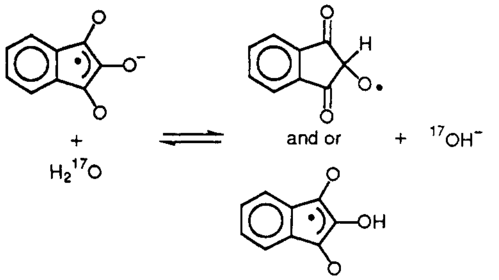
solution of the ninhydrin anion radical in HMPA, the expected changes in the coupling constants are accompanied by the nine-line spectrum being slowly replaced by that of the ^{17}O-substituted anion radical (A_0 = 3.94 G). The intensity of the ^{17}O-substituted system continues to grow for a period of about 30 h, and the two spectra can be observed simultaneously without apparent loss of total anion radical concentration. When the same reaction is carried out with a solution containing 0.1 M neutral triketone, the reaction is complete within 10 min. The anion radical solutions generated in the presence of excess neutral ninhydrin exhibit large line widths due to rapid electron exchange between neutral molecule and anion radical. The much more rapid appearance of the ^{17}O-labeled anion radical in the ESR spectra when the neutral molecule concentration in the anion radical solution is high, further supports the mechanism proposed in Scheme I and provides evidence against proton transfer from water to the anion radical to form hydroxide followed by direct reversible addition of hydroxide to the semiquinones and semidiones thereby exchanging oxygen. This dependance upon neutral molecule concentration also indicates that this same mechanism with the modification in step A indicated in reaction 4 is applicable for those systems that are kinetically stable in water. Once the labeled hydroxide ion is formed, the reaction can proceed in exactly the same manner as shown in Scheme I.



(4)

Several hours after the addition of large amounts (>10 μL) of labeled water, the ESR analysis clearly shows the presence of a third anion radical. This new system exhibits the same proton coupling constants and contains one ^{17}O with a much larger coupling constant (A_0 = 11.63 G). Given the relative slowness of the appearance of the second, larger ^{17}O splitting, it is statistically logical to assign this coupling constant to the unique carbonyl oxygen of the three. This is consistent with calculated Hückel and McLachlan type spin densities for the unique oxygen being more than double those of the matched pair of oxygens.[10] In our preliminary communication,[11] we misinterpreted the observation (at that time) of only one ^{17}O coupling constant in terms of the two oxygens being equivalent. This has proven not to be the case.

We were not able to observe a spectrum for any species containing two ^{17}O's on the same radical. This is due to statistical considerations coupled with the fact that the unlabeled material is always in much larger abundance than the labeled material. However, the reduction of specifically prepared dilabeled benzoquinone in liquid ammonia clearly shows the 11 five-line patterns due to four equivalent protons and two equivalent oxygen-17 nuclei.

Acknowledgment. We thank the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this work.

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[10] Sioda, R. E.; Koski, W. S. *J. Am. Chem. Soc.* **1967**, *89*, 475.

[11] Stevenson, G. R.; Wang, Z. Y.; Reiter, R. C. *J. Am. Chem. Soc.* **1988**, *110*, 6581.

Synthesis of 1,1-Bishomoadamant-3-ene (Tricyclo[5.3.1.1^{3,9}]dodec-3-ene)

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Formation of the silyl enol ether of 1,1-bishomoadamantan-4-one (4) under thermodynamically controlled conditions gives 4-(trimethylsiloxy)-1,1-bishomoadamant-4-ene. Generation of the silyl enol ether of 4 under kinetically controlled conditions provides 4-(trimethylsiloxy)-1,1-bishomoadamant-3-ene. Consequently, 1,1-bishomoadamant-3-ene (3) can be prepared in two steps from 4 by Ireland's method for the conversion of a ketone to the corresponding olefin via the kinetic enolate. As predicted by the criteria of both Wiseman and Schleyer, 3 is a tricyclic bridgehead olefin that is kinetically stable at room temperature.

Since Bredt noted that double bonds tend to avoid the ring junctions in camphane and pinane systems,[1] the synthesis of bridgehead olefins has received considerable attention.[2] According to Wiseman's modification of Bredt's rule, the strain in *bicyclic* bridgehead alkenes can be related to the strain of *trans*-cycloalkenes.[3] Wiseman recognized that all isolable bicyclic bridgehead olefins possess a *trans*-cycloalkene moiety that has at least eight carbon atoms. Wiseman also predicted that bicyclic bridgehead olefins in which the *trans*-cycloalkene unit contains seven or less carbon atoms should not be observable at room temperature.

