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: ^1H 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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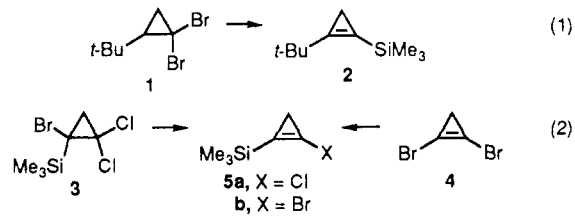
1,2-Bis(trimethylsilyl)cyclopropene (**7**), 1,2,3-tris(trimethylsilyl)cyclopropene (**11**), and 3,3-dibromo-1,2-bis(trimethylsilyl)cyclopropene (**13a**) were prepared from 1,2-bis(trimethylsilyl)acetylene (**6**) by the addition of the appropriate carbene. 1-Bromo-2-(trimethylsilyl)cyclopropene (**5b**) 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.

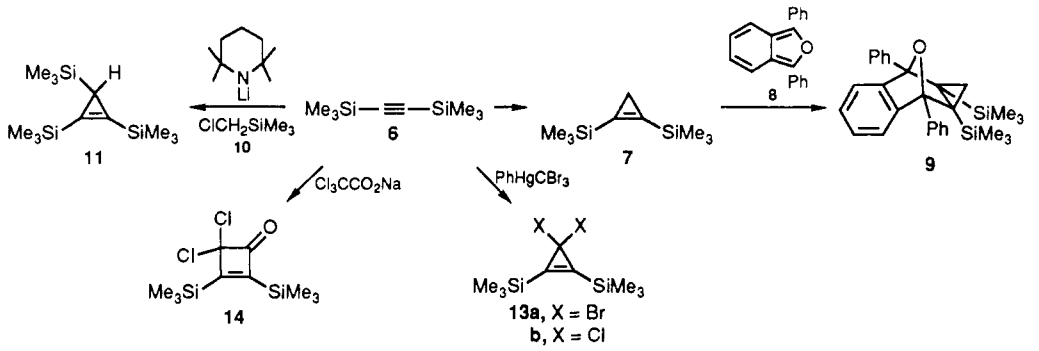


From the Addition of Carbenes to (Trimethylsilyl)acetylenes. Bis(trimethylsilyl)acetylene (**6**) was heated with a suspension of (iodomethyl)mercuric iodide[7] and diphenylmercury[8] to give 1,2-bis(trimethylsilyl)-cyclopropene (**7**) in 10% yield as a clear, colorless oil which resinified on standing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

(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.
(5) Dent, B. R.; Halton, B.; Smith, A. M. F. *Aust. J. Chem.* **1986**, *39*, 1621.
(6) Both the successful accomplishment of and the problems encountered with, the addition of carbenes to acetylenes is well documented. See, Kirmse, W. *Carbene Chemistry*, 2nd ed.; Academic Press: New York, 1971; Chapter 9.
(7) Simmons, H. E.; Blanchard, E. P., Jr.; Smith, R. D. *J. Am. Chem. Soc.* **1964**, *86*, 1347. Blanchard, E. P., Jr.; Blomstrom, D. C.; Simmons, H. E. *J. Organomet. Chem.* **1965**, *3*, 97.
(8) Seyferth, D.; Burlitch, J. M.; Minasz, R. J.; Mui, J. Y.-P.; Simmons, H. D., Jr.; Treiber, A. J. H.; Dowd, S. R. *J. Am. Chem. Soc.* **1965**, *87*, 4259.

0022-3263/90/1955-0084$02.50/0

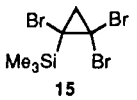
Scheme I



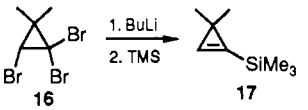
When the experiment was repeated in the presence of 1,3-diphenylisobenzofuran (**8**) the adduct **9** was isolated in 35% yield, identical in all observed respects with that previously reported.[5] We next examined the addition of (trimethylsilyl)carbene to **6**. Bis(trimethylsilyl)acetylene (**6**) and (chloromethyl)trimethylsilane (**10**) were added to lithium 2,2,6,6-tetramethylpiperidine in hexanes to give 1,2,3-tris(trimethylsilyl)cyclopropene (**11**) in 15% yield as a yellow oil, stable at room temperature for about a month. The mass, IR, and ^{1}H NMR spectra were in accord with the assigned structure.

