - N_2)^+$; Calcd for $C_{11}H_{13}F_3Si$ 230.0739, Found 230.0734.

Bis(trimethylsilyl)acetylene

A 2.5 M solution of *n*-BuLi (40.8 mL, 0.102 mol) was added dropwise to 10 g (0.102 mol) of trimethylsilylacetylene[23] in 200 mL of anhydrous THF at −78 °C. The reaction was stirred for 40 min at −78 °C and then 15.4 mL (1.2 equiv.) of TMSCl was slowly added. The resulting mixture was stirred for an additional 1 h at −78 °C before allowing it to slowly warm up to room temperature. HCl (50 mL 1 M) and then 100 mL of water were used to quench the reaction, subsequently, the aqueous layer was extracted with pentane (3 × 100 mL). The combined organic material was washed with water (10 × 60 mL) and dried over anhydrous $MgSO_4$. Fractional distillation provided 15.6 g (90%) of the disubstituted acetylene: ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.16 (s); ^{13}C NMR (75 MHz, $CDCl_3$) δ 113.7 (s), −0.06 (q); IR (neat) 2962, 2901, 1409, 1251, 1033, 842 cm^{-1}.

3-(*p*-Tolyl)-1,2,3-tris(trimethylsilyl)cyclopropene 5a

Bis(trimethylsilyl)acetylene (27 g, 0.159 mol) was combined with 0.9 g (4.4 mmol) of (*p*-tolyl)trimethylsilyldiazomethane and the solution was degassed with nitrogen before being irradiated at room temperature with a 450 W slide projection lamp for 1 day. Infrared spectroscopy was used to monitor the progress of the reaction and when **4a** was consumed the excess bis(trimethylsilyl)acetylene was removed by distillation under reduced pressure (~20 mm) at ~70 °C. The remaining material was chromatographed on a silica gel column using pentane as the eluting solvent to afford 0.84 g (56%) of the cyclopropene as a liquid: ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.98 (br m, 4 H), 2.28 (s, 3 H), 0.18 (s, 18 H), 0.008 (s, 9 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 147.8 (s), 135.9 (s), 130.2 (s), 128.4 (d), 127.5 (d), 37.1 (s), 20.9 (q), −0.34 (q), −0.39 (q); IR (neat) 3048, 2957, 2896, 1885, 1724, 1508, 1406, 1248, 893, 838, 756 cm^{-1}; HRMS-CI (isobutane) M^+ Calcd for $C_{19}H_{34}Si_3$ 346.1968, Found 346.1988; $M + H^+$ Calcd for $C_{19}H_{35}Si_3$ 347.2047, Found 347.2031.

3-(*p*-Tolyl)-3-trimethylsilylcyclopropene 1a

3-(*p*-Tolyl)-1,2,3-tris(trimethylsilyl)cyclopropene (0.15 g, 0.43 mmol) was dissolved in 8 mL of anhydrous THF under an argon atmosphere and 1.53 mL (3 equiv.) of 1 M TBAF in THF was added to it at room temperature. The solution quickly changed to a dark reddish color and was stirred for an additional 20 min before being quenched with water. The product was extracted with pentane (3 × 15 mL) and the combined organic material was washed with water and dried over anhydrous $MgSO_4$. Removal of the solvent with a rotary evaporator at ~0 °C was followed by column chromatography (pentane) to yield 0.066 g of **1a** (75%) as a liquid: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.38 (s, 2 H), 7.05 (br s, 4 H), 2.31 (s, 3 H), 0.004 (s, 9 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 146.4 (s), 134.4 (s), 128.9 (d), 127.5 (d), 113.6 (d), 20.9 (q), 18.0 (s), −1.54 (q); IR (neat) 3104, 3028, 2955, 2923, 2854, 1656, 1510, 1454, 1247, 1108, 837, 735 cm^{-1}; HRMS-EI M^+ Calcd for $C_{13}H_{18}Si$ 202.1177, Found 202.1162.

