1220, 980, 755, 695 cm^{-1}. Anal. Calcd for $C_{16}H_{16}OS$: C, 74.98; H, 6.29. Found: C, 74.95; H, 6.29.

3-((Phenylthio)methyl)-2,3-dihydrobenzofuran (5g). Benzenethiol (132 mg) and copper powder (170 mg) were added to a stirred mixture of sodium hydride (30 mg) in dry Me_2SO (6.0 mL) at room temperature. After 15 min, when the evolution of hydrogen had ceased, a solution of **4a** (298 mg) in Me_2SO (6.0 mL) was added. The mixture was stirred vigorously for 30 min, by which time the evolution of nitrogen had subsided. The mixture was then diluted with water and extracted 3 times with ether. After the combined extracts had been washed successively with water, 10% aqueous sodium hydroxide solution, and water, they were dried and concentrated. The concentrate was subjected to flash chromatography (15% CH_2Cl_2/petroleum ether) to afford **5g** (155 mg, 53%) as an oil: bp 105 °C (block) (0.1 mm); n^{20}_D 1.6214; MS (relative intensity), m/z 242 (19%, M^+), 124 (44%), 119 (100%), 91 (55%), 77 (24%); ^1H NMR δ 2.7-3.3 (m, 2 H), 3.3-3.8 (m, 1 H), 4.1-4.8 (m, 2 H), 6.6-7.4 (m, 9 H); ^{13}C NMR δ 39.0 (t), 41.7 (d) 76.2 (t), 110.0 (d), 120.7 (d), 124.7 (d), 126.7 (d) 129.1 (d), 129.3 (d), 130.1 (d), 135.8 (s), 160.3 (s); IR 1595, 1585, 1480, 1460, 1230, 965, 750, 695 cm^{-1}. Anal. Calcd for $C_{15}H_{14}OS$: C, 74.36; H, 5.82. Found: C, 74.09; H, 5.91. A similar experiment, carried out without the copper powder, gave identical results.

3-((Butylthio)methyl)-3-methyl-2,3-dihydrobenzofuran (5h). 1-Butanethiol (36 mg) was added to a stirred suspension of sodium hydride (10 mg) in Me_2SO (2.0 mL). After 15 min, a solution of **4b** (105 mg) in Me_2SO (2.0 mL) was added, and the resultant mixture was stirred for a further 10 min. The mixture was worked up as in the previous experiment and was subjected to flash chromatography to give **5h** (39 mg, 41%) as an oil: bp 110 °C (block) (0.1 mm); n^{15}_D 1.5422; MS (relative intensity), m/z 236 (4%, M^+), 134 (14%), 133 (100%), 132 (36%), 105 (57%); ^1H NMR δ 0.7-1.9 (m, 7 H), 2.40 (t, J = 7 Hz, 2 H), 2.70 (s, 2 H), 4.06 and 4.43 (AB q, J_{AB} = 9 Hz, 2 H), 6.5-7.3 (m, 4 H); IR 1610, 1600, 1485, 1460, 1215, 1020, 980, 840, 760 cm^{-1}. Anal. Calcd for $C_{14}H_{20}OS$: C, 71.16; H, 8.53. Found: C, 71.13; H, 8.28.

An experiment identical with the one above, except that copper powder was present (as described in the preparation of **5g**), afforded **5h** in 64% yield. The spectral data and refractive index were identical with those of the sample prepared above.

***S*-((3-Methyl-2,3-dihydrobenzofuran-3-yl)methyl) *O*-Ethyl Dithiocarbonate (5i).** A solution of **4b** (315 mg) in acetone (6.0 mL) was added to a stirred solution of potassium *O*-ethyl dithiocarbonate (240 mg) in acetone (6.0 mL). The evolution of nitrogen was instantaneous. The mixture was stirred for 10 min at room temperature and then was boiled for 3 min under reflux. After the solvent had been removed under reduced pressure from the cooled mixture, ether and water were shaken with the residue. The organic phase was separated and dried. The solvent was then removed, and the resultant oil was subjected to flash chromatography (30% CH_2Cl_2/petroleum ether) to give **5i** (242 mg, 75%) as an oil: n^{26}_D 1.5905; MS (relative intensity), m/z 268 (6%, M^+), 133 (100%), 105 (46%), 91 (13%), 77 (9%); ^1H NMR δ 1.35 (t, J = 7 Hz, 3 H), 1.43 (s, 3 H), 3.46 (s, 2 H), 4.11 and 4.39 (AB q, J_{AB} = 9 Hz, 2 H), 4.53 (q, J = 7 Hz, 2 H), 6.5-7.2 (m, 4 H); ^{13}C NMR δ 13.7 (q), 24.5 (q), 45.7 (t), 46.0 (s), 70.3 (t), 81.7 (t), 110.2 (d), 120.9 (d), 123.2 (d), 129.1 (d), 133.4 (s), 160.6 (s), 177.2 (s); IR 1610, 1595, 1480, 1455, 1220, 1110, 1050, 980, 755 cm^{-1}. Anal. Calcd for $C_{13}H_{16}O_2S_2$: C, 58.20; H, 6.01. Found: C, 58.07; H, 5.58.

(3-Methyl-2,3-dihydrobenzofuran-3-yl)methanethiol (5j). A solution of **5i** (220 mg) in 1,2-diaminomethane (1.5 mL) was stirred under nitrogen overnight at ambient temperature. The mixture was then poured into water and extracted 3 times with ether. After the combined ether extracts had been washed successively with 10% aqueous hydrochloric acid and water, they were dried and concentrated. The resultant oil was purified by flash chromatography (80% CH_2Cl_2/petroleum ether) to afford **5j** as an oil (144 mg, 77%). Although this compound was homogeneous on GLC (column B, 125 °C), ^1H NMR examination indicated that an unidentified minor impurity was present (<20%). Further purification was inefficient, but distillation of a portion, afforded a small analytical sample: bp 110 °C (block) (0.5 mm); MS (relative intensity), m/z 180 (4%, M^+), 133 (61%), 105 (100%), 79 (20%), 77 (30%); ^1H NMR δ 1.23 (t, J = 9 Hz, 1 H), 1.43 (s, 3 H), 2.73 (d, J = 9 Hz, 2 H), 4.14 and 4.51 (AB q, J_{AB} = 9 Hz, 2H), 6.6-7.3 (m, 4 H); IR 2570, 1610, 1600, 1480, 1450, 1225, 1000, 985, 840, 755 cm^{-1}. Anal. Calcd for $C_{10}H_{12}OS$: C, 66.65; H, 6.71. Found: C, 66.65; H, 6.67.

Registry No. 4a, 25125-40-0; **4b**, 56182-25-3; **5a**, 78739-85-2; **5b**, 78739-86-3; **5c**, 78739-87-4; **5d**, 78739-88-5; **5e**, 78739-90-9; **5g**, 103304-48-9; **5h**, 78739-89-6; **5i**, 103304-49-0; **5j**, 103304-50-3; BuSH, 109-79-5; EtOC(S)SK, 140-89-6; $H_2NCH_2CH_2NH_2$, 107-15-3.

Formation of Some Bi- and Tricyclic Systems by Radical Ring Closure[1]

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Contribution from the Research School of Chemistry, Australian National University, Canberra, A.C.T. 2601, Australia. *Received March 6, 1986*

Abstract: Reductive alkylation of methyl benzoate with 1,3-dibromopropane affords a (bromopropyl)cyclohexadiene **3a** treatment of which with tributylstannane gives the hydroindane derivative **4a** via ring closure of the radical **25**. Similar reactions of suitable substituted dienes (e.g., **3b,c**), dienones (e.g., **23**), and related compounds (e.g., **14**) with tributylstannane or tributylgermane give mixtures of cyclized products the relative amounts of which allow the effects of substituents on the rate of cyclization to be determined. The results show that vinylic substituents at the seat of attack (α-substituents) strongly retard addition, that the β-methyl substituent in **6b** is weakly activating, that the β-methoxy substituents in **6** and **12** have a negligible effect, and that dienone radicals (e.g., **31**) are much more reactive than the corresponding diene radicals (e.g., **25**). The rate constants, k_c, for ring closure and activation parameters were determined by comparison with k_H the rate constant for reaction of alkyl radicals with tributylstannane. Captodative stabilization of the product radical **43** has only a small rate-enhancing effect on cyclization of the radical **32**, containing both methoxy and carbonyl groups.

Numerous recent examples[2,3] have illustrated the increasing importance of free radical methods in synthetic chemistry. Ring formation by intramolecular homolytic addition[3-5] has attracted particular interest since it can often be carried out efficiently under mild conditions and with such chemoselectivity that the use of protecting groups is minimized. Furthermore, cyclization fre-

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(1) For a preliminary account of this work, see: Beckwith, A. L. J.; O'Shea, D. M.; Roberts, D. H. *J. Chem. Soc., Chem. Commun.* **1983**, 1445-1446.

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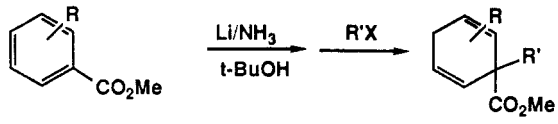
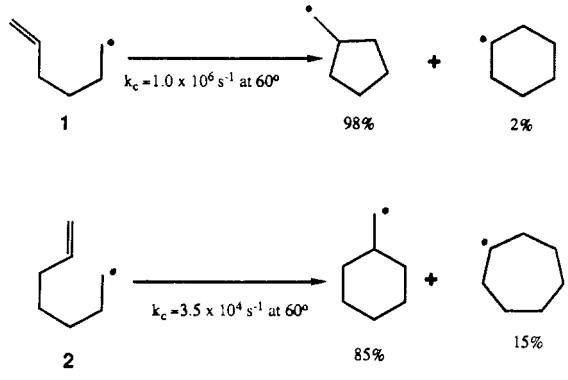
Scheme I



quently occurs with high, predictable, regio- and stereoselectivity.[4-6]

Much of the foundation for these synthetic applications was laid by fundamental work on the ring closure of simple ω-alkenyl radicals.[4-7] Cyclization of 5-hexen-1-yl radical (**1**), which proceeds mainly in the exo mode[6] to afford cyclopentylmethyl radical, is one of the most thoroughly scrutinized and most accurately kinetically defined[8] organic radical processes. This reaction is now widely employed as a mechanistic probe and kinetic yardstick; it is the best known of the radical "clocks".[9] Ring closure of hept-6-en-1-yl radical (**2**) is considerably slower at ordinary temperatures than that of its lower homologue (**1**) and is less selective giving some 15% of the endo product.[10] Nevertheless, under favorable circumstances such as those described below, the heptenyl system can afford good yields of cyclic products.



In the present work we have examined the application of radical ring closure methodology to the synthesis of a variety of substituted decalins, hydroindanes, and related compounds. Our aim was to illuminate those special features of kinetics, regiochemistry, and stereochemistry that pertain to the formation of bi- or tricyclic systems and hence to lay the groundwork for the synthesis of complex systems by radical ring closure. In pursuing these goals we have examined the stereochemical and regiochemical course of ring closure of 15 suitably constituted radicals and have determined the kinetics, including Arrhenius parameters, of many of them, thereby calibrating a range of new radical clocks. Finally, we have uncovered some interesting new radical transformations and have examined the effect of captodative stabilization[11] on the rate of radical ring closure.