We then turned our attention to the preparation of 3,3-dihalo-1,2-bis(trimethylsilyl)cyclopropenes. Phenyl(tribromomethyl)mercury (**12**) was heated to 80 °C in a benzene solution of **6**, and 3,3-dibromo-1,2-bis(trimethylsilyl)cyclopropane (**13a**) was isolated in 45% yield as a colorless oil. The mass, IR, and ^{1}H and ^{13}C NMR spectra were in accord with the assigned structure. We had initially attempted to apply the same sequence of reactions to the preparation of 3,3-dichloro-1,2-bis(trimethylsilyl)cyclopropene (**13b**) but had obtained none of the desired compound, isolated only an ill-defined material containing trimethylsilyl groups. Reaction of sodium trichloroacetate with **6** at 80 °C also gave none of the desired product, but in this case 4,4-dichloro-2,3-bis(trimethylsilyl)cyclobutenone (**14**) was obtained in 45% yield. The mass, IR, and ^{13}C and ^{1}H NMR spectra were in accord with the assigned structure. Ring expansion of 3,3-dihalocyclopropenes to 4,4-dihalocyclobutanones during dihalocarbene additions to acetylenes is well-known[9] and may occur via the cyclopropenone or by direct attack on the 3,3-dihalocyclopropene by the trihalomethyl anion.

From Halocyclopropanes. As mentioned earlier, 1-bromo-2-(trimethylsilyl)cyclopropene (**5b**) had been prepared by lithiation and trimethylsilation of 1,2-dibromocyclopropene (**4**).[5] We have found that **5b** can be prepared directly from 1,1,2-tribromo-2-(trimethylsilyl)cyclopropane (**15**), the precursor of **4**, by treatment with *n*-butyllithium



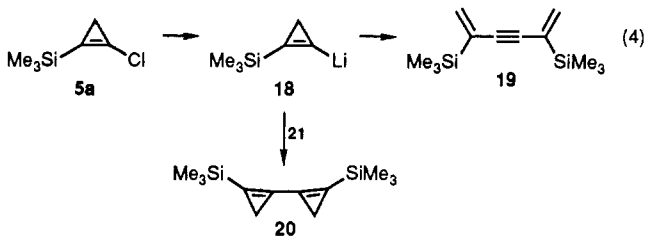
in ether at −78 °C for 2 min. The ^{1}H NMR spectrum exhibited two singlets at δ 1.47 (2 H) and 0.18 (9 H) and is consistent with that previously reported.[5] The corresponding chlorocyclopropene **5a** could be prepared from **3** by Billup's method, gas-phase treatment with methyllithium on glass helixes, or in solution by treatment with methyllithium at −78 °C. 3,3-Dimethyl-1-(trimethylsilyl)cyclopropene (**17**), previously prepared from 3,3-dimethylcyclopropene by lithiation and trimethylsilylation, was obtained in 73% yield by treatment 3,3-dimethyl-1,1,2-tribromocyclopropane (**16**, eq 3) with *n*-butyllithium followed by trimethylchlorosilane and was identical in all observed respects with that prepared by the previous route.[10]



(3)

Reactions of (Trimethylsilyl)cyclopropenes

Dimerization via Lithium–Halogen Exchange. Treatment of 1-chloro-2-(trimethylsilyl)cyclopropene (**5a**) with *n*-butyllithium at −78 °C gave a yellow solution, attributed to the organolithium **18**. Treatment of this solution with a copper(I) iodide–copper(II) chloride medium gave the acetylene **19** in 14% yield (eq 4). The mass



(4)

spectrum molecular ion at m/e 222 and the spectral properties were in accord with the assigned structure. The acetylene **19** may arise from reaction of the desired bicyclopropenyl **20** with copper ions leading to a ring-opened carbocation that subsequently rearranges. Treatment of **5a** with the tri-*n*-butylphosphine copper(I) complex **21** and then dioxygen by the method of Whitesides et al.[11] gave the desired bicyclopropenyl **20** but only in 5% yield. Although satisfactory analytical or mass spectral data could not be obtained because of the instability of **20**, the spectral properties were in accord with the assigned structure. The IR spectrum showed strong bands at 2980, 1680, and 850 cm^{-1}, and the ^{1}H NMR spectrum had two singlets at δ 1.50 and 0.16 in the ratio 2:9. Particularly supportive was the ^{13}C NMR spectrum, which showed four signals at 135.2, 130.6, 27.15, and −0.85. Compound **20** could also be prepared in 8% yield from the corresponding bromo derivative **5b**.

Dimerization of 3,3-dimethyl-1-(trimethylsilyl)cyclopropene (**17**) had been previously reported to give the

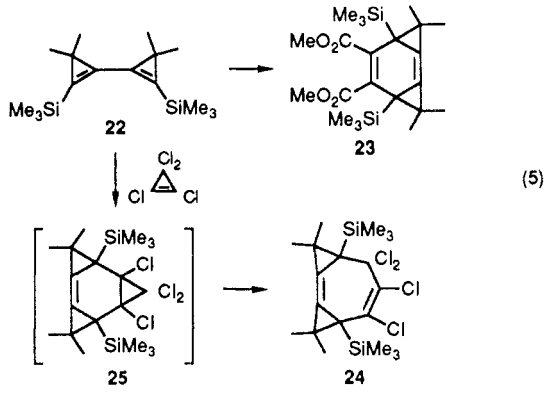
(9) Dehmlow, E. V. *Tetrahedron Lett.* **1965**, 4003.