1,2-Dibenzoyl-3-(*p*-tolyl)-3-trimethylsilylcyclopropene 2a

To a solution of 0.28 g (0.8 mmol) of **5a** and 4.5 g (42 mmol) of benzaldehyde in 12 mL of anhydrous THF was added 2.4 mL (3 equiv.) of 1 M tetra-*n*-butylammonium fluoride (TBAF) at room temperature under an argon atmosphere. The reaction mixture was stirred for an additional 6 h, quenched with water, and extracted with ether (3 × 20 mL). The combined organic material was washed with water, dried over anhydrous magnesium sulfate, and concentrated under reduced pressure to afford the crude diol (**10a**). Purification by column chromatography (100% hexane to 80% hexane and 20% ether) gave 0.14 g (42%) of the desired product as a mixture of three diastereomers. The individual compounds were not separated, and the mixture of diols was used for the subsequent oxidation.

Dichloromethane (10 mL) and 0.1 g of **10a** was treated with 0.42 g (20 equiv.) of activated MnO_2 at 0 °C under an argon atmosphere. The resulting heterogeneous solution was stirred for an additional 40 min at 0 °C and then was filtered through a plug of silica gel. Removal of the solvent under reduced pressure gave the crude dibenzoyl cyclopropene which was purified by chromatography using a silica gel column (100% hexane to 95% hexane and 5% ether) to yield 0.06 g (60%) of **2a** as a yellow oil: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.95 (dd, 4 H, J = 8.5 Hz and 1.5 Hz), 7.54 (tt, 2 H, J = 7.5 Hz and 1.5 Hz), 7.37 (dd, 4 H, J = 8.5 Hz and 7.5 Hz), 7.31 (d, 2 H, J = 8.5 Hz), 7.10 (d, 2 H, J = 8.5 Hz), 2.32 (s, 3 H), 0.15 (s, 9 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 185.3 (s), 141.6 (s), 135.99 (s), 135.95 (s), 134.2 (d), 129.4 (d), 129.3 (d), 128.7 (d), 128.4 (d), 127.9 (s), 37.9 (s), 21.2 (q), −1.29 (q); HRMS-CI (isobutane) M^+ Calcd for $C_{27}H_{26}O_2Si$ 410.1701, Found 410.1694.

3-(4-Trifluoromethylphenyl)-1,2,3-tris(trimethylsilyl)cyclopropene 5b

The procedure for the synthesis of **5a** was followed. In this case, 0.7 g (2.7 mmol) of **4b** in 26 g of bis(trimethylsilyl)acetylene was irradiated for 23 h to afford 0.71 g (65%) of the desired cyclopropene: bp 85–88 °C (0.1 mm); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.43 (d, 2 H, J = 8.4 Hz), 7.18 (d, 2 H, J = 8.4 Hz), 0.20 (s, 18 H), 0.054 (s, 9 H); ^{19}F NMR (282 MHz, $CDCl_3$, $CFCl_3 = \delta$ 0.00) δ −62.3 (s); ^{13}C NMR (75 MHz, $CDCl_3$) δ 155.7 (s), 134.6 (s), 127.4 (d), 126.0 (s; q, $^2J_{C-F}$ = 32.3 Hz§), 124.7 (s; q, $^1J_{C-F}$ = 271.6 Hz), 124.5 (d; q, $^3J_{C-F}$ = 3.6 Hz), 21.0 (s), −0.31 (q), −0.48 (q); IR (neat) 3069, 2957, 2900, 1885, 1730, 1612, 1407, 1328, 1164, 1123, 1069, 1016, 843 cm^{-1}; HRMS-CI (isobutane) M^+ Calcd for $C_{19}H_{31}F_3Si_3$ 400.1685, Found 400.1670; $M + H^+$ Calcd for $C_{19}H_{32}F_3Si_3$ 401.1764, Found 401.1721.