Results and Discussion

Precursors. The 15 compounds used as radical precursors were all synthesized expeditiously by Birch reductive alkylation of suitable aromatic esters (Scheme I). Good results were obtained with esters containing ortho or meta alkyl or alkoxy substituents, but the reaction fails with para-substituted compounds. Initially, alkylations were conducted with the tetrahydropyranyl ether of 3-iodopropanol (Scheme I, R′ = $CH_2CH_2CH_2OTHP$) to give a product which could be readily converted into radical precursors by standard procedures. However, we later found it faster and more convenient to use either 1,4-dibromobutane or 1,3-dibromopropane [Scheme I, R′ = $(CH_2)_3Br$ or $(CH_2)_4Br$] in excess as the alkylating agent. Disubstitution sometimes occurred to a relatively small extent (up to 10%). Neverthless, the required radical precursors were readily purified and isolated in yields of 40–80%. Although they are thermally stable, the substituted cyclohexadienes are very suceptible to autoxidation because of their biallylic structure and are best stored in solution under an argon atmosphere at <0 °C. In the presence of air they are rapidly converted into aromatic esters and 4-ketocyclohexadienes. Mechanistic features of this reaction will appear elsewhere.[12]

The cyclohexadienones **9a**, **9c**, and **23** were conveniently prepared by oxidation of the corresponding dienes with chromium trioxide/dimethylpyrazole,[13] while the aldehyde **18** was obtained by oxidation of the corresponding alcohol with pyridinium chlorochromate.[14] Other compounds were prepared by standard methods.

Products. Table I shows the nature and yield of cyclic products formed when each of the precursors was heated in degassed benzene with tributylstannane (ca. 0.05 M). Reaction mixtures were treated with 10% potassium fluoride solution to remove tin compounds,[15] and products were separated and isolated by flash chromatography. In some cases the relative amounts of epimers were estimated by NMR spectroscopy.

The data in Table I show that under these conditions the reaction affords solely cyclized products in good total yield. Uncyclized products are obtained only when higher concentrations of stannane are used (see below).

The stereochemistry of the newly formed ring junction was rigorously determined in two cases. Hydrogenation and hydrolysis of **4a** gave a product identical with authentic *cis*-biscyclo[4.3.0]nonane-1-carboxylic acid,[16] while hydrogenation of **21** gave methyl *cis*-decalin-9-carboxylate. The cis stereochemistry of the ring junction in each of the other products was assigned on the basis of the similarity of their NMR spectra to those of **4a** and **21** and because MM2 force-field calculations show the strain energy of the transition structure for the cis ring closures to be markedly less than those for their trans counterparts.[7]

A noteworthy feature of these ring closures is their high regioselectivity. Each of the compounds containing the hex-5-en-1-yl system gave exclusively the product or products of 1,5-cyclization and no trace of 1,6-cyclization products could be detected. The compound (**20**) containing the hept-6-en-1-yl system gave a minor product tentatively assigned the structure **22** arising from endo cyclization, but when a carbonyl group was incorporated in the molecule **23** only the exo-cyclization product **24** was obtained.

(2) See inter alia: Barton, D. H. R.; Crich, D.; Motherwell, W. B. *Tetrahedron* **1985**, *41*, 3901–3924. Giese, B.; Horler, H. *Ibid.* **1985**, *41*, 4025–4038. Bunnett, J. F.; Mitchell, E.; Galli, C. *Ibid.* **1985**, *41*, 4119–4132. Palacios, S. M.; Alonso, R. A.; Rossi, R. A. *Ibid.* **1985**, *41*, 4147–4156. Baldwin, J. E.; Adlington, R. M.; Basak, A. *J. Chem. Soc., Chem. Commun.* **1984**, 1284.

(3) For recent examples of ring formation, see: Curran, D. P.; Rakiewicz, D. M. *Tetrahedron* **1985**, *41*, 3943–3958. Choi, J. K.; Hart, D. J. *Ibid.* **1985**, *41*, 3959–3972. Beckwith, A. L. J.; Roberts, D. H.; Schiesser, C. H.; Wallner, A. *Tetrahedron Lett.* **1985**, *26*, 3349–3352. Beckwith, A. L. J.; Boate, D. R. *Ibid.* **1985**, *26*, 1761–1764. Bachi, M. D.; Frolow, F.; Hoornaert, C. *J. Org. Chem.* **1983**, *48*, 1841–1849. Angoh, A. G.; Clive, D. L. J. *J. Chem. Soc., Chem. Commun.* **1985**, 980–982; Stork, G.; Kaku, M. *J. Am. Chem. Soc.* **1985**, *107*, 500–501. Moeller, K. D.; Little, R. D. *Tetahedron Lett.* **1985**, *26*, 3417–3420. Franz, J. A.; Barrows, R. D.; Camaioni, D. M. *J. Am. Chem. Soc.* **1984**, *106*, 3964–3967; Corey, E. J.; Pine, S. G. *Tetrahedron Lett.* **1983**, *24*, 2821–2824.

(4) For recent reviews, see: Surzur, J.-M. In *Reactive Intermediates*; Abramovitch, A. A., Ed.; Plenum: New York, 1981; Vol. 2, pp 121–295. Beckwith, A. L. J.; Ingold, K. U. In *Rearrangements of Ground and Excited States*; de Mayo, P., Ed.; Academic Press: New York, 1980; Vol. 1, pp 161–310. Hart, D. J. *Science (Washington, D.C.)* **1984**, *223*, 883.

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(6) Beckwith, A. L. J.; Easton, C. J.; Serelis, A. K. *J. Chem. Soc., Chem. Commun.* **1980**, 482–483.

(7) Beckwith, A. L. J.; Schiesser, C. H. *Tetrahedron Lett.* **1985**, *26*, 375–378; *Tetrahedron* **1985**, *41*, 3925–3942.

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(10) Beckwith, A. L. J.; Moad, G. *J. Chem. Soc., Chem. Commun.* **1974**, 472–473.

(11) Viehe, H. G.; Janousek, Z.; Merenyi, R.; Stella, L. *Acc. Chem. Res.* **1985**, *18*, 148–154 and references cited.

(12) Beckwith, A. L. J.; Roberts, D. H. *J. Am. Chem. Soc.*, in press.

(13) Salmond, W. G.; Barta, M. A.; Havens, J. L. *J. Org. Chem.* **1978**, *43*, 2057–2059.

(14) Corey, E. J.; Suggs, J. W. *Tetrahedron Lett.* **1975**, *16*, 2647–2650.

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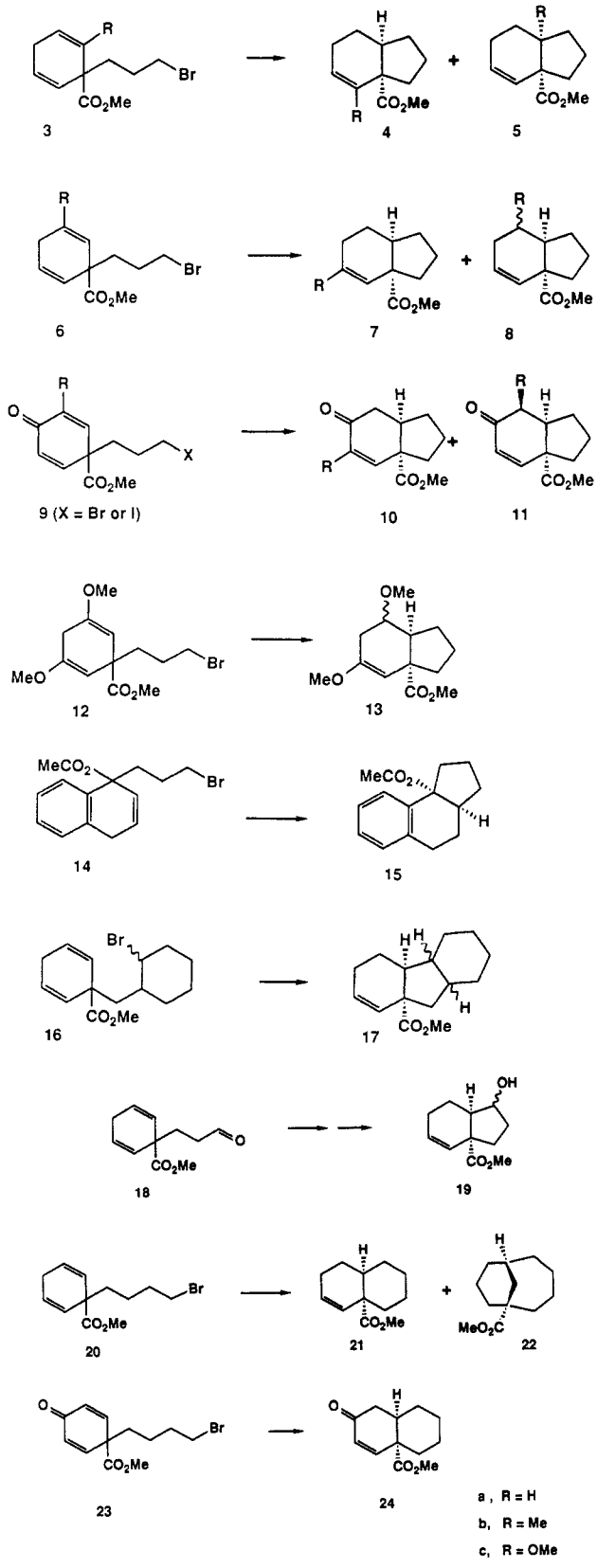


This result illustrates the powerful activating effect of the carbonyl group on homolytic addition, further evidence for which is outlined in the kinetics section below.

When the cyclohexadiene moiety bears a substituent at the 2-position (compounds **3b,c**) the reaction shows very high preference for ring closure onto the unsubstituted olefinic bond, but this is not so for the 3-monosubstituted systems (**6b,c**) when all three possible exo-cyclization products are formed. In these cases the stereochemistry of the epimers of **8b,c** was assigned on the

Table I. Yields of Products from Radical Cyclizations[a]

precursor	product	rel yield, %	total yield, %
3a	**4a**	100	96
3b	**4b**	97	85
	5b	3	
3c	**4c**	>97	92
	5c	<3	
6b	**7b**	32	80
	8b (β-Me)	54	
	8b (α-Me)	14	
6c	**7c**	48	89
	8c (β-OMe)	39	
	8c (α-OMe)	13	
9a (X = I)	**10a**	100	81
9c (X = Br)	**10c**	42	65
	11c	58	
12	**13** (β-OMe)	74	60
	13 (α-OMe)	26	
14	**15**	100	97
16	**17** (cis,anti,cis)[b]	60	92
	17 (cis,syn,cis)[b]	24	
	17 (cis,anti,trans)[b]	16	
18	**19** (β-OH)	55	90
	19 (α-OH)	45	
20	**21**	85	79
	22	15	
23	**24**	100	76

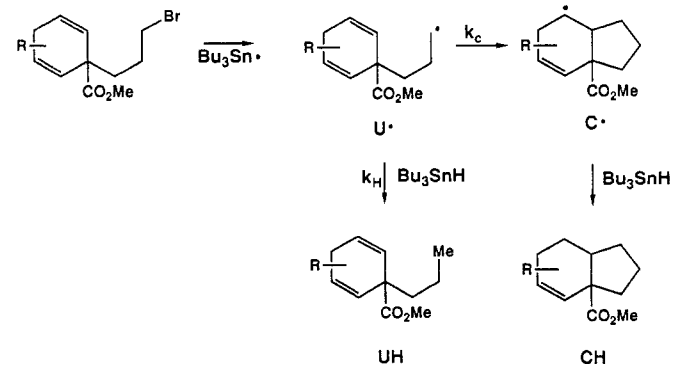
[a] Typical reaction conditions: AIBN/precursor/Bu_3SnH (ca. 0.05 M in benzene) = 0.01/1.0/1.2 at 80 °C for 12 h. [b] Tentative assignment of stereochemistry based on MM2 calculations.[7]

Table II. Kinetic Data for Ring Closure onto the Unsubstituted Double Bond of Cyclohexadienylalkyl Radicals and Related Species

precursor	radical	product[a]	k_c(70 °C), s^{-1}	log A	E, kcal·mol^{-1}
b	**1**	methylcyclopentane	1.0×10^6	10.4	6.9
b	**34**	1,2,2-trimethylcyclopentane	1.3×10^7	10.5	5.5
3a	**25**[c]	**4a**	4.1×10^6	10.5 ± 0.3	6.1 ± 0.4
3b	**29**	**4b**	4.5×10^6	ca. 10.5[d]	ca. 6.0[d]
3c	**30**	**4c**	4.4×10^6	ca. 10.5[d]	ca. 6.0[d]
6b	**26**	**7b**	4×10^6	ca. 10.5[d]	ca. 6.0[d]
6c	**27**	**7c**	3.8×10^6	ca. 10.5[d]	ca. 6.0[d]
14	**33**	**15**	4.2×10^6	ca. 10.5[d]	ca. 6.0[d]
9a (X = I)	**31**[c]	**10a**	1.6×10^8	10.5 ± 0.4	3.6 ± 0.6
e	**2**	methylcyclohexane	2.9×10^4	9.5	7.9
20	**35**[c]	**21**	5.8×10^3	9.5 ± 0.4	9.0 ± 0.5
23	**36**[c]	**24**	2.5×10^6	9.4 ± 0.2	4.7 ± 0.2

[a] Products formed by reaction of cyclized radicals with tributylstannane. [b] Data from ref 19. [c] A statistical correction has been applied to data for this radical (see text). [d] These radicals gave scattered data, but within experimental error the kinetic parameters are the same as those for radical **25**. [e] Data from ref 10.

