Strain-Activated 1,3-Butadienes. Synthesis and Dienic Reactivity of Dicyclobutylideneethane

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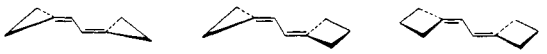
A synthesis of dicyclobutylideneethane (**13**) is described. An approach involving 1-(trimethylsilyl)-substituted cyclobutanes was first examined and shown not to be conducive for gaining access to this strained diene. A Wittig approach involving condensation of cyclobutylideneacetaldehyde (**18**) with cyclobutylidenetriphenylphosphorane (**20**) did deliver **3**, whose dienic behavior toward several dienophiles was examined. The electronic spectum of **3** resembles that of the bicyclohexylidene analogue and its relative reactivity in a representative Diels–Alder reaction was shown to be lower than that of **1**. Despite the obvious steric congestion at its bonding centers, however, **3** has reasonable reactivity. Various approaches to cyclobutylidenecyclopropylideneethane (**2**) have been examined without success. These efforts are briefly summarized.

Dicyclopropylideneethane (**1**), a 1,3-butadiene derivative with three-membered rings annealed to its termini, has commanded attention recently.[2,3] The consequences of juxtaposing two methylenecyclopropanes in this manner are reflected in the spectral properties of **1** and its significantly enhanced reactivity toward various dienophiles in [4 + 2] cycloaddition reactions. As a direct consequence, we have been interested in the preparation of **2** and **3**. We

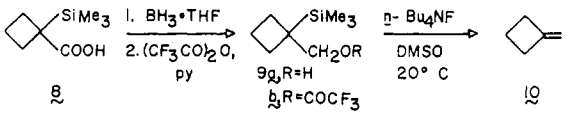


herein describe an expedient route to **3** and briefly detail those complications encountered in gaining access to **2**. Qualitative comparison is also made of the electronic properties of **1** and **3** and their relative ability to capture dienophiles.

Results

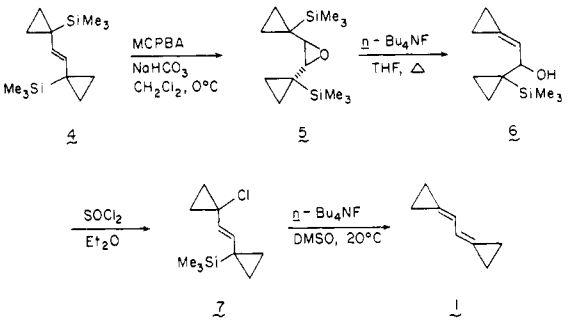
Evaluation of 1-(Trimethylsilyl)cyclobutane Precursors to 3. Earlier, we had shown that **1** could be arrived at conveniently by the sequence outlined in Scheme I.[3] Both key olefination steps are dependent upon mild fluoride ion induced desilylative elimination of a 1-(trimethylsilyl)cyclopropane subunit.[4]

As a direct extension of the use of these chemospecific processes, we sought initially to prepare **3** by a comparable protocol. This particular synthetic pathway is obviously dependent upon the availability of 1-(trimethylsilyl)-cyclobutane derivatives. However, the carboxylic acid **8**[5] represented the sole reported number of this potentially useful group of conjunctive reagents. In a preliminary set of experiments, **8** was reduced with the borane–tetrahydrofuran complex and the resulting alcohol (**9a**) was transformed into its trifluoroacetate **9b**. Under rather

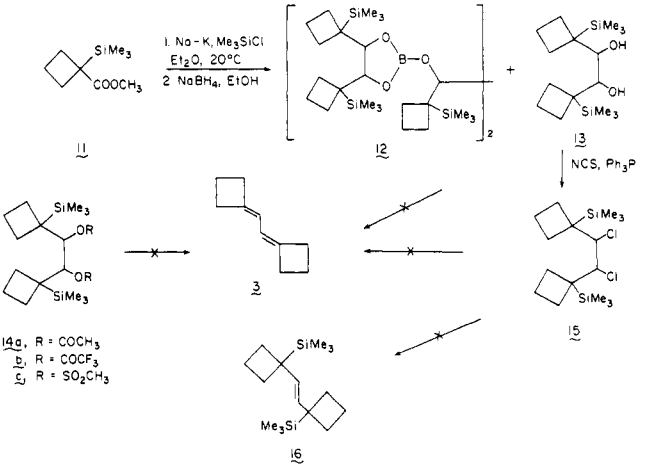


unsophisticated, nonpreparative conditions in an NMR tube, **9b** was seen to be transformed in the presence of

Scheme I



Scheme II



excess tetra-*n*-butylammonium fluoride completely to methylenecyclobutane (**10**)[6] during 60 h at room temperature. The intrinsic capability of suitably functionalized 1-(trimethylsilyl)cyclobutane derivatives to undergo elimination was thereby demonstrated.

Following this observation, we proceeded to subject ester **11** to acyloin condensation. Treatment with an ethereal suspension of sodium–potassium alloy containing chlorotrimethylsilane afforded a rather labile coupling product that was directly reduced with sodium borohydride in ethanol.[7] Under these conditions, the unexpected borate ester **12** was obtained in addition to the desired diol

(1) The Ohio State University Postdoctoral Fellow, 1983–1984.
(2) Heinrich, F.; Lüttke, W. *Angew. Chem., Int. Ed. Engl.* **1972**, *11*, 234.
(3) Paquette, L. A.; Wells, G. J.; Wickham, G. *J. Org. Chem.* **1984**, *49*, 3618.
(4) Review of silylcyclopropane chemistry: Paquette, L. A. *Isr. J. Chem.* **1981**, *21*, 128.
(5) Ainsworth, C.; Kuo, Y. N. *J. Organomet. Chem.* **1972**, *46*, 73.
(6) (a) Roberts, J. D.; Sauer, C. W. *J. Am. Chem. Soc.* **1949**, *71*, 3925. (b) Erickson, K. L.; Markstein, J.; Kim, K. *J. Org. Chem.* **1971**, *36*, 1024. (c) "The Aldrich Library of NMR Spectra", Vol. 1, 40D, Aldrich Chemical Co., Inc., 1974.
(7) Chasey, K. L.; Paquette, L. A.; Blount, J. F. *J. Org. Chem.* **1982**, *47*, 5262.