3-(4-Trifluoromethylphenyl)-3-trimethylsilylcyclopropene 1b

The procedure for the synthesis of **1a** was followed. In this case, 0.2 g (0.5 mmol) of **5b** in 9 mL of THF and 1 mL (2 equiv.) of 1.0 M TBAF were used, and 0.09 g (70%) of liquid cyclopropene was obtained: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.47 (d, 2 H, J = 8.0 Hz), 7.40 (s, 2 H), 7.21 (d, 2 H, J = 8.0 Hz), −0.007 (s, 9 H); ^{19}F NMR (282 MHz, $CDCl_3$, $CFCl_3 = \delta$ 0.00) δ −62.57 (s); ^{13}C NMR (75 MHz, $CDCl_3$) δ 153.8 (s), 127.9 (d), 127.2 (s; q, $^2J_{C-F}$ = 32.3 Hz), 125.1 (d; q, $^3J_{C-F}$ = 3.6 Hz), 124.5 (s; q, $^1J_{C-F}$ = 271.6 Hz), 113.2 (d), 18.8 (s), −1.68 (q); IR (neat) 3116, 2959, 2899, 1647, 1613, 1406, 1326, 1250, 1164, 1124, 1066, 1014, 943, 840 cm^{-1}; HRMS-CI (isobutane) M^+ Calcd for $C_{13}H_{15}F_3Si$ 256.0895, Found 256.0906; $M + H^+$ Calcd for $C_{13}H_{16}F_3Si$ 257.0973, Found 257.0927.

1,2-Dibenzoyl-3-(4-trifluoromethylphenyl)-3-trimethylsilylcyclopropene 2b

The procedure for the synthesis of **2a** was followed. In this case, a solution of 0.32 g (0.8 mmol) of **5b** and 4.5 g of benzaldehyde (42 mmol) in 12 mL of THF was treated with 1.4 mL (2 equiv.) of 1 M TBAF. The resulting diol (**10b**) was obtained as a mixture of three diastereomers in a 44% yield (0.11 g). After MnO_2 oxidation of **10b**, 0.09 g (82%) of **2b** was realized as a yellow oil: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.90 (m, 4 H), 7.56–7.53 (m, 6 H), 7.36 (m, 4 H), 0.15 (s, 9 H); ^{19}F NMR (282 MHz, $CDCl_3$, $CFCl_3 = \delta$ 0.00) δ −62.79 (s); ^{13}C NMR (75 MHz, $CDCl_3$) δ 184.9 (s), 148.9 (s), 135.7 (s), 134.5 (d), 129.3 (d), 129.0 (d), 128.8 (d), 128.6 (s; q, $^2J_{C-F}$ = 32.4 Hz), 126.6 (s), 125.6 (d; q, $^3J_{C-F}$ = 3.6 Hz), 124.3 (s; q, $^1J_{C-F}$ = 272.2 Hz), 37.3 (s), −1.49 (q); IR (neat) 3062, 2961, 2934, 1795, 1642, 1614, 1598, 1580, 1450, 1326, 1252, 1165, 1125, 1067, 845 cm^{-1}; HRMS-CI (isobutane) M^+ Calcd for $C_{27}H_{23}F_3O_2Si$ 464.1419; Found 464.1419.

Thermal isomerization and dimerization of 1a and 1b

The cyclopropenes were injected into a preparative gas chromatograph on to a 10% SE-30 on Chrom W column at 160 °C. Two main products, an indene and a dimer, were obtained. Intramolecular isomerization afforded the solid indene, which eluted in 15 min. The intermolecular [2 + 2] cyclization dimer was attained as a white solid after trapping the effluent for about 12 h. A small amount of **1b** also was recovered after 10 min, whereas **1a** was completely consumed under the same conditions.

6-Methyl-3-trimethylsilylindene 6a

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.37 (d, 1 H, J = 7.5 Hz), 7.32 (br s, 1 H), 7.10 (d, 1 H, J = 7.5 Hz), 6.69 (t, 1 H, J = 1.8 Hz), 3.38 (m, 2 H), 2.39 (s, 3 H), 0.29 (s, 9 H); ^{13}C NMR (75 MHz,

§ Quaternary carbon (s) split by fluorine into a quartet.

