Nickel(0)-Catalyzed Cycloaddition of 1-(Trimethylsilyl)-1,7-decadiyne (5) with Carbon Dioxide to the Bicyclic α-Pyrone 6. The reaction was carried out under nitrogen. In a 50-mL stainless steel autoclave were placed a THF solution (1.05 mL) of $Ni(cod)_2$ (0.025 mmol), the ligand **1** (0.013 mL, 0.050 mmol), and THF (19.0 mL). After the mixture was stirred for several minutes, **5** (0.068 mL, 0.250 mmol) was added and then CO_2 gas was compressed up to 50 kg/cm^2 at room temperature. The reaction mixture was magnetically stirred for 20 h at 120 °C. The remaining CO_2 gas was purged off and the reaction mixture was transferred to a flask using ether (20 mL). Addition of *n*-docosane (0.0388 g, 0.125 mmol) as a GC internal standard and subsequent GC analysis (a silicone DC 550 column) showed formation of **6** in 80% yield. The solution was concentrated to give a residue that was purified by PLC (hexane/ether = 2:1 (v/v)) to give **6** (0.0358 g, 57%): IR (neat, cm^{-1}) 1690, 1595, 1550; ^{1}H NMR 0.32 (s, 9 H), 1.08 (t, J = 7.5, 3 H), 1.59–1.83 (m, 4 H), 2.41–2.57 (m, 4 H), 2.62 (t, J = 6.4, 2 H); MS *m/e* (relative intensity) 250 (M$^+$, 97), 235 (52), 222 (100), 207 (81), 73 (58); HRMS (*m/e*) 250.1398, calcd for $C_{14}H_{22}O_2Si$ 250.1389. The purity of the product **6** was judged to be ≥95% by ^{1}H NMR spectral determination.

The reactions of **2a**, **2b**, **7a**, and **7b** were carried out as described above and the corresponding bicyclic α-pyrones were identified as follows. The product purity was judged to be ≥95% for the products **3a** and **8a** by ^{1}H NMR spectral determinations. **3a** (PLC, hexane/ether = 1:1 (v/v)): IR (neat, cm^{-1}) 1680, 1630, 1560; ^{1}H NMR 0.27 (s, 9 H), 1.97 (quint, J = 7.4, 2 H), 2.65 (t, J = 7.4, 4 H), 6.09 (s, 1 H); MS, *m/e* (relative intensity) 208 (M$^+$, 60), 193 (100), 165 (14), 135 (17), 73 (88); HRMS (*m/e*) 208.0928, calcd for $C_{11}H_{16}O_2Si$ 208.0919. **4a** (PLC, hexane/ether = 1:1 (v/v)): IR (neat, cm^{-1}) 1665, 1630, 1540; ^{1}H NMR 0.27 (s, 9 H), 1.96 (quint, J = 7.4, 2 H), 2.56 (t, J = 7.3, 2 H), 2.75 (t, J = 7.4, 2 H), 7.30 (s, 1 H); MS, *m/e* (relative intensity) 208 (M$^+$, 24), 193 (100), 165 (48), 73 (11), 57 (11); HRMS (*m/e*) 208.0913, calcd for $C_{11}H_{16}O_2Si$ 208.0919. Anal. Calcd for $C_{11}H_{16}O_2Si$: C, 63.42; H, 7.74. Found: C, 63.34; H, 7.89. **3b** (PLC, hexane/ether = 1:1 (v/v)): IR (neat, cm^{-1}) 1710, 1605, 1535; ^{1}H NMR 0.31 (s, 9 H), 1.60–1.71 (m, 4 H), 2.50 (t, J = 6.3, 2 H), 2.58 (t, J = 6.1, 2 H), 6.00 (s, 1 H); MS, *m/e* (relative intensity) 222 (M$^+$, 45), 207 (36), 179 (65), 73 (100); HRMS (*m/e*) 222.1086, calcd for $C_{12}H_{18}O_2Si$ 222.1076. Anal. Calcd for $C_{12}H_{18}O_2Si$: C, 64.83; H, 8.16. Found: C, 64.63; H, 8.25. **8a** (PLC, hexane/ether = 3:1 (v/v), a white solid): mp 87.2–89.3 °C; IR (Nujol paste, cm^{-1}) 1670, 1605, 1540; ^{1}H NMR 0.29 (s, 18 H), 1.95 (quint, J = 7.4, 2 H), 2.61 (t, J = 7.4, 2 H), 2.72 (t, J = 7.5, 2 H); MS, *m/e* (relative intensity) 280 (M$^+$, 46), 265 (42), 147 (30), 133 (37), 73 (100); HRMS (*m/e*) 280.1295, calcd for $C_{14}H_{24}O_2Si_2$ 280.1314. **8b** (PLC, hexane/ether = 2:1 (v/v)): IR (neat, cm^{-1}) 1680, 1575, 1520; ^{1}H NMR 0.29 (s, 18 H), 1.60–1.70 (m, 4 H), 2.45 (t, J = 6.6, 2 H), 2.64 (t, J = 6.6, 2 H); MS, *m/e* (relative intensity) 294 (M$^+$, 6), 279 (55), 266 (91), 133 (26), 73 (100); HRMS (*m/e*) 294.1456, calcd for $C_{15}H_{26}O_2Si_2$ 294.1471. Anal. Calcd for $C_{15}H_{26}O_2Si_2$: C, 61.17; H, 8.90. Found: C, 61.07; H, 8.88.

