transferred into a 60-mL separatory funnel with ether, and the ethereal solution was washed with 20 mL of 1.0 M HCl followed by 20 mL of 1.0 M sodium hydroxide. Drying with brine and $MgSO_4$, followed by solvent removal, gave a thick oil. The crude product (nearly pure by TLC) was purified by flash chromatography on silica gel (1:9 hexanes/ethyl acetate) to yield 103 mg (96% yield) of pure product. This material was further purified by recrystallization from spectral grade methanol, to give the target compound 1; R_1 = *n*-decyl, R_2 = *n*-pentyl, of sufficient purity for liquid crystal studies: mp 42 °C; IR ($CHCl_3$, cm^{-1}) 3060, 2960, 2930, 2760, 1730, 1605, 1510, 1500, 1260, 1225, 1210, 1195, 1175, 1075; ^1H NMR (500 MHz, $CDCl_3$) δ 0.885 (t, J = 7.5 Hz, 3 H), 0.929 (t, J = 9.5 Hz, 3 H), 1.25–1.40 (large m, alkyl region), 1.47 (m, CH_2), 1.62 (m, CH_2), 1.83 (m, CH_2), 2.09 (m, $OCH(CN)CH_2$), 4.04 (t, J = 6.5 Hz, 2 H, CH_2O), 4.739 (t, $OCH(CN)CH_2$, J = 6.7 Hz, 1 H), 6.96 (d, J = 8.5 Hz, 2 H), 7.055 (d, J = 8.5 Hz, 2 H), 7.179 (d, J = 9.0 Hz, 2 H), 8.127 (d, J = 9.0 Hz, 2 H); mass spectrum (CI^+, methane, m/z) 480 ($(M + 1)^+$), 261.

Anal. Calcd for $C_{30}H_{41}O_4N$: C, 75.12; H, 8.62. Found: C, 74.65; H, 8.59.

Acknowledgment. This work was supported by the National Science Foundation (Grant DMR-8611192), by the NSF Engineering Research Center program (Optoelectronic Computing Systems Center, Grant CDR-8622236), and by the Office of Naval Research.

Supplementary Material Available: Details of the crystal structure determination of compound **10**, including tables of atomic coordinates, bond lengths and angles, anisotropic displacement parameters, H-atom coordinates and isotropic displacement parameters, and an ORTEP drawing of the structure showing the numbering scheme used in the tables (9 pages). Ordering information is given on any current masthead page.

Reaction Pathways of 3-(3′-Methylenecyclobutyl)propyl and 2-(3′-Methylenecyclobutyl)ethyl Radicals

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Molecular mechanics (MM2) calculations were used to predict the efficacy and regiochemical outcome of radical cyclizations involving the title radicals and others with further substitution at C_1 on the ring. The MM2 results were generally ratified by experiment and showed the preference for exo closure to give the bicyclo[3.1.1]-heptylmethyl and bicyclo[2.1.1]hexylmethyl radicals, respectively. However, due to subsequent radical rearrangements and, in the case of the former, internal H transfer, these cyclizations are not synthetically viable.

Introduction

Currently there is a great deal of interest in free-radical cyclizations from their extensive use as kinetic and mechanistic probes[1] and successful application in synthesis.[2] Similarly, small-ring bicyclic alkanes have also commanded considerable attention due to the intriguing chemistry attributed to them over recent years. Most of the interest has arisen through NMR[3] and photoelectron spectra,[4] gas-phase ion studies,[5] and solvolytic chemistry[6] in which transannular bridgehead–bridgehead interactions have been implicated, with substantial theoretical support,[7] to explain observations. It seemed appropriate to investigate the possibility of ring-forming reactions of the type

Scheme I

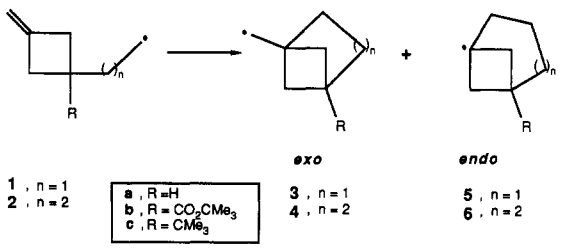


Table I. Transition Structure MM2 Strain Energies for the Ring Closure of 1 and 2

radical	ΔE_s^a (radical) exo	endo
1a	11.1 (3a)	27.4 (5a)
1b	9.5 (3b)	26.3 (5b)
1c	6.4 (3c)	24.2 (5c)
2a	13.1 (4a)	16.9 (6a)
2b	10.8 (4b)	14.5 (6b)
2c	9.6 (4c)	12.9 (6c)

[a] Kilocalories/mole.

(1) (a) See: Newcomb, M.; Curran, D. P. *Acc. Chem. Res.* **1988**, *21*, 206 for a review on the use of alkenyl halides as mechanistic probes. (b) Beckwith, A. L. J.; Abeywickrema, A. N. *J. Org. Chem.* **1987**, *52*, 2568. (c) Jewell, D. R.; Mathew, L.; Warkentin, J. *Can. J. Chem.* **1987**, *65*, 311. (d) Beckwith, A. L. J.; O'Shea, D. M. *Tetrahedron Lett.* **1987**, *28*, 4525. (e) Stork, G.; Mook, R., Jr. *Tetrahedron Lett.* **1987**, *28*, 4529. (f) Park, S.-U.; Chung, S.-K.; Newcomb, M. *J. Org. Chem.* **1987**, *52*, 3275. (g) Tsang, R.; Dickson, J. K., Jr.; Pak, H.; Walton, R.; Fraser-Reid, B. *J. Am. Chem. Soc.* **1987**, *109*, 3484. (h) Chuang, C.-P.; Gallucci, J. C.; Hart, D. J.; Hoffman, C. *J. Org. Chem.* **1988**, *53*, 3218.

(2) (a) Geise, B. *Radicals in Organic Synthesis: Formation of Carbon–Carbon Bonds*; Baldwin, J. E., Ed.; Pergamon: New York, 1986. (b) For a review, see: Curran, D. P. *Synthesis* **1988**, 417–439 and 489–513. (c) Wantanabe, Y.; Endo, T. *Tetrahedron Lett.* **1988**, *29*, 321. (d) Middleton, D. S.; Simpkins, N. S. *Tetrahedron Lett.* **1988**, *29*, 1315. (e) Cekovic, Z.; Ilijev, D. *Tetrahedron Lett.* **1988**, *29*, 1441. (f) Crich, D.; Fortt, S. M. *Tetrahedron Lett.* **1988**, *29*, 2585. (g) Narasimhan, N. S.; Aidhen, I. S. *Tetrahedron Lett.* **1988**, *29*, 2987. (h) Chuang, C.-P.; Gallucci, J. C.; Hart, D. J. *J. Org. Chem.* **1988**, *53*, 3210. (i) Boger, D. L.; Mathrink, R. J. *J. Org. Chem.* **1988**, *53*, 3379.

(3) (a) Della, E. W.; Gangodawila, H.; Pigou, P. E. *J. Org. Chem.* **1988**, *53*, 592. (b) Della, E. W.; Kasum, B.; Kirkbride, K. P. *J. Am. Chem. Soc.* **1987**, *109*, 2746. (c) Barfield, M.; Della, E. W.; Pigou, P. E.; Walter, S. R. *J. Am. Chem. Soc.* **1982**, *104*, 3549 for leading references.

(4) Abeywickrema, R. A.; Della, E. W.; Pigou, P. E.; Livett, M. K.; Peel, J. B. *J. Am. Chem. Soc.* **1984**, *106*, 7321 and references therein.

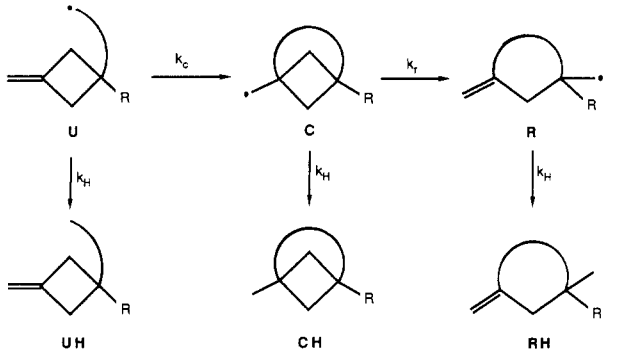
(5) Tsanaktsidis, J. Ph.D. Thesis, Flinders University of South Australia, 1987.

(6) Della, E. W.; Elsey, G. M. *Tetrahedron Lett.* **1988**, *29*, 1299.

(7) Della, E. W.; Pigou, P. E.; Tsanaktsidis, J. *J. Chem. Soc., Chem. Commun.* **1987**, 833. (b) Della, E. W.; Schiesser, C. H. *Tetrahedron Lett.* **1987**, *28*, 3869 and references cited therein. (c) Della, E. W.; Gill, P. M. W.; Schiesser, C. H. *J. Org. Chem.* **1988**, *53*, 4354.

0022-3263/89/1954-4943$01.50/0

Scheme II



illustrated in Scheme I. Apart from the intrinsic interest in radical chemistry of this kind, the expected bicyclic products are of the type required for the synthesis of thromboxane A_2 analogues.[8]

Method

Molecular mechanics calculations[9] on model ground and transition states, as described by Beckwith and Schiesser,[10] were used to estimate the likelihood of cyclization occurring and the degree of selectivity to be expected between the two possible modes of closure (Table I). As the radicals **1** and **2** were to be generated by the action of tributylstannane on a suitable substrate, there would be competition between internal radical addition to the double bond and hydrogen transfer from the stannane. From the results of Beckwith and Schiesser[10] it appears that a calculated strain-energy difference between the ground and transition state (ΔE_s) of less than 10 kcal mol^{-1} is necessary for synthetically useful rates of cyclization to be attained. Similarly ΔE_s differences of greater than 1 kcal mol^{-1} between the exo and endo paths result in useful levels of selectivity.

