Regiochemistry in Aryl Radical Cyclization onto Methylenecycloalkanes

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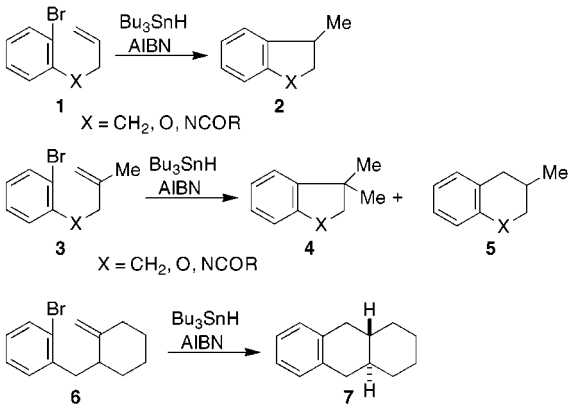
Bu_3SnH-mediated aryl radical cyclization onto methylenecycloalkanes having a phenylthio, an ester, or a nitrile group at the terminus of the alkenic bond provides exclusively *exo* cyclization products. The results are in sharp contrast to those reported for nonsubstituted methylenecycloalkanes, which give exclusively *endo* cyclization products. Formation of *endo* cyclization products has been suggested to be a result of a consecutive 5-*exo* cyclization of an aryl radical and neophyl rearrangement. The *exo*-selective aryl radical cyclization offers a new method for synthesizing fused aromatic compounds containing a benzylic quaternary carbon atom.

Introduction

Aryl radical cyclizations are now widely used in organic synthesis for the construction of fused aromatic compounds.[1] It has been recognized that a 5-*exo* cyclization is generally preferred over a 6-*endo* ring closure in those systems having an alkenic bond at the 5-position relative to the aryl radical center. For example, *o*-bromo(3-butenyl)benzene and related compounds **1**, upon treatment with Bu_3SnH in the presence of AIBN, gave almost exclusively the 5-*exo* cyclization products **2**.[2−4] This was also the case for the cyclizations of 3-methyl-3-butenyl congeners **3**, in which X = O[2a] or NAc,[4a] giving predominantly or exclusively the 5-*exo* cyclization product **4**, respectively. However, when X = CH_2 in **3**, the 6-*endo* cyclization predominated to give mixtures of **5** and the 5-*exo* cyclization product **4** in a ratio of (1.3−1.8):1.[5] Ghatak and co-workers reported that the aryl radical cyclization onto methylenecyclohexane **6** gave exclusively the 6-*endo* cyclization product **7**.[6] Formation of **7** from **6**



was considered to be a result of the preferred attack of an aryl radical at the least-substituted methylene center. On the other hand, we recently reported that methylenecyclohexane **9**, having a phenylthio group at the terminus of the alkene bond, affords exclusively the 5-*exo* cyclization product **15**.[7] The difference between the modes of cyclization of **6** and **9** led us to further investigate the role of the substituents in determining the course of the cyclization onto methylenecycloalkanes. Here, we present full details of the results with a range of methylenecycloalkanes, showing that a 5-*exo* cyclization is essentially preferred over a 6-*endo* ring closure for the cyclization onto methylenecycloalkanes and that the formation of 6-*endo* products is not a result of a direct 6-*endo* cyclization of aryl radicals but is explained in terms of a consecutive 5-*exo* cyclization and neophyl rearrangement.

Results and Discussion

The requisite radical precursors **9**−**14** were prepared as follows. Reactions of ketone **8**[8] with $Ph_2P(O)CH(Li)R$

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(1) For reviews, see: (a) Giese, B. *Radicals in Organic Synthesis: Formation of Carbon- Carbon Bonds*; Pergamon: New York, 1986. (b) Fossey, J.; Lefort, D.; Sorba, J. *Free Radicals in Organic Chemistry*; Wiley: New York, 1995. (c) Curran, D. P. *Synthesis* **1988**, 417, 489. (d) Jasperse, C. P.; Curran, D. P.; Fevig, T. L. *Chem. Rev.* **1991**, *91*, 1237.

