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Competitive Intermolecular Pericyclic Reactions of Free and Complexed Cyclopentyne

John C. Gilbert* and Duen-Ren Hou[1]

Department of Chemistry and Biochemistry, The University of Texas at Austin, 1 University Station Stop A5300, Austin, Texas 78712

jgilbert@mail.utexas.edu

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Intermolecular competition for cyclopentyne by different alkenes supports the hypothesis that organolithium-promoted decomposition of precursors to cyclopentyne affords one or more lithium-ion-complexed species. Competition reactions with mixtures of 2,3-dihydropyran do not clearly differentiate between complexed and unencumbered (free) forms of cyclopentyne, but those involving spirodiene **2** and cyclohexene do. Remarkably, the cycloaddition reactions of free cyclopentyne are not diffusion-controlled despite its high reactivity.

Introduction

We recently reported [2 + 2] and [2 + 4] cycloaddition reactions involving cyclopentyne (**1**) and spiro-1,3-dienes.[2] For example, reaction of **1** with spiro[4.4]nona-1,3-diene (**2**) afforded **3** and **4** (Scheme 1).[2b] The competition between the two reaction channels for cycloaddition, which nominally represent [2 + 2] and [2 + 4] pericyclic processes (vide infra), was strongly dependent on the precursor used to produce **1**. Substrates **5** and **6** both afforded a 1:1.6 ratio of **3**:**4**, a ratio that proved to be independent of the temperature at which the cycloaddition occurred. Precursors **7** and **8** afforded ratios of **3**:**4** that also were similar to one another but were very different from that provided by **5** and **6**. For example, the ratio of **3** and **4** at room temperature was 27:1 when **7** was used to produce **1**. The ratios of cycloadducts using **7** and **8** showed a significant temperature dependence and favored the [2 + 2] product **3** over the temperature range studied**.** The dramatic differences in the ratios of cycloadducts as a function of the precursor used and the fact that organolithium reagents were used to generate **1** from **7** and **8** led us to propose a lithium bromide complexed species **9** as a key reactive intermediate (Scheme 1).[3] In our model, the ratio resulting from **5** and **6** defines the intrinsic reactivity of unencumbered cyclopentyne in the competing cycloadditions, whereas those from **7** and **8** represent the reactivity of one or more lithium bromide-complexed species, i.e., an encumbered cyclopentyne.

Because of the stereospecificity of the process with diastereomeric acyclic alkenes as traps for the cycloalkyne,[4] the formation of the adduct **3** had originally been interpreted mechanistically as being consistent with an unprecedented concerted pericyclic [2 + 2] process, and a theoretical rationale for this in terms of the theory of orbital isomerism[5] was developed.[6] However, more recent experimental[7a] and theoretical[7b] results support an alternate multistep process for forming this adduct, as outlined in Scheme 2. In this sequence, both the initial [2 + 1] cycloaddition and the ring expansion are allowed as concerted thermal processes according to the tenets of orbital symmetry.[8] This modification of our original explanation for the formation of [2 + 2] cycloadducts such as **3** does not affect our conclusion that free and lithium-encumbered cyclopentynes behave differently toward 1,3-dienes. Rather, it provides orbital symmetry-allowed pathways for formation of both [2 + 2] and [2 + 4] cycloadducts in the reaction of cyclopentynes with conjugated dienes.

Given our results with 1,3-dienes, it was clearly of interest to determine whether free and complexed cyclopentynes reacted differentially in [2 + 2] cycloadditions with monoenes. Literature precedent suggested they would. Thus, Fitjer and co-workers in 1983 reported that the cyclopentyne derived from 1-(dibromomethylene)-cyclobutane (**8**) reacted some three times faster with cyclohexene (**10**) than with 2,3-dihydropyran (**11**) in affording a [2 + 2] cycloadduct (eq 1).[9] Based on our aforementioned study of the cycloadditions of cyclopen-

(1) Present address: Department of Chemistry, National Central University. No. 300, Jung-Da Rd., Jung-Li City, Taoyuan, Taiwan 320.

(2) (a) Gilbert, J. C.; McKinley, E. G.; Hou, D.-R. *Tetrahedron* **1997**, *53*, 9891−9902. (b) Gilbert, J. C.; Hou, D.-R.; Grimme, J. W. *J. Org. Chem*. **1999**, *64*, 1529−1534.

