described for 11a was employed with 50 mg (0.17 mmol) of alcohol 4e, 90 mg (0.34 mmol) of Ph_3P, 32 mg (0.34 mmol) of chloroacetic acid, and 54 μL (0.34 mmol) of DEAD affording 54 mg (86%) of ester 11e: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.32-7.18 (m, aryl H's), 6.23 (d, J = 6.2 Hz, H1), 5.75-5.51 (m, H3 and H4), 3.97 (d, J = 2.2 Hz, CH_2Cl), 3.55 (dd, J = 14.6, 8.3 Hz, H2), 1.65 (d, J = 7.2 Hz, H5), 0.73 (s, $SiC(CH_3)_3$), -0.06 (d, J = 29.0 Hz, $Si(CH_3)_2$); HRMS (EI$^+$) calcd for $C_{15}H_{20}{}^{35}ClO_3Si$ (M - t-Bu) 311.0870, found 311.0874.

Acknowledgment. This research was supported by grants (R01-AI31422 and R01-GM29475) from the National Institute for Allergy and Infectious Diseases and the National Institute of General Medical Sciences. G.S.W. is grateful to the ACS Division of Organic Chemistry and Glaxo, Inc., for a graduate fellowship (1991-1992). We thank Molecular Design, Ltd., for the use of their reaction databases.

Supplementary Material Available: Representative ^{1}H NMR spectra (16 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

Free-Radical Ring Expansion of Fused Cyclobutanones: Stereospecific Construction of 5,7-, 6,7-, 7,7-, 8,7-, and 5,8-Cis-Fused Bicyclic Systems[1]

Paul Dowd* and Wei Zhang

Department of Chemistry, University of Pittsburgh, Pittsburgh, Pennsylvania 15260

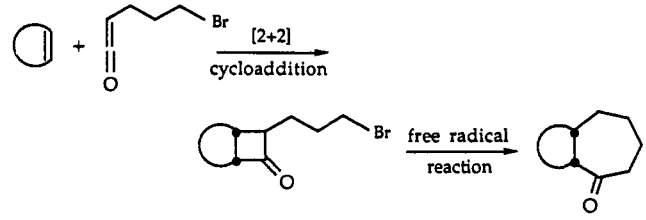
Received August 31, 1992

A new method of appending seven- and eight-membered rings to cycloalkenes is described. Treatment of selected alkene precursors with an ω-bromoalkyl ketene or a keteniminium salt leads to haloalkyl cyclobutanone formation. Tri-*n*-butyltin hydride promoted ring expansion then yields the annulated product. Since the initial cyclobutanone is cis fused, the final product is also produced stereospecifically with a cis ring fusion.

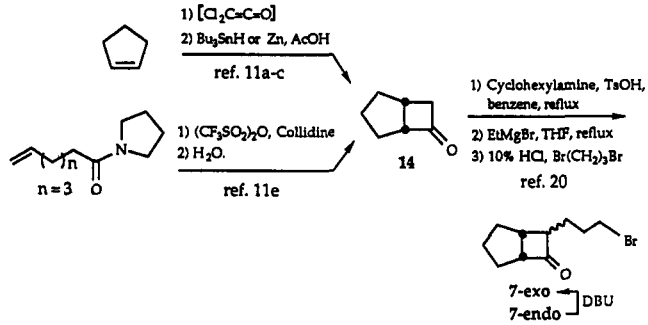
Introduction

Development of methods for the synthesis of carbocyclic molecules containing fused seven- and eight-membered rings[2,3] is currently an area of active investigation. Such carbon skeletons form the basic structures of many biologically active natural products.[4] During a study of the free-radical reactions of cyclobutanones,[5] we discovered a free-radical-based[6] ring expansion[7,8] reaction which

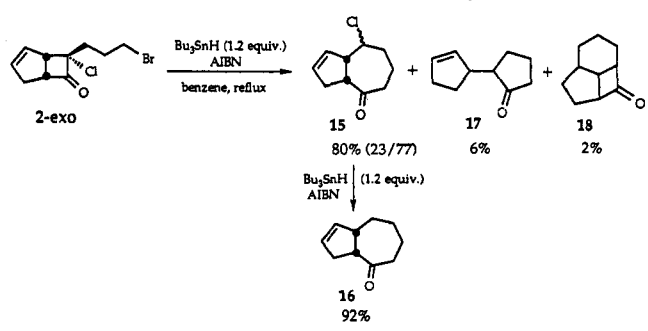
Scheme I. [2 + 2] Cycloaddition and Subsequent Ring Expansion



Scheme II. Preparation and Subsequent Alkylation of 17



Scheme III. Free-Radical Reaction of Cyclobutanone



(1) Preliminary communication: Dowd, P.; Zhang, W. *J. Am. Chem. Soc.* **1991**, *113*, 9875.

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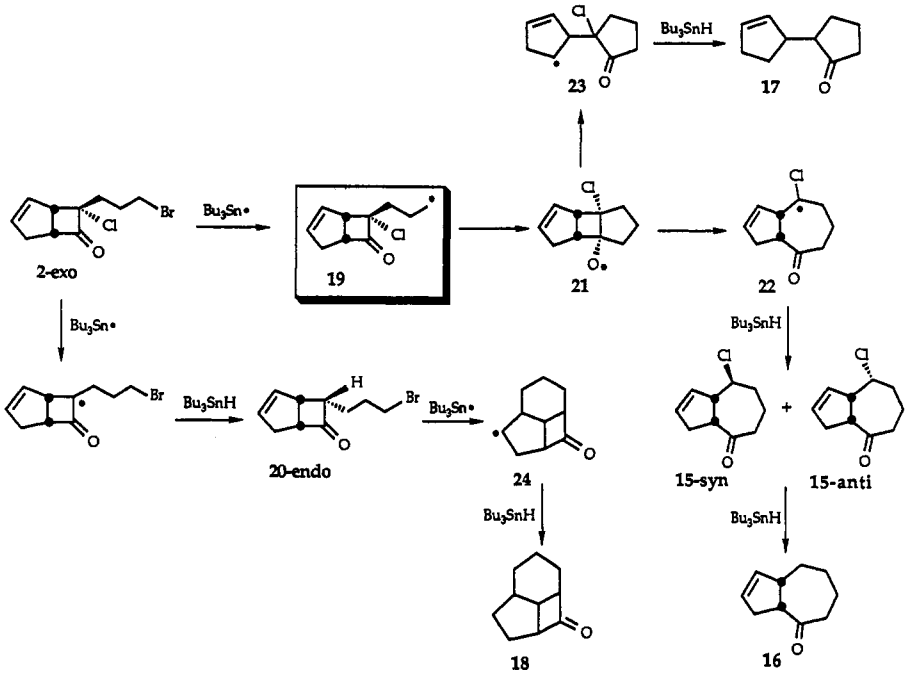
0022-3263/92/1957-7163$03.00/0

Scheme IV. Mechanism for the Free-Radical Reaction of 2-exo



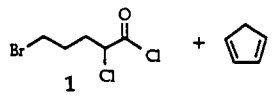
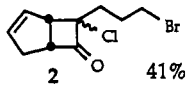
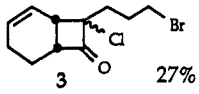
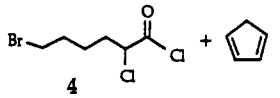
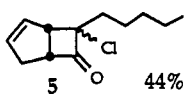
generates fused seven- and eight-membered rings in stereospecific fashion.

The procedure is straightforward. First, an ω-bromoalkyl ketene is generated in the presence of an alkene to form a haloalkyl cyclobutanone. Free-radical reaction of the cyclobutanone then yields the ring-expanded annulation product (Scheme I). The reaction sequence leading to the ring fusion is stereospecific; the cis stereochemistry is enforced by the requirements of the cyclobutanone ring and, once established, is then translated to the ring-expansion product.

Results and Discussion

Preparation of Haloalkyl Cyclobutanones. Cyclobutanones can be prepared by [2 + 2] intermolecular cycloaddition of stabilized ketenes to active alkenes. The ketene cycloaddition[9,10] has been suggested to be a concerted reaction, yielding as the major adduct that with the larger group in the endo position. In our experiments, mixtures of endo and exo side chain adducts were obtained (Table I).

Table I. Ketene–Cyclic Diene Cycloaddition[a]

starting materials	product, yield, and ratio (exo/endo)
	 41% (42/58)
	 27% (51/49)
	 44% (33/67)

[a] 1.8 equiv of Et_3N, CH_2Cl_2, 25 °C.

Cycloaddition of keteniminium salts[9a,b] with alkenes[11] provides an alternative method for preparing cyclobutanones. Keteniminium salts are more electrophilic than ketenes, and they react with unactivated alkenes. Examples in Table II show that cycloadditions of keteniminium salts usually give higher ratios of exo to endo diastereomers than those of ketenes.

Either cycloaddition of dichloroketene to cyclopentene, followed by tin hydride reduction or intramolecular cycloaddition of the keteniminium salt can be used to prepare the fused cyclobutanone 14 (Scheme II). Formation

(4) Examples include: *5,7-fused* ring compounds 9-*epi*-dictyol B,[2a] daucene,[2b] aphanamol I,[2b] dolatriol,[2b] bulnesol,[2c] guaiol,[2c] reiswigin A,[2d] tanzanene;[2e] *5,8-fused* ring compounds precapnelladiene,[2f] epoxydictynene,[2g] ophiobolin C,[2h-i] dectylol,[2c] poitediol;[2c] *6,7-fused* ring compounds α-himachalene,[2c] perforenone,[2c] widdrol;[2c] and *6,8-fused* ring compound taxol.[2j-l]

(5) Zhang, W.; Dowd, P. Unpublished results.

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(7) For reviews on ring expansion, see: (a) Hesse, H. *Ring Enlargement in Organic Chemistry*; VCH: Weinheim, 1991. (b) Stach, H.; Hesse, M. *Tetrahedron* **1988**, *44*, 1573.

(8) (a) Zhang, W.; Dowd, P. *Tetrahedron Lett.* **1992**, 3285. (b) Dowd, P.; Choi, S.-C. *Tetrahedron* **1991**, *47*, 4847. (c) Dowd, P.; Choi, S.-C. *Tetrahedron* **1989**, *45*, 77. (d) Dowd, P.; Choi, S.-C. *J. Am. Chem. Soc.* **1987**, *109*, 6548. (e) Bowman, W. R.; Westlake, P. J. *Tetrahedron* **1992**, *48*, 4027. See also refs 3c, 3i, 3k, 3l, 3p, and 3q.

(9) For general reviews on ketene cycloadditions, see: (a) Snider, B. B. *Chemtracts—Org. Chem.* **1991**, *4*, 403. (b) Carruthers, W. In *Cycloaddition Reactions in Organic Synthesis*; Pergamon: Oxford, 1990; pp 332–369. (c) Snider, B. B. *Chem. Rev.* **1988**, *88*, 793. (d) Ghosez, L.; O'Donnell, M. J. *Pericyclic Reactions*; Marchand, A. P., Lehr, R. E., Eds.; Academic: New York, 1977; Vol. II, pp 79–140. (e) Brady, W. T. In *The Chemistry of Ketenes, Allenes and Related Compounds*; Patai, S., Eds.; Interscience: New York, 1980; pp 278–308.

