Pericyclic Reactions of Free and Complexed Cyclopentyne

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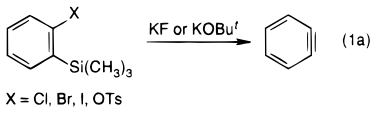
The selectivity between [2 + 2] and [2 + 4] cycloadditions of cyclopentyne with spiro[2.4]nona-2,4-diene depends on the mode of generating the cycloalkyne. Using diazomethylenecyclobutane and (bromocyclobutylidenemethyl)trimethylsilane as precursors affords cyclopentyne in an unencumbered form, whereas using dibromomethylenecyclobutane and 1,2-dibromocyclopentene yields a cyclopentyne−lithium bromide complex.

Introduction

We recently described the cycloaddition of cyclopentyne (**3**) with spiro[2.4]hepta-4,6-diene (**4**) (Scheme 1), wherein competing [2 + 2] and [2 + 4] reaction channels are observed to provide **5** and **6**, respectively.[1] As seen in Scheme 1, two protocols were used for accessing the cycloalkyne. One approach involved conversion of cyclobutanone (**1**)[2] to cyclobutylidenecarbene by way of diazomethylenecyclobutane and afforded a temperature-*independent* ratio of **5**:**6** of about 1:3. An alternate approach through dehalogenation of 1,2-dibromocyclopentene (**2**)[3] provided a ratio of **5**:**6** that was temperature-*dependent*, ranging from 20:1 at 25 °C to 9.4:1 at 80 °C. A tentative explanation for the differing results was that the latter method generated a cyclopentyne−lithium bromide complex **7**, which then served as a key reactive intermediate in the cycloaddition process. The present report describes studies with two additional precursors to cyclopentyne, one of which is novel, that provide persuasive evidence for the intervention of lithium-containing complexes when the cycloalkyne is generated via alkyllithium chemistry.

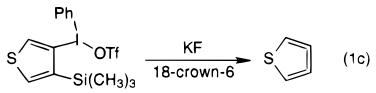
Results and Discussion

The initial goal of our work was to prepare precursors whose decomposition to cyclopentyne could be effected in the absence of lithium cations. With this in mind, we were intrigued by reports that benzyne[4a] as well as five- and six-membered cyclic cumulenes[4b,c] may be generated via desilylation of vinylsilanes bearing leaving groups at the β-position (eq 1).[4] The necessary substrate **8** was prepared in 90% yield by quenching 1-bromo-2-lithiocyclopentene[3c] with TMSCl at −78 °C (eq 2). Unfortunately, all attempts to effect elimination of **8** by using fluoride ion failed.[5] The failure of **8** to undergo the desired β-elimination is presumably associated with the increased strain in cyclopentyne as compared to benzyne.[6]

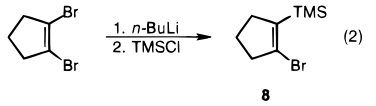


(1a)

(1b)



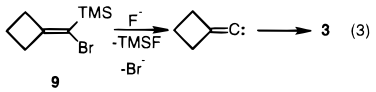
(1c)



(2)

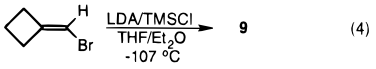
8

We then considered α-desilylation of 1-(bromotrimethylsilylmethylene)cyclobutane (**9**) as a possible lithium cation-free approach to cyclopentyne according to eq 3. Two groups have reported using this type of elimination to prepare alkylidenecarbenes,[7] although neither has applied it for generating an alkylidenecarbene that might rearrange to a cycloalkyne. To explore this approach to cyclopentyne, the previously unknown **9** was readily prepared in 33% yield by treating bromomethylenecyclobutane with LDA/TMSCl at −107 °C (eq 4).



(3)

9



(4)

The reaction of **9** with anhydrous benzyltrimethylammonium fluoride[8] was subsequently effected in the presence of spiro[4.4]-nona-1,3-diene (**10**, eq 5) as the trapping

(1) Gilbert, J. C.; McKinley, E. G.; Hou, D.-R. *Tetrahedron* **1997**, *53*, 9891−9902.

(2) (a) Gilbert, J. C.; Baze, M. E. *J. Am. Chem. Soc.* **1983**, *105*, 664. (b) Gilbert, J. C.; Baze, M. E. *J. Am. Chem. Soc.* **1984**, *106*, 1885−1886.

(3) (a) Krebs, A.; Wittig, G. *Chem. Ber.* **1961**, *94*, 3260−75. (b) Wittig, G.; Pohlke, R. *Chem. Ber.* **1961**, *94*, 3276−86. (c) Wittig, G.; Weinlich, J.; Wilson, E. R. *Chem. Ber.* **1965**, *98*, 458−470. (d) Wittig, G.; Heyn, J. *Liebigs Ann. Chem.* **1969**, *726*, 57−68.

