layer was washed with saturated aqueous $NaHCO_3$ (25 mL), dried ($MgSO_4$), and concentrated in vacuo to afford 1.04 g of a brown foam that was purified by silica gel chromatography (80 g). Elution with hexane/ethyl acetate (20:1) gave 820 mg (84%) of the aldehyde **12** as a colorless foam.

Dimethyl Acetal 2. To a solution of aldehyde **12** (2.07 g, 1.60 mmol) at 0 °C in 105 mL of THF was added methanol (155 mL), trimethyl orthoformate (3.13 mL, 28.6 mmol), and pyridinium *p*-toluenesulfonate (PPTS, 555 mg, 2.21 mmol) and the mixture was warmed to 18 °C. After 2 h, 444 mg of PPTS was added, and the mixture was warmed to 25 °C. After 3 h at 25 °C, pyridine (4.9 mL, 60 mmol) was added with ice bath cooling and the mixture was poured into 250 mL of saturated aqueous $NaHCO_3$ and extracted with CH_2Cl_2 (3 × 200 mL). The combined CH_2Cl_2 layer was washed with 3% aqueous $NaHCO_3$ (120 mL), dried ($MgSO_4$), and concentrated in vacuo. The resulting crude oil was chromatographed on 200 g of silica gel, eluting with hexanes/ethyl acetate ((15:1), 1.6 L; (8:1), 850 mL; (3:1), flush) to afford 1.64 g (84%) of the dimethyl acetal **2** as a colorless oil: ^1H NMR (300.1 MHz, $CDCl_3$) 5.42 (br d, J = 8.8, 1 H), 4.36 (m, 1 H), 4.24 (br s, 1 H), 4.06 (d, J = 5.9, 1 H), 3.90 (br s, 1 H), 3.86 (dd, J = 5.9, 1.0, 1 H), 3.45, 3.40, 3.35, 3.34, 3.31 (5 × s, 5 × 3 H), 2.43 (m, 1 H), 1.59 (br s, 3 H), 1.57 (br s, 3 H), 0.94 (d, J = 6.8, 3 H), 0.82 (d, J = 6.4, 3 H), 0.76 (d, J = 6.8, 3 H); ^{13}C NMR (75.5 MHz, $CDCl_3$) 137.3, 135.6, 133.3, 128.9, 126.8, 115.7, 109.3, 84.7, 81.1, 81.0, 79.3, 76.3, 75.2, 73.7, 72.5, 58.9, 57.5, 56.9, 54.9, 53.5, 47.1, 45.2, 39.5, 38.9, 36.6, 36.5, 36.4, 35.1, 34.4, 33.2, 32.6, 30.9, 27.2, 26.0, 20.1, 18.2, 18.1_1, 18.0_8, 16.6, 16.3, 14.4, 13.4, 12.6, 3.7, -3.5, -4.1, -4.6, -4.7. Anal. Calcd for $C_{68}H_{138}O_{10}Si_4$: C, 66.50; H, 11.32. Found: C, 66.43; H, 11.68.

***N*-Boc-pipecolate 13.** To a -20 °C solution of alcohol **2** (308 mg, 0.251 mmol) in 4.4 mL of CH_2Cl_2 was added solid (*S*)-*N*-Boc-pipecolinic acid (231 mg, 1.00 mmol), dicyclohexylcarbodiimide (208 mg, 1.00 mmol) and 4-(dimethylamino)pyridine (6.0 mg, 0.050 mmol). The initially homogeneous solution was aged at -20 °C for 21 h and then filtered and the filter cake washed with hexane/ethyl acetate solution (12:1). The combined organic phase was concentrated in vacuo and the residue chromatographed on 95 g of silica gel. Elution with hexanes/ethyl acetate (3:1) gave 436 mg (97%) of the pipecolinic ester **13** as a colorless foam: ^{13}C NMR (75.5 MHz, $CDCl_3$, many resonances are broadened (br) or doubled (dbl) due to 1/1 carbamate rotamers; these doubled resonances precede (dbl)) 170.6 (br), 155.4 (br), 137.5 (br), 136.6, 136.2 (dbl), 135.1, 135.0 (dbl), 130.9, 130.8 (dbl), 127.5, 127.4 (dbl), 115.6 (br), 109.3, 84.4, 82.3, 82.1 (dbl), 81.1, 81.0, 79.7, 79.6 (dbl), 74.7, 73.8, 72.8, 69.7, 69.3 (dbl), 58.9, 57.1, 56.9, 54.9, 53.5, 47.1, 44.5, 44.3 (dbl), 42.0, 41.0 (dbl), 40.4 (br), 38.9, 38.4, 38.1 (dbl), 35.9, 35.7 (dbl), 35.6, 35.1, 34.1, 33.1, 32.6, 30.3, 28.3, 27.1, 27.0, 26.8 (dbl), 25.9_5, 25.9_1, 25.0, 24.7 (dbl), 20.8, 20.4 (dbl), 20.1, 18.6, 18.5, 18.2, 18.0_9, 18.0_6, 16.6, 16.3, 13.3, 12.6, 12.1 (br), 9.3, 9.2 (dbl), -3.7, -4.4, -4.5, -4.7; IR 1740, 1700. Anal. Calcd for $C_{79}H_{155}Si_4O_{13}N$: C, 65.92; H, 10.85; N, 0.97. Found:[11] C, 65.86; H, 10.72; N, 1.01.

Aldehyde 14. To a solution of dimethyl acetal **13** (348 mg, 0.242 mmol) in 11 mL of CH_2Cl_2 at 25 °C were added glyoxylic acid monohydrate (225 mg, 2.44 mmol) and acetic acid (140 μL). The resulting suspension was heated to 40 °C and aged for 2 h. The suspension was cooled to 0 °C, diluted with CH_2Cl_2 (100 mL), and washed with saturated aqueous $NaHCO_3$ (3 × 50 mL). The solution was dried ($MgSO_4$) and concentrated in vacuo to afford 330 mg of crude product that was chromatographed on 29 g of silica gel. Elution with hexanes/ethyl acetate (12:1) gave 318 mg (94%) of the aldehyde **14** as a colorless oil. For spectral data, see ref 2b. Anal. Calcd for $C_{77}H_{149}Si_4O_{12}N$: C, 66.38; H, 10.78; N, 1.01. Found:[11] C, 66.32; H, 10.69; N, 1.09.

Acknowledgment. We wish to thank J. Wu, J. Perkins, and M. Valenciano for performing combustion analysis and R. Borris for supplying us with natural FK-506.

Supplementary Material Available: Copies of ^1H and/or ^{13}C NMR spectra for compounds **2**, **4**, **5**, **7a,b**, **8a,b**, **10a,b**, **11a**, **12**, and **13** (15 pages). Ordering information is given on any current masthead page.

(11) The combustion analyses for these compounds in a prior paper[2b] by one of us (R.R.) was that obtained from this naturally derived material.

Rearrangement of Rigid Cyclopropylcarbinyl Radicals: Investigation of a Reporter System for the Detection of Very Short Lived Radicals

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The ring-opening rearrangements of the spiro[cyclopropane-1,1′-indan]-2′-yl radicals **1** and **2**, the dispiro-[cyclopropane-1,1′-indan-3′,1″-cyclopropane]-2′-yl radical **3**, and the 3′,4′-dihydrospiro[cyclopropane-1,1′-(2′*H*)-naphthalen]-2′-yl radicals **4** and **5** were investigated by the tin hydride method. At 75 °C, the following unimolecular rate constants (k_r) were obtained: 2.1×10^9 s^{-1} (**1**), 8.6×10^9 s^{-1} (**2**), 5.3×10^8 s^{-1} (**3**), 3.0×10^9 s^{-1} (**4**), and 3.6×10^9 s^{-1} (**5**). The rate of ring opening of the 3′,3′-dimethylspiro[cyclopropane-1,1′-indan]-2′-yl radical **2** is comparable to that of the bicyclo[2.1.0]pent-2-yl radical and is one of the fastest cyclopropylcarbinyl radical rearrangements currently known.

Introduction

A central issue for a number of reactions that can be formulated either as two sequential inner-sphere single-electron transfers or as a one-step two-electron process is how these conceptually different pathways can be distinguished experimentally.[1,2] The difficulty of this distinction is well recognized; an in-cage process of two sequential single-electron transfers in which the second electron transfer is more rapid than molecular reorientation will not differ from a concerted two-electron-transfer process with presently available mechanistic probes. Because of our interest in halogen–lithium interchange, a reaction for which this mechanistic dichotomy exists, we initiated a

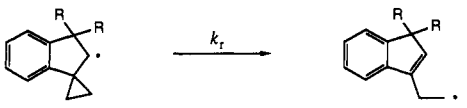
(1) For summaries, see: (a) Andrieux, C. P.; Gelis, L.; Saveant, J.-M. *J. Am. Chem. Soc.* **1990**, *112*, 786. (b) Lehmann, R. E.; Bockman, T. M.; Kochi, J. K. *Ibid.* **1990**, *112*, 458. (c) Pross, A. *Acc. Chem. Res.* **1985**, *18*, 212. (d) Eberson, L. *Adv. Phys. Org. Chem.* **1982**, *18*, 79.