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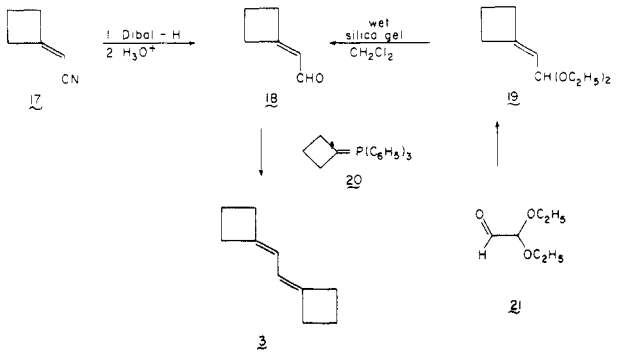
Scheme III



(Scheme II). The amount of highly crystalline borate species produced varied significantly (25–65%) from run to run. Although **12** proved surprisingly resistant to typical hydrolysis conditions,[8] efficient conversion to **13** was realized by heating for 24 h at the reflux temperature with 5% sulfuric acid in tetrahydrofuran.

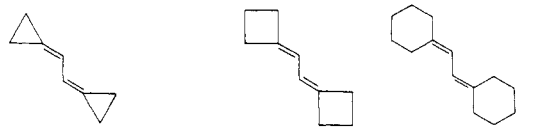
Diol **13** proved to be a somewhat sensitive molecule. Although it could be stored at 0 °C for several weeks without apparent decomposition, attempts to induce direct conversion to **3** under either basic (e.g., KH or KO-*t*-Bu in THF) or acidic (e.g., $SnCl_4$, $TiCl_4$, or BF_3-Et_2O in CH_2Cl_2 at −78 °C) conditions resulted only in its total destruction. On the other hand, **13** was generally amenable to esterification, giving diacetate **14a**, bis(trifluoroacetate) **14b**, and dimesylate **14c** in good yields. Unfortunately, these derivatives were either unreactive to anhydrous fluoride salts in various dipolar solvents or, in the case of **14b**, reverted to free diol as the sole observable product.

Conversion to dichloride **15** was achieved through the combined action of *N*-chlorosuccinimide and triphenylphosphine. However, this intermediate proved equally unserviceable as a precursor to **3**. Moreover, all attempts to arrive at **16** by reductive dechlorination gave no indication that the olefin had been produced. When the action of activated titanium metal[9] on diol **13** failed to produce **16**, our efforts were redirected.

Why is this collective group of molecules unsuitable as direct precursors of **3**? Models suggest that they may be constrained to exist in rigid conformations where the trimethylsilyl–vicinal X combinations are unable to attain either the cis- or trans-periplanar arrangement so necessary to successful desilylative elimination. This rationalization gains some support from their spectral features. Thus, alcohol **9a** is characterized by five ^{13}C signals, in complete agreement with the presence of a C_2 plane that bisects C(1) and C(3). On the other hand, the ^{13}C NMR spectra of **13–15** clearly indicate the presence of four uniquely different cyclobutyl carbons in each instance (see Experimental Section). Evidently, a C_2 plane bisects only the central bond of these dimeric structures.

Wittig Approach to Dicyclobutylideneethane (3). Although the readily available cyclobutylideneacetonitrile (**17**)[10] can be satisfactorily reduced to air-sensitive aldehyde **18** with diisobutylaluminum hydride, the alternative route via acetal **19** proved more reproducible and amenable to scale-up (Scheme III). Cyclobutylidenetriphenylphosphorane (**20**)[11] could be conveniently generated from

Table I. Electronic Spectra of 1, 3, and Dicyclohexylideneethane (Cyclohexane Solution, nm)

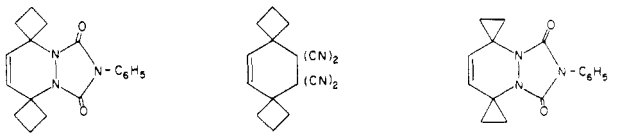


λ_{max}	ϵ^a	λ_{max}	ϵ	λ_{max}^a
230	25 900	244	7700	241
238	34 700	252	9600	250
247	29 100	262	7000	259

[a] See ref 2.

(4-bromobutyl)triphenylphosphonium bromide with 2 equiv of either phenyllithium in dimethoxyethane–ether or *n*-butyllithium in dimethoxyethane–hexane. Following condensation with glyoxal diethyl acetal (**21**),[12] the hydrolysis of **19** was effected with wet silica gel in dichloromethane solution.[13] Subsequent condensation of **18** with **20** delivered **3** in 21% yield after purification. The 300-MHz ^1H NMR spectrum (in $CDCl_3$) of this entirely stable 1,3-diene is characterized by a broad olefinic singlet of area 2 at δ 5.64, an eight-proton triplet at δ 2.72 due to the allylic hydrogens, and a quintet of area 4 at δ 1.98. These data compare favorably to those recently reported for 6,6-trimethylenefulvene.[14] The ultraviolet data for **3** are compiled in Table I. Interestingly, the three absorptions of dicyclobutylideneethane appear at longer wavelengths relative to those exhibited by 1 and bear remarkably close similarity to those of the "unstrained" dicyclohexylideneethane.