(4) (a) Cunico, R. F.; Dexheimer, E. M. *J. Organomet. Chem.* **1973**, *59*, 153−160. (b) Shakespeare, W. C.; Johnson, R. P. *J. Am. Chem. Soc.* **1990**, *112*, 8578−8579. (c) Wong, H. N. C.; Ye, X.-S. *J. Org. Chem.* **1997**, *62*, 1940−1954.

(5) This result was unexpected, given the reports of generating cyclohexynes using this type of methodology as described in ref 4a,b.

(6) It is possible that the elimination might be successful with a better leaving group. This is being investigated.

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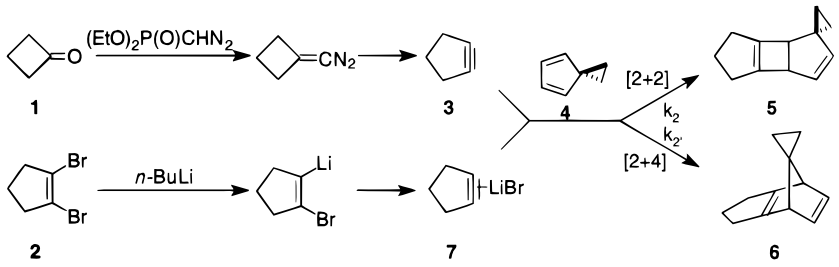
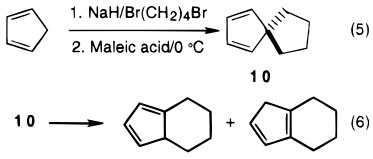
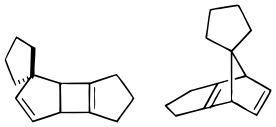
Scheme 1



reagent. We elected to use this diene rather than **4** to exclude the possibility that the spiroconjugation associated with the latter substrate[9] might influence the results. Although the reported synthesis of **10** is unexceptional (eq 5),[10] in our hands the isolated product was contaminated with some 15% of dienes derived by [1,5] sigmatropic rearrangements of the desired product (eq 6). Fortunately, these byproducts could be removed through Diels−Alder reaction with maleic acid.



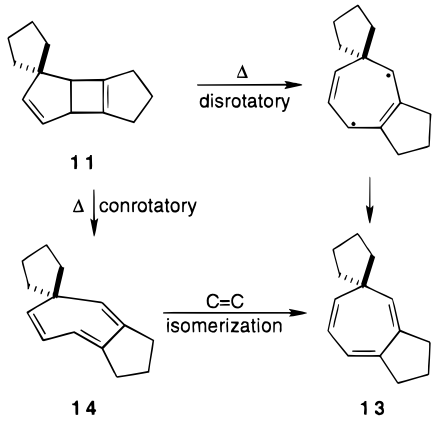
In analogy with our earlier results,[1] executing the α-elimination of **9** in the presence of **10** afforded two cycloadducts according to GC/MS analysis of the reaction mixture. Upon isolation by preparative GC and spectroscopic analysis, the cycloadducts were found to have structures corresponding to the [2 + 2] and [2 + 4] cycloadducts **11** and **12**, respectively. Purification of 11 proved to somewhat troublesome as this cycloadduct



was prone to thermal isomerization under the GC conditions used at first. Thus, the purified material initially isolated provided a ^{1}H NMR spectrum exhibiting four vinylic one-proton resonances and a ^{13}C NMR spectrum with six magnetically distinct sp^2-carbon atoms. These spectral data are consistent with those expected for the cycloheptatriene **13** (Scheme 2), an isomer of **11**.

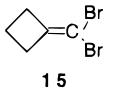
The isomerization presumably occurs by way of thermally induced ring-opening of **11**. The rules of orbital symmetry[11] would dictate that the initial product of an

Scheme 2



allowed process would be the *cis*,*trans*,*cis*-triene **14**, which could afford **13** by isomerization of the trans double bond (Scheme 2). Alternatively, a thermally disallowed route could produce **13** directly from **11** by way of a biradical. Reports from the groups of Gajewski and Baldwin on the thermal isomerization of various bicyclo[3.2.0]hepta-2,5-dienes suggest that both mechanistic routes are operative, with the disallowed disrotatory pathway predominating.[12] Fortunately, we found that the thermal isomerization **11** could be avoided by maintaining the temperature of the GC column and detector below 180 °C so that the pure [2 + 2] cycloadduct could be isolated.