(3) The structure shown for **9** is a generalization; we have no data showing it to be a simple 1:1 complex.

(4) Fitjer, L.; Modaressi, S. *Tetrahedron Lett*. **1983**, *24*, 5495−5498. Gilbert, J. C.; Baze, M. E. *J. Am. Chem. Soc.* **1984**, *106*, 1885.

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(8) Woodward, R. B.; Hoffmann, R. *Angew. Chem., Int. Ed. Eng.* **1969**, *8*, 781−853.

(9) Fitjer, L.; Kliebisch, U.; Wehle, D.; Modaressi, S. *Tetrahedron Lett*. **1982**, *23*, 1661−1664.

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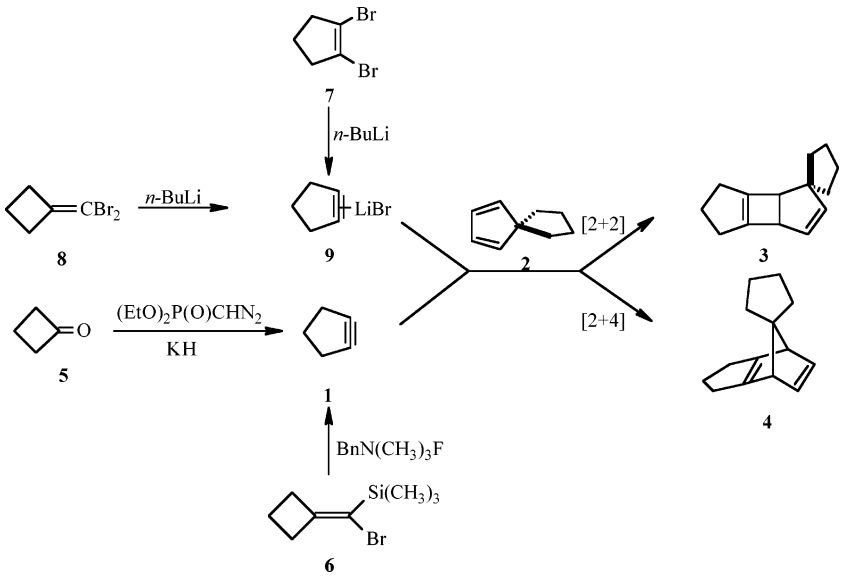
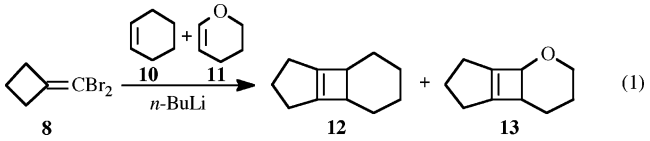
SCHEME 1



SCHEME 2

tyne with **2**,[2] this selectivity may be that of an encumbered species **9**. The present report elaborates on the question of the chemoselectivity of both free and complexed forms of cyclopentyne toward mixtures of alkenes. Because theory supports the reaction pathway of Scheme 2 for forming [2 + 2] cycloadducts, the results will be interpreted in this manner.



(1)

Results and Discussion

The competition between the cyclopentyne generated from precursors **5**, **7**, and **8** and an equimolar mixture of cyclohexene and 2,3-dihydropyran was studied first. The cycloadducts **12** and **13** were independently isolated, and their spectroscopic data are consistent with those reported previously.[9] Analysis of the ratios of **12** and **13** was effected using capillary GC and electronic integration. A check on the accuracy of the analytical method was our ability to replicate the result of Fitjer et al., in which cyclopentyne was produced by treating **8** with *n*-butyllithium (Table 1, entries 1 and 7).[9] The additional data we obtained are summarized in Table 1.