As may be seen from the data (Table I), the cyclizations of radicals **1a** and **2a** are predicted to exhibit good discrimination between the exo and endo modes. However, the overall ring-forming process is expected to be unfavorable as ΔE_s is quite high in each case.

The cyclization pathway is often facilitated by substitution in the alkyl chain. The energy of the ground state is raised relative to the transition state through nonbonded interactions which are partially relieved as ring formation proceeds. The subsequent enhancement in the rate of ring closure is known as the Thorpe–Ingold effect.[11] To test the effect of substitution at C1 of the cyclobutyl ring ΔE_s was calculated for the *tert*-butyl compounds **1c** and **2c** and the sterically less demanding, but synthetically more versatile, esters **1b** and **2b**. The results (Table I) were quite encouraging as ΔE_s was lowered significantly, in each case, to values which should allow the observation of ring closures. As expected the reduction in ΔE_s was greater for the bulky tertiary substituent.

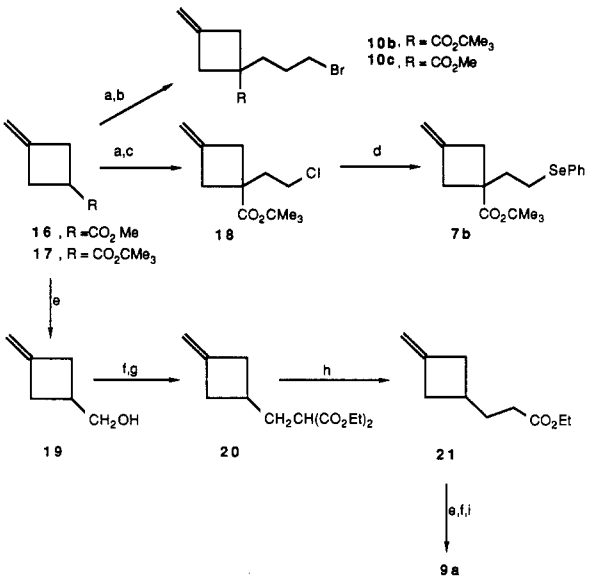
If, as predicted, the cyclization proceeds via the exo mode then the expected product radicals from **1** and **2** would be the cyclobutylcarbinyl radicals **3** and **4**, respectively. However, such species are known to undergo ring opening at modest rates[12] so the appearance of the products arising from **12** and **13** could be anticipated. The balance of the product distribution would be determined primarily by the relative rates of ring closure (k_c) and ring opening (k_r), assuming that the rate of hydrogen transfer (k_H) varies only slightly between the radical species. This seems a reasonable approximation as they are all primary carbon-centered radicals.[13] Given that Scheme II represents all of the processes involved, and that each step is irreversible, then, under pseudo-first-order conditions ([stannane] > 10[substrate]), the required kinetic details can be simply determined from the product ratios where $[SH]_{eff}$ is the effective stannane concentration throughout the reaction.

$$\frac{k_c}{k_H} = \frac{([CH] + [RH])[SH]_{eff}}{[UH]}$$

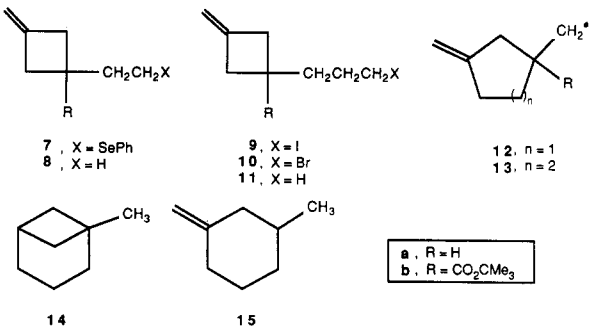
$$\frac{k_r}{k_H} = \frac{[RH][SH]_{eff}}{[CH]}$$

Experimentally, the *tert*-butyl esters **7b** and **10b** were used to assess the theoretical predictions. From the data

Scheme III[a]



[a] Reagents: (a) LDA; (b) $Br(CH_2)_3Br$; (c) $Br(CH_2)_2Cl$; (d) $(PhSe)_2/NaBH_4/EtOH$; (e) $LiAlH_4$; (f) p-$C_6H_4SO_2Cl$/pyridine; (g) $NaCH(CO_2Et)_2$/p-dioxane; (h) NaCl/H_2O/DMSO/140 °C; (i) NaI/acetone.



(8) For a review, see: Newton, R. F.; Roberts, S. M. *Synthesis* **1984**, 449.

(9) (a) Allinger, N. L. *J. Am. Chem. Soc.* **1977**, *99*, 8127. (b) Allinger, N. L.; Yuh, Y. H. QCPE No. 395, 423.

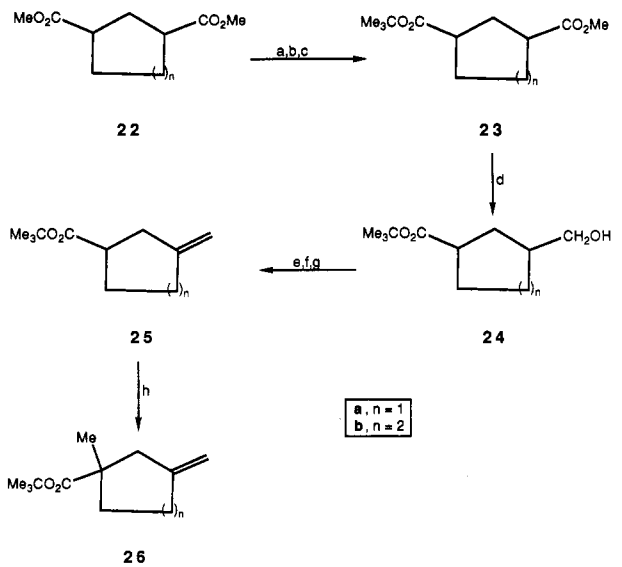
(10) (a) Beckwith, A. L. J.; Schiesser, C. H. *Tetrahedron Lett.* **1985**, *26*, 373. (b) Beckwith, A. L. J.; Schiesser, C. H. *Tetrahedron* **1985**, *41*, 3925.

(11) (a) Beesley, R. M.; Ingold, C. K.; Thorpe, J. F. *J. Chem. Soc.* **1915**, *107*, 1080. (b) Ingold, C. K. *J. Chem. Soc.* **1921**, *119*, 305.

(12) (a) Beckwith, A. L. J.; Moad, G. *J. Chem. Soc., Perkin Trans. 2* **1980**, 1083. (b) Bews, J. R.; Glidewell, C.; Walton, J. C. *J. Chem. Soc., Perkin Trans. 2* **1982**, 1447. (c) Maillard, B.; Walton, J. C. *J. Chem. Soc., Perkin Trans. 2* **1985**, 443. (d) Walton, J. C. *J. Chem. Soc., Perkin Trans 2* **1987**, 231.

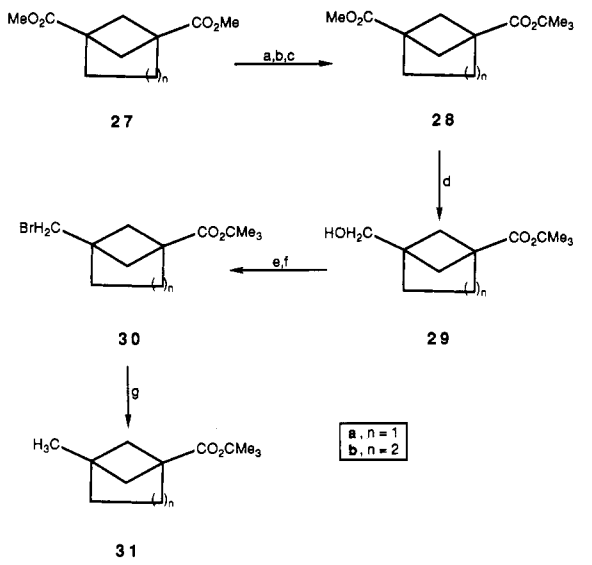
(13) Chatgilialoglu, C.; Ingold, K. U.; Scaiano, J. C. *J. Am. Chem. Soc.* **1981**, *103*, 7739.

Scheme IV[a]



[a] Reagents: (a) $Ba(OH)_2/H_3O^+$; (b) $SOCl_2$; (c) *t*-BuOH/$PhNMe_2$; (d) $LiAlH_4$/THF/−40 °C; (e) *p*-$C_6H_4SOCl_2$/pyridine; (f) NaI/acetone; (g) *t*-BuOK; (h) LDA/MeI.

Scheme V[a]



[a] Reagents: (a) $Ba(OH)_2/H_3O^+$; (b) $SOCl_2$; (c) *t*-BuOH/$PhNMe_2$; (d) $LiAlH_4$/THF/−40 °C; (e) *p*-$C_6H_4SO_2Cl$/pyridine; (f) LiBr/DME/80 °C; (g) Bu_3SnH.

of Table I it was anticipated that an ester function would induce a moderate Thorpe–Ingold enhancement in the cyclization rate and, furthermore, the ester group could be easily manipulated to other functionalities in subsequent steps. The *tert*-butyl ester was chosen as it also facilitated the alkylation of **17** to **10b** and **18** as described in the Syntheses section.

The radicals were generated by the abstraction of phenyl selenide or halide by the tributylstannyl radical under conditions of low stannane concentration conducive to intramolecular radical reactions. The reaction mixtures were analyzed by VPC and the products identified by comparison with authentic samples.