The demonstration that fluoride-induced decomposition of **9** afforded the cycloadducts **11** and **12** set the stage for exploring the competition between the two modes of cycloaddition as a function of four different precursors to cyclopentyne, namely **1**, **2**, **9**, and dibromomethylenecyclobutane (**15**).[13] The data obtained as a function



of these precursors and reaction temperature are contained in Table 1. As can be seen,the yields of the reactions are poor but represent data under conditions that have not been optimized. Substantial loss of products in all cases is believed to attend the removal of excess diene by reaction with maleic anhydride (see Experimental Section). Moreover, considerable amounts of bromomethylenecyclobutane and 1-bromocyclopentene are formed

(7) (a) Stang, P. J.; Fox, D. P. *J. Org. Chem.* **1977**, *42*, 1667−1669. (b) Stang, P. J.; Madsen, J. R.; Mangum, M. G.; Fox, D. P. *J. Org. Chem.* **1977**, *42*, 1802−1804. (c) Seyferth, D.; Lefferts, J. L.; Lambert, R. L. *J. Organomet. Chem.* **1977**, *142*, 39−53. (d) Cunico, R. F.; Han, Y.-K. *J. Organomet. Chem.* **1976**, *105*, C29−C31. (e) Cunico, R. F.; Han, Y.-K. *J. Organomet. Chem.* **1978**, *162*, 1−16. (f) Gajewski, J. J.; Paul, G. C.; Chang, M. J.; Gortva, A. M. *J. Am. Chem. Soc.* **1994**, *116*, 5150−5154.

(8) Kuwajima, I.; Nakamura, E.; Shimizu, M. *J. Am. Chem. Soc.* **1982**, *104*, 1025−1030.

(9) Harmony, M. D.; Mathur, S. N.; Choe, J.-I.; Kattija-Ari, M.; Howard, A. E.; Staley, S. W. *J. Am. Chem. Soc.* **1981**, *103*, 2961−2966 and references cited therein.

(10) Wilcox, C. F.; Craig, R. R. *J. Am. Chem. Soc.* **1961**, *83*, 3866−3870.

(11) Woodward, R. B.; Hoffmann, R. *The Conservation of Orbital Symmetry*; Verlag Chemie: Weinheim, Germany, 1970.

(12) Baldwin, J. E.; Kaplan, W. S. *J. Am. Chem. Soc.* **1971**, *93*, 3969−3977. Otterbacher, E. W.; Gajewski, J. *J. Am. Chem. Soc.* **1981**, *103*, 5862−5866. Baldwin, J. E.; Belfield, K. D. *J. Org. Chem.* **1987**, *52*, 4772−4775.

(13) (a) Fitjer, L.; Kliebisch, U.; Wehle, D.; Modaressi, S. *Tetrahedron Lett.* **1982**, *23*, 1661−1664. (b) Fitjer, L.; Modaressi, S. *Tetrahedron Lett.* **1983**, *24*, 5495−5498.

Table 1. Ratios of Cycloadducts 11 and 12 as a Function of Precursor and Temperature

run	source of cyclopentyne	*T* (°C)	solvent	yield[a] (%)	ratio[b] **11**:**12**
1	**2**	0	hexanes		36:1
2	**2**	25	hexanes	15	27:1
3	**2**	60	hexanes		21:1
4	**15**	−78	hexanes		54:1
5	**15**	−40	hexanes		27:1
6	**15**	0	hexanes	14	12:1
7	**1**	−40	CH_2Cl_2		1:1.5
8	**1**	0	CH_2Cl_2		1:1.5
9	**1**	25	CH_2Cl_2	4	1:1.6
10	**9**	−40	CH_2Cl_2	4	1:1.5
11	**9**	25	CH_2Cl_2		1:1.6
12	**9**	25	pentane		1:2.5

[a] GLC yield. [b] Average of two or more trials; the estimated error in the percentages from which these ratios are derived is ±5%.

when **9** is used; these byproducts are thought to result from protonation of anionic intermediates by adventitious moisture present in the ammonium salt used for desilylation. Despite the disappointingly low yields, multiple runs under the same reaction conditions show that the observed ratios are repeatable, thereby lending confidence to our interpretations of the data.

The results from **2** and **15** (runs 1−6), both of which involve *n*-BuLi for transmetalation and the use of hydrocarbon solvents, are comparable to one another and track those previously obtained with **2** in the presence of diene **4**.[1] Specifically, the reaction channel affording the [2 + 2] cycloadduct **11** is strongly favored,[14] and there is a conventional temperature-dependence of the ratio of **11**:**12** that reflects a higher activation barrier for generating the [2 + 4] cycloadduct. It is to be noted that there does appear to be a slight but experimentally meaningful difference in the selectivity between the two reaction channels as a function of whether **2** or **15** is used. Comparing the data of runs 1 and 6, both of which were performed at 0 °C, shows that **2** affords a more selective reactive intermediate. A similar conclusion results by noting that the same 27:1 ratio of **11** and **12** results from these two precursors (cf. runs 2 and 5) but the temperatures for producing this ratio differ by 65 °C.