(10) (a) Grüger, F.; Sziemies, G. *Tetrahedron Lett.* **1986**, *27*, 1563. (b) Baird, M. S.; Hussain, H. H. *Tetrahedron Lett.* **1986**, *27*, 5143. (c) Kirms, M. A.; Prinke, H.; Stohlmeier, M.; de Meijere, A. *Recl. Trav. Chim. Pays-Bas* **1986**, *105*, 462.

(11) Whitesides, G. M.; SanFilippo, J., Jr.; Casey, C. P.; Panek, E. J. *J. Am. Chem. Soc.* **1967**, *89*, 5302.

bicyclopropenyl **22** in 30% yield.[10a] Using **17** prepared by our alternative synthesis and replacing THF for ether in the lithiating sequence gave **22** in 57% yield.

A number of attempts were made to react the bicyclopropenyl **20** with dienophiles, but these all led to nondefinable material, probably through decomposition of **20** before the Diels–Alder reaction could occur. The bicyclopropenyl **22** did react in a Diels–Alder manner with dimethyl acetylenedicarboxylate in boiling toluene to give **23** but in only 6% yield (eq 5). The analytical and mass

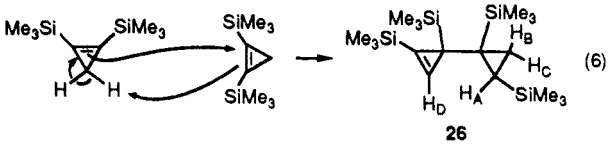


(5)

spectral data were in accord with the assigned structure, the mass spectrum showing a fragment ion at m/e 278, attributed to an ion arising from a retro-Diels–Alder process. Although **22** did not give any recognizable product with 1,2-dibromocyclopropene, it did react with tetrachlorocyclopropene in boiling toluene to give **24** as colorless crystals in 33% yield. The analytical and mass spectral data are in accord with the desired tetracyclic system **25**, but the spectral data firmly indicate that **24** has the structure shown. In particular, the ^{13}C NMR spectrum shows signals at δ 148.4, 143.3, 135.2, 84.35, 34.2, 28.1, 2.37, and −0.65, consistent with **24** but not with **25**.

This facile rearrangement finds ample precedent in the observations of Law and Tobey[12] on the reaction of tetrachlorocyclopropene with cyclopentadiene and furan, the observed products being derived in the same way. Substitution of 3,3-difluoro-1,2-dichlorocyclopropene as the dienophile may lead to isolation of the desired unrearranged adduct, but this has not been investigated.

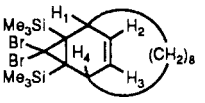
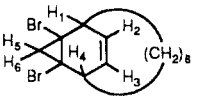
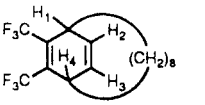
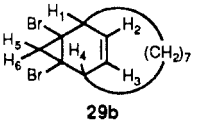
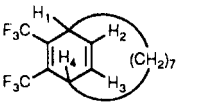
Ene Reactions of (Trimethylsilyl)cyclopropenes. Cyclopropenes having a hydrogen atom at C-3 often undergo a facile ene reaction involving the transfer of the hydrogen to the double bond of another molecule with concurrent C–C bond formation between them.[13] When 1,2-bis(trimethylsilyl)cylcopropene (**7**) is allowed to stand in $CDCl_3$ for a few minutes at room temperature, the original ^1H NMR spectrum disappears and a new spectrum develops, consistent with the dimeric structure **26** (eq 6). The mass spectrum and analytical data are also in accord with this dimerized structure.



(6)

In contrast, the tris(trimethylsilyl)cyclopropene **11** was stable in $CDCl_3$ even after prolonged heating at 100 °C in a sealed tube. Steric interaction is presumably too severe to allow transfer of the hydrogen from one sterically hindered site to another.