More recently, molecular mechanics calculations have been employed to predict the stability of bridgehead olefins.[4] The olefinic strain (OS) of an alkene is calculated by subtracting the total strain energy of the most stable conformer of the corresponding saturated hydrocarbon from the total strain energy of the most stable conformer of the olefin. For calculations performed with the MM1 force field, Maier and Schleyer concluded that if OS ≤ 17 kcal/mol, then the olefin will be "isolable" at room temperature. If 17 kcal/mol ≤ OS ≤ 21 kcal/mol, then the

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[1] Bredt, J.; Thouet, H.; Schmitz, J. *Liebigs Ann. Chem.* **1924**, *437*, 1.

[2] Recent reviews: (a) Szeimes, G. In *Reactive Intermediates*; Abramovitch, R. A., Ed.; Plenum: New York, 1983; Vol. III, Chapter 5, p 299. (b) Shea, K. J. *Tetrahedron* **1980**, *36*, 1683.

[3] Wiseman, J. R.; Pletcher, W. A. *J. Am. Chem. Soc.* **1970**, *92*, 956.

[4] Maier, W. F.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1981**, *103*, 1891.

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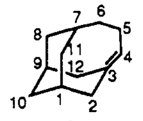
olefin should be spectroscopically "observable" at a reduced temperature but not isolable at room temperature. An olefin with OS $\geqslant$ 21 kcal/mol would be "unstable" and should be observable only in a matrix at a very low temperature.

The homologous series of adamantene (1), homoadamant-3-ene (2), and 1,1-bishomoadamant-3-ene (3)

1

2



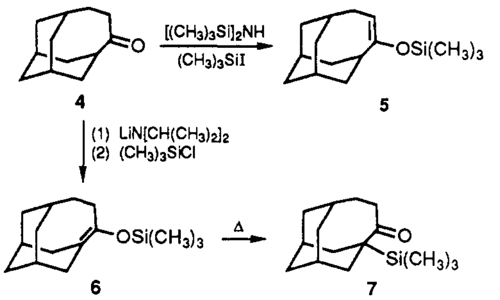
3

provides an opportunity to test these predictions with a family of *tricyclic* bridgehead olefins. Adamantene (OS: 39.5 kcal/mol by MM1,[4] 34.3 kcal/mol by MM2[5]) contains a trans double bond in a six-membered ring. Michl and co-workers succeeded in generating 1 in an argon matrix at −263 °C by treating 1,2-diiodoadamantane with sodium vapor.[6] This olefin survives for at least 1 h at −203 °C. However, when it is warmed to room temperature, a mixture of [2 + 2] dimers of 1 is obtained. Homoadamant-3-ene (OS: 20.2 kcal/mol by MM1,[4] 18.5 kcal/mol by MM2[5]) has a trans double bond in a seven-membered ring. This olefin was prepared by Martella et al. by pyrolyzing 1-adamantyldiazomethane at 375 °C and then condensing the product on a sodium chloride plate that was maintained at −196 °C.[7] When 2 is warmed to −20 °C, dimerization takes place. By the criteria of both Wiseman and Schleyer, 1,1-bishomoadamant-3-ene, which contains a trans double bond in an eight-membered ring and has an OS of 1.2 kcal/mol by MM2,[5] should be kinetically stable and isolable at room temperature. We now wish to report the preparation of 3.

Results and Discussion

A potential synthetic precursor for 3 is 1,1-bishomoadamantan-4-one (4). This ketone is readily prepared by the Tiffeneau–Demjanov homologation of 4-homoadamantanone.[8] Normally, the kinetic enolate of a ketone is formed preferentially at the less substituted carbon that is α to the carbonyl, and the thermodynamic enolate is produced preferentially at the more substituted carbon that is α to the carbonyl. We have found exactly the opposite behavior for ketone 4.