Precursors **1** and **9** also mimic one another in terms of the ratios of cycloadducts obtained. In analogy to our previous studies with precursor **1** and diene **4**,[1] there is a slight preference for the reaction channel affording the [2 + 4] cycloadduct **12** and no dependence of the product ratio on temperature in experiments performed with dichloromethane as solvent (Table 1, runs 7−11). Because this solvent affords a reaction medium having somewhat greater polarity than that used with **2** and **15**, one study (run 12) was performed with **9** in pentane solvent. The [2 + 4] cycloadduct 12 still predominated in this case, demonstrating that the more lipophilic medium used with **2** and **15** does not account for the preference for the [2 + 2] cycloaddition channel with these precursors.[15]

A rationale for our observations is that cyclopentyne, when generated from **1** and **9**, is in an uncomplexed, free state, since with neither precursor is there intimate association with a cation at the birth of cyclopentyne. Thus, the experimental results using these precursors represent the intrinsic reactivity of the unencumbered species. We believe the temperature-independence of the product ratios signals a negligible value of $\Delta\Delta H^{\ddagger}$ for the two reaction channels affording the cycloaddition products.[16]

On the other hand, the organolithium-promoted dehalogenation of **2** and **15** affords a lithium−cycloalkyne complex, and we propose that this species rather than free cyclopentyne effects the cycloaddition reactions leading to **11** and **12**. Complexes of alkynes with transition metals are known,[17] and Schleyer et al. have recently demonstrated the existence of intramolecular π-interactions between Li^+ and an acetylenic moiety on the basis of analysis of the X-ray crystal structure of the hexamer of $Li-OCMe_2CCH$.[18−20] This group also reported calculations predicting a stabilization of some 20 kcal/mol from the π-interaction between lithium cation and acetylene. In our case, the generation of cyclopentyne in close association with lithium cation and the nonpolar reaction media provide an environment conducive for forming a complex. In any case, the lithium ion must be intimately involved in the cycloaddition process itself to account for the differing temperature-dependence and product ratios observed relative to those obtained when **1** and **9** are used.[21] Moreover, the difference in ratios observed for runs 1 and 6 may be interpreted as implying differing aggregations of the complex as a function of its mode of generation.[23−25] That this might be the case is not surprising, given that the conversion of **2** and **15** to a complex does not involve a common intermediate: **15** affords cycloadducts at temperatures where 1-bromo-2-lithiocyclopentene, prepared by transmetalation of **2**, is thermally stable,[26] a fact noted previously by Fitjer and Modaressi.[13b]

The results we have obtained using four different precursors to cyclopentyne differ from those observed for benzyne. For example, generating this aryne from five different precursors in the presence of 1,4-dimethoxyan-

(14) The basis for the high selectivity toward the [2 + 2] process is presently not obvious but is being explored computationally.

(15) The similarity of results with dienes **4** and **10** implies that possible stereoelectronic effects associated with spiroconjugation in **4** have no significant influence on the cycloaddition reactions.

(16) Whether or not the cycloaddition reactions involving free cyclopentyne are diffusion-controlled will be addressed in a subsequent publication.

(17) This subject has recently been reviewed: Melikyan, G. G.; Nicholas, K. M. In *Modern Acetylene Chemistry*; Stang, P. J., Diederich, F., Eds.; VCH: Weinheim, 1995; Chapter 4.

(18) Goldfuss, B.; Schleyer, P. v. R.; Hampel, F. *J. Am. Chem. Soc.* **1997**, *119*, 1072−1080.

(19) A reviewer has suggested that Roberts et al. have reported complexation of lithium cation with benzyne.[20] They indeed proposed such a complex but had no evidence for its existence and certainly did not uncover different reactivities for free and a possibly complexed species.

(20) Roberts, J. D.; Semenow, D. A.; Simmons, H. E.; Carlsmith, L. A. *J. Am. Chem. Soc.* **1956**, *78*, 601−611.

(21) Adding lithium bromide to a mixture in which **1** and DAMP were used to prepare cyclopentyne did not affect the product ratio.[1] However, the low solubility of LiBr in the reaction medium and short lifetime of cyclopentyne make it doubtful that this effort to mimic the in situ generation of LiBr as in dehalogenation of **2** is effective. Attempts to increase the concentration of dissolved lithium bromide by the use of 12-crown-4 failed to provide meaningful data.[22]

(22) Barnes, B. Unpublished results.

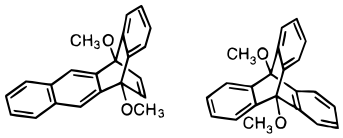
(23) Aggregation phenomena for organolithium species in hydrocarbon solvents are known,[24] and aggregation of lithium bromide with a lithium enolate has been described.[25]

(24) DeLong, G. T.; Pannell, D. K.; Clarke, M. T.; Thomas, R. D. *J. Am. Chem. Soc.* **1993**, *115*, 7013−7014 and references therein.

(25) Abu-Hasanayn, F.; Streitwieser, A. *J. Am. Chem. Soc.* **1996**, *118*, 8136−8137.