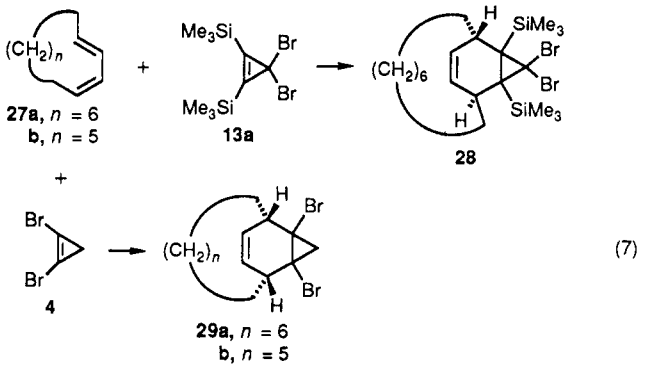
Table I. ^1H NMR Spectra of In–Out Diels–Alder Adducts

compound	chem shifts,[a] δ, multiplicity, assignment	ref
 **28**	0.17 (s, $SiMe_3$), 1.28–1.68 (m, $(CH_2)_8$), 2.05 (m, H-4), 2.14 (m, H-1), 5.22 (m, H-3/2),[b] 5.28 (br s, H-2/3)	
 **29a**	0.87 (m, H-5,6), 1.26–1.60 (m, $(CH_2)_8$), 2.12 (m, 4-H), 2.20 (m, H-1), 5.40 (m, H-3/2), 5.73 (br s, H-2/3)	
	1.20–2.28 (m, $(CH_2)_8$), 3.03 (m, H-4), 3.51 (m, H-1), 5.99 (br s, H-3/2), 6.02 (m, H-2/3)	17
 **29b**	0.90 (m, H-5,6), 1.2–1.57 (m, $(CH_2)_7$), 2.81 (m, H-4), 2.89 (m, H-1), 5.99 (m, H-3/2), 6.12 (br s, H-2/3)	
	1.05–2.20 (m, $(CH_2)_7$), 2.92 (m, H-4), 3.48 (m, H-1), 6.02 (m, H-3/2), 6.25 (m, H-2/3)	17

[a] Spectra taken in $CDCl_3$ as solvent. [b] 2/3 (3/2) indicates that it was not possible to distinguish between H-2 and H-3 in the assignment.

Diels–Alder Reactions of (Trimethylsilyl)cyclopropenes. Cyclopropenes readily act as dienophiles, cycloaddition leading to relief of ring strain. The ease of reaction depends on the nature and position of substituents; electron-withdrawing groups on the double bond increase the reactivity while substituents at C-3 decrease reactivity.[14-16] As we have previously mentioned, the bis(trimethylsilyl)cyclopropene **7** reacts with 1,3-diphenylisobenzofuran (**8**) to give the adduct **9**. Treatment of tris(trimethylsilyl)cyclopropene **11** or 3,3-dibromo-1,2-bis(trimethylsilyl)cyclopropene (**13a**) with **9** under a variety of conditions gave none of the desired products even at elevated temperatures. Although these results were not very encouraging, we nevertheless decided to examine some of these cyclopropenes with strained cyclic dienes, trusting that the relief of strain energy might overcome the lack of reactivity of the cyclopropene. Gassman and co-workers[17] have reported that (*E,Z*)-cyclododeca-1,3-diene (**27a**) is more reactive than either the *E,E* or *Z,Z* isomer and that the products have the unusual in–out stereochemistry. Treatment of **27a** with the cyclopropene **13a** and a trace of hydroquinone in a Carius tube at 100 °C gave the adduct **28** in 10% yield plus 15% of unreacted **27a** (eq 7). Despite many attempts, **28** could not be freed from a small amount of impurity, but otherwise the spectral properties are in accord with the assigned structure. The ^1H NMR spectral data are shown in Table I in comparison with the ^1H NMR spectrum of in–out bridged cyclohexadiene prepared by Gassman and co-workers.[17] The reactivity of **13a** prompted us to examine cyclopropene **7** in this reaction. Treatment of **7** with **27a** at low temperatures followed by warming to 0 °C gave ony an intractable polymer and none

(12) Law, D. F. C.; Tobey, S. W. *J. Am. Chem. Soc.* **1968**, *90*, 2376.
(13) See: Breslow, R.; Dowd, P. *J. Am. Chem. Soc.* **1963**, *85*, 2729. Yoshida, Z.; Miyahara, H. *Chem. Lett.* **1972**, 335.
(14) Closs, G. L.; Closs, L. E.; Böll, W. A. *J. Am. Chem. Soc.* **1963**, *85*, 3796.
(15) Battiste, M. A. *Tetrahedron Lett.* **1964**, 3795.
(16) Cijanek, E. *J. Am. Chem. Soc.* **1966**, *88*, 1979.
(17) Gassman, P. G.; Bailey, T. F.; Hoye, R. C. *J. Org. Chem.* **1980**, *45*, 2923, and references therein.