(10) For regio- and stereoselectivities of ketene–alkene cycloadditions, see: (a) Wang, X.; Houk, K. N. *J. Am. Chem. Soc.* **1990**, *112*, 1754. (b) Valenti, E.; Pericas, M. A.; Moyano, A. *J. Org. Chem.* **1990**, *55*, 3582. (c) Bernardi, F.; Bottoni, A.; Robb, M. A.; Venturini, A. *J. Am. Chem. Soc.* **1990**, *112*, 2106. (d) Tidwell, T. T. *Acc. Chem. Res.* **1990**, *23*, 273.

(11) Cycloaddition of dichloroketenes to olefins, see: (a) Mehta, G.; Rao, H. S. P. *Synthetic Commun.* **1985**, *15*, 991. (b) Brady, W. T. *Tetrahedron* **1981**, *37*, 2949. (c) Ghosez, L.; Montaigne, R.; Roussel, A.; Vanlierde, H.; Mollet, P. *Tetrahedron* **1971**, *27*, 615. (d) Brady, W. T.; Roe, R., Jr. *J. Am. Chem. Soc.* **1971**, *93*, 1662. Intramolecular cycloaddition of keteniminiums to olefins, see: (e) Marko, I.; Ronsmans, B.; Hesbain-Frisque, A.-M.; Dumas, S.; Ghosez, L. *J. Am. Chem. Soc.* **1985**, *107*, 2192. (f) L. Gobeaux, B.; Ghosez, L. *Heterocycles* **1989**, *28*, 29.

Scheme V. 1,5-H Transfer of 12-exo

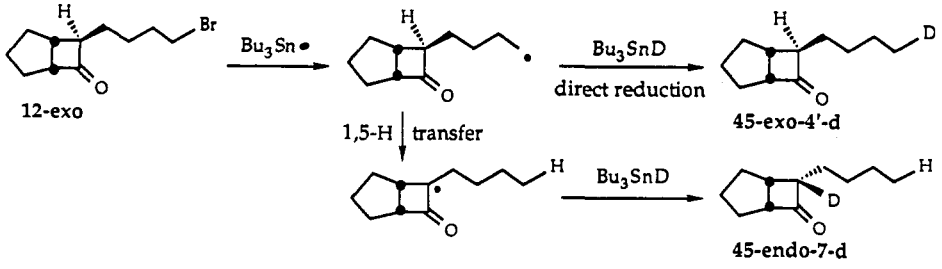
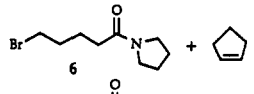
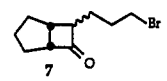
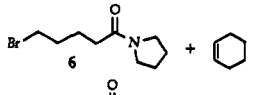
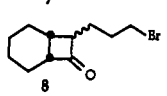
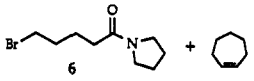
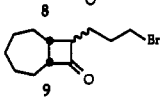
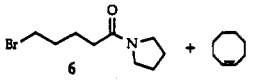
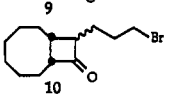
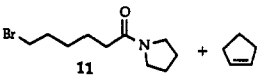
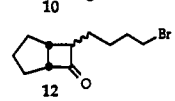
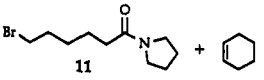
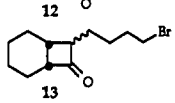


Table II. Keteniminium Salt–Cyclic Alkene Cycloaddition[a]

starting materials	product, yield, and ratio (exo/endo)
	 53% (76/24)
	 26% (73/27)
	 37% (71/29)
	 22% (58/42)
	 62% (73/27)
	 72% (72/28)

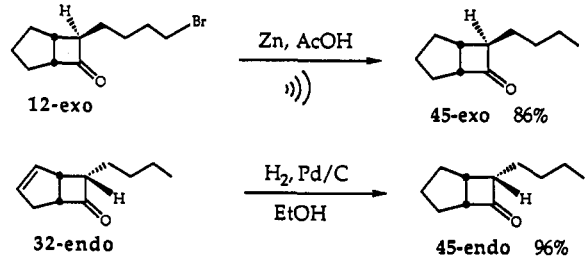
[a] 1.5 equiv of $(CF_3SO_2)_2O$, 1.1 equiv of collidine, CH_2ClCH_2Cl, 25 °C; hydrolyzed with CCl_4/H_2O, reflux. Reactions not optimized.

of the imine and subsequent alkylation afforded **7** (49%) as a 60:40 mixture of exo and endo diastereomers. The **7-exo** isomer can be recovered from the **7-endo** isomer by treatment of **7-endo** with a 5 M ether solution of DBU to form a 2:1 mixture of **7-exo** and **7-endo**.

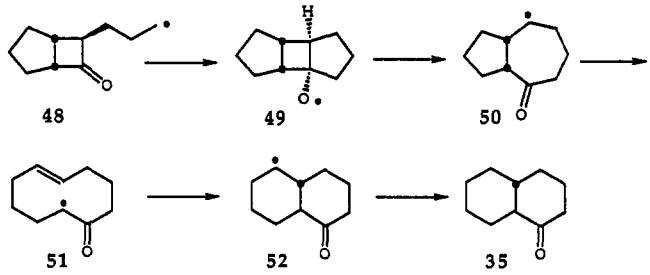
Free-Radical Reaction of Fused Cyclobutanones. The exo cycloadducts undergo smooth free-radical ring expansion. In a typical example (Scheme III) the exo adduct **2-exo** was treated by slow addition with 1.2 equiv of tri-*n*-butyltin hydride and a catalytic amount of AIBN in refluxing benzene. Ring annulation leading to the chlorine-bearing ring-expansion product **15** (80%) was the major reaction course. Minor amounts of the alternative ring opening product **17** and the product **18** of cyclization to the carbon–carbon double bonds were also formed. None of the direct reduction product was observed. The chloro ketone **15** was then treated with 1.2 equiv of tri-*n*-butyltin hydride to give reduction product **16** (92%).

In designing this sequence, we anticipated that the initial primary radical in **19** would attack the four-membered ketone[12] to give the alkoxyl radical[13] **21** (Scheme IV). The

Scheme VI. Synthesis of Authentic Samples of 45-exo and 45-endo



Scheme VII



latter can then open in either of two ways (to **22** or **23**) to yield the ring-expanded annulation product **15** accompanied by the minor product **17** of ring attachment. In order to form the tricyclic ketone **18**, prior reduction of the cyclobutyl chloride must occur with inversion at carbon, as the hydrogen atom from tin hydride is delivered from the least hindered face.

Table III summarizes the results of other examples and demonstrates that in every instance ring expansion is the major pathway in the sequence. A substantial driving force is provided by the relief of strain in the four-membered rings.

Annulation to cycloheptene (Table III, entry 6) and to cyclooctene (entry 7) offer attractive extensions of the method.

Entry 3 shows that four-carbon annulation of eight-membered rings is also possible following this strategy. The chloro substituent is required in this sequence to forestall internal hydrogen abstraction. Thus, free-radical reaction of **12-exo** (Table IV) suffered from a 1,5-hydrogen transfer reaction that precluded ring expansion. With relatively high concentrations of tri-*n*-butyltin hydride (19 mM), the ratio of 1,5-hydrogen transfer product, **45-endo**, to direct reduction product, **45-exo**, is 64:36. Slow addition will favor the former, and under these conditions tri-*n*-butyltin deuteride leads to a 91:9 ratio of **45-endo-*7-d*** to **45-exo-*4'-d*** (Scheme V). Authentic samples of **45-exo** and **45-endo** were prepared as shown in Scheme VI.

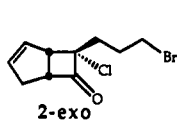
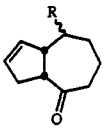
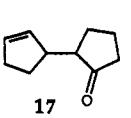
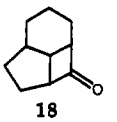
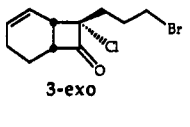
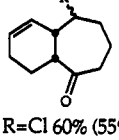
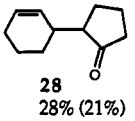
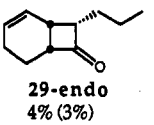
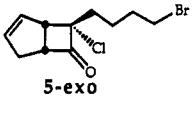
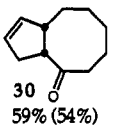
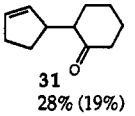
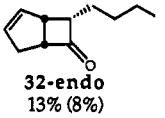
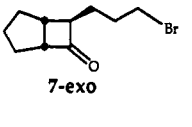
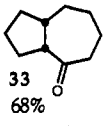
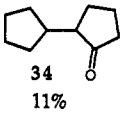
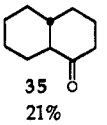
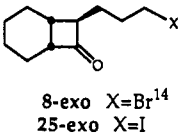
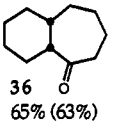
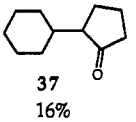
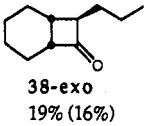
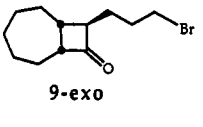
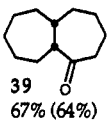
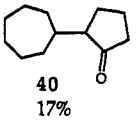
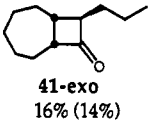
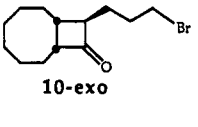
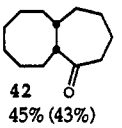
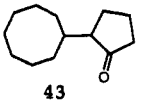
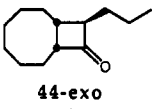
The outcome of ring annulation can be quite sensitive to the reaction conditions. Thus, if bromide **9-exo** (Table V) is irradiated at 350-nm with tributyltin hydride (7.5M), reduction to **47** (57%) is the major reaction path (Table V, entry 1). By contrast, if the bromide **9-exo** is heated

(12) For intramolecular addition of alkyl radicals to carbonyl groups, see: (a) Walton, R.; Fraser-Reid, B. *J. Am. Chem. Soc.* **1991**, *113*, 5791. (b) Beckwith, A. L. J.; Hay, B. P. *J. Am. Chem. Soc.* **1989**, *111*, 2674. (c) Beckwith, A. L. J.; Hay, B. P. *J. Am. Chem. Soc.* **1989**, *111*, 230. (d) Tsang, R.; Dickson, J. K., Jr.; Pak, H.; Walton, R.; Fraser-Reid, B. *J. Am. Chem. Soc.* **1987**, *109*, 3484.

(13) For β-scission of alkoxy radicals, see: (a) Suginome, H.; Senboku, H.; Yamada, S. *Tetrahedron Lett.* **1988**, *29*, 79. (b) O'Dell, D. E.; Loper, J. T.; MacDonald, T. L. *J. Org. Chem.* **1988**, *53*, 5125. (c) MacDonald, T. L.; O'Dell, D. E. *J. Org. Chem.* **1981**, *46*, 1501. (d) Beckwith, A. L. J.; Kazlauskas, R.; Syner-Lyons, M. R. *J. Org. Chem.* **1983**, *48*, 4718. See also ref 3i.