(2) For discussion of a representative case, see: (a) Newcomb, M.; Curran, D. P. *Acc. Chem. Res.* **1988**, *21*, 206. (b) Ashby, E. C. *Ibid.* **1988**, *21*, 414.

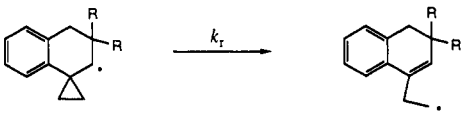
0022-3263/90/1955-5454$02.50/0

study of mechanistic probes that can report the occurrence of radical intermediates on a shorter time scale than heretofore.[3] We sought radical clocks that could undergo rearrangement within the estimated lifetime of a radical pair solvent cage, i.e., with rate constants equal to or greater than 10^{11} s^{-1} at ambient temperatures.[4,5]

Our approach is based on the ring opening of the cyclopropylmethyl radical, a reaction that was the fastest known radical clock at the time we began this study and that has since been confirmed to proceed with a rate constant of 9.4×10^7 s^{-1} at 25 °C.[6] Walton and Roberts have shown that rigid spirocyclopropylcarbinyl radicals undergo ring opening more rapidly than acyclic systems and attributed this to a greater relief of ring strain and a favorable alignment of the reacting orbitals.[7] It is also known that alkyl or aryl substituents on the cyclopropane ring can accelerate the ring opening of cyclopropylcarbinyl radicals.[8,9] Accordingly, we first investigated the radical clocks **1–5**. These systems should undergo ring opening faster than acyclic cyclopropylcarbinyl radicals under the considerations of Walton and Roberts and might show a further enhanced rate due to developing conjugation with the aromatic ring.

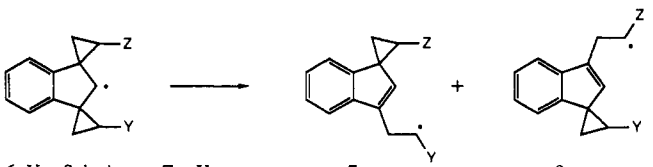


1, R = H; **2**, R = CH_3
3, R, R = CH_2CH_2



4, R = H; **5**, R = CH_3

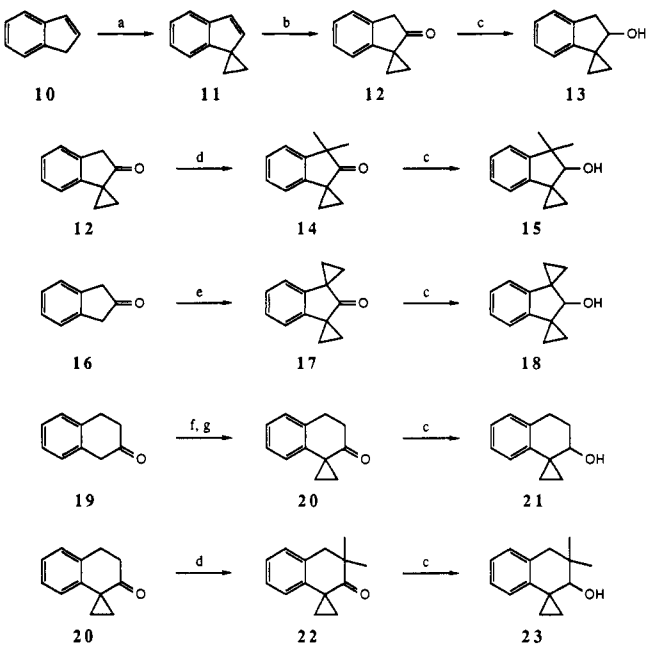
In order to determine the effect of cyclopropane ring substituents on the rates of ring opening of **1–3**, we also planned to carry out competitive experiments with the radical clock system **6**. In this system, the two cyclopropane rings have the same geometry with respect to the radical center, and the rate of opening of the unsubstituted ring might be used as an internal radical clock against which the intramolecularly competitive opening of the



6, Y = Substituent, Z = H
9, Y, Z = Substituent

7 **8**

Scheme I[a]



[a] (a) 50% aqueous NaOH, $Br_2(CH_2)_2$, TEBA; (b) HCO_2H, 30% H_2O_2, steam distillation; (c) $LiAlH_4$, Et_2O, 25 °C; (d) KH, CH_3I, THF, 25 °C; (e) 50% aqueous KOH, $Br_2(CH_2)_2$, TEBA; (f) KO-*t*-Bu, DMSO, 50 °C; (g) $Br_2(CH_2)_2$, 50 °C.

substituted ring can be calibrated. In this "double clock" experiment, the relative rates of the two ring-opening reactions of **6** could be determined from the ratio of products derived from the ring-opened radicals **7** and **8**. Assuming that irreversible opening of the unsubstituted ring in **6** does proceed with a rate on the order of 10^8 s^{-1} and that a product ratio of 1000:1 is measurable, ring opening rates of up to 10^{11} s^{-1}, on the scale of radical cage diffusion, might be measurable by this experiment. During the course of our work, Castellino and Bruice reported essentially the same approach to calibrate the ring opening of an acyclic (*trans*-2, *trans*-3-diphenylcyclopropyl)carbinyl radical and estimated the rate of that ring opening to be greater than 2×10^{10} s^{-1} at 30 °C.[9,10]

Another potential advantage of this approach for the investigation of metal–halogen interchange reactions is that, for a mechanistic probe with the general structure **9** in which Y and Z are anion- and radical-stabilizing substituents, respectively, a distinction between the one-electron- and two-electron-transfer pathways might be provided by the structures of the products formed.[11] In this paper, we report the synthesis of stable precursors to the cyclopropylcarbinyl radicals **1–5** and the measurement of rate constants at 75 °C for the ring-opening rearrangements of these radicals by the tin hydride method.[12]

(3) Beak, P.; Allen, D. J.; Lee, W.-K. *J. Am. Chem. Soc.* **1990**, *112*, 1629.
(4) For a review of radical clocks and their use as mechanistic probes, see: (a) Surzur, J. M. In *Reactive Intermediates*; Abramovitch, R. A., Ed.; Plenum Press: New York, 1982; Vol. 2, p 253. (b) Beckwith, A. L. J.; Ingold, K. U. In *Rearrangements in Ground and Excited States*; De Mayo, P., Ed.; Academic Press: New York, 1980; Vol. I, Essay 4. (c) Griller, D.; Ingold, K. U. *Acc. Chem. Res.* **1980**, *13*, 317.
(5) The lifetime of a radical pair solvent cage has been estimated at ca. 10^{-11} s. Noyes, R. M. *J. Am. Chem. Soc.* **1955**, *77*, 2042.
(6) Newcomb, M.; Glenn, A. G. *J. Am. Chem. Soc.* **1989**, *111*, 275 and references cited therein.
(7) Roberts, C.; Walton, J. C. *J. Chem. Soc., Perkin Trans. 2* **1985**, 841.
(8) (a) Newcomb, M.; Glenn, A. G.; Williams, W. G. *J. Org. Chem.* **1989**, *54*, 2675. (b) Beckwith, A. L. J.; Bowry, V. W. *Ibid.* **1989**, *54*, 2681.
(9) Castellino, A. J.; Bruice, T. C. *J. Am. Chem. Soc.* **1988**, *110*, 7512.
(10) For other examples of radical rearrangements competing intramolecularly, see: (a) Tsang, R.; Dickson, J. K., Jr.; Pak, H.; Walton, R.; Fraser-Reid, B. *J. Am. Chem. Soc.* **1987**, *109*, 3484. (b) Johns, A.; Murphy, J. A.; Patterson, C. W.; Wooster, N. F. *J. Chem. Soc., Chem. Commun.* **1987**, 1238.
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Results of our investigation of the methyl-substituted double clock **6** (Y = CH_3) are also presented.