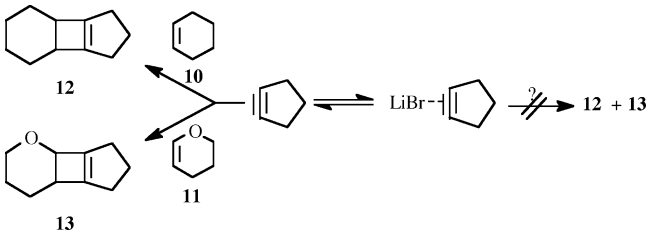
Our initial investigations revealed that the cyclopentyne from precursors **5**, **7**, and **8** gave very similar product ratios when the reactions were performed at room temperature (Table 1, entries 3, 6, and 7). This could be interpreted as reflecting the intervention of a common reactive intermediate, presumably the free form of cyclopentyne. Thus, one might propose an equilibrium between free and complexed cyclopentyne, with only the unencumbered form being sufficiently reactive to generate cycloadducts **12** and **13** (Scheme 3). This would imply

TABLE 1. Ratios of 12 and 13 as Function of Precursor and Temperature

entry	source of cyclopentyne	*T* (°C)	ratio[a,b] 12:13
1[9]	**8**	25	1:3.7
2	**5**	60	1:3.3
3	**5**	25	1:3.2
4	**5**	0	1:3.3
5	**5**	−40	1:3.2
6	**7**	25	1:3.3
7	**8**	25	1:3.7
8	**8**	−40	1:3.1
9	**8**	−78	1:2.9

[a] Average of two or more trials and a minimum of three separate analytical runs. The estimated error in the percentages from which these ratios are derived is ±5%. [b] The ratios derived from the raw integrations of products were multiplied by a factor of 1.28 to account for the lower sensitivity of the FID to **13** as compared to **12**. An uncorrected value was previously reported.[9]

SCHEME 3



that the ratio of cycloadducts would be temperature-independent, in analogy with the reactions of unencumbered cyclopentyne with diene **2**.[2a] Although this was the case with cyclobutanone as the source of cyclopentyne (Table 1, entries 2−5), the ratios are modestly temperature-dependent when **8** is used to produce the cycloalkyne (Table 1, entries 7−9). This excludes the hypothesis summarized in Scheme 3, demonstrating instead that both free and complexed cyclopentynes are directly involved in formation of cycloadducts **12** and **13**.

The results compiled in Table 1 show that both free and what we believe are complexed cyclopentynes have very similar selectivities toward the two alkenes. For example, the ratios from precursors **5** (source of free

cyclopentyne) and **7** and **8** (sources of complexed cyclopentyne) were within 10% of one another at room temperature (Table 1, entries 3, 6, and 7, respectively). This contrasts sharply with the dramatic variation in selectivities seen in the intramolecular competitions between [2 + 2] and [2 + 4] cycloadditions of free and complexed cyclopentyne with diene **2**.[2] In addition, the results with precursor **5** (entries 2−5) clearly show that the reaction of free cyclopentyne with alkenes is not diffusion-controlled but rather selectively favors the more electron-rich 2,3-dihydropyran by a factor of greater than three. Were the competing cycloadditions subject to diffusion control, a 1:1 ratio of cycloadducts **12** and **13** should have been observed.

The temperature independence of the ratio of cycloadducts from free cyclopentyne and alkenes **10** and **11** (Table 1, entries 2−5) mirrors that noted for the ratio of [2 + 2] and [2 + 4] cycloadducts obtained with unencumbered cyclopentyne and diene **2**.[2b] However, the ratios from complexed cyclopentyne show a modest temperature dependence, with the selectivity decreasing as the reaction temperature is lowered (entries 7−9). This trend may reflect a change in the aggregation of the complex.[10] Differences in aggregation may also account for the fact that the complexes derived from dibromides **7** and **8** afford different ratios of cycloadducts in reactions performed at identical temperatures (entries 6 and 7). If this is true, the selectivities observed when the dibromides serve as sources of cyclopentyne may reflect differing reactivities of varying aggregates of complexed cyclopentyne rather than that of a simple monomeric complex.

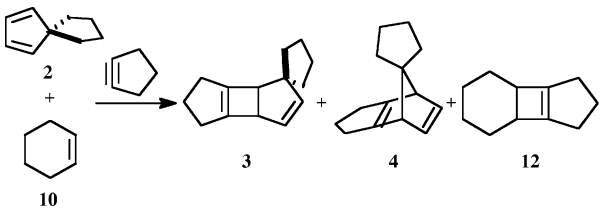
The preferred product in the competition between cyclohexene and 2,3-dihydropyran is cycloadduct **13**, regardless of the source of the cyclopentyne. This selectivity is consistent with the hypothesis contained in Scheme 2, wherein [2 + 1] cycloaddition occurs to provide a cyclopropylcarbene. If this cycloaddition is concerted, a reflection of dicarbene character of the cyclopentyne, as posited previously for norbornyne,[7] or diradical character of the cycloalkyne, reaction with the more nucleophilic **11** is expected to be faster than with **10**.