(7)

of the desired adduct. Wishing to obtain a pure in–out precursor, we retreated from the (trimethylsilyl)cyclopropenes and examined the reaction of 1,2-dibromocyclopropene (**4**) and **27a**. Treatment of **4** with **27a** in THF containing hydroquinone at −50 °C gave none of the desired adduct **29a**. When, however, the precursor of **4**, the tribromo(trimethylsilyl)cyclopropane **15**, was dissolved in THF with the diene **28** at −78 °C and the solution treated with tetra-*n*-butylammonium fluoride, the adduct **29a** was obtained in 26% yield as a colorless oil. The analytical data and mass and IR spectra were in accord with the proposed structure. The ^{1}H NMR spectral data are shown in Table I.

We then examined the reaction of the cyclopropenes with (*E,Z*)-cycloundea-1,3-diene (**27b**).[18] None of the desired adduct could be obtained with either of the (trimethylsilyl)cyclopropenes **7** or **11**. In the latter case, reaction in a Carius tube at 100 °C as before led to an intractable resin, the diene also having decomposed. 1,2-Dibromocyclopropene (**4**) did, however, react with **27b** to give the desired adduct **29b** in 44% yield. The analytical data and mass and IR spectra were in accord with the assigned structure. The ^{1}H NMR spectral data are shown in Table I.

Preliminary attempts to dehydrobrominate adducts **29a** and **29b** to the corresponding cyclopropacyclophanes using KO-*t*-Bu in THF or DMSO were unsuccessful, only intractable materials being obtained. We believe, however, that these compounds warrant more extensive investigation, but not currently having the wherewithal to do this we publish these results hoping that they will stimulate others with an interest in this area and the means to pursue these studies.

Experimental Section

Mass spectra were obtained on a VG 7070H spectrometer. ^{1}H NMR spectra were recorded on a Varian XL-200 or XVR-400 spectrometer in $CDCl_3$ as solvent with Me_4Si as internal standard except when recording the spectra of TMS-containing compounds. ^{13}C NMR spectra were recorded on a Varian XL-200 spectrometer in $CDCl_3$ as solvent with Me_4Si as standard except when recording the spectra of TMS-containing compounds, where the residual peak of $CHCl_3$ was taken as the reference. IR spectra were recorded on a Perkin-Elmer 983 spectrophotometer. Melting points were taken on a Kofler hot-stage melting point apparatus and are uncorrected. Spinning plate preparative thin-layer chromatography was performed on a Chromatatron instrument using silica gel as adsorbant. Solvents were purified by standard methods, and all reactions were carried out under an atmosphere of dry N_2 unless stated otherwise. *n*-Butyllithium was used dissolved in hexanes.

Preparation of 1,2-Bis(trimethylsilyl)cyclopropane (7). Bis(trimethylsilyl)acetylene (**6**, 0.62 g, 3.65 mmol) was added to a stirred mixture of (iodomethyl)mercuric iodide (0.09 g, 0.20 mmol) and diphenylmercury (0.07 g, 0.20 mmol) in benzene (5 mL) at room temperature. The mixture was warmed to 35 °C and stirred for 3 days. After cooling to room temperature, the precipitate was removed by filtration, and the residue concentrated under reduced pressure and chromatographed by spinning plate chromatography, eluting with cyclohexane, to give a colorless oil, 0.004 g (0.02 mmol, 10%); ^{1}H NMR δ 0.25 (s, 18 H), 1.41 (s, 2 H).

The experiment was repeated but with the addition of 1,3-diphenylisobenzofuran (**8**, 0.99 g, 3.66 mmol). The mixture was worked up as before, and the resulting brown oil chromatographed by spinning plate chromatography, eluting with cyclohexane, to give **9**, 0.026 g (0.07 mmol, 35%), as yellow crystals; mp 158–160 °C (lit.[5] mp 150–155 °C). The mass and ^{1}H NMR spectra were in accord with those reported.

Preparation of 1,2,3-Tris(trimethylsilyl)cyclopropene (11). Bis(trimethylsilyl)acetylene (**6**, 10.31 g, 1.82 mmol) was added to a stirred suspension of lithium 2,2,6,6-tetramethylpiperidide (prepared from 2,2,6,6-tetramethylpiperidine (0.26 g, 1.82 mmol)) in hexanes. (Chloroethyl)trimethylsilane (**10**, 0.22 g, 1.82 mmol) was then added, and the resulting mixture was heated at 85 °C for 24 h before being allowed to cool to room temperature. The resulting dark suspension was diluted with ether (10 mL), washed with saturated aqueous citric acid (5 mL) and water (10 mL), and dried ($MgSO_4$). The solvents were removed under reduced pressure to give a brown oil that was chromatographed by spinning plate chromatography, eluting with *n*-hexane, to give **11**, 0.070 g (0.27 mmol, 15%); MS *m/e* 256 (M^+), 241, 183, 110, 73 (100%); ^{1}H NMR δ 0.89 (s, 1 H), 0.20 (s, 18 H), 0.17 (s, 9 H); IR (liquid film) 2990, 2924, 1653, 1412, 1250, 842 cm^{-1}. Anal. Calcd for $C_{12}H_{28}Si_3$: C, 56.16; H, 10.99. Found: C, 55.72; H, 11.35.