Results

Synthesis and Reactions of the Radical Precursors. The alcohols **13**, **15**, **18**, **21**, and **23** were prepared by reduction of the corresponding ketones, as shown in Scheme I, and were characterized by ^1H and ^{13}C NMR, IR, MS, and elemental analysis. The spiroindanone **12** was obtained in 33% overall yield by treatment of 1*H*-indene (**10**) under phase-transfer conditions with 1,2-dibromoethane in 50% aqueous sodium hydroxide to afford **11**, followed by performic acid oxidation to **12**.[13] Further elaboration of **12** to the dimethylspiroindanone **14** was achieved in situ in 66% yield by treatment of **12** with a 2-fold excess of potassium hydride and methyl iodide at room temperature.[14] The dispiroindanone **17** was obtained in 56% yield by treatment of 2-indanone (**16**) with 50% aqueous potassium hydroxide and 1,2-dibromoethane under phase-transfer conditions.[15] The spirotetralone **20** was obtained in 48% yield by treatment of β-tetralone (**19**) with potassium *tert*-butoxide in DMSO, followed by trapping with 1,2-dibromoethane.[16] Further elaboration of **20** to the dimethylspirotetralone **22** was also carried out in situ with excess potassium hydride and methyl iodide and proceeded in 87% yield.[14]

Treatment of the alcohols with methyl oxalyl chloride and pyridine under mild conditions afforded the methyl oxalates **24–28** in 91% to 94% yield. Dolan and MacMillan have reported that methyl oxalate derivatives of secondary and tertiary alcohols are reduced to the corresponding hydrocarbons by Bu_3SnH/AIBN via a radical-chain mechanism when heated in refluxing benzene or toluene.[17,18] Indeed, preliminary tests showed that **24**, **26**, **27**, and **28** undergo reduction cleanly with Bu_3SnH/AIBN in benzene at 75 °C. Unexpectedly, the reaction of **25** under the same conditions produced only trace amounts of reduced products. As an alternative, the phenyl thiocarbonate **29** was prepared in 85% yield by treatment of **15** with *o*-phenyl chloromethanethioate and pyridine under mild conditions.[19] This function is analogous to the thiocarbonyl ester precursors originally used by Barton for the generation of radicals by deoxygenation, and **29** undergoes reduction cleanly with Bu_3SnH/AIBN in benzene at 75 °C.[20] For the double clock experiment, the methyl-substituted dispiro alcohol was prepared by treatment of **18** with 2.6 equiv of *sec*-BuLi in refluxing ether, followed by reaction with methyl iodide.[21] Treatment of this alcohol with methyl oxalyl chloride/pyridine afforded the precursor **30** in 94% yield.

Scheme II

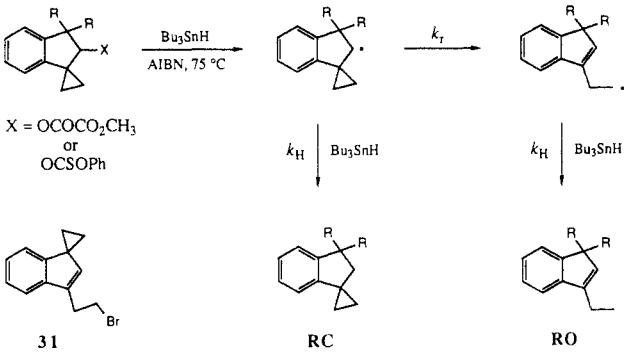
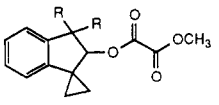


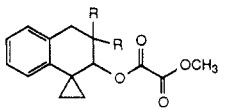
Table I. First-Order Rate Constants (k_r) for the Rearrangements of Radicals 1–5 at 75 ± 0.1 °C

radical	[Bu_3SnH], mol/L	[RO]/[RC][a,b]	10^9k_r,[a,c] s^{-1}
 1	2.0	190 ± 36	2.1 ± 0.4
 2	2.5	616 ± 76[d]	8.6 ± 1.4
 3	2.0	47 ± 4	0.53 ± 0.08
 4	2.0	270 ± 42	3.0 ± 0.6
 5	2.0	317 ± 20	3.6 ± 0.4
			0.52[e]

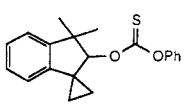
[a] Errors as ±2 standard deviations. [b] Determined by capillary GC and corrected for differences in detector response factors. [c] Calculated from eq 1. [d] The reliability of GC product ratios as high as 600:1 was verified by injection of standardized mixtures of authentic products. [e] Reference 6.



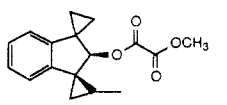
24, R = H
25, R = CH_3
26, R, R = CH_2CH_2



27, R = H
28, R = CH_3



29



30

Kinetics Measurements. The tin hydride method was used to generate and trap the cyclopropylcarbinyl radicals **1–5** at 75 °C in benzene, as illustrated in Scheme II.[12] Rate constants for the ring-opening rearrangements (k_r) were obtained from the product ratios [RO]/[RC] using eq 1, where k_H was estimated at 5.6×10^6 M^{-1} s^{-1}. This

$$k_r = k_H[Bu_3SnH][RO]/[RC] \quad (1)$$

value was obtained from Arrhenius parameters previously

(12) For recent use of the tin hydride method, see: (a) Beckwith, A. L. J.; Wang, S.; Warkentin, J. *J. Am. Chem. Soc.* **1987**, *109*, 5289. (b) Park, S.-U.; Chung, S.-K.; Newcomb, M. *Ibid.* **1986**, *108*, 240. (c) Beckwith, A. L. J.; O'Shea, D. M. *Tetrahedron Lett.* **1986**, 4525. (d) Abeywickrema, A. N.; Beckwith, A. L. J. *J. Chem. Soc., Chem. Commun.* **1986**, 464. (e) Newcomb, M.; Williams, W. G. *Tetrahedron Lett.* **1985**, 1179.

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(15) Klages, C.-P.; Voss, J. *Chem. Ber.* **1980**, *113*, 2255.

(16) Keely, S. L.; Martinez, A. J.; Tahk, F. C. *Tetrahedron* **1970**, *26*, 4729.

(17) Dolan, S. C.; MacMillan, J. *J. Chem. Soc., Chem. Commun.* **1985**, 1588.

(18) Conversion of the alcohols to the corresponding halides, a more common radical precursor, in this protocol led to substantial rearrangement and ring opening.

(19) Robins, M. J.; Wilson, J. S.; Hansske, F. *J. Am. Chem. Soc.* **1983**, *105*, 4059.

(20) Barton, D. H. R.; McCombie, S. W. *J. Chem. Soc., Perkin Trans. 1* **1975**, 1574.

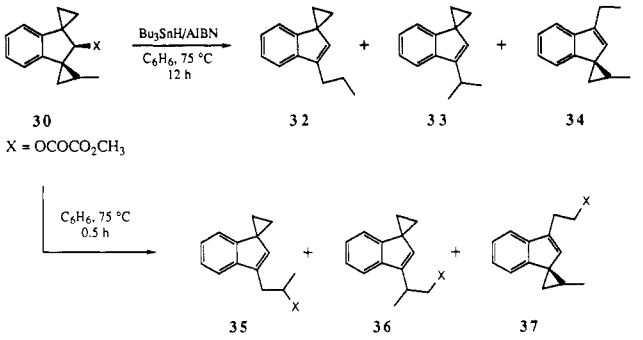
(21) (a) Gallagher, D. J.; Garrett, C. G.; Lemieux, R. P.; Beak, P. *J. Org. Chem.*, submitted for publication. (b) Klumpp, G. W. *Rec. Trav. Chim. Pays-Bas* **1986**, *105*, 1.

reported by Ingold and co-workers for the reaction of a cyclohexyl radical with Bu_3SnH, with the reasonable assumption that k_H is insensitive to the structure of the radical being trapped.[12,22]

The reductions were carried out in sealed ampules with a 10-fold excess of Bu_3SnH and a catalytic amount of AIBN (1.5% M) in dry, deoxygenated benzene.[23] The ampules were kept in a thermostated bath maintained at 75 ± 0.1 °C until completion of the reaction, after which the excess tin hydride was removed in the form of insoluble Bu_3SnF by treatment of the reaction mixtures with *t*-BuBr, followed by addition to a saturated aqueous solution of KF.[24] Four identical runs were made for each experiment. The product mixtures were analyzed by capillary GC, and the product ratios were corrected for differences in detector response factors. Authentic ring-closed and ring-opened compounds were synthesized for each case and used to establish the identities of the products. The relative stabilities of the reduction products in the presence of excess Bu_3SnH/AIBN under the above reaction conditions were determined by control experiments using mixtures of authentic materials.[25] The thermal stability of each radical precursor was demonstrated by ^1H NMR analysis after allowing the compounds to stand in benzene at 75 °C for the corresponding time of reaction. The bromide **31** was allowed to react with Bu_3SnH/AIBN under the reaction conditions used for the reduction of **26** to test the assumption that the radical ring-opening reaction is irreversible in these systems. This reaction proceeded without formation of any ring-closed product, as determined by capillary GC.