Competitions between Monoene and Diene. The similarity in ratios as a function of the precursor to cyclopentyne (Table 1) appeared to thwart our goal of using an intermolecular competition between monoenes of differing nucleophilicity to differentiate between free and complexed cyclopentyne. However, applying the concept from organometallic chemistry that bidentate ligands form more stable complexes than do monodentates[13] suggested that differentiation might be possible using a diene and a monoene. To test this possibility, mixtures of spiro[4.4]nona-1,3-diene (**2**) and cyclohexene (**8**) were used to study this type of intermolecular competition (eq 2). The results are summarized in Table 2.

TABLE 2. Ratios of 3, 4, and 12 at 25 °C as Function of Precursor

entry	source of cyclopentyne	ratio[a] (12:3:4)	**3**:**4**[b]	**12**:(**3** + **4**)
1	**5**	6.0:1:1.6	1:1.6	2.3:1
2	**6**	7.1:1:1.6	1:1.6	2.7:1
3	**7**	32:36:1	36:1	0.83:1
4	**8**	6.1:10:1	12:1[c]	0.56:1

[a] Average of two or more trials and a minimum of three separate analytical GC runs. The ratios are derived from integration data that have been corrected for detector response. The estimated error in the percentages from which the ratios are derived is ±5%. [b] Taken from ref 2b. [c] Ratio obtained at 0 °C; the ratio is expected to be lower at 25 °C but was not determined.[2b]

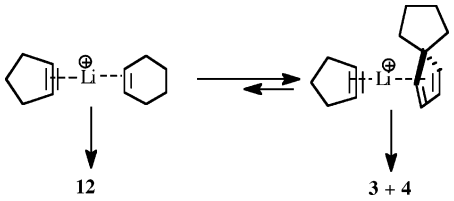


(2)

Comparing the ratios of products **3** and **4** (Table 2, column 4) with those reported earlier[2b] shows that the competition between the two modes of cycloaddition of diene **2** is not affected by the presence of cyclohexene. The next comparison is the selectivity of cyclopentyne toward cyclohexene and diene **2**, data for which are shown in the last column of Table 2. In contrast to the competition between **10** and **11**, the selectivities of free and complexed cyclopentyne are clearly different for monoene and diene. The free species derived from **5** and **6** preferentially reacts with cyclohexene by a factor of ca. 2.5 (entries 1 and 2), whereas the complexed analogue arising from **7** and **8** favors reaction with diene **2** by a factor of 1.5 (entries 3 and 4). Although the selectivities are relatively modest, they are opposite to one another and are outside of experimental error. The intermolecular competition involved in this set of experiments therefore serves to differentiate free and complexed forms of cyclopentyne.

The preference of the encumbered species to react with **2** may be a result of the diene being a more effective ligand for lithium ion (Scheme 4). In this scenario, a

SCHEME 4



complex or aggregate involving cyclopentyne, lithium bromide and the diene is posited to be more stable than an analogous array with cyclohexene. Cycloadducts derived from the diene consequently are formed preferentially.

The modest selectivity of free cyclopentyne for cyclohexene relative to the diene is interesting because the latter is more electron-rich, as measured by HOMO energies of the diene **2** and cyclohexene of 8.38 and 8.35 eV, respectively.[14] Given the electrophilic character of

(10) Aggregation phenomena for organolithium species in hydrocarbon solvents are known,[11] and aggregation of lithium bromide with a lithium enolate has been described.[12]

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

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(13) Collman, J. P.; Hegedus, L. S.; Norton, J. R.; Finke, R. G. *Principles and Application of Organotransition Metal Chemistry*, 2nd ed.; University Science Books, Mill Valley, 1987; pp 150, 548.