Syntheses

The radical precursors **7b**, **9a**, and **10b** were prepared by the routes illustrated in Scheme III. The lithium enolate of the methyl ester **16**, which was generated under standard conditions,[14] failed to give **10c** when quenched with 1,3-dibromopropane, whereas, under similar conditions, the *tert*-butyl ester **17** delivered **10b** in good yield (60%) after distillation. Alkylation of this enolate by 1-bromo-2-chloroethane gave **18**, which was then converted into the radically-more-reactive selenide[15] **7b**. The iodopropyl substrate **9a** was derived from **16** by the standard conversion illustrated in Scheme III.

Authentic samples of the open-chain reduced compounds **8b**, **11a**, and **11b** were prepared by reduction of the corresponding radical precursors **7b**, **9a**, and **10b** in an excess of neat tributylstannane. Specimens of the expected rearrangement products were synthesized by the sequences outlined in Schemes IV and V. Dimethyl cycloalkane-1,3-dicarboxylate (**22**) was converted to the mixed-ester **23** via barium hydroxide hydrolysis[16] to the half-ester and reesterification of the derived acid chloride with *tert*-butyl alcohol.[17] The methyl ester was then selectively reduced, in the presence of the *tert*-butyl ester, by treatment with 1 molar equiv of lithium aluminum hydride (LAH) in THF at −40 °C, to give the alcohol **24**. The modified hydride reagent produced was relatively unreactive toward the ester functions as addition of 0.5 molar equiv of LAH in THF at −78 °C, followed by 16 h at room temperature, left 55% of **23** unreacted.

The tosylate, derived from **24**, when treated with potassium *tert*-butoxide in 1,4-dioxane, gave the *tert*-butyl ether substitution product rather than elimination to the exocyclic alkene. However, under similar conditions, the iodide gave the required elimination product **25**, which was in turn converted to the enolate with LDA and alkylated with iodomethane to deliver the standards *tert*-butyl 1-methyl-3-methylenecyclopentanecarboxylate (**26a**) and *tert*-butyl 1-methyl-3-methylenecyclohexanecarboxylate (**26b**) (Scheme IV). A specimen of 1-methylbicyclo[3.1.1]heptane (**14**) was available from earlier work,[18] while 3-methylmethylenecyclohexane (**15**) was prepared by a Wittig reaction on 3-methylcyclohexanone.

Functional group manipulations for the conversion of **27** to **29** (Scheme V) were carried out as described above for **22** to **24**. Although the tosylate, derived from **29**, failed to react with lithium bromide after 1 h in refluxing acetone, substitution occurred smoothly at reflux in 1,2-dimethoxyethane. The standards *tert*-butyl 4-methylbicyclo[2.1.1]hexane-1-carboxylate (**31a**) and *tert*-butyl 5-methylbicyclo[3.1.1]heptane-1-carboxylate (**31b**) were prepared by reduction of the corresponding bromides (**30**) in neat tributylstannane. That the radicals **3b** and **4b** rearrange, as illustrated in Scheme II, was confirmed by conducting the bromide reductions at lower tributylstannane concentrations (0.05–0.2 M). Such conditions allowed these radicals sufficient time for some rearrangement to occur in competition with hydride transfer.

Results and Discussion

Experiments carried out to verify the predictions discussed above unearthed some interesting results. As predicted, the radical **2a** failed to give any more than traces of the bicyclic (**14**) or ring-opened (**15**) products arising from intramolecular alkene addition. However, the simple

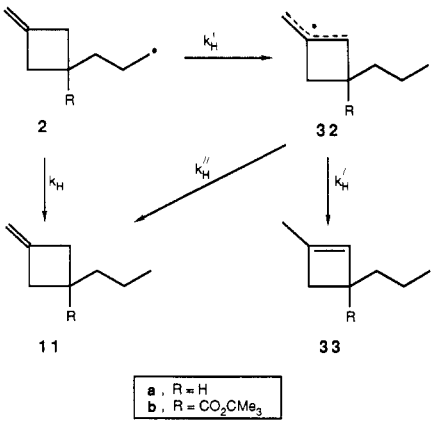
(14) Della, E. W.; Tsanaktsidis, J. *Aust. J. Chem.* **1985**, *38*, 1705.
(15) (a) Beckwith, A. L. J.; Pigou, P. E. *Aust. J. Chem.* **1986**, *39*, 77. (b) Beckwith, A. L. J.; Pigou, P. E. *Aust. J. Chem.* **1986**, *39*, 1151.
(16) Della, E. W.; Tsanaktsidis, J. *Aust. J. Chem.* **1986**, *39*, 2061.
(17) The acid chloride was treated as described by Vogel, A. I. *Practical Organic Chemistry*, 3rd ed.; Longman: London, 1970; pp 384–5.
(18) Della, E. W.; Pigou, P. E. *J. Am. Chem. Soc.* **1984**, *106*, 1085.

Table II. Product Distribution for the Reaction of 9a and 10b with Bu_3SnH[a]

	products[b] [intermediate radical]					
	from 9a		from 10b			
T, °C	(11a) [2a]	(33a) [32a]	11b [2b]	33b [32b]	31b [4b]	26b [13b]
60	(97)	(3)	65	35	nd	nd
80	(97)	(3)	70	25	3	2
100	(96)	(4)	68	25	5	2
120			77	13	7	3

[a] [Bu_3SnH] = 0.02 and 0.023 M, respectively, and [substrate] < 2 mM. [b] Values in parentheses are products arising from **9a**; **14** and **15** were not detected. nd = not determined.

Scheme VI



reduction product **11a** was contaminated with another component. Both product species were removed from the gas chromatogram by the addition of bromine to the analysis sample. A similar situation arose with the substituted species **2b**, with the gas chromatogram indicating four products, three of which were identified as **11b**, **26b**, and **31b** by gas chromatographic comparison with authentic samples. Treatment of the mixture with bromine removed **11b**, **26b**, and the unknown from the chromatogram. Gas chromatographic high-resolution mass spectrometry showed the unknown to be isomeric with the others (calculated for $C_{13}H_{22}O_2$ 210.1620, found 210.1634, spectrum m/z (relative intensity) 210 (2), 154 (20), 137 (2), 125 (7), 109 (100)). Proton NMR of the crude mixture suggested two alkene resonances, a terminal alkene at δ 4.8 and another at 5.7 ppm, which is consistent with a cyclobutene derivative. The ^{13}C NMR spectrum also supported such an alkene mixture with the relevant peaks at δ 143.1 (C3) and 107.4 ppm (=CH_2) for **11b** and δ 131.9 and 107.6 ppm for the other. The minor constituents **26b** and **31b** were present in concentrations too low to allow their assignment in the spectrum (see Table II).

It appears reasonable to suppose that the source of the alkene isomerisation is internal H transfer from the allylic position to the radical side chain, as illustrated in Scheme VI, to give the delocalized radical **32**. Hydrogen transfer to this species by tributylstannane will deliver a mixture of exocyclic (**11**) and endocyclic (**33**) alkenes. However, **11** can also arise from direct transfer of hydrogen to the first-formed radical **2** from stannane. Hence determination of the rate of internal abstraction (k_H^i) relative to the reaction with stannane (k_H) is not straightforward as the importance of k_H'' is not known.

The presence of the alkenes **11b** and **33b** was further substantiated when catalytic hydrogenation of the reaction mixture afforded isomeric products identical with those derived from hydrogenation of **10b**.

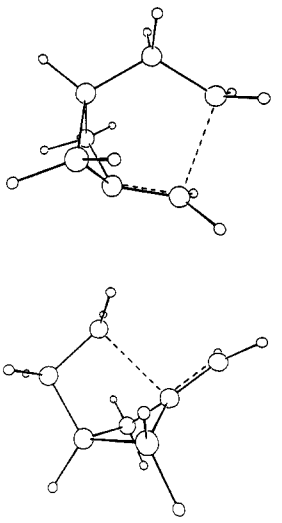


Figure 1. Transition-state structures leading to **5a** (endo), top, and **3a** (exo), bottom.

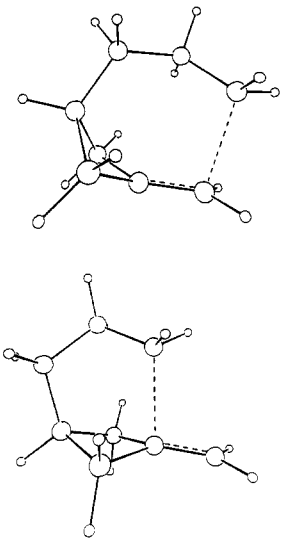


Figure 2. Transition-state structures leading to **6a** (endo), top, and **4a** (exo), bottom.

The relative proportions of the products arising from these reactions are listed in Table II. Iodide **9a** gave almost exclusively the simple reduction product **11a** with no evidence of the bicyclic (**14**) or cyclopentyl (**15**) compounds and traces of H-abstraction product (**33a**) whereas the ester (**10b**) provided traces of the cyclised (**31b**) and ring-expanded (**26b**) products, with a significant amount of allylic rearrangement to **33b**. This illustrates the accelerating effect of the ester substituent on the rates of cyclization and internal H transfer.

Treatment of the lower homologue **7b** with 0.05 M tributylstannane resulted in the formation of three reduction products in ratios dependent on the reaction conditions. The two major components of the mixture were removed from the gas chromatogram by treatment with bromine, but only the exocyclic alkene resonance was observed in the ^1H NMR spectrum. This was substantiated by the carbon spectrum which showed alkene resonances at δ 143.5 (C3) and 107.4 (=CH_2) for **8b** and 150.8 (C3) and 108.0 ppm (=CH_2) for **26a**, the remaining component being the bicyclic compound **31a**.