Rate constants for the ring opening of radicals **1–5** at 75 °C are provided in Table I along with the rate constant for ring opening of the cyclopropylmethyl radical at 75 °C.[6] These results show that four of the spirocyclopropylcarbinyl radicals do undergo rearrangement at somewhat faster rates than that reported for the rearrangement of the acyclic cyclopropylmethyl radical. The rearrangement of the *gem*-dimethylspiroindanyl radical **2** proceeds ca. four times more rapidly than that of the unsubstituted system **1**, whereas for the spirotetrahydronaphthyl system **4**, similar *gem*-dimethyl substitution has a negligible effect on the rate of rearrangement. These results also show that the rearrangement of the dispiroindanyl radical **3** is slower than that of the corresponding spiroindanyl radical **1** by a factor of 4, and statistical correction suggests that ring opening in **3** is eight times slower than in **1**.

Treatment of the methyl oxalate **30** with 1.1 equiv of Bu_3SnH and a catalytic amount of AIBN for 12 h in benzene at 75 °C gave the products **32**, **33**, and **34**, apparently arising from all possible ring openings of the dispiro radical, in a ratio of 3.5:1:1, respectively. The products were identified by comparison with authentic materials using ^1H NMR and GC/MS. These results might be interpreted to show that ring opening of **6** (Y = CH_3) to the secondary radical is favored by a factor of 5.2:1 after statistical correction. However, a control experiment showed that **30** isomerizes completely to a mixture of the ring-opened oxalates **35**, **36**, and **37** after standing in



benzene at 75 °C for 30 min. The structural assignments of these compounds are based on ^1H NMR decoupling experiments and on a GC/MS analysis of the mixture. Hence, the formation of **32–34** in this experiment does not represent the ring opening of the putative radical, but reflects at least in part the isomerization of the reactant **30** prior to radical formation.[26] Further efforts to provide a precursor to radical **6** (Y = CH_3) that is stable under these conditions were unsuccessful. This observation offers a caution to the use of mechanistic probes that incorporate a cyclopropylcarbinyl radical precursor to detect the occurrence of radical intermediates. The possibility that such a probe undergoes rearrangement prior to radical formation should be investigated by appropriate control experiments.

Discussion

The rate of ring opening of the cyclopropylcarbinyl radical **2** of (8.6 ± 1.4) × 10^9 s^{-1} at 75 °C is comparable to that of 6.2 × 10^9 s^{-1} at 75 °C for the ring opening of the bicyclo[2.1.0]pent-2-yl radical, one of the fastest cyclopropylcarbinyl radical rearrangements currently known, and is about 1 order of magnitude faster than that of the acyclic cyclopropylmethyl radical.[6,27] The explanations provided by Roberts and Walton concerning the favorable frontier orbital overlap and greater relief of ring strain in the rearrangements of rigid spirocyclopropylcarbinyl radical systems, along with the potential for stabilization of the developing double bond by the adjacent phenyl ring, provide a rationale for the rate enhancements observed in the rearrangements of radicals **1**, **2**, **4**, and **5**.[7] The slower rate of **3** however, is not consistent with this rationale and could be attributed to ground-state stabilization of the ring-closed radical due to the presence of two cyclopropyl rings adjacent to the radical center or to increased strain in the transition state for ring opening.[28] We have attempted to correlate these results by open-shell semiempirical MNDO and AM1 calculations without success and provide the details and a note of caution about such correlations in the supplementary material.[29]

Although the radical clock **2** is comparable to the fastest unsubstituted cyclopropylcarbinyl radical clocks that have

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

(23) In this study, we are interested in order of magnitude comparisons. The effects of thermal expansion of the solution, changes in tributyltin hydride concentration, and the errors in the use of the cyclohexyl radical as a model for the cyclopropylcarbinyl radicals **1–5** are assumed to be negligible.

(24) Leibner, J. E.; Jacobus, J. *J. Org. Chem.* **1979**, *44*, 449.

(25) Variations in the product ratios over the corresponding reaction time periods are small and fall within the experimental errors given in Table I.

(26) We believe that the rearrangement of **30** to **35–37** is consistent with the formation of ion pairs in solution. (a) Mazur, R. H.; White, W. N.; Semenov, D. A.; Lee, C. C.; Silver, M. S.; Roberts, J. D. *J. Am. Chem. Soc.* **1959**, *81*, 4390. (b) Schleyer, P. v. R.; Van Dine, G. W. *Ibid.* **1966**, *88*, 2321.

(27) A rate constant of 2.4 × 10^9 s^{-1} at 37 °C was recently obtained by competition kinetics for the bicyclo[2.1.0]pent-2-yl radical rearrangement using TEMPO as the radical trapping agent. This corresponds to an estimated E_A value of 5.1 kcal/mol, assuming a preexponential of 13.0 s^{-1}. Bowry, V. W.; Lusztyk, J.; Ingold, K. U. *J. Am. Chem. Soc.* **1989**, *111*, 1927.

(28) The stabilization energy of a cyclopropylmethyl radical was recently estimated to be 2.4 kcal/mol, based on EPR measurements. Walton, J. C. *Magn. Reson. Chem.* **1987**, *25*, 998.

(29) (a) Dewar, M. J. S.; Thiel, W. *J. Am. Chem. Soc.* **1977**, *99*, 4899. (b) Dewar, M. J. S.; Zoebisch, E. G.; Healy, E. F.; Stewart, J. J. P. *Ibid.* **1985**, *107*, 3902.

been calibrated, it is several times slower than the phenyl-substituted cyclopropylcarbinyl system of Castellino and Bruice.[9] The radical clock **2** is still 2 orders of magnitude slower than what we believe is needed to provide a mechanistic probe capable of differentiating between sequential one-electron- and two-electron-transfer processes on the time scale of inner-sphere single-electron-transfer reactions. Nonetheless, the double clock approach does appear to provide a framework by which faster radical clocks can be calibrated.[4,5,9]

Experimental Section

General. ^{1}H NMR and ^{13}C NMR spectra were recorded on a Varian XL-200, General Electric QE-300, or General Electric GN-500 spectrometer in deuteriochloroform or deuterated benzene. The chemical shifts are reported in δ (ppm) relative to tetramethylsilane as internal standard. Infrared spectra were recorded on a IBM IR/32 FT-IR spectrometer as thin films or as KBr pellets. Peaks are reported in units of cm^{-1} with the following relative intensities: s, strong; m, medium; w, weak. Low-resolution EI mass spectra were recorded on a Finnigan-MAT CH-5 or Finnigan-MAT 731 mass spectrometer with an ionization voltage of 10 or 70 eV. Peaks are reported as *m/e* (% intensity relative to the base peak). Low-resolution EI GC/MS analyses were carried out on a Hewlett-Packard 5970 mass selective detector coupled to a Hewlett-Packard 5890 gas chromatograph with a 12 m × 0.20 mm i.d. HP-1 capillary column. The elemental analyses were performed by the University of Illinois Microanalytical Service Laboratory.

Gas chromatographic analyses were carried out on a Hewlett-Packard 5790 or 5890 instrument, each fitted with a flame ionization detector, using bonded phase FSOT capillary columns: Alltech Associates 30 m × 0.25 mm i.d. RSL-200 (column A); 60 m × 0.25 mm i.d. RSL-200 (column B); Hewlett-Packard 12 m × 0.20 mm i.d. HP-1 (column C); 30 m × 0.20 mm i.d. Ultra-2 (column D). For each column, the head pressure was adjusted for a column gas flow of 1.0 mL/min. Peak integrations were obtained on a Hewlett-Packard 3390A or 3396A integrator and were corrected individually for detector response factors. Medium-pressure liquid chromatography (MPLC) separations were carried out with homemade 12 in. × 1 in. and 36 in. × 1 in. columns packed with 32–63-mesh Woelm silica gel. Melting points were measured on a Thomas-Hoover apparatus and are uncorrected.