(26) Temperatures greater than −20 °C are required under our conditions for 2-lithio-1-bromocyclopentyne to generate cycloaddition products. Wittig et al. noted similar thermal stability of this species in ethereal solvents.[3]

thracene afforded a mixture of **21** and **22** in a ratio of approximately 2.4.[27] On the basis of the relative constancy of the ratio, unencumbered benzyne was taken as the common intermediate. This study depended on competitive intramolecular cycloadditions of benzyne, in close analogy to our work, but unfortunately the formation of the aryne did not involve intervention of an organolithium species. However, Huisgen and Knorr studied the intermolecular competition of furan and 1,3-cyclohexadiene for the benzyne generated from four different precursors, one of which was **23**, and found a near-constant ratio of cycloadducts **24** and **25**.[28] This result also indicates that benzyne does not form a lithium complex analogous to **7**. This apparent difference may be a reflection of differing electronic characteristics of the in-plane π-bond of the two systems, an issue that we are presently addressing computationally.



21 **22**

23 **24** **25**

Conclusions

The data collected in Table 1 show that the classical preparation of cyclopentyne as reported by Wittig et al.[3] apparently does not generate free cyclopentyne, nor does that developed by Fitjer et al.[13] Rather, these protocols lead to complexes and/or aggregates involving association between the cycloalkyne and lithium cations. Only the methods involving cyclobutanone (**1**) and 1-(bromotrimethylsilylmethylene)cyclobutane (**9**) appear to provide the unencumbered cycloalkyne. Further research to define the effects of complexation on the reactivity of cyclopentyne and its close relatives is in progress.

Experimental Section

All cyclopentyne reactions were performed under an atmosphere of dry nitrogen in one-neck flamed-dried flasks. Low-temperature baths of −40 °C were obtained with an immersion cooler using acetone as the bath liquid. Ice/water, dry ice/acetone, and isooctane/N_2(l) were used for 0, −78, and −107 °C baths, respectively. Commercial chemicals were used without further purification unless noted otherwise. Solvents were dried and distilled under an inert atmosphere before use. Diethyl ether (Et_2O) and THF were distilled from sodium benzophenone ketyl, dichloromethane (CH_2Cl_2) from CaH_2, and diisopropylamine from KOH. Concentration of solutions was accomplished by rotary evaporation at water aspirator pressures.

Preparative GC purification was accomplished with a 4-ft × 0.125-in. column containing 5% OV-101 on Chromsorb P-AW-DMCS (80/100 mesh). Helium was used as the carrier gas (45 mL/min). Quantitative GC analyses were obtained on an analytical gas chromatograph interfaced with a recording integrator and equipped with a 25-m × 0.25-mm AT-1 (100% dimethylpolysiloxane) capillary column using helium as the carrier gas (1.2 mL/min) and a flame-ionization detector (FID). The yields of the reactions were determined by the integrated area of the cycloadducts vs an internal standard (di-*n*-hexyl ether or dodecane).

GC/MS analyses were performed using a 12-m × 0.22-mm GB-5 (95% dimethyl-, 5% diphenylpolysiloxane) capillary column with helium as the carrier gas (1.0 mL/min) and interfaced with an electron-impact ion trap detector mass spectrometer. High-resolution MS analyses were obtained in the EI mode (70 eV).

^{1}H NMR spectra were obtained at 250 and 500 MHz (^{1}H), and ^{13}C NMR spectra were measured at 62.5 and 125 MHz. All chemical shifts are referenced to the NMR solvent, which was $CDCl_3$ unless otherwise noted.

1-Bromo-2-trimethylsilylcyclopentene (8). In a 100-mL round-bottom flask equipped with a stirbar, septum, and thermometer, *n*-BuLi (20.1 mL of a 1.5 M solution in hexanes) was stripped of its solvent in vacuo and then dissolved in 25 mL of diethyl ether under argon and cooled to −78 °C. 1,2-Dibromocyclopentene (**2**, 5.7 g, 0.025 mol) was added via syringe, and the mixture was stirred for 45 min at −78 °C. The mixture was slowly warmed to 0 °C and again cooled to −78 °C before the addition of 3.3 g (0.030 mol, 3.3 mL) of TMSCl in six portions. The resulting mixture was stirred at −78 °C for 45 min before removal of the cooling bath. As the solution warmed, a colorless precipitate was formed at −15 °C. After being stirred for 2 h at room temperature under argon, the reaction mixture was quenched with 15 mL of ethanol and diluted with 40 mL of saturated NH_4Cl solution. Extraction of the aqueous phase with 20 mL of Et_2O was followed by washing with water and brine, drying ($MgSO_4$), and distillation of the solvent under normal pressure. The residual was subjected to a bulb-to-bulb distillation to afford 4.9 g of **8** as a colorless oil (bp 32−35 °C/5 Torr): R_f (alumina/pentane) 0.81.