Preparation of 3,3-Dibromo-1,2-bis(trimethylsilyl)cyclopropane (13a). Bis(trimethylsilyl)acetylene (**6**, 0.85 g, 5.00 mmol) in benzene (5 mL) was added dropwise to a stirred mixture of phenyl(tribromomethyl)mercury (1.86 g, 5.00 mmol) and hydroquinone (4.00 mg, 0.04 mmol) in benzene (5 mL) at 80 °C. After addition, the mixture was stirred at 80 °C for 1 h and cooled, and the resulting precipitate removed by filtration. Ethanol (6 mL) was added to the filtrate, the mixture heated to reflux for 5 min and cooled, and the resulting precipitate again removed by filtration. The filtrate was concentrated under reduced pressure, cyclohexane (5 mL) added, and the mixture filtered. The filtrate was chromatographed by spinning plate chromatography, eluting with cyclohexane, to give **13a**, 0.77 g (2.24 mmol, 45%) as a colorless oil: MS, *m/e* 344, 342, 340 (M^+, 53, 90, 57), 263, 261 (M^+ − Br), 182, 73 (100); ^{1}H NMR δ 0.14 (s); ^{13}C NMR δ 113.7, 27.1, 0.13; IR (liquid film) 2930, 2843, 1780, 1742, 1438, 1250, 845, 772, 628 cm^{-1}. Anal. Calcd for $C_9H_{18}Br_2Si_2$: C, 31.59; H, 5.30; Br, 46.70. Found: C, 31.62; H, 5.28; Br, 46.55.

Reaction of Bis(trimethylsilyl)acetylene (6) with Sodium Trichloroacetate. Preparation of 4,4-Dichloro-2,3-bis(trimethylsilyl)cyclobutenone (14). The acetylene **6** (0.62 g, 3.65 mmol) was added to a mixture of sodium trichloroacetate (0.67 g, 3.65 mmol) and hydroquinone (2.00 mg, 0.02 mmol) in a mixture of glyme:diglyme (10:1, 10 mL) at 25 °C. The mixture was warmed to 90 °C and maintained at this temperature for 10 h. After cooling, the dark mixture was diluted with pentane (5 mL) and water (5 mL), stirred for 30 min, and then filtered through glass wool. The residue was washed with pentane (10 mL), the combined filtrates were separated, and the aqueous phase was extracted with pentane (8 mL). The organic layers were washed with water (5 × 10 mL) and dried ($CaCl_2$), and the solvent was removed under reduced pressure to give **14**, 0.46 g (1.64 mmol, 45%), as a pale yellow oil: MS, *m/e* 284, 282, 280 (M^+, 1, 5, 8), 247, 247 (M^+ − Cl), 210, 207, 73 (100); ^{1}H NMR δ 0.18 (s); ^{13}C NMR δ 209.0, 139.25, 107.7, −0.65; IR (liquid film) 2982, 2922, 1790, 1610, 1410, 1268, 865 cm^{-1}. Anal. Calcd for $C_{10}H_{18}Cl_2OSi_2$: C, 42.69; H, 6.45; Cl, 25.20. Found: C, 42.85; H, 6.91; Cl, 25.33.

Preparation of 1-Bromo-2-(trimethylsilyl)cyclopropene (5b). *n*-Butyllithium (1.17 M, 6.90 mL, 5.00 mmol) was added dropwise to a magnetically stirred solution of 1,1,2-tribromo-2-(trimethylsilyl)cyclopropane (**15**, 2.81 g, 8.00 mmol) in THF (15 mL) at −78 °C. Stirring was continued for approximately a further 2 min, and the mixture was then treated with hydrochloric acid (2 M, 0.5 mL) and water (10 mL) and allowed to warm to room temperature. The organic layer was separated and dried, and the

(18) Gassman, P. G.; Korn, S. R.; Bailey, T. F.; Johnson, T. H.; Finer, J.; Clardy, J. *Tetrahedron Lett.* **1979**, 3401.

solvent removed under reduced pressure to give **5b**, 0.20 g (1.05 mmol, 13%), as a pale yellow oil, identical in all observed respects with that previously reported.[5]