From the transition state representation for the exo closures of radicals **1** and **2** (Figures 1 and 2) it is clear that, in its rotational arc above the unsaturated centre, the radical side chain must pass in close proximity to the allylic

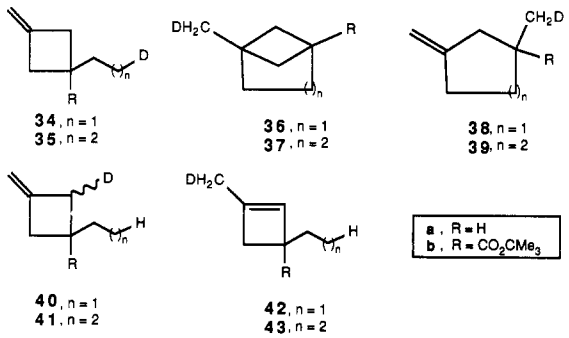
Table III. ^{2}H NMR Analysis of Reaction Mixtures from 7b, 9a, and 10b with Bu_3SnD[a] at 90 °C

entry	substrate	initial radical	[Bu_3SnD], M	rearranged radicals	deuterium chemical shift[b]	products (%)
1	**7b**	**1b**	0.05	**3b, 12b**	0.9	**34b + 36b** (65)
					1.2	**38b** (35)
2	**9a**	**2a**	0.05	**4a, 13a**	0.9	**35a + 37a + 39a** (97)
				32a	1.7	**43a** (3)
3	**10b**	**2b**	0.05	**4b, 13b**	0.9	**35b + 37b + 39b** (79)
				32b	1.7	**43b** (21)
4	**10b**	**2b**	0.16		0.9	**35b + 37b + 39b** (78)
					1.7	**43b** (14)
					2.4	**41b** (4)
					2.5	unknown (2)
					3.0	**41b** (2)

[a] 1.1 equiv. [b] Ppm, δ, internal standard C_6D_6 (δ 7.3 ppm).

hydrogen atoms. In the case of **2**, the H transfer is a 1,5-shift, of which there are numerous examples in the literature,[19] and proceeds because C–H bond breaking and formation can occur in a collinear fashion.[19] The shorter side chain of **1** requires a 1,4-hydrogen transfer, but achievement of the necessary near-collinear arrangement between the interacting centers introduces too much small-angle strain into the transition state for reaction to proceed by that path.

As an additional check **7b**, **9a**, and **10b** were reduced with 1.1 equiv of tributyltin deuteride (0.05–0.16 M). If internal H transfer was indeed occurring then deuterium should be incorporated at an allylic site as well as on the side chain. The reaction was carried out in hexane at 90 °C and the ^{2}H NMR spectra of the reaction mixtures recorded with benzene-d_6 as the internal standard. Of the likely products, **34–39** would be expected to have deuterium resonances around δ 0.9 ppm based on proton spectra. However, the endocyclic (**42**, **43**) and exocyclic (**40**, **41**) allylic deuteride resonances should be distinguishable with expected chemical shifts of δ 1.7 for the former and 2.4 or 3.0 ppm for the latter, depending onto which face the deuterium is delivered.



The data of Table III confirm that only the longer radical side chain gives rise to internal H abstraction, and hence deuterium incorporation, at an allylic site. Additionally, from the ratio of the deuterides **43b** and **41b** (entry 4), the delivery of deuterium to the exocyclic carbon center is preferred by a factor of about 2 over the alternative site on the ring (C2).

The details of the product distribution for the reaction between **7b** and tributylstannane are displayed in Table IV. The data clearly illustrate two features: that the proportion of products (**31a** + **26a**) arising from the cyclization process (k_c) increases with temperature and that the importance of the subsequent rearrangement (k_r) increases at an even greater rate with temperature. From

Table IV. Product Distribution for the Reaction of 7b with Equimolar Bu_3SnH (0.02 M) at Various Temperatures

T, °C	products 8b	31a[a]	26a	$10^3k_c/k_H$, M
1.5	89.6	6.9	3.5	0.58
51	73.7	6.6	19.7	2.33
70	64.7	5.7	29.6	3.89
90	56.3	4.5	39.2	5.92
110	49.8	3.4	46.8	8.73

[a] The proportion of **31a** present was calculated from its known rate of rearrangement[20] to **26a** as **8b** and **31a** were coincident on VPC. The amount of **8b** was adjusted accordingly.

these data approximate Arrhenius parameters for the cyclization of **1b** have been determined,

$$\log \frac{k_c}{k_H} = 0.91\ (\pm 0.12) - \frac{5.23\ (\pm 0.18)}{2.3RT}$$

with errors expressed at the 95% confidence level and E_a in kcal mol^{-1}. Using Ingold's rate expression for H transfer from stannane to a primary carbon-centered radical,[13]

$$\log k_H = 9.07\ (\pm 0.24) - \frac{3.69\ (\pm 0.32)}{2.3RT}$$

the cyclization expression becomes

$$\log k_c = 10.0\ (\pm 0.3) - \frac{8.9\ (\pm 0.4)}{2.3RT}$$

As anticipated from the MM2 calculations, cyclization to the bicyclo[2.1.1]hexyl radical **3b** was much more facile than the analogous formation of the higher homologue **4b**, but so was the subsequent ring opening, of the former, to give **12b**.[20] Consequently, neither route is synthetically viable in its present form for the preparation of bicyclic alkanes.

Experimental Section

Molecular mechanics calculations were carried out on a PRIME 9955 computer. Melting points and boiling points are uncorrected. Infrared (IR) spectra were recorded on a Perkin-Elmer 237 grating spectrometer. Routine ^{1}H NMR spectra were obtained on a Varian EM-360A spectrometer. ^{2}H, ^{13}C, and some ^{1}H NMR data were collected on a JEOL FX90Q instrument. All IR and NMR measurements were determined in CCl_4 solution unless otherwise stated, and chemical shifts relative to TMS are reported in ppm (δ). Mass spectra and high-resolution mass spectra (HRMS) were recorded on a Kratos MS25RF spectrometer, chemical ionization mass spectra (CIMS) were obtained using NH_3, and gas chromatographic samples were introduced via a Carlo Erba GC 6000 chromatograph equipped with an Alltech Associates RSL-150 (0.32 mm × 25 m) fused silica column. Analytical GC were performed on a Perkin-Elmer 8410 chromatograph using an Alltech Asso-

(19) Beckwith, A. L. J.; Ingold, K. U. In *Rearrangements in the Ground and Excited States*; de Mayo, P., Ed.; Academic Press: New York, 1980.

(20) Pigou, P. E., manuscript in preparation.

ciates RSL-300 (0.53 mm × 30 m) fused silica column. Elemental analyses were carried out by the Australian Microanalysis Service, Melbourne.

***tert*-Butyl 1-(3′-Bromopropyl)-3-methylenecyclobutanecarboxylate (10b).** A solution of LDA was prepared by the addition of *n*-BuLi (11 mmol) in hexane (7 mL) to diisopropylamine (1.2 g, 12 mmol) in dry THF (14 mL) at −40 °C under a nitrogen atmosphere. The mixture was then cooled to −80 °C, and *tert*-butyl 3-methylenecyclobutanecarboxylate[17] (1.68 g, 10 mmol) in THF (5 mL) was introduced, followed by HMPA (1 mL) in THF (4 mL) with the temperature maintained below −70 °C throughout the addition. After 20 min excess 1,3-dibromopropane (2 mL) was added, and the mixture was allowed to warm slowly to room temperature. Aqueous ammonium chloride workup and extraction with petroleum ether afforded pure **10b** (1.6 g, 55%) after distillation: bp (Kugelrohr) 145 °C (1 mm); IR 3070, 2975, 2920, 1725, 1680, 1365, 1330, 1255, 1150 cm^{-1}; ^{1}H NMR δ 4.95–4.7 (m, 2 H), 3.28 (perturbed t, J = 5.5 Hz, 2 H), 2.96 (perturbed d, J = 16 Hz, 2 H), 2.37 (perturbed d, J = 16 Hz, 2 H), 2.05–1.65 (m, 4 H), 1.45 (s, 9 H); ^{13}C NMR 173.64 (CO), 142.43 (C_3), 107.87 (=CH_2), 79.43 (CMe_3), 43.03 (C_1), 40.21, ($C_{2,4}$), 35.82 ($C_{3'}$), 32.63 ($C_{1'}$), 28.62 ($C_{2'}$), 27.91 (CH_3); mass spectrum, m/z (relative intensity) 235, 233 (10), 234, 232 (32), 217, 215 (8), 189, 187 (7), 153 (8), 125 (55), 111 (34), 107 (26), 57 (100); CIMS 308, 306 (m + NH_4^+, 25, 28), 291, 289 (m + H^+, 22). Anal. Calcd for $C_{13}H_{21}BrO_2$: C, 53.9; H, 7.3. Found: C, 54.0; H, 7.1.