(2) For X = CH_2, see: (a) Abeywickrema, A. N.; Beckwith, A. L. J.; Gerba, S. *J. Org. Chem.* **1987**, *52*, 4072. See also: (b) Beckwith, A. L. J.; Gara, W. B. *J. Am. Chem. Soc.* **1969**, *91*, 5691. (c) Beckwith, A. L. J.; Gara, W. B. *J. Chem. Soc., Perkin Trans. 2* **1975**, 593, 795. (d) Beckwith, A. L. J.; O'Shea, D. M.; Roberts, D. H. *J. Chem. Soc., Chem. Commun.* **1983**, 1445. (e) Abeywickrema, A. N.; Beckwith, A. L. J. *J. Chem. Soc., Chem. Commun.* **1986**, 464. (f) Meijs, G. F.; Bunnet, J. F.; Beckwith, A. L. J. *J. Am. Chem. Soc.* **1986**, *108*, 4899.

(3) For X = O, see: (a) Chung, S.-K.; Chung, F. *Tetrahedron Lett.* **1979**, 2473. See also: (b) Beckwith, A. L. J.; Meijs, G. F. *J. Chem. Soc., Chem. Commun.* **1981**, 136, 595. (c) Ueno, Y.; Chino, K.; Okawara, M. *Tetrahedron Lett.* **1982**, *23*, 2575. (d) Shankaran, K.; Sloan, C. P.; Snieckus, V. *Tetrahedron Lett.* **1985**, *26*, 6001. (e) Meijs, G. F.; Beckwith, A. L. *J. Am. Chem. Soc.* **1986**, *108*, 5890. (f) Beckwith, A. L. J.; Meijs, G. F. *J. Org. Chem.* **1987**, *52*, 1922. (g) Parker, K. A.; Spero, D. M.; Epp, J. V. *J. Org. Chem.* **1988**, *53*, 4628. (h) Bhandal, H.; Patel, V. F.; Pattenden, G.; Russell, J. J. *J. Chem. Soc., Perkin Trans. 1* **1990**, 2691. (i) Clark, A. J.; Davies, D. I.; Jones, K.; Millbanks, C. *J. Chem. Soc., Chem. Commun.* **1994**, 41. (j) Yorimitsu, H.; Shinokubo, H.; Oshima, K. *Chem. Lett.* **2000**, 104. See also refs 2a,c,e.

(4) For X = NAc, see: (a) Dittami, J. P.; Ramanathan, H. *Tetrahedron Lett.* **1988**, *29*, 45. (b) Özlü, Y.; Cladingboel, D. E.; Parsons, P. J. *Tetrahedron* **1994**, *50*, 2183. See also: Inanaga, J.; Ujikawa, O.; Yamaguchi, M. *Tetrahedron Lett.* **1991**, *32*, 1737. See also ref 2c.

(5) (a) Miura, K.; Ichinose, Y.; Nozaki, K.; Fugami, K.; Oshima, K.; Utimoto, K. *Bull. Chem. Soc. Jpn.* **1989**, *62*, 143. (b) Rigollier, P.; Young, J. R.; Fowley, L. A.; Stille, J. R. *J. Am. Chem. Soc.* **1990**, *112*, 9441.

(6) (a) Pal, S.; Mukherjee, M.; Podder, D.; Mukherjee, A. K.; Ghatak, U. R. *J. Chem. Soc., Chem. Commun.* **1991**, 1591. (b) Pal, S.; Mukhopadhyaya, J. K.; Ghatak, U. R. *J. Org. Chem.* **1994**, *59*, 2687.

(7) Ishibashi, H.; Kobayashi, T.; Takamasu, D. *Synlett* **1999**, 1286.

(8) Booth, S. E.; Jenkins, P. R.; Swain, C. J.; Sweeney, J. B. *J. Chem. Soc., Perkin Trans. 1* **1994**, 3499.

