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Synthesis and Thermolysis of 3-Substituted 3-Trimethylsilylcyclopropenes

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Abstract: The synthesis of 3-substituted-3-(trimethylsilyl)cyclopropenes (X = CO_2Et, CHO, CN) is described. Their acid sensitivity and thermal stability was probed and the reaction products were identified. In one case, a novel rearrangement to a Dewar furan maybe involved and this pathway was explored via kinetics and computations.

Keywords: Cyclopropenes; Rearrangements; Kinetics; X-Ray crystallography

INTRODUCTION

The synthesis, reactivity, and physical characterization of small strained ring compounds is an ongoing area of interest which has been explored over the course of many years. A variety of synthetic methods have been developed for the preparation of cyclopropenes, but their thermal stability and Lewis acid sensitivity varies widely with the exact nature of the substituents on the three-membered ring. 3-Trimethylsilyl derivatives are of particular interest because they can serve as cyclopropenyl anion precursors. For example, Borden and co-workers[1] have concluded that the cyclopropenyl anion rapidly pseudorotates, in accord with theoretical predictions, by examining the reaction of ^{13}C-labeled 1,2,3-triphenyl-3-(trimethylsilyl)cyclopropene with tetrabutylammonium fluoride (eq 1). In a similar vein, Sachs and Kass[2] prepared the first stable cyclopropenyl

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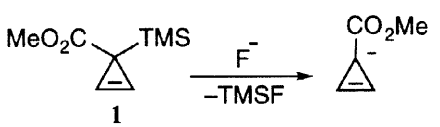
anion by reacting fluoride ion with 3-carbomethoxy-3-(trimethylsilyl)cyclopropene (**1**) in the gas phase (eq 2).



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In order to explore additional cyclopropenyl anion derivatives, functional group transformations were carried out on the ethyl ester analog of **1**. In this report we describe the syntheses of 3-substituted-3-(trimethylsilyl)cyclopropenes (X = CO_2Et, CHO, and CN), their thermolyses and acid-catalyzed reactions, and a novel rearrangement.

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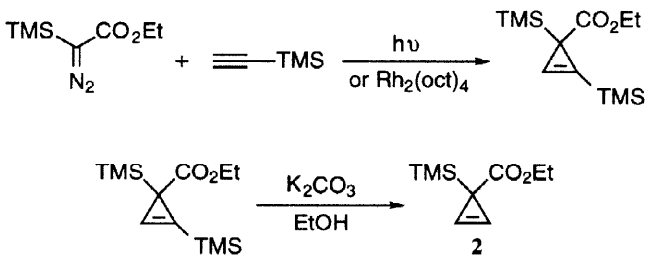
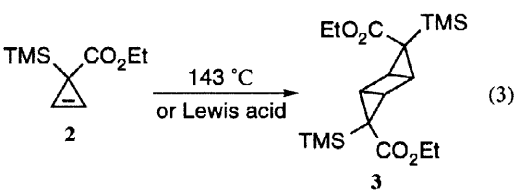
RESULTS AND DISCUSSION

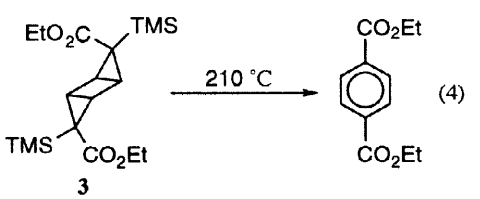
3-Carboethoxy-3-(trimethylsilyl)cyclopropene (**2**) was prepared in a reasonably efficient sequence. Irradiation of ethyl trimethylsilyldiazoacetate in the presence of trimethylsilylacetylene followed by selective removal of the vinyl trimethylsilyl group affords the desired cyclopropene in an overall yield of 48% (Scheme 1). Alternatively, the substituted bis(trimethylsilyl)cyclopropene can be formed under thermal conditions using a metal catalyst such as rhodium(II) octanoate dimer.[3] Either way, these reactions can be carried out to produce **2** in gram quantities.