$CDCl_3$) δ 145.4 (s), 145.0 (s), 144.9 (s), 143.1 (d), 133.9 (s), 126.8 (d), 124.7 (d), 121.5 (d), 40.5 (t), 21.4 (q), −1.1 (q); IR (neat) 3024, 3005, 2957, 2897, 1731, 1611, 1472, 1387, 1249, 1106, 1035, 985, 838 cm^{-1}; HRMS-CI (isobutane) M^+ Calcd for $C_{13}H_{18}Si$ 202.1177, Found 202.1175.

anti-3,6-Bis(4-methylphenyl)-3,6-bis(trimethylsilyl)tricyclo-[3.1.0.0^{2,4}]hexane (7a)

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.05 (br s, 8 H), 2.32 (s, 6 H), 1.44 (s, 4 H), −0.31 (s, 18 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 137.7 (s), 133.7 (s), 130.1 (d), 128.2 (d), 38.2 (s), 27.3 (d), 21.1 (q), −3.2 (q); IR (KBr) 3032, 2958, 1617, 1509, 1385, 1248, 1102, 1066, 978, 876, 834 cm^{-1}; HRMS-CI (isobutane) M^+ Calcd for $C_{26}H_{36}Si_2$ 404.2355; Found 404.2353.

6-Trifluoromethyl-3-trimethylsilylindene (6b)

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.74 (br s, 1 H), 7.55–7.54 (d, 2 H, J = 0.9 Hz), 6.92 (t, 1 H, J = 1.9 Hz), 3.48 (dd, 2 H, J = 1.8 Hz and 0.9 Hz), 0.32 (s, 9 H); ^{19}F NMR (282 MHz, $CDCl_3$, $CFCl_3 = \delta$ 0.00) δ −61.84 (s); ^{13}C NMR (75 MHz, $CDCl_3$) δ 151.4 (s), 146.8 (d), 144.9 (s), 126.5 (s), 126.4 (s; q, $^2J_{C-F}$ = 31.8 Hz), 124.9 (s; q, $^1J_{C-F}$ = 271.6 Hz), 123.5 (d; q, $^3J_{C-F}$ = 3.7 Hz), 121.7 (d), 120.4 (d; q, J_{C-F} = 4.3 Hz), 40.8 (t), −1.23 (q); IR (KBr) 2972, 2963, 1625, 1432, 1385, 1334, 1279, 1249, 1155, 1113, 1059, 887, 838 cm^{-1}; HRMS-EI M^+ Calcd for $C_{13}H_{15}F_3Si$ 256.0895, Found 256.0896.

anti-3,6-Bis(4-trifluoromethylphenyl)-3,6-bis(trimethylsilyl)-tricyclo[3.1.0.0^{2,4}]hexane (7b)

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.53 (d, 4 H, J = 8.4 Hz), 7.27 (d, 4 H, J = 8.4 Hz), 1.51 (s, 4 H), −0.29 (s, 18 H); ^{19}F NMR (282 MHz, $CDCl_3$, $CFCl_3 = \delta$ 0.00) δ −62.48 (s); ^{13}C NMR (75 MHz, $CDCl_3$) δ 145.3 (s), 130.3 (d), 127.1 (s; q, $^2J_{C-F}$ = 32.4 Hz), 124.7 (d; q, $^3J_{C-F}$ = 3.6 Hz), 124.6 (s; q, $^1J_{C-F}$ = 271.6 Hz), 46.6 (s), 27.6 (d), −3.3 (q); IR (KBr) 3039, 3023, 2963, 2904, 1616, 1409, 1325, 1272, 1250, 1165, 1117, 1067, 1016, 980, 874, 845 cm^{-1}; HRMS-CI (isobutane) M^+ Calcd for $C_{26}H_{30}F_6Si_2$ 512.1790, Found 512.1782.