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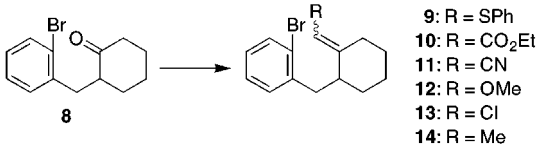
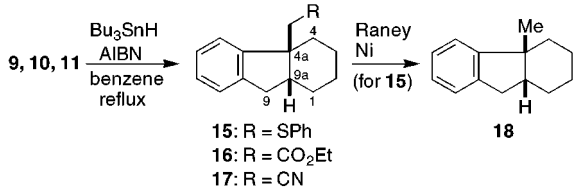
(for R = SPh, OMe) gave **9** (91%) and **12** (72%), and reactions with $(EtO)_2P(O)CH(Li)R$ (for R = CO_2Et, CN) gave **10** (76%) and **11** (86%), respectively. On the other



hand, reaction of **8** with $Ph_3P{=}CHR$ (for R = Cl or Me) gave **13** and **14** in 92% and 76% yields, respectively (see Supporting Information). ^{1}H NMR spectra of compounds **9**, **12**, and **14** showed them to be mixtures of two stereoisomers with respect to the alkene bond in ratios of 22:1, 5:4, and 8:1, respectively, and compounds **10**, **11**, and **13** were shown to be single stereoisomers.

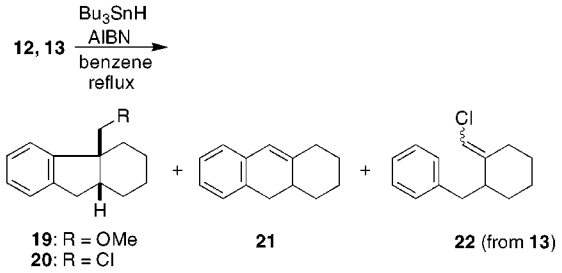
When a mixture of Bu_3SnH (1.2 equiv) and a catalytic amount of AIBN in benzene was added slowly to a solution of ((phenylthio)methylene)cyclohexane **9** in boiling benzene over a period of 1 h and the whole solution was further heated at reflux for 3 h, the 5-*exo* cyclization product **15** was obtained in 91% yield. The structure of



15 was readily confirmed by its ^{1}H NMR spectrum, which showed signals due to the methylene protons α to the PhS group as two parts of an AB quartet at δ 3.13 and 3.16 (J = 12.2 Hz). Desulfurization of **15** with Raney Ni gave the known compound **18**,[9] thereby confirming the *cis* stereochemistry of the ring juncture of **15**. In addition, the whole sequence of the reactions (**18** from **9** via **15**) can be regarded in a formal sense as a 5-*exo* cyclization of methylenecyclohexane **6**.

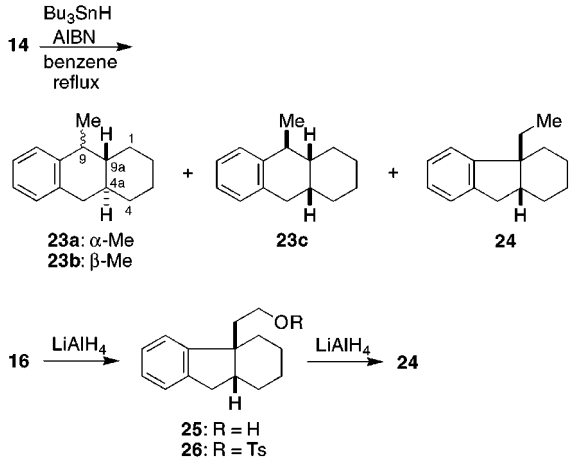
The ester and nitrile congeners **10** and **11** also gave the 5-*exo* cyclization products **16** and **17** in 87 and 81% yields, respectively.

The methoxy-substituted congener **12** gave the 5-*exo* cyclization product **19** (55% yield) along with hexahydroanthracene **21**[10] (15% yield). The NOE difference