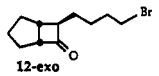
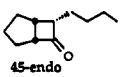
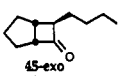
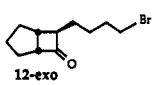
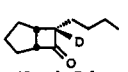
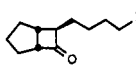
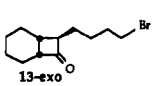
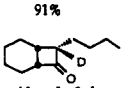
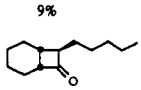
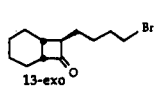
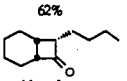
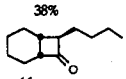
(14) Based on the finding of Porter et al. (Porter, N. A.; Magnin, D. R.; Wright, B. T. *J. Am. Chem. Soc.* **1986**, *108*, 2787) that alkyl iodides often give significantly better yields as a consequence of improved chain transfer. In this case, the iodide afforded the same yield as the bromide.

Table III. Free-Radical Ring Expansion of Haloalkyl Cyclobutanones

entry	starting material	condns[a]	products and yields[b]		
1	 2-exo	A	 15 R=Cl 87% (80%)	 17 11% (6%)	 18 2% (2%)
		B	16 R=H 74%	18%	8%
2	 3-exo			 28	 29-endo
		A	26 R=Cl 60% (55%)	28% (21%)	4% (3%)
		B	27 R=H 55%	23%	14%
3	 5-exo	B	 30 59% (54%)	 31 28% (19%)	 32-endo 13% (8%)
4	 7-exo	C	 33 68%	 34 11%	 35 21%
5	 8-exo X=Br[14] 25-exo X=I	A	 36 65% (63%) 68%	 37 16% 15%	 38-exo 19% (16%) 17%
6	 9-exo	A	 39 67% (64%)	 40 17%	 41-exo 16% (14%)
7	 10-exo	A	 42 45% (43%)	 43 32%	 44-exo 9% (7%)

[a] A. 1.2–1.5 equiv of Bn_3SnH with AIBN, 4–7 h slow addition to refluxing benzene solution. B. 2.0–3.3 equiv of Bu_3SnH with AIBN, 7–10 h slow addition to refluxing benzene solution. C. 1.5 equiv of Bu_3SnH (7.5 mM), AIBN, benzene, reflux. [b] Yields refer to normalization on GC. Figures in parentheses are isolated yields after flash chromatography.

Table IV. Free-Radical Reaction of 12-exo and 13-exo[a]

starting material	condns	products and relative yields: 1,5-H transfer	products and relative yields: direct reduction
 12-exo	Bu_3SnH (19 mM), $h\nu$, 350-nm, 25 °C	 45-endo 64%	 45-exo 36%
 12-exo	Bu_3SnD, slow addition, 80 °C	 45-endo-7-d 91%	 45-exo-4'-d 9%
 13-exo	Bu_3SnD (25 mM), $h\nu$, 350-nm, 25 °C	 46-endo-8-d 62%	 46-exo-4'-d 38%
 13-exo	Bu_3SnH, slow addition, 80 °C	 46-endo 96%	 46-exo 4%

[a] Free-radical initiator: AIBN. Solvent: benzene.

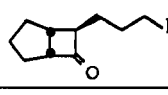
with the same concentration of tributyltin hydride (7.5 mM), ring annulation yielding **33** is the main reaction course (68%) (entry 3). If the reaction is carried out under conditions of slow addition of tributyltin hydride, *trans*-α-decalone **35** becomes the major product (65%) (entry 5). We suggest that the reaction leading to *trans*-α-decalone

Scheme VIII. Free-Radical Reaction of Unsaturated *endo*-Bromide

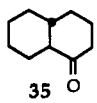
35 proceeds through the radical intermediates shown in Scheme VII. Thus, the initial primary radical **48** adds to the cyclobutanone carbonyl group yielding the reactive alkoxyl radical **49**. Ring opening leads to the fused bicyclo[5.3.0]decanone radical **50** which can then revert to the cyclodecenone acyl-substituted radical[15] **51**. Ring closure

(15) For acyl-substituted radicals, see: (a) Curran, D. P.; Morgan, T. M.; Schwartz, C. E.; Snider, B. B.; Dombrowski, M. *J. Am. Chem. Soc.* **1991**, *113*, 6607. (b) Broeker, J. L.; Houk, K. N. *J. Org. Chem.* **1991**, *56*, 3651. (c) Curran, D. P.; Chang, C.-T. *J. Org. Chem.* **1989**, *54*, 3140. (d) Porter, N. A.; Chang, V. H.-T.; Magnin, D. R.; Wright, B. T. *J. Am. Chem. Soc.* **1988**, *110*, 3554. (e) Clive, D. L. J.; Cheshire, D. R. *J. Chem. Soc., Chem. Commun.* **1987**, 1510.

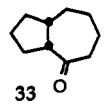
Table V. Free-Radical Reaction of 9-exo[a]



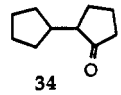
9-exo



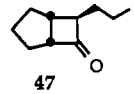
35



33



34



47

Entry	Bu_3SnH (1.5 equiv.)	Temp./°C	Time/h	35	33	34	47
1	7.5 mM, hν, 350-nm	25	0.5	n.d.	31%	12%	57%
2	9.8 mM, Δ	80	6	5%	61%	8%	26%
3	7.5 mM, Δ	80	9	21%	68%	11%	n.d.
4	5.0 mM, Δ	80	9	29%	66%	5%	n.d.
5	slow addition Δ	80	9	65%	23%	12%	n.d.

[a] Free-radical initiator: AIBN. Solvent: benzene. Relative yields on GC. n.d. indicates none detected.

in the alternative sense to **52** is then followed by hydrogen atom chain transfer yielding *trans*-α-decalone **35**.[16]

Unlike the *exo*-bromides, which undergo smooth ring expansion, the saturated *endo*-bromides are prone to undergo direct reduction as a consequence of steric hindrance to ring closure.[17] Unsaturated *endo*-bromides undergo cyclization to double bonds to form tricyclic products (Scheme VIII). Tricyclic product **18**, generated as a major product from **2-endo**, is the same as that generated as a byproduct from **2-exo** (Scheme III).

Conclusion

We have discovered a new stereospecific means of appending five and six carbons to cyclic alkenes, leading to bicyclic products carrying useful levels of functionality. In principle, wherever a compound has a carbon–carbon double bond, a haloalkyl cyclobutanone can be generated by [2 + 2] cycloaddition. Free-radical reaction of the cyclobutanone then leads to the formation of the cis-fused ring-expansion product. The intensively studied [2 + 2] cycloadditions[9-11] provide a broad field in which to develop this new synthetic method.

Experimental Section

Materials and Methods. All reactions were performed under a nitrogen atmosphere. THF, benzene, and diethyl ether were distilled from Na/benzophenone. CH_2Cl_2, CH_2ClCH_2Cl, and Et_3N were distilled from CaH_2. Pyrrolidine, cyclohexylamine, and collidine were distilled from Na and stored over molecular sieves. $(CF_3SO_2)_2O$ was freshly distilled prior to use. Cyclopentadiene was obtained from the distillation of dicyclopentadiene and stored in an ultracold refrigerator at −70 °C.

^1H and ^{13}C NMR spectra were obtained on FT-Bruker WH-300, AF-300, and AM-500 Aspect-300 spectrometers (300 MHz for ^1H NMR, 75 MHz for ^{13}C NMR). *J* values are given in Hz. Infrared (IR) spectra were obtained on an IBM IR/32 FTIR spectrometer. Gas chromatography and low-resolution mass spectra (GC–MS) were obtained using a Hewlett-Packard 5890 series II gas chromatograph equipped with a Hewlett-Packard 5970 series mass spectrometer. The GC column was a 12-m × 0.2-mm i.d. × 0.33-μm film thickness fused silica capillary column coated with 100% dimethyl polysiloxane (HP-1, Hewlett-Packard). Injection was made into the injection port at 250 °C while the column was maintained at 120 °C. After 2 min the column oven was heated to its final temperature of 250 °C with a heating rate of about 15 °C/min. The detector was set at 280 °C. Oxygen-free helium was used as a carrier gas (inlet pressure 7 psi and flow rate 55 mL/min). The ratios of isomers and the relative yields were determined on the GC. High-resolution mass spectra were obtained on a Varian MAT CH-5DF spectrometer.

α-Chloro acid chlorides **1** and **4** were prepared in 94% and 98% yields by the method of Harpp et al.[18] from the acid chlorides. Amides **6** and **11** were prepared in 97% and 99% yields by a standard amidation procedure[19] from the acid chlorides. Bicyclo[3.2.0]heptan-6-one **14** was prepared in 91% yield by intramolecular [2 + 2] cycloaddition.[11e]

General Procedure for Intermolecular Cycloaddition of Ketenes to Cyclic Dienes.[11d] **7-Chloro-7-(3′-bromopropyl)bicyclo[3.2.0]hept-2-en-6-one (2).** A solution of α-chloro acid chloride **1** (3.47 g, 16 mmol) in CH_2Cl_2 (10 mL) was added to a solution of Et_3N (4.0 mL, 29 mmol) and cyclopentadiene (5.0 g, 76 mmol) in CH_2Cl_2 (15 mL) at 25 °C over 1 h. The reaction mixture was stirred at 25 °C for 3 h after the addition was complete. After the solvent was removed, the residual oil was extracted with ether (3 × 15 mL). The combined ether layers were washed with H_2O and saturated NH_4Cl solution and dried over $MgSO_4$. Evaporation of the solvent gave **2** as a 42:58 mixture of exo and endo diastereomers. The crude product was purified by flash chromatography on silica gel (elution with 20:1 hexanes–ether) to give *exo*-bromide **2-exo** (0.70 g, 17%) and *endo*-bromide **2-endo** (1.01 g, 25%).

Data for *exo*-bromide **2-exo**: ^1H NMR ($CDCl_3$) δ 2.05–2.25 (4 H), 2.53 (m, 1 H), 2.77 (m, 1 H), 3.46 (m, 2 H), 3.64 (m, 1 H), 3.96 (td, *J* = 8.3 and 0.9, 1 H), 5.76 (m, 1 H), 5.93 (m, 1 H); ^{13}C NMR ($CDCl_3$) δ 27.6 (t, *J* = 131), 32.9 (t, *J* = 127), 35.1 (t, *J* = 133), 36.0 (t, *J* = 131), 51.9 (d, *J* = 150), 57.3 (d, *J* = 145), 82.0 (s), 129.3 (d, *J* = 169), 134.6 (d, *J* = 159), 206.4 (s); IR (neat) 1786 (vs, C=O) cm^{-1}; MS *m/e* (rel intensity) 262 (1, M^+), 229 and 227 (5, M^+ – Cl), 201 and 199 (14), 155 (9), 119 (25), 91 (100), 66 (91, $M^+ - C_5H_6BrClO$); HRMS calcd for $C_{10}H_{12}{}^{79}Br^{35}ClO$ 261.9760, found 261.9760.