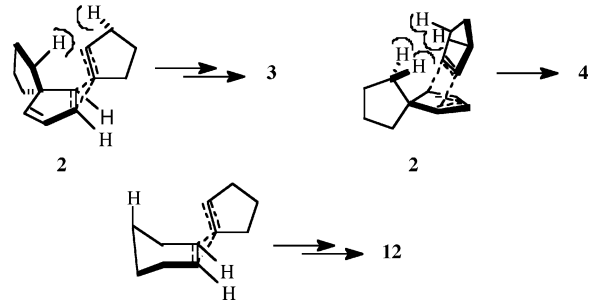
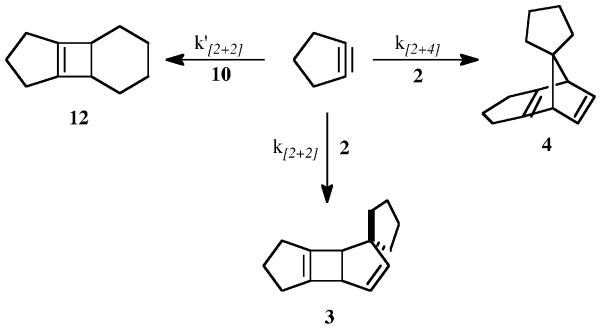


FIGURE 1. Potential steric effects for reaction of **2** and cyclohexene with cyclopentyne.

cyclopentyne, as reflected in the competition between cyclohexene and 2,3-dihydropyran (Table 1), the preference of the free cycloalkyne for cyclohexene compared to the diene suggests that factors other than the relative nucleophilicities of the substrates may be at work.

Analyzing these factors is complicated owing to the existence of three reaction channels in this competition (Scheme 5). The [2 + 2] cycloaddition is the only known

SCHEME 5



reaction channel for cyclopentyne and cyclohexene (**11**), but both [2 + 2] and [2 + 4] cycloaddition pathways are available for reaction of cyclopentyne with diene **2**. The fact that **12** was the major product in this three-way competition indicates that the rate constant for [2 + 2] cycloaddition with cyclohexene, $k'_{[2+2]}$, is greater than the sum, $k_{[2+4]} + k_{[2+2]}$, of those for the [2 + 4] and [2 + 2] cycloadditions with diene **2** (Scheme 5). In addition, the rate constant $k_{[2+4]}$ is greater than $k_{[2+2]}$, based on the observed ratio of the two cycloadducts **3** and **4**. The slower rate of reaction of free cyclopentyne with diene **2** as compared to cyclohexene may be due to steric hindrance associated with the spiroannulated cyclopentadienyl moiety that hampers access of the diene to the incoming cyclopentyne (Figure 1).[15] This hypothesis suggests that increasing the steric bulk of the substitutents at the 5-position of a 1,3-cyclopentadiene should favor reaction of cyclopentyne with cyclohexene in an intermolecular competition experiment.

Conclusions

Our previously reported results involving *intramolecular* competition between formation of [2 + 2] and [2 + 4] cycloadducts from reaction of spiroannulated 1,3-cyclopentadienes with cyclopentyne demonstrated a dependence of product ratios on the precursor used to produce the alkyne.[2] This led us to posit the existence of free and complexed forms of cyclopentyne. The present study involving *intermolecular* competition for cyclopentyne by different alkenes augments the intramolecular data reported previously.[2] The evidence obtained herein is consistent with our earlier hypothesis that organolithium-promoted decomposition of precursors to the cycloalkyne affords one or more lithium bromide complexed species that are capable of cycloadditions with cyclohexene and 2,3-dihydropyran. Although the competition reaction with mixtures of these alkenes does not clearly differentiate between the complexed and unencumbered forms of cyclopentyne, the comparable study using spirodiene **2** and cyclohexene does. Thus, the cyclopentyne generated from precursors **5** and **6** is believed to be the free species, whereas that derived from **7** and **8** is in the form of a complex. The present results also reveal that despite the high reactivity of free cyclopentyne, its cycloaddition reactions are not diffusion controlled.

Experimental Section

All reactions involving generation of cyclopentyne 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 effected with a 4-ft × 0.125-in. column containing 5% OV-101 on Chromosorb P-AW-DMCS (80/100 mesh), using helium 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 and a flame-ionization detector (FID); helium was the carrier gas (1.2 mL/min). Yields of 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 and interfaced with an electron impact ion trap detector mass spectrometer; helium was the carrier gas (1.0 mL/min). High-resolution MS analyses were obtained in the EI mode (70 eV).