Materials. All solvents and reagents were obtained from commercial sources and used without further purification, unless otherwise noted. Benzene, diethyl ether (ether), and tetrahydrofuran (THF) were freshly distilled from sodium/benzophenone under an atmosphere of dry nitrogen. For the kinetics experiments, benzene was further degassed by three freeze–pump–thaw cycles under high vacuum. Methylene chloride (CH_2Cl_2) and pyridine were distilled from calcium hydride and stored under dry nitrogen. The ethyl acetate and hexane solvents used for column chromatography were distilled over sodium carbonate and 3-Å molecular sieves, respectively. Spiro[cyclopropane-1,1′-indan]-2′-one (**12**), dispiro[cyclopropane-1,1′-indan-3′,1″-cyclopropan]-2′-one (**17**), 3′,4′-dihydrospiro[cyclopropane-1,1′(2′*H*)-naphthalen]-2′-one (**20**), and *anti*-2-methyldispiro[cyclopropane-1,1′-indan-3′,1″-cyclopropan]-*syn*-2′-ol (**38**) were prepared by literature procedures and shown to have the expected physical and spectral properties.[13,15,16,21]

Spiro[cyclopropane-1,1′-indan]-2′-ol (13). Under a N_2 atmosphere, a solution of **12** (2.85 g, 18 mmol) in 50 mL of dry ether was added dropwise over 0.5 h to a mechanically stirred suspension of lithium aluminum hydride (0.47 g, 12.0 mmol) in 140 mL of dry ether cooled to 0 °C. The mixture was stirred overnight at 25 °C and quenched by addition of an aqueous Na_2SO_4 slurry until the liquid phase turned clear. The mixture was filtered, and the filtrate was dried ($MgSO_4$). Removal of the solvent in vacuo afforded 2.7 g (94%) of **13** as a white solid: mp 85–87 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.84–0.90 (m, 1 H), 0.96–1.03 (m, 1 H), 1.07–1.14 (m, 1 H), 1.20–1.27 (m, 1 H), 1.76 (br s, OH), 2.94 (dd, J = 1.9, 16.6 Hz, 1 H), 3.36 (dd, J = 6.1, 16.5 Hz, 1 H), 4.08 (br d, CHO-), 6.70–6.74 (m, 1 H), 7.11–7.18 (m, 2 H), 7.19–7.23 (m, 1 H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 9.7, 16.9, 34.1, 41.2, 78.1, 118.8, 124.6, 126.1, 126.9, 140.6, 145.4; IR (KBr) 3299 (s), 3004 (w), 2940 (w), 2913 (w), 1607 (w), 1483 (m), 1458 (m), 1426 (w), 1331 (m), 1287 (m), 1240 (m), 1206 (w), 1169 (m), 1084 (m), 1040 (s), 1024 (m), 988 (m), 941 (m), 911 (m), 870 (w), 758 (s), 752 (s), 731 (m) cm^{-1}; MS (70 eV) *m/e* 160 (M^+, 68), 145 (100), 142 (70), 132 (82), 131 (82), 129 (44), 117 (66), 115 (85), 103 (25), 91 (63), 89 (14), 77 (66), 65 (19), 63 (26), 51 (32).

Anal. Calcd for $C_{11}H_{12}O$: C, 82.47; H, 7.55. Found: C, 82.55; H, 7.57.

3′,3′-Dimethylspiro[cyclopropane-1,1′-indan]-2′-one (14). Under an Ar atmosphere, a solution of **12** (3.18 g, 20 mmol) in 25 mL of dry THF was added dropwise to 5.9 g (50 mmol) of 35% potassium hydride oil dispersion stirred in 40 mL of dry THF that was being cooled with a water bath. The mixture was stirred at 25 °C for 5 min, and 7.3 g (51 mmol) of methyl iodide dissolved in 10 mL of dry THF was added dropwise over 15 min while cooling was continued. The mixture was stirred for an additional 20 min at 25 °C, carefully quenched with water (20 mL), and extracted with ether (2 × 75 mL). The combined extracts were washed with saturated aqueous NH_4Cl (100 mL) and brine (100 mL), dried ($MgSO_4$), and concentrated to give a crude oil. Distillation under reduced pressure using a 6-in. Vigreux column afforded 2.46 g (66%) of **14** as a colorless oil: bp 70–71 °C (0.3 Torr); ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.36 (s, 2 CH_3), 1.36–1.38 (m, 2 H), 1.67–1.70 (m, 2 H), 6.82–6.83 (m, 1 H), 7.25–7.28 (m, 3 H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 22.0, 25.6, 32.5, 49.3, 118.4, 122.5, 126.8, 127.5, 140.7, 147.1, 221.4; IR (neat) 3048 (w), 2967 (s), 2928 (m), 2867 (w), 1736 (s), 1613 (w), 1480 (m), 1460 (m), 1416 (w), 1379 (w), 1350 (w), 1321 (s), 1219 (m), 1196 (w), 1117 (m), 1082 (m), 1036 (m), 1024 (w), 1011 (m), 939 (w), 752 (s) cm^{-1}; MS (70 eV) *m/e* 186 (M^+, 100), 171 (39), 158 (16), 143 (54), 128 (11), 125 (9), 107 (5), 81 (10).

Anal. Calcd for $C_{13}H_{14}O$: C, 83.83; H, 7.58. Found: C, 84.07; H, 7.61.

3′,3′-Dimethylspiro[cyclopropane-1,1′-indan]-2′-ol (15). The procedure described for the preparation of **13** was used with 4.46 g (24 mmol) of **14** and 0.64 g (16 mmol) of lithium aluminum hydride to afford 3.68 g (82%) of **15** as a white solid: mp 78–80 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.81–0.85 (m, 1 H), 0.96–1.00 (m, 1 H), 1.03–1.07 (m, 1 H), 1.17–1.22 (m, 1 H), 1.26 (s, CH_3), 1.32 (s, CH_3), 1.48 (d, J = 8.0 Hz, OH), 3.78 (d, J = 8.0 Hz, CHO-), 6.71–6.73 (m, 1 H), 7.14–7.20 (m, 3 H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 10.5, 13.6, 22.1, 27.2, 30.6, 46.6, 85.2, 118.8, 122.1, 126.4, 127.0, 143.6, 149.8; IR (KBr) 3281 (s), 3069 (w), 2994 (w), 2955 (m), 2865 (w), 1607 (w), 1480 (m), 1456 (m), 1426 (w), 1379 (w), 1360 (w), 1300 (w), 1242 (w), 1123 (w), 1061 (s), 1022 (w), 1001 (m), 955 (m), 907 (m), 750 (s), 727 (w) cm^{-1}; MS (10 eV) *m/e* 188 (M^+, 99), 173 (87), 170 (20), 160 (88), 157 (11), 155 (19), 145 (100), 129 (7), 117 (16), 91 (3).

Anal. Calcd for $C_{13}H_{16}O$: C, 82.94; H, 8.57. Found: C, 82.74; H, 8.47.

Dispiro[cyclopropane-1,1′-indan-3′,1″-cyclopropan]-2′-ol (18). The procedure described for the preparation of **13** was used with 9.55 g (52 mmol) of **17** and 1.27 g (31.8 mmol) of lithium aluminum hydride to afford 8.65 g (90%) of **18** as a white solid: mp 136–137 °C; ^{1}H NMR (200 MHz, $CDCl_3$) δ 0.98–1.38 (m, 8 H), 1.54 (d, J = 7.3 Hz, OH), 3.67 (d, J = 7.1 Hz, CHO-), 6.65–6.70 (m, 2 H), 7.09–7.13 (m, 2 H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 10.5, 18.1, 32.9, 83.4, 118.3, 126.4, 145.4; MS (70 eV) *m/e* 186 (M^+, 40), 171 (22), 168 (6), 158 (100), 155 (9), 153 (10), 143 (13), 141 (17), 129 (46), 115 (48), 102 (5), 91 (6), 89 (5), 77 (11), 63 (10).

Anal. Calcd for $C_{13}H_{14}O$: C, 83.83; H, 7.58. Found: C, 83.86; H, 7.50.

3′,4′-Dihydrospiro[cyclopropane-1,1′(2′*H*)-naphthalen]-2′-ol (21). The procedure described for the preparation of **13** was used with 3.73 g (21.7 mmol) of **20** and 0.64 g (16 mmol) of lithium aluminum hydride to afford 3.28 g (87%) of **21** as a white solid: mp 98–99 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.82–0.86 (m, 1 H), 0.95–0.99 (m, 1 H), 1.06–1.11 (m, 1 H), 1.20–1.24 (m, 1 H), 1.61 (s, OH), 1.98–2.05 (m, 1 H), 2.07–2.13 (m, 1 H), 2.78–2.83 (m, 1 H), 3.18–3.25 (m, 1 H) 3.42 (br s, CHO-), 6.68–6.69 (m, 1 H), 7.06–7.12 (m, 3 H); irradiation of the signal at 2.07–2.13 ppm simplified the signals at 2.78–2.83 and 3.18–3.25 ppm to doublets; ^{13}C NMR (125 MHz, $CDCl_3$) δ 13.2, 19.6, 24.7, 25.3, 28.4, 73.8, 122.3, 125.0, 126.3, 128.6, 136.2, 138.5; IR (KBr) 3243 (s), 3077 (m), 2934 (s), 2843 (m), 1603 (w), 1493 (s), 1456 (m), 1441 (m), 1428 (m), 1308 (m), 1260 (m), 1248 (m), 1178 (w), 1088 (m), 1067

(s), 1043 (m), 1013 (m), 951 (s), 934 (s), 752 (s) cm^{-1}; MS (70 eV) *m/e* 174 (M^+, 93), 159 (17), 156 (60), 146 (100), 141 (44), 130 (69), 117 (31), 115 (20), 91 (8).