Data for *endo*-bromide **2-endo**: ^1H NMR ($CDCl_3$) δ 1.90–2.10 (3 H), 2.27 (m, 1 H), 2.49 (m, 1 H), 2.73 (m, 1 H), 3.35–3.55 (m, 2 H), 3.68 (m, 1 H), 4.28 (td, *J* = 8.5 and 1.3, 1 H), 5.79 (m, 1 H), 6.03 (m, 1 H); ^{13}C NMR ($CDCl_3$) δ 27.2 (t, *J* = 131), 30.1 (t, *J* = 127), 33.1 (t, *J* = 151), 33.9 (t, *J* = 133), 54.4 (d, *J* = 153), 59.2 (d, *J* = 144), 82.6 (s), 127.8 (d, *J* = 167), 136.8 (d, *J* = 155), 206.0 (s); IR (neat) 1790 (vs, C=O) cm^{-1}; MS *m/e* (rel intensity) 262 (<1, M^+), 229 and 227 (2, M^+ – Cl), 201 and 199 (13), 155 (8), 119 (17), 91 (100), 66 (94, $M^+ - C_5H_6BrClO$); HRMS calcd for $C_{10}H_{12}{}^{79}Br^{35}ClO$ 261.9760, found 261.9760.

8-Chloro-8-(3′-bromopropyl)bicyclo[4.2.0]oct-2-en-7-one (3). Following the general procedure above, treatment of α-chloro acid

(16) For formation of **33** and **35** via transannular reaction of carbonium ions in medium-size rings, see: (a) Hannack, M.; Harding, C. E.; Derocque, J.-L. *Chem. Ber.* **1972**, *105*, 421. (b) Rao, B.; Weiler, L. *Tetrahedron Lett.* **1971**, 927. (c) Balf, R. J.; Rao, B.; Weiler, L. *Can. J. Chem.* **1971**, *49*, 3135.

(17) For analogous cases, see: Cossy, J.; Belotti, D.; Pete, J. P. *Tetrahedron Lett.* **1979**, *28*, 4889. See also: Ribar, D. P. Thesis, University of Pittsburgh, 1990.

(18) Harpp, D. N.; Bao, L. Q.; Black, C. J.; Gleason, J. G.; Smith, R. A. *J. Org. Chem.* **1975**, *40*, 3420.

(19) Stevens, R. V.; Beaulieu, N.; Chan, W. H.; Daiewski, A. R.; Takeda, T.; Waldner, A.; Williard, P. G.; Zutter, U. *J. Am. Chem. Soc.* **1986**, *108*, 1039.

chloride 1 (11.7 g, 50 mmol) with 1,3-cyclohexadiene (19 mL, 200 mmol) and Et_3N (12.5 mL, 90 mmol) in CH_2Cl_2 at 25 °C afforded **3** as a 51:49 mixture of exo and endo diastereomers. Flash chromatography (30:1 hexanes-ether) of the crude product gave *exo*-bromide **3-exo** (1.8 g, 13%) and *endo*-bromide **3-endo** (1.9 g, 14%).

Data for *exo*-bromide **3-exo**: ^1H NMR ($CDCl_3$) δ 1.59 (m, 1 H), 1.95–2.25 (m, 7 H), 3.01 (m, 1 H), 3.46 (m, 2 H), 3.75 (m, 1 H), 5.78 (m, 1 H), 6.03 (m, 1 H); ^{13}C NMR ($CDCl_3$) δ 18.7 (t, J = 131), 20.6 (t, J = 133), 27.7 (t, J = 132), 33.0 (t, J = 148), 36.3 (d, J = 174), 36.8 (t, J = 130), 52.2 (d, J = 127), 79.6 (s), 124.1 (d, J = 164), 130.1 (d, J = 160), 206.0 (s); IR (neat) 1784 (vs, C=O) cm^{-1}; MS m/e (rel intensity) 276 (2, M^+), 243 and 241 (4, M^+ – Cl), 169 (1), 105 (19), 80 (31, $M^+ - C_5H_6BrClO$), 55 (100); HRMS calcd for $C_{11}H_{14}{}^{79}Br^{35}ClO$ 275.9917, found 275.9919.

Data for *endo*-bromide **3-endo**: ^1H NMR ($CDCl_3$) δ 1.55 (m, 1 H), 1.90–2.35 (m, 7 H), 3.15 (m, 1 H), 3.42 (m, 2 H), 4.16 (m, 1 H), 5.91 (m, 1 H), 6.07 (m, 1 H); ^{13}C NMR ($CDCl_3$) δ 18.7 (t, J = 130), 21.3 (t, J = 128), 27.7 (t, J = 132), 31.0 (t, J = 127), 33.3 (t, J = 151), 40.3 (t, J = 149), 54.4 (d, J = 137), 80.8 (s), 123.6 (d, J = 161), 132.5 (d, J = 171), 205.3 (s); IR (neat) 1784 (vs, C=O) cm^{-1}; MS m/e (rel intensity) 278 and 276 (4, M^+), 169 (3), 105 (21), 80 (51, $M^+ - C_5H_6BrClO$), 55 (100); HRMS calcd for $C_{11}H_{14}{}^{79}Br^{35}ClO$ 275.9917, found 275.9857.

7-Chloro-7-(4′-bromobutyl)bicyclo[3.2.0]hept-2-en-6-one (5). Following the general procedure above, treatment of α-chloro acid chloride **2** (3.56 g, 14.4 mmol) with cyclopentadiene (5.6 g, 85 mmol) and Et_3N (4.2 mL, 30 mmol) in CH_2Cl_2 at 25 °C afforded **5** as a 33:67 mixture of exo and endo diastereomers. Flash chromatography (30:1 hexanes–ether) of the crude product gave *exo*-bromide **5-exo** (0.538 g, 14%) and *endo*-bromide **5-endo** (1.21 g, 30%).

Data for *exo*-bromide **5-exo**: ^1H NMR ($CDCl_3$) δ 1.70 (m, 2 H), 1.91 (m, 2 H), 2.04 (t, J = 8.4, 2 H), 2.51 (m, 1 H), 2.76 (m, 1 H), 3.41 (t, J = 6.6, 2 H), 3.63 (m, 1 H), 3.90 (t, J = 8.2, 1 H), 5.77 (m, 1 H), 5.93 (m, 1 H); ^{13}C NMR ($CDCl_3$) δ 23.3 (t, J = 120), 32.2 (t, J = 126), 33.1 (t, J = 157), 35.4 (t, J = 132), 36.9 (t, J = 126), 51.9 (d, J = 146), 57.5 (d, J = 144), 82.7 (s), 129.6 (d, J = 169), 134.7 (d, J = 165), 207.2 (s); IR (neat) 1788 (vs, C=O) cm^{-1}; MS m/e (rel intensity) 276 (<1, M^+), 243 and 241 (3, M^+ – Cl), 215 and 213 (7), 197 (1, M^+ – Br), 135 (17), 91 (97), 66 (100, $M^+ - C_6H_8BrClO$); HRMS calcd for $C_{11}H_{14}{}^{79}Br^{35}ClO$ 275.9917, found 275.9917.

Data for *endo*-bromide **5-endo**: ^1H NMR ($CDCl_3$) δ 1.50–2.00 (m, 6 H), 2.48 (m, 1 H), 2.71 (m, 1 H), 3.41 (t, J = 6.6, 2 H), 3.69 (m, 1 H), 4.27 (td, J = 8.5 and 1.2, 1 H), 5.78 (m, 1 H), 6.01 (m, 1 H); ^{13}C NMR ($CDCl_3$) δ 22.5, 30.4, 32.4, 33.3, 34.1, 54.5, 59.2, 83.4, 128.2, 136.9, 206.8; IR (neat) 1788 (vs, C=O) cm^{-1}; MS m/e (rel intensity) 276 (<1, M^+), 243 and 241 (2, M^+ – Cl), 215 and 213 (11), 197 (2, M^+ – Br), 135 (15), 91 (91), 66 (100, $M^+ - C_6H_8BrClO$); HRMS calcd for $C_{11}H_{14}{}^{79}Br^{35}ClO$ 275.9917, found 275.9882.

General Procedure for Intermolecular Cycloaddition of Keteniminium Salts to Cyclic Alkenes. 7-(3′-Bromopropyl)bicyclo[3.2.0]heptan-6-one (7). Following the method established by Ghosez,[11f] a solution of amide **6** (0.468 g, 2.0 mmol) in CH_2ClCH_2Cl (20 mL) was added over 20 min to a solution of triflic anhydride (0.42 mL, 3.0 mmol) and cyclopentene (1.48 mL, 20 mmol) in CH_2ClCH_2Cl (20 mL) at 25 °C. A solution of collidine (0.26 mL, 2.2 mmol) in CH_2ClCH_2Cl (20 mL) was then added over 20 min to the reaction mixture. After the addition was completed, the mixture was stirred at 25 °C for 6 h. The solvent was removed under vacuum, and the residue was hydrolyzed in a two-phase system of H_2O (20 mL) and CCl_4 (20 mL) at reflux for 6 h. The reaction mixture was decanted, and the aqueous layer was extracted with CCl_4 (3 × 10 mL). The organic layers were washed with H_2O and brine and dried over $MgSO_4$. Evaporation of the solvent gave **7** as a 76:24 mixture of exo and endo diastereomers. The crude product was purified by flash chromatography on silica gel (elution with 40:1 hexanes–ether) to give *exo*-bromide **7-exo** (182 mg, 39%) and *endo*-bromide **7-endo** (63 mg, 14%).

Data for *exo*-bromide **7-exo**: ^1H NMR ($CDCl_3$) δ 1.55–2.05 (m, 10 H), 2.54 (m, 1 H), 2.58 (m, 1 H), 3.40 (m, 2 H), 3.49 (m, 1 H); ^{13}C NMR ($CDCl_3$) δ 25.1 (t, J = 133), 28.1 (t, J = 125), 29.3 (t, J = 136), 30.2 (t, J = 128), 32.7 (t, J = 129), 33.2 (t, J = 151), 36.3 (d, J = 151), 61.7 (d, J = 142), 62.8 (d, J = 132), 216.3 (s); IR (neat) 1770 (vs, C=O) cm^{-1}; MS m/e (rel intensity) 232 and 230 (1, M^+), 164 and 162 (31), 151 (3, M^+ – Br), 95 (14), 83 (64), 67 (54), 55 (100); HRMS calcd for $C_{10}H_{15}{}^{79}BrO$ 230.0306, found 230.0306.

Data for *endo*-bromide **7-endo**: ^1H NMR ($CDCl_3$) δ 1.35–2.10 (m, 10 H), 2.97 (q, J = 7.9, 1 H), 3.26 (m, 1 H), 3.41 (m, 2 H), 3.58 (m, 1 H); IR (neat) 1770 (vs, C=O) cm^{-1}; MS m/e (rel intensity) 232 and 230 (2, M^+), 164 and 162 (33), 151 (2, M^+ – Br), 95 (18), 83 (70), 67 (58), 55 (100); HRMS calcd for $C_{10}H_{15}{}^{79}BrO$ 230.0306, found 230.0306.

8-(3′-Bromopropyl)bicyclo[4.2.0]octan-7-one (8). Following the general procedure above, treatment of amide **6** (2.34 g, 10 mmol) and cyclohexene (10.2 mL, 100 mmol) with triflic anhydride (2.1 mL, 15 mmol) and collidine (1.26 mL, 11 mmol) in CH_2Cl-CH_2Cl at reflux afforded **8**, after hydrolysis, as a 73:27 mixture of exo and endo diastereomers. Flash chromatography (40:1 hexanes–ether) of the crude product gave *exo*-bromide **8-exo** (290 mg, 12%) and a mixture of *exo*- and *endo*-bromides **8** (348 mg, 14%).