Scheme 1

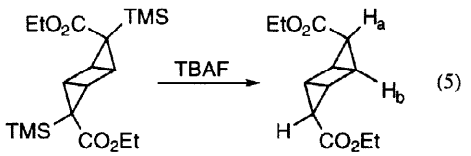
Thermolysis of **2** in refluxing xylene at 143 °C slowly leads to the formation of tricyclo-[3.1.0.0^{2,4}]hexane **3** over a 50 hour period (eq 3). In the presence of Lewis acids this dimerization is more facile and takes place over 30 minutes at room temperature with trimethylaluminum or 2 hours at 85 °C with trimethylsilyl triflate. Upon further heating at 210 °C, **3** is converted to diethyl terephthalate (eq 4). Both the thermal and acid-catalyzed cycloadditions, and the subsequent aromatization are consistent with related observations on other cyclopropenes.[4] The stereoselectivity in these reactions, however, has not been extensively examined. Our observation of **3** and not the other stereoisomers in both the thermal and acid-catalyzed reactions contrasts with the thermal dimerization of 3-ethynyl-3-methylcyclopropene, which leads to a 24 : 10 : 1 mixture of dimers, but is the same as what was observed for 3-aryl-3-trimethylsilylcyclopropenes.[5,6]





The structure of **3** could not be determined unambiguously by ^{1}H NMR spectroscopy since there is no coupling information, and the ester and trimethylsilyl groups are chemically equivalent. Presumably, the two

three-membered rings are *anti* to each other (as opposed to *syn*) because this is the less strained arrangement and all of the tricyclo[3.1.0.0^{2,4}]hexanes reported to date have this geometry. The relative positions of the carboethoxy and trimethylsilyl groups, however, are uncertain. In order to make this assignment, the trimethylsilyl groups were cleaved with tetrabutylammonium fluoride (eq 5). The resulting coupling between H_a and H_b is 4.2 Hz which indicates that H_a is exo; in the parent hydrocarbon, $J(H_bH_{exo})$ = 3.5 Hz and $J(H_bH_{endo})$ = 0 Hz.[7] This suggests that the trimethylsilyl groups are in the exo positions in **3**, but epimerization might accompany the fluoride-induced desilylation and thus this assignment is not conclusive.



(5)

In order to unequivocally establish the structure of **3**, an x-ray crystal determination was carried out. Suitable prismatic crystals were obtained by slowly recrystallizing **3** from hexanes at -20 °C and the structure was solved at 173 K with a reasonable R factor of 0.0526 (Figure 1).[8] The cyclopropane rings are *anti* as expected and the bulkier trimethylsilyl groups (A = 2.4 - 2.6 kcal/mol [TMS] and 1.1 - 1.2 kcal/mol [CO_2Et])[9] are in the exo positions as indicated by the fluoride-induced cleavage results. The carbon–carbon bonds in the ring system of **3** span from 1.507 - 1.546 Å with the bridging bonds (C1–C2 and C(1A)–C(2A)) being somewhat elongated. This is consistent with the relative ease in which **3** is converted to diethyl terephthalate upon further heating. It contrasts, however, to a previously reported x-ray structure for *anti*-1,2,4,5-tetraphenyl-3,6-dicarbomethoxytricyclo[3.1.0.0^{2,4}]hexane in which the C–C ring bonds are uniform in length and only vary from 1.525 - 1.536 Å.[10]

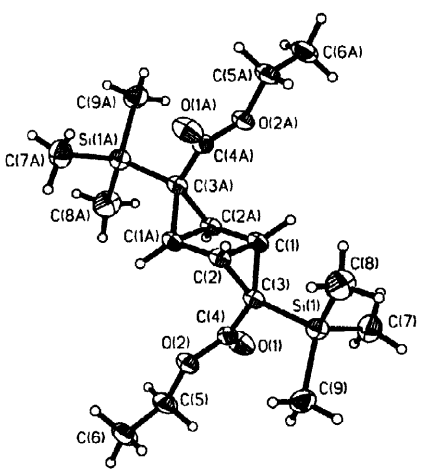
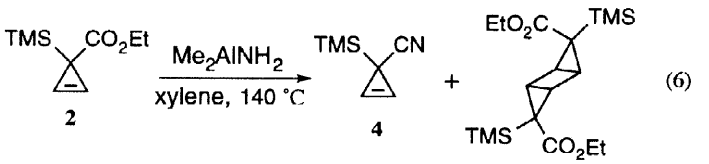


