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Silicon in Organic Synthesis. 24. Preparation and Selected Reactions of Functionalized 1-(Trimethylsilyl)-Substituted Cyclopropanes[1]

Gregory J. Wells, Tu-Hsin Yan, and Leo A. Paquette*

Evans Chemical Laboratories, The Ohio State University, Columbus, Ohio 43210

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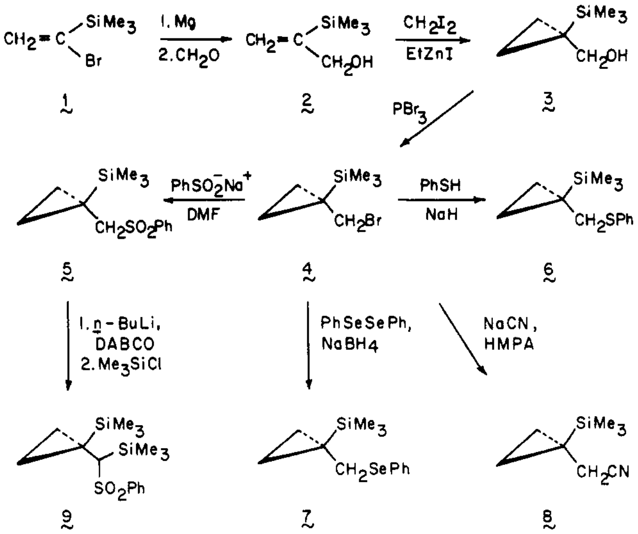
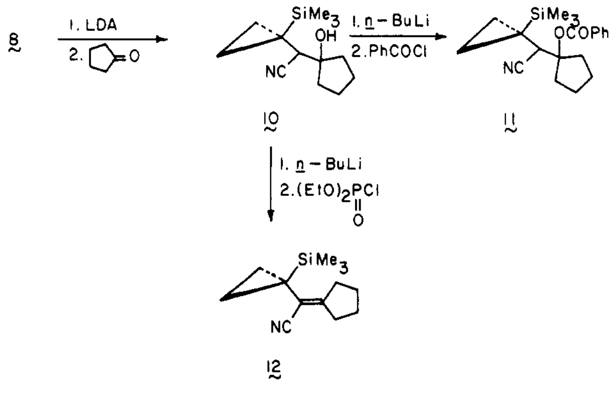
Several methods for preparing bifunctional 1-(trimethylsilyl)-substituted cyclopropanes are described. The methyl bromide **4**, available by Simmons–Smith cyclopropanation of **2** and bromination with phosphorus tribromide, is shown to be highly reactive to S_N2 displacement and therefore easily transformed into a variety of other derivatives including the phenyl sulfide, phenyl sulfone, nitrile, and phenyl selenide. Ring-closure protocols have been applied to gain access to the triphenylphosphonium salt, phosphonate ester, and carboxaldehyde (**22**). The dimethyl acetal **23** of this aldehyde gives every indication of being an excellent conjunctive reagent as exemplified by its conversion to **24**, **26**, and **30**. Reactive anions of type A (X = SO_2Ph, SPh, SePh, CN) have been generated and in certain cases utilized for additional chemical transformations.

Recent reports from these laboratories have described several synthetic[2-4] and physical–organic studies[5,6] involving silylcyclopropanes. In line with the recent general upsurge of interest in varied applications of organosilicon reagents,[7] the boundaries of our previously limited knowledge of silyl-substituted small-ring compounds[8] have begun to expand. The efficient preparation of this class of molecules remains, as always, the fundamental cornerstone of their broad-scale utilization. As a small contribution to this technology, we describe here synthetic approaches to a number of functionalized 1-(trimethylsilyl)cyclopropanes with the intent of illustrating their ready accessibility. Some chemical transformations of selected structures are also included to emphasize further their potential usefulness in molecular construction.

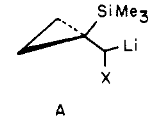
Scheme I



Scheme II



Displacement Reactions of [1-(Trimethylsilyl)-cyclopropyl]methyl Bromide. The addition of functionalized organolithium reagents to carbonyl compounds followed by reductive elimination comprises a large class of olefin-forming reactions whose most important characteristic is assurance of double-bond positional selectivity. The Wittig reaction[9] and its modifications[10] are the most well-known of these, but reactions involving silane,[11] sulfide,[12] sulfoxide,[13] sulfone,[14] selenide,[15] selenoxide,[16] and nitrile eliminations[17] have recently been developed. Thus, the availability of a selection of functionalized organolithium reagents of general formula A assumes specific interest. The transformations outlined in Scheme I, which can be easily realized, pertain to this particular synthon concept.



A

In order to arrive at carbinol **3**, the Grignard reagent of **1**[18] was condensed with gaseous formaldehyde to give **2**.[19]