Data for *exo*-bromide **8-exo**: ^1H NMR ($CDCl_3$) δ 1.25–2.08 (m, 12 H), 2.14 (m, 1 H), 2.98 (m, 1 H), 3.20 (m, 1 H), 3.40 (m, 2 H); ^{13}C NMR ($CDCl_3$) δ 21.4 (t, J = 129, 2 C), 22.1 (t, J = 126), 26.5 (t, J = 128), 28.3 (t, J = 128), 28.9 (d, J = 140), 30.5 (t, J = 128), 33.2 (t, J = 151), 53.2 (d, J = 136), 61.8 (d, J = 133), 212.1 (s); IR (neat) 1769 (vs, C=O) cm^{-1}; MS m/e (rel intensity) 246 and 244 (2, M^+), 165 (16, M^+ – Br), 164 and 162 (64), 95 (16), 83 (76), 67 (76), 50 (100); HRMS calcd for $C_{11}H_{17}{}^{79}BrO$ 244.0463, found 244.0463.

9-(3′-Bromopropyl)bicyclo[5.2.0]nonan-8-one (9). Following the general procedure above, treatment of amide **6** (0.583 g, 2.5 mmol) and cycloheptene (2.4 mL, 20 mmol) with triflic anhydride (0.6 mL, 3.8 mmol) and collidine (0.37 mL, 2.8 mmol) in CH_2-ClCH_2Cl at reflux afforded **9**, after hydrolysis, as a 71:29 mixture of exo and endo diastereomers. Flash chromatography (35:1 hexanes–ether) of the crude product gave *exo*-bromide **9-exo** (103 mg, 16%) and a mixture of *exo*- and *endo*-bromides **9** (138 mg, 21%).

Data for *exo*-bromide **9-exo**: ^1H NMR ($CDCl_3$) δ 1.10–2.10 (m, 14 H), 2.28 (m, 1 H), 2.77 (m, 1 H), 3.33 (m, 1 H), 3.41 (m, 2 H); ^{13}C NMR ($CDCl_3$) δ 25.8 (t, J = 128), 28.3 (t, J = 123), 28.9, 29.2 (t, J = 130), 30.4 (t, J = 127), 31.9, 32.9 (t, J = 144), 33.2 (t, J = 150), 36.9 (d, J = 136), 61.2 (d, J = 132), 62.3 (d, J = 131), 214.8 (s); IR (neat) 1771 (vs, C=O) cm^{-1}; MS m/e (rel intensity) 260 and 258 (2, M^+), 217 and 215 (1), 179 (1, M^+ – Br), 164 and 162 (49), 95 (20), 81 (61), 67 (68), 55 (100); HRMS calcd for $C_{12}-H_{19}{}^{79}BrO$ 258.0619, found 258.0619.

10-(3′-Bromopropyl)bicyclo[6.2.0]decan-9-one (10). Following the general procedure above, treatment of amide **6** (2.40 g, 10 mmol) and cyclooctene (10 mL, 80 mmol) with triflic anhydride (2.6 mL, 15 mmol) and collidine (1.5 mL, 11 mmol) in CH_2ClCH_2Cl at reflux afforded **10**, after hydrolysis, as a 58:42 mixture of exo and endo diastereomers. Flash chromatography (30:1 hexanes–ether) of the crude product gave *exo*-bromide **10-exo** (212 mg, 8%) and a mixture of *exo*- and *endo*-bromides **10** (395 mg, 14%).

Data for *exo*-bromide **10-exo**: ^1H NMR ($CDCl_3$) δ 1.10–2.10 (m, 16 H), 2.72 (qd, J = 7.3 and 2.7, 1 H), 3.06 (m, 1 H), 3.40 (m, 2 H), 3.54 (m, 1 H); ^{13}C NMR ($CDCl_3$) δ 23.3 (t, J = 128), 25.3, 26.0, 28.2, 28.7, 29.6, 29.8, 30.5, 33.4, 36.5 (d, J = 131), 60.6 (d, J = 136), 63.7 (d, J = 128), 215.8 (s); IR (neat) 1767 (vs, C=O) cm^{-1}; MS m/e (rel intensity) 274 and 272 (<1, M^+), 164 and 162 (27), 98 (56), 81 (45), 67 (54), 55 (100); HRMS calcd for $C_{13}-H_{21}{}^{79}BrO$ 272.0776, found 272.0776.

7-(4′-Bromobutyl)bicyclo[3.2.0]heptan-6-one (12). Following the general procedure above, treatment of amide **11** (1.04 g, 4.2 mmol) and cyclopentene (3.7 mL, 42 mmol) with triflic anhydride (1.05 mL, 6.3 mmol) and collidine (0.63 mL, 4.6 mmol) in CH_2-ClCH_2Cl at 25 °C afforded **15**, after hydrolysis, as a 73:27 mixture of exo and endo diastereomers. Flash chromatography (30:1 hexanes–ether) of the crude product gave a mixture of *exo*- and *endo*-bromides **12** (641 mg, 62%). For spectroscopic purposes a small amount of **12-exo** was isolated, contaminated with 9% of **12-endo**.

Data for *exo*-bromide **12-exo**: ^1H NMR ($CDCl_3$) δ 1.45–1.90 (m, 11 H), 2.02 (m, 1 H), 2.49 (m, 1 H), 2.59 (m, 1 H), 3.40 (t, J = 6.8, 2 H), 3.46 (m, 1 H); IR (neat) 1771 (vs, C=O) cm^{-1}; MS

m/e (rel intensity) 246 and 244 (3, M^+), 176 and 174 (27), 165 (6, $M^+ - Br$), 97 (86), 81 (29), 67 (69), 55 (100); HRMS calcd for $C_{11}H_{17}{}^{79}BrO$ 244.0463, found 244.0482.

8-(4'-Bromobutyl)bicyclo[4.2.0]octan-6-one (13). Following the general procedure above, treatment of amide **11** (0.50 g, 2.0 mmol) and cyclohexene (3.2 mL, 31 mmol) with triflic anhydride (0.50 mL, 3.0 mmol) and collidine (0.30 mL, 2.2 mmol) in CH_2ClCH_2Cl at reflux afforded **13**, after hydrolysis, as a 72:28 mixture of exo and endo diastereomers. Flash chromatography (30:1 hexanes–ether) of the crude product gave a mixture of *exo*- and *endo*-bromides **13** (374 mg, 72%). For spectroscopic purposes a small amount of **13-exo** was isolated, contaminated with 11% of **13-endo**.

Data for *exo*-bromide **13-exo**: ^1H NMR ($CDCl_3$) δ 1.30–2.00 (m, 14 H), 2.13 (m, 1 H), 2.97 (m, 1 H), 3.18 (m, 1 H), 3.40 (t, J = 6.7, 2 H); IR (neat) 1771 (vs, C=O) cm^{-1}; MS *m/e* (rel intensity) 179 (20, $M^+ - Br$), 134 (6), 97 (86), 79 (30), 67 (80), 55 (100); HRMS calcd for $C_6H_9{}^{79}BrO$ ($M^+ - C_6H_{10}$) 175.9837, found 175.9839.

Alkylation of 14 was conducted by the procedure of Stork and Dowd.[20] A solution of ketone **14** (300 mg, 2.7 mmol), cyclohexylamine (0.62 mL, 5.4 mmol), and a catalytic amount of *p*-toluenesulfonic acid (2.5 mg) in benzene (5 mL) was refluxed for 2 h with azeotropic removal of H_2O. The cold reaction mixture was diluted with benzene (5 mL) and quickly washed with H_2O (5 mL). The benzene layer was dried and concentrated to give the imine (510 mg, purity >98%, yield: 99%). A portion of the resulting imine (100 mg, 0.5 mmol) in THF (1.5 mL) was added over 20 min to a refluxing solution of 2.8 M EtMgBr (0.22 mL, 0.6 mmol) in THF. The reaction mixture was refluxed 2 h further after the addition was complete and then cooled to 0 °C. 1,3-Dibromopropane (0.20 mL, 2.0 mmol) was added rapidly to the cold reaction mixture. After the mixture was stirred at 25 °C for 2 h, 10% HCl (0.5 mL) was added and the reaction mixture was refluxed for 10 h. Ether workup afforded crude **7** as a 60:40 mixture of exo and endo diastereomers. Flash chromatography (35:1 hexanes–ether) of the crude product gave *exo*-bromide **7-exo** (35.0 mg, 30%) and *endo*-bromide **10** (21.4 mg, 19%).

General Free-Radical Reaction Procedure. Free-Radical Reaction of (1*SR*,5*RS*,7*SR*)-7-Chloro-7-(3'-bromopropyl)bicyclo[3.2.0]hept-2-en-6-one (2-exo). Procedure A: Slow Addition of 1.2 equiv of Bu_3SnH. A solution of Bu_3SnH (135 μL, 0.5 mmol) and AIBN (ca. 10 mg) in benzene (5 mL) was added to a stirring, refluxing solution of *exo*-bromide **2-exo** (132 mg, 0.50 mmol) in benzene (30 mL) over 4 h using a syringe pump. The reaction was followed by GC while another 28 μL (0.1 mmol) of Bu_3SnH with AIBN (1 mg) in benzene (1.5 mL) was added to the reaction mixture. The reaction was stopped when the GC showed no more starting material. An 87:11:2 mixture of chlorine-bearing ring-expansion product **15**, ring-attachment product **17**, and cyclization product **18** was obtained. The ratio of **15-syn** to **15-anti** was 23:77. The GC retention times of **15-syn** and **15-anti** were 2.82 and 3.16 min, respectively. The tin products were removed by standard KF workup,[8c] and flash chromatography of the crude product on silica gel (elution with 50:1 hexanes–ether) gave **15-syn** (15 mg, 16%) as a colorless oil, **15-anti** (59 mg, 64%) as a white solid, **17** (4.5 mg, 6%) as a pair of diastereomers, and **18** (1.5 mg, 2%).

Data for **15-syn**: ^1H NMR ($CDCl_3$) δ 1.76–1.98 (3 H), 2.33–2.69 (4 H), 2.82–3.07 (m, 2 H), 3.14 (q, J = 9.2, 1 H), 3.89 (m, 1 H), 5.81 (m, 2 H); ^{13}C NMR ($CDCl_3$) δ 21.6, 33.1, 40.5, 42.9, 53.9, 56.6, 66.0, 130.8, 131.0, 210.7; IR (neat) 1705 (vs, C=O); MS *m/e* (rel intensity) 184 (28, M^+), 149 (37, $M^+ - Cl$), 131 (29), 121 (32), 107 (100), 91 (53), 79 (53), 66 (67), 55 (58); HRMS calcd for $C_{10}H_{13}{}^{35}ClO$ 184.0659, found 184.0645.