Dicyclobutylideneethane (**3**) reacts rapidly with *N*-phenyltriazolinedione in ether solution at −78 °C to give **22**. When **3** was codissolved with tetracyanoethylene in



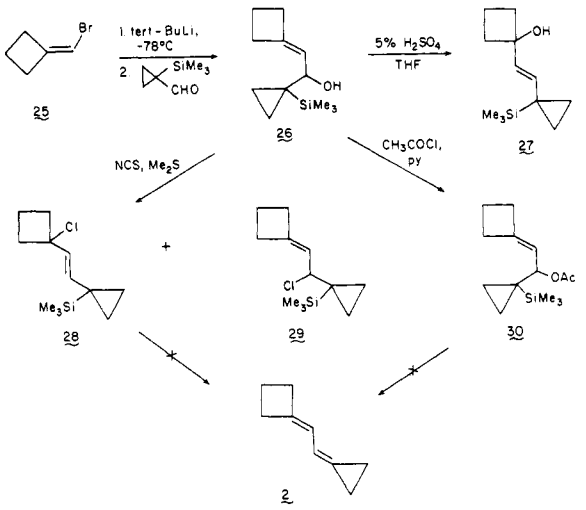
carbon tetrachloride in the absence of oxygen at room temperature, a deep blue color formed immediately. After 48 h, this color disappeared and adduct **23** was isolated. Diels–Alder cycloaddition to dimethyl acetylenedicarboxylate was not observed, forcing conditions notwithstanding. As in the case of **1**, adducts **22** and **23** were obtained only in low yields. However, no other well-defined substances were produced.

A competition experiment was subsequently carried out involving the addition of a limited quantity (0.4 equiv) of *N*-phenyltriazolinedione to a 1:1 mixture of **1** and **3** in chloroform solution at −78 °C. Under these conditions, **24** was produced to the virtual exclusion of **22**, thereby signaling the superior dienic reactivity of **1** toward this dienophile.

Unsuccessful Attempts To Synthesize Cyclobutylidenecyclopropylideneethane (2). As before, silicon-based approaches to **2** were initially examined (Scheme IV). Lithiation of (1-bromomethylene)cyclobutane (**25**)[6] followed by condensation with 1-(trimethylsilyl)cyclopropanecarboxaldehyde,[15] delivered al-

(8) Hoffman, R. W.; Ziess, H. J. *J. Org. Chem.* **1981**, *46*, 1309.
(9) Walborsky, H. M.; Wüst, H. H. *J. Am. Chem. Soc.* **1982**, *104*, 5807.
(10) Erickson, K. L.; Markstein, J.; Kim, K. *J. Org. Chem.* **1971**, *36*, 1024.
(11) (a) Scherer, K. V., Jr.; Lunt, R. S., III. *J. Org. Chem.* **1965**, *30*, 3215. (b) Schmidbaur, H.; Schier, A.; Neugebauer, D. *Chem. Ber.* **1983**, *116*, 2173.
(12) Fisher, H. O. L.; Baer, E. *Helv. Chim. Acta* **1935**, *18*, 514.
(13) (a) Huet, F.; Lechevallier, A.; Pellet, M.; Conia, J. M. *Synthesis* **1978**, 63. (b) Bestmann, H. J.; Roth, K.; Ettlinger, M. *Chem. Ber.* **1982**, *115*, 161.
(14) Stone, K. J.; Little, R. D. *J. Org. Chem.* **1984**, *49*, 1849.

Scheme IV



cohol **26** in 85% yield after silica gel chromatography. In the presence of 5% sulfuric acid, clean rearrangement of **26** to the more stable isomeric cyclobutanol **27** was effected, as expected from thermodynamic considerations. In order to activate **26** for elimination, several chemical transformations were performed. Chlorination with the *N*-chlorosuccinimide–dimethyl sulfide complex provided a mixture of chlorides enriched in **29**, as indicated by the characteristic ^{1}H NMR signal of its olefinic proton at δ 6.0. Attempts to purify this substance by chromatography on neutral alumina led in part to equally unstable isomer **28**. Considerable decomposition occurred as well. When alternative methods of chlorination were observed to be less satisfactory than the above, unpurified samples of **29** were utilized in the studies to follow.

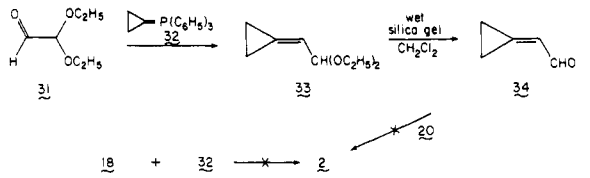
Simple esterification of **26** also produced complications. Thus, treatment with trifluoroacetic anhydride in pyridine (with and without 4-(dimethylamino)pyridine as catalyst) or with methanesulfonyl chloride in pyridine was not successful in providing the corresponding esters. Reaction with acetyl chloride in pyridine did give rise to **30**. However, attempted chromatographic purification of the latter returned mixtures of alcohols **26** and **27**. Consequently, **30** was employed after Kugelrohr distillation only. Tertiary alcohol **27** proved resistant to esterification.

Exposure of **29** and **30** to tetra-*n*-butylammonium fluoride,[16] benzyltrimethylammonium fluoride,[17] or potassium fluoride/18-crown-6[18] in numerous solvents at various temperatures gave no indication of delivering **2**. Most often, olefinic protons were not observed for the resultant viscous oils. Much decomposition was seen. In certain cases, *N*-phenylmaleimide was introduced after an appropriate lapse of time in order to trap **2** if formed. However, no Diels–Alder adduct was found.