***tert*-Butyl 1-(2′-Chloroethyl)-3-methylenecyclobutanecarboxylate (18).** The lithium enolate of **17** was prepared as described above and then quenched with excess 1-bromo-2-chloroethane to provide **18** (1.2 g, 52%), after flash chromatography (silica gel/hexane) and Kugelrohr distillation: IR (neat) 3075, 2960, 2930, 1725, 1680, 1365, 1150 cm^{-1}; ^{1}H NMR δ 4.77 (sym m, 2 H), 3.40 (perturbed t, J = 7.5 Hz, 2 H), 3.05–2.85 (m, 2 H), 2.75–2.45 (m, 2 H), 2.15 (perturbed t, J = 7.5 Hz, 2 H), 1.45 (s, 9 H); ^{13}C NMR 172.99 (CO), 141.94 (C_3), 107.98 (=CH_2), 79.75 (CMe_3), 42.59 (C_1), 40.31 ($C_{2,4}$), 40.04 ($C_{1'}$ or $C_{2'}$), 39.77 ($C_{1'}$ or $C_{2'}$), 27.75 (CH_3); mass spectrum, m/z (relative intensity) 177, 175 (4, 12), 176, 174 (24, 72), 159, 157 (13, 38), 139 (5), 129 (12), 125 (100), 111 (40); CIMS 250, 248 (m + NH_4^+, 13, 39), 233, 231 (m + H^+, 18, 54). Anal. Calcd for $C_{12}H_{19}ClO_2$: C, 62.5; H, 8.3. Found: C, 62.1; H, 8.5.

***tert*-Butyl 1-(2′-(Phenylseleno)ethyl)-3-methylenecyclobutanecarboxylate (7b).** Sodium borohydride was added portionwise to a solution of diphenyl diselenide (0.35 g, 1.1 mmol) in ethanol (5 mL) until the yellow color just disappeared. The chloride (**18**) (0.5 g, 2.17 mmol) was then introduced, and the mixture was warmed to 70 °C overnight. The cooled mixture was diluted with ether and washed with water. Evaporation of the ether followed by flash chromatography (silica gel/40% dichloromethane in hexane) and distillation (Kugelrohr, bp 123 °C (0.1 mm)) of the residue gave the selenide **7b** (700 mg, 92%): IR (neat) 3060, 2960, 2925, 1720, 1675, 1570, 1470, 1360, 1145 cm^{-1}; ^{1}H NMR δ 7.6–7.0 (m, 5 H), 4.75 (sym m, 2 H), 3.25–1.85 (m, 8 H, major resonances at 3.17, 2.9, 2.57, 2.2), 1.40 (s, 9 H); ^{13}C NMR δ 173.20 (CO), 142.22 (C_3), 132.30 (C_o), 130.13 (C_{ipso}), 128.62 (C_m), 126.40 (C_p), 107.87 (=CH_2), 79.37 (CMe_3), 44.05 (C_1), 39.99 ($C_{2,4}$), 38.20 ($C_{1'}$), 27.80 (CH_3), 22.28 ($C_{2'}$); mass spectrum, m/z (relative intensity) 352 (6), 279 (6), 233 (7), 171 (6), 158 (7), 157 (6), 147 (5), 140 (10), 139 (100); CIMS 353 (m + H^+, 18). Anal. Calcd for $C_{18}H_{24}O_2Se$: C, 61.5; H, 6.9. Found: C, 61.2; H, 6.7.

Ethyl 2-(Ethoxycarbonyl)-3-(3′-methylenecyclobutyl)propanoate (20). 3-Methylenecyclobutanecarboxylic acid was reduced by LAH to the corresponding alcohol, which was then converted to the tosylate[21] (mp 45–6 °C) by treatment with *p*-toluenesulfonyl chloride and pyridine in dichloromethane. Diethyl malonate (14 mL) was added dropwise to a stirred suspension of sodium hydride (1.5 g) in dry 1,4-dioxane (45 mL) under nitrogen. When the last traces of hydride had been consumed, the tosylate (10 g, 39.7 mmol), dissolved in 1,4-dioxane (20 mL), was administered, and the mixture was heated under reflux overnight. The thick white suspension was diluted with petroleum ether, and the precipitate was dissolved in water. The organic phase was dried ($MgSO_4$), and the solvent was evaporated. Distillation of the residue afforded the diester **20** (8.65 g, 91%) as a colorless liquid, bp 98–102 °C (0.3 mm); IR 3070, 2980, 2950, 2910, 1750, 1732, 1675 cm^{-1}; ^{1}H NMR δ 4.85–4.4 (m, 2 H), 4.15 (q, J = 7 Hz, 4 H), 3.13 (t, J = 7 Hz, 1 H), 3.0–1.85 (m, 7 H), 1.27 (t, J = 7 Hz, 6 H); ^{13}C NMR δ 167.84 (CO), 145.25 ($C_{3'}$), 105.93 (=CH_2), 60.36 (OCH_2), 49.85 (C_2), 37.12 ($C_{2',4'}$), 34.84 (C_3), 28.13 ($C_{1'}$), 13.93 (CH_3); mass spectrum, m/z (relative intensity) 240 (10), 194 (12), 167 (14), 166 (36), 149 (25), 148 (25), 137 (15), 123 (12), 121 (31), 120 (25), 93 (100). Anal. Calcd for $C_{13}H_{20}O_4$: C, 65.0; H, 8.4. Found: C, 65.1; H, 8.1.

Ethyl 3-(3′-Methylenecyclobutyl)propanoate (21). Diester **20** was converted into **21** by the method of Krapcho and Lovey[22] in 65% yield (recovered **20** (8%)). Monoester **21**: bp (Kugelrohr) 95–100 °C (25 mm); IR 3075, 2985, 2950, 1737, 1677, 1175, 875 cm^{-1}; ^{1}H NMR δ 4.8–4.6 (m, 2 H), 4.05 (q, J = 7 Hz, 2 H), 3.1–2.5 (m, 9 H), 1.25 (t, J = 7 Hz, 3 H); ^{13}C NMR δ 171.46 (C_1), 145.73 ($C_{3'}$), 105.97 (=CH_2), 59.32 (OCH_2), 37.06 ($C_{2',4'}$), 31.26 (C_3), 29.58 ($C_{1'}$), 14.14 (CH_3). Anal. Calcd for $C_{10}H_{16}O_2$: C, 71.4; H, 9.6. Found: C, 71.0; H, 9.7.

3-(3′-Iodopropyl)-1-methylenecyclobutane (9a). Ethyl ester **21** (3.2 g, 19.0 mmol) was reduced with LAH (0.5 g, 13 mmol) in ether (70 mL) to the corresponding alcohol, 3-(3′-hydroxypropyl)-1-methylenecyclobutane (2.1 g) (88%): bp (Kugelrohr) 105–110 °C (25 mm); IR 3325, 3070, 2930, 1675, 1055, 905, 875 cm^{-1}; ^{1}H NMR δ 4.85–4.6 (m, 2 H), 3.90 (br, 1 H, OH), 3.7–3.35 (m, 2 H), 3.15–1.95 (m, 5 H), 1.7–1.2 (m, 4 H); ^{13}C NMR δ 146.22 (C_1), 105.75 (=CH_2), 61.66 ($C_{3'}$), 37.33 ($C_{2,4}$), 32.51 ($C_{1'}$), 30.40 ($C_{2'}$), 29.91 (C_3). Anal. Calcd for $C_8H_{14}O$: C, 76.1; H, 11.2. Found: C, 76.0; H, 10.8.

The alcohol (1.9 g, 15 mmol) in dichloromethane (5 mL) and pyridine (2 g) was cooled in an ice bath and then treated with *p*-toluenesulfonyl chloride (3.8 g, 20 mmol) in the usual manner to afford 3-(3′-(tosyloxy)propyl)-1-methylenecyclobutane (4.1 g, 98%) as a colorless oil: IR 3080, 2960, 2865, 1680, 1600, 1370, 1185, 1170, 1095 cm^{-1}; ^{1}H NMR δ 7.9–7.2 (sym m, 4 H), 4.8–4.6 (m, 2 H), 3.95 (perturbed t, J = 6 Hz, 2 H), 2.9–2.0 (m, 8 H, with s at 2.45), 1.7–1.3 (m, 2 H); ^{13}C NMR δ 145.90 (C_1), 143.79 (CS), 133.76 (C_p), 129.43 (C_o), 127.59 (C_m), 105.97 (=CH_2), 69.57 ($C_{3'}$), 37.17 ($C_{2,4}$), 31.92 ($C_{1'}$), 29.43 (C_3), 26.83 ($C_{2'}$), 21.36 (CH_3).

The tosylate (4.0 g, 14.3 mmol) was then treated with sodium iodide (3.2 g, 21.3 mmol) in refluxing acetone (100 mL) for 90 min, and the cooled mixture was diluted with water and extracted with pentane. The organic fraction was then washed with aqueous sodium bisulfite solution, water, and brine, dried, ($MgSO_4$) and evaporated. Distillation of the residue delivered the iodide **9a** (2.7 g, 88%) as a colorless liquid: bp (Kugelrohr) 95 °C (10 mm); IR 3080, 2930, 2850, 1675, 875 cm^{-1}; ^{1}H NMR δ 4.85–4.6 (m, 2 H), 3.15 (t, J = 6 Hz, 2 H), 3.0–1.4 (m, 9 H); ^{13}C NMR δ 145.74 (C_1), 106.19 (=CH_2), 37.39 ($C_{2,4}$), 37.06 ($C_{1'}$), 31.49 ($C_{2'}$), 29.26 (C_3), 5.64 ($C_{3'}$); mass spectrum, m/z (relative intensity) 236 (21), 208 (4), 155 (9), 127 (4), 109 (100), 81 (69), 67 (86). Anal. Calcd for $C_8H_{13}I$: C, 40.7; H, 5.5. Found: C, 40.9; H, 5.4.