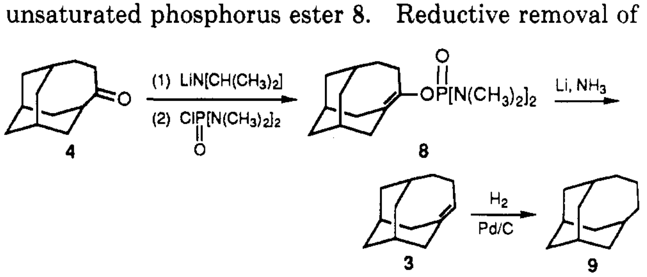
Miller and McKean have shown that treating a cyclic ketone with trimethylsilyl iodide and hexamethyldisilizane at room temperature leads to the predominant formation of the more substituted silyl enol ether.[9] However, reaction of 4 under these thermodynamically controlled conditions gives 4-(trimethylsiloxy)-1,1-bishomoadamant-4-ene (5) exclusively. The assignment of the carbon skeleton of 5 follows from the observation that acidic hydrolysis of 5 regenerates 4. Consistent with the presence of a plane of symmetry in 5, the proton decoupled ^{13}C NMR spectrum of 5 contains only 10 resonances. The ^{13}C NMR spectrum of 5 features one methine carbon and one quaternary carbon in the olefinic region, and the ^{1}H NMR spectrum of 5 has only one proton in this region.



Fleming and Paterson have reported that the less substituted silyl enol ether of a cyclic ketone can be prepared by slowly adding the ketone to a solution of lithium diisopropylamide in tetrahydrofuran at −78 °C and then quenching the resulting enolate with chlorotrimethylsilane.[10] Reaction of 4 under these kinetically controlled conditions provides only 4-(trimethylsiloxy)-1,1-bishomoadamant-3-ene (6). Although the ^{1}H NMR spectrum of 6 shows no protons in the olefinic region, the ^{13}C NMR spectrum of 6 contains signals for two quaternary carbons in this region. Since this compound contains no element of symmetry, the proton decoupled ^{13}C NMR spectrum of 6 consists of 13 signals. Acidic hydrolysis of 6 also provides only the starting ketone 4.

The considerable strain present in 6 is apparent from its unusual thermal behavior. Normally, an α-silyl ketone thermally rearranges to its corresponding silyl enol ether.[11] However, heating 6 at 200 °C in a sealed ampule for 1 h gives 3-(trimethylsilyl)-1,1-bishomoadamantan-4-one (7). The infrared spectrum of 7 shows a carbonyl absorption at 1708 cm^{-1}. Consistent with the presence of a plane of symmetry in 7, the proton decoupled ^{13}C NMR spectrum of 7 contains only 10 resonances.

As a result of these studies, it appeared that Ireland's method for the conversion of a ketone to the corresponding olefin[12] might provide a route from ketone 4 to 1,1-bishomoadamant-3-ene. According to this procedure, a ketone is initially treated with lithium diisopropylamide at −78 °C to generate the kinetic enolate, which is then trapped as the corresponding vinyl phosphoramidate by the addition of bis(dimethylamino)phosphorochloridate. Reductive removal of the phosphorus ester moiety with lithium in liquid ammonia provides the corresponding alkene. Generation and trapping of the kinetic enolate of ketone 4 by this method occurred smoothly to give the unsaturated phosphorus ester 8. Reductive removal of the phosphorus ester group of 8 with lithium in liquid ammonia provided crude 3. The alkene was isolated by initially dissolving the crude reduction product in ether and then complexing 3 with silver nitrate in water. This complex was destroyed with an aqueous potassium cyanide solution, and 3 was recovered by extraction with ether.[13]



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(5) The MM2 calculations were performed by Professor James Damewood of the University of Delaware.

(6) Conlin, R. T.; Miller, R. D.; Michl, J. *J. Am. Chem. Soc.* **1979**, *101*, 7637.

(7) Martella, D. J.; Jones, M., Jr.; Schleyer, P. v. R.; Maier, W. F. *J. Am. Chem. Soc.* **1979**, *101*, 7634.

(8) Sasaki, T.; Eguchi, S.; Toru, T.; Itoh, K. *J. Am. Chem. Soc.* **1972**, *94*, 1357.

(9) Miller, R. D.; McKean, D. R. *Synthesis* **1979**, 730.

(10) Fleming, I.; Paterson, I. *Synthesis* **1979**, 736.

(11) Little, J. L.; Moran, J. T.; Todd, L. J. *J. Am. Chem. Soc.* **1967**, *89*, 5493.