Spectral data: ^{1}H NMR (250 MHz) δ 0.17 [s, 9H, $Si(CH_3)_3$], 1.87 [q, J = 7.6 Hz, 2H, (H-3)], 2.39 [m, J = 2.8 Hz, 2H, (H-4)], 2.67 [m, J = 2.6 Hz, 2H, (H-5)]; ^{13}C NMR (72.5 MHz) δ −1.42 ($Si(CH_3)_3$), 23.5 (C-4), 37.6 (C-3), 43.7 (C-5), 130.1 (C-2), 139.9 (C-1); MS (70 eV) *m*/*z* 219 (5) [$M^+ + 1$], 203 (15), 139 (10), 73 (19), 57 (100); HRMS calcd for $C_8H_{15}SiBr$ 218.0126, found 218.0118.

1-(Bromotrimethylsilylmethylene)cyclobutane (9). Diisopropylamine (0.38 g, 3.7 mmol), THF (10 mL), and Et_2O (5 mL) were added to a 50-mL flask equipped with a stirbar. The flask was cooled to −78 °C, *n*-BuLi (4.6 mL of 0.82 M solution in hexane, 3.8 mmol) was added, and the solution was stirred at −78 °C for 0.5 h. The flask was placed in a −107 °C bath, and TMSCl (0.41 g, 3.7 mmol) was added. Bromomethylenecyclobutane (0.5 g, 3.4 mmol) in THF (5 mL) was added dropwise to the flask at −107 °C, and the mixture was stirred at −107 °C for another 0.5 h. After being stirred at −78 °C for an additional 2 h, the reaction mixture was quenched with water (10 mL). The aqueous layer was separated and extracted with pentane (2 × 10 mL). The combined organic layer was washed sequentially with 1.5 N HCl (20 mL), saturated $NaHCO_3$ (10 mL), and water (10 mL). The organic solution was dried ($MgSO_4$), filtered, and concentrated. The crude product was purified by silica gel column chromatography using pentane as eluant, R_f (silica gel/pentane) 0.70. After concentration, 0.36 g (1.6 mmol) of **9** was isolated as a colorless oil.

Spectral data: ^{1}H NMR (250 MHz) δ 2.70 (4H, m), 1.93 (2H, m), 0.16 (9H, s); ^{13}C NMR δ 154.8, 118.5, 35.1, 32.18, 15.1, −0.95; HRMS *m*/*z* calcd for $C_8H_{15}SiBr$ 218.0126, found 218.0118.

Spiro[4.4]nona-1,3-diene (10). Sodium hydride (110.5 g, 2.76 mmol, 60% in mineral oil) in a 2-L round-bottom flask was washed with hexane (100 × 3 mL) and flushed by nitrogen gas, and then the flask was equipped with a condenser, an addition funnel, and a stirbar. THF (450 mL) was added to the flask and cooled to 0 °C. Freshly distilled 1,3-cyclopentadiene (83 g, 1.26 mol) and 1,4-dibromobutane (193.2 g, 0.84 mol) were added dropwise to the flask sequentially during 4−5 h. After the reaction mixture was stirred for 2 h at 0 °C, water

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(500 mL) was added, and the biphasic mixture was extracted with pentane (3 × 200 mL). The organic solution was dried (Na_2SO_4), filtered, and concentrated. The residual liquid was distilled to yield 55 g (bp 25−30 °C, 3 Torr) of crude dienes. The crude product was added to a solution of maleic acid (8.6 g, 0.074 mol) in acetonitrile (100 mL) and CH_2Cl_2 (100 mL), and the reaction mixture was stirred at 0 °C for 2 h. Aqueous sodium hydroxide (0.9 M, 200 mL) was added, and the resulting mixture was stirred for 20 min and then extracted with pentane (3 × 30 mL). The organic layer was separated, dried (Na_2SO_4), concentrated, and distilled to yield 23.1 g of **10** (bp 28−30 °C, 3 Torr). Spectral data were consistent with those provided in the literature.[26]

Cyclopentyne from Cyclobutanone (1): 2′,3′,4′,7′-Tetrahydrospiro[cyclopentane-1,8′-[4.7]methano[1H]-indene] (12). General Procedure. Potassium hydride (405 mg, 3.54 mmol, 35% in mineral oil) in a 10-mL round-bottom flask containing a stirbar was washed with pentane (3 × 8 mL) and flushed by nitrogen gas. Dry CH_2Cl_2 (1.0 mL) was added and the resulting solution was cooled to −78 °C. Diethyl (diazomethyl)phosphonate (470 mg, 2.65 mmol) in 0.5 mL of CH_2Cl_2 was transferred into the reaction mixture. The slurry was stirred for 10 min at −78 °C. Spiro[4.4]nona-1,3-diene (**10**, 1.70 g, 14.2 mmol) and cyclobutanone (**1**, 124 mg, 1.77 mmol) were added sequentially, and the solution was stirred at −78 °C for 15 min. The flask was transferred to a room-temperature water bath, and stirring was continued for 1 h. After the bath was removed, nitrogen evolution was observed in 2 min, and the solution became orange. The reaction mixture was treated with a solution of maleic anhydride (2.77 g, 28.3 mmol) in acetonitrile (15 mL), and this mixture was stirred for 1 h. The resulting mixture was extracted with pentane (3 × 8 mL), dried (Na_2SO_4), filtered, and concentrated to about 1.5 mL. This solution was passed through a short silica plug using pentane as eluant until TLC (silica gel/pentane) showed that no more compounds were eluting.