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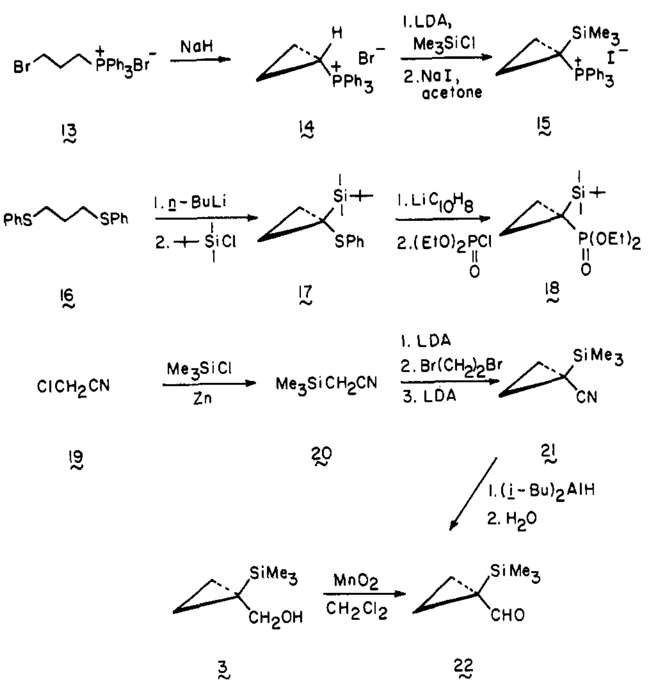
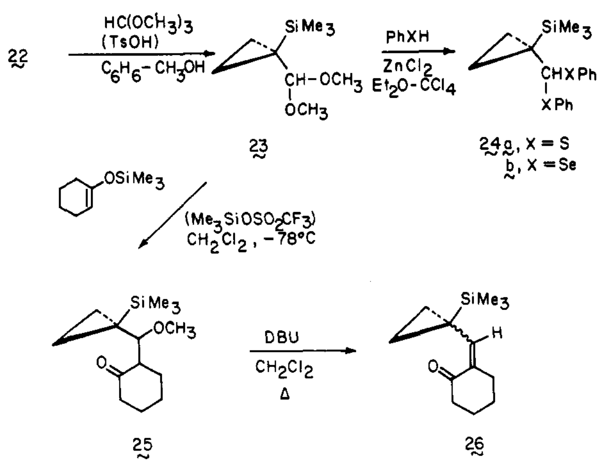
Scheme III



Scheme IV



This allylic alcohol smoothly underwent Simmons–Smith cyclopropanation when the modified form of this procedure which utilizes ethylzinc iodide[20] was applied. It is worth noting that no methyl ether formation was observed as in the case of the homoallylic alcohol.[4] Access to 4 was gained in 71% yield by reaction of 3 with phosphorus tribromide.[21]

Despite the neopentyl nature of the halogen-substituted carbon in 4, reaction with sodium benzenesulfinate in dimethylformamide[22] led quantitatively to 5. Because further deployment of 5 is dependent upon formation of the α-lithio species,[14] the sulfone was metalated with *n*-butyllithium in tetrahydrofuran solution containing Dabco. Quenching with chlorotrimethylsilane delivered 9 (90%), a possible precursor to vinyl sulfones of unusual structure.[23] Since additional displacement reactions on 4 involving thiophenoxide, phenyl selenoxide, and cyanide ion also proceeded in very good to excellent yield, it appears that this bromide is a respectable electrophilic reagent.

Condensation of the anion of 8 with cyclopentanone afforded cyanohydrin 10 (Scheme II). Presumably because of steric strain factors and the ready enolizability of a cyclopentanone, approximately 50% of 8 was recovered unchanged. Although 10 could be conveniently benzoylated as 11,[24] spontaneous dehydration occurred during attempted formation of the diethyl phosphate. It should be recognized that 12 so incorporates allylsilane and acrylonitrile functional groups that they work in electronic opposition.

Ring-Closure Processes. In view of the considerable interest which has developed in five-membered ring formation via nucleophilic attack on activated cyclopropanes with subsequent intramolecular ring closure,[26-31] we have ventured to prepare phosphonium salt 15 and phosphonate 18. These doubly activated three-carbon synthons might be expected to undergo regiospecific nucleophilic ring opening with concomitant generation of a reactive phosphorus ylide or phosphonate carbanion; subsequent cyclization completes the annulation process. It may prove necessary to contend with the possible lability of the C–Si bond in 15 toward nucleophilic attack, a phenomenon which should be less likely in the case of 18.

Preparation of these materials can be conveniently accomplished by the pathways outlined in Scheme III. Following synthesis of phosphonium salt 14 by the Schweizer procedure,[32] the derived ylide can be efficiently silylated (97%) to give the mixed halide salt. Exposure of this material to sodium iodide in acetone provided 15.

Synthetic entry to 18 is founded upon the readiness with which 16 undergoes cyclization to 1-lithio-1-(phenylthio)cyclopropane when treated with 2 equiv of *n*-butyllithium.[33] Direct addition[4] of *tert*-butyldimethylchlorosilane furnished 17. Reduction of this substrate with lithium naphthalenide[34] provided the α-silyl carbanion which was converted to 18 by condensation with diethyl chlorophosphate. In this instance, chromatography was necessary to separate naphthalene and other hydrocarbons from the more polar product. The overall yield of phosphonate from 16 was low because of the need for extensive purification after each of the two steps.

A different type of cyclization methodology was utilized to arrive at nitrile 21 and aldehyde 22. (Trimethylsilyl)-

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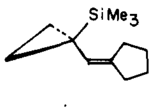
[24] Exposure of 11 to sodium or lithium in liquid ammonia[17] or to potassium in hexamethylphosphoramide[25] gave no i.



i

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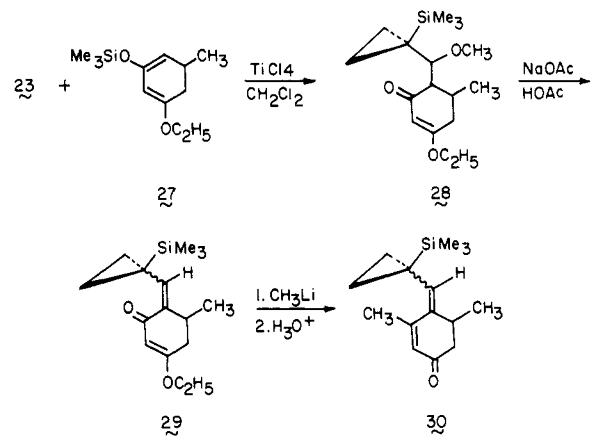
acetonitrile (**20**) is available by reductive coupling of chlorotrimethylsilane and chloroacetonitrile with zinc dust in refluxing benzene–tetrahydrofuran (1:1) solution.[35] Application of standard spirocyclopropanation methodology to this intermediate gave **21**. Best results (70%) were realized when **20** was treated sequentially with 1 equiv of lithium diisopropylamide, 1.5 equiv of 1,2-dibromoethane, and finally a second equivalent of lithium diisopropylamide. Diisobutylaluminum hydride reduction of **21** followed by hydrolysis of the resulting imine with dilute sulfuric acid gave **22**. The same aldehyde could be prepared by manganese dioxide oxidation[36] of **3**. However, whereas **22** obtained by the first method proved to be quite stable in air, samples produced oxidatively underwent quantitative air oxidation to the carboxylic acid at room temperature during 1–2 days. Trace amount of metal ions which persisted during purification are evidently responsible for this pronounced difference in shelf stability.