Preparation of Standards for GC and NMR Experiments: 1-Methylene-3-propylcyclobutane (11a). Iodide **9a** (1 mmol) was added to neat tributylstannane (2 mmol) containing AIBN (1 mg) and sealed in a glass ampoule after deoxygenation. The ampoule was irradiated with UV light (Hanovia 450-W mercury lamp at 15-cm separation) for 5 min. The reduced product was pumped from the mixture at room temperature (0.5 mm) and collected in a cold trap (−78 °C): ^{1}H NMR ($CDCl_3$) δ 4.7 (m, 2 H), 3.0–1.9 (m, 5 H), 1.7–1.2 (m, 4 H), 1.1–0.8 (m, 3 H); ^{13}C NMR ($CDCl_3$) δ 148.00 (C_3), 105.26 (=CH_2), 38.90 ($C_{1'}$), 37.76 ($C_{2,4}$), 30.18 (C_3), 20.75 ($C_{2'}$), 14.09 ($C_{3'}$); mass spectrum, m/z (relative intensity) 110 (1), 109 (6), 95 (59), 82 (20), 81 (96), 69 (15), 68 (39), 67 (52), 55 (100); HRMS calcd for C_8H_{14} 110.1095, found 110.1094.

1-Methylbicyclo[3.1.1]heptane (14) was available from previous work.[18]

3-Methyl-1-methylenecyclohexane (15). Sodium hydride (60 mg, 2.5 mmol) was added to dry DMSO (2 mL) under nitrogen, and the mixture was heated to 70 °C. On cessation of hydrogen evolution methyltriphenylphosphonium iodide (0.67 g, 1.65 mmol) in DMSO (4 mL) was added followed by 3-methylcyclohexanone (0.1 g, 0.87 mmol) after 15 min. A sample of **15** was obtained by

(21) Wiberg, K. B.; Connor, D. S. *J. Am. Chem. Soc.* **1966**, *88*, 4437.

(22) Krapcho, A. P.; Lovey, A. J. *Tetrahedron Lett.* **1973**, 957.

passing a gentle stream of nitrogen through the mixture and trapping the volatile product in a cold trap (−78 °C). Spectral data were in accord with literature values.[23]

***tert*-Butyl 1-Ethyl-3-methylenecyclobutanecarboxylate (8b).** The enolate of *tert*-butyl 3-methylenecyclobutanecarboxylate[17] was prepared, as described above for **10b**, and quenched with excess bromoethane. The crude product was distilled (Kugelrohr) (bp 120 °C (15 mm)) to give a sample of **8b**: IR ($CDCl_3$) 3080, 2980, 2930, 1715, 1680 cm^{-1}; ^1H NMR ($CDCl_3$) δ 4.75 (m, 2 H), 3.02 (d, J = 16 Hz, 2 H), 2.40 (d, J = 16 Hz, 2 H), 1.75 (q, J = 7 Hz, 2 H), 1.42 (s, 9 H), 0.84 (t, J = 7 Hz, 3 H); ^{13}C NMR ($CDCl_3$) δ 175.63 (CO), 143.56 (C_3), 107.54 (=CH_2), 79.96 (CMe_3), 44.54 (C_1), 40.03 ($C_{2,4}$), 30.50 ($C_{1'}$), 28.06 (3 CH_3), 9.43 ($C_{2'}$); mass spectrum, m/z (relative intensity) 140 (35), 125 (17), 111 (28), 95 (52), 67 (30), 57 (100); HRMS calcd for (m − C_4H_8) 140.0837, found 140.0836; CIMS 214 (m + NH_4^+, 28), 197 (m + H^+, 60).

***tert*-Butyl 3-Methylene-1-propylcyclobutanecarboxylate (11b).** An authentic sample of **11b** was prepared by tributylstannane reduction of **10b** as described above for **31a**. **11b**: ^1H NMR δ 4.75 (m, 2 H), 3.05 (perturbed d, J = 16 Hz, 2 H), 2.40 (perturbed d, J = 16 Hz, 2 H), 1.85–0.8 (m, 16 H, includes at 1.44, s, 9 H); ^{13}C NMR δ 173.90 (CO), 143.13 (C_3), 107.37 (=CH_2), 78.77 (CMe_3), 43.45 (C_1), 40.20 ($C_{2,4}$), 39.76 ($C_{1'}$), 27.90 (3 CH_3), 18.37 ($C_{2'}$), 14.30 ($C_{3'}$); mass spectrum, m/z (relative intensity) 154 (30), 137 (26), 125 (69), 111 (32), 109 (40), 57 (100); CIMS 211 (m + H^+, 39). Anal. Calcd for $C_{13}H_{22}O_2$: C, 74.2; H, 10.5. Found: C, 74.5; H, 10.7.

***tert*-Butyl 4-(Methoxycarbonyl)bicyclo[2.1.1]hexane-1-carboxylate (28a) and *tert*-Butyl 5-(Methoxycarbonyl)bicyclo[3.1.1]heptane-1-carboxylate (28b).** The diesters **27a** and **27b**[14] were half-hydrolyzed as described previously,[16] and the derived acids were converted to the *tert*-butyl esters **28a** and **28b** by the method described.[17] The NMR data were consistent with those of **27a** and **27b**.

28a: ^1H NMR δ 3.67 (s, 3 H), 2.25–1.9 (m, 6 H), 1.8–1.5 (m, 2 H), 1.4 (s, 9 H); ^{13}C NMR δ 171.20, 170.22, 79.10, 50.77, 49.90, 48.39, 44.21, 29.59, 29.48, 27.91; mass spectrum, m/z (relative intensity) 209 (10), 185 (75), 167 (34), 166 (23), 152 (29), 139 (14), 125 (12), 107 (50), 79 (47), 57 (100).

28b: ^1H NMR δ 3.63 (s, 3 H), 2.6–2.2 (m, 2 H), 1.90 (br s, 4 H), 1.85–1.6 (m, 2 H), 1.4 (s, 9 H); ^{13}C NMR δ 173.80, 172.88, 78.89, 50.94, 42.76, 41.56, 38.42, 37.66, 29.43, 27.81, 15.83; mass spectrum, m/z (relative intensity) 199 (39), 181 (16), 180 (11), 155 (14), 154 (22), 153 (37), 139 (19), 122 (25), 121 (20), 95 (30), 94 (20), 93 (100), 57 (90).

***tert*-Butyl 4-(Hydroxymethyl)bicyclo[2.1.1]hexane-1-carboxylate (29a) and *tert*-Butyl 5-(Hydroxymethyl)bicyclo[3.1.1]heptane-1-carboxylate (29b).** The mixed diesters **29a** (230 mg, 0.96 mmol) and **29b** (0.7 g, 2.76 mmol) were reduced with LAH, as described below for the preparation of **24a**, to afford **29a** (150 mg, 58%) and **29b** (0.5 g, 81%) after purification. Physical data for **29a**: IR (neat) 3370, 2970, 2930, 2880, 1715, 1370, 1355, 1260, 1165 cm^{-1}; ^1H NMR δ 3.62 (s, 1 H, OH), 3.46 (s, 2 H), 2.0–1.2 (m, 17 H, includes at 1.4, s, 9 H); ^{13}C NMR δ 172.28 (C=O) 78.99 (CMe_3), 63.50 (OCH_2), 50.01 ($C_{1,4}$), 42.16 ($C_{5,6}$), 30.24 (C_3), 29.05 (C_2), 27.96 (CH_3); mass spectrum, m/z (relative intensity) 157 (3), 156 (5), 139 (20), 138 (27), 110 (16), 93 (65), 57 (100); HRMS calcd for (m − C_4H_8) 156.0786, found 156.0806; CIMS 230 (m + NH_4^+, 18), 213 (m + H^+, 47). Physical data for **29b**: IR 3425, 2950, 2870, 1725, 1370, 1300, 1160 cm^{-1}; ^1H NMR δ 3.3 (s, 2 H), 3.0 (s, 1 H, OH), 2.2–1.3 (m, 19 H, includes at 1.4, s, 9 H); ^{13}C NMR δ 174.34 (C=O), 78.67 (CMe_3), 68.27 (OCH_2), 43.13 (C_1), 40.15 (C_5), 35.98 ($C_{6,7}$), 30.40 (C_4), 30.08 (C_2), 27.91 (CH_3), 16.32 (C_3); mass spectrum, m/z (relative intensity) 170 (20), 153 (25), 152 (87), 125 (30), 124 (44), 107 (90), 95 (29) with 57 (100); CIMS 227 (m + H^+, 20). Anal. Calcd for $C_{13}H_{21}BrO_2$: C, 69.0; H, 9.8. Found: C, 68.8; H, 9.6.

***tert*-Butyl 4-(Bromomethyl)bicyclo[2.1.1]hexane-1-carboxylate (30a) and *tert*-Butyl 5-(Bromomethyl)bicyclo[3.1.1]heptane-1-carboxylate (30b).** The alcohols **29a** and **29b** were converted quantitatively to the corresponding tosylates as described in the preparation of **9a**. Physical properties of *tert*-butyl 4-((tosyloxy)methyl)bicyclo[2.1.1]hexane-1-carboxylate: mp 96–98 °C; IR 2980, 2880, 1723, 1370, 1345, 1190, 1180, 1165 cm^{-1}; ^1H NMR δ 7.9–7.2 (sym m, 4 H), 3.97 (s, 2 H), 2.4 (s, 3 H), 2.0–1.0 (m, 17 H includes at 1.4, s, 9 H); ^{13}C NMR δ 170.77 (C=O), 143.89 (CS), 133.55 (C_p), 129.48 (C_o), 127.59 (C_m), 79.05 (CMe_3), 70.87 (OCH_2), 50.23 (C_1), 46.38 (C_4), 42.48 ($C_{5,6}$), 29.81 (C_3), 28.94 (C_2), 27.86 (3 CH_3), 21.30 ($ArCH_3$).