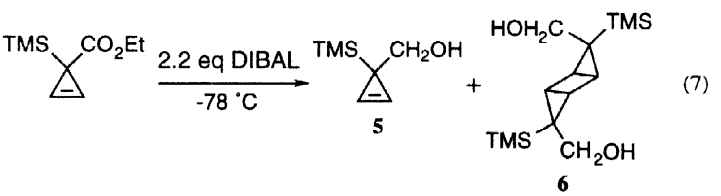
Fig. 1. X-Ray crystal structure of the dimer of **2** displaying C_i symmetry. Selected distances (Å) and angles (degrees) with standard deviations in parentheses are: Si(1)-C(3), 1.896 (3); C(3)-C(4), 1.494 (4); C(3)-C(1), 1.517 (4); C(3)-C(2), 1.516 (4); C(2)-C(1), 1.546 (4); C(1)-C(2A), 1.507 (4); angles, C(1)-C(3)-C(2), 61.3 (2); C(2)-C(1)-C(3), 59.3 (2); C(1)-C(2)-C(3), 59.4 (2); C(2)-C(1)-C(2A), 90.3 (2); C(1A)-C(2)-C(1), 89.7 (2).

The facile synthesis and thermal stability of **2** make it a suitable starting material for further transformations. Dimethylaluminum amide converts the ester to its corresponding nitrile (**4**) in one step in a modest 27% yield (eq 6).[11] The dimer of **2** is a competing side-product which is formed in variable amounts depending upon the quality of the aluminum reagent (i.e., the presence of a small amount of Lewis acid). Like the ester, **4** is thermally robust and can be heated to 150 °C for 1.5 hours before unidentified decomposition products are observed in the ^{1}H NMR spectrum.



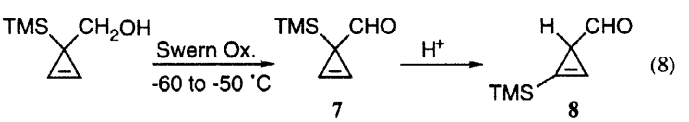
2 4 (6)

Direct conversion of 3-carboethoxy-3-(trimethylsilyl)cyclopropene to the corresponding aldehyde using one equivalent of diisobutylaluminum hydride (DIBAL) at -78 °C was unsuccessful; unreacted starting material and the over reduced alcohol (**5**) were isolated. A two-step sequence starting with lithium aluminum hydride also was problematic in that the double bond was reduced in addition to the ester. This contrasts with a previous report in which the ester in 1,2-disubstituted-3-carbomethoxycyclopropenes were successfully reduced with lithium aluminum hydride without affecting the ring double bond.[12] In any case, the synthesis of **5** was achieved in a 62% yield by using 2.2 equivalents of DIBAL at -78 °C (eq 7). This reaction requires special care



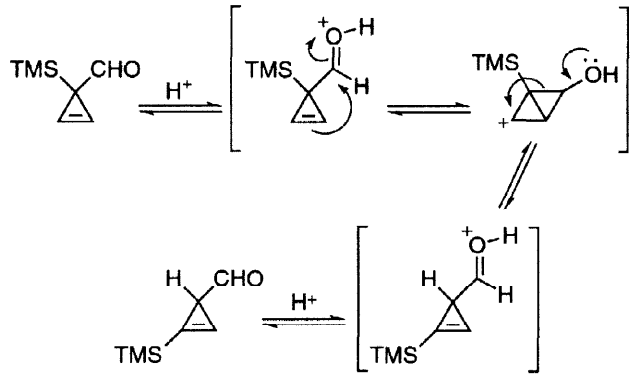
5 6 (7)

in that, if the addition of the ester to the DIBAL solution is carried out too rapidly an undesired by-product (**6**) is produced. Since **5** is unreactive when treated with trimethylaluminum, it appears that the mechanism for the formation of **6** involves the dimerization of **2** and then its reduction. Swern oxidation of **5** affords the desired aldehyde (**7**) in a 40% yield after chromatography but upon exposure to traces of acid **7** rearranges to a more stable derivative (eq 8).[13] A reasonable mechanism for this transformation is illustrated in Scheme 2. Proton



7 8 (8)

transfer to the carbonyl oxygen catalyzes the bond rearrangement to the vinyltrimethylsilane derivative in a stepwise (as shown) or concerted manner. The latter isomer (**8**) is more stable because the electropositive silicon is attached to the more electronegative carbon (i.e., electronegativity decreases with hybridization in the order sp > sp^2 > sp^3).