Cationic entry to **2** also proved unworkable. Thus, treatment of **29** with solutions of silver perchlorate and silver trifluoroacetate in benzene only induced extensive decomposition and tar formation.

These negative results made an approach to **2** based on phosphorus ylide chemistry seem attractive. Cyclopropylideneacetaldehyde (**34**) was therefore prepared as described earlier by Conia and co-workers[19] (Scheme V).

Scheme V



However, **34** proved exceptionally sensitive to cyclobutylidenetriphenylphosphorane (**20**) in a wide range of solvents. Dark sludgy material invariably deposited from solution and none of the desired diene was observed. Quite unexpectedly, alternative recourse to the condensation of aldehyde **18** with cyclopropylidenetriphenylphosphorane (**32**)[20] was equally unproductive. In the several Wittig reactions attempted, small amounts of olefinic materials could be isolated, but none proved to be **2** (^{1}H NMR and GC–MS analysis).

The failures encountered in the above experiments suggest that access to **2** will have to be gained from yet another direction. It is unlikely that **2** is appreciably more labile than **1** (quite prone to polymerization) and **3** (stable for prolonged periods at 0 °C and above). The heightened reactivity of those precursors prepared in this study is more likely responsible for the present inability to obtain and characterize **2**.

Experimental Section

[1-(Trimethylsilyl)cyclobutyl]methanol (9a). To a solution of 26 mL of borane–tetrahydrofuran complex (1 M in THF) cooled to 0 °C was added **8** (3.0 g, 17.4 mmol) in tetrahydrofuran (10 mL) dropwise over 30 min. After being stirred for an additional 2 h at 0 °C and 1 h at room temperature, the reaction mixture was quenched by the addition of water and poured into a separatory funnel containing 50 mL of ether. The organic phase was washed in turn with 25 mL each of 1 N sodium hydroxide, 2 N hydrochloric acid, and saturated sodium bicarbonate solution before being dried, filtered, and concentrated to afford a clear oil. MPLC on silica gel (elution with 20% ether in hexane) gave 2.4 g (85%) of **9a** as a white crystalline compound. Further purification for analysis was accomplished by sublimation at 0.05 torr (T = 20 °C): mp 74–75 °C; IR (KBr, cm^{-1}) 3390, 2955, 1860, 1678, 1440, 1401, 1252, 1148, 1110, 1059, 1010, 838, 746, 687; ^{1}H NMR ($CDCl_3$) δ 3.60 (s, 2 H), 2.80 (br s, 1 H), 1.90 (m, 6 H), 0.0 (s, 9 H); ^{13}C NMR ($CDCl_3$) ppm 69.28, 31.67, 24.45, 17.13, 3.87; MS, m/z calcd (M^+ – $SiMe_3$) 85.0653, obsd 84.9684.

Anal. Calcd for $C_8H_{18}OSi$: C, 60.68; H, 11.48. Found: 60.60; H, 11.51.

Methylenecyclobutane (10). To a solution of **9a** (100 mg, 0.63 mmol) in dry pyridine (2 mL) cooled to 0 °C was added trifluoroacetic anhydride (1.46 mg, 0.69 mmol). The reaction mixture was stirred for 8 h while it slowly warmed to room temperature and was poured into a separatory funnel containing ether and 10% aqueous citric acid solution. The organic phase was washed with saturated aqueous sodium bicarbonate solution, dried, filtered, and evaporated. The residual oil was distilled in a Kugelrohr apparatus at 100 °C and 0.5 torr to give 133 mg (83%) of **9b** as a colorless liquid: IR (neat, cm^{-1}) 2960, 2875, 1785, 1445, 1400, 1349, 1259, 1227, 1162, 843, 780, 753, 740, 691; ^{1}H NMR ($CDCl_3$) δ 4.35 (s, 2 H), 2.00 (m, 6 H), 0.05 (s, 9 H).

Into a dry NMR tube was placed 82 mg (0.32 mmol) of **9b** and 0.1 mL of dry dimethyl-d_6 sulfoxide. To this mixture was added 0.1 mL of benzene-d_6, whereupon 0.2 mL (0.52 mmol) of anhydrous 2.6 M tetra-*n*-butylammonium fluoride in dimethyl-d_6 sulfoxide was introduced. The tube was sealed at 30 torr and maintained at room temperature. Periodic spectral scans revealed a gradual

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(16) Sharma, R. K.; Fry, J. L. *J. Org. Chem.* **1983**, *48*, 2112.
(17) (a) Kuwajima, I.; Nakamura, E.; Shimizu, M. *J. Am. Chem. Soc.* **1982**, *104*, 1025. (b) Paquette, L. A.; Blankenship, C.; Wells, G. J. *Ibid.* **1984**, *106*, 6442.
(18) Liotta, D., private communication.
(19) Rousseau, G.; Lechevallier, A.; Huet, F.; Conia, J. M. *Tetrahedron Lett.* **1978**, 3287.
(20) (a) Maercker, A. *Angew. Chem., Int. Ed. Engl.* **1967**, *6*, 557. (b) Bestmann, H. J.; Denzel, Th.; Kunstmann, R., Lengyel, J. *Tetrahedron Lett.* **1968**, 2895.

decline in the intensity of the singlet at δ 4.35 with concomitant increase of that for a multiplet at δ 4.50 diagnostic of the olefinic protons for methylenecyclobutane.[5c] After 60 h, the conversion to **10** was complete.