Protodesilylation of the Silyl Bicyclic α-Pyrone 6 to the Bicyclic α-Pyrone 9. A THF solution (1.2 mL) of tetrabutylammonium fluoride trihydrate (0.38 g, 1.2 mmol) was added to a magnetically stirred THF solution (5.0 mL) of **6** (0.146 g, 0.583 mmol) at 0 °C under nitrogen. The mixture was stirred for 15 min, treated with water (30 mL), and extracted with ether (30 mL). The ether solution was dried over anhydrous magnesium sulfate, filtered, and concentrated. A residue was purified by PLC (hexane/ether = 1:1 (v/v)) to give **9** (0.101 g, 97%): IR (neat, cm^{-1}) 1705, 1630, 1535; ^{1}H NMR 1.02 (t, J = 7.5, 3 H), 1.49–1.80 (m, 4 H), 2.32–2.52 (m, 4 H), 2.57 (t, J = 6.4, 2 H), 7.08 (s, 1 H); MS, *m/e* (relative intensity) 178 (M$^+$, 100), 150 (38), 135 (75); HRMS (*m/e*) 178.1006, calcd for $C_{11}H_{14}O_2$ 178.0994. The purity of the product **9** was judged to be ≥95% by ^{1}H NMR spectral determination.

Diels–Alder Reaction of the Silyl Bicyclic α-Pyrone 3b with 5-Hydroxy-1,4-naphthoquinone. The reaction was carried out under nitrogen. In a 50-mL stainless steel autoclave were placed **3b** (0.0422 g, 0.190 mmol), 5-hydroxy-1,4-naphthoquinone (0.0693 g, 0.398 mmol), and xylenes (5.0 mL). The reaction mixture was magnetically stirred for 7 days at 130 °C. Then Ag_2O (0.20 g, 0.86 mmol) and $MgSO_4$ (0.20 g, 1.7 mmol) were added. The reaction mixture was magnetically stirred for 1 day at room temperature. The reaction mixture was filtrated. The filtrate was concentrated to give a residue, which was purified by PLC (hexane/ethyl acetate = 5:1 (v/v)) to give the mixture of regioisomeric Diels–Alder cycloadducts **10** and **11**. Regioisomers **10** (0.025 g, 38%) and **11** (0.010 g, 16%) were separated by MPLC (hexane/ethyl acetate = 10:1 (v/v)) and were crystallized in hexane at 0 °C as yellow prisms. The structure of **10** was determined by X-ray crystallography. **10** (mp 138.5–141.2 °C): IR (KBr, cm^{-1}) 3433, 1668, 1633, 1570; ^{1}H NMR 0.38 (s, 9 H), 1.65–1.90 (m, 4 H), 2.92 (t, J = 6.4, 2 H), 2.95 (t, J = 6.2, 2 H), 7.25 (dd, J = 7.5, 1.6, 1 H), 7.60 (t, J = 7.8, 1 H), 7.74 (dd, J = 7.3, 1.5, 1 H), 7.95 (s, 1 H), 12.28 (s, 1 H); MS, *m/e* (relative intensity) 350 (M$^+$, 3.6), 335 (100), 319 (4.3), 149 (4.6); HRMS (*m/e*) 350.1309, calcd for $C_{21}H_{22}O_3Si$ 350.1332. **11** (mp 180.7–183.0 °C): IR (KBr, cm^{-1}) 3444, 1662, 1633, 1566; ^{1}H NMR 0.37 (s, 9 H), 1.70–1.90 (m, 4 H), 2.92 (t, J = 6.6, 2 H), 2.95 (t, J = 6.2, 2 H), 7.23, (dd, J = 7.3, 2.2, 1 H), 7.55–7.65 (m, 2 H), 7.96 (s, 1 H), 12.49 (s, 1 H); MS, *m/e* (relative intensity) 350 (M$^+$, 1.8), 355 (100), 307 (8.9); HRMS (*m/e*) 350.1309, calcd for $C_{21}H_{22}O_3Si$ 350.1332. The purity of the products **10** and **11** was judged to be ≥95% by ^{1}H NMR determinations.