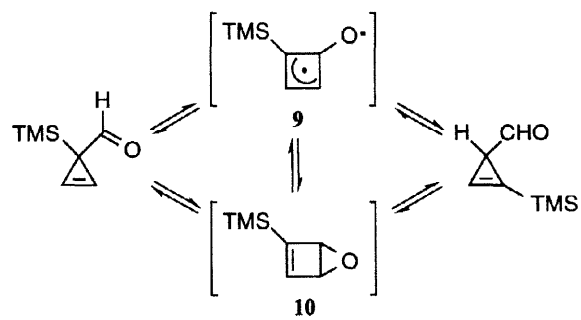
Scheme 2

The isomerization of **7** to **8** also occurs under thermal conditions. First-order rate coefficients were measured by dissolving **7** in toluene-d_8, heating the mixture in the probe of an NMR at temperatures ranging from 82° to 102 °C, and monitoring the disappearance of the starting aldehyde (Table 1). An Eyring plot of the

Table 1. First-order Rearrangement Rates for the Conversion of **7** to **8**.

Temperature (°C)	k (s^{-1})
82	$(4.89 \pm 0.05) \times 10^{-5}$
92	$(1.01 \pm 0.01) \times 10^{-4}$
102	$(2.31 \pm 0.02) \times 10^{-4}$

data is linear and the resulting activation parameters are $\Delta H^{\ddagger}$ = 19.8 ± 1.1 kcal/mol and $\Delta S^{\ddagger}$ = -23 ± 3 cal/mol K.[14] The large negative entropy of activation probably is over estimated (too negative) due to the limited temperature range (20 °C), but does indicate that the rate determining step proceeds via a tight transition state. A concerted or stepwise pathway which may involve a Dewar furan intermediate is illustrated in Scheme 3. This



Scheme 3

mechanism is consistent with a previous report that Dewar furan thermally isomerizes to 3-formylcyclopropene at temperatures below -65 °C[15] and the relative ease which many cyclopropenes undergo homolytic cleavage. In

order to further substantiate it, high-level G2(MP2)[16] and B3LYP/6-31G(d) calculations were carried out on 3-formylcyclopropene, Dewar furan, biradical **9**, and a reaction pathway which interconnects these species (Figure 2); this last point was confirmed by carrying out intrinsic reaction coordinate calculations which link the TS's to the reactants and products they interconnect at the Hartree Fock level.[17] Both computational methods indicate the presence of an intermediate with little, if any, barrier to its formation. Based upon these results, the fact that single configuration methods were used, and that a model system was employed, it is difficult to distinguish between a concerted or a stepwise pathway.

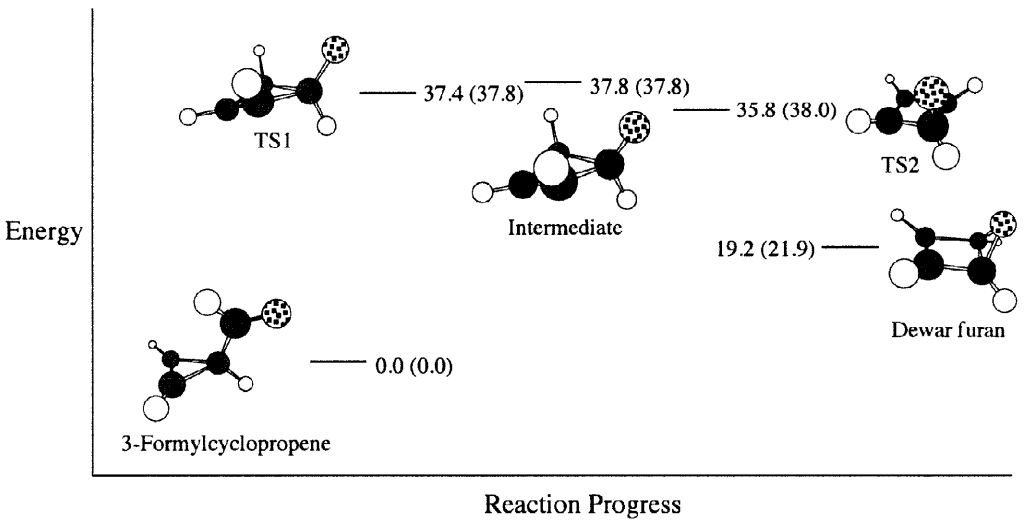


Fig. 2. Computed G2(MP2) potential energy surface for the degenerate thermal isomerization of 3-formylcyclopropene. All energies are in kcal/mol and parenthetical values correspond to B3LYP/6-31G(d) results.