Data for **15-anti**:[22] mp 100–101.5 °C; ^1H NMR ($CDCl_3$) δ 1.19 (m, 1 H), 2.00 (m, 2 H), 2.25 (m, 1 H), 2.42 (dd, J = 17.0 and 9.3, 1 H), 2.57 (t, J = 5.0, 2 H), 2.80–2.94 (m, 1 H), 3.27 (q, J = 9.2, 1 H), 3.48 (br d, J = 9.5, 1 H), 4.33 (d, J = 6.3, 1 H), 5.58 (m, 1 H), 5.94 (m, 1 H); ^{13}C NMR ($CDCl_3$) δ 20.9 (t, J = 131), 34.2 (t, J = 131), 36.7 (t, J = 122), 43.0 (t, J = 129), 51.9 (d, J = 137), 54.1 (d, J = 124), 64.8 (d, J = 147), 129.9 (d, J = 171), 132.5 (d, J = 158), 210.5 (s); IR (neat) 1705 (vs, C=O); MS *m/e* (rel intensity) 184 (48, M^+), 149 (50, $M^+ - Cl$), 131 (35), 121 (43), 107 (76), 91 (65), 79 (61), 66 (100), 55 (63); HRMS calcd for $C_{10}H_{13}{}^{35}ClO$ 184.0659, found 184.0657.

Data for **18**: ^1H NMR ($CDCl_3$) δ 1.25–1.70 (m, 8 H), 1.97 (m, 1 H), 2.12 (m, 1 H), 2.47 (m, 1 H), 2.78 (q, J = 8.9, 1 H), 3.23 (m, 1 H), 3.56 (m, 1 H); ^{13}C NMR ($CDCl_3$) δ 16.3 (t, J = 130), 21.8 (t, J = 125), 25.1 (t, J = 124), 28.8 (t, J = 130), 29.2 (t, J = 132), 32.0 (d, J = 149), 35.1 (d, J = 128), 55.2 (d, J = 129), 64.8 (d, J = 142), 217.7 (s); IR (neat) 1773 (vs, C=O); MS *m/e* (rel intensity) 150 (22, M^+), 132 (11), 122 (10), 104 (12), 93 (46), 79 (100), 67 (40); HRMS calcd for $C_{10}H_{14}O$ 150.1045, found 150.1045.

Ring-expansion product 16 was prepared by the reduction of the chlorine-bearing ring-expansion product **15** with Bu_3SnH. A solution of **15-anti** (18.4 mg, 0.1 mmol), Bu_3SnH (35 μL, 0.13 mmol), and AIBN (ca. 2 mg) in benzene (5 mL) was heated to reflux for 5 h. Tin products were removed by DBU workup,[21] and flash chromatography (40:1 hexanes–ether) of the crude product gave ring-expansion product **16** (13.8 mg, 92%): ^1H NMR ($CDCl_3$) δ 1.08 (m, 1 H), 1.52 (m, 2 H), 1.68 (m, 1 H), 1.70–1.95 (m, 2 H), 2.30 (m, 1 H), 2.40–2.60 (m, 2 H), 2.89 (m, 1 H), 3.07 (m, 1 H), 3.44 (m, 1 H), 5.46 (m, 1 H), 5.63 (m, 1 H); ^{13}C NMR ($CDCl_3$) δ 25.6 (t, J = 125), 28.4 (t, J = 128), 31.5 (t, J = 132), 32.0 (t, J = 128), 43.1 (t, J = 129), 46.8 (d, J = 131), 54.0 (d, J = 126), 128.7 (d, J = 164), 133.3 (d, J = 168), 213.0 (s); IR 1705 (vs, C=O) cm^{-1}; MS *m/e* (rel intensity) 150 (87, M^+), 135 (15), 121 (32), 107 (100), 91 (50), 79 (88), 66 (57); HRMS calcd for $C_{10}H_{14}O$ 150.1045, found 150.1045.

Procedure B: Slow Addition of 3.3 equiv of Bu_3SnH. A solution of Bu_3SnH (810 μL, 2.97 mmol) and AIBN (ca. 20 mg) in benzene (15 mL) was added to a stirring, refluxing solution of *exo*-bromide **2-exo** (238 mg, 0.90 mmol) in benzene (70 mL) over 10 h using a syringe pump. The reaction mixture was refluxed for an additional 2 h after the addition was complete to gave ring-expansion product **16**, ring-attachment product **17**, and cyclization product **18** as a 74:18:8 mixture.

Free-Radical Reaction of (1*SR*,6*RS*,8*SR*)-8-Chloro-8-(3'-bromopropyl)bicyclo[4.2.0]oct-2-en-7-one (3-exo). Procedure A: Slow Addition of 1.3 equiv of Bu_3SnH. A solution of Bu_3SnH (421 μL, 1.6 mmol) and AIBN (ca. 15 mg) in benzene (25 mL) was added to a stirring, refluxing solution of *exo*-bromide **3-exo** (440 mg, 1.6 mmol) in benzene (80 mL) over 4 h using a syringe pump. The reaction was followed by GC while another 134 μL (0.5 mmol) of Bu_3SnH with AIBN (6 mg) in benzene (10 mL) was added to reaction mixture. The reaction was stopped when the GC showed no more starting material. A 60:28:4 mixture of chlorine-bearing ring-expansion product **26**, ring-attachment product **28**, and direct reduction product **29-endo** was obtained. The ratio of **26-syn** to **26-anti** was 51:49. The GC retention times of **26-syn** and **26-anti** were 4.05 and 4.08 min, respectively. After KF workup, flash chromatography of the crude product on silica gel (elution with 50:1 hexanes–ether) gave **26-syn** (89 mg, 28%) as a colorless oil, **26-anti** (86 mg, 27%) as a low-melting white solid, **28** (55 mg, 21%) as a pair of diastereomers not isolated in a pure state, and **29-endo** (7.8 mg, 3%).

Data for **26-syn**: ^1H NMR ($CDCl_3$) δ 1.68 (m, 1 H), 1.80–2.24 (7 H), 2.45–2.66 (m, 2 H), 2.94 (m, 1 H), 3.40 (m, 1 H), 4.43 (m, 1 H), 5.72 (m, 1 H), 5.84 (m, 1 H); ^{13}C NMR ($CDCl_3$) δ 19.2 (t, J = 128), 23.3 (t, J = 125), 25.3 (t, J = 131), 34.5 (t, J = 127), 42.1 (d, J = 131), 43.1 (t, J = 133), 47.6 (d, J = 130), 64.7 (d, J = 150), 127.7 (d, J = 158), 128.7 (d, J = 159), 214.6 (s); IR (neat) 1705 (vs, C=O) cm^{-1}; MS *m/e* (rel intensity) 198 (16, M^+), 163 (14, $M^+ - Cl$), 144 (22), 133 (31), 107 (36), 91 (56), 79 (100), 55 (47); HRMS calcd for $C_{11}H_{15}{}^{35}ClO$ 198.6925, found 198.6925.

Data for **26-anti**: ^1H NMR ($CDCl_3$) δ 1.58 (m, 1 H), 1.84–2.23 (7 H), 2.46–2.66 (m, 2 H), 2.69 (m, 1 H), 3.13 (m, 1 H), 4.18 (m, 1 H), 5.58 (m, 1 H), 5.93 (m, 1 H); ^{13}C NMR ($CDCl_3$) δ 22.4 (t, J = 127), 22.8 (t, J = 123), 25.6 (t, J = 132), 36.7 (t, J = 131), 42.2 (d, J = 126), 43.5 (t, J = 128), 49.3 (d, J = 126), 64.6 (d, J = 150), 126.2 (d, J = 159), 129.8 (d, J = 158), 214.0 (s); IR (neat) 1704 (vs, C=O) cm^{-1}; MS *m/e* (rel intensity) 198 (42, M^+), 163 (17, $M^+ - Cl$), 144 (23), 133 (30), 107 (47), 91 (83), 79 (100), 55

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(21) Curran, D. P.; Chang, C.-T. *J. Org. Chem.* **1989**, *54*, 3140.

(22) The chlorine-bearing ring expansion product **15** was also isolated by Dr. K. Mahmood. A satisfactory X-ray structure of the **15-anti** isomer has been obtained by Dr. Steven J. Geib, unpublished results.

(50); HRMS calcd for $C_{11}H_{15}{}^{35}ClO$ 198.6925, found 198.6925.

Data for **28** (pair of diastereomers): ^1H NMR ($CDCl_3$) δ 1.18–2.48 (11 H), 2.50–2.82 (2 H), 3.60 (m, 1 H), 5.58–5.85 (m, 2 H); ^{13}C NMR ($CDCl_3$) δ 20.7, 20.9, 21.8, 22.0, 24.8, 25.0, 25.4, 25.6, 27.9, 28.1, 35.3, 35.3, 39.1, 39.2, 53.4, 53.6, 128.2, 129.3, 130.2, 130.5, 220.8, 221.3; IR (neat) 1736 (vs, C=O) cm^{-1}; MS *m/e* (rel intensity) 164 (51, M^+), 149 (9), 136 (15), 121 (23), 108 (23), 93 (32), 80 (100), 67 (23), 53 (21); HRMS calcd for $C_{11}H_{16}O$ 164.1201, found 164.1201.

Data for **29-endo**: ^1H NMR ($CDCl_3$) δ 0.89 (t, *J* = 7.0, 3 H), 1.20–1.70 (5 H), 1.90–2.05 (3 H), 3.01 (br s, 1 H), 3.32 (m, 1 H), 3.53 (m, 1 H), 5.77 (m, 1 H), 5.93 (m, 1 H); ^{13}C NMR ($CDCl_3$) δ 14.0, 18.6, 21.3, 21.5, 27.0, 27.6, 54.9, 61.3, 125.6, 130.4, 214.2; IR (neat) 1769 (vs, C=O) cm^{-1}; MS *m/e* (rel intensity) 164 (3, M^+), 136 (2), 107 (2), 91 (4), 80 (4, $M^+ - C_5H_8O$), 67 (8); HRMS calcd for $C_{11}H_{16}O$ 164.1201, found 164.1201.

Ring-expansion product 27 was prepared by the reduction of chlorine-bearing ring-expansion product **26** with Bu_3SnH. A solution of **26-anti** (30 mg, 0.15 mmol), Bu_3SnH (49 μL, 0.18 mmol), and AIBN (ca. 3 mg) in benzene (7 mL) was heated to reflux for 6 h. DBU workup gave ring-expansion product **27** (23.4 mg, 95%) as a single product: ^1H NMR ($CDCl_3$) δ 1.10–1.67 (6 H), 1.74–2.18 (4 H), 2.38 (m, 1 H), 2.56 (m, 1 H), 2.60–2.73 (m, 2 H), 5.55–5.73 (m, 2 H); ^{13}C NMR ($CDCl_3$) δ 19.7 (t, *J* = 128), 24.8 (t, *J* = 127), 26.9 (t, *J* = 127), 30.1 (t, *J* = 123), 32.3 (t, *J* = 125), 36.1 (d, *J* = 127), 42.2 (t, *J* = 136), 50.7 (d, *J* = 123), 126.6 (d, *J* = 157), 131.4 (d, *J* = 158), 215.0 (s); IR (neat) 1701 (vs, C=O) cm^{-1}; MS *m/e* (rel intensity) 164 (27, M^+), 146 (11), 135 (20), 117 (27), 104 (34), 91 (39), 79 (100); HRMS calcd for $C_{11}H_{16}O$ 164.1201, found 164.1201. The spectral properties of **27** compared favorably with those reported by Smith and Houk.[23]

Procedure B: Slow Addition of 3.3 equiv of Bu_3SnH. A solution of Bu_3SnH (516 μL, 1.90 mmol) and AIBN (ca. 10 mg) in benzene (20 mL) was added to a stirring, refluxing solution of *exo*-bromide **3-exo** (178 mg, 0.64 mmol) in benzene (70 mL) over 8 h using a syringe pump. The reaction mixture was refluxed for an additional 2 h after the addition was complete to give ring-expansion product **27**, ring-attachment product **28**, and direct-reduction product **29-endo** as a 55:23:14 mixture.