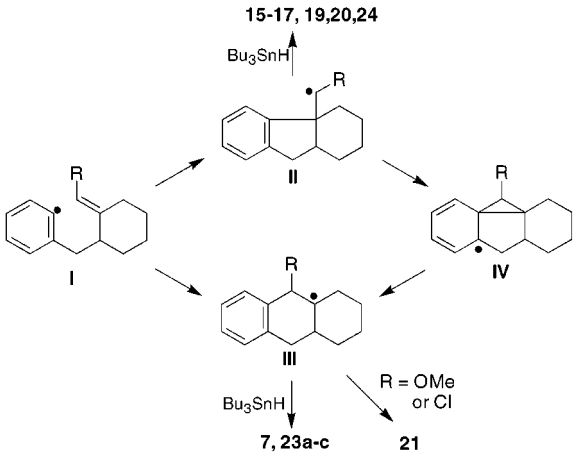


spectroscopy showed the ring juncture of **19** to be a *cis* relationship. ^{1}H NMR spectral properties of **21** were identical with the literature values.[10]

Scheme 1



Scheme 2



The chloro-substituted congener **13** gave a mixture of the 5-*exo* cyclization product **20** and the reduction product **22** in a ratio of ca. 2:1 and in 55% combined yield. The ^{1}H NMR spectrum of the mixture showed that it also contained a small quantity of **21**.

Ethylidenecyclohexane **14** gave almost exclusively the 6-*endo* cyclization products **23a**−**c** in 79% combined yield as an inseparable mixture containing a trace amount of the 5-*exo* cyclization product **24**. The stereochemistries of **23a**−**c** were tentatively assigned as depicted in Scheme 1 by a comparison of the chemical shifts of their methyl protons (δ 1.10 (J = 7.3 Hz), 1.31 (J = 6.9 Hz), and 1.32 (J = 6.9 Hz)) with those reported for **23a** (δ 1.08), **23b** (δ 1.28), and **23c** (δ 1.31), respectively.[11] The structure of **24** was established by its independent synthesis from ester **16** through $LiAlH_4$ reduction, tosylation of the resulting alcohol **25**, and $LiAlH_4$ reduction of tosylate **26**.

The results by Ghatak and us showed that nonsubstituted and alkyl-substituted methylenecyclohexanes **6** and **14** gave almost exclusively the 6-*endo* cyclization products, whereas compounds **9**−**13** gave exclusively or predominantly the 5-*exo* cyclization products. Formation of the observed 5-*exo* and 6-*endo* cyclization products was rationalized by an attack of Bu_3SnH on the intermediate radicals **II** and **III** formed from aryl radical **I**, respectively (Scheme 2). Compound **21** from **12** or **13** might have arisen due to elimination of a methoxyl radical or chlorine

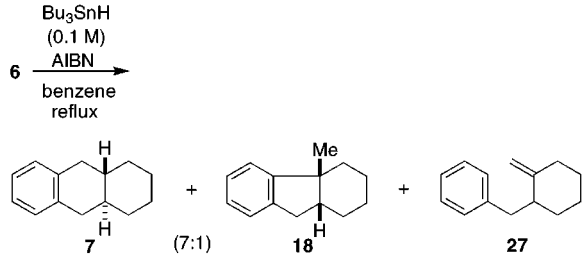
(9) Barrow, C. J.; Bright, S. T.; Coxon, J. M.; Steel, P. J. *J. Org. Chem.* **1989**, *54*, 2542.

(10) Clive, D. L. J.; Zhang, C.; Murthy, K. S. K.; Hayward, W. D.; Daigneault, S. *J. Org. Chem.* **1991**, *56*, 6447.

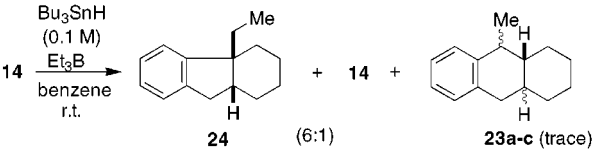
(11) Hagishita, S.; Kuriyama, K. *Bull. Chem. Soc. Jpn.* **1982**, *55*, 3216.

atom from the intermediate radicals **III**. The obvious question, however, is whether the intermediate radicals **III** are formed directly by a 6-*endo* cyclization of aryl radicals **I** (R = H, Me) or by a consecutive 5-*exo* cyclization of **I** and neophyl rearrangement[12] of the resulting radicals **II** via the intermediates **IV**.[13] We therefore examined the cyclizations of **6** and **14** in more detail.