Scheme II



assumption that approach of tributylstannane to the intermediate radicals would occur most readily from the exo face and that the

Table III. Effect of Substituents on Rate of Ring Closure

precursor	radical	substituent	rel rate (70 °C)	k_c (70 °C), s^{-1}
3a	25	H	1.0	4.1×10^6
3b	29	2-Me	0.04	1.4×10^5
3c	30	2-OMe	0.09	3.7×10^5
6b	26	3-Me	1.7	7×10^6
6c	27	3-OMe	0.93	3.8×10^6
12	28	3-OMe	0.95	3.9×10^6

major products would consequently contain the substituents in the orientation trans to the carboxymethyl group. The stereochemistry of the product (**13**) obtained from the dimethoxy compound **12** was similarly assigned. Surprisingly, the methoxy ketone **9** (X = Br) gave only one (**11c**) of the stereoisomers of the cyclized product. Its structure was assigned to it on the basis of its NMR spectrum.

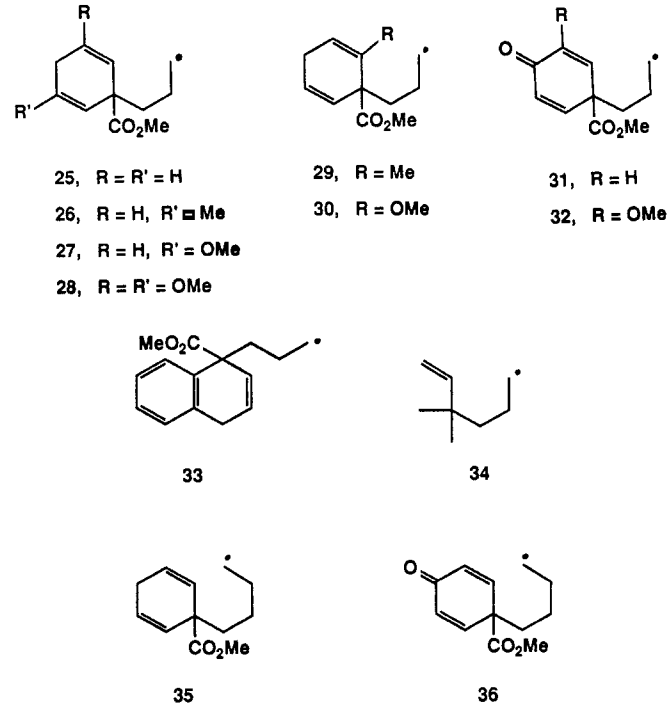
The utility of the method for construction of tricyclic systems was demonstrated by the formation of **15** in high yield from the precursor **14**, readily derived from 1-naphthoic acid. Treatment of the mixture of epimeric bromides **16** with tributylstannane in the usual way gave three isomers of the tricyclic product **17**. The stereochemistry tentatively assigned to them is consistent with the formation of a new cis ring junction as occurs in all of these reactions and is supported by MM2 force-field calculations.[7]

Kinetics. The reaction of tributylstannane with each of the compounds listed in Table I is believed to follow the general mechanism adumbrated in Scheme II which shows that the initially generated radical, U•, is partitioned between ring closure leading via C• to the cyclized product, CH, and direct formation of the uncyclized product, UH, by hydrogen atom transfer from stannane. In most cases the reaction was conducted with a large excess of stannane under which conditions $k_c/k_H = [CH]_f[S]/[UH]_f$ where $[CH]_f$ and $[UH]_f$ represent final concentrations of cyclized and uncyclized products, respectively, and [S] is the concentration of stannane. However, preliminary experiments showed that products derived from the cyclohexadienones **9** and **23** reacted slowly with tributylstannane by addition of $Bu_3Sn^•$ to the α,β-unsaturated carbonyl system (see below). Accordingly, kinetic experiments with these compounds were conducted with a slight deficiency of stannane, and values of k_c were obtained by an iterative method based on the appropriate integrated rate equation.[10]

To obtain values of k_c from k_c/k_H we noted previous evidence[8,17] that the rate of reaction of alkyl radicals with tributylstannane is relatively insensitive to radical structure and assumed that all of the primary radicals studied here will have the same reactivity as butyl radical,[8] e.g., $\log k_H = (9.07 - 3.69)/\theta$, where k_H is the rate constant for hydrogen transfer from stannane to alkyl radical and $\theta = 2.3RT$ kcal·mol^{-1}.

Representative analytical data obtained from the kinetic runs are given in the Experimental Section, while values of rate constants are given in Tables II and III. Because of the difficulty of obtaining completely resolved gas chromatograms from some of the reaction mixtures, Arrhenius plots of rate constants showed considerable scatter and gave variable results. Eventually, we decided to concentrate on a few key compounds which were carefully studied over a very wide temperature range (0–150 °C). The resultant values for the Arrhenius parameters are given in Table II. For convenient comparison with data for simple acyclic systems the values of k_c for symmetrical radicals (e.g., **25**, **28**, and **31**) have been halved to give k_c *per double bond*. Likewise the corresponding values of log A have been reduced by log 2.

The data in Tables II and III show that the values of k_c for ring closure of the cyclohexadienylpropyl radical **25** and related species are greater than that for 1,5-ring closure of hex-5-enyl radical (**1**). This is undoubtedly because of the "*gem*-dimethyl" effect[18] of the substituents at the 4-position in the hexenyl system



of **25**, which raise its ground-state energy relative to that of the unsubstituted radical **1**. As expected on these grounds the increase in rate is almost completely due to a lowering of the activation energy. It is not so low, however, as that for ring closure of 4,4-dimethylhex-5-enyl radical (**34**),[19] nor is the rate constant so large. Presumably a 4-methyl group in **34** has larger gauche interactions than the ring vinyl substituent in the equivalent position of **25**.

Unlike its lower homologue **25**, the radical **35** containing a 6-heptenyl system undergoes ring closure more slowly than its simple acyclic analogue **2**. In this case it appears that other factors outweigh the rate enhancement expected from the "*gem*-dimethyl" effect. Inspection of models and MM2 calculations[7] suggest that in the transition structure for ring closure of **35** there is a serious steric interaction between one of the protons on C-3 of the side chain and a vinylic proton on the double bond not undergoing attack.

Interestingly, the value of the rate constants for ring closure per double bond of **25** and **28** are similar to each other and to the values (in Table II) for ring closure onto the unsubstituted double bond in the unsymmetrical radicals, **26**, **27**, **29**, and **30**. We conclude that substitution of one double bond has little effect on the reactivity of the other; i.e., each double bond behaves as though it were an isolated system. This observation is relevant to the suggestion[20] that the double bonds in 1,4-dienes may, under some circumstances, experience mutual through-bond and through-space interactions.

As expected, incorporation of a carbonyl group into the cyclohexadienyl system as in radicals **31** and **36** causes a substantial increase in the rate of ring closure. The Arrhenius data show this increase, of the order of 40-fold, to be associated with a significant lowering of the activation energy. This probably reflects the lower energy of the π^* orbital (LUMO) of an α,β-unsaturated ketone by comparison with that of an isolated double bond.

Ring closures of the radicals **25** and **31** are important additions to the "horlogerie" of radical clocks[9] available as kinetic and mechanistic probes. They are readily generated from easily obtainable precursors, and they cyclize at convenient rates. In particular ring closure of **31** with a total value of k_c of 3×10^8 s^{-1} at 70 °C appears to be one of the most rapid of the 5-exo clocks.

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(19) Beckwith, A. L. J.; Easton, C. J.; Lawrence, T.; Serelis, A. K. *Aust. J. Chem.* **1983**, *36*, 545–556.
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Indeed, its rate approaches that of cyclopropylmethyl radical ring opening ($k = 5 \times 10^8$ s^{-1} at 70 °C),[21] but it has the distinct advantage of being irreversible.

Substituent Effects. The radicals **26**, **27**, **29**, and **30** are of special interest because they allow direct determination by internal competition of the effect of substituents on the rate of ring closure. In each of these species one double bond is unsubstituted while the other bears one substituent. Since the cyclized radicals are converted quantitatively into products, the ratio of their yields, (substituted %)/(unsubstituted %) gives the ratio of rate constants, k(sub)/k(unsub). There are then two procedures by which absolute values can be obtained. One is to use the normal method to determine $\sum k_c/k_H$ and hence the value of k(sub) + k(unsub) from which, together with the ratio of products, the individual values of each can be determined. Table III lists values of k(sub) obtained in this way.

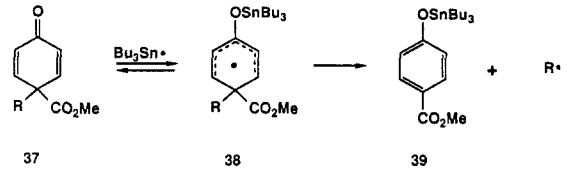
The other is to assume that k(unsub) has the same value for each radical and that the apparent small variations recorded in Table II represent experimental error. If we assume that k(unsub) = 4.3×10^6 s^{-1} at 70 °C, the values of k(sub) can then be determined directly from the ratio of products. Qualitatively, both methods lead to the same conclusions.

The data in Table III for radicals **29** and **30** accord with previous evidence[5,22] that substituents at the seat of attack retard the rate of alkyl radical addition to olefins, both inter- and intramolecularly. Steric blocking is probably the dominant factor.[7] We believe that the difference in experimental rate constants for ring closure onto the substituted double bonds of **29** and of **30** is real and reflects mainly the difference in effective size between the methyl and methoxy substituents. Nevertheless, it is probable that electronic effects make a less significant but, at this stage, indeterminate contribution.

The substituents at the remote termini of the double bonds in **26**–**28** have a less dramatic effect. Indeed, within experimental error the methoxy group neither retards nor enhances the rate of ring closure. Since the radicals initially formed by ring closure of **28** or to the substituted double bond of **27** are undoubtedly stabilized by interaction of the unpaired electron with the adjacent oxygen lone pair, these data reinforce the view[4-7] that the relative rates of homolytic processes cannot be deduced from simple thermochemical data. Possibly the activating effect expected to arise from stabilization of the product radical by the methoxy group is nullified by its electron donation to the π system which retards interaction with nucleophilic alkyl radicals.