Energetically, Dewar furan is 19.2 kcal/mol (G2(MP2)) higher in energy than 3-formylcyclopropene and there is a 37 kcal/mol barrier for the latter species isomerizing to the former one. This rearrangement barrier maybe overestimated as it is 20 kcal/mol greater than our measured value for the conversion of **7** to **8**, but the discrepancy maybe due to the trimethylsilyl substituent which would be expected to facilitate this unimolecular process. Preliminary B3LYP calculations on **7** and **10**, where the $Si(CH_3)_3$ group has been replaced by SiH_3, indicate that the energy difference between these compounds drops by 7.2 kcal/mol.

ACKNOWLEDGMENTS

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SUPPLEMENTARY MATERIAL AVAILABLE

X-ray crystallographic data for **3** (6 pages).

EXPERIMENTAL

Ethyl 1,3-bis(trimethylsilyl)cyclopropene-3-carboxylate. *Photochemical method.* Ethyl (trimethylsilyl)diazoacetate[18] (4.0 g, 0.0215 mol) and trimethylsilylacetylene (35 ml) were placed in a Pyrex photolysis tube and the mixture was degassed with argon at 0 °C for 30 minutes. Irradiation of this solution with a Rayonet™ photochemical reactor containing 16 350 nm lamps was carried out for 54 hours or until the diazo peak at 2092 cm^{-1} in the IR disappeared. The excess trimethylsilylacetylene was recovered by simple atmospheric distillation and 3.5 g of the product (63% yield) was obtained after vacuum distillation (b.p. 51-52 °C at 0.4 mm Hg).

Thermal method.[2] A three-necked round bottomed flask equipped with a reflux condenser, two septa, and a magnetic stir bar was charged with 0.10 g (0.13 mmol) of rhodium(II) octanoate dimer and 12 ml of trimethylsilylacetylene. The slurry was heated to 45 °C and a solution of ethyl (trimethylsilyl)diazoacetate (4.5 g, 0.0242 mol) in 25 ml of trimethylsilylacetylene was added slowly via a syringe pump (2.5 ml/hour). After all of the diazo compound was added heating was continued for at least an additional two hours. Trimethylsilylacetylene was recovered by simple distillation, and vacuum distillation of the residue afforded 4.0 g (65%) of the disilylester. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.15 (s, 1H), 4.02 (q, 2H, J = 7.1 Hz), 1.22 (t, 3H, J = 7.1 Hz), 0.21 (s, 9H), -0.01 (s, 9H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 178.4, 115.7, 114.5, 60.0, 17.4, 14.4, -0.8, -1.2. IR (neat) 2957, 2900, 1732, 1695, 1578, 1504, 1248, 1203, 840. HRMS-EI M^+ calcd for $C_{12}H_{24}O_2Si$ 256.1313, found 256.1318.

Ethyl 3-trimethylsilylcyclopropene-3-carboxylate (2). A solution of 3.0 g (0.0117 mol) of ethyl 1,3-bis(trimethylsilyl)cyclopropene-3-carboxylate in 80 ml of ethanol was stirred with a large excess of potassium carbonate at reflux for 5 hours. Upon cooling, 100 ml of water was added and the solution was extracted three times with methylene chloride. The combined organic material was washed three times with water to help remove the ethanol, once with a saturated sodium chloride solution and then dried over anhydrous magnesium sulfate. Vacuum distillation (58-60 °C at 2 mm Hg) yielded 1.7 g (80%) of **2** [Note: If methanol is used and longer reaction times are employed (36 h) this method leads to desilylation and trans-esterification to the methyl ester]. ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.86 (2H, s), 4.10 (2H, q, J = 7.1 Hz), 1.25 (3H, t, J = 7.1), 0.01 (9H, s). ^{13}C NMR (75 MHz, $CDCl_3$) δ 178.1, 104.5, 60.4, 16.7, 14.3, -1.7. IR (neat) cm^{-1} 3162, 3118, 2954, 2900, 1720, 1446, 1246, 1214, 840. HRMS-EI M^+ calcd for $C_9H_{16}O_2Si$ 184.0920, found 184.0928.

***anti*-1,6-bis(trimethylsilyl)-1,6-dicarbomethoxytricyclo[3.1.0.0^{2,4}]hexane (3)**. *Thermal dimerization.* A solution of **2** (0.10 g, 0.54 mmol) in 10 ml of xylene was heated to 143 °C for 50 h under argon; the reaction was monitored by gas chromatography using a capillary column. Xylene was removed by column chromatography (silica gel with hexanes as the eluting solvent) and the dimer was subsequently eluted with 5% ethyl acetate in hexanes.