Free-Radical Reaction of (1*SR*,5*RS*,7*SR*)-7-Chloro-7-(4′-bromobutyl)bicyclo[3.2.0]hept-2-en-6-one (5-exo). A solution of Bu_3SnH (249 μL, 0.78 mmol) and AIBN (ca. 10 mg) in benzene (13 mL) was added to a stirring, refluxing solution of *exo*-bromide **5-exo** (100 mg, 0.36 mmol) in benzene (22 mL) over 7 h using a syringe pump. The reaction mixture was refluxed for an additional 2 h after the addition was complete to give ring-expansion product **30**, ring-attachment product **31**, and direct reduction product **32-endo** as a 59:28:13 mixture. After DBU workup, flash chromatography (45:1 hexanes–ether) of the crude product gave **30** (31.9 mg, 54%) and **31** (11.2 mg, 19%) as a pair of diastereomers, and **32-endo** (5.0 mg, 8%).

Data for **30**: ^1H NMR ($CDCl_3$) δ 1.10–1.85 (6 H), 1.90 (m, 2 H), 2.30 (m, 2 H), 2.56 (m, 1 H), 2.76–2.90 (1 H), 3.15 (m, 1 H), 3.47 (m, 1 H), 5.40 (m, 1 H), 5.18 (m, 1 H); ^{13}C NMR ($CDCl_3$) δ 24.3, 27.5, 28.7, 30.3, 34.5, 45.4, 51.1, 128.5, 134.6, 216.8; IR (neat) 1700 (vs, C=O) cm^{-1}; MS *m/e* (rel intensity) 164 (51, M^+), 135 (7), 121 (41), 101 (100), 79 (99), 66 (69, $M^+ - C_6H_{10}O$); HRMS calcd for $C_{11}H_{16}O$ 164.1201, found 164.1201.

Data for **31** (pair of diastereomers): ^1H NMR ($CDCl_3$) δ 1.30–2.45 (m, 12 H), 1.88 (m, 1 H), 3.18 (br, 1 H), 5.67 (m, 1 H), 5.78 (m, 1 H); ^{13}C NMR ($CDCl_3$) δ 24.8, 24.9, 26.9, 27.0, 28.1, 28.3, 28.6, 30.7, 31.1, 32.1, 32.2, 42.4, 44.4, 44.7, 55.7, 56.2, 131.3, 132.0, 132.1, 133.6, 213.4; IR (neat) 1707 (vs, C=O) cm^{-1}; MS *m/e* (rel intensity) 164 (16, M^+), 135 (32), 107 (39), 98 (100), 79 (34), 67 (84, $M^+ - C_6H_9O$); HRMS calcd for $C_{11}H_{16}O$ 164.1201, found 164.1172.

Data for **32-endo**: ^1H NMR ($CDCl_3$) δ 0.88 (t, *J* = 7.0, 3 H), 1.20–1.60 (m, 6 H), 2.36 (m, 1 H), 2.61 (m, 1 H), 3.42 (m, 1 H), 3.58 (m, 1 H), 3.77 (m, 1 H), 5.73 (m, 1 H), 5.87 (m, 1 H); ^{13}C NMR ($CDCl_3$) δ 14.0 (q, *J* = 124), 22.6 (t, *J* = 120), 24.6 (t, *J* = 127), 29.8 (t, *J* = 124), 34.0 (t, *J* = 132), 42.2 (d, *J* = 148), 59.2 (d, *J* = 142), 65.2 (d, *J* = 129), 129.8 (d, *J* = 164), 134.8 (d, *J* = 153), 216.1 (s); IR (neat), 1773 (vs, C=O) cm^{-1}; MS *m/e* (rel intensity) 164 (0, M^+), 136 (10), 93 (3), 79 (21), 66 (100, $M^+ - C_6H_{10}O$); HRMS calcd for $C_9H_{12}O$ ($M^+ - C_2H_4$) 164.1201, found 164.1201.

Free-Radical Reaction of (1*SR*,5*RS*,7*SR*)-7-(3′-Bromopropyl)bicyclo[3.2.0]heptan-6-one (7-exo). Procedure A: Single Addition of Bu_3SnH. A solution of *exo*-bromide **7-exo** (6.5 mg, 0.028 mmol), Bu_3SnH (12 μL, 0.038 mmol, 7.5 mM), and AIBN (ca. 1 mg) in benzene (5 mL) was heated to reflux for 9 h to give ring-expansion product **33**, ring-attachment product **34**, and *trans*-α-decalone **35** in the ratio of 68:11:21. The experiment was repeated using different concentrations of Bu_3SnH and irradiation using 350-nm UV lamps instead of heating. The results are presented in Table V.

Procedure B: Slow Addition of Bu_3SnH. A solution of Bu_3SnH (250 μL, 0.79 mmol) and AIBN (ca. 10 mg) in benzene (10.5 mL) was added to a stirring, refluxing solution of *exo*-bromide **7-exo** (120 mg, 0.52 mmol) in benzene (40 mL) over 6.7 h using a syringe pump. The reaction mixture was refluxed for an additional 2 h after the addition was complete to give ring-expansion product **33**, ring-attachment product **34**, and *trans*-α-decalone **35** as a 23:12:65 mixture. After DBU workup, flash chromatography (50:1 hexanes–ether) of the crude product gave **33** (6.8 mg, 9%), a mixture of **33** and **34** (5.1 mg), and **35** (46.0 mg, 58%).

^1H NMR, IR, and MS of **33** agree with those of literature values:[24] HRMS calcd for $C_{10}H_{11}O$ 152.1201, found 152.1201.

^1H NMR, ^{13}C NMR, IR, and MS of **35** are identical with those of an authentic sample of *trans*-α-decalone (Aldrich).

Free-Radical Reaction of (1*SR*,6*RS*,8*SR*)-8-(3′-Bromopropyl)bicyclo[4.2.0]octan-7-one (8-exo). A solution of Bu_3SnH (410 μL, 1.3 mmol) and AIBN (ca. 20 mg) in benzene (10 mL) was added to a stirring, refluxing solution of *exo*-bromide **8-exo** (244 mg, 1.0 mmol) in benzene (80 mL) over 6.7 h using a syringe pump. The reaction mixture was refluxed for an additional 2 h after the addition was complete to give ring-expansion product **36**, ring-attachment product **37**, and direct-reduction product **38-exo** in the ratio 65:16:19. After DBU workup, flash chromatography (50:1 hexanes–ether) of the crude product gave **36** (25.5 mg, 15%), a 74:26 mixture of **36** and **37** (105.6 mg, 47% for **36**, 16% for **37**), and **38-exo** (26.5 mg, 16%). The experiment was repeated using iodide **25-exo** instead of bromide **8-exo** to give ring-expansion product **36**, ring-attachment product **37**, and direct-reduction product **38-exo** in the ratio of 68:15:17.

Data for **36**: ^1H NMR ($CDCl_3$) δ 1.15–1.90 (13 H), 1.96 (m, 1 H), 2.25–2.42 (m, 3 H), 2.72 (td, *J* = 12.7 and 3.2, 1 H); ^{13}C NMR ($CDCl_3$) δ 21.5 (t, *J* = 127), 24.0 (t, *J* = 127), 25.6 (t, *J* = 127), 26.0 (t, *J* = 131), 29.1 (t, *J* = 124), 31.4 (t, *J* = 130), 34.1 (t, *J* = 124), 35.7 (d, *J* = 128), 42.3 (t, *J* = 123), 51.3 (d, *J* = 123), 216.3 (s); IR (neat) 1694 (vs, C=O) cm^{-1}; MS *m/e* (rel intensity) 166 (12, M^+), 151 (9), 137 (11), 124 (24), 111 (61), 109 (55), 98 (91), 81 (76), 67 (100); HRMS calcd for $C_{11}H_{18}O$ 166.1358, found 166.1358.

Data for **38-exo**: ^1H NMR ($CDCl_3$) δ 0.89 (t, *J* = 7.2, 3 H), 1.25–1.70 (11 H), 1.92 (m, 1 H), 2.12 (m, 1 H), 2.97 (qd, *J* = 7.1 and 2.4, 1 H), 3.08 (qd, *J* = 8.8 and 2.3, 1 H); ^{13}C NMR ($CDCl_3$) δ 14.0, 20.8, 21.8 (2 C), 22.4, 27.1, 29.2, 32.2, 53.4, 63.1, 214.0; IR (neat) 1771 (vs, C=O) cm^{-1}; MS *m/e* (rel intensity) 166 (6, M^+), 138 (3), 109 (2), 95 (8), 84 (42), 67 (53), 55 (100); HRMS calcd for $C_{11}H_{18}O$ 166.1358, found 166.1358.

Free-Radical Reaction of (1*SR*,7*RS*,9*SR*)-9-(3′-Bromopropyl)bicyclo[5.2.0]nonan-8-one (9-exo). A solution of Bu_3SnH (150 μL, 0.48 mmol) and AIBN (ca. 5 mg) in benzene (20 mL) was added to a stirring, refluxing solution of *exo*-bromide **9-exo** (95.5 mg, 0.37 mmol) in benzene (40 mL) over 7 h using a syringe pump. The reaction mixture was refluxed for an additional 2 h after the addition was complete to afford ring-expansion product **39**, ring-attachment product **40**, and direct reduction product **41-exo** in the ratio of 67:17:16. After DBU workup, flash chromatography (35:1 hexanes–ether) of the crude product gave **39** (19.1 mg, 29%), a 76:24 mixture of **39** and **40** (30.6 mg, 35% for **39**, 11% for **40**), and **41-exo** (9.3 mg, 14%).

Data for **39**: ^1H NMR ($CDCl_3$) δ 1.18–1.90 (15 H), 2.04 (m, 1 H), 2.20 (br s, 1 H), 2.36 (m, 1 H), 2.55–2.70 (m, 2 H); ^{13}C NMR

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($CDCl_3$) δ 24.6, 26.2, 26.9, 28.5, 28.9, 30.3, 34.5, 34.9, 38.8, 42.4, 56.5, 215.6; IR (neat) 1698 (vs, C=O) cm^{-1}; MS *m/e* (rel intensity) 180 (15, M^+), 165 (8), 151 (20), 137 (36), 123 (32), 111 (60), 98 (75), 95 (50), 81 (68), 67 (100); HRMS calcd for $C_{12}H_{20}O$ 180.1514, found 180.1514.