The methyl group in radical **26** weakly enhances the rate of ring closure. In this case, when polar effects are minimal, the increase in rate probably does reflect the favorable effect of the substituent on the stability of the product radical.

Interaction of Germanium- and Tin-Centered Radicals with (Haloalkyl)cyclohexadienones. When the (bromoalkyl)cyclohexadienones **9a** (X = Br), **9c** (X = Br), and **23** were heated with tributylstannane in degassed benzene, major amounts of aromatic esters were formed. Thus **9a** (X = Br) and **23** gave methyl *p*-hydroxybenzoate in yields of 40% and 36%, respectively, while **9c** (X = Br) gave 35% of methyl 4-hydroxy-3-methoxybenzoate. In each case the only other product was the desired bicyclic ketone (**10a**, **10c**, **11c**, or **24**). These results indicate that addition of tributyltin radicals to the carbonyl oxygen of the cyclohexadienone system occurs sufficiently rapidly to compete effectively with S_H2 attack on bromine. The adducts (e.g., **38**) so formed then undergo



37 38 39

β-fission in a step formally the reverse of the first step of aromatic homolytic *cine* substitution to form the stannyl ether of the aromatic ester (e.g., **39**) and a bromoalkyl radical which propagates the chain in the usual way by reaction with stannane. In accord with this mechanism generation of tributyltin radicals in the presence of the cyclohexadienone **37** (R = Me) in the ESR cavity gave a strong signal consistent in g value (2.0028) and multiplicity [a(2 H) 8.5, a(2 H) 2.2 G] with that expected for the adduct **38** (R = Me).

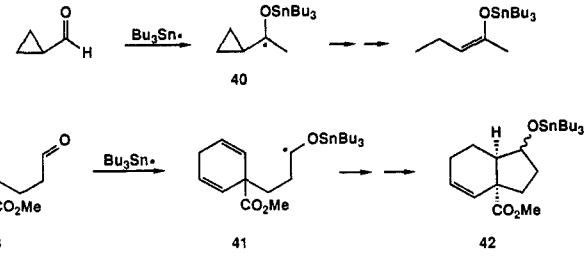
The formation of adducts between tributyltin radicals and (bromoalkyl)cyclohexadienones was not unexpected, for although typical rate constants for reaction with simple ketones ($k \approx 10^5$ M^{-1}·s^{-1} at 25 °C) are considerably less than those for S_H2 attack on bromine ($k \approx 10^7$ M^{-1}·s^{-1} at 25 °C), that for addition to duroquinone is greater ($k \approx 1 \times 10^9$ M^{-1}·s^{-1}).[23] It appears that the cyclohexadienones used here resemble quinones in reactivity presumably because of the presence of the extended π system.

In order to overcome this problem, iodine was substituted for bromine in the substrates. Since iodides have been shown previously to react with tributyltin radicals about 100 times more rapidly than corresponding bromides,[23] we expected that adduct formation would no longer compete effectively with halogen transfer. In fact, when the iodides **9a** (X = I) and **9c** (X = I) were treated in the usual way with 1 molar equiv of tributylstannane they each gave more than 95% of the expected cyclized product.

Alternatively, tributylgermanium could be used in place of tributyltin. In accord with recent results[23,24] indicating that tributylgermanium radicals react a little more rapidly than tributyltin radicals with bromides, but less rapidly with ketones, treatment of the bromides **9a**, **9c** (X = Br), and **23** with tributylgermanium hydride gave less than 5% of aromatic esters.

Ring Closure of a (Stannyloxy)alkyl Radical. Although simple aliphatic carbonyl compounds are relatively inert toward attack by tributyltin radicals, it is sometimes possible to induce homolytic rearrangements in suitably constituted aldehydes and ketones by treatment with tributylstannane. Cyclopropanecarboxaldehyde, for example, is converted in this way into ring-opened products via β-fission of the stannyloxy radical **40**.[25]

We have now observed that the aldehyde **18** upon heating with tributylstannane in the usual way is converted in 90% yield into an approximately equimolar mixture of the epimers of the tin alkoxide **42**. Hydrolysis of the product affords the corresponding alcohols **19**. The reaction undoubtedly involves ring closure of the radical **41**.



At present we are unable to obtain values of the rate constants for formation of **41** or for its ring closure. However, the fact that the reaction proceeds more slowly than those of halides such as **3a** and requires more initiator to go to completion suggests that either or both of these rate constants has a relatively low value or that the formation of **41** is rapidly reversible.

Effect of Captodative Stabilization. The captodative effect[11] is the synergistic stabilization of a radical center flanked by both an electron-accepting and an electron-donating substituent. Although substituents of either type are well-known to interact

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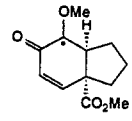
(24) Beckwith, A. L. J.; Pigou, P. E. *Aust. J. Chem.* **1986**.
(25) Castaing, M.; Pereyre, M.; Ratier, M.; Blum, P. M.; Davies, A. G. *J. Chem. Soc., Perkin Trans. 2* **1979**, 589–592 and references cited. See also: Beckwith, A. L. J.; Moad, G. *Ibid.* **1980**, 1473–1482.

conjugatively with an adjacent unpaired electron, it has been suggested that when both types operate simultaneously on a radical center an extended π system is created which bestows stabilization greater than would be expected from the sum of the two individual effects. There has been extensive debate about the magnitude of captodative stabilization and its effect on reactivity.

The methoxy ketone **9c** (X = Br or I) affords the opportunity to examine the effect of captodative stabilization of the product radical on the rate of cyclization. Ring closure of the radical **32** derived from **9c** (X = Br) can give either the acyl stabilized radical **44** or the captodative radical **43**. Since the data for radicals **27**



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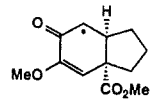

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and **28** show that a β-methoxy substituent of itself has a negligible effect on the rate of 5-exo ring closure, any regiopreference displayed in the cyclization of **32** must be ascribed to captodative stabilization of the radical product.

Oxidation[13] of the methoxycyclohexadiene **6c** gave **9c** (X = Br), which was treated with tributylgermane in the usual way. The ratio of yields of the two products **10c** and **11c** was 1.0:1.4; i.e., the rate of cyclization onto the more substituted double bond is about 40% greater than would have been expected from simple addition of the rates for radicals containing a single methoxy substituent or a single acyl substituent. Clearly, captodative stabilization of the radical **43** has only a minor effect on its rate of formation. It might be argued that the transition state for radical addition is very reactant-like, and its energy, therefore, will reflect only to a minor degree the extent of stabilization of the product. This argument, however, appears to fail when applied to radicals such as **31** in which the presence of the carbonyl group causes a very large rate enhancement by comparison with those from which it is absent.

It is not possible, therefore, to draw firm conclusions about the magnitude of captodative stabilization of the radical **43**. What is clear is that it has a minor effect on the chemical reactivity of the radical **32**. Very similar effects have recently been recorded[26] for the effect of captodative stabilization on the rates of ring closure of some appropriately substituted simple hexenyl radicals.

Conclusion. The results presented above show that compounds such as **3a** and **23**, readily prepared by reductive alkylation of aromatic esters, give good yields of cyclized products when treated with tributylstannane or tributylgermane. The nature and relative yields of such products illustrate the high degree of stereo- and regioselectivity attainable in the formation of bi- and tricyclic systems by radical ring closure. They also reflect substituent effects on the rates of intermolecular homolytic addition processes. By and large the results are similar to those previously recorded for intermolecular addition.[27] They indicate that substituents at the seat of attack strongly retard addition, that β-alkyl or β-alkoxy substituents are weakly activating, and that a β-acyl substituent powerfully increases the rate of addition. However, captodative stabilization of the product radical has little kinetic effect.

Experimental Section

GLC analyses were carried out on a Varian 6000 chromatograph equipped with either a 25-m SE-30 microbore fused silica column or a 30-m SE-30 SCOT column. Chromatograms were recorded and integrated on a HP 3390A electronic integrator. Proton and carbon-13 NMR spectra were recorded on a JEOL FX200 spectrometer at 200 and 50 MHz, respectively. Tetrahydrofuran was freshly distilled from sodium metal. Benzene was washed with sulfuric acid and with water, then dried, distilled, and stored over molecular sieve. *tert*-Butyl alcohol was dried over anhydrous Na_2CO_3. Tributyltin hydride (Aldrich) was stored under nitrogen in the freezer. Tributylgermanium hydride, prepared by LAH reduction of Bu_3GeI,[28] was similarly stored and handled. Merck Kieselgel 60 was used for flash chromatography and Merck LiChroprep Si60 columns were used for HPLC separations.

Reductive Alkylation: General Procedure. A solution of methyl arenecarboxylate (8.0 mmol) and 600 mg (8.1 mmol) of *tert*-butyl alcohol in 10 mL of dry THF was cooled to −78 °C, and 60 mL of liquid ammonia was added by distillation from sodamide. While the mixture was vigorously stirred, 120 mg (17.3 mmol) of lithium metal cut into small pieces was added in one portion. The lithium rapidly dissolved, and after about 10 min, when reduction was complete, a persistent dark blue color was formed. Alkyl halide dissolved in an equal volume of THF was then added in one portion. For monohalides, 1 equiv (8.1 mmol) was used, and for di-halides, 2.5 equiv (20 mmol) were used. Immediately after the addition the solution became yellow. After 20 min the cooling bath was removed and the mixture was allowed to warm up. When the ammonia had evaporated, the residue was concentrated in a rotary evaporator and then diluted with 50 mL of ether and with water. The ether layer was washed with brine, dried (Na_2SO_4), and evaporated to afford the crude product, which was usually purified by flash chromatography using 10% ethyl acetate in hexane as elutant.

Methyl 1-(3-Bromopropyl)cyclohexa-2,5-diene-1-carboxylate (3a). Alkylation of methyl benzoate (1.0 g) with 1,3-dibromopropane as described above gave 1.36 g (72%) of **3a** as a clear oil: ^{1}H NMR ($CDCl_3$) δ 1.8 (m, 4 H), 2.6 (br s, 2 H), 3.4 (m, 2 H), 3.7 (s, 3 H), 5.7 (dt, 2 H), 5.9 (dt, 2 H); ^{13}C NMR ($CDCl_3$) δ 26.10, 27.94, 37.78, 47.5, 52.24, 126.29 (2 C), 126.67 (the carbonyl carbon resonance was not detected). Anal. Calcd for $C_{11}H_{15}O_2Br$: C, 50.98; H, 5.83. Found: C, 51.25; H, 5.82.

Methyl 1-(3-Bromopropyl)-4-ketocyclohexa-2,5-diene-1-carboxylate (9a, X = Br). 3,5-Dimethylpyrazole (2.24 g, 23.3 mmol) was added in one portion with stirring to a cold (−20 °C) suspension of 2.33 g (23.3 mmol) of dry chromium trioxide in 20 mL of dichloromethane.[13] After the solution had been stirred at −20 °C for 10 min, 603 mg (2.33 mmol) of **3a** was added, and the mixture was kept at −20 °C for 30 min. Sodium hydroxide solution (10 mL, 5 N) was then added and the mixture was stirred at 0 °C for 1 h. After addition of ether and water, the organic layer was separated, washed, dried, and evaporated. Flash chromatography of the residue gave **9a** (X = Br) as a pale yellow oil: ^{1}H NMR ($CDCl_3$) δ 1.65–1.85 (m, 2 H), 2.1–2.25 (m, 2 H), 3.35 (t, 2 H), 3.77 (s, 3 H), 6.4 (d, 2 H), 7.0 (d, 2 H); ^{13}C NMR ($CDCl_3$) δ 27.30, 32.47, 36.50, 51.71 (q), 53.26, 130.67 (2C), 147.22 (2C), 170.44, 184.74; exact mass calcd for $C_{11}H_{13}O_3Br$ 272.0054, found 272.0048.