Acknowledgment. We thank Dr. Kazuhide Kamiya and Dr. Masayuki Takamoto of Chemistry Research Laboratories, Takeda Chemical Industries, Limited, for X-ray diffraction analysis of the compound **10**.

Supplementary Material Available: Crystal structure data of compound **10** and ^{1}H NMR spectra showing the purity of the products **3a**, **6**, **8a**, **9**, **10**, and **11** (18 pages). Ordering information is given on any current masthead page.

A New Method for Coupling Aromatic Aldehydes and Ketones To Produce α-Glycols Using Zn–$ZnCl_2$ in Aqueous Solution and in the Solid State

Koichi Tanaka, Satoshi Kishigami, and Fumio Toda*

Department of Industrial Chemistry, Faculty of Engineering, Ehime University, Matsuyama 790, Japan

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The coupling of aromatic aldehydes and ketones to afford α-glycols has been carried out by heating with Zn–AcOH,[1] Mg–MgX_2,[2] or Al(Hg).[3] These methods were improved by using more active metals such as Al,[4] $TiCl_4$,[5] or $TiCl_4$–Zn.[6] However, these reactions should be carried out at low temperature and in the presence of an inert gas, since the active reagents are sensitive to oxygen and the reaction with the reagents at high temperature gives an olefin.

Previously, we have reported that Zn–$ZnCl_2$ is an effective reagent for the reduction of activated olefins[7] and ketones.[8] Recently, we found further that the reagent is effective for the coupling of aromatic aldehydes and ketones to produce α-glycols, both in solution and in the solid state. Since the Zn–$ZnCl_2$ reagent is effective at room temperature and not sensitive to oxygen, its handling is easy.

For example, when a solution of benzaldehyde (**1a**), commercially available Zn powder, and $ZnCl_2$ in 50%

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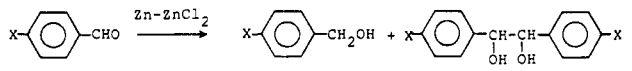
Table I. Yield of 2 and 3 Produced by Treatment of 1 with Zn–$ZnCl_2$ at Room Temperature for 3 h in 50% Aqueous THF and in the Solid State

1	solvent	yield, % 2	yield, % 3	meso:dl ratio[b] in 3
a, X = H	A[a]	39	11	50:50
		trace	46	60:40
b, X = Me	A	81	7	50:50
		trace	87	70:30
c, X = Cl	A	82	16	50:50
		25	65	80:20
d, X = Br	A	72	27	50:50
		19	55	70:30
e, X = CN	A	0	90	c
		0	93	c
f, X = Ph	A	49	38	80:20
		2	64	70:30

[a] A = 50% aqueous THF. [b] The meso:dl ratio was determined by NMR spectroscopy. [c] The meso:dl ratio was not determined.

aqueous THF was stirred for 3 h at room temperature, benzyl alcohol (**2a**) and α-glycol (**3a**) were obtained in 39 and 11% yields, respectively. When the reaction was

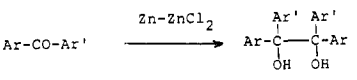


1 2 3

carried out without using solvent, more α-glycol was produced than in solution. For example, when a mixture of **1a**, Zn, and $ZnCl_2$ was kept at room temperature for 3 h, **3a** was obtained in 46% yield. Similar treatment of benzaldehyde derivatives **1b–f** gave **2b–f** and **3b–f** in the yields shown in Table I. In all cases except **1e**, **2** is the main reaction product in aqueous solution, although **3** is always the main product in the solid state. Since the reaction in the solid state is a high-concentration reaction, the intermolecular reaction of **1** would occur more easily to produce the coupling product **3** mainly.