Preparation of 3,3-Dimethyl-1-(trimethylsilyl)cyclopropane (17). *n*-Butyllithium (2.70 M, 0.22 mL, 0.59 mmol) was added over 5 min to a stirred solution of 3,3-dimethyl-1,1,2-tribromocyclopropane (**18**, 0.18 g, 0.59 mmol) in hexane at −78 °C. The resulting mixture was allowed to warm to room temperature, and then, after 15 min, it was cooled to −40 °C and chlorotrimethylsilane (0.07 g, 0.64 mmol) was added over 5 min. The mixture was then allowed to warm to room temperature, and water (0.5 mL) was added. The organic layer was separated, washed with water (3 × 3 mL), and dried ($MgSO_4$), and the solvents were removed under reduced pressure to give **17**, 0.60 g (0.43 mmol, 73%) as a colorless oil, identical in all observed respects with that prepared previously.[10]

Reaction of 1-Chloro-2-(trimethylsilyl)cyclopropene (5a) with *n*-Butyllithium and Copper Salts. A. Preparation of 2,5-Bis(trimethylsilyl)hexa-1,5-dien-3-yne (19). *n*-Butyllithium (2.70 M, 0.66 mL, 1.83 mmol) was added to a stirred solution of **5a** (0.27 g, 1.83 mmol) in THF (1 mL) at −78 °C. The mixture was then allowed to warm to −23 °C and stirred for 1 h. After recooling to −78 °C, copper(I) iodide (0.38 g, 1.83 mmol) was added, and the solution stirred for 1 h. The temperature was then allowed to rise to −23 °C, copper(II) chloride (0.27 g, 1.83 mmol) added, and the mixture stirred for 1 h. The mixture was then allowed to reach ambient temperature overnight, and hydrochloric acid (2 M, 0.5 mL) was added followed by water (20 mL). The organic layer was separated and dried ($MgSO_4$), and the solvents removed under reduced pressure. Bulb-to-bulb distillation under reduced presure gave **19**, 0.06 g (0.27 mmol, 15%): MS, *m/e* 222 (M^+, 7), 149, 76, 73 (100); ^1H NMR δ 5.43, 5.40 (AB q, 4 H, J = 3.2 Hz), 0.01 (s, 18 H); ^{13}C NMR δ 156.2, 124.1, 92.3, −0.60. Anal. Calcd for $C_{12}H_{22}Si_2$: C, 64.78; H, 9.97. Found: C, 64.53; H, 9.91.

B. Preparation of 2,2′-Bis(trimethylsilyl)bicyclopropenyl (20). The reaction was carried out as for method A except that tetrakis[iodo(tri-*n*-butylphosphine)]copper(I) replaced copper(I) iodide and excess dioxygen replaced copper(II) chloride. Compound **20**, 0.02 g (0.09 mmol, 5%) was isolated as a yellow oil: ^1H NMR δ 1.50 (s, 4 H), 0.16 (s, 18 H); ^{13}C NMR δ 135.2, 130.6, 27.15, −0.85; IR (liquid film) 2980, 1680, 1265, 850 cm^{-1}. The same product, 0.01 g (0.045 mmol, 7%) was also prepared from **5b** (0.12 g, 0.63 mmol), identical in all observed respects.

Diels–Alder Reaction of 3,3,3′,3′-Tetramethyl-2,2′-bis(trimethylsilyl)bicyclopropenyl (22) with Dimethyl Acetylenedicarboxylate. Dimethyl acetylenedicarboxylate (0.006 g, 0.05 mmol) in toluene (1 mL) was added to **23** (0.028 g, 0.10 mmol) and hydroquinone (2.00 mg, 0.02 mmol) in toluene (1 mL). The mixture was heated to reflux for 12 h and allowed to cool. A white, crystalline solid precipitated as **23**, 0.002 g (0.005 mmol, 10%); mp 189–191 °C; MS, *m/e* 420 (M^+, 4), 278, 73, (100); ^1H NMR δ 3.92 (s, 6 H), 1.15 (s, 12 H), 0.15 (s, 18 H). Anal. Calcd for $C_{22}H_{36}O_4Si_2$: C, 62.81; H, 8.62. Found: C, 63.21; H, 8.58.

Diels–Alder Reaction of 3,3,3′,3′-Tetramethyl-2,2′-bis(trimethylsilyl)bicyclopropenyl (22) with Tetracyclopropene. Tetrachlorocyclopropene (0.75 g, 4.22 mmol) in toluene (2 mL) was added dropwise to a stirred mixture of **22** (1.17 g, 4.20 mmol) and hydroquinone (0.01 g, 0.09 mmol) in toluene (6 mL). The reaction mixture was heated at 110 °C for 15 h, and the solvent then removed under reduced pressure. The residue was triturated with methanol, the insoluble material removed by filtration, and the filtrate reduced in volume. A dark solid crystallized that was separated by filtration, washed with a small amount of acetone, and air dried. Recrystallization from 1-propanol gave **24**, 0.63 g (1.38 mmol, 33%), as almost colorless crystals: mp 157–158 °C; MS, *m/e* 460, 458, 456, 454 (M^+, 2, 6, 12, 9), 425, 423, 421, 419 (M^+ − Cl), 388, 386, 384 (M^+ − 2Cl), 351, 349 (M^+ − 3Cl), 314, 248, 73 (100); ^1H NMR δ 1.20 (s, 12 H), 0.22 (s, 18 H); ^{13}C NMR, see discussion; IR (KBr) 2975, 1602, 1382, 1360, 1263, 825 cm^{-1}. Anal. Calcd for $C_{19}H_{30}Cl_4Si_2$: C, 50.00; H, 6.62; Cl, 31.07. Found: c, 49.75; H, 6.56; Cl, 30.97.