Methyl 1-(3-Iodopropyl)-4-ketocyclohexa-2,5-diene-1-carboxylate (9a, X = I). A solution of 30 mg of the bromide **9a** (X = Br) and an excess of sodium iodide in 3 mL of dry acetone was refluxed under nitrogen for 15 h, then cooled, and diluted with ether and water. The ether layer was washed with brine, dried, and evaporated to give 32 mg (91%) of the iodide **9a** (X = I) as a pale yellow oil: ^{1}H NMR ($CDCl_3$) δ 1.6–1.8 (m, 2 H), 2.0–2.2 (m, 2 H), 3.13 (t, 2 H), 3.77 (s, 3 H), 6.4 (d, 2 H), 7.0 (d, 2 H). Exact mass calcd for $C_{11}H_{13}O_3I$ 319.9909, found 319.9917.

Methyl 1-(3-Bromopropyl)-2-methylcyclohexa-2,5-diene-1-carboxylate (3b). Alkylation of 1.0 g of methyl *o*-toluate with 1,3-dibromopropane gave 1.0 g (55%) of **3b** as a clear oil: ^{1}H NMR ($CDCl_3$) δ 1.5–1.9 (m, 3 H), 1.7 (s, 3 H), 2.1 (m, 1 H), 2.5–2.8 (m, 2 H), 3.4 (m, 2 H), 3.7 (s, 3 H), 5.4 (d, 1 H), 5.7 (s, 1 H), 5.9 (dt, 1 H): ^{13}C NMR ($CDCl_3$) δ 19.59, 26.89, 27.74, 33.17, 33.96, 52.35, 123.63, 126.67, 127.10, 130.52 (quaternary and carbonyl carbons were not detected). Anal. Calcd for $C_{12}H_{17}O_2Br$: C, 52.76; H, 6.27. Found: C, 52.58; H, 6.10.

Methyl 1-(3-Bromopropyl)-2-methoxycyclohexa-2,5-diene-1-carboxylate (3c). Alkylation of 1.0 g of methyl *o*-methoxybenzoate with 1,3-dibromopropane gave 1.15 g (66%) of **3c** as a clear oil: ^{1}H NMR ($CDCl_3$) δ 1.5–1.9 (m, 3 H), 2.0–2.2 (m, 1 H), 2.7–3.0 (m, 2 H), 3.35 (t, 2 H), 3.5 (s, 3 H), 3.7 (s, 3 H), 4.85 (br s, 1 H), 5.4 (d, 1 H), 5.9 (dt, 1 H); ^{13}C NMR ($CDCl_3$) δ 26.45, 28.15, 33.11, 33.75, 51.33 (q), 52.44, 54.31, 93.85, 126.67, 127.19, 152.24, 173.71. Anal. Calcd for $C_{12}H_{17}O_3Br$: C, 49.84; H, 5.93. Found: C, 49.78; H, 6.15.

Methyl 1-(3-Bromopropyl)-3-methylcyclohexa-2,5-diene-1-carboxylate (6b). Methyl *m*-toluate (1.0 g), upon alkylation with 1,3-dibromopropane, gave 1.07 g (59%) of **6b** as a colorless oil: ^{1}H NMR ($CDCl_3$) δ 1.6–2.0 (m, 7 H), 2.35–2.7 (m, 2 H), 3.35 (t, 2 H), 3.65 (s, 3 H), 5.4 (s, 1 H), 5.7 (d, 1 H), 5.9 (dt, 1 H); ^{13}C NMR ($CDCl_3$) δ 23.18, 28.00, 30.92, 33.70, 37.99, 51.95 (q), 52.09, 121.32, 126.11, 126.49, 133.70, 175.08. Anal. Calcd for $C_{12}H_{17}O_2Br$: C, 52.76; H, 6.27. Found: C, 52.94; H, 6.20.

Methyl 1-(3-Bromopropyl)-3-methoxycyclohexa-2,5-diene-1-carboxylate (6c). Alkylation of 1.0 g of methyl *m*-methoxybenzoate with

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(28) Anderson, H. H. *J. Am. Chem. Soc.* **1951**, *73*, 5800–5802.

1,3-dibromopropane gave 1.04 g (60%) of **6c** as a colorless oil: ^{1}H NMR ($CDCl_3$) δ 1.6–1.9 (m, 4 H), 2.55–2.8 (m, 2 H), 3.35 (t, 2 H), 3.6 (s, 3 H), 3.7 (s, 3 H), 4.65 (s, 1 H), 5.7 (d, 1 H), 5.85 (dt, 1 H); ^{13}C NMR ($CDCl_3$) δ 27.97, 28.64, 33.78, 38.54, 49.61, 52.24, 54.08, 94.61, 124.74, 126.99, 154.70, 175.49. Anal. Calcd for $C_{12}H_{17}O_3Br$: C, 49.84; H, 5.93. Found: C, 49.80; H, 5.60. This compound is very sensitive to traces of acid. Upon standing in $CDCl_3$ it isomerizes to an equilibrium mixture of **6c** (33%) and the conjugated 2,4-diene (66%).

Methyl 1-(3-Bromopropyl)-3-methoxy-4-ketocyclohexa-2,5-diene-1-carboxylate (9c, X = Br). Oxidation of the preceding diene (**6c**) with chromium trioxide and dimethylpyrazole[13] as described above gave 50% of **9c** (X = Br) as a pale yellow oil: ^{1}H NMR ($CDCl_3$) δ 1.65–1.9 (m, 2 H), 2.1–2.3 (m, 2 H), 3.4 (t, 2 H), 3.73 (s, 3 H), 3.77 (s, 3 H), 5.9 (d, 1 H, J = 2.5 Hz), 6.4 (d, 1 H, J = 10.0 Hz), 7.0 (dd, 1 H, J = 10.0 and 2.5 Hz); ^{13}C NMR ($CDCl_3$) δ 27.3, 32.6, 37.1, 52.2 (q), 53.2, 55.0, 114.3, 130.0, 147.5, 152.0, 171.1, 180.0; exact mass calcd for $C_{12}H_{15}O_4Br$ 302.0154, found 302.0156.

Methyl 1-(3-Bromopropyl)-3,5-dimethoxycyclohexa-2,5-diene-1-carboxylate (12). Alkylation of 1.0 g of methyl 3,5-dimethoxybenzoate with 1,3-dibromopropane gave 545 mg (33%) of **12** as a clear oil: ^{1}H NMR ($CDCl_3$) δ 1.65–1.9 (m, 4 H), 2.75 (s, 2 H), 3.4 (t, 2 H), 3.6 (s, 6 H), 3.8 (s, 3 H), 4.65 (s, 2 H); ^{13}C NMR ($CDCl_3$) δ 28.0, 31.1, 33.9, 39.4, 49.7, 52.3, 54.5 (2 C), 94.75 (2 C), 153.4 (2 C) (the carbonyl carbon was not detected). Anal. Calcd for $C_{13}H_{19}O_4Br$: C, 48.92; H, 6.00. Found: C, 48.65; H, 5.99. This compound undergoes rapid decomposition in the presence of a trace of acid.

Methyl 1-(3-Bromopropyl)-1,4-dihydro-1-naphthoate (14). Alkylation of 1.0 g of methyl 1-naphthoate with 1,3-dibromopropane gave 90 mg (55%) of **14** as a clear oil: ^{1}H NMR ($CDCl_3$) δ 1.2–1.5 (m, 1 H), 1.6–1.85 (m, 1 H), 1.95–2.15 (m, 1 H), 2.2–2.4 (m, 1 H), 3.2 (t, 2 H), 3.4 (br s, 2 H), 3.6 (s, 3 H), 5.65 (d, 1 H), 6.15 (dt, 1 H), 7.05–7.35 (m, 4 H) (in this compound the diastereotopic protons of the side chain methylenes show markedly different shifts); ^{13}C NMR ($CDCl_3$) δ 27.80, 29.61, 33.70, 38.08, 50.60 (q), 52.50, 126.49, 126.64, 126.99, 127.37, 128.62, 133.85, 134.52, 174.87. Anal. Calcd for $C_{15}H_{17}O_2Br$: C, 58.27; H, 5.54. Found: C, 58.50; H, 5.78.

Methyl 1-[(2-Bromocyclohexyl)methyl]cyclohexa-2,5-diene-1-carboxylate (16). Alkylation of methyl benzoate (1.0 g) with 1-bromo-2-(bromomethyl)cyclohexane gave 1.44 g (63%) of a mixture of the two diastereoisomers of **16** as a colorless oil: ^{1}H NMR ($CDCl_3$) δ 1.0–2.4 (m, 11 H), 2.65 (br s, 2 H), 3.4–3.55 (m, 1 H, CHBr minor isomer), 3.69 (s, 3 H), 3.75–3.95 (m, 1 H, CHBr major isomer), 5.65–6.0 (m, 4 H); ^{13}C NMR resonances for the two diastereoisomers could not be distinguished in the upfield region, but in the downfield region they occurred at δ 125.47, 125.58, 127.37, 127.42, 174.89 for the major isomer and at 125.8, 126.2, 127.8 (2 C), 174.82 for the minor; exact mass calcd for $C_{15}H_{21}O_2Br$ 312.0725, found 312.0725.

3-(1-Carbomethoxycyclohexa-2,5-dienyl)propanal (18). Methyl benzoate (1.0 g) was alkylated with the tetrahydropyranyl ether of 3-iodopropanol, and the crude product was stirred with 30 mg of *p*-toluenesulfonic acid in 40 mL of dry methanol for 6 h. The mixture was then diluted with brine and extracted twice with ether, and the organic layers were washed with brine, dried, and evaporated. Flash chromatography of the residue gave 715 mg (50%) of methyl 1-(3-hydroxypropyl)cyclohexa-2,5-diene-1-carboxylate as a clear oil: ^{1}H NMR ($CDCl_3$) δ 1.35–1.55 (m, 2 H), 1.65–1.8 (m, 2 H), 2.6 (br s, 2 H), 3.55 (t, 2 H), 3.7 (t, 3 H), 5.7 (d, 2 H), 5.9 (dt, 2 H); ^{13}C NMR ($CDCl_3$) δ 16.1, 27.5, 35.7, 52.1, 62.3, 125.9 (2 C), 127.0 (2 C) (the quaternary and carbonyl carbon resonances were not detected). Anal. Calcd for $C_{11}H_{16}O_3$: C, 67.32; H, 8.22. Found: C, 67.32; H, 8.37.

Treatment of the preceding alcohol with pyridinium chlorochromate by the usual procedure[14] gave 70% of **18** as a colorless oil: ^{1}H NMR ($CDCl_3$) δ 2.0 (t, 2 H), 2.4 (t, 2 H), 2.65 (br s, 2 H), 3.71 (s, 3 H), 5.65 (dt, 2 H), 5.95 (dt, 2 H), 9.2 (br s, 1 H). Anal. Calcd for $C_{11}H_{14}O_3$: C, 68.02; H, 7.26. Found: C, 67.82; H, 7.33.