(12) (a) Ireland, R. E.; O'Neil, T. H.; Tolman, G. L. *Org. Syn.* **1983**, *61*, 116. (b) Ireland, R. E.; Muchmore, D. C.; Hengartner, U. *J. Am. Chem. Soc.* **1972**, *94*, 5098.

Pure **3** was obtained after crystallization of the resulting residue from aqueous acetone.

The structure of **3** is consistent with its spectral characteristics. The infrared spectrum of **3** shows a C=C stretching frequency at 1655 cm^{-1}. The presence of a methine carbon and a quaternary carbon in the olefinic region of the ^{13}C NMR spectrum of **3** is indicative of a bridgehead alkene. Moreover, the ^1H NMR spectrum of **3** has only one proton in the olefinic region. The proton decoupled ^{13}C NMR spectrum of **3** consists of 12 resonances. The carbon skeleton of **3** was unequivocally confirmed by catalytic hydrogenation of **3** to give the known hydrocarbon[8] 1,1-bishomoadamantane (**9**).

Experimental Section

Infrared spectra were recorded with Perkin-Elmer 180 or Unicam SP1100 spectrophotometers. Proton magnetic resonance spectra were obtained with a Bruker AM 250-MHz spectrometer. Apparent splittings are reported in all cases. Carbon magnetic resonance spectra were recorded with the Bruker instrument at 62.9 MHz. Both the ^1H and ^{13}C NMR spectra were obtained with $CDCl_3$ as the solvent and are referenced to an internal standard of tetramethylsilane. Electron impact mass spectra were recorded with a Du Pont 21-492B mass spectrometer at an ionization potential of 70 eV. The purity of each of the title compounds was judged to be >90% by ^1H and ^{13}C NMR spectroscopy.

4-(Trimethylsiloxy)-1,1-bishomoadamant-4-ene (5). Trimethylsilyl iodide (0.32 mL, 2.26 mmol) was added dropwise to a stirred solution of **4**[8] (100 mg, 0.57 mmol) in dry pentane (6.7 mL, distilled from lithium aluminum hydride) and freshly distilled hexamethyldisilizane (0.48 mL, 2.28 mmol) that was maintained at −20 °C under nitrogen. After stirring at −20 °C for 0.5 h, the reaction mixture was allowed to warm to room temperature, and then it was stirred at this temperature for 17 h. At this time, stirring was stopped and the pentane layer was decanted. This solution was washed with ice-cold, saturated aqueous sodium bicarbonate (2 × 6 mL) and then dried over anhydrous magnesium sulfate. Evaporation of the solvent at reduced pressure provided 141 mg (99% yield) of **5** as an oil: ^1H NMR δ 4.66 (t, J = 10.4 Hz, 1 H, CH=C), 2.7–1.3 (complex m, 16 H), 0.11 [s, 9 H, $OSi(CH_3)_3$]; ^{13}C NMR δ 156.5 (C-4), 105.4 (C-5), 37.7 (C-6), 35.3 (C-2 and C-11), 34.7 (C-8 and C-12), 34.7 (C-3), 33.3 (C-10), 25.3 (C-7), 24.7 (C-1 and C-9), 0.3 [$OSi(CH_3)_3$]; exact mass calcd for $C_{15}H_{26}OSi$ 250.175, found 250.175.

Hydrolysis of 5. Silyl enol ether **5** (145 mg, 0.58 mmol) was dissolved in a solution of tetrahydrofuran/1 M hydrochloric acid (20/1, 1.64 mL), and the resulting solution was stirred for 20 h at room temperature. Water (5 mL) was then added, and the reaction mixture was extracted with ether (3 × 10 mL). The ether extracts were combined, washed with water (10 mL), and dried over anhydrous magnesium sulfate. Evaporation of the solvent at reduced pressure provided a solid which was sublimed (100 °C, 0.02 mmHg) to give 83 mg (80% yield) of **4**.