Thermal Reaction of 1,2-Bis(trimethylsilyl)cyclopropane (7). The cyclopropene **7** (0.0050 g, 0.027 mmol) was dissolved in $CDCl_3$ (0.05 mL) and allowed to stand at room temperature for 10 min. The solvent was removed under reduced pressure to give **26**, 0.0047 g (0.013 mmol, 94%) as a pale yellow oil: MS, *m/e* 368 (M^+, 6), 295, 292, 149, 73 (100); ^1H NMR δ 6.43 (s, 1 H), 1.08 (dd, 1 H, J = 4.8, 6.4 Hz), 0.82 (dd, 1 H, J = 3.5, 6.4 Hz), 0.62 (t, 1 H, J = 3.5, 4.8 Hz), 0.35 (s, 3 H), 0.03 (s, 9 H); IR (liquid film) 3029, 2990, 1773, 1430, 1255, 842 cm^{-1}. Anal. Calcd for $C_{18}H_{40}Si_4$: C, 58.61; H, 10.93. Found: C, 58.49; H, 10.96.

Diels–Alder Reaction of 3,3-Dibromo-1,2-bis(trimethylsilyl)cyclopropene (13a) and (*E*,*Z*)-Cyclododeca-1,3-diene (27a). A mixture of **13a** (0.21 g, 0.61 mmol), **28a** (0.1 g, 0.61 mmol), and hydroquinone (0.0030 g, 0.03 mmol) was heated in a sealed tube at 100 °C for 5 days. Cyclohexane (5 mL) was added to the resulting dark material, and the mixture filtered. The filtrate was concentrated under reduced pressure to give a solid which was purified by spinning plate chromatography to give **28**, 0.0123 g (0.024 mmol, 4%) contaminated with a minor component; ^1H NMR, see Table I; IR (KBr) 3015, 2988, 1430, 848, 710, 605 cm^{-1}.

Diels–Alder Reaction of 1,2-Dibromocyclopropene (4) with 27a. A solution of tetra-*n*-butylammonium fluoride (1.00 M, 1.50 mL, 1.50 mmol) in THF was added dropwise to a stirred solution of the tribromocyclopropane **15** (0.33 g, 0.95 mmol), the diene **27a** (0.16 g, 0.97 mmol), and hydroquinone (0.003 g, 0.03 mmol) in THF (5 mL) at −78 °C. The solution was allowed to warm to room temperature and was then kept at ambient temperature for a further 1.5 h. The mixture was then diluted with CH_2Cl_2 (20 mL), extracted with sodium hydroxide (2 M, 2 × 5 mL) and water (15 mL), and dried ($MgSO_4$). The solvents were then removed under reduced pressure to give **29a**, 0.09 g (0.25 mmol, 26%) as a colorless oil: MS, *m/e* 362, 360, 358 (M^+ − 2 H, 2,2,2), 283, 281 (M^+ − Br), 202 (M^+ − 2Br), 57 (100%); ^1H NMR, see Table I; IR (liquid film) 3010, 2928, 712, 690 cm^{-1}. Anal. Calcd for $C_{15}H_{22}Br_2$: C, 49.57; H, 6.12; Br, 44.13. Found: C, 49.69; H, 6.15; Br, 44.09.

Diels–Alder Reaction of 4 with (*E*,*Z*)-Cycloundeca-1,3-diene (27b). This reaction was carried out in the same manner as described above for **4** with **27a**. The adduct **29b**, 0.15 g (0.43 mmol, 44%), was isolated as an almost colorless oil: MS, *m/e* 350, 348, 346 (M^+, 5, 10, 4), 269, 267 (M^+ − Br), 188 (M^+ − 2Br), 49 (100); ^1H NMR, see Table I; IR (liquid film) 3005, 2925, 714, 685 cm^{-1}. Anal. Calcd for $C_{14}H_{20}Br_2$: C, 48.30; H, 5.79; Br, 45.91. Found: C, 48.22; H, 5.81; Br, 45.68.

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Supplementary Material Available: ^1H NMR spectra of **7** and **20** (3 pages). Ordering information is given on any current masthead page.