As water content decreases, the ratio of **2**:**3** decreases. For example, when the coupling reaction of **1d** with Zn–$ZnCl_2$ was carried out at room temperature for 3 h in THF containing 50, 20, 10, 5, and 0% water, the ratios of the yields of **2d** and **3d** were 55:22, 67:32, 72:27, 50:49, and 19:55, respectively. However, the reason for the effect of water on the product ratio is not clear.

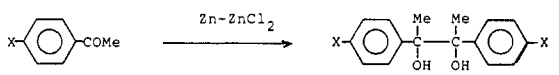
The coupling reaction of aromatic ketones (**4**) with Zn–$ZnCl_2$ is more selective, and only the α-glycols (**5**) were produced (Table II). In this case, the reaction in aqueous



4 5

THF is more effective than in the solid state. In many cases of the reaction in the solid state, heating for a long time is necessary (Table II).

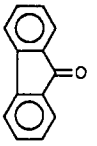
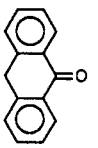
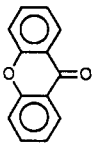
The Zn–$ZnCl_2$ reagent is also effective for the coupling of acetophenone derivatives (**6**), and their coupling reaction products (**7**) were obtained in good yields (Table III).



6 7

In conclusion, it is clear that the coupling method with Zn–$ZnCl_2$ is effective, simple, and economical and has many advantages in comparison to usual methods.

Table II. Yield of 5 Produced by Treatment of 4 with Zn–$ZnCl_2$ in 50% Aqueous THF and in the Solid State

4 Ar	4 Ar'	solvent	reacn time, h	temp, °C	yield of 5, %
C_6H_5	C_6H_5	A[a]	1	rt[b]	84
			6	rt	86
p-MeC_6H_4	p-MeC_6H_4	A	3	rt	84
			84	70	30
p-ClC_6H_4	p-ClC_6H_4	A	1	rt	92
			6	70	39
C_6H_5	p-ClC_6H_4	A	2	rt	90[c]
			6	70	26[c]
		A	0.5	rt	94
			3	rt	92
		A	1	rt	95
			84	70	43
		A	2	rt	94
			84	70	20

[a] A = 50% aqueous THF. [b] rt = room temperature. [c] The meso:dl ratio was not determined.

Table III. Yield of 7 Produced by Treatment of 6 with Zn–$ZnCl_2$ in 50% Aqueous THF and in the Solid State

6	solvent	reacn time, h	temp, °C	yield of 7,[c] %
X = H	A[a]	3	rt[b]	0
		24	70	89
X = Br	A	3	rt	62
		3	70	77
X = CN	A	3	rt	100
		3	70	65

[a] A = 50% aqueous THF. [b] rt = room temperature. [c] The meso:dl ratio was not determined.

Experimental Section

General Procedure. Commercially available Zn powder and $ZnCl_2$ were used for the coupling reaction. The structure of the reaction product (**2**, **3**, **5**, and **7**) was elucidated by comparison of its IR spectrum with that of an authentic sample. The meso:dl ratio of **3** was determined by ^1H NMR spectroscopy.

General Coupling Procedure in 50% Aqueous THF. A mixture of **1** (1 g), Zn powder (5 g), $ZnCl_2$ (1 g), and 50% aqueous THF (10 mL) was stirred at room temperature for 3 h. The reaction mixture was combined with 3 N HCl (5 mL) and filtered to remove the Zn powder. The filtrate was extracted with toluene, and the toluene solution was washed with water and dried over $MgSO_4$. The toluene solution was evaporated to give a mixture of **2** and **3**. Since the solubilities of **2** and **3** in organic solvents are different, **2** and **3** were easily separated to give pure **2** and **3** in the yields shown in Table I.

Similar treatment of **4** and **6** with the Zn–$ZnCl_2$ reagent as above gave **5** and **7** in the yields shown in Tables II and III, respectively.

General Coupling Procedure in the Solid State. A mixture of **1** (1 g), Zn powder (5 g), and $ZnCl_2$ (1 g) was kept at room temperature for 3 h. The reaction mixture was combined with 3 N HCl (5 mL) and toluene (10 mL) and filtered to remove Zn powder. The filtrate was worked up as above to give **2** and **3** in the yields shown in Table I.