The eluant was concentrated to approximately 0.5 mL, and the residue was subjected to preparative gas chromatography. GC conditions: injector temperature, 170 °C; detector temperature, 170 °C; detector current, 150 mA; initial column temperature 100 °C. The temperature was ramped at 10 °C/min to 240 °C. The [2 + 4] cycloadduct 12 (retention time 7.3 min) was collected in Teflon tubes cooled in an ice−water bath. The condensates were transferred into NMR tubes with C_6D_6 (0.6 mL).

Spectral data for **12**: ^{1}H NMR (C_6D_6, 500 MHz) δ 1.46−1.49 (m, 4H), 1.54−1.72 (m, 4H), 1.99−2.03 (m, 2H), 2.00−2.04 (m, 1H), 2.09−2.14 (m, 1H), 2.36−2.39 (m, 2H), 2.92 (t, J = 1.9 Hz, 2H), 6.67 (t, J = 1.9 Hz, 2H); ^{13}C NMR δ 25.8, 25.9, 28.3, 30.6, 34.3, 35.2, 58.0, 96.4, 142.93, 158.4; HRMS (CI) calcd for $C_{14}H_{19}$ (MH^+) 187.1487, found 187.1490.

Variable-Temperature Experiments. The general procedure described above was followed.

(i) −40 °C Trapping. After 15 min at −78 °C, the flask was placed in a −50 °C bath, where it remained for 3 h prior to workup and analysis.

(ii) 0 °C Trapping. After the 15 min at −78 °C, the flask was placed in a 0 °C bath, where it remained for 1 h prior to workup and analysis.

(iii) 25 °C Trapping. The procedure was the same as the general procedure.

Cyclopentyne from 1,2-Dibromocyclopentene (2); 4,5,6,-6b-Tetrahydrospiro[cyclobuta[1,2:3,4]dicyclopentene-1(3a*H*), 1′-cyclopentane] (11) and 2,3-Dihydrospiro-[azulene-5(1*H*),1′-cyclopentane] (13). General Procedure. 1,2-Dibromocyclopentene (400 mg, 1.77 mmol) was added to a 10-mL flask containing a stirbar. Spiro[4.4]nona-1,3-diene (10, 1.70 g, 14.1 mmol) was added to the flask, which was then cooled to −78 °C. The solution was stirred for 10 min. A solution of *n*-BuLi (2.2 mL of a 1.6 M solution in hexane, 3.52 mmol) was added by syringe. The solution was first stirred at −78 °C for 0.5 h, after which the flask was transferred to a room-temperature water bath. A yellow precipitate was observed after 5 min. The mixture was stirred at room temperature for 1 h and then treated with a solution of maleic anhydride (2.77 g, 28.3 mmol) in acetonitrile (15 mL). After being stirred for 1 h, the mixture was extracted with pentane (3 × 10 mL), dried (Na_2SO_4), filtered, and concentrated to about 1.5 mL. This solution was passed through a short silica plug using pentane as eluant until TLC (silica gel/pentane) showed that no more compounds were eluting.

The eluant was concentrated to approximately 0.5 mL, and the residue was subjected to preparative gas chromatography. GC conditions: injector temperature: 170 °C; detector temperature, 170 °C; detector current, 150 mA; initial column temperature, 100 °C. The temperature was ramped at 10 °C/min to 240 °C. The [2 + 4]cycloadduct **11** (retention time 7.7 min) was collected in Teflon tubes cooled by an ice−water bath. The condensates were transferred into NMR tubes with C_6D_6 (0.6 mL).

Spectral data for 11: ^{1}H NMR (C_6D_6, 500 MHz) δ 1.24−1.32 (m, 1H), 1.32−1.44 (m, 1H), 1.49−1.62 (m, 2H), 1.62−1.67 (m, 4H), 1.92−2.07 (m, 2H), 2.17−2.36 (m, 4H), 3.06 (br, 1H), 3.69 (br, 1H), 5.40 (d, J = 5.8 Hz), 5.79 (dd, J = 5.8, 2.2 Hz); ^{13}C NMR δ 23.7, 25.0, 26.2, 30.0, 31.5, 38.4, 41.8, 53.4, 53.5, 54.2, 130.6, 139.7, 152.1, 159.3; HRMS (CI) calcd for $C_{14}H_{19}$ (MH^+) 187.1487, found 187.1480.

GC Isolation of 13. The purification procedure was same as for **11** except that the detector temperature was 250 °C. A trace of **11** was removed by silica gel chromatography using pentane as the eluant: R_f values (silica gel/pentane) 0.63 (**13**) and 0.72 (**11**).