When compound **6** was treated with Bu_3SnH at a concentration of 0.1 M, which was much higher than that (0.007−0.02 M) employed by Ghatak and co-workers,[6] a small quantity of the 5-*exo* cyclization product **18** was obtained along with the 6-*endo* cyclization product **7** in a ratio of ca. 1:7, along with small quantities of the recovered **6** and the simple reduction product **27**.



Formation of **18** from **6** suggested that radical **I** (R = H) (Scheme 2) cyclized in a 5-*exo* manner and that the resulting radical **II** (R = H) was rapidly attacked by a large quantity of Bu_3SnH. It is assumed that when the concentration of Bu_3SnH is low (0.007−0.02 M), as employed by Ghatak, radical **II** undergoes a neophyl rearrangement before an attack by Bu_3SnH resulting in the formation of **III**. A more distinguishing result was obtained by treating **14** with 1.2 equiv. of Bu_3SnH (not using the slow addition technique) in the presence of triethylborane at room temperature for 12 h. This gave predominantly the 5-*exo* cyclization product **24** together with the recovered starting material **14** in a ratio of ca. 6:1. The ^1H NMR spectrum of this mixture also showed

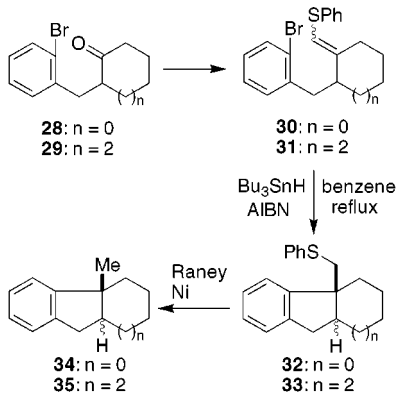


a negligibly small signal due to the methyl protons for **23a**, and accordingly, it seemed reasonable to assume that the reaction also provided small quantities of the 6-*endo* cyclization product **23a**−**c**. This result strongly suggests that the 5-*exo* cyclization of **I** (R = Me) giving **II** (R = Me) (Scheme 2) is kinetically favored over the 6-*endo* cyclization and that the formation of the 6-*endo* cyclization products **23a**−**c** under the usual radical reaction conditions (slow addition of Bu_3SnH) is a result of a consecutive 5-*exo* cyclization and neophyl rearrangement.

Several explanations can be offered for the effect of the substituent (R) of radicals **II** on the tendency to undergo a neophyl rearrangement. One possible explanation is derived from the consideration of a steric factor of the substituent. A sterically more demanding substituent such as an OMe, Cl, SPh, or COOEt group prevents an attack of a radical center on the aromatic ring, thereby retarding the neophyl rearrangement. However, despite its small size, a CN group did not bring out the neophyl rearrangement. Another explanation involves the relative stability of radicals **II**. The nonsubstituted or alkyl-substituted radical **II** (R = H, Me) might be less stable than the others,[14] so that these radicals immediately attacked the neighboring aromatic ring to give relatively stable cyclohexadienyl radicals **IV**, which then afforded the much more stable tertiary radicals **III**. Although the radical **II** (R = OMe) is expected to be stabilized significantly, the radical underwent the neophyl rearrangement to some extent. Consequently, an additional possibility may be derived from the consideration of the nucleophilicity of radicals. The radical adjacent to the OMe group is given nucleophilicity by interacting with the lone pair of electrons of the oxygen atom, and hence, the radical has some tendency to attack on the aromatic ring, giving **IV**.[15]

As noted above, vinyl sulfide **9** gave **15** and **18** (by desulfurization of **15**), and this method therefore provides a new synthesis of fused aromatic compounds containing a benzylic quaternary carbon atom.[16] We then examined an extended application of this method to the cyclization of vinyl sulfides **30** and **31** having a methylenecyclopentane or -cycloheptane ring.

Treatment of compounds **30** and **31** with Bu_3SnH in the presence of AIBN in boiling benzene gave the expected 5-*exo* cyclization products **32** and **33** in 75 and 82% yields, respectively. Desulfurization of compounds



32 and **33** with Raney Ni afforded **34** and **35**, respectively. The NOE difference spectra showed compound **34** to be a single *cis* isomer and compound **35** to be a mixture of *cis* and *trans* isomers in a ratio of 4.3:1.