4-(Trimethylsiloxy)-1,1-bishomoadamant-3-ene (6). A solution of lithium diisopropylamide in tetrahydrofuran was prepared by the dropwise addition of *n*-butyllithium (4.80 mL of a 1.48 M solution in hexane, 7.11 mmol) to a stirred solution of dry diisopropylamine (1.13 mL, 8.04 mmol, distilled from calcium hydride) in anhydrous tetrahydrofuran (8.25 mL, distilled from sodium benzophenone ketyl) that was maintained at −78 °C under nitrogen. The resulting solution was sitrred at −78 °C for 15 min and then at 0 °C for 15 min, before it was recooled to −78 °C. At this point, a solution of **4** (300 mg, 1.68 mmol) in dry tetrahydrofuran (1.4 mL) was added dropwise to this reaction mixture. The resulting solution was stirred at −78 °C for 5 h. Freshly distilled chlorotrimethylsilane (0.72 mL, 5.67 mmol) was then added dropwise to the reaction mixture. The resulting solution was allowed to warm to room temperature, and it was stirred at that temperature for 2 h. The solvent was then evaporated at reduced pressure, and dry pentane (10 mL) was added to the residue. This material was filtered, and the pentane was evaporated at reduced pressure. The resulting yellow oily residue was column chromatographed on basic alumina (15 g) with hexane as eluent to give 287 mg (68% yield) of **6** as a colorless oil: ^1H NMR δ 2.89 (br d, J = 9 Hz, 1 H), 2.72 (dt, J = 13 and 5.5 Hz, 1 H), 2.37–1.30 (complex m, 15 H), 0.10 [s, 9 H, $OSi(CH_3)_3$]; ^{13}C NMR δ 146.6 (C-4), 121.6 (C-3), 43.6 (t), 40.3 (t), 38.8 (d), 36.9 (t), 36.2 (t), 35.0 (t), 33.5 (d), 32.4 (t), 30.0 (t), 27.7 (d), 0.2 [$OSi(CH_3)_3$]; exact mass calcd for $C_{15}H_{26}OSi$ 250.175, found 250.176.

Hydrolysis of 6. Treatment of **6** (125 mg, 0.50 mmol) with a solution of tetrahydrofuran/1 M hydrochloric acid (20/1, 1.25 mL) according to the procedure described for **5** → **4** gave a solid which was sublimed (100 °C, 0.01 mmHg) to afford 52 mg (59% yield) of **4**.

3-(Trimethylsilyl)-1,1-bishomoadamantan-4-one (7). A neat sample of **6** (60 mg, 0.24 mmol) was heated in a sealed glass ampule at 200 °C for 1 h. The resulting yellow oil was Kugelrohr distilled (60–65 °C, 0.2 mmHg) to provide 20 mg (33% yield) of **7** as a colorless oil: ^1H NMR δ 2.60 (t, J = 6.7 Hz, 2 H), 2.33 (d, J = 14.5 Hz, 2 H), 2.17–1.35 (complex m, 13 H), −0.03 [s, 9 H, $Si(CH_3)_3$]; ^{13}C NMR δ 217.1 (C-4), 76.7 (C-3), 45.0 (C-2 and C-11), 38.7 (C-5), 35.3 (C-6 or C-10), 35.1 (C-6 or C-10), 34.1 (C-8 and C-12), 28.4 (C-1 and C-9), 25.8 (C-7), 2.8 [$-Si(CH_3)_3$]; IR ($CHCl_3$) ν 2920, 1708, 1250, 1110, 1095, 985 cm^{-1}; exact mass calcd for $C_{15}H_{26}OSi$ 250.175, found 250.176.

1,1-Bishomoadamant-3-ene (3). *n*-Butyllithium (6.40 mL of a 1.48 M hexane solution, 9.49 mmol) was added dropwise to a stirred solution of dry diisopropylamine (1.52 mL, 10.72 mmol) in dry tetrahydrofuran (11.0 mL) that was maintained at −78 °C under nitrogen. The resulting solution was stirred at −78 °C for 15 min and then at 0 °C for 15 min, before it was recooled to −78 °C. At this point, a solution of **4** (400 mg, 2.25 mmol) in dry tetrahydrofuran (1.9 mL) was added dropwise to this reaction mixture. The resulting solution was stirred for 5 h at −78 °C. Bis(dimethylamino)phosphorochloridate (1.17 mL, 7.6 mmol) was then added dropwise, and the solution was allowed to warm to room temperature. It was stirred at room temperature for 2 h. Saturated aqueous sodium bicarbonate (6.7 mL) was then added, and stirring was continued for 5 min. The resulting milky mixture was extracted with ether (3 × 20 mL). The ether extracts were combined, washed with brine (15 mL), and dried over anhydrous magnesium sulfate. Evaporation of the solvent at reduced pressure afforded 1.51 g of a yellow oil which showed no carbonyl absorption in the infrared.