Methyl 1-(4-Bromobutyl)cyclohexa-2,5-diene-1-carboxylate (20). Alkylation of 1.0 g of methyl benzoate with 1,4-dibromobutane gave 686 mg (34%) of **20** as an oil: ^{1}H NMR ($CDCl_3$) δ 1.2–1.5 (m, 2 H), 1.55–1.9 (m, 4 H), 2.45–2.8 (m, 2 H), 3.35 (t, 2 H), 3.65 (s, 3 H), 5.7 (d, 2 H), 5.9 (dt, 2 H); ^{13}C NMR ($CDCl_3$) δ 22.98, 26.13, 32.88, 33.37, 38.51, 47.77 (q), 52.12, 125.91 (2 C), 126.99 (2 C), 175.05. Anal. Calcd for $C_{12}H_{17}O_2Br$: C, 52.76; H, 6.27. Found: C, 52.45; H, 6.19.

Methyl 1-(4-Bromobutyl)-4-ketocyclohexa-2,5-diene-1-carboxylate (23). Oxidation of the preceding diene (**20**) with chromium trioxide and dimethylpyrazole[13] as described above gave 86% of **23** as a pale yellow oil: ^{1}H NMR ($CDCl_3$) δ 1.25–1.5 (m, 2 H), 1.75–2.05 (m, 4 H), 3.37 (t, 2 H), 3.76 (s, 3 H), 6.3 (d, 2 H), 6.95 (d, 2 H); ^{13}C NMR ($CDCl_3$) δ 22.9, 32.4, 32.8, 37.4, 52.3 (q), 53.3, 130.5 (2 C), 147.7 (2 C), 170.8, 185.1.

Methyl 1-(4-Iodobutyl)-4-ketocyclohexa-2,5-diene-1-carboxylate. Treatment of the preceding bromide (**23**) with sodium iodide as described above gave 95% of the required iodide as an oil: ^{1}H NMR ($CDCl_3$) δ 1.2–1.45 (m, 2 H), 1.8 (p, 2 H), 2.0 (m, 2 H), 3.14 (t, 2 H), 3.77 (s, 3 H), 6.4 (d, 2 H), 7.0 (d, 2 H); ^{13}C NMR ($CDCl_3$) δ 5.49, 25.11, 32.94, 37.00, 52.12 (q), 53.17, 130.41, 147.55, 70.64, 184.92. Anal. Calcd for $C_{12}H_{15}O_3I$: C, 43.13; H, 4.52. Found: C, 43.26, H, 4.58.

Methyl 1-Propylcyclohexa-2,5-diene-1-carboxylate. Alkylation of 500 mg of methyl benzoate with 1-bromopropane gave 460 mg (70%) of the require diene as a clear oil: ^{1}H NMR ($CDCl_3$) δ 0.9 (t, 3 H), 1.1–1.35 (m, 2 H), 1.55–1.7 (m, 2 H), 2.63 (br s, 2 H), 3.68 (s, 3 H), 5.75 (d, 2 H), 5.85 (dt, 2 H); ^{13}C NMR ($CDCl_3$) δ 14.25, 17.55, 26.11, 42.02, 47.92 (q), 52.04, 125.38 (2 C), 127.40 (2 C), 175.40. Anal. Calcd for $C_{11}H_{16}O_2$: C, 73.30; H, 8.95. Found: C, 73.31; H, 8.73.

Methyl 1-Propyl-4-ketocyclohexa-2,5-diene-1-carboxylate. Oxidation of the preceding diene with chromium trioxide and dimethylpyrazole[13] as described above gave 73% of the required dienone as a pale yellow oil: ^{1}H NMR ($CDCl_3$) δ 0.8 (t, 3 H), 1.0–1.3 (m, 2 H), 1.75–1.9 (m, 2 H), 3.65 (s, 3 H), 6.25 (d, 2 H), 6.95 (d, 2 H); ^{13}C NMR ($CDCl_3$) δ 13.70, 17.44, 40.27, 52.15, 52.68, 129.65 (2 C), 147.90 (2 C), 170.50, 184.75. Anal. Calcd for $C_{11}H_{14}O_3$: C, 68.02; H, 7.26. Found: C, 68.33; H, 7.32.

Methyl 1-Propyl-2-methylcyclohexa-2,5-diene-1-carboxylate. Alkylation of methyl *o*-toluate (1.30 g) with 1-bromopropane gave 1.28 g (76%) of the required diene as a colorless oil: ^{1}H NMR ($CDCl_3$) δ 0.9 (t, 3 H), 1.1–1.35 (m 2 H), 1.5–1.7 (m, 2 H), 1.7 (s, 3 H), 2.65 (m, 2 H), 3.7 (s, 3 H), 5.4 (d, 1 H), 5.7 (s, 1 H), 5.9 (dt, 1 H). Anal. Calcd for $C_{12}H_{18}O_2$: C, 74.19; H, 9.34. Found: C, 74.49; H, 9.36.

Methyl 1-Propyl-2-methoxycyclohexa-2,5-diene-1-carboxylate. Alkylation of 1.20 g of methyl *o*-methoxybenzoate with 1-bromopropane gave 1.08 g (73%) of the required diene as a colorless oil: ^{1}H NMR ($CDCl_3$) δ 0.9 (t, 3 H), 1.2 (m, 2 H), 1.65 (m, 2 H), 2.8 (m, 2 H), 3.5 (s, 3 H), 3.7 (s, 3 H), 4.85 (br s, 1 H), 5.4 (d, 1 H), 5.9 (dt, 1 H). Anal. Calcd for $C_{12}H_{18}O_3$: C, 68.55; H, 8.63. Found: C, 68.65; H, 8.62.

Methyl 1-Propyl-3-methylcyclohexa-2,5-diene-1-carboxylate. Alkylation of 1.40 g of methyl *m*-toluate with 1-bromopropane and Kugelrohr distillation of the crude product gave 1.50 g (85%) of the required diene as a colorless oil: ^{1}H NMR ($CDCl_3$) δ 0.9 (t, 3 H), 1.6–2.0 (m, 7 H), 2.5–2.7 (m, 2 H), 3.65 (s, 3 H), 5.4 (s, 1 H), 5.8 (m, 2 H). Anal. Calcd for $C_{12}H_{18}O_2$: C, 74.19; H, 9.34. Found: C, 74.45; H, 9.45.

Methyl 1-Propyl-3-methoxycyclohexa-2,5-diene-1-carboxylate. Alkylation of 1.46 g of methyl *m*-methoxybenzoate with 1-bromopropane and Kugelrohr distilllation of the product gave 1.59 g (71%) of the required diene as a colorless oil: ^{1}H NMR ($CDCl_3$) δ 0.88 (t, 3 H), 1.2 (m, 2 H), 1.65 (m, 2 H), 2.68 (br s, 2 H), 3.59 (s, 3 H), 3.68 (s, 3 H), 4.70 (s, 1 H), 5.75 (m, 2 H); ^{13}C NMR ($CDCl_3$) δ 14.25, 17.58, 28.65, 42.84, 50.05 (q), 51.98, 53.93, 95.31, 123.75, 127.63, 153.99, 175.96. Anal. Calcd for $C_{12}H_{18}O_3$: C, 68.55; H, 8.63. Found: C, 68.66; H, 8.97.

Methyl 1-Propyl-3,5-dimethoxycyclohexa-2,5-diene-1-carboxylate. Alkylation of 1.55 g of methyl 3,5-dimethoxybenzoate with 1-bromopropane gave, after distillation of the crude product in a Kugelrohr apparatus, the required diene, mp 33–35 °C: ^{1}H NMR ($CDCl_3$) δ 0.88 (t, 3 H), 1.2 (m, 2 H), 1.65 (m, 2 H), 2.75 (br s, 2 H), 3.60 (s, 6 H), 3.68 (s, 3 H), 4.70 (s, 2 H). Anal. Calcd for $C_{12}H_{20}O_4$: C, 64.98; H, 8.39. Found: C, 64.99; H, 8.62.

Methyl 1-Propyl-1,4-dihydronaphthoate. Alkylation of 1.4 g of methyl 1-naphthoate with 1-bromopropane and distillation of the crude product in a Kugelrohr apparatus gave 1.32 g (76%) of the required ester as a colorless oil: ^{1}H NMR ($CDCl_3$) δ 0.8–1.0 (m, 3 H), 1.1–1.3 (m, 1 H), 1.8–2.2 (m, 3 H), 3.4 (m, 2 H), 3.62 (s, 3 H), 5.7 (dt, 1 H, J = 2.2, 10.0 Hz), 6.1 (dt, 1 H, J = 3.66, 10.0 Hz), 7.1–7.4 (m, 4 H); ^{13}C NMR ($CDCl_3$) δ 14.28, 17.38, 29.67, 41.93, 51.19 (q), 52.33, 125.65, 126.35, 126.61 (2 C), 127.98, 128.45, 133.94, 135.31, 175.37. Anal. Calcd for $C_{15}H_{18}O_2$: C, 78.23; H, 7.88. Found: C, 78.48; H, 7.95.

Methyl 1-(Cyclohexylmethyl)cyclohexa-2,5-diene-1-carboxylate. Alkylation of 500 mg of methyl benzoate with (bromomethyl)cyclohexane gave 555 mg (65%) of the required diene as a colorless oil: ^{1}H NMR ($CDCl_3$) δ 0.8–1.9 (m, 13 H), 2.65 (br s, 2 H), 3.67 (s, 3 H), 5.7–5.9 (m, 4 H); ^{13}C NMR ($CDCl_3$) δ 26.08, 26.22, 26.37 (2 C), 33.93, 34.58 (2 C), 47.25, 47.59 (q), 52.03, 124.97 (2 C), 128.01 (2 C), 175.63; exact mass calcd for $C_{15}H_{22}O_2$ 234.1620, found 234.1619.

Methyl 1-Butylcyclohexa-2,5-diene-1-carboxylate. Alkylation of 500 mg of methyl benzoate with 1-bromobutane gave 530 mg (75%) of the required diene as a colorless oil: ^{1}H NMR ($CDCl_3$) δ 0.9 (t, 3 H), 1.1–1.4 (m, 4 H), 1.6–1.75 (m, 2 H), 2.65 (br s, 2 H), 3.69 (s, 3 H), 5.75 (d, 2 H), 5.9 (dt, 2 H); ^{13}C NMR ($CDCl_3$) δ 13.96, 22.89, 26.14, 26.40, 39.51, 47.83 (q), 52.03, 125.41 (2 C), 127.40 (2 C), 175.43. Anal. Calcd for $C_{12}H_{18}O_2$: C, 74.19; H, 9.34. Found: C, 73.88; H, 9.30.

Methyl 1-Butyl-4-ketocyclohexa-2,5-diene-1-carboxylate. Oxidation of the preceding diene with chromium trioxide and dimethylpyrazole[13] as described above gave 73% of the required dienone as a pale yellow oil:

^{1}H NMR ($CDCl_3$) δ 0.8 (t, 3 H), 1.0–1.3 (m, 4 H), 1.8–1.95 (m, 2 H), 3.67 (s, 3 H), 6.25 (d, 2 H), 6.95 (d, 2 H); ^{13}C NMR ($CDCl_3$) δ 13.44, 22.34, 26.08, 37.96, 52.06, 52.71, 129.73 (2 C), 147.90 (2 C), 170.55, 184.75. Anal. Calcd for $C_{12}H_{16}O_3$: C, 69.21; H, 7.74. Found: C, 69.40; H, 7.75.