1,2-Bis[1-(trimethylsilyl)cyclobutyl]-1,2-ethanediol (13). Esterification of **8** (2.5 g, 14.5 mmol) with excess ethereal diazomethane in the usual manner gave 2.5 g (92%) of **11** as a clear oil following workup and distillation at 0.9 torr: bp 50–52 °C; ^{1}H NMR ($CDCl_3$) δ 3.60 (s, 3 H), 2.80–1.65 (m, 6 H), 0.05 (s, 9 H).

An alloy of freshly cut potassium (5.2 g, 0.11 mol) and sodium (2.5 g, 0.11 mol) was prepared in a Morton flask by heating the combined metal until molten in an oxygen-free atmosphere. After cooling, dry ether (400 mL) was added, and the mixture was stirred vigorously. A solution of 10.0 g (53.7 mmol) of **11** in ether (100 mL) containing 36 g (0.33 mol) of chlorotrimethylsilane was added dropwise over 1 h. A mildly exothermic reaction occurred. The mixture was stirred an additional 8 h before being filtered with suction through Celite. The violet solids (caution: pyrophoric!) were washed with ether and the organic phase was concentrated in vacuo to afford the labile silylated enediol (13 g) as a pale yellow, odoriferous liquid which was used without further purification: IR (CCl_4, cm^{-1}) 2960, 2910, 1640, 1405, 1250, 1150, 1100, 900, 740; ^{1}H NMR ($CDCl_3$) δ 2.60 (m, 6 H), 1.85 (m, 6 H), 0.05 (2 s, 36 H).

The crude product obtained above was dissolved in absolute ethanol (270 mL), whereupon 4.4 g (0.12 mol) of sodium borohydride was added in one portion. A mildly exothermic reaction ensued and the mixture was stirred for 8 h at room temperature. The solution was concentrated in vacuo and the white solid residue was dissolved in ether (250 mL) and water (100 mL). The excess reducing agent was destroyed by careful addition of 1 N hydrochloric acid. The organic phase was washed with saturated aqueous sodium bicarbonate solution, dried, filtered, and concentrated to afford a mixture of **12** and **13** in variable ratios over several trials.

MPLC on silica gel (elution with hexane then 5% ether in hexane) gave two major bands. The first (eluted almost with the solvent front) gave a viscous concentrate which slowly crystallized over several days and was found to be **12**. Recrystallization from ethyl acetate–methanol gave a white powder which was further purified for analysis by sublimation at 0.05 torr and 55 °C; mp 71–72 °C; IR (KBr, cm^{-1}) 2960, 2860, 1400, 1365, 1330, 1310, 1250, 1120, 1075, 977, 840, 745, 690, 649; ^{1}H NMR ($CDCl_3$) δ 3.85 (d, J = 6 Hz, 2 H), 2.75–2.40 (m, 2 H), 2.10–1.70 (m, 10 H), 0.0 (s, 18 H); ^{13}C NMR ($CDCl_3$) ppm 69.5, 38.8, 25.9, 25.2, 18.3, 2.9.

Anal. Calcd for $C_{48}H_{96}B_2O_6Si_6$: C, 60.08; H, 10.10. Found: C, 59.76; H, 10.64.

A solution of 1.0 g (1.0 mmol) of **12** in 50 mL each of tetrahydrofuran and 5% sulfuric acid was heated at reflux for 24 h. After being allowed to cool, the mixture was diluted with ether (50 mL), and the organic phase was washed with saturated aqueous sodium bicarbonate solution, dried, filtered, and concentrated to afford nearly 1.0 g of a colorless oil, identical in all respects to **13**, which had eluted last during the MPLC procedure described above. Attempts to purify this nonvolatile diol, either by distillation or preparative VPC, failed.

The overall yield of pure **13** was 7.6 g (90%); IR (CCl_4, cm^{-1}) 3620, 2500, 2970, 2880, 1450, 1415, 1370, 1255, 980, 840; ^{1}H NMR ($CDCl_3$) δ 3.05 (d, J = 7 Hz, 2 H), 2.60–2.25 (m, 2 H), 1.95–1.65 (m, 10 H), 1.20 (s, 2 H), 0.0 (s, 18 H); ^{13}C NMR ($CDCl_3$) ppm 70.2, 39.2, 26.2, 25.2, 18.4, 3.3. The molecular peak was observed in high resolution mass spectroscopy but was too transient for high resolution measurement.

1,2-Bis[1-(trimethylsilyl)cyclobutyl]-1,2-diacetoxyethane (14a). To a solution of 150 mg (0.48 mmol) of **13** in dry pyridine (5 mL) cooled to 0 °C was added 107 mg (1.05 mmol) of acetic anhydride. The solution was stirred for 8 h while being allowed to warm slowly to room temperature. The mixture was poured into a separatory funnel containing ether and 10% aqueous citric acid solution. The organic phase was washed with saturated aqueous sodium bicarbonate solution, dried, filtered, and concentrated. The residue was further purified by Kugelrohr distillation at 0.1 torr and 110 °C to afford 180 mg (95%) of **14a** as a colorless oil; IR (neat, cm^{-1}) 2960, 2870, 1735, 1430, 1370, 1240, 1015, 840; ^{1}H NMR ($CDCl_3$) δ 4.65 (d, J = 8 Hz, 2 H), 2.80–2.30 (m, 2 H), 2.05 (s, 6 H), 2.00–1.65 (m, 10 H), 0.05 (s, 18 H). The molecular peak was observed in high resolution mass spectroscopy but was too transient for high resolution.