(12) (a) Ruchardt, C.; Hecht, R. *Chem. Ber.* **1965**, *98*, 2471. (b) Parker, K. A.; Spero, D. M.; Inman, K. C. *Tetrahedron Lett.* **1986**, *27*, 2833. (c) McNab, H. *J. Chem. Soc., Chem. Commun.* **1990**, 543. (d) Crich, D.; Yao, Q. *J. Org. Chem.* **1995**, *60*, 84. (e) Ishibashi, H.; Ohata, K.; Niihara, M.; Sato, T.; Ikeda, M. *J. Chem. Soc., Perkin Trans. 1* **2000**, 547. See also ref 2a.

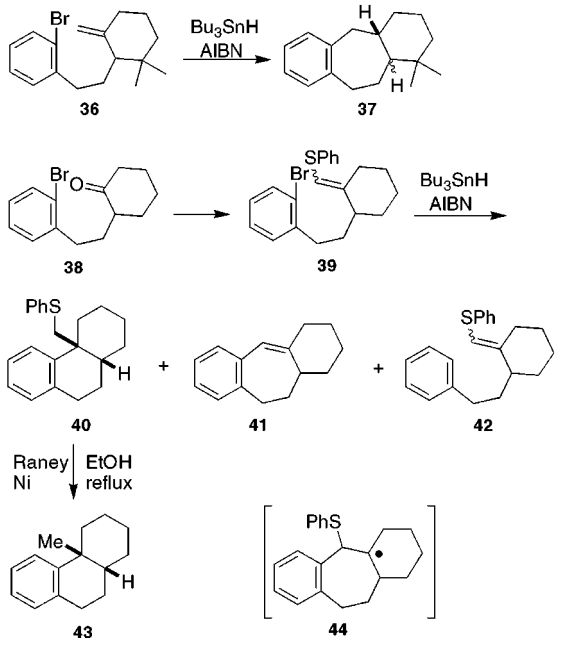
(13) In Scheme 2, reverse processes of the radicals **II** and **III** to the aryl radical **I** are not considered, since it is well-known that a primary or a secondary radical is much more stable than is an aryl radical (bond dissociation energies: Et−H, 101 kcal/mol; cyclo-C_6H_{11}−H, 99 kcal/mol; Ph−H, 111 kcal/mol).[1b] For a similar discussion, see ref 2a.

(14) (a) McMillen, D. F.; Golden, D. M. *Annu. Rev. Phys. Chem.* **1982**, *33*, 493. (b) Bordwell, F. G.; Zhang, X.-M. *Acc. Chem. Res.* **1993**, *26*, 510. (c) Leroy, G.; Sana, M.; Wilante, C. *J. Mol. Struct. (THEOCHEM)* **1989**, *198*, 159. See also ref 1b, pp 31−38.

(15) Kurz, M. E.; Baru, V.; Nguyen, P.-N. *J. Org. Chem.* **1984**, *49*, 1603. See also ref 1a, pp 4−35.

(16) For other sulfur-controlled *exo* selective radical cyclizations, see: (a) Ishibashi, H.; Kameoka, C.; Iriyama, K.; Kodama, K.; Sato, T.; Ikeda, M. *J. Org. Chem.* **1995**, *60*, 1276. (b) Ishibashi, H.; Kameoka, C.; Kodama, K.; Ikeda, M. *Tetrahedron* **1996**, *52*, 489. (c) Ishibashi, H.; Kawanami, H.; Nakagawa, H.; Ikeda, M. *J. Chem. Soc., Perkin Trans. 1* **1997**, 2291.

Ghatak and co-workers reported that the homologous system **36** cyclized also in an *endo* manner to give the product **37**.[17,18] We found that vinyl sulfide **39** gave the



exo cyclization product **40** in 40% yield along with small amounts of **41** and the reduction product **42**. The *cis* stereochemistry of the ring juncture of **40** was established by transforming it to the known compound **43**.[19] Formation of **41** may be rationalized in terms of an elimination of the benzenethiyl radical from the intermediate radical **44** formed by a 7-*endo* cyclization of an aryl radical.