Similar treatment of **4** and **6** with the Zn–$ZnCl_2$ reagent as above gave **5** and **7** in the yields shown in Tables II and III, respectively.

Registry No. **1a**, 100-52-7; **1b**, 104-87-0; **1c**, 104-88-1; **1d**, 1122-91-4; **1e**, 105-07-7; **1f**, 3218-36-8; **2a**, 100-51-6; **2b**, 589-18-4; **2c**, 873-76-7; **2d**, 873-75-6; **2f**, 3597-91-9; *meso*-**3a**, 579-43-1; (±)-**3a**,

655-48-1; *meso*-**3b**, 5173-29-5; (±)-**3b**, 5173-28-4; *meso*-**3c**, 37580-81-7; (±)-**3c**, 69483-09-6; *meso*-**3d**, 37580-82-8; (±)-**3d**, 126082-50-6; *meso*-**3e**, 86001-18-5; (±)-**3e**, 86001-17-4; *meso*-**3f**, 126082-51-7; (±)-**3f**, 126082-52-8; zinc, 7440-66-6; zinc dichloride, 7646-85-7; benzophenone, 119-61-9; *p*-tolyl ketone, 611-97-2; *p*-chlorophenyl ketone, 90-98-2; *p*-chlorobenzophenone, 134-85-0; fluoren-9-one, 486-25-9; anthrone, 90-44-8; 9-xanthone, 90-47-1; 1,1,2,2-tetraphenylethylene glycol, 464-72-2; 1,1,2,2-tetra-*p*-tolylethylene glycol, 913-86-0; 1,1,2,2-tetrakis(*p*-chlorophenyl)-ethylene glycol, 5418-23-5; *meso*-1,2-bis(*p*-chlorophenyl)-1,2-diphenylethylene glycol, 126082-53-9; *dl*-1,2-bis(*p*-chlorophenyl)-1,2-diphenylethylene glycol, 126082-54-0; fluorenopinacol, 3073-51-6; anthrapinacol, 4393-30-0; xanthopinacol, 6272-59-9; acetophenone, 99-90-1; *p*-bromoacetophenone, 99-90-1; *p*-cyanoacetophenone, 1443-80-7; *meso*-2,3-diphenyl-2,3-butanediol, 4217-65-6; *dl*-2,3-diphenyl-2,3-butanediol, 22985-90-6; *meso*-2,3-bis(*p*-bromophenyl)-2,3-butanediol, 126082-55-1; *dl*-2,3-bis(*p*-bromophenyl)-2,3-butanediol, 126082-56-2; *meso*-2,3-bis(*p*-cyanophenyl)-2,3-butanediol, 93453-78-2; *dl*-2,3-bis(*p*-cyanophenyl)-2,3-butanediol, 93453-76-0.

Bromo[3]cumulene and Bromo Enyne Radical Cyclization to Cyclopentenyne Products†

Carl B. Ziegler, Jr.

American Cyanamid Company, Medical Research Division, Lederle Laboratories, Pearl River, New York 10965

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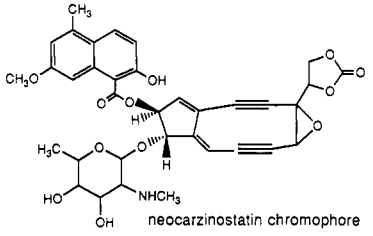
The synthetic utilization of halo[3]cumulenes is new and holds considerable potential for the development of novel methodology.[1] Recently, we reported a new halo enyne synthesis in which the key step was a regioselective S_N2' halide displacement on bromo[3]cumulenes.[2] In this work we present our studies directed toward the vinyl radical cyclization of appropriately substituted bromo[3]cumulene and bromo enyne intermediates. The synthetic targets chosen are substituted cyclopentenynes. This structural moiety is part of the highly strained fused ring system of neocarzinostatin, an extremely potent antitumor antibiotic, whose structure was recently elucidated.[3] The methodology described herein could find an application that compliments the present synthetic approaches to neocarzinostatin.[4]