Derivatization of 1-(Trimethylsilyl)cyclopropanecarboxaldehyde. Rather surprisingly, direct condensation of aldehyde **22** with thiophenol[37] or benzeneselenol[38] afforded the desired products **24a** and **24b** only with low efficiency. However, when recourse was made to the exchange reaction[39] between dimethyl acetal **23** and thiophenol in the presence of ethereal zinc chloride, **24a** was obtained quantitatively. Under similar conditions, selenoacetal **24b** was produced in 80% yield (Scheme IV). Preliminary studies involving reductive lithiation of **24a** with lithium naphthalenide[33,34,40] have shown that formation of A (X = SPh) can be readily achieved. Quenching with water resulted in essentially complete conversion to **6**. Lithiation of **24b** with *n*-butyllithium in tetrahydrofuran at −78 °C[41] led similarly to **7** following protonation. Thus, A (X = SePh) can also be prepared without difficulty. The successful 1,2 addition of these anions to carbonyl compounds will require that steric hindrance and competitive enolization not interfere with C–C bond formation. This difficulty, which has surfaced in several other contexts,[42–44] does merit concern, at least until the proper experimental tests are applied.

In order to engage **22** in an exemplary crossed-aldol condensation, equimolar amounts of acetal **23** and 1-(trimethylsilyloxy)cyclohexene were admixed in the presence of 1–5 mol % of trimethylsilyl trifluoromethanesulfonate.[45] When adduct **25** (90%) was treated with 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) in refluxing dichloromethane containing molecular sieves,[46] β-elimination of methanol occurred to give conjugated enone **26** (90%).

This protocol was extended to include dienone **30** which exhibited no tendency to aromatize under ordinary conditions of handling (Scheme V). Thus, 5-methyl-1,3-cyclohexanedione[47] was transformed into the β-ethoxy enone by an established procedure[48] and subsequently O-silylated[49] to generate **27**. Coupling of **23** with diene **27** in the presence of titanium tetrachloride at −78 °C[50] proceeded uneventfully to deliver **28** as a 1:1 mixture of diastereomers. In this example, β-elimination was effected with sodium acetate in acetic acid. Sequential treatment of **29** with methyllithium and aqueous acid gave rise to the targeted **30** (85%).

Scheme V



Summary. The methodology detailed herein has resulted in the convenient preparation of a diverse collection of bifunctional 1-(trimethylsilyl)cyclopropane reagents. These synthetic intermediates are expected to lend themselves to additional chemical manipulation and to play a role in the future development of silylcyclopropane chemistry. Derived anions where feasible appear to be adequately nucleophilic, despite prevailing steric hindrance, to undergo reaction with a diverse array of electrophilic partners. The operations already carried out on acetal **23** reveal that it is generally possible to engage its derived carbocation in condensation reactions without danger of cyclopropylcarbinyl cation rearrangement. Overall there exists a reasonable degree of functional group compatibility in either context to allow reliable extension to the synthesis of compounds possessing more complex molecular architecture. The ensuing paper[51] describes the feasibility of extending aspects of this methodology to the preparation of spirocyclic sesquiterpenes.

Experimental Section

2-(Trimethylsilyl)-2-propen-1-ol (2). To a slurry of magnesium (5.2 g, 0.22 mol) in anhydrous tetrahydrofuran (150 mL) was added a solution of **1** (40 g, 0.22 mol) in dry tetrahydrofuran (50 mL) during 1 h. The reaction mixture was heated at reflux for 1.5 h and cooled to 0 °C. Gaseous formaldehyde, generated by heating paraformaldehyde at 160 °C, was passed through the reaction flask under a slow nitrogen flow. Upon completion of the addition, the reaction mixture was stirred for an additional 10 h at room temperature and treated with water (20 mL). The solvent was decanted and the salts were washed with ether (3 × 200 mL). The combined organic phases were washed with water and brine before drying. Solvent evaporation followed by distillation afforded 23 g (80%) of **2** as a clear, colorless oil; bp 62–64 °C at 9 torr (lit.[19] bp 74–75 °C at 30 torr).

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[1-(Trimethylsilyl)cyclopropyl]carbinol (3). A stock solution of ethylzinc iodide was prepared as follows. Ethyl iodide (156 g, 1 mol) was treated with zinc–copper couple (70 g) in dry ether (550 mL), and the mixture was stirred at room temperature for 36 h. The supernatant liquid was withdrawn free of the sludge and stored in a stoppered flask.

To the above stock solution (300 mL, 1.66 M) containing 500 mmol of active ethylzinc iodide was added methylene iodide (50 g, 186 mmol) at a rate which maintained the reaction mixture at gentle reflux. After the addition was complete, the mixture was stirred at room temperature for 4 h, cooled to 0 °C, and treated with **2** (10 g, 77 mmol). The reaction mixture was allowed to warm to room temperature and stirred for an additional 15 h. The flask contents were poured into cold (0 °C) 5% sodium hydroxide solution, filtered, and extracted with ether (3 × 200 mL). The combined ethereal layers were washed with 5% sodium hydroxide solution (40 mL) and brine, dried, and evaporated. Distillation of the residue afforded 11 g (99%) of **3** as a colorless oil: bp 84–85 °C at 9 torr; IR (neat, cm^{-1}) 3360, 3070, 3002, 2960, 1255, 850; ^1H NMR (CCl_4) δ 3.39 (s, 2 H), 2.08 (s, 1 H), 0.48–0.28 (series of m, 4 H), 0.03 (s, 9 H); MS, *m/e* ($M^+ - CH_3$) calcd 129.0735, obsd 129.0731.