The yellow oil, which was the crude 1,1-bishomoadamant-3-ene-4-bis(dimethylamino)phosphoroamidate (**8**), was dissolved in dry tetrahydrofuran (20 mL), and the solution was cooled to −78 °C. As this solution was stirred under nitrogen at −78 °C, ammonia gas (ca. 30 mL) was condensed into it. The resulting solution was then allowed to warm to reflux, dry *tert*-butyl alcohol (0.88 mL, distilled under nitrogen from sodium metal) was added, and small pieces (3–5 mg each) of lithium (total of ca. 50 mg) were introduced over 2 h so as to maintain a dark blue color. At this time, enough ammonium chloride was added to the reaction mixture to dissipate the blue color, and the ammonia was allowed to evaporate. Ether (25 mL) and water (25 mL) were then added, the layers were separated, and the aqueous layer was extracted with ether (2 × 20 mL). The ether layer and the ether extracts were combined, washed with brine (20 mL), and dried over anhydrous magnesium sulfate. Evaporation of the solvent at reduced pressure (water aspirator) at 10 °C provided 1.22 g of a clear oil which was dissolved in ether (20 mL). This solution was extracted with 2 M aqueous silver nitrate (3 × 8 mL). The combined silver nitrate extracts were poured into ice-cold 4 M aqueous potassium cyanide (35 mL). The resulting suspension was stirred for 5 min, and then it was extracted with ether (3 × 20 mL). The combined ether extracts were washed with water (2 × 10 mL), dried over anhydrous magnesium sulfate, and concentrated at reduced pressure (water aspirator) at 10 °C to give 240 mg of a clear colorless oil. Crystallization of this material from aqueous acetone afforded 29 mg (8% yield) of **3** as a white solid:[14] ^1H NMR δ 5.42 (dd, J = 11.7 and 4.4 Hz, 1 H, CH=C), 2.55–0.98 (complex m,

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[13] This procedure follows that developed in: Franzus, B.; Baird, W. C., Jr.; Snyder, E. I.; Surridge, J. H. *J. Org. Chem.* **1967**, *32*, 2845.

[14] An attempt to obtain the melting point of **3** by digital scanning calorimetry indicated two exothermic transitions between 60 and 250 °C. These were followed by an endothermic transition that began at about 365 °C and reached a maximum at 381 °C.

17 H); ^{13}C NMR δ 142.0 (C-3), 124.8 (C-4), 48.4 (t), 46.2 (t), 39.1 (d), 36.1 (t), 35.7 (t), 35.6 (t), 34.1 (t), 32.2 (d), 27.2 (d), 26.7 (t); IR ($CHCl_3$) ν 2930, 2865, 1655, 1475, 1455, 1440, 1265, 1100, 975, and 865 cm^{-1}; exact mass calcd for $C_{12}H_{18}$ 162.141, found 162.141.

1,1-Bishomoadamantane (9). A solution of **3** (20 mg, 0.12 mmol) in ether (10 mL) was stirred at room temperature with 10% palladium on carbon (5 mg) under an atmosphere of hydrogen for 48 h. The reaction mixture was then filtered through a small amount of Celite to remove the catalyst. Evaporation of the solvent at reduced pressure provided an off-white solid which was sublimed (65 °C, 1.0 mmHg) to give 17 mg (83% yield) of **9**. The spectroscopic characteristics of this material were identical with those of a sample of **9** that was prepared by an independent route.[7]

Acknowledgment. This work was supported by grants from the United Parkinson Foundation and the University of Delaware Research Foundation.

Registry No. **3**, 123411-72-3; **4**, 36071-45-1; **5**, 123411-68-7; **6**, 123411-69-8; **7**, 123411-70-1; **8**, 123411-71-2; **9**, 36071-50-8.

Supplementary Material Available: ^{1}H and ^{13}C NMR spectra for compounds **3**, **5**, **6**, and **7** (8 pages). Ordering information is given on any current masthead page.