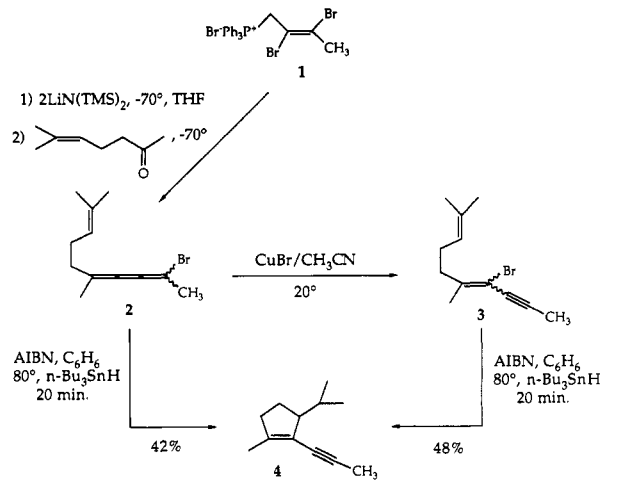


neocarzinostatin chromophore

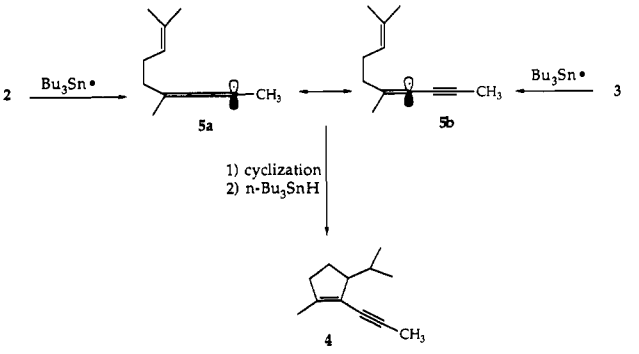
The synthetic method to be described is presented in Scheme I. The bromo[3]cumulene **2** was prepared from phosphonium salt **1** and 6-methyl-5-hepten-2-one by a Wittig condensation. Thus, **2** was converted to the bromo enyne **3** as reported.[2,5] When either **2** or **3** was treated with 1.1 equiv of *n*-Bu_3SnH (AIBN initiation) in refluxing benzene (0.02 M) for 20 min, the 5-(*π-Endo*)-*Exo-Trig* cyclization[6] product **4** was isolated. Yields of **4** in each case were based on the starting phosphonium salt **1**. Cyclopentene formation via **2** (42%, two steps) was similar to that via the intermediacy of **3** (48%, three steps).[7,8]

†Dedicated to the memory of Dr. Daniel F. Lieberman, a friend and colleague.

Scheme I



Scheme II



A logical mechanistic rational for this radical cyclization is presented in Scheme II. Bromo[3]cumulene **2** and bromo enyne **3** are converted to the same planar radical intermediate represented as forms **5a** and **5b** under these

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(5) As was demonstrated in ref 2, the bromo[3]cumulene products of unsymmetrical ketones are formed as a 1:1 geometrical pair. Thus, bromo enynes synthesized from them are isomeric.

(6) The term (*π-Endo*) used here to describe this type of vinyl radical has been coined by Crich; see: Crich, D.; Fortt, S. M. *Tetrahedron Lett.* **1987**, *27*, 2895. Intramolecular vinyl radical cyclizations have been demonstrated by many. For some pertinent examples, see: Julia, M. *Acc. Chem. Res.* **1971**, *4*, 1971. Stork, G.; Baine, N. H. *J. Am. Chem. Soc.* **1982**, *104*, 2321. Beckwith, A. L. J.; O'Shea, D. M. *Tetrahedron Lett.* **1986**, *27*, 4525. Curran, D. P.; Rakiewicz, D. M. *J. Am. Chem. Soc.* **1985**, *107*, 1448. Curran, D. P.; Kuo, S.-C. *Ibid.* **1986**, *108*, 1106. Stork, G.; Mook, R., Jr. *Ibid.* **1987**, *109*, 2829: Munt, S. P.; Thomas, E. J. *J. Chem. Soc., Chem. Commun.* **1989**, 480.

(7) It was not prudent to determine the isolated yield of **2** in this work. The bromo[3]cumulene **2** readily decomposed when concentrated. Ease and expediency were best served when **2** was kept unpurified in solution. The yield of **3**, however, from **1** was 57%. Cyclization of **3** to **4** occurred in 85% isolated yield, thus giving a combined total of 48% from **1**.

(8) The cyclopentene **4** was also prepared in 44% overall yield from **1** via syringe pump addition of *n*-Bu_3SnH plus 5 mol % AIBN to **2** (0.2 mmol/min).

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