Lewis acid dimerization (trimethylaluminum): Trimethylaluminum (1.5 ml of a 1M solution in hexane) was added to 0.45 g (2.4 mmol) of **2** in 40 ml of xylene at room temperature. The reaction was monitored by GC and after 2 h at room temperature no change was seen in the **3/2** ratio. Upon warming to 80 °C the ratio changed slightly but total conversion to the dimer was not obtained.

(Trimethylsilyl triflate (TMSOTf)): A mixture of 0.24 g (1.3 mmol) of **2**, 25 ml of xylene and 0.3 ml of

TMSOTf was heated to 85 °C for 1 h and 120 °C for 1 h (where dimer formation was much faster). The reaction was quenched with water and the product was obtained via column chromatography as described in the Me_3Al procedure. ^1H NMR (500 MHz, $CDCl_3$) δ 4.15 (q, 4H, J = 7.0 Hz), 1.92 (s, 4H), 1.25 (t, 6H, J = 7.0 Hz), -.01 (s, 18H). ^{13}C NMR δ 171.9, 60.0, 45.0, 27.7, 14.7, −2.9. IR (KBr) 2957, 1713, 1259, 1133, 843. HRMS-CI (isobutane) M+H$^+$ calcd for $C_{18}H_{33}O_4Si_2$ 369.1917, found 369.1918.

Dimethylaluminum amide.[11] A solution of trimethylaluminum (35 ml of a 2.0 M solution in hexanes) and methylene chloride (25 ml) was cooled to -78 °C in a 100 ml three-necked round bottomed flask fitted with a dry ice condenser and a magnetic stir bar. Approximately 8 ml of liquid ammonia (purified from sodium) was condensed into the flask. At the half-way point the cooling bath was removed and when the addition was finished the dry ice condenser was taken away. The resulting reaction mixture was allowed to warm to room temperature thereby enabling the excess ammonia to escape. The reagent (approximately 1.2 M) was used without any subsequent purification and could be stored in a -20 °C freezer for up to 2 weeks without any noticeable loss in activity [Note: Preparation of dimethylaluminum amide using a solution of trimethylaluminum in toluene did not afford a reactive reagent].

3-Trimethylsilyl-3-cyanocyclopropene (4). A solution of **2** (0.5 g, 2.7 mmol) in 55 ml of xylene was placed into a 250 ml three-necked round bottomed flask and 5.4 ml of dimethylaluminum amide was added with stirring. This solution was heated to 140 °C and the reaction progress was monitored by GC. After 1.25 h all of the starting material was consumed and the reaction mixture was allowed to cool to room temperature before being slowly quenched with water. The organic material was washed twice with water, three times with 2 M HCl, and dried over magnesium sulfate. Column chromatography on silica gel first with hexanes (to elute the xylene) and then 5% ethyl acetate in hexanes afforded **3** and **4**; the former compound elutes before the latter one. MPLC using the same solvents can be used to further purify **4**. Reaction yields 0.10 g (27%) of **4** were typical, but in some cases depending upon the batch of the dimethylaluminum reagent, more **3** was produced at the expense of **4**. ^{1}NMR (300 MHz, $CDCl_3$) δ 7.04 (s, 2H), 0.08 (s, 9H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 125.1, 104.8, 1.1, -3.2. IR (neat) 3115, 2958, 2207, 1660, 1252, 844. HRMS-CI (isobutane) M$^+$ calcd for $C_7H_{11}NSi$ 137.0660, found 137.0657.

3-Hydroxymethyl-3-(trimethylsilyl)cyclopropene (5). A -78 °C solution of **2** (2.0 g, 0.0109 mol) in 100 ml of ether was slowly added to 23 ml (0.023 mol) of diisobutylaluminum hydride (1 M in hexanes) in 100 ml of freshly distilled ether at -78 °C. After approximately 2 h the solution was slowly quenched with water. The organic layer was washed twice with 2 M HCl, three times with water, once with saturated sodium bicarbonate, and once with saturated sodium chloride before being dried over magnesium sulfate and concentrated *in vacuo*. The crude alcohol was purified by MPLC (silica gel and 20% ethyl acetate in hexanes) to give 1.0 g (62%) of **5**. ^1H NMR (300 MHz, $CDCl_3$) δ 7.25 (t, 2H, J = 0.5 Hz), 3.57 (t, 2H, J = 0.5 Hz), 1.24 (bs, 1H), -0.6 (s, 9H). ^{13}C NMR (75 MHz,$CDCl_3$) δ 113.3, 68.6, 16.6, -2.5. IR (neat) 3359, 2954, 1247, 1066, 1016, 895. HRMS-CI (isobutane) M+H$^+$ calcd for $C_7H_{15}OSi$ 143.0892, found 143.0888.