Physical properties of *tert*-butyl 5-((tosyloxy)methyl)bicyclo[3.1.1]heptane-1-carboxylate: IR 2950, 2870, 1725, 1370, 1190, 1180, 1155 cm^{-1}; ^1H NMR δ 7.9–7.2 (sym m, 4 H), 3.77 (s, 2 H), 2.47 (s, 3 H), 2.1–1.3 (m, 19 H, includes at 1.4, s, 9 H); ^{13}C NMR δ 172.98 (C=O), 143.62 (CS), 133.87 (C_p), 129.37 (C_o), 127.64 (C_m), 78.82 (CMe_3), 75.09 (OCH_2), 43.39 (C_1), 37.71 (C_5), 36.57 ($C_{6,7}$), 29.90 (C_2), 29.69 (C_4), 27.85 (3 CH_3), 21.34 ($ArCH_3$), 15.98 (C_3). These tosylates (1 mmol) were treated with lithium bromide (2 mmol) in DME (7 mL) at reflux. After 2 h, TLC of the reaction mixture indicated that the conversion was essentially complete. The solvent was evaporated, and the solids were dissolved in water and extracted with hexane. Filtration of the hexane fraction through silica gel followed by distillation gave **30a** (55% from **29a**) and **30b** (70% from **29b**), respectively.

Physical data for **30a**: bp (Kugelrohr) 60 °C (1 mm); ^1H NMR δ 3.5 (s, 2 H), 2.1–1.5 (m, 17 Hz, includes at 1.44, s, 9 H); ^{13}C NMR δ 170.66 (CO), 78.94 (CMe_3), 49.36 (C_4), 48.06 (C_1), 44.16 ($C_{5,6}$), 35.55 (CBr), 30.67 (C_2 or C_3), 30.51 (C_2 or C_3), 27.96 (CH_3); mass spectrum, m/z (relative intensity) 220, 218 (7), 203, 201 (12), 173, 171 (12), 139 (58), 138 (26), 128 (54), 79 (14), 77 (14), 57 (100); CIMS 294, 292 (m + NH_4^+, 10, 9), 277, 275 (m + H^+, 71, 67). Anal. Calcd for $C_{12}H_{19}BrO_2$: C, 52.4; H, 7.0. Found: C, 52.8; H, 6.8.

Physical data for **30b**: bp (Kugelrohr) 95 °C (1 mm); IR 2975, 2950, 2870, 1725, 1365, 1300, 1155 cm^{-1}; ^1H NMR δ 3.32 (s, 2 H), 2.2–1.2 (m, 19 H, includes at 1.4, s, 9 H); ^{13}C NMR δ 172.88 (CO), 78.78 (CMe_3), 42.48 (C_1), 42.10 (CBr), 39.01 (C_5), 38.63 ($C_{6,7}$), 31.43 (C_4), 29.54 (C_2), 27.86 (CH_3), 16.43 (C_3); mass spectrum, m/z (relative intensity) 235, 233 (9), 234, 232 (10), 217, 215 (10), 189, 187 (25), 153 (93), 152 (49), 107 (61), 79 (20), 57 (100); CIMS 291, 189 (m + H^+, 17, 15). Anal. Calcd for $C_{13}H_{21}BrO_2$: C, 53.9; H, 7.3. Found: C, 54.1; H, 7.0.

***tert*-Butyl 4-Methylbicyclo[2.1.1]hexane-1-carboxylate (31a) and *tert*-Butyl 5-Methylbicyclo[3.1.1]heptane-1-carboxylate (31b).** The bromide **30a** (or **30b**) (1 mmol) was added to neat tributylstannane (2 mmol) containing AIBN (1 mg) and sealed in a glass ampoule after deoxygenation. The ampoule was irradiated with UV light (450-W Hanovia mercury lamp at 15-cm separation) for 30 min. Excess stannane was quenched with 2-bromo-2-chloro-1,1,1-trifluoroethane, and the reduced product **31a** (80%) (or **31b** (76%)) was recovered by Kugelrohr distillation of the crude mixture.

Physical data for **31a**: bp (Kugelrohr) 125 °C (15 mm); IR ($CHCl_3$) 2990, 2890, 1710, 1375, 1340, 1275, 1175 cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.0–1.3 (m, 17 H), 1.17 (s, 3 H); ^{13}C NMR ($CDCl_3$) δ 173.58 (CO), 79.64 (CMe_3), 50.54 (C_1), 46.32 ($C_{5,6}$), 44.75 (C_4), 33.91 (C_3), 31.31 (C_2), 28.12 (3 CH_3), 19.39 (CH_3); mass spectrum, m/z (relative intensity) 140 (44), 125 (49), 123 (33), 122 (18), 95 (100), 94 (30), 82 (49), 80 (50), 79 (23), 57 (92); HRMS calcd for (m − C_4H_8) 140.0837, found 140.0845; CIMS 197 (m + H^+, 23).

Physical data for **31b**: bp (Kugelrohr) 125 °C (15 mm); IR (neat) 2950, 2870, 1725 cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.0–1.5 (m, 8 H), 1.4 (s, 9 H), 1.0 (s, 3 H), 1.05–0.73 (m, 2 H); ^{13}C NMR ($CDCl_3$) δ 175.7 (CO), 79.47 (CMe_3), 43.56 (C_1), 41.01 ($C_{6,7}$), 35.43 (C_5), 35.21 (C_4), 29.85 (C_2), 28.06 (3 CH_3), 27.30 (CH_3), 16.85 (C_3); mass spectrum, m/z (relative intensity) 154 (33), 137 (7), 136 (7), 112 (20), 109 (57), 94 (22), 69 (55), 57 (100); HRMS calcd for (m − C_4H_8) 154.0994, found 154.1008; CIMS 211 (m + H^+, 59).

***cis-tert*-Butyl 3-(Methoxycarbonyl)cyclopentanecarboxylate (23a).** The diester **22a**[14] was half-hydrolyzed as described previously,[16] and the derived acid was converted to the acid chloride and then the *tert*-butyl ester by the method described:[17] IR (neat) 2960, 1725, 1445, 1430, 1365, 1150 cm^{-1}; ^1H NMR δ 3.62 (s, 3 H), 3.0–2.35 (m, 2 H), 2.3–1.8 (m, 6 H), 1.4 (s, 9 H); ^{13}C NMR δ 174.07 (CO), 173.04 (CO), 78.99 (CMe_3), 50.98 (OCH_3), 44.48 (C_1 or C_3), 43.35 (C_1 or C_3), 33.17 (C_2), 28.78 ($C_{4,5}$), 27.80 (3 CH_3).

***cis-tert*-Butyl 3-(Hydroxymethyl)cyclopentanecarboxylate (24a).** The mixed ester **23** (3.23 g, 14.2 mmol) in dry ether (15 mL) was cooled to −40 °C, and a solution of LAH (0.09 M) in THF was added until all the starting material had

(23) (a) Smith, G. V.; Trotter, P. J. *J. Org. Chem.* **1963**, *28*, 2450. (b) Grover, S. H.; Stothers, J. B. *Can. J. Chem.* **1975**, *53*, 589.

been consumed (17 mL, 15.3 mmol) (monitored by VPC). The mixture was then quenched with ethyl acetate and allowed to attain room temperature. The crude product was dissolved in dichloromethane, filtered through a short silica gel column, and then distilled to give **24a** (1.9 g, 71%): IR (neat) 3400, 2950, 2860, 1720, 1370, 1150 cm^{-1}; ^1H NMR δ 3.7–3.3 (m, 2 H), 3.1–2.4 (m, 3 H, includes OH), 2.4–1.5 (m, 6 H), 1.4 (s, 9 H); ^{13}C NMR δ 174.88 (C=O), 78.99 (CMe_3), 65.72 (CH_2O), 44.59 (C_1), 42.21 (C_3), 32.94 (C_2), 29.10 (C_4), 28.45 (C_5), 27.96 (CH_3); mass spectrum, *m/z* (relative intensity) 170 (2), 159 (7), 145 (14), 144 (16), 141 (39), 128 (15), 127 (100); HRMS calcd for (m – C_4H_8) 144.0786, found 144.0771; CIMS 218 (m + NH_4^+, 5), 201 (m + H^+, 13).

***tert*-Butyl 3-Methylenecyclopentanecarboxylate (25a).** Alcohol **24a** was converted to the corresponding tosylate (92%) and then the iodide (90%) as described in the preparation of **9a**. Physical data for *tert*-butyl 3-((tosyloxy)methyl)cyclopentanecarboxylate: IR 2940, 1710, 1360, 1185, 1170, 1145, 955 cm^{-1}; ^1H NMR δ 7.85–7.15 (m, 4 H), 3.89 (perturbed d, J = 6.5 Hz, 2 H), 2.7–1.2 (m, 20 H, includes at 2.43, s, 3 H and 1.4, s, 9 H); ^{13}C NMR δ 173.58 (CO), 143.51 (CS), 134.03 (C_p), 129.32 (C_o), 127.69 (C_m), 78.99 (CMe_3), 72.71 (CH_2O), 44.16 (C_1), 38.90 (C_3), 32.46 (C_2), 28.83 (C_4), 28.39 (C_5), 27.91 (3 CH_3), 21.35 ($ArCH_3$).