^{1}H NMR spectra were obtained at 250 and 500 MHz, 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. The preparation and characterization of 1-(bromotrimethylsilylmethylene)cyclobutane (**6**) and of the cycloadducts **3** and **4** were reported previously.[2b]

(14) (a) Lambert, J. B.; Xue, L.; Bosch, R. J.; Taba, K. M.; Marko, D. E.; Urano, S.; LeBerton, P. R. *J. Am. Chem. Soc.* **1986**, *108*, 7575−7579. (b) Planckaert, A. A.; Doucet, J.; Sandorfy, C. *J. Chem. Phys.* **1974**, *60*, 4846−4853. (c) Batich, C.; Heilbronner, E.; Rommel, E.; Semmelhack, M. F.; Foos, J. S. *J. Am. Chem. Soc.* **1974**, *96*, 7662−7668. Generalized frontier orbitals of alkenes and dienes: Houk, K. N. *J. Am. Chem. Soc.* **1973**, *95*, 4092−4094.

(15) To the extent that formation of [2 + 2] cycloaddition products with cyclopentyne is initiated by formation of a cyclopropylcarbene, further support for the role of steric factors is provided by the known preference of dichlorocarbene to react twice as fast with 1,3-cyclohexadiene than with cyclohexene.[16] This would imply that $k_{[2+2]}$ should be greater than $k'_{[2+2]}$, a result opposite to that observed experimentally.

Competition Reactions of Cyclopentyne between Cyclohexene and 2,3-Dihydropyran. A. Tricyclo[6.3.0.0^{2,7}]-undec-1(8)-ene (12). 1-(Dibromomethylene)cyclobutane (**8**, 100 mg, 0.44 mmol) was added to a dry 10-mL flask containing a magnetic stirbar. Cyclohexene (0.29 g, 3.55 mmol) was added, and the solution was cooled to −78 °C. After the solution was stirred for 10 min, a solution of *n*-BuLi (0.66 mL of a 1.3 M solution in diethyl ether/hexane, 0.88 mmol) was added dropwise by syringe. A yellow precipitate was observed immediately after the *n*-BuLi addition. The solution was stirred in the ice−water bath for 2 h, and the reaction mixture was then treated with a mixture of pentane (5 mL) and water (0.1 mL). The solution was dried (Na_2SO_4), filtered, and concentrated. The crude product was purified by silica gel column chromatography using pentane as eluant; R_f 0.74. After concentration, 9.8 mg (0.066 mmol, 15%) of **12** was isolated as a colorless liquid. Yield: 3.7%. The NMR spectra were consistent with those reported.[9] HRMS (CI): calcd for $C_{11}H_{17}$ (MH^+) 149.1326, found 149.1330.

B. 3-Oxatricyclo[6.3.0.0^{2,7}]undec-1(8)-ene (13). Potassium hydride (408 mg, 3.56 mmol, 35% in mineral oil) in a 10-mL round-bottom flask equipped with a magnetic stirbar was washed with pentane (3 × 8 mL) and flushed by nitrogen gas. Dry dichloromethane (1.0 mL) was added, and the resulting solution was cooled to −78 °C. Diethyl (diazomethyl)-phosphonate (DAMP)[17] (470 mg, 2.65 mmol) in 0.5 mL of dichloromethane was added by syringe, and the resulting slurry was stirred for 10 min at −78 °C. 2,3-Dihydropyran (**11**, 1.01 g, 12.0 mmol) and cyclobutanone (**5**, 124 mg, 1.77 mmol) were added sequentially to the reaction flask, and the solution was stirred at −78 °C for an additional 15 min. The flask was transferred to a room-temperature water bath; vigorous nitrogen evolution occurred within 2 min and the solution became orange. The reaction mixture was stirred at 25 °C for 1 h, acetonitrile (5 mL) was added, and the resulting solution was extracted with pentane (3 × 5 mL), dried (Na_2SO_4), filtered, and concentrated to about 1.5 mL. The crude product was purified by silica gel column chromatography using pentane/ethyl acetate (9:1) as eluant; R_f 0.83. After concentration, 9.7 mg (0.46 mmol, 3.7%) of **13** was isolated as a colorless liquid. The NMR spectra were consistent with those reported.[9] HRMS (CI): calcd for $C_{10}H_{15}O$ (MH^+) 151.1114, found 151.1123.