[1-(Trimethylsilyl)cyclopropyl]methyl Bromide (4). To a solution of **3** (2.8 g, 20 mmol) in dry ether (100 mL) cooled to −78 °C was added phosphorus tribromide (1.8 g, 6.7 mmol) during 5 min. The reaction mixture was allowed to warm to room temperature during 3 h and kept at 25 °C for 2 h. Water was added and the product was extracted into ether. The combined organic extracts were dried and concentrated to give 2.7 g (71%) of **4** whose purity was suitable for subsequent use: IR (neat, cm^{-1}) 3080, 3005, 2963, 1258, 845; ^1H NMR (CCl_4) δ 3.34 (s, 2 H), 0.72–0.52 (series of m, 4 H), 0.07 (s, 9 H); MS, *m/e* (M^+) calcd 190.9892, obsd 190.9896.

[1-(Trimethylsilyl)cyclopropyl]methyl Phenyl Sulfone (5). To a slurry of sodium benzenesulfinate (1.87 g, 11.4 mmol) in dry dimethylformamide (15 mL) was added **4** (1.57 g, 7.6 mmol) at room temperature. After 7 h at 25 °C, the reaction mixture was diluted with ether (30 mL) and the filtered salts were rinsed with ether (2 × 20 mL). The combined organic phases were washed with 5% potassium hydroxide solution (3 × 5 mL) and brine, dried, and evaporated. There was obtained 1.92 g (100%) of **5** as a colorless oil. Kugelrohr distillation provided the analytical sample: IR (neat, cm^{-1}) 3060, 2950, 1582, 1470, 1440, 1310, 1240, 1150, 830; ^1H NMR (CCl_4) δ 8.0–7.4 (series of m, 5 H), 3.05 (s, 2 H), 0.64–0.44 (series of m, 4 H), 0.12 (s, 9 H); MS, *m/e* ($M^+ - CH_3$) calcd 253.0718, obsd 253.0724.

Anal. Calcd for $C_{13}H_{20}O_2SSi$: C, 58.16; H, 7.51. Found: C, 58.27; H, 7.59.

[1-(Trimethylsilyl)cyclopropyl]methyl Phenyl Sulfide (6). To a dry, 25-mL, three-necked, round-bottomed flask containing a stirring bar and two serum caps was added dry tetrahydrofuran (20 mL) and a 50% oil dispersion of sodium hydride (0.72 g, 15 mmol). The system was placed under a nitrogen atmosphere, allowed to stir for 2 min, and then allowed to settle for 5 min. The oil/tetrahydrofuran mixture was removed by pipet and replaced by additional dry tetrahydrofuran (20 mL). This procedure was repeated twice. At this point, 20 mL of dry tetrahydrofuran was added to the remaining sodium hydride. The mixture was again stirred and cooled to 0 °C, and thiophenol (1.65 g, 15 mmol) was added slowly. A solution of **4** (2.07 g, 10 mmol) in 10 mL of tetrahydrofuran was added and the mixture was allowed to warm to room temperature. After 8 h at 25 °C, the tetrahydrofuran was evaporated under reduced pressure and the excess sodium hydride was quenched with water (10 mL). The resulting basic solution was extracted with ether (300 mL). The combined ethereal layers were washed with 5% potassium hydroxide solution and brine, dried, and evaporated. There was obtained 2.31 g (100%) of **6** as an oil which was purified for analysis by Kugelrohr distillation: IR (neat, cm^{-1}) 3060, 2940, 1580, 1470, 1430, 1240, 820; ^1H NMR (CCl_4) δ 7.4–7.1 (series of m, 5 H), 3.05 (s, 2 H), 0.55 (s, 4 H), 0.1 (s, 9 H); MS, *m/e* (M^+) calcd 236.1054, obsd 236.1061.

Anal. Calcd for $C_{13}H_{20}SSi$: C, 66.04; H, 8.53. Found: C, 65.90; H, 8.49.

[1-(Trimethylsilyl)cyclopropyl]methyl Phenyl Selenide (7). To a cold (0 °C), magnetically stirred suspension of diphenyl diselenide (1.71 g, 5.5 mmol) in absolute ethanol (20 mL) was added sodium borohydride (0.42 g, 11 mmol) in small batches. After the addition was complete, the reaction mixture was allowed to warm to room temperature. A clear, colorless solution resulted. (Caution! Reduction of the selenide is exothermic and vigorous hydrogen evolution occurs.) Bromide **4** (2.07 g, 10 mmol) was added. After 4 h of stirring at 25 °C, the ethanol was evaporated under reduced pressure and the residue was taken up in ether (100 mL), washed with 5% sodium hydroxide solution (40 mL), dried, and concentrated. Selenide **7** was obtained as a colorless oil (2.83 g, 100%): IR (neat, cm^{-1}) 3060, 1580, 1475, 1435, 1245, 830; ^1H NMR (CCl_4) δ 7.6-7.1 (series of m, 5 H), 3.07 (s, 2 H), 0.52 (s, 4 H), 0.13 (s, 9 H); MS, *m/e* (M^+) calcd 284.0492, obsd 284.0506.

Anal. Calcd for $C_{13}H_{20}SeSi$: C, 55.11; H, 7.11. Found: C, 55.11; H, 7.08.

[1-(Trimethylsilyl)cyclopropyl]acetonitrile (8). To a cold (5 °C) slurry of sodium cyanide (0.75 g, 15 mmol) in hexamethylphosphoric triamide (5 mL) was added **4** (2.06 g, 10 mmol). The reaction mixture was allowed to warm to room temperature and stirred for an additional 15 h before being diluted with ether (150 mL). After filtration, the filtrate was washed with 10% hydrochloric acid, water, and saturated sodium bicarbonate solution prior to drying and solvent evaporation. There was obtained 1.15 g (75%) of **8** as a colorless oil which was purified for analysis by Kugelrohr distillation: IR (neat, cm^{-1}) 3060, 2950, 2222, 1245, 830; ^1H NMR ($CDCl_3$) δ 2.37 (s, 2 H), 0.62 (s, 4 H), 0.12 (s, 9 H); MS, *m/e* (M^+) calcd 153.0973, obsd 153.0979.