Alcohol by-product (6). ^1H NMR (300 MHz, DMSO-d_6) δ 4.21 (t, 2H, J = 5.1 Hz), 3.78 (d, 4H, J = 5.4 Hz), 1,46 (s, 4H), 0.078 (s, 18H). ^{13}C NMR (75 MHz, DMSO-d_6) δ 59.3, 38.2, 23.9, -1.6. IR (KBr) 3390, 2957, 1247, 1023, 839 HRMS-CI (NH_3) M+NH_4^+ calcd for $C_{14}H_{32}O_2NSi_2$ 302.1972, found 302.1951.

3-Formyl-3-(trimethylsilyl)cyclopropene (7). Oxalyl chloride (0.26 ml, 2.9 mmol) in 6.5 ml of freshly distilled methylene chloride (from CaH) was cooled to between -60 ° - -50 °C in a 25 ml flask; an isopropyl alcohol bath was used and was cooled by periodically adding chunks of dry ice. At this temperature, 0.43 ml (6.0 mmol) of dimethyl sulfoxide in 1.3 ml of methylene chloride was added dropwise and bubbles were observed with each added drop. After 5 minutes, **5** (0.250 g, 1.76 mmol) in 2.5 ml of methylene chloride was slowly added. The solution turned cloudy and was stirred for an additional 35 minutes. Dimethylethyl amine (1.4 ml, 12.9 mmol) was then added, and the mixture was allowed to warm to room temperature. The resulting solution was quenched with water and the organic layer was extracted with saturated sodium bicarbonate and then water (3x). The organic material was dried over magnesium sulfate and concentrated at 0 °C using a rotorary evaporator. The crude product was mixed with 2.5% dimethylethylamine in pentane and applied to an MPLC column packed with silica gel which had been equilibrated with the same amine/pentane solvent; silica gel alone causes the aldehyde to rearrange to **8**. A 40% yield, 0.10 g, of the product was obtained. ^{1}H NMR (300 MHz, C_6D_6) δ 8.74 (s, 1H), 6.07 (s, 2H), 0.13 (s, 9H). ^{13}C NMR (300 MHz, toluene-d_8) δ 206.0, 106.2, 28.6, -2.4. IR (neat) 3120, 2957, 2773, 2675, 1705, 1686, 1248, 841. HRMS-EI M^+ calcd for $C_7H_{12}OSi$ 140.0657, found 140.0656.

1-Trimethylsilyl-3-formylcyclopropene (8). ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.67 (d, 1H, J = 7.2 Hz), 7.35 (s, 1H), 2.17 (d, 1H, J = 7.2 Hz), 0.23 (s, 9H). ^{13}C NMR (300 MHz, $C_6D_5CD_3$) δ 205.8, 116.0, 114.8, 30.2, -2.0. HRMS-EI M^+ calcd for $C_7H_{12}OSi$ 140.0657, found 140.0660.

Thermolysis of 7. A solution of **7** in approximately 0.5 ml of toluene-d_8 was degassed and sealed under vacuum in an NMR tube. The probe of a 300 MHz Varian™ NMR was heated to the desired thermolysis temperature and calibrated with an ethylene glycol external standard before and after each kinetic run. The temperature did not vary more than a half of a degree during the time period of the experiment. After the sample was inserted into the NMR probe, it was allowed to equilibrate 5 minutes prior to collecting data. Two runs each were made at 82° and 102° C and three at 92° C by collecting a series of 15 to 20 single scan spectra at appropriate intervals over a period of at least one half-life. The disappearance of **7** was monitored by comparing the integration of the vinyl protons of **7** to the aromatic protons of toluene [Note: the toluene was present in the toluene-d_8 solvent]. Base washing of the NMR tubes did not lead to a change in the reaction rate data. Eyring parameters were determined from the rate constants measured at the three temperatures.