Preparation and Reactions of Some (Trimethylsilyl)cyclopropenes. Synthesis of In-Out Tricyclic $[n.3.2.0^{2,4}]$ Compounds, Potential Precursors to Cyclopropaparacyclophanes

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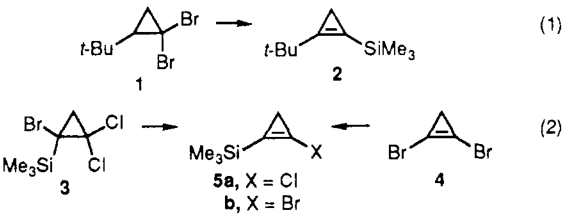
Received February 21, 1989

1,2-Bis(trimethylsilyl)cyclopropene (**7**), 1,2,3-tris(trimethylsilyl)cyclopropene (**11**), and 3,3-dibromo-1,2-bis(trimethylsilyl)cyclopropene (**13a**) were prepared from 1,2-bis(trimethylsilyl)acetylene (**6**) by the addition of the appropriate carbene. 1-Bromo-2-(trimethylsilyl)cyclopropene (**5b**) and 3,3-dimethyl-1-(trimethylsilyl)cyclopropene (**17**) were prepared by modification of previous routes from tribromocyclopropanes. 2,2′-Bis(trimethylsilyl)bicyclopropenyl (**20**) and 3,3,3′,3′-tetramethyl-2,2′-bis(trimethylsilyl)bicyclopropenyl (**22**) were prepared by metalation of the appropriate halocyclopropene, but Diels–Alder addition to these bicyclopropenyls did not give the desired adducts. Diels–Alder addition of **13a** to (*E*,*Z*)-cyclododeca-1,3-diene (**27a**) gave the tricyclic in-out adduct **28** and addition of 1,2-dibromocyclopropene (**4**) to **27a** and to (*E*,*Z*)-cycloundeca-1,3-diene (**27b**) gave the corresponding tricyclic in-out adducts **29a** and **29b**.

Cyclopropenes are useful precursors to aryl compounds strained by the annelation of three-membered rings.[1] We have been interested in preparing such compounds for some time and considered that cyclopropenes substituted with silicon would be desirable intermediates for this purpose because of the synthetic possibilities and ease of removal of the silicon group.[2] We consequently explored the preparation of (trimethylsilyl)cyclopropenes and describe herein their synthesis and some of their reactions. In particular, the Diels–Alder reaction with *E*,*Z*-cyclic dienes of 1,2,3-tris(trimethylsilyl)cyclopropene and 1,2-dibromocyclopropene leads to in-out tricyclo$[n.3.2.0^{2,4}]$ systems, potential precursors of cyclopropaparacyclophanes.

Synthesis of (Trimethylsilyl)cyclopropenes

A number of (trimethylsilyl)cyclopropenes are known, most of them prepared by the trimethylsilylation of a preformed cyclopropane or cyclopropene. Thus 1-(trimethylsilyl)-2-*tert*-butylcyclopropene (**2**) has thus been prepared by reaction of 1,1-dibromo-2-*tert*-butylcyclopropane (**1**) with 2 mol of methyllithium and trimethylsilyl chloride (eq 1).[3] 1-Chloro-2-(trimethylsilyl)cyclopropene (**5a**) has been prepared from 2-bromo-1,1-dichloro-2-(trimethylsilyl)cyclopropane (**3**),[4] and the corresponding bromocyclopropene **5b** from 1,2-dibromocyclopropene (**4**, eq 2).[5] We were interested in a general method for the synthesis of (trimethylsilyl)cyclopropenes and decided to examine the addition of carbenes to (trimethylsilyl)acetylenes[6] as well as previous methods.



From the Addition of Carbenes to (Trimethylsilyl)acetylenes. Bis(trimethylsilyl)acetylene (**6**) was heated with a suspension of (iodomethyl)mercuric iodide[7] and diphenylmercury[8] to give 1,2-bis(trimethylsilyl)cyclopropene (**7**) in 10% yield as a clear, colorless oil which resinified on standing at room temperature (Scheme I).

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(1) See: Billups, W. E.; Rodin, W. A.; Haley, M. M. *Tetrahedron* **1988**, *44*, 1305.

(2) See: Fleming, I. *Comprehensive Organic Chemistry*; Barton, D., Ollis, W. D., Eds.; Pergamon: Oxford, 1979; Vol. 3, Jones, D. N. Ed., Chapter 13.

(3) Baird, M. S.; Nethercott, W. *Tetrahedron Lett.* **1983**, 605. Baird, M. S.; Hussain, H. H.; Nethercott, W. *J. Chem. Soc., Perkin Trans. 1* **1986**, 1845.

(4) Billups, W. E.; Lin, L.-J. *Tetrahedron* **1986**, *42*, 1575.

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