C. GC Response Factor. Three independent GC analyses (isothermal, 100 °C, FID) of a solution of cycloadducts **12** (13.0 mg, 0.088 mmol) and **13** (9.7 mg, 0.065 mmol) in pentane (5 mL) provided a relative molar response factor of 1:1.28 ± 5%.

D. Cyclopentyne from 1,2-Dibromocyclopentene (1). 1,2-Dibromocyclopentene (**7**, 100 mg, 0.45 mmol), 2,3-dihydropyran (149 mg, 1.77 mmol), and cyclohexene (145 mg, 1.77 mmol) were combined in a dry 10-mL flask containing a magnetic stirbar. The solution was cooled to −78 °C and stirred for 10 min, after which a solution of *n*-BuLi (0.6 mL of a 1.2 M solution in hexane, 0.72 mmol) was added by syringe. The resulting solution was stirred at −78 °C for 15 min and at room temperature for 1 h. Water (0.1 mL) and pentane (15 mL) were added, the mixture was filtered through a cotton plug, and the filtrate was subjected to GC analysis (isothermal, 100 °C).

E. Cyclopentyne from 1-(Dibromomethylene)cyclobutane (8). General Procedure. 1-(Dibromomethylene)cyclobutane (**8**, 100 mg, 0.45 mmol) was placed in a dry 10-mL flask containing a magnetic stirbar, and 2,3-dihydropyran (149 mg, 1.77 mmol) and cyclohexene (145 g, 1.77 mmol) were added by syringe; the solution was maintained at 25 °C. A solution of *n*-BuLi (0.6 mL of a 1.2 M solution in hexane, 0.72 mmol) was added dropwise by syringe, and the reaction mixture was stirred at 25 °C for 1 h; a yellow precipitate formed immediately upon addition of the alkyllithium. Workup and analysis followed the procedure of part D.

Variable temperature experiments were performed at −78 and −40 °C using the above procedure and the appropriate cooling baths.

F. Cyclopentyne from Cyclobutanone (5). Potassium hydride (405 mg, 3.54 mmol, 35% in mineral oil) in a 10-mL round-bottom flask was washed with pentane (3 × 8 mL) and flushed by nitrogen gas. Dry dichloromethane (1.0 mL) was added, the resulting solution was cooled to −78 °C, and a solution of DAMP (470 mg, 2.65 mmol) in 0.5 mL dichloromethane was transferred by syringe into the reaction flask. The slurry was stirred for 10 min at −78 °C, cyclohexene (581 mg, 7.07 mmol), 2,3-dihydropyran (596 mg, 7.07 mmol), and cyclobutanone (**5**, 124 mg, 1.77 mmol) were added sequentially, and the solution was stirred at −78 °C for an additional 15 min. The flask was transferred to a room-temperature water bath; vigorous nitrogen evolution occurred within 2 min and the solution became orange. The reaction mixture was stirred at 25 °C for 1 h, water (5 mL) was added, and the resulting solution was extracted with dichloromethane (1 × 10 mL, 5 × 2 mL). The combined extracts were dried (Na_2SO_4), filtered, and concentrated to about 1.0 mL, after which the residue was subjected to GC analysis (isothermal, 100 °C).

Variable temperature experiments were performed at −40, 0, and 60 °C using the above procedure and the appropriate cooling or heating baths. The reaction mixtures were first held at −78 °C for 15 min and then kept at the specified temperature for 120, 60, and 5 min, respectively.

Competition between Cyclohexene and Diene 2. A. GC Response Factor. Three independent GC analyses (isothermal, 250 °C, FID) of a solution of cycloadduct **12** (3.4 mg, 0.023 mmol) and dodecane (11.8 mg, 0.069 mmol) in pentane (5 mL) provided a relative molar response factor of 1:2.0 ± 5%. The corresponding analysis under the same GC conditions of a solution of cycloadducts **3** and **4** (4.6 mg, 0.025 mmol) and dodecane (19.4 mg, 0.114 mmol) in pentane (5 mL) yielded a relative response factor of 1:1.17 ± 5%. These data provide a relative response factor of 1:1.70 ± 5% for **12**:**3**.