Anal. Calcd for $C_8H_{15}NSi$: C, 62.68; H, 9.86. Found: C, 62.55; H, 9.85.

[1-(Trimethylsilyl)cyclopropyl](trimethylsilyl)methyl Phenyl Sulfone (9). To a cold (0 °C) solution of **5** (0.51 g, 1.9 mmol) and 1,4-diazabicyclo[2.2.2]octane (0.22 g, 2 mmol) in dry tetrahydrofuran (15 mL) was added *n*-butyllithium (1.5 mL of 1.4 M). The reaction mixture was stirred at 0 °C for an additional hour, cooled to −78 °C, and quenched with trimethylsilyl chloride (420 mg, 3.9 mmol). After 2 h at −78 °C, the mixture was allowed to warm to 25 °C and was partitioned between water (10 mL) and ether (100 mL). The organic phase was washed with cold 10% hydrochloric acid, dried, and evaporated. There was obtained 0.58 g (90%) of **9** as a clear, colorless oil which was purified for analysis by Kugelrohr distillation: IR (neat, cm^{-1}) 3060, 2970, 1583, 1475, 1442, 1300, 1245, 1135, 837; ^1H NMR ($CDCl_3$) δ 8.0–7.4 (series of m, 5 H), 2.45 (br s, 1 H), 0.8–0.3 (series of m, 4 H), 0.45 (s, 9 H), 0.05 (s, 9 H); MS, *m/e* ($M^+ - CH_3$) calcd 325.1113, obsd 325.1119.

Anal. Calcd for $C_{16}H_{28}O_2SSi_2$: C, 56.42; H, 8.28. Found: C, 56.44; H, 8.23.

(1-Hydroxycyclopentyl)[1-(trimethylsilyl)cyclopropyl]acetonitrile (10). To a cold (−78 °C) solution of diisopropylamine (0.92 mL, 6 mmol) in dry tetrahydrofuran (20 mL) was added *n*-butyllithium (2.94 mL of 2.05 M). The reaction mixture was allowed to warm to 0 °C over a 0.5-h period and recooled to −78 °C. A solution of **8** (0.76 g, 5 mmol) in dry tetrahydrofuran (3 mL) was added dropwise. After 1 h, a solution of cyclopentanone (0.42 g, 5 mmol) in tetrahydrofuran (3 mL) was added and stirring was continued at −78 °C for 3 h. Water was introduced and the product was extracted into ether. The combined organic layers were dried and evaporated to leave a residue which was purified by chromatography on silica gel (elution with hexane–ether, 10:1). There was obtained 0.4 g of unreacted **8** and 0.35 g (70%) of **10** as a colorless oil: IR (neat, cm^{-1}) 3590, 3460, 3060, 2950, 2218, 1434, 1245, 830; ^1H NMR ($CDCl_3$) δ 2.2–1.5 (series of m, 10 H), 0.88–0.48 (series of m, 4 H), 0.13 (s, 9 H); MS, *m/e* ($M^+ - CH_3$) calcd 222.1314, obsd 222.1320.

Anal. Calcd for $C_{13}H_{23}NOSi$: C, 65.76; H, 9.76. Found: C, 65.57; H, 9.75.

Benzoylation of 10. To a cold (−78 °C) solution of **10** (0.31 g, 1.3 mmol) in dry tetrahydrofuran (10 mL) was added *n*-butyllithium (0.93 mL of 1.4 M). After an additional 0.5 h, benzoyl chloride (0.18 g, 1.3 mmol) was introduced via syringe and the mixture was allowed to warm to room temperature (ca. 2 h). Conventional workup followed by preparative liquid chromatography on silica gel (elution with hexane–ether, 4:1) gave 0.43 g (97%) of **11** as a colorless oil: IR (neat, cm^{-1}) 3070, 2960, 2240, 1720, 1600, 1584, 1452, 1285, 1260, 850; ^1H NMR ($CDCl_3$) δ 8.1–7.25 (series of m, 5 H), 3.61 (s, 1 H), 2.8–1.6 (series of m, 8 H), 0.95–0.8

(series of m, 4 H), 0.07 (s, 9 H); MS, *m/e* ($M^+ - C_6H_5COOH$) calcd 219.1443, obsd 219.1450.

Anal. Calcd for $C_{20}H_{27}NO_2Si$: C, 70.34; H, 7.97. Found: C, 69.98; H, 8.06.

[1-Cyano-1-[1-(trimethylsilyl)cyclopropyl]methylene]cyclopentane (12). A cold (−40 °C) solution of **10** (100 mg, 0.42 mmol) in anhydrous tetrahydrofuran (5 mL) was treated with *n*-butyllithium (0.42 mL of 1.4 M in hexane, 0.6 mmol). Following 10 min of stirring, freshly distilled diethyl chlorophosphate (103 mg, 0.60 mmol) was added dropwise via syringe. The reaction mixture was slowly allowed to warm to room temperature and stirred overnight. Water (5 mL) was added and the product was extracted into ether (50 mL). The organic phase was washed sequentially with 10% hydrochloric acid, saturated sodium bicarbonate solution, water, and brine prior to drying and evaporation. Preparative TLC on silica gel (elution with ether–hexane, 1:4) returned 32 mg of unreacted **10** and gave 35 mg (56%) of **12** as a colorless oil: ^{1}H NMR (CDCl$_3$) δ 2.78–2.24 (m, 4 H), 1.9–1.58 (m, 4 H), 0.85–0.68 (narrow m, 4 H), 0.05 (s, 9 H); MS, *m/e* calcd (M^+) 219.1443, obsd 219.1458.