Physical data for *tert*-butyl 3-(iodomethyl)cyclopentanecarboxylate: bp (Kugelrohr) 115 °C (0.5 mm); ^1H NMR ($CDCl_3$) δ 3.18 (perturbed d, J = 6 Hz, 2 H), 2.9–1.6 (m, 8 H), 1.4 (s, 9 H); ^{13}C NMR ($CDCl_3$) δ 174.94 (CO), 79.85 (CMe_3) 44.70 (C_1), 42.91 (C_3), 36.96 (C_2), 32.57 (C_4), 28.99 (C_5), 27.91 (CH_3), 11.93 (CI); mass spectrum, *m/z* (relative intensity) 255 (5), 254 (2), 238 (2), 209 (13), 141 (14), 127 (86), 109 (30), 81 (76), 57 (100); HRMS calcd for (m – C_4H_7) 254.9881, found 254.9885; CIMS 328 (m + NH_4^+, 43), 311 (m + H^+, 30).

tert-Butyl alcohol (2 mL) was added to a stirred suspension of oil-free potassium hydride (400 mg) in DME (200 mL) to prepare a solution of potassium *tert*-butoxide, to which the above iodide (2 g, 6.7 mmol) was added. The mixture was warmed at 40 °C for 30 min by which time all of the starting iodide had been consumed (VPC). The contents were diluted with hexane and washed with water. The crude product was filtered through silica gel with hexane, and evaporation of the solvent left **25** (1.22 g, 65%): ^1H NMR ($CDCl_3$) δ 4.9–4.7 (m, 2 H), 2.8–1.8 (m, 7 H), 1.4 (s, 9 H); ^{13}C NMR ($CDCl_3$) δ 174.62, 150.56, 105.65, 79.81, 45.14, 36.31, 32.09, 29.92, 27.97, which are in accord with the literature data of the corresponding methyl ester.[24]

***tert*-Butyl 1-Methyl-3-methylenecyclopentanecarboxylate (26a).** The lithium enolate of **25** was formed as described above in the preparation of **10b**. In this instance the enolate was quenched with excess methyl iodide to give **26a**: bp (Kugelrohr) 125 °C (15 mm); ^1H NMR ($CDCl_3$) δ 4.8 (m, 2 H), 2.7–1.6 (m, 6 H), 1.42 (s, 9 H), 1.2 (s, 3 H); ^{13}C NMR ($CDCl_3$) δ 174.8 (CO), 150.1 (C_3), 106.1 (=CH_2), 79.85 (CMe_3), 49.81 (C_1), 44.42 (C_2), 36.78 (C_5), 30.99 (C_4), 28.01 (3 CH_3), 23.62 (CH_3), which are in accord with literature data.[24]

***tert*-Butyl 3-(Methoxycarbonyl)cyclohexanecarboxylate (23b).** The diester **22b**[14] (2.7 g, 13.5 mmol) was half-hydrolyzed as described previously,[21] and the derived acid (1.4 g, 7.53 mmol) (56%) was converted to the acid chloride and then to the *tert*-butyl ester **23b** (1.5 g, 82%) as described:[17] IR 2945, 2865, 1735, 1370, 1250, 1150 cm^{-1}; ^1H NMR δ 3.55 (s, 3 H), 2.5–0.9 (m, 19 H, includes at 1.4, s, 9 H); ^{13}C NMR δ 173.74, 172.77, 78.83, 50.82, 43.24, 42.21, 30.94, 28.13, 27.91, 24.71, which is in accord with the literature data for the dimethyl ester.[25]

***tert*-Butyl 3-(Hydroxymethyl)cyclohexanecarboxylate (24b).** The mixed diester **23b** (1.04 g, 4.31 mmol) in dry THF (10 mL) was selectively reduced by LAH (4.5 mmol) as described for **24a**. The crude product was contaminated by a few percent of the diol resulting from the slight excess of reducing agent. Pure **24b** (0.6 g, 68%) was obtained by flash chromatography (silica gel/3:12:2 acetone/CH_2Cl_2/hexane) followed by distillation: bp (Kugelrohr) 111 °C (0.3 mm); IR 3440, 2980, 2935, 2865, 1730, 1365, 1155 cm^{-1}; ^1H NMR δ 3.73 (s, 1 H, OH), 3.27 (perturbed d, J = 5 Hz, 2 H), 2.2–0.8 (m, 19 H, includes at 1.4, s, 9 H); ^{13}C NMR δ 174.34 (C=O), 78.78 (CMe_3), 67.29 (OCH_2), 43.62 (C_1), 39.61 (C_3), 31.76 (C_2), 28.99 (C_4 or C_6), 28.72 (C_4 or C_6), 27.96 (C_5), 24.99 (CH_3); mass spectrum, *m/z* (relative intensity) 159 (3), 141 (20), 123 (5), 95 (32), 81 (7), 67 (9), 57 (100); HRMS calcd for (m – C_4H_7) 159.1021, found 159.1027; CIMS 215 (m + H^+, 21).

***tert*-Butyl 3-Methylenecyclohexanecarboxylate (25b).** Alcohol **24b** (450 mg, 2.10 mmol) was converted to the corresponding tosylate (0.8 g, 98%) and then iodide (0.64 g, 91%) as described in the preparation of **9a**.

Physical data for *tert*-butyl 3-((tosyloxy)methyl)cyclohexanecarboxylate: IR 2975, 2955, 2880, 1725, 1365, 1185, 1175, 1155 cm^{-1}; ^1H NMR δ 7.9–7.2 (sym m, 4 H), 3.77 (perturbed d, J = 5.5 Hz, 2 H), 2.45 (s, 3 H), 2.1–0.8 (m, 19 H, includes at 1.4, s, 9 H); ^{13}C NMR δ 172.99 (C=O), 143.46 (CS), 133.87 (C_p), 129.27 (C_o), 127.70 (C_m), 78.72 (CMe_3) 73.79 (OCH_2), 43.08 (C_1), 36.52 (C_3), 31.05 (C_2), 28.56 (C_4 or C_6), 28.29 (C_4 or C_6), 27.86 (C_5), 24.55 ($ArCH_3$), 21.36 (3 CH_3).

Physical data for *tert*-butyl 3-(iodomethyl)cyclohexanecarboxylate: IR (neat) 2945, 2870, 1720, 1455, 1375, 1270, 1170, 1155 cm^{-1}; ^1H NMR δ 3.1 (d, J = 5 Hz, 2 H), 2.3–0.9 (m, 19 H, includes at 1.4, s, 9 H); ^{13}C NMR ($CDCl_3$) δ 174.77 (CO), 80.02 (CMe_3), 43.99 (C_1), 39.38 (C_3), 35.54 (C_2), 32.78 (C_4), 28.77 (C_6), 28.12 (CH_3), 25.14 (C_5), 14.68 (CI); mass spectrum, *m/z* (relative intensity) 269 (3), 252 (2), 223 (21), 141 (100), 123 (14), 95 (87); HRMS calcd for (m – C_4H_7) 269.0038, found 269.0029; CIMS 342 (m + NH_4^+, 42), 325 (m + H^+, 23). The above iodide was treated with potassium *tert*-butoxide as described above for **25a** and gave, after filtration through silica gel with hexane, the alkene **25b** (97%): IR 3080, 2980, 2940, 2865, 1730, 1655 cm^{-1}; ^1H NMR δ 4.65 (br s, 2 H), 2.6–1.0 (m, 18 H, includes at 1.4, s, 9 H), which is in accord with the literature data for the methyl ester;[26] ^{13}C NMR δ 172.72, 146.45, 108.41, 75.67, 44.70, 37.17, 34.36, 29.54, 27.91, 26.39.

***tert*-Butyl 1-Methyl-3-methylenecyclohexanecarboxylate (26b).** The lithium enolate of **25b** (235 mg, 1.19 mmol) was formed as described above in the preparation of **10b**. In this instance methyl iodide was the alkylating agent. The crude product was a dark red-brown oil (200 mg, 80%), which, when filtered through a short column of silica gel with hexane, furnished pure **26b** (180 mg, 72%) as a colorless oil: IR 3080, 2940, 1725, 1655, 1370, 1165 cm^{-1}; ^1H NMR δ 4.6 (br s, 2 H), 2.6–1.0 (m, 20 H, includes at 1.4, s, 9 H, and 1.1, s, 3 H), which is in accord with the literature data for the methyl ester;[27] ^{13}C NMR δ 174.50, 145.41, 109.17, 78.45, 44.54, 43.78, 34.52.

Typical Kinetic Experiment. Method A. A standard solution of Bu_3SnH containing the substrate (1.1 or <0.1 equiv) and a few milligrams of AIBN, in benzene, was portioned (ca 0.5 mL) into Pyrex ampoules, which were then degassed by repeated freeze–thaw cycles in a vacuum, sealed, and heated in a constant-temperature bath for 0.25–5 h. Reactions at <60 °C were initiated photochemically for 15 min, and hexane solvent was employed for runs carried out at 1.5 °C.

Method B. A septum-sealed Pyrex vial was purged with N_2 and charged with a measured quantity (0.5 mL) of a deoxygenated standard solution of Bu_3SnH in benzene (or hexane for reaction temperatures < 5 °C). The vial was then thermally equilibrated in a constant-temperature bath for 10–20 min before a solution of the substrate and AIBN in benzene (typically 2 μL) such that <0.1 equiv of substrate is injected into the vial and the volume is not changed significantly. The samples were then analyzed by VPC and in some instances by NMR, on larger scale reactions. Where excess Bu_3SnH had been used this was first quenched by the addition of methyl iodide.

Bu_3SnD Experiment. The halides **7a**, **9a**, and **10b** (ca. 0.15 mmol) were treated with Bu_3SnD (1.1 equiv and then made to 0.05 or 0.16 M) using method A.

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(24) Trost, B. M.; Chan, D. M. T. *J. Am. Chem. Soc.* **1983**, *105*, 2315.
(25) James, D. E.; Stille, J. K. *J. Org. Chem.* **1976**, *41*, 1504.
(26) Brown, J. M.; Hall, S. A. *J. Organomet. Chem.* **1985**, *285*, 333.
(27) Nerdel, F.; Frank, D.; Metasch, W.; Gerner, K.; Marschall, H. *Tetrahedron* **1970**, *26*, 1589.