3-Methoxycarbonyl-1,2-diphenyl-3-trimethylsilylcyclopropene

Diphenylacetylene (5.65 g, 31.7 mmol) and Rh(II) octanoate (30 mg) were heated to 150 °C under nitrogen with stirring. Methyl trimethylsilyldiazoacetate[24] (5.8 g, 33 mmol) was added to the acetylene solution *via* a syringe pump at a rate of 0.74 mL h^{-1}. The disappearance of the diazo compound was monitored by IR spectroscopy. After 30 h the heat was removed and the reaction was allowed to cool to room temperature. The product was separated by flash column chromatography using hexane and dichloromethane (100% hexane to 80% hexane and 20% CH_2Cl_2) as the eluting solvents. After recrystallization from hexane, 0.94 g (9%) of the pure cyclopropene was obtained: mp 126–127 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.65 (d, 4 H, J = 7.9 Hz), 7.46 (t, 4 H, J = 7.5 Hz), 7.36 (t, 2 H, J = 7.5 Hz), 3.66 (s, 3 H), 0.14 (s, 9 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 176.9 (s), 129.7 (d), 128.9 (d), 128.7 (d), 127.6 (s), 109.8 (s), 51.5 (q), 23.2 (s), −0.6 (q); IR (KBr) 3186, 2955, 1695, 1490, 1446, 1435, 1395, 1242, 1067, 920, 845, 753, 688 cm^{-1}; HRMS-CI (isobutane) M^+ Calcd for $C_{20}H_{22}O_2Si$ 322.1388, Found 322.1384.

Fluoride-induced desilylation of 3-methoxycarbonyl-1,2-diphenyl-3-trimethylsilyl-cyclopropene

3-Methoxycarbonyl-1,2-diphenyl-3-trimethylsilylcyclopropene (70 mg, 0.22 mmol) and benzaldehyde (1.7 g, 16 mmol) in 3 mL of anhydrous THF was treated with 1.1 mL of 1 M TBAF in THF. After the starting material had been consumed, the reaction was quenched with water and the aqueous layer was extracted with ether. The combined ethereal solution was washed with water, dried over anhydrous magnesium sulfate, and concentrated *in vacuo*. After column chromatography (100% hexane to 80% hexane and 20% dichloromethane) 60 mg (78%) of 3-methoxycarbonyl-3-[phenyl(hydroxy)methyl]-1,2-diphenylcyclopropene (**11**) was obtained: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.68 (dm, 2 H, J = 8.0 Hz), 7.49–7.33 (m, 8 H), 7.13 (dm, 2 H, J = 8.0 Hz), 7.05 (m, 3 H), 5.77 (d, 1 H, J = 4.5 Hz), 3.76 (d, 1 H, J = 4.5 Hz), 3.63 (s, 3 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 176.2 (s), 141.1 (s), 130.3 (d), 129.7 (d), 129.4 (d), 129.2 (d), 128.8 (d), 128.7 (d), 127.7 (d), 127.2 (d), 127.1 (s), 126.8 (d), 126.6 (s), 110.2 (s), 108.7 (s), 75.7 (d), 52.1 (q), 38.1 (s); IR (KBr) 3463, 3020, 2951, 2913, 2913, 1698, 1495, 1446, 1433, 1396, 1266, 1177, 1060, 1023, 758 cm^{-1}; HRMS (MALDI, DHBA matrix) $(M + Na)^+$ Calcd for $C_{24}H_{20}O_3Na$ 379.1305, Found 379.1307. 3-Methoxycarbonyl-1,2-diphenyl-cyclopropene (**12**) was also obtained as a minor product: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.69 (dm, 4 H, J = 7.2 Hz), 7.48 (tm, 4 H, J = 7.5 Hz), 7.40 (tm, 2 H, J = 7.5 Hz), 3.71 (s, 3 H), 2.84 (s, 1 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 175.4 (s), 130.0 (d), 129.4 (d), 128.9 (d), 127.0 (s), 107.5 (s), 51.8 (q), 21.4 (d); HRMS (EI) M^+ Calcd for $C_{17}H_{14}O_2$ 250.0993, Found 250.0982.

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