Spectral data for 13: ^{1}H NMR ($CDCl_3$, 500 MHz) δ 1.45−1.60 (m, 4H), 1.60−1.62 (m, 4H), 1.78 (q, J = 7.2 Hz, 2H), 2.50 (dt, J = 7.2, 1.8 Hz, 2H), 2.60 (mt, J = 7.2, 2H), 5.12 (d, J = 10 Hz, 1H), 5.17 (br, 1H), 6.02 (dd, J = 10, 6.4 Hz, 1H), 6.26 (br d), J = 6.4 Hz, 1H); ^{13}C NMR (C_6D_6, 125 MHz) δ 23.0, 25.1, 33.6, 35.3, 38.6, 46.5, 123.0, 124.2, 124.3, 129.1, 140.7, 145.9; HRMS (CI) calcd for $C_{14}H_{19}$ (MH^+) 187.1487, found 187.1490.

Variable-Temperature Experiments. The general procedure described above was followed, but with reduced quantities of reagents: 1,2-Dibromocyclopentene (100 mg, 0.44 mmol), spiro[4.4]nona-1,3-diene (460 mg, 3.83 mmol), and *n*-BuLi 0.6 mL (1.6 M solution in hexane, 0.96 mmol).

(i) 0 °C Trapping. After 15 min at −78 °C, the flask was placed in a 0 °C bath. The reaction mixture was stirred at this temperature for 1 h prior to workup and analysis.

(ii) 25 °C Trapping. The procedure was the same as the general procedure.

(iii) 60 °C Trapping. After 15 min at −78 °C, the flask was placed in a 60 °C oil bath, where it remained for 0.5 prior to workup and analysis.

Cyclopentyne from 1-Dibromomethylenecyclobutane (15). General Procedure. 1-Dibromomethylenecyclobutane (**15**, 150 mg, 0.66 mmol) was added to a dry 10-mL flask containing a stirbar. Spiro[4.4]nona-1,3-diene (**10**; 0.64 g, 5.3 mmol) was added, and the flask was cooled in an ice−water bath. The solution was stirred for 10 min. A solution of *n*-BuLi (0.83 mL of a 1.6 M solution in hexane, 1.33 mmol) was added dropwise. A yellow precipitate was observed immediately. The solution was stirred in the ice−water bath for 1 h before being treated with a solution of maleic anhydride (1.04 g, 10.6 mmol) in acetonitrile (6 mL). This mixture was stirred for 1 h, followed by extraction with pentane (3 × 6 mL), drying of the extracts (Na_2SO_4), filtration, and concentration to about 1.5 mL. The concentrate was passed through a short silica plug using pentane as eluant until TLC (silica gel/pentane) showed that no more compounds were eluting.

Variable-Temperature Experiments. These experiments were performed according to the general procedure, using the appropriate baths to maintain the desired temperature.

Cyclopentyne from 1-(Bromotrimethylsilylmethylene)-cyclobutane (9). General Procedure. Benzyltrimethylammonium fluoride (85 mg, 0.5 mmol) and 4 Å molecular sieves (0.5 g) were added to a 5-mL flask equipped with a stirbar. THF (2 mL) was added, and the resulting slurry was stirred at room temperature for 14 h. After THF was removed in vacuo, dichloromethane (2 mL) was added, followed by a solution of (bromocyclobutylidenemethyl)trimethylsilane (9, 100 mg, 0.45 mmol) and spiro[4.4]nona-1,3-diene (10, 0.43 g,

3.6 mmol), which was transferred by cannulation. The color of the solution became brown immediately. After being stirred at room temperature for 1.5 h, the mixture was treated with a solution of maleic anhydride (0.5 g, 5 mmol) in acetonitrile (5 mL) and stirred for 1 h. The resulting mixture was extracted with pentane (3 × 6 mL), and the extracts were dried (Na_2SO_4), filtered, and concentrated to about 1.5 mL. This residue was passed through a short silica plug using pentane as eluant until TLC (pentane) showed that no more compounds were eluting.

Variable-Temperature Experiments. (i) −40 °C Trapping. The general procedure to dry the benzyltrimethylammonium fluoride and workup procedure was the same as in general procedure. After removal of THF, the flask was placed in a −40 °C bath, and the mixture of (bromocyclobutylidenemethyl)trimethylsilane and spiro[4.4]nona-1,3-diene was precooled in a −40 °C bath before being added to the flask. The reaction was stirred at −40 °C for 4 h.

(ii) 25 °C Trapping. This procedure was according to the general procedure.

Variable-Solvent Experiments. (i) In THF. The general procedure was followed except that the THF was not replaced by CH_2Cl_2. The bromosilane **9** and diene **10** were added to the flask immediately after the drying procedure.

(ii) In Pentane. The general procedure was followed except that pentane instead of CH_2Cl_2 was added to the reaction flask. However, the reaction was not complete after 24 h at room temperature, and cycloadducts were produced in low yields.

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