B. Cyclopentyne from 1,2-Dibromocyclopentene (7). 1,2-Dibromocyclopentene (**7**, 200 mg, 0.89 mmol) was combined with spiro[4.4]nona-1,3-diene (**2**, 0.36 g, 3.0 mmol) and cyclohexene (0.246 g, 3.0 mmol) in a dry 10-mL flask containing a magnetic stirbar, and the solution was cooled to −78 °C and stirred for 10 min. A solution of *n*-BuLi (1.5 mL of a 1.2 M solution in hexane, 1.8 mmol) was added by syringe, and the resulting mixture was stirred at −78 °C for 30 min and at room temperature for 1 h; a yellow precipitate was observed after 5 min. A solution of maleic anhydride (0.36 g, 3.7 mmol) in acetonitrile (5 mL) solution was added, and the resulting mixture was stirred for 1 h and then extracted with pentane (3 × 5 mL). The combined extracts were dried (Na_2SO_4), filtered, and concentrated to about 1.0 mL. The residue was passed through a short silica plug using pentane as eluant until no compounds could be detected in the eluate by TLC analysis (pentane). The concentrated eluate was subjected to GC analysis (isothermal, 100 °C).

C. Cyclopentyne from 1-(Dibromomethylene)cyclobutane (8). 1-(Dibromomethylene)cyclobutane (**8**, 100 mg, 0.45 mmol) was combined with spiro[4.4]nona-1,3-diene (**2**, 180 mg, 1.50 mmol) and cyclohexene (123 mg, 1.50 mmol) in a dry 10-mL flask containing a magnetic stirbar, and the solution was maintained at 25 °C. A solution of *n*-BuLi (0.79 mL of a 1.12 M solution in hexane, 0.88 mmol) was added dropwise by syringe, and the resulting mixture was stirred at 25 °C for 1 h; yellow precipitate was observed immediately after addition of the alkyllithium. Workup and analysis followed the procedure of part C, with removal of excess diene **2** being effected by addition of a solution of maleic anhydride (0.30 g, 3.0 mmol) in acetonitrile (5 mL).

D. Cyclopentyne from Cyclobutanone (5). Potassium hydride (202 mg, 1.77 mmol, 35% in mineral oil) in a 10-mL round-bottom flask was washed with pentane (3 × 5 mL) and flushed by nitrogen gas. Dry dichloromethane (1.0 mL) was

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added, the resulting slurry was cooled to −78 °C, and a solution of DAMP (235 mg, 1.32 mmol) in dichloromethane (0.5 mL) was introduced via syringe. The slurry was stirred for 10 min at −78 °C, after which spiro[4.4]nona-1,3-diene (**2**, 360 mg, 3.0 mmol), cyclohexene (246 mg, 3.0 mmol), and cyclobutanone (**5**, 62 mg, 0.88 mmol) were added sequentially. The reaction mixture was stirred at −78 °C for an additional 15 min and at room temperature for 1 h. Nitrogen evolution was observed 2 min after removal of the flask from the cooling bath, and the solution became orange. Workup and analysis followed the procedure of part C, with removal of excess diene **2** being effected by addition of a solution of maleic anhydride (0.60 g, 6.0 mmol) in acetonitrile (5 mL).

E. Cyclopentyne from (Bromocyclobutylidenemethyl)trimethylsilane (6). Benzyltrimethylammonium fluoride (85 mg, 0.5 mmol) and 4Å molecular sieves (0.5 g) were added to a 5-mL flask equipped with a stirbar. THF (2 mL) was added, and the slurry was stirred at room temperature for 14 h. After THF was removed under vacuum, dichloromethane (2 mL) was added, and a solution of (bromocyclobutylidenemethyl)trimethylsilane (**6**, 100 mg, 0.45 mmol) in spiro[4.4]nona-1,3-diene (**2**, 180 mg, 1.50 mmol) and cyclohexene (123 mg, 1.50 mmol) was introduced by cannulation. The reaction mixture, which became brown immediately after the reagents were combined, was stirred at room temperature for 1.5 h. Workup and analysis followed the procedure of part C, with removal of excess diene **2** being effected by addition of a solution of maleic anhydride (0.20 g, 2.0 mmol) in acetonitrile (5 mL).

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