Cyclizations: General Procedure. A mixture of the halide, azobis(isobutyronitrile) (0.05 molar equiv), and tributylstannane (1.2 molar equiv) as a benzene solution of appropriate molarity (in each cyclization the concentration of stannane was chosen so as to maximize the formation of cyclized product without sacrificing experimental convenience) was degassed and refluxed under N_2 or argon until the reaction as monitored by TLC or GLC was complete (usually 2–8 h). The solvent was then removed in a rotary evaporator and the residue was dissolved in ether and stirred with an excess of 60% aqueous potassium fluoride[15] for 3 h, during which time a white precipitate was formed. The precipitate was removed by filtration, and the two layers were separated. The aqueous layer was extracted with ether, and the combined organic layers were washed with brine, dried, filtered, and stripped to afford crude product which was usually purified or separated into its components by flash chromatography with ethyl acetate–hexane or ether–hexane mixtures as elutant.

Cyclization of 3a. Heating of **3a** (270 mg) with Bu_3SnH (0.05 M) in benzene gave 181 mg (96%) of methyl [3aα,7aα]-1,2,3,6,7,7a-hexahydro-3a*H*-indene-3a-carboxylate (**4a**) as a colorless oil: ^{1}H NMR ($CDCl_3$) δ 1.35–2.2 (m, 10 H), 2.58 (m, 1 H, bridge head), 3.68 (s, 3 H), 5.6 (d, 1 H, J = 10.0 Hz), 5.8 (dt, 1 H); ^{13}C NMR ($CDCl_3$) δ 20.76, 23.39, 28.79, 37.70, 40.60, 51.97, 52.85 (q), 128.21, 129.35, 177.12. Anal. Calcd for $C_{11}H_{16}O_2$: C, 73.30; H, 8.95. Found: C, 73.45; H, 8.92.

Cyclization of 3b. Heating of **3b** (183 mg) with Bu_3SnH [0.05 M] in benzene gave 111 mg (85%) of methyl [3aα,7aα]-1,2,3,6,7,7a-hexahydro-4-methyl-3a*H*-indene-3a-carboxylate (**4b**) as a colorless oil: ^{1}H NMR ($CDCl_3$) δ 1.3–1.8 (m, 10 H), 2.00 (br s, 2 H), 2.2–2.5 (m, 2 H), 3.68 (s, 3 H), 5.55 (br s, 1 H); ^{13}C NMR ($CDCl_3$) δ 20.35, 22.22, 23.27, 24.12, 29.84, 34.22, 43.10, 52.00, 56.73, 123.89, 134.08, 177.30. Anal. Calcd for $C_{12}H_{18}O_2$: C, 74.19; H, 9.34. Found: C, 73.85; H, 9.23.

Cyclization of 3c. Heating of **3c** (181 mg) with Bu_3SnH (0.05 M) in benzene gave 140 mg (92%) of methyl [3aα,7aα]-1,2,3,6,7,7a-hexahydro-4-methoxy-3a*H*-indene-3a-carboxylate (**4c**) as a colorless oil: ^{1}H NMR ($CDCl_3$) δ 1.4–1.9 (m, 7 H), 2.1 (m, 2 H), 2.25–2.5 (m, 2 H), 3.49 (s, 3 H, ether CH_2), 3.68 (s, 3 H, ester CH_3), 4.75 (t, 1 H, J = 4.1 Hz); ^{13}C NMR ($CDCl_3$) δ 20.53, 23.74, 24.09, 29.78, 34.02, 44.65 (methine), 52.15, 54.40, 56.12 (q), 94.52, 155.92, 176.42. Anal. Calcd for $C_{12}H_{18}O_3$: C, 68.55; H, 8.63. Found: C, 68.43; H, 3.89.

Cyclization of 6b. Heating of **6b** (220 mg) with Bu_3SnH (0.05 M) in benzene gave an inseparable mixture (123 mg; 80%) of methyl [3aα,7aα]-1,2,3,6,7,7a-hexahydro-5-methyl-3a*H*-indene-3a-carboxylate (**7b**), methyl [3aα,7β,7aα]-1,2,3,6,7,7a-hexahydro-7-methyl-3a*H*-indene-3a-carboxylate (**8b**, β-Me), and its 7α isomer (**8b**, α-Me) in the ratio 2.3:3.8:1.0 (GLC) as a clear oil: ^{1}H NMR ($CDCl_3$) δ 1.4–2.1 (m, CH_2), 2.3–2.6 (m, CH), 3.66 (s, OCH_3, **7b**), 3.67 [s, OCH_3, **8b** (β-Me)], 3.68 [s, OCH_3, **8b** (α-Me)], 5.35 (s, vinyl H, **7b**), 5.50 [m, vinyl H, **8b** (α-+ β-Me)], 5.75 [(m, vinyl H, **8b** (α + β-Me)]; ^{13}C NMR ($CDCl_3$) (downfield region only) δ 123.51, 126.75, 128.09, 129.03, 135.57. Anal. Calcd for $C_{12}H_{18}O_2$: C, 74.19; H, 9.34. Found: C, 74.41; H, 9.41.

Cyclization of 6c. Heating of **6c** (210 mg) with Bu_3SnH (0.05 M) in benzene gave a clear oil (136 mg, 89%) containing the following three compounds in the ratio 3.7:1.0:3.0 respectively [GLC]: (i) Methyl [3aα,7aα]-1,2,3,6,7,7a-hexahydro-5-methoxy-3a*H*-indene-3a-carboxylate (**7c**); ^{1}H NMR ($CDCl_3$) δ 1.35–2.2 (m, 8 H), 2.5 (m, 1 H), 3.5 (2, 3 H, ether CH_3), 3.7 (s, 3 H, ester CH_3), 4.5 (s, 1 H); ^{13}C NMR ($CDCl_3$) δ 23.35, 23.71, 24.09, 28.44, 38.92, 39.51 (methine), 51.92, 53.14 (q), 54.02, 96.98, 156.65 (the carboxyl carbon was not detected). Anal. Calcd for $C_{12}H_{18}O_3$: C, 68.55; H, 8.63. Found: C, 68.82; H, 8.57. (ii) Methyl [3aα,7α,7aα]-1,2,3,5,6,7a-hexahydro-7-methoxy-3a*H*-indene-3a-carboxylate (**8c**, α-OMe); ^{1}H NMR ($CDCl_3$) δ 1.3–1.9 (m, 6 H), 2.0–2.4 (m, 2 H), 2.94 (m, 1 H, bridge head), 3.31 (s, 3 H, ether CH_3), 3.3–3.4 (m, 1 H, ether methine), 3.69 (s, 3 H, ester CH_3), 5.7 (m, 2 H); exact mass calcd for $C_{12}H_{18}O_3$ 210.1256, found 210.1255. (iii) Methyl [3aα,7β,7aα]-1,2,3,5,6,7a-hexahydro-7-methoxy-3a*H*-indene-3a-carboxylate (**8c**, β-OMe); ^{1}H NMR ($CDCl_3$) δ 1.3–1.85 (m, 6 H), 2.0 (m, 2 H), 2.3 (dt, 1 H), 2.9 (m, 1 H, bridge head), 3.37 (s, 3 H, ether CH_3), 3.6–3.75 (m, 1 H, ether methine), 3.70 (s, 3 H, ester CH_3), 5.45 (dm, 1 H), 5.65(ddd, 1 H); ^{13}C NMR ($CDCl_3$) δ 23.24, 23.51, 29.70, 37.78, 42.86 (bridge head), 52.06, 55.83, 75.60 (ether methine), 125.44, 129.09 (quaternary and carbonyl carbon resonances not detected); exact mass found 210.1258.

Cyclization of 9a (X = I). Heating of 80 mg of **9a** (X = I) with Bu_3SnH (0.034 M) gave 46 mg (81%) of methyl [3aα,7aα]-6-keto-1,2,3,6,7,7a-hexahydro-3a-carboxylate (**10a**) as a pale yellow oil: ^{1}H NMR (C_6D_6) δ 1.4–1.8 (m, 5 H), 1.95 (m, 1 H), 2.25 (m, 1 H), 2.6 (m, 2 H), 3.23 (s, 3 H), 6.1 (dd, 1 H), 5.9 (d, 1 H). Anal. Calcd for $C_{11}H_{14}O_3$: C, 68.02; H, 7.26. Found: C, 68.03; H, 7.15.

Cyclization of 9c (X = Br). Heating of 60 mg of **9c** (X = Br) with Bu_3SnH [0.5 M] in benzene gave a mixture of methyl vanillate, **10c**, and **11c**, in the ratio of 1.3:1.0:1.4. Methyl vanillate was identified by comparison with an authentic sample. Methyl [3aα,7aα]-6-keto-5-methoxy-1,2,3,6,7,7a-hexahydro-3a*H*-indene-3a-carboxylate (**10c**) was a clear oil: ^{1}H NMR ($CDCl_3$) δ 1.3–2.3 (m, 6 H), 2.55 (dd, 1 H), 2.85 (m, 2 H), 3.64 (s, 3 H), 3.74 (s, 3 H), 5.51 (s, 1 H); ^{13}C NMR ($CDCl_3$) δ 23.16, 30.08, 39.48, 39.74, 40.68, 52.33, 54.99, 115.75 (quaternary, carbonyl and one vinyl carbon were not detected). Anal. Calcd for $C_{12}H_{16}O_4$: C, 64.27; H, 7.19. Found: C, 64.53; H, 7.19. Methyl [3aα,7β,7aα]-6-keto-7-methoxy-1,2,3,6,7,7a-hexahydro-3a*H*-indene-3a-carboxylate (**11c**) was a clear oil: ^{1}H NMR ($CDCl_3$) δ 1.3–1.9 (m, 3 H), 1.95 (m, 2 H), 2.15 (m, 1 H), 3.2 (m, 1 H), 3.55 (s, 3 H), 7.78 (s, 3 H), 4.21 (d, 1 H, J = 5.6 Hz), 5.95 (d, 1 H, J = 10 Hz), 6.55 (dd, 1 H, J = 10.0, 2.7 Hz); ^{13}C NMR ($CDCl_3$) δ 23.51, 25.52, 39.01, 45.61 (bridge head methine), 52.70, 58.54, 81.1 (ether methine), 128.1, 147.2 (the quaternary and carbonyl carbons could not be detected). Anal. Calcd for $C_{12}H_{16}O_4$: C, 64.27; H, 7.19. Found: C, 64.08; H, 7.43.

Cyclization of 12. Heating of 78 mg of **12** with Bu_3SnH (0.05 M) in benzene gave a mixture (35 mg, 60%) of the two epimers of **13** in the ratio of 2.8:1.0. The major isomer, methyl [3aα,7β,7aα]-5,7-dimethoxy-1,2,3,6,7,7a-hexahydro-3a*H*-indene-3a-carboxylate (**13**, β-OMe) was a clear oil: ^{1}H NMR ($CDCl_3$) δ 1.4–1.8 (m, 5 H), 1.9–2.2 (m, 2 H), 2.3 (dd, 1 H), 2.85 (m, 1 H, bridge head), 3.37 (s, 3 H), 3.53 (s, 3 H), 3.69 (s, 3 H), 3.8 (m, 1 H, ether methine), 4.56 (d, 1 H, J = 1.7 Hz); ^{13}C NMR ($CDCl_3$) δ 23.04, 23.27, 29.02, 39.10, 42.57 (bridge head), 52.03, 53.73, 54.40, 56.03, 75.74 (ether methine), 96.53, 153.79, 176.95. Anal. Calcd for $C_{13}H_{20}O_4$: C, 64.98; H, 8.39. Found: C, 65.16; H, 8.42.