Anal. Calcd for $C_{12}H_{14}O$: C, 82.72; H, 8.10. Found: C, 82.81; H, 8.10.

3′,4′-Dihydro-3′,3′-dimethylspiro[cyclopropane-1,1′-(2′*H*)-naphthalen]-2′-one (22). The procedure described for the preparation of **14** was used with 3.44 g (20 mmol) of **20**, 5.2 g (45 mmol) of 35% potassium hydride oil dispersion, and 6.4 g (45 mmol) of methyl iodide. After workup, the crude product was distilled under reduced pressure to afford 3.5 g (87%) of **22** as a colorless oil: bp 105–107 °C (1.5 Torr); ^1H NMR (300 MHz, $CDCl_3$) δ 1.14 (s, 2 CH_3), 1.27–1.31 (m, 2 H), 1.74–1.78 (m, 2 H), 2.94 (s, 2 H), 6.71 (d, *J* = 7.1 Hz, 1 H), 7.13–7.20 (m, 3 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 23.9, 24.3, 29.2, 42.6, 43.2, 121.2, 125.6, 126.8, 128.2, 134.8, 138.3, 213.4; IR (neat) 3009 (w), 2967 (m), 2928 (m), 2836 (w), 1698 (s), 1607 (w), 1493 (m), 1468 (m), 1458 (m), 1418 (w), 1383 (m), 1366 (w), 1348 (w), 1310 (m), 1250 (m), 1094 (m), 1055 (s), 1040 (m), 1026 (w), 1003 (m), 754 (s) cm^{-1}; MS (70 eV) *m/e* 200 (M^+, 48), 185 (100), 170 (18), 157 (20), 152 (4), 142 (22), 129 (28), 128 (28), 115 (26), 102 (4), 91 (8), 89 (5), 77 (9), 63 (8).

Anal. Calcd for $C_{14}H_{16}O$: C, 83.96; H, 8.05. Found: C, 83.95; H, 8.07.

3′,4′-Dihydro-3′,3′-dimethylspiro[cyclopropane-1,1′-(2′*H*)-naphthalen]-2′-ol (23). The procedure described for the preparation of **13** was used with 3.5 g (17.5 mmol) of **22** and 0.52 g (13.1 mmol) of lithium aluminum hydride to afford 2.91 g (82%) of **23** as a white solid: mp 93–94 °C; ^1H NMR (500 MHz, $CDCl_3$) δ 0.87–0.92 (m, 1 H) 0.97 (s, CH_3), 1.01–1.05 (m, 1 H), 1.10–1.15 (m, 2 H), 1.12 (s, CH_3), 1.56 (d, *J* = 3.6 Hz, OH), 2.44 (d, *J* = 16.4 Hz, 1 H), 2.83 (d, *J* = 3.4 Hz, CHO-), 3.08 (d, *J* = 16.4 Hz, 1 H), 6.64 (d, *J* = 7.5 Hz, 1 H), 7.06–7.12 (m, 3 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 12.4, 20.9, 24.4, 24.9, 26.4, 34.6, 38.9, 82.0, 122.0, 125.1, 126.2, 129.0, 135.6, 137.8; IR (KBr) 3343 (m), 3063 (w), 2957 (w), 2901 (w), 1491 (m), 1472 (w), 1383 (w), 1364 (w), 1246 (w), 1088 (m), 1038 (s), 1009 (m), 961 (w), 932 (w), 893 (w), 752 (s), 718 (m) cm^{-1}; MS (70 eV) *m/e* 202 (M^+, 48), 187 (18), 184 (8), 174 (51), 169 (64), 159 (100), 157 (30), 154 (12), 146 (24), 141 (32), 129 (63), 117 (23), 115 (57), 103 (8), 91 (34), 89 (7), 77 (15), 65 (8).

Anal. Calcd for $C_{14}H_{18}O$: C, 83.12; H, 8.97. Found: C, 83.12; H, 9.01.

Methyl Spiro[cyclopropane-1,1′-indan]-2′-yl Oxalate (24). Under a N_2 atmosphere, 1.74 mL (2.3 g, 18 mmol) of methyl oxalyl chloride was added to a stirred solution of **13** (2.4 g, 15 mmol) and pyridine (1.22 g, 15 mmol) in 75 mL of dry benzene. The mixture was stirred at 25 °C for 3.0 h and washed with 1 M aqueous HCl (2 × 75 mL). The aqueous washings were extracted with ether, and the combined organic layers were washed with saturated aqueous $NaHCO_3$ (2 × 100 mL) and brine (100 mL) and dried ($MgSO_4$). Removal of the solvents in vacuo afforded 3.35 g (91%) of **24** as a white solid: mp 97–98 °C; ^1H NMR (300 MHz, $CDCl_3$) δ 0.89–0.93 (m, 1 H), 1.18–1.29 (m, 3 H), 3.14 (d, *J* = 17.6 Hz, 1 H), 3.56 (dd, *J* = 6.3, 17.6 Hz, 1 H), 3.85 (s, OCH_3), 5.36 (d, *J* = 6.1 Hz, CHO-), 6.71–6.74 (m, 1 H), 7.16–7.24 (m, 3 H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 10.9, 18.6, 31.8, 38.5, 53.4, 84.4, 118.5, 124.3, 126.4, 127.3, 139.4, 144.9, 157.9, 158.3; IR (KBr) 3048 (w), 2996 (w), 2944 (w), 1759 (s), 1485 (w), 1439 (w), 1318 (s), 1223 (m), 1175 (m), 1159 (m), 994 (m), 980 (w), 953 (w), 939 (m), 843 (w), 752 (m), 716 (w) cm^{-1}; MS (70 eV) *m/e* 246 (M^+, 3), 142 (100), 131 (4), 128 (32), 115 (21), 103 (4), 91 (6), 89 (3), 77 (4), 65 (3), 63 (4).

Anal. Calcd for $C_{14}H_{14}O_4$: C, 68.28; H, 5.73. Found: C, 68.36; H, 5.84.

Methyl 3′,3′-Dimethylspiro[cyclopropane-1,1′-indan]-2′-yl Oxalate (25). The procedure described for the preparation of **24** was used with 2.82 g (15 mmol) of **15**, 1.22 g (15 mmol) of pyridine, and 1.74 mL (2.3 g, 18 mmol) of methyl oxalyl chloride to afford 3.8 g (92%) of **25** as a white solid: mp 114–115 °C; ^1H NMR (500 MHz, $CDCl_3$) δ 0.5–0.98 (m, 1 H), 1.10–1.17 (m, 2 H), 1.28–1.32 (m, 1 H), 1.36 (s, 2 CH_3), 3.85 (s, OCH_3), 5.11 (s, CHO-), 6.70–6.72 (m, 1 H), 7.15–7.23 (m, 3 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 10.2, 17.7, 21.6, 28.7, 29.6, 47.2, 53.3, 91.4, 118.5 121.7, 126.8, 127.4, 143.2, 149.1, 158.1, 158.4; IR (KBr) 3187 (w), 3027 (w), 2959 (w), 1761 (s), 1482 (w), 1458 (w), 1439 (w), 1350 (w), 1312 (m), 1217 (m), 1173 (m), 982 (w), 955 (w), 938 (w), 928 (w), 746 (m) cm^{-1}; MS (10 eV) *m/e* 274 (M^+, 8), 170 (100), 155 (22), 143 (6), 129 (3).

Anal. Calcd for $C_{16}H_{18}O_4$: C, 70.06; H, 6.61. Found: C, 70.20; H, 6.66.

Methyl Dispiro[cyclopropane-1,1′-indan-3′,1″-cyclopropan]-2′-yl Oxalate (26). The procedure described for the preparation of **24** was used with 1.86 g (10 mmol) of **18**, 0.83 g (10.5 mmol) of pyridine, and 1.15 mL (1.5 g, 12 mmol) of methyl oxalyl chloride to afford 2.56 g (94%) of **26** as a white solid: mp 117–118 °C; ^1H NMR (300 MHz, $CDCl_3$) δ 0.96–1.02 (m, 2 H), 1.19–1.30 (m, 4 H), 1.35–1.41 (m, 2 H), 3.86 (s, OCH_3), 5.08 (s, CHO-), 6.68–6.71 (m, 2 H), 7.13–7.16 (m, 2H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 11.0, 19.8, 31.0, 53.3, 91.1, 118.0, 126.7, 144.8, 158.4, 158.5; IR (KBr) 3002 (w), 2955 (w), 2851 (w), 1759 (s), 1485 (w), 1439 (w), 1354 (m), 1306 (m), 1215 (s), 1171 (m), 1073 (w), 986 (w), 968 (m), 949 (w), 938 (w), 856 (w), 746 (s) cm^{-1}; MS (70 eV) *m/e* 272 (M^+, 18), 244 (5), 206 (8), 204 (22), 186 (26), 171 (18), 168 (77), 165 (14), 158 (70), 155 (100), 153 (77), 141 (76), 139 (15), 129 (67), 115 (69), 102 (7), 91 (10), 89 (8), 84 (57), 77 (18).