[1-(Trimethylsilyl)cyclopropyl]triphenylphosphonium Iodide (15). A cold (−20 °C) solution of lithium diisopropylamide in anhydrous tetrahydrofuran (20 mL) [from 1.45 g (14.3 mmol) of diisopropylamine and 8.7 mL of 1.5 M *n*-butyllithium in hexane (13.05 mmol)] was slowly syringed into a cold (−20 °C) stirred suspension of **14**[32] (5.0 g, 13.05 mmol) in 30 mL of dry tetrahydrofuran. After 90 min, chlorotrimethylsilane (1.66 mL, 13.05 mmol) was introduced and the reaction mixture was allowed to warm slowly to room temperature. The flocculent white precipitate was separated by filtration and washed with tetrahydrofuran. Evaporation of the filtrate gave 5.48 g (97%) of **15** as the mixed chloride/bromide salt, mp 180–190 °C dec.

A solution of the mixed halide (2.0 g, ca. 4.62 mmol) in acetone (15 mL) (dissolution requires warming) was titrated with 0.5 M sodium iodide in acetone until no additional precipitate was produced. Repeated centrifugation was required to acquire a clear supernatant solution. The reaction mixture was passed through a short plug of glass wool and concentrated to leave 2.3 g of oily solid. Recrystallization of this material from acetone–ether gave 1.6 g (70%) of **15** as colorless crystals, mp 232–235 °C dec. The combustion analysis disclosed that trace amounts of the mixed halide salt persisted.

Anal. Calcd for $C_{24}H_{28}IPSi$: C, 57.36; H, 5.63. Found: C, 58.76; H, 5.82.

1-(*tert*-Butyldimethylsilyl)cyclopropyl Phenyl Sulfide (17). To a cold (0 °C) solution of **16** (10.0 g, 38.4 mmol) in dry tetrahydrofuran (50 mL) was added 55 mL of 1.4 M *n*-butyllithium (76.8 mmol) dropwise over 1 h. Following 2 h at 0 °C, *tert*-butyldimethylchlorosilane (5.79 g, 38.4 mmol) was added. The reaction mixture was stirred at 0 °C for 2 h and allowed to warm to room temperature over an additional 8 h. Water was added, the organic phase was evaporated, and the product was extracted into ether. The ethereal solution was washed with 1 N sodium hydroxide solution and brine prior to drying and evaporation. The residual dark liquid was purified by column chromatography on silica gel (pentane elution). There was isolated 4.75 g (46%) of **17** as a clear, strongly odoriferous liquid: ^{1}H NMR (CDCl$_3$) δ 7.45–7.1 (m, 5 H), 1.2–0.85 (br m, 13 H), 0.0 (s, 6 H); MS, *m/e* (M^+) calcd 264.1368, obsd 264.1376.

1-(Trimethylsilyl)cyclopropanenitrile (21). To a cold (−78 °C) solution of lithium diisopropylamide (14.6 mmol) in dry tetrahydrofuran (50 mL) was added slowly over 20 min a solution of **20**[35] (1.5 g, 13.2 mmol) in the same solvent (5 mL). The reaction mixture was allowed to warm to −30 °C and held there for 15 min before 1,2-dibromoethane (3.73 g, 1.5 equiv) was introduced in one portion. After 3 h, a second 1.1 equiv of lithium diisopropylamide was added dropwise during 10 min. The solution was recooled to −78 °C and allowed to warm slowly to room temperature overnight. Saturated brine (50 mL) was added and the dark reaction mixture was diluted with ether. The organic phase was washed with 50 mL each of 4 N hydrochloric acid and saturated sodium bicarbonate solution, dried, and concentrated to leave 2.2 g of a dark liquid. Kugelrohr distillation of this material at 100 °C and 10 mm gave **21** as a clear colorless liquid (1.34 g, 73%). The analytical sample was obtained following preparative VPC (6 ft × 0.25 in. 10% SE-30 on Chromosorb G, 100 °C): IR (neat, cm^{-1}) 2950, 2205, 1250, 940, 850, 835; ^{1}H NMR (CDCl$_3$) δ 1.1 (m, 2 H), 0.8 (m, 2 H), 0.0 (s, 9 H); MS, *m/e* (M^+) calcd 139.0817, obsd 139.0821.

Anal. Calcd for $C_7H_{13}NSi$: C, 60.35; H, 9.43. Found: C, 60.21; H, 9.40.

1-(Trimethylsilyl)cyclopropanecarboxaldehyde (22). A. Reduction of 21. Into a solution of **21** (10 g, 72 mmol) in dry ether (400 mL) cooled to −78 °C was syringed diisobutylaluminum hydride (79 mL of 1 M in hexane) over ca. 30 min. The reaction mixture was stirred for an additional 2 h before being quenched with 200 mL of 5% sulfuric acid. After 1 h of stirring, the separated organic phase was washed with saturated sodium bicarbonate solution, dried, filtered, and concentrated to give 9.6 g (94%) of **22** as a clear colorless oil: IR (CCl$_4$, cm^{-1}) 3085, 3005, 2965, 2690, 1710, 1445, 1252, 1051, 1030, 919, 645; ^{1}H NMR (CDCl$_3$) δ 8.70 (s, 1 H), 1.15–0.9 (series of m, 4 H), 0.09 (s, 9 H); MS, *m/e* ($M^+ - CH_3$) calcd 127.0579, obsd 127.0582.

The semicarbazone of **22** was isolated as colorless needles, mp 179.5–180.5 °C (from ethanol): ^{1}H NMR (Me$_2$SO-d_6) δ 9.18 (br s, 1 H), 6.78 (s, 1 H), 5.85 (br s, 2 H), 0.79 (s, 4 H), 0.09 (s, 9 H); MS, *m/e* (M^+) calcd 199.1140, obsd 199.1146.

Anal. Calcd for $C_8H_{17}N_3OSi$: C, 48.20; H, 8.60. Found: C, 48.33; H, 8.62.