1,2-Bis[1-(trimethylsilyl)cyclobutyl]-1,2-bis(trifluoroacetoxy)ethane (14b). This derivative was prepared in a manner analogous to that described above. From 0.50 g (1.59 mmol) of **13** and 0.73 g (3.5 mmol) of trifluoroacetic anhydride in pyridine (15 mL) was obtained 0.69 g (86%) of **14b** as a colorless liquid following workup and distillation on a Kugelrohr apparatus at 0.1 torr and 100 °C: IR (CCl_4, cm^{-1}) 2960, 2870, 1785, 1370, 1250, 1220, 1170, 910, 840; ^{1}H NMR ($CDCl_3$) δ 4.90 (d, J = 8 Hz, 2 H), 2.85–2.50 (m, 2 H), 2.15–1.65 (m, 10 H), 0.15 (s, 18 H); ^{13}C NMR ($CDCl_3$) ppm 159.1, 78.5, 36.3, 26.2, 25.6, 18.3, 3.3. The molecular peak was observed in high resolution mass spectroscopy but was too transient for high resolution measurement.

1,2-Bis[1-(trimethylsilyl)cyclobutyl]-1,2-ethanediol Dimesylate (14c). To a solution of 87 mg (0.28 mmol) of **13** in dry dichloromethane (3 mL) and triethylamine (1 mL) was added 76 mg (0.66 mmol) of methanesulfonyl chloride followed by 2 mg of 4-(dimethylamino)pyridine. After being stirred for 5 h, the reaction mixture was poured into a separatory funnel conaining ether (25 mL) and 10% aqueous citric acid solution (25 mL). The organic phase was washed further with saturated aqueous sodium bicarbonate and sodium chloride solutions, dried, filtered, and concentrated. The crude residue was purified by distillation on a Kugelrohr apparatus at 0.1 torr and 110 °C to afford 112 mg (86%) of **14c** as a pale yellow oil: IR (CCl_4, cm^{-1}) 2960, 2880, 1455, 1369, 1320, 1250, 1189, 1130, 1090, 961, 908, 835, 634; ^{1}H NMR ($CDCl_3$) δ 4.55 (d, J = 8 Hz, 2 H), 3.00 (br s, 6 H), 2.90–2.50 (m, 2 H), 2.20–1.70 (m, 10 H), 0.15 (s, 18 H). The molecular peak was observed in high resolution mass spectroscopy but was too transient for high resolution measurement.

1,2-Bis[1-(trimethylsilyl)cyclobutyl]-1,2-dichloroethane (15). To a solution of 4.02 g (30.1 mmol) of *N*-chlorosuccinimide in dry tetrahydrofuran (200 mL) was added a solution of 7.89 g (30.1 mmol) of triphenylphosphine in tetrahydrofuran (25 mL) dropwise during 15 min, whereupon a solution of 4.30 g (13.7 mmol) of **13** in tetrahydrofuran (25 mL) was added dropwise over several minutes. After 3 h, the precipitate had dissolved and the clear red solution was diluted with ether (250 mL). The organic phase was washed with water and saturated aqueous sodium chloride solution, dried, filtered, and concentrated to provide a solid residue. This was extracted with hexane, and the resulting light yellow solution was passed through a column of Florisil (25 g) and eluted with additional hexane (200 mL). The eluate was concentrated and the residue was distilled at 0.75 torr to provide 2.95 g (62%) of **15** as a colorless liquid, mp 44–46 °C. A sample for analysis was prepared by VPC (2 ft × 0.25 in. 10% SE-30 Chromosorb G, 90 °C): IR (CCl_4, cm^{-1}) 2970, 2900, 2870, 1450, 1410, 1255, 1150, 1125, 865, 840, 690; ^{1}H NMR ($CDCl_3$) δ 3.20 (d, J = 8 Hz, 2 H), 2.85–2.45 (m, 2 H), 2.15–1.70 (m, 10 H), 0.10 (s, 18 H); ^{13}C NMR ($CDCl_3$) ppm 57.0, 39.0, 28.1, 27.4, 17.7, 2.8.

Anal. Calcd for $C_{16}H_{32}Cl_2Si_2$: C, 54.66; H, 9.19. Found: C, 54.86; H, 9.48.

Cyclobutylideneacetaldehyde (18). A. Reduction of 17. To a cold (−78 °C) solution of **17** (161 mg, 1.73 mmol) in anhydrous ether (6 mL) under argon was added diisobutylaluminum hydride (1.92 mL of 1 M in hexane) via syringe during 60 min. After 2 h at −78 °C, cold 5% sulfuric acid solution was added dropwise, yielding a bright lime-green solution. The organic phase was separated, washed twice with saturated sodium bicarbonate solution, dried, and evaporated. The residual pale yellow oil (59 mg) was immediately purified by MPLC on silica gel (elution with 5% ethyl acetate in petroleum ether). There was isolated 59.2 mg (36%) of the air-sensitive aldehyde: ^{1}H NMR (300 MHz, $CDCl_3$) δ 9.56 (d, J = 8.2 Hz, 1 H), 5.73 (d, with small additional coupling, J = 8.2 Hz, 1 H), 3.11 (br t, J = 7.9 Hz, 2 H), 2.90 (br t, J = 7.9 Hz, 2 H), 2.12 (quintet, J = 7.9 Hz, 2 H); ^{13}C NMR ($CDCl_3$) ppm 190.05, 173.44, 123.30, 33.35, 31.12, 17.51; the molecular peak was observed in high resolution mass spectroscopy but was too transient for high resolution measurement.