Data for **41-exo**: ^1H NMR ($CDCl_3$) δ 0.89 (t, *J* = 7.2, 3 H), 1.15–1.90 (13 H), 2.01 (m, 1 H), 2.26 (m, 1 H), 2.77 (m, 1 H), 3.28 (m, 1 H); IR (neat) 1773 (vs, C=O) cm^{-1}; MS *m/e* (rel intensity) 180 (9, M^+), 151 (3), 137 (7), 96 (14), 84 (56), 81 (59), 67 (73), 55 (100); HRMS calcd for $C_{12}H_{20}O$ 180.1514, found 180.1514.

Free-Radical Reaction of (1*SR*,8*RS*,10*SR*)-10-(3′-Bromopropyl)bicyclo[6.2.0]decan-9-one (10-exo). A solution of Bu_3SnH (327 μL, 1.04 mmol) and AIBN (ca. 10 mg) in benzene (20 mL) was added to a stirring, refluxing solution of *exo*-bromide **10-exo** (190 mg, 0.69 mmol) in benzene (60 mL) over 7 h using a syringe pump. The reaction mixture was refluxed for an additional 2 h after the addition was complete to afford ring-expansion product **42**, ring-attachment product **43**, and direct-reduction product **44-exo** in the ratio of 45:32:9. After DBU workup, flash chromatography (30:1 hexanes–ether) of the crude product gave **42** (25.4 mg, 19%), a 45:55 mixture of **42** and **43** (72.4 mg, 24% for **42**, 30% for **43**), and **44-exo** (9.4 mg, 7%).

Data for **42**: ^1H NMR ($CDCl_3$) δ 1.25–1.90 (16 H), 1.90–2.10 (m, 2 H), 2.20 (br, 1 H), 2.43 (m, 1 H), 2.57–2.72 (m, 2 H); ^{13}C NMR ($CDCl_3$) δ 24.3, 25.1, 26.4, 27.2 (2 C), 27.5, 27.7, 32.7, 35.1, 38.0, 42.8, 53.3, 216.3; IR (neat) 1698 (vs, C=O) cm^{-1}; MS *m/e* (rel intensity) 194 (14, M^+), 151 (20), 137 (57), 124 (29), 111 (71), 98 (94), 81 (51), 55 (100); HRMS calcd for $C_{13}H_{22}O$ 194.1671, found 194.1671.

Data for **44-exo**: ^1H NMR ($CDCl_3$) δ 1.10–1.90 (m, 17 H), 2.00 (m, 2 H), 2.31 (m, 1 H), 2.72 (m, 1 H), 3.02 (m, 1 H); IR (neat) 1773 (vs, C=O) cm^{-1}; MS *m/e* (rel intensity) 194 (8, M^+), 165 (7), 151 (11), 137 (6), 123 (6), 111 (8), 98 (32), 82 (36), 72 (60), 55 (100); HRMS calcd for $C_{13}H_{22}O$ 194.1671, found 194.1671.

Free-Radical Reaction of (1*SR*,5*RS*,7*SR*)-7-(4′-Bromobutyl)bicyclo[3.2.0]heptan-6-one (12-exo). Procedure A: Single Addition of Bu_3SnH. A solution of **12-exo** (5.0 mg, 0.02 mmol), Bu_3SnH (8.0 μL, 0.03 mmol), and AIBN (ca. 0.5 mg) in benzene (1.1 mL) was irradiated in an NMR tube placed in a photochemical reactor (Rayonet) using RPR 350-nm lamps (Southern New England Ultraviolet Co.) for 25 min to give direct reduction product **45-exo** and 1,5-hydrogen transfer product **45-endo** as a 36:64 mixture of exo and endo diastereomers. The GC retention times of **45-exo** and **45-endo** were 1.36 and 1.50 min, respectively.

Authentic Sample of 45-exo. A mixture of *exo*-bromide **12-exo** (122 mg, 0.50 mmol) and zinc dust (260 mg, 4.0 mmol) in 4 mL of acetic acid was irradiated in an ultrasonic water bath at 40 °C for 42 h. The reaction mixture was filtered, and the filtrate was washed with H_2O and saturated $NaHCO_3$ solution. After the organic layer was dried over $MgSO_4$, the solvent was removed to give direct reduction product **45-exo** (75 mg, purity >95%, yield: 86%): ^1H NMR ($CDCl_3$) δ 0.87 (t, *J* = 7.0, 3 H), 1.20–1.40 (4 H), 1.40–1.85 (7 H), 1.99 (d, *J* = 6.7, 1 H), 2.50 (m, 1 H), 2.58 (m, 1 H), 3.43 (m, 1 H). ^{13}C NMR ($CDCl_3$) δ 14.0 (q, *J* = 124), 22.6 (t, *J* = 120), 25.3 (t, *J* = 128), 29.3 (t, *J* = 130, 2 C), 29.4 (t, *J* = 130), 33.0 (t, *J* = 130), 36.5 (d, *J* = 143), 61.6 (d, *J* = 141), 64.1 (d, *J* = 131), 218.1 (s); IR (neat) 1769 (vs, C=O) cm^{-1}; MS *m/e* (rel intensity) 166 (8, M^+), 138 (2), 124 (8), 109 (4), 99 (34), 80 (39), 67 (71), 55 (100); HRMS calcd for $C_{11}H_{18}O$ 166.1358, found 166.1361.

Authentic Sample of 45-endo. To a solution of **32-endo** (50 mg, 0.3 mmol) in absolute ethanol (4 mL) was added 10% Pd/C (15 mg). The mixture was stirred under H_2 balloon for 40 h at 25 °C. The catalyst was removed by filtration and the filtrate was concentrated to give **45-endo** (48 mg, purity >95%, yield: 96%) as a clear oil: ^1H NMR ($CDCl_3$) δ 0.87 (t, *J* = 6.8, 3 H), 1.20–1.70 (9 H), 1.82 (td, *J* = 13.9, 7.9, 2 H), 2.01 (m, 1 H), 2.94 (q, *J* = 9.7, 1 H), 3.24 (m, 1 H), 3.53 (td, *J* = 7.1 and 2.9, 1 H); ^{13}C NMR ($CDCl_3$) δ 14.0 (q, *J* = 125), 22.6 (t, *J* = 122), 23.2 (t, *J* = 125), 26.8 (t, *J* = 125), 29.0 (t, *J* = 131), 30.0 (d, *J* = 153), 60.8 (d, *J* = 124), 62.8 (d, *J* = 141), 218.7 (s); IR (neat) 1773 (vs, C=O) cm^{-1}; MS *m/e* (rel intensity) 166 (10, M^+), 138 (4), 124 (10), 109 (2), 99 (34), 80 (36), 67 (64), 55 (100); HRMS calcd for $C_{11}H_{18}O$ 166.1358, found 166.1358.

Procedure B: Slow Addition of Bu_3SnD. A solution of Bu_3SnD (32 μL, 0.12 mmol) and AIBN (ca. 2 mg) in benzene (2 mL) was added to a stirring, refluxing solution of *exo*-bromide **12-exo** (20.0 mg, 0.08 mmol) in benzene (2 mL) over 2 h using a syringe pump. The reaction mixture was refluxed an additional 1.5 h after the addition was complete to afford direct reduction product **45-exo-*4′-d*** and 1,5-hydrogen transfer product **45-endo-*7-d*** as a 9:91 mixture. The GC retention time of **45-exo-*4′-d*** and **45-endo-*7-d*** were 1.39 and 1.53 min, respectively.

MS of direct reduction product **45-exo-*4′-d***: *m/e* (rel intensity) 167 (19, M^+), 139 (8), 124 (15), 109 (4), 100 (52), 81 (69), 67 (92), 55 (100). MS of 1,5-hydrogen transfer product **45-endo-*7-d***: *m/e* (rel intensity) 167 (12, M^+), 139 (2), 125 (12), 110 (2), 100 (35), 81 (46), 67 (73), 56 (100).

Free Radical Reaction of (1*SR*,6*RS*,8*SR*)-8-(4′-Bromobutyl)bicyclo[4.2.0]octan-6-one (13-exo). Procedure A: Single Addition of Bu_3SnD. A solution of **13-exo** (4.3 mg, 0.016 mmol), Bu_3SnD (6.7 μL, 0.025 (mmol), and AIBN (ca. 0.5 mg) in benzene (1.0 mL) was irradiated in an NMR tube placed in a photochemical reactor using 350-nm lamps for 20 min to give direct reduction product **46-exo-*4′-d*** and 1,5-hydrogen transfer product **46-endo-*8-d*** as a 38:62 mixture. The GC retention times of **46-exo-*4′-d*** and **46-endo-*8-d*** were 2.42 and 2.65 min, respectively.

MS of direct reduction product **46-exo-*4′-d***: *m/e* (rel intensity) 181 (M^+, 8), 163 (2), 152 (2), 138 (17), 124 (1), 109 (6), 100 (75), 81 (67), 67 (77), 55 (100). MS of 1,5-hydrogen transfer product **46-endo-*8-d***: *m/e* (rel intensity) 181 (M^+, 6), 163 (3), 153 (3), 139 (19), 124 (3), 110 (9), 100 (100), 81 (81), 67 (75), 56 (88).

Procedure B: Slow Addition of Bu_3SnH. A solution of Bu_3SnH (31 μL, 0.098 mmol) and AIBN (ca. 2 mg) in benzene (2 mL) was added to a stirring, refluxing solution of *exo*-bromide **13-exo** (20 mg, 0.082 mmol) in benzene (3 mL) over 5.7 h using a syringe pump. The reaction mixture was refluxed for an additional 1.5 h after the addition was complete to afford direct reduction product **46-exo** and 1,5-hydrogen transfer product **46-endo** as a 4:96 mixture of exo and endo diastereomers. The GC retention times of **46-exo** and **46-endo** were 2.38 and 2.61 min, respectively.

MS of the exo diastereomer **46-exo**: *m/e* (rel intensity) 180 (6, M^+), 162 (2), 152 (1), 138 (4), 123 (3), 109 (7), 99 (70), 80 (50), 67 (75), 55 (100). MS of the endo diastereomer **46-endo**: *m/e* (rel intensity) 180 (7, M^+), 162 (4), 152 (5), 138 (14), 123 (3), 109 (7), 99 (64), 80 (50), 67 (75), 55 (100).

Free-Radical Reaction of (1*SR*,5*RS*,7*RS*)-7-Chloro-7-(3′-bromopropyl)bicyclo[3.2.0]hept-2-en-6-one (2-endo). A solution of Bu_3SnH (722 μL, 2.6 mmol) and AIBN (ca. 10 mg) in benzene (10 mL) was added to a stirring, refluxing solution of *endo*-bromide **2-endo** (320 mg, 1.2 mmol) in benzene (50 mL) over 8 h using a syringe pump. The reaction mixture was refluxed for an additional 2 h after the addition was complete to give tricyclic product **18**, direct-reduction product **53-endo**, ring-expansion product **16**, and ring-attachment product **17** as a 74:20:3:3 mixture. After DBU workup, flash chromatography of the crude product on silica gel (elution with 50:1 hexanes–ether) gave **18** (124 mg, 69%) as a clear colorless oil. The ^1H NMR, IR, and GC–MS data of **18** agree with those obtained from the minor product isolated from the reaction of **2-exo**.

Acknowledgment. This work was generously supported by the Institute of General Medical Sciences of the National Institutes of Health under Grant No. GM 39825.

Supplementary Material Available: ^1H NMR, ^{13}C NMR, or GC data of compounds described in the Experimental Section (32 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.