Anal. Calcd for $C_{16}H_{16}O_4$: C, 70.58; H, 5.92. Found: C, 70.51; H, 6.02.

3′,4′-Dihydrospiro[cyclopropane-1,1′(2′*H*)-naphthalen]-2′-yl Methyl Oxalate (27). The procedure described for the preparation of **24** was used with 1.74 g (10 mmol) of **21**, 0.88 g (11 mmol) of pyridine, and 1.15 mL (1.53 g, 12 mmol) of methyl oxalyl chloride to afford 2.36 g (91%) of **27** as a white solid: mp 78–79 °C; ^1H NMR (500 MHz, $CDCl_3$) δ 0.88–0.92 (m, 1 H), 1.07–1.11 (m, 1 H), 1.16–1.21 (m, 1 H), 1.32–1.36 (m, 1 H), 2.11–2.18 (m, 1 H), 2.23–2.28 (m, 1 H), 2.82–2.87 (m, 1 H), 3.12–3.19 (m, 1 H), 3.84 (s, OCH_3), 4.82–4.83 (m, CHO-), 6.66–6.68 (m, 1 H), 7.10–7.15 (m, 3 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 14.4, 21.2, 22.7, 24.7, 26.2, 53.4, 80.8, 121.8, 125.3, 126.6, 128.6, 135.6, 137.9, 157.8, 158.5; IR (KBr) 3065 (w), 2963 (w), 2921 (w), 2842 (w), 1759 (s), 1497 (w), 1441 (w), 1331 (m), 1314 (m), 1219 (m), 1173 (m), 1034 (w), 982 (w), 910 (w), 876 (w), 752 (w) cm^{-1}; MS (70 eV) *m/e* 260 (M^+, 4), 156 (100), 141 (40), 129 (23), 117 (3), 115 (6).

Anal. Calcd for $C_{15}H_{16}O_4$: C, 69.22; H, 6.20. Found: C, 69.20; H, 6.19.

3′,4′-Dihydro-3′,3′-dimethylspiro[cyclopropane-1,1′-(2′*H*)-naphthalen]-2′-yl Methyl Oxalate (28). The procedure described for the preparation of **24** was used with 0.202 g (1.0 mmol) of **23**, 0.088 g (1.1 mmol) of pyridine, and 0.12 mL (0.16 g, 1.25 mmol) of methyl oxalyl chloride to afford 0.27 g (94%) of **28** as a white solid: mp 87–88 °C; ^1H NMR (500 MHz, $CDCl_3$) δ 0.93–0.97 (m, 1 H), 1.05 (s, CH_3), 1.07 (s, CH_3), 1.08–1.12 (m, 1 H), 1.20–1.29 (m, 2 H), 2.51 (d, *J* = 16.3 Hz, 1 H), 3.15 (d, *J* = 16.4 Hz, 1 H), 3.84 (s, OCH_3), 4.58 (s, CHO-), 6.62–6.63 (m, 1 H), 7.08–7.14 (m, 3 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 13.3, 22.1, 22.2, 24.7, 26.4, 34.4, 39.1, 53.3, 87.5, 121.4, 125.3, 126.4, 129.0, 134.9, 137.2, 158.2, 158.6; IR (KBr) 3006 (w), 2953 (w), 1765 (s), 1497 (w), 1437 (w), 1354 (w), 1308 (s), 1208 (m), 1169 (m), 986 (w), 930 (w), 903 (w), 760 (m) cm^{-1}; MS (70 eV) *m/e* 288 (M^+, 2), 184 (33), 169 (100), 157 (12), 154 (14), 143 (15), 141 (18), 129 (21), 115 (14), 91 (6), 77 (4).

Anal. Calcd for $C_{17}H_{20}O_4$: C, 70.81; H, 6.99. Found: C, 70.91; H, 7.03.

***O*-(3′,3′-Dimethylspiro[cyclopropane-1,1′-indan]-2′-yl) *O*-Phenyl Carbonothioate (29).** Under a N_2 atmosphere, 0.38 mL (0.474 g, 2.74 mmol) of *O*-phenyl chloromethanethioate was added to a stirred solution of **15** (0.465 g, 2.47 mmol) and pyridine (0.72 g, 9.1 mmol) in 15 mL of dry CH_2Cl_2. The mixture was stirred at 25 °C overnight and washed with 1 M aqueous HCl (2 × 25 mL). The aqueous washings were extracted with ether (2 × 25 mL), and the combined organic layers were washed with saturated aqueous $NaHCO_3$ (2 × 25 mL) and brine (25 mL), dried ($MgSO_4$), and concentrated to give a crude oil. Purification by MPLC with 5% (v/v) EtOAc/hexane as eluent afforded 0.68 g (85%) of **29** as a yellow oil: ^1H NMR (300 MHz, $CDCl_3$) δ 0.95–1.00 (m, 1 H), 1.14–1.20 (m, 1 H), 1.35–1.48 (m, 2 H), 1.40 (s, CH_3), 1.45 (s, CH_3), 5.63 (s, CHO-), 6.71–6.74 (m, 1 H), 7.06–7.45 (m, 3 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 10.0, 18.0, 21.6, 28.9, 29.9, 47.8, 98.9, 118.4, 121.6, 121.9, 126.4, 126.7, 127.4, 129.4, 143.4, 153.4, 196.0; IR (neat) 3071 (w), 2961 (m), 2867 (w), 1592 (m), 1489 (s), 1456 (m), 1364 (m), 1343 (m), 1287 (s), 1200 (s), 1157 (m), 1125 (w), 1071 (w), 1015 (m), 1001 (m), 961 (w), 922 (w), 839 (m), 770 (m), 752 (s) cm^{-1}; MS (70 eV) *m/e* 324 (M^+, 1), 202 (15), 171 (100),

155 (15), 153 (4), 143 (38), 141 (26), 137 (17), 129 (44), 115 (18), 109 (23), 94 (8), 91 (6), 77 (65), 65 (19).

Anal. Calcd for $C_{20}H_{20}O_2S$: C, 74.04; H, 6.21; S, 9.88. Found: C, 74.02; H, 6.16; S, 9.90.

Methyl *anti*-2-Methyldispiro[cyclopropane-1,1′-indan-3′,1″-cyclopropan]-*syn*-2′-yl Oxalate (30). The procedure described for the preparation of **24** was used with 1.45 g (7.2 mmol) of **38**, 0.59 g (7.4 mmol) of pyridine, and 0.84 mL (1.12 g, 8.8 mmol) of methyl oxalyl chloride to afford 1.94 g (94%) of **30** as a white solid: mp 84–86 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.87–0.93 (m, 1 H), 0.98 (dd, J = 4.4, 8.6 Hz, 1 H) 1.06 (dd, J = 4.5, 6.2 Hz, 1 H), 1.15–1.31 (m, 2 H), 1.21 (d, J = 6.3 Hz, CH_3), 1.42–1.49 (m, 1 H), 1.77–1.84 (m, 1 H), 3.83 (s, OCH_3), 5.21 (s, CHO-), 6.67–6.76 (m, 2 H), 7.11–7.17 (m, 2 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 9.7, 15.7, 18.0, 19.8, 26.7, 32.3, 33.8, 53.3, 91.3, 118.07, 118.13, 126.6, 126.7, 144.5, 145.7, 158.5, 158.6; IR (KBr) 3004 (w), 1759 (s), 1607 (w), 1482 (w), 1464 (w), 1437 (m), 1350 (m), 1306 (s), 1208 (s), 1165 (s), 1098 (w), 1084 (w), 1024 (w), 974 (m), 951 (m), 938 (m), 912 (m), 878 (m), 754 (s), 746 (m) cm^{-1}; MS (10 eV) m/e 286 (M^+, 12), 213 (11), 200 (100), 182 (39), 171 (4), 167 (26), 155 (9), 153 (5), 141 (20), 70 (60).

Anal. Calcd for $C_{17}H_{18}O_4$: C, 71.31; H, 6.34. Found: C, 71.35; H, 6.38.