B. Oxidation of 3. To a solution of **3** (5.0 g, 34.7 mmol) in dry dichloromethane (150 mL) was added activated manganese dioxide[52] (39 g, 450 mmol). The reaction mixture was stirred at room temperature for 2 days, diluted with dichloromethane (200 mL), and filtered. The solid was washed with dichloromethane (3 × 200 mL) and the combined filtrates were concentrated to give 4.0 (80%) of **22** as a colorless oil.

1-(Trimethylsilyl)cyclopropanecarboxaldehyde Dimethyl Acetal (23). To a solution of **22** (3.6 g, 25 mmol) in dry methanol–benzene (1:1, 15 mL) was added pyridinium tosylate (0.5 g, 2 mmol) and trimethyl orthoformate (3.18 g, 30 mmol). The reaction mixture was stirred at room temperature for 15 h and the solvent was evaporated. The residue was taken up in ether, washed with 5% sodium hydroxide solution (10 mL) and brine, dried, and concentrated. Dimethyl acetal **23** was isolated as a colorless oil (4.25 g, 90%): ^{1}H NMR (CCl$_4$) δ 4.1 (s, 1 H), 3.35 (s, 6 H), 0.7–0.3 (series of m, 4 H), 0.05 (s, 9 H); MS, *m/e* ($M^+ - CH_3$) calcd 173.0998, obsd 173.0961.

1-[Bis(phenylseleno)methyl]-1-(trimethylsilyl)cyclopropane (24). Benzeneselenol (3.14 g, 20 mmol) was slowly added at −30 °C under nitrogen to a solution of **23** (1.8 g, 9.5 mmol) in dry ether (50 mL) in which was suspended anhydrous zinc chloride (1.36 g, 10 mmol). The reaction mixture was allowed to warm to 0 °C (ca. 4 h), diluted with ether (100 mL), and washed with 5% sodium hydroxide solution (2 × 30 mL) and brine prior to drying. Solvent evaporation left a thick yellow oil which was dissolved in dry ether (20 mL). The reaction mixture was cooled to 10 °C, treated with sodium borohydride (0.08 g, 2 mmol), and kept at 10 °C for 20 min. Water was added and the product was extracted into ether. Evaporation followed by chromatography on silica gel (elution with hexane) gave 3.5 g (80%) of **24b** as a clear, colorless oil: IR (neat, cm^{-1}) 3040, 2938, 1572, 1468, 1430, 1240, 830; ^{1}H NMR (CCl$_4$) δ 7.6–7.2 (series of m, 10 H), 4.5 (s, 1 H), 0.08–0.6 (series of m, 4 H), 0.2 (s, 9 H).

Anal. Calcd for $C_{19}H_{24}Se_2Si$: C, 52.05; H, 5.52. Found: C, 52.08; H, 5.48.

1-[Bis(phenylthio)methyl]-1-(trimethylsilyl)cyclopropane (24a). Treatment of cold (−30 °C) **23** (2.0 g, 10.6 mmol) with zinc chloride (1.5 g, 11 mmol) and thiophenol (2.75 g, 25 mmol) as described above gave **24a** as a clear, colorless oil (3.6 g, 98%): IR (neat, cm^{-1}) 3040, 2940, 1580, 1485, 1430, 1240, 830; ^{1}H NMR (CCl$_4$) δ 7.45–7.15 (series of m, 10 H), 4.59 (s, 1 H), 0.8–0.6 (series of m, 4 H), 0.2 (s, 9 H); MS, *m/e* (M^+) calcd 344.1088, obsd 344.1095.

Anal. Calcd for $C_{19}H_{24}S_2Si$: C, 66.22; H, 7.02. Found: C, 66.18; H, 7.10.

2-[Methoxy[1-(trimethylsilyl)cyclopropyl]methyl]cyclohexanone (25). To a cooled (−78 °C) solution of 1-(trimethylsiloxy)cyclohexene (0.32 g, 1.9 mmol) and **23** (0.37 g, 2.0 mmol) in dry dichloromethane (10 mL) was added trimethylsilyl tri-

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fluoromethanesulfonate (0.05 g, 0.2 mmol). After 8 h at −78 °C, water (2 mL) was introduced and the product was extracted into ether (100 mL). The organic extracts were washed with aqueous sodium bicarbonate solution, dried, and concentrated. There was obtained 0.43 g (90%) of **25** as a clear colorless oil after MPLC on silica gel (elution with 20% ether in hexane): IR (neat, cm^{-1}) 2959, 2900, 2860, 2819, 1718, 1450, 1250, 1127, 1093, 1026, 835, 750, 685; ^{1}H NMR ($CDCl_3$) δ 3.4 (d, $J = 4$ Hz, 1 H), 3.3 (s, 3 H), 2.5–1.5 (m, 9 H), 0.6–0.2 (m, 4 H), 0.05 (s, 9 H); MS, m/e (M^+) calcd 254.1702, obsd 254.1711.

2-[[1-(Trimethylsilyl)cyclopropyl]methylene]cyclohexanone (26). To a solution of **25** (140 mg, 0.55 mmol) in dry dichloromethane (10 mL) were added 3-Å molecular sieves (250 mg) and DBU (150 mg, 1.2 mmol). The mixture was gently refluxed for 18 h before being diluted with dichloromethane, washed with 10% hydrochloric acid and saturated sodium bicarbonate solution, dried, filtered, and concentrated. Further purification on silica gel (elution with 20% ether in hexane) gave 100 mg (90%) of **26** as a clear oil: IR (neat, cm^{-1}) 3039, 3000, 2960, 1690, 1600, 1440, 1415, 1317, 1252, 1140, 840, 750, 686, 650; ^{1}H NMR ($CDCl_3$) δ 6.7 (br s, 1 H), 2.8–2.3 (m, 4 H), 1.9–1.6 (m, 4 H), 0.8–0.6 (m, 4 H), 0.05 (s, 9 H); MS, m/e (M^+) calcd 222.1440, obsd 222.1447.