B. Hydrolysis of 19. To a suspension of (4-bromobutyl)-triphenylphosphonium bromide (17.9 g, 37.6 mmol) in anhydrous dimethoxyethane (135 mL) at room temperature under nitrogen was added freshly prepared phenyllithium (116 mL of 0.65 M in ether) dropwise. The blood-red solution was stirred overnight, cooled in ice, and treated dropwise with a solution of freshly

distilled glyoxal diethyl acetal (4.5 g, 34.1 mmol) in dimethoxyethane (45 mL). The resulting mixture was gently refluxed for 48 h, cooled to room temperature, and filtered to remove insolubles. The filtrate was evaporated and the residue was flash distilled. Fractional distillation of the condensate provided 1.76 g (30%) of **19** as a colorless oil: bp 48 °C at 5 torr; ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.20 (m, 1 H), 4.85 (d, J = 7 Hz, 1 H), 3.65 (q, J = 7 Hz, 2 H), 3.45 (q, J = 7 Hz, 2 H), 2.70 (m, 4 H), 1.95 (m, 2 H), 1.15 (t, J = 7 Hz, 6 H); ^{13}C NMR ($CDCl_3$) ppm 145.76, 119.51, 99.50, 60.36, 31.44, 30.62, 17.77, 15.64.

To a suspension of silica gel (600 mg, Kieselgel 60, 70–230 mesh) in dichloromethane (1 mL) and water (2 drops) was added **19** (200 mg, 1.18 mmol) in one portion. The reaction mixture was stirred for 48 h and filtered. Following washing of the silica gel with dichloromethane, the combined filtrates were evaporated to leave a yellow oil (112 mg), the ^{1}H NMR spectrum of which was identical with the product from part A.

Dicyclobutylideneethane (3). To a suspension of (4-bromobutyl)triphenylphosphonium bromide (11.3 g, 23.7 mmol) in deoxygenated (argon) and anhydrous dimethoxyethane (77 mL) was added n-butyllithium (30.6 mL of 1.55 M in hexane, 47.4 mmol) dropwise. The blood-red solution was stirred overnight, cooled in ice, and treated dropwise with a solution of **18** (2.07 g, 21.5 mmol) in deoxygenated dimethoxyethane (26 mL). Precipitation occurred immediately. The reaction mixture was stirred overnight at 40 °C, cooled to room temperature, and vacuum filtered. The salts were washed thoroughly with petroleum ether and the combined filtrates were evaporated. Flash distillation of the residue at 25 °C and 0.05–0.1 torr delivered 1.12 g of impure diene. Purification was achieved by MPLC on silica gel (elution with 5% ethyl acetate in petroleum ether). There was isolated 600 mg (21%) of **3** as a colorless oil: ^{1}H NMR (300 MHz, $CDcl_3$) δ 5.64 (br s, 2 H), 2.72 (t, J = 7.8 Hz, 8 H), 1.98 (quintet, J = 7.8 Hz, 4 H); ^{13}C NMR ($CDCl_3$) δ 5.64 (br s, 2 H), 2.72 (t, J = 7.8 Hz, 8 H), 1.98 (quintet, J = 7.8 Hz, 4 H); ^{13}C NMR ($CDCl_3$) ppm 141.28, 116.95, 31.29, 29.72, 17.21; $\lambda_{max}^{cyclohexane}$ 244 (ϵ 7700), 252 (9600), 262 nm (7000).

Anal. Calcd for $C_{10}H_{16}$: C, 89.49; H, 10.51. Found: C, 89.34; H, 10.68.

***N*-Phenyltriazolinedione Adduct of 3.** To a solution of *N*-phenyltriazolinedione (196 mg, 1.12 mmol) in cold (−78 °C), deoxygenated (argon) ether (6 mL) was added dropwise a solution of **3** (150 mg, 1.12 mmol) in the same solvent (3 mL). Upon completion of the addition, the reaction mixture was stirred at −78 °C for 10 min at which time a precipitate was present. The solvent was evaporated under reduced pressure and the residue was filtered through a short column of neutral alumina (chloroform elution). Evaporation of the chloroform followed by MPLC on silica gel (elution with 25% ethyl acetate in petroleum ether) gave 47 mg (14%) of **22**: mp 169–170 °C (from petroleum ether); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.50–7.18 (m, 5 H), 5.94 (s, 2 H), 3.30–3.16 (m, 4 H), 2.13–2.00 (m, 4 H), 2.00–1.69 (m, 4 H); ^{13}C NMR ($CDCl_3$) ppm 151.43, 131.25, 128.93, 127.91, 126.82, 125.71, 59.19, 32.68, 12.42.

Anal. Calcd for $C_{18}H_{19}N_3O_2$: C, 69.88; H, 6.19. Found: C, 69.68; H, 6.41.

Tetracyanoethylene Adduct of 3. Admixture of **3** (150 mg, 1.12 mmol) and sublimed tetracyanoethylene (143 mg, 1.12 mmol) in deoxygenated (argon) carbon tetrachloride (4 mL) at room temperature resulted in formation of a deep blue color that faded after 48 h. The CCl_4-insoluble material (169 mg) was separated by filtration and the filtrate was evaporated to give 58 mg (20%) of adduct. Sublimation and recrystallization from chloroform–hexane gave **23** as a colorless solid: mp 176.5–177 °C; ^{1}H NMR (300 MHz, $CDcl_3$) δ 6.17 (s, 2 H), 2.81–2.64 (m, 2 H), 2.32–2.04 (m, 10 H); ^{13}C NMR ($CDCl_3$) ppm 127.34, 110.18, 46.51, 44.06, 33.18, 15.04.