3′-(2-Bromoethyl)spiro[cyclopropane-1,1′-[1*H*]indene] (31). To a solution of **18** (0.94 g, 5.0 mmol) and LiBr (0.88 g, 10.0 mmol) in 20 mL of THF cooled to 0 °C was added 2.0 mL of 48% aqueous HBr. The mixture was stirred at 0 °C for 3.0 h, poured into water (25 mL), and extracted with ether (3 × 25 mL). The combined extracts were washed with saturated aqueous $NaHCO_3$ (2 × 50 mL) and brine (50 mL), dried ($MgSO_4$), and concentrated to give a yellow solid. Recrystallization from pentane afforded 1.14 g (92%) of **31** as a white solid: mp 50–51 °C; ^{1}H NMR (200 MHz, $CDCl_3$) δ 1.55–1.63 (m, 4 H), 3.17 (t, J = 7.9 Hz, CH_2CH_2Br), 3.64 (t, J = 7.7 Hz, CH_2CH_2Br), 5.99 (s, 1 H), 6.93–6.98 (m, 1 H), 7.15–7.38 (m, 3 H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 14.6, 30.8, 31.6, 32.1, 117.5, 118.9, 124.6, 125.4, 136.6, 137.8, 143.0, 148.4; IR (KBr) 3073 (w), 2998 (w), 2961 (w), 1609 (w), 1460 (s), 1439 (m), 1381 (w), 1235 (w), 1208 (s), 1102 (w), 1065 (w), 1053 (w), 1018 (m), 951 (s), 909 (w), 791 (m), 750 (s); MS (70 eV) m/e 250 (M^{+2}, 34), 248 (M^+, 34), 169 (46), 167 (9), 165 (9), 155 (100), 141 (84), 139 (10), 128 (16), 115 (27), 83 (14), 63 (8).

Anal. Calcd for $C_{13}H_{13}Br$: C, 62.67; H, 5.26; Br, 32.07. Found: C, 62.83; H, 5.34; Br, 32.14.

Reductions of 24 and 26–28 with Bu_3SnH/AIBN. The following procedure is representative. A 0.45 M stock solution was prepared by mixing 0.554 g (2.25 mmol) of **24** and 0.056 g (0.34 mmol) of AIBN with dry, oxygen-free benzene in a 5.0-mL volumetric flask. In each of four 5-mL glass ampules previously swept with argon for 30 min, 1.10 mL of stock solution was mixed with 1.4 mL (1.51 g, 5.0 mmol) of neat Bu_3SnH. The ampules were frozen, sealed, and placed in a thermostated bath kept at 75 ± 0.1 °C for 12.0 h. The ampules were then cooled in ice and opened, and their contents were transferred to reaction flasks. Workup consisted of treatment with 1.0 mL (1.2 g, 8.4 mmol) of *tert*-butyl bromide for 5 h at 25 °C, followed by treatment with saturated aqueous KF (25 mL) with vigorous stirring overnight. The mixtures were filtered under vacuum, and the solid tin fluoride residues were washed twice with ether. The organic phases were separated, dried ($MgSO_4$), and concentrated to oily residues that were analyzed by capillary GC. The products were identified by coelution with authentic samples, and the product ratios were corrected for detector response factors.

Reduction of 29 with Bu_3SnH/AIBN. A 0.68 M stock solution was prepared by mixing 0.444 g (1.37 mmol) of **29** and 0.041 g (0.25 mmol) of AIBN with dry, oxygen-free benzene in a 2.0-mL volumetric flask. In each of four 5-mL ampules previously swept with argon for 30 min, 0.73 mL of stock solution was mixed with 1.67 mL (1.8 g, 6.0 mmol) of neat Bu_3SnH. The ampules were frozen, sealed, and placed in a thermostated bath maintained at 75 ± 0.1 °C for 4.0 h. The ampules were then cooled in ice and their content worked up and analyzed as previously described.

Reduction of 30 with Bu_3SnH/AIBN. A 0.5 M stock solution was prepared by mixing 0.715 g (2.5 mmol) of **30** and 0.01 g (0.06 mmol) of AIBN with dry, oxygen-free benzene in a 5.0-mL volumetric flask. In each of four 2-mL glass ampules previously swept with Ar for 30 min, 1.0 mL of stock solution was mixed with 0.16 mL (0.168 g, 0.58 mmol) of neat Bu_3SnH. The ampules were frozen, sealed, and placed in a thermostated bath kept at 75 ± 0.1 °C for 12 h. The ampules were then cooled in ice and opened, and their contents were analyzed by capillary GC. The products were identified by coelution with authentic samples, and the product ratios were corrected for detector responses factors.

Control Experiment: Stability of 30 at 75 °C. A 2-mL ampule previously swept with argon for 30 min was charged with 1.0 mL of a 0.5 M solution of **30** in dry, oxygen-free benzene. The ampule was frozen, sealed, and placed in a thermostated bath kept at 75 °C for 0.5 h. After cooling, the solution was concentrated to an oily residue that consisted of a 1.2:1:1.3 mixture of 3′-(2-(methoxalyloxy)-*n*-propyl)spiro[cyclopropane-1,1′-[1*H*]indene] (**35**), 3′-(2-(methoxalyloxy)-1-methylethyl)spiro[cyclopropane-1,1′-[1*H*]indene] (**36**), and 3′-(2-(methoxalyloxy)ethyl)-*anti*-2-methylspiro[cyclopropane-1,1′-[1*H*]indene] (**37**), as determined by ^{1}H NMR integration of the signals at 4.26, 5.38, and 4.42 ppm, respectively, and by capillary GC (column A, 225 °C). No trace of **30** was detected in the residue.

35: t_R 5.47 min; ^{1}H NMR (500 MHz, C_6D_6, mixture) δ 1.09 (d, J = 6.4 Hz, CH_3), 1.24 (br s, 4 H, overlap), 2.57 (dd, J = 7.3, 14.8 Hz, 1 H), 2.91 (dd, J = 5.8, 14.7, Hz, 1 H), 3.17 (s, OCH_3), 5.34–5.41 (m, 1 H), 5.63 (s, 1 H), 6.66–7.46 (m, 4 H, overlap); irradiation of the signal at 5.34–5.41 ppm simplified the signals at 2.57 and 2.91 ppm to doublets and the signal at 1.09 ppm to a singlet; GC/MS (70 eV) m/e 286 (M^+, 52), 182 (78), 167 (100), 165 (15), 155 (30), 153 (39), 141 (36), 139 (6), 128 (20), 115 (21), 91 (2), 89 (4), 77 (7).

36: t_R 5.90 min; ^{1}H NMR (500 MHz, C_6D_6, mixture) δ 1.18 (d, J = 6.9 Hz, CH_3), 1.24 (br s, 4 H, overlap), 3.10–3.13 (m, 1 H), 3.19 (s, OCH_3), 4.04 (dd, J = 8.4, 10.8 Hz, 1 H), 4.42 (dd, J = 5.1, 10.7 Hz, 1 H), 5.57 (s, 1 H), 6.66–7.46 (m, 4 H, overlap); irradiation of the signal at 3.10–3.13 ppm simplified the signals at 4.04 and 4.42 ppm to doublets and the signal at 1.18 ppm to a singlet; GC/MS (70 eV) m/e 286 (M^+, 65), 182 (100), 169 (33), 167 (87), 165 (20), 155 (11), 153 (35), 141 (70), 139 (8), 128 (19), 115 (25), 91 (5), 89 (4), 77 (5).

37: t_R 6.51 min; ^{1}H NMR (500 MHz, C_6D_6, mixture) δ 1.07 (d, J = 6.2 Hz, CH_3), 1.16 (dd, J = 4.4, 7.0 Hz, 1 H), 1.41 (dd, J = 4.2, 8.6 Hz, 1 H), 1.63–1.67 (m, 1 H)8, 2.73 (t, J = 7.5 Hz, CH_2CH_2O), 3.19 (s, OCH_3), 4.26 (t, J = 7.4 Hz, CH_2CH_2O), 5.88 (s, 1 H), 6.66–7.46 (m, 4 H, overlap); irradiation of the signal at 4.26 ppm simplified the signal at 2.73 ppm to a singlet; GC/MS (70 eV) m/e 286 (M^+, 28), 182 (61), 167 (100), 165 (17), 155 (15), 153 (39), 141 (23), 139 (5), 128 (14), 115 (15), 91 (3), 89 (3), 77 (4).

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Supplementary Material Available: Procedures for the preparation of authentic compounds and gas chromatographic conditions and tables of MNDO-UHF and AM1-UHF calculation results (21 pages). Ordering information is given on any current masthead page.