1-Ethoxy-3-(trimethylsiloxy)-5-methyl-1,3-cyclohexadiene (27). To a solution of lithium diisopropylamide (43 mmol) in dry 1,2-dimethoxyethane (50 mL) cooled to −78 °C was added a solution of 3-ethoxy-5-methyl-2-cyclohexenone[48] in dimethoxyethane (10 mL) dropwise over 10 min. After an additional 30 min, a solution of freshly distilled (from calcium hydride) chlorotrimethylsilane (8.2 g, 75.3 mmol) in dimethoxyethane (20 mL) was introduced via syringe. The reaction mixture was allowed to warm slowly to ambient temperature and poured into a separatory funnel containing 200 mL of hexane. The organic phase was washed with saturated sodium bicarbonate solution, dried, filtered, and concentrated. Distillation of the crude residue gave 4.50 g (93%) of **27** as a clear liquid: bp 49–50 °C (0.1 torr); ^{1}H NMR ($CDCl_3$) δ 4.55 (br s, 1 H), 4.35 (m, 1 H), 3.65 (q, $J = 7$ Hz, 2 H), 2.30–1.90 (m, 3 H), 1.25 (t, $J = 7$ Hz, 3 H), 0.95 (d, $J = 6$ Hz, 3 H), 0.10 (s, 9 H).

3-Ethoxy-5-methyl-6-[methoxy[1-(trimethylsilyl)cyclopropyl]methyl]cyclohex-2-enone (28). To a solution of titanium tetrachloride (1.38 g, 7.29 mmol) in dry dichloromethane (50 mL) cooled to −78 °C was added a solution of **23** (1.37 g, 7.29 mmol) in dichloromethane (5 mL) via syringe. To this clear yellow solution was added a solution of **27** (1.50 g, 6.62 mmol) in dichloromethane (5 mL) via syringe. The reaction mixture was stirred in the cold for 4 h before being quenched with several grams of water at this temperature. The solution was allowed to warm to room temperature before being poured into a separatory funnel containing 100 mL of ether and 25 mL of water. The organic phase was washed with water, dried, filtered, and concentrated to afford the crude product. MPLC on silica gel (elution with 40% ethyl acetate in hexane) gave 1.45 g (70%) of **28** as a mixture of stereoisomers: IR (CCl_4, cm^{-1}) 3060, 2980, 2815, 1660, 1610, 1471, 1440, 1371, 1326, 1241, 1210, 1170, 1095, 1019, 900, 840, 830, 720; ^{1}H NMR ($CDCl_3$) δ 5.25 (br s, 1 H), 3.90 (q, $J = 7$ Hz, 2 H), 3.40 (d, $J = 4$ Hz, 1 H), 3.35 (s, 3 H), 2.70–2.20 (m, 4 H), 1.40 (t, $J = 7$ Hz, 3 H), 1.10 (d, $J = 6$ Hz, 3 H), 0.50 (m, 4 H), 0.10 (s, 9 H); MS, m/e (M^+) calcd 310.1964, obsd 310.1973.

3-Ethoxy-5-methyl-6-[[1-(trimethylsilyl)cyclopropyl]methylene]cyclohex-2-enone (29). To a solution of **28** (680 mg, 2.17 mmol) in glacial acetic acid (7 mL) was added 375 mg (4.57 mmol) of anhydrous sodium acetate. The reaction mixture was refluxed for 10 h before being allowed to cool to room temperature and poured into a separatory funnel containing 50 mL of ether. The organic phase was washed several times with water and saturated sodium bicarbonate solution until nonacidic, dried, filtered, and concentrated. The product was purified by MPLC on silica gel (elution with 40% ethyl acetate in hexane) and isolated as a pale yellow oil (535 mg, 81%): IR (neat, cm^{-1}) 3062, 2960, 2895, 1655, 1600, 1472, 1401, 1380, 1360, 1315, 1244, 1228, 1183, 1103, 1021, 1007, 904, 835, 625, 681, 646; ^{1}H NMR ($CDCl_3$) δ 6.50 (s, 1 H), 5.35 (s, 1 H), 3.9 (q, $J = 7$ Hz, 2 H), 3.5–2.0 (m, 3 H), 1.4 (t, $J = 7$ Hz, 3 H), 1.15 (d, $J = 7$ Hz, 3 H), 0.7 (m, 4 H), 0.05 (s, 9 H); MS, m/e (M^+) calcd 278.1746, obsd 278.1751.

3,5-Dimethyl-4-[[1-(trimethylsilyl)cyclopropyl]methylene]cyclohex-2-enone (30). A solution of **29** (1.9 g, 6.1 mmol) in dry ether (35 mL) cooled to 0 °C was treated dropwise during 10 min with 7.8 mL of 1.25 M methyllithium in ether (19.8 mmol). The reaction mixture was stirred for 1 h and carefully quenched with water. The organic phase was washed with saturated sodium bicarbonate solution, dried, filtered, and concentrated. MPLC purification on silica gel (elution with 40% ethyl acetate in hexane) afforded 1.16 g (77%) of **30** as a pale yellow oil which was further purified for analysis by Kugelrohr distillation at 0.07 torr and 115 °C: IR (neat, cm^{-1}) 3065, 2950, 2885, 1670, 1610, 1440, 1393, 1246, 1165, 1061, 841, 745, 685, 651; ^{1}H NMR ($CDCl_3$) δ 6.0 (s, 1 H), 5.8 (s, 1 H), 3.5 (m, 1 H), 2.4 (m, 2 H), 2.05 (d, $J = 1$ Hz, 3 H), 1.05 (d, $J = 7$ Hz, 3 H), 0.65 (m, 4 H), 0.05 (s, 9 H); ^{13}C NMR ($CDCl_3$) ppm 199.2, 154.0, 141.9, 135.4, 125.1, 44.8, 31.2, 20.8, 20.2, 11.4, 10.3, 0.0, −3.0; MS, m/e (M^+) calcd 248.1596, obsd 248.1602.

Anal. Calcd for $C_{15}H_{24}OSi$: C, 72.50; H, 9.70. Found: C, 72.13; H, 9.70.

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