COMPUTATIONS

Ab initio and density functional calculations were carried out using GAMESS[19] and Gaussian 94.[20] All structures were fully optimized and verified as minima or transition structures by examining the analytically computed vibrational frequencies; minima only have positive values while transition structures have one and only one negative frequency. Intrinsic reaction coordinate (IRC) calculations were carried out at the Hartree-Fock level to verify the reactant and prodcut for a given transition structure. G2(MP2) energies were calculated as previously described[15] and were not corrected for the finite temperature change from 0 to 298 K. Likewise, the B3LYP/6-31G(d) energies have been zero-point energy corrected (using unscaled B3LYP/6-31G(d) vibrational frequencies) but were not temperature corrected.

REFERENCES AND NOTES

1. Köser, H. G., Renzoni, G. E., Borden, W. T. *J. Am. Chem. Soc.* **1983**, *105*, 6359-6360.
2. Kass, S. R. and Sachs, R. K. *J. Am. Chem. Soc.* **1994**, *116*, 783-784.
3. Clauberg, H. Ph.D. Thesis. Harvard University, 1993.
4. Thermal dimerization: Flowers, M. C., Frey, H. M., Höpf, H. *J. C. S. Chem. Comm.* **1972**, 1284-1285. Lewis acid dimerization: *Tetrahedron Lett.* **1975**, *52*, 4673-4676.
5. Ivanov, A. L., Domin, I. N. J. Org. Chem. USSR **1988**, *24*, 2298-2303.
6. Han, S.; Kass, S. submitted for publication.
7. Schipperijn, A. J. and Lukas, J. *Tetrahedron Lett.* **1972**, 231-232.
8. Crytallographic data along with the refined coordinates and bond distances can be found in the supplemental material.
9. March, J. *Advanced Organic Chemistry*, 4th ed.; Wiley Interscience: New York, 1992; p. 145.
10. Bennett, M. J.; Purdham, J. T.; Takada, S.; Masamune, S. *J. Am. Chem. Soc.* **1971**, *93*, 4063-4065.
11. Wood, J. L.; Khatri, N. A.; Weinreb, S. M. *Tetrahedron Lett.* **1979**, *51*, 4907-4910.
12. Zefirov, N. S.; Averina, N. A.; Boganov, A. M.; Laryukova, M. V.; Rashchupkin, Z. A.; Tetent'ev, P. B.; Sharbatyan, P. A. *Zh. Org. Khim.* **1981**, *17*, 1450-1462.
13. In order to obtain NMR spectra of **6** in $CDCl_3$ we found that it was necessary to filter the solvent through neutral alumina so as to neutralize it.
14. The cited errors represent the standard errors in the slope and intercept of the Erying plot.
15. Ritt, I. G.; Russell, R. A.; Warrener, R. N. *J. Am. Chem. Soc.* **1985**, *107*, 7176-7178.
16. Curtiss, L. A.; Raghavachari, K.; Pople, J. A. *J. Chem. Phys.* **1993**, *98*, 1293-1298.
17. Other intermediates such as the biradical formed by making a σ bond between the two ends of the allylic radical in **9** (the radical equivalent of the possible intermediate suggested in the acid-catalyzed pathway) or the tricyclic compound formed by combining the two radical centers were explored. In each case either a higher energy species was obtained or the compound reverted without a barrier to one of the substrates we had already examined.
18. Regitz, M.; Gümbel, H.; Allspach, T. *J. Organomet. Chem.* **1985**, *290*, 33-39.
19. Schmidt, M. W.; Baldridge, K. K.; Boatz, J. A.; Elbert, S. T.; Gordon, M. S.; Jensen, J. H.; Koseki, S.; Matsunaga, N.; Nguyen, K. A.; Su, S.; Windus, T. L.; Dupuis, M.; Montgomery, Jr., J. A. *J. Comput. Chem.* **1993**, *14*, 1347-1363.
20. Gaussian 94, Revisions B and D, Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Gill, P. M. W.; Johnson, B. G.; Robb, M. A.; Cheeseman, J. R.; Keith, T.; Petersson, G. A.; Montgomery, J. A.; Raghavachari, K.; Al-Laham, M. A.; Zakrzewski, V. G.; Ortiz, J. V.; Foresman, J. B.; Cioslowski, J.; Stefanov, B. B.; Nanayakkara, A.; Challacombe, M.; Peng, C. Y.; Ayala, P. Y.; Chen, W.; Wong, M. W.; Andres, J. L.; Replogle, E. S.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Binkley, J. S.; Defrees, D. J.; Baker, J.; Stewart, J. P.; Head-Gordon, M.; Gonzalez, C.; Pople, J. A. Gaussian, Inc., Pittsburgh, PA, 1995.