1-[1-(Trimethylsilyl)cyclopropyl]-2-cyclobutylideneethanol (26). To a solution of 1-(bromoethylene)cyclobutane[6] (1.0 g, 6.80 mmol) in anhydrous ether (30 mL) cooled to −78 °C was added 3.1 mL of *tert*-butyllithium solution (2.6 M in pentane). After 3 h of stirring, a solution of 1-(trimethylsilyl)cyclopropanecarboxaldehyde (0.97 g, 6.80 mmol) in 5 mL of ether was added via syringe. The reaction mixture was allowed to warm slowly to room temperature during 1 h and quenched with water. The organic phase was washed with saturated sodium bicarbonate solution, dried, filtered, and concentrated to leave a clear yellow oil. MPLC on silica gel (elution with 10% ether in hexane) gave 0.85 g (59%) of **26** as a colorless liquid: ^{1}H NMR ($CDCl_3$) δ 5.20 (m, 1 H), 3.80 (d, J = 8 Hz, 1 H), 1.65 (m, 4 H), 2.0 (m, 2 H), 1.50 (s, 1 H), 0.40 (m, 4 H), 0.05 (s, 9 H); MS, m/z calcd ($M^+ - CH_3$) 195.1205, obsd 195.1235.

1-(1-Hydroxycyclobutyl)-2-(1-(trimethylsilyl)cyclopropyl)ethylene (27). Treatment of **26** (300 mg, 1.43 mmol) in tetrahydrofuran (5 mL) with 5% sulfuric acid (1 mL) for 1 h at room temperature gave, following workup and chromatography as above, 240 mg (80%) of **27** as a colorless oil: ^{1}H NMR ($CDCl_3$) δ 5.75 (dd, J = 14 and 4 Hz, 2 H), 2.30–1.50 (m, 7 H), 0.60 (m, 4 H), 0.05 (s, 9 H); ^{13}C NMR ($CDCl_3$) ppm 133.80, 132.32, 74.97, 36.43, 12.21, 9.85, 3.16; MS, m/z calcd ($M^+ - CH_3$) 195.1205, obsd 195.1203.

Chlorination of 26. To a solution of *N*-chlorosuccinimide (352 mg, 2.63 mmol) in anhydrous dichloromethane (5 mL) under nitrogen at 0 °C was added dropwise via syringe 210 μL (2.88 mmol) of dimethyl sulfide (freshly distilled from CaH_2). The milky white mixture was cooled to −20 °C and **26** (500 mg, 2.38 mmol) dissolved in dichloromethane (2 mL) was slowly introduced. Upon completion of the addition, the reaction mixture was stirred at 0 °C for 1 h, poured into ice-cold brine (5 mL), and extracted with ether (2 × 10 mL). The combined ethereal extracts were washed with cold brine (2 × 5 mL), dried, and evaporated at reduced pressure to leave a viscous yellow oil. This material was predominantly **30**: ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.0 (dt, J = 7 and 1 Hz, 1 H), 3.45 (d, J = 7 Hz, 1 H), 2.85 (m, 4 H), 2.10 (m, 2 H), 0.85 (br t, 2 H), 0.50 (m, 2 H), −0.02 (s, 9 H).

Chromatographic purification by elution (petroleum ether) through a short column of neutral alumina provided 99 mg of a colorless oil now enriched in **29**: ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.25 (dd, J = 12 Hz, 2 H), 2.80–2.40 (m, 6 H), 0.85 (m, 2 H), 0.55 (m, 2 H), −0.02 (s, 9 H). Considerable loss was incurred in this process.

1-[1-(Trimethylsilyl)cyclopropyl]-2-cyclobutylideneethanol Acetate (30). To a solution of **26** (200 mg, 0.95 mmol) in cold (0 °C) anhydrous pyridine (2 mL) under argon was added freshly distilled acetyl chloride (75.4 mg, 0.96 mmol). The mixture was stirred at 0 °C for 1 h prior to dilution with water and ether. The aqueous phase was extracted with ether (2 × 30 mL), and the combined organic layers were washed with saturated cupric nitrate and sodium chloride solutions before drying. Solvent evaporation left **30** as a colorless oil (157 mg, 62%), which was partially purified by Kugelrohr distillation at 106 °C and 1.4 torr: ^{1}H NMR (300 MHz, $CDCl_3$) δ 4.89 (m, 1 H), 2.69 (m, 4 H), 2.29–1.65 (m, 2 H), 0.45 (m, 4 H), 0.04 (s, 9 H); ^{13}C NMR ($CDCl_3$) ppm 170.18, 145.78, 118.31, 34.50, 30.09, 21.47, 17.13, 7.99, 6.20, −1.84.

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Registry No. **3**, 97592-31-9; **8**, 97592-20-6; **9a**, 97592-21-7; **9b**, 97592-22-8; **10**, 1120-56-5; **11**, 97592-23-9; **12**, 97592-25-1; **13**, 97613-80-4; **13** (silylated enediol), 97592-24-0; **14a**, 97613-81-5; **14b**, 97592-26-2; **14c**, 97592-27-3; **15**, 97592-28-4; **17**, 27784-69-6; **18**, 97592-29-5; **19**, 97592-30-8; **22**, 97592-32-0; **23**, 97592-33-1; **26**, 97592-34-2; **27**, 97592-35-3; **28**, 97592-36-4; **29**, 97592-37-5; **30**, 97592-38-6; chlorotrimethylsilane, 75-77-4; (4-bromobutyl)triphenylphosphonium bromide, 7333-63-3; glyoxal diethyl acetal, 5344-23-0; *N*-phenyltriazolinedione, 4233-33-4; tetracyanoethylene, 670-54-2; 1-(bromomethylene)cyclobutane, 1905-06-2; 1-(trimethylsilyl)cyclopropanecarboxaldehyde, 81236-83-1.