The minor component methyl [3aα,7α,7aα]-5,7-dimethoxy-1,2,3,6,7,7a-hexahydro-3a*H*-indene-3a-carboxylate (**13**, α-OMe) was a clear oil: ^{1}H NMR ($CDCl_3$) δ 1.3–1.9 (m, 5 H), 2.0–2.2 (m, 2 H), 2.4 (dd, 1 H), 2.9 (m, 1 H, bridgehead), 3.3 (s, 3 H), 3.4 (m, 1 H, ether methine), 3.55 (s, 3 H), 3.7 (s, 3 H, 4.65 (s, 1 H); ^{13}C NMR ($CDCl_3$) δ 23.65, 27.83, 30.10, 40.47, 44.06 (bridge head), 54.16, 56.65, 77.85 (ether methine), 96.36; exact mass calcd for $C_{13}H_{20}O_4$ 240.1363, found 240.1370.

Cyclization of 14. Heating of **14** (82 mg) with Bu_3SnH (0.05 M) in benzene gave 59 mg (97%) of methyl [3aα,9bα]-2,3,3a,4,5,9b-hexahydro-1*H*-benz[*e*]indene-9b-carboxylate (**15**) as a clear oil: ^{1}H NMR ($CDCl_3$) δ 1.35–2.1 (m, 10 H), 2.55–2.85 (m, 5 H), 3.61 (s, 3 H), 7.0–7.25 (m, 4 H); ^{13}C NMR ($CDCl_3$) δ 233.83, 26.98, 28.15, 31.42, 38.66, 42.72 (bridge head), 52.27, 56.97 (q), 126.14, 126.29, 127.89, 128.71, 136.95 (the carbonyl and one vinyl carbon were not detected). Anal. Calcd for $C_{15}H_{18}O_2$: C, 78.23; H, 7.88. Found: C, 78.23; H, 7.46.

Cyclization of 16. Heating of 279 mg of **16** with Bu_3SnH (0.030 M) gave 192 mg (92%) of an inseparable mixture of the three diastereoisomers of methyl [4bα,8aα]-2,3,4,4a,4b,5,6,8a,9,9a-decahydro-1*H*-fluorene-8a-carboxylate (**17**) in the ratio 3.75:1.5:1.0 (GLC) as a clear oil: ^{1}H NMR ($CDCl_3$) δ 0.8–2.0 (m, 16 H), 2.5–2.6 (m, 1 H), 3.55–3.65 [3 singlets at 3.59 (medium), 3.60 (weak), and 3.61 (strong) totaling 3 H], 5.55–5.60 (m, 2 H); exact mass calcd for $C_{15}H_{22}O_2$ 234.1620, found 234.1617.

Cyclization of 18. The reaction of **18** with 1.1 molar equiv of 0.05 M Bu_3SnH in benzene was very inefficient. Additional portions (0.05 molar equiv) of AIBN were added after 5, 10, and 20 h, and an additional portion (1.0 molar equiv) of Bu_3SnH after 20 h. The reaction was complete after 40 h. Flash chromatography of the crude products on silica gel gave the alcohols tentatively assigned the structures **19** β-OH and **19** α-OH in the ratio 1.2:1.0. Methyl [1$\alpha\beta$,3aα,7aα]-1-hydroxy-1,2,3,6,7,7a-hexahydro-3a*H*-indene-3a-carboxylate (**19**, β-OH) was a colorless oil: ^{1}H NMR ($CDCl_3$) δ 1.4–2.3 (m, 8 H), 2.6 (m, bridge head), 3.93 (s, 3 H), 4.4 (m, 1 H, C*H*OH), 5.75 (d, 1 H, J = 10 Hz), 5.9 (dt, 1 H, J = 10.0, 3.7 Hz); exact mass calcd for $C_{11}H_{16}O_3$ 196.1099, found 196.1103.

The epimeric alcohol **19** (α-OH) was a colorless oil: ^{1}H NMR ($CDCl_3$) δ 1.5–2.15 (m, 7 H), 2.35 (m, 2 H), 3.71 (s, 3 H), 4.0 (br s, 1 H), 5.65 (d, 1 H), 5.8 (dt, 1 H). Anal. Calcd for $C_{11}H_{16}O_3$: C, 67.32; H, 8.22. Found: C, 67.23, H, 8.14.

Cyclization of 20. Heating of 24.8 mg of **20** with Bu_3SnH (0.008 M) gave a mixture of the direct reduction product, methyl [4a,9a]-1,2,4a,5,6,7,8,8a-octahydronaphthalene-4a-carboxylate (**21**), and a compound tentatively identified as methyl bicyclo[4,3,1]dec-8-ene-1-carboxylate (**22**) in the ratio 21:68:11 (GLC) as an oil: ^{1}H NMR ($CDCl_3$) δ 0.9 (t, 22), 1.2–1.8 (m), 2.0 (m, allylic CH_2 in **21** and **22**), 2.05–2.35 (m, bridge head CH in **21** and **22**), 2.6 (br s, 2.6), 3.61, 3.68, 3.69 (3s, OCH_3), 5.5 (d, 21), 5.95 (m). Anal. Calcd for $C_{12}H_{18}O_2$: C, 74.19; H, 9.34. Found: C, 74.15; H, 9.59. When the reaction was carried out with tributylgermane (0.01 M) the yields of **21** and **22** were 83% and 8%, respectively.

A small sample (5 mg) of **21**, isolated by preparative GLC, was dissolved in hexane (3 mL) and hydrogenated over 10% Pd/C at 40 lb. After 2 h the solution was filtered through Celite, concentrated, and analyzed by GLC. Only one component was detected, which was identified as methyl *cis*-decalin-9-carboxylate by comparison with authentic specimens of the cis and trans compounds.

Cyclization of 23 (X = I). Heating of 58 mg of **23** (X = I) with 1.1 molar equiv of Bu_3SnH (0.05 M) gave a mixture of methyl *p*-hydroxybenzoate (4%) and methyl 2-keto-*cis*-decahydronaphthalene-4a-carboxylate (**24**; 76%) as a clear oil: ^1H NMR (C_6D_6) δ 1.3-1.8 (m, 7 H), 2.0-2.3 (m, 2 H), 2.4-2.6 (m, 2 H), 3.22 (s, 3 H), 5.95 (d, 1 H, J = 10.3 Hz), 6.15 (dd, 1 H, J = 10.3, 1.2 Hz). Anal. Calcd for $C_{12}H_{16}O_3$: C, 69.21; H, 7.74. Found: C, 69.48; H, 7.95.

Kinetic Experiments: General Procedure. A solution was prepared which contained the halide, about 10 molar equiv of tributylstannane of known molarity, and about 0.05 molar equiv of azobis(isobutyronitrile) in purified benzene. Where possible, the concentration of stannane was chosen so as to give comparable amounts of cyclized and direct reduction products. Small aliquots of the solution were then placed in vials and degassed by freeze/thawing. The vials were sealed under vacuum and heated in constant temperature baths until the reaction was complete. The mixtures were then analyzed by GLC on a capillary column. For experiments conducted at low temperatures the reaction was initiated by UV irradiation. For those carried out at temperatures above 100 °C di-*tert*-butyl peroxide was used as initiator instead of azobis(isobutyronitrile). In some cases deuteriobenzene was used as solvent, and the reaction mixtures were directly analyzed by ^1H NMR spectroscopy as well as GLC.

From the relative yields of cyclized and uncyclized products and the mean value of the stannane concentration, the value of k_c/k_H was determined by means of the appropriate pseudo first-order integrated rate equation (see text).

In the case of compounds containing an unsaturated ketone group a slight deficiency of stannane was employed. In these cases the final concentration of cyclized product was determined from the analytical results, and values of k_c/k_H were obtained from the appropriate integrated rate equation by an iterative technique as previously described.[10] Values of k_H were calculated from the appropriate Arrhenius equation[8] and used to determine k_c. Arrhenius parameters for the cyclization reactions were obtained in the usual way from the straight line of best fit obtained by plotting log k_c against $1/T$ (K).

In a typical experiment 20.0 mg (0.077 mmol) of **3a** and 1.0 mg (0.006 mmol) of AIBN were added to 1.25 mL of 0.671 M tributylstannane solution (0.84 mmol), and the mixture was divided between four vials. The aliquots were then degassed, sealed, irradiated with UV light or heated, and analyzed as described above. A second mixture prepared from 18.3 mg (0.071 mmol) of **3a**, 0.5 mg (0.004 mmol) of di-*tert*-butyl peroxide, and 1.25 mL of 0.0667 M tributylstannane solution (0.83 mmol) was similarly treated. The results obtained and the values of rate constants calculated from the expression $k_c/k_H = S_n(CH/UH)$, where S_n is the mean concentration of stannane and CH/UH is the ratio of yields of cyclized and uncyclized products, were as follows: (temperature, S_n, CH/UH, k_c/k_H) (I) 0 °C, 0.640 M, 0.8947, 0.573; (II) 40 °C, 0.640 M, 1.808, 0.157; (III) 75 °C, 0.640 M, 2.706, 1.732; (IV) 110 °C, 0.639 M, 3.271, 2.090; (V) 150 °C, 0.639 M, 4.875, 3.115. The reaction was carried out similarly at other concentrations of stannane. The values of k_c/k_H so obtained together with those listed above were used to obtain values of k_c by multiplying each by appropriate values of k_H.[8] Some typical values of k_c are 7.87×10^5 s^{-1} at 0 °C, 3.76×10^6 s^{-1} at 40 °C, 1.02×10^7 s^{-1} at 75 °C, 1.89×10^7 s^{-1} at 110 °C, and 4.76×10^7 at 150 °C. An Arrhenius plot gave log $A = 10.82 \pm 0.27$ (s^{-1}) and $E = 6.12 \pm 0.38$ kcal·mol^{-1}.

Synthesis, Bromination, and Photoelectron Spectra of Meso-Bridgehead Dienes[1]

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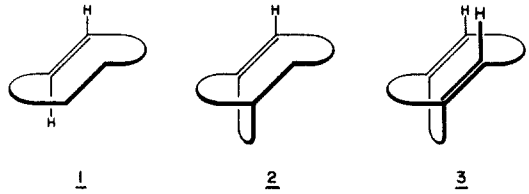
Abstract: The Cope rearrangement of 1,*n*-divinylbicycloalkanes has been employed for the synthesis of a series of meso-bridgehead dienes, molecules that contain two torsionally distorted carbon-carbon double bonds held in proximate relationship. The rate of Cope rearrangement does not correlate with reaction exothermicity or release of strain energy. A frontier molecular orbital explanation is one of several considerations offered to account for these observations. Spectroscopic (UV and photoelectron spectra) and chemical studies have permitted documentation of the progressive transannular interactions of the two bridgehead double bonds.

Reactivity of carbon-carbon double bonds can be modified in a predictable manner by direct attachment of substituents to the olefinic linkage. Considerably less is understood regarding the chemical and spectroscopic response of alkenes to a torsional distortion of the double bond. Indeed a consideration of these factors can provide new insight into subtle yet important chemical behavior of the carbon-carbon double bond.[2]

Torsionally distorted carbon-carbon double bonds are embodied in such compounds as *trans*-cycloalkenes **1**[3] and bridgehead alkenes **2**.[4] Incorporation of two distorted bridgehead olefinic linkages in the same molecule results in compounds that have been termed bridgehead dienes.[4a,5] Bridgehead dienes include such topologically interesting species as meso-bridgehead diene **3**, a molecule that contains two torsionally distorted carbon-carbon double bonds "locked" in close proximate relationship. Not only would the availability of molecules of this type allow for the study of distorted double bonds but it would also permit evaluation of the chemical



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(2) The chemical response to a distortion (i.e., change in facial or regioselectivity) may originate from electronic factors that arise from changes in the energy levels and coefficients of the orbitals and/or from steric factors that stem from a concentration of substituents on one face of the olefin plane. For leading references to these matters see: *Stereochemistry and Reactivity of Systems Containing π Electrons*; Watson, W., Ed.; Verlag Chemie International: Deerfield Beach, FL, 1983.

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