In conclusion, we revealed that aryl radical cyclization onto methylenecycloalkanes occurred initially in a 5-*exo* manner[20] and that formation of *endo* cyclization products was a result of a consecutive *exo* cyclization and neophyl rearrangement. In adidition, the whole sequence of the reactions for vinyl sulfides **9**, **30**, **31**, and **39** can be regarded in a formal sense as an *exo* cyclization of the corresponding nonsusbtituted methylenecycloalkanes, since the products could readily be desulfurized to give **18**, **34**, **35**, and **43**, respectively. Moreover, the *exo* selective aryl radical cyclization herein described offers a new method for synthesizing fused aromatic compounds containing a benzylic quaternary carbon atom.

Experimental Section

Melting points are uncorrected. ^{1}H and ^{13}C NMR spectra were measured for solutions in $CDCl_3$. Column chromatography was performed on silica gel 60 PF_{254} (Nacalai Tesque) or alumina 90 (70−230 mesh) (E. Merck, No. 1097) under pressure.

Radical Cyclization of 9 with Bu_3SnH−AIBN in Boiling Benzene. General Procedure. To a boiling solution of **9** (301 mg, 0.807 mmol) in benzene (75 mL) was added dropwise a solution of Bu_3SnH (282 mg, 0.969 mmol) and AIBN (15.9 mg, 0.097 mmol) in benzene (38 mL) via a syringe over 1 h, and the mixture was further heated under reflux for 3 h. After evaporation of the solvent, Et_2O (50 mL) and an 8% aqueous KF solution (50 mL) were added to the residue, and the whole mixture was vigorously stirred at room temperature for 16 h. The organic phase was separated, and the aqueous phase was further extracted with Et_2O. The combined organic phase was washed with brine, dried ($MgSO_4$), and concentrated. The residue was chromatographed on silica gel (hexane/AcOEt, 50:1) to give *cis*-1,2,3,4,4a,9a-hexahydro-4a-((phenylthio)-methyl)fluorene (**15**) (216 mg, 91%) as a colorless oil: ^{1}H NMR (500 MHz) δ 1.14−1.27 (2 H, m), 1.29−1.37 (1 H, m), 1.44−1.55 (2 H, m), 1.65−1.72 (1 H, m), 1.78 (1 H, ddd, J = 14.2, 10.3, 3.9 Hz), 1.95−2.01 (1 H, m), 2.46−2.52 (1 H, m), 2.53 (1 H, dd, J = 15.1 4.4 Hz), 3.01 (1 H, dd, J = 15.1 6.4 Hz), 3.13 (1 H, d, J = 12.2 Hz), 3.16 (1 H, d, J = 12.2 Hz), 7.09−7.26 (9 H, m); ^{13}C NMR (125.7 MHz) δ 22.1, 23.5, 28.2, 32.2, 36.3, 42.8, 44.3, 50.5, 122.9, 125.5, 125.6, 126.1, 126.7, 128.7 (2C), 129.0 (2C), 138.2, 142.8, 148.1. Anal. Calcd for $C_{20}H_{22}S$: C, 81.58; H, 7.53. Found: C, 81.27; H, 7.67.

Radical Cyclization of 10. Following the general procedure, compound **10** (111 mg, 0.33 mmol) was treated with Bu_3SnH (122 mg, 0.42 mmol) in the presence of AIBN (6.6 mg, 0.042 mmol) in benzene (51 mL). After workup, the crude material was chromatographed on silica gel (hexane/AcOEt, 20:1) to give ethyl *cis*-1,2,3,4,4a,9a-hexahydrofluorene-4a-acetate (**16**) (75.9 mg, 87%) as a colorless oil: IR ($CHCl_3$) ν 1720 cm^{-1}; ^{1}H NMR (500 MHz) δ 1.15 (3 H, t, J = 6.3 Hz), 1.18−1.53 (5H, m), 1.66−1.73 (2 H, m), 1.95−2.01 (1 H, m), 2.39−2.45 (1 H, m), 2.47 (1 H, d, J = 13.7 Hz), 2.53 (1 H, d, J = 13.7 Hz), 2.55 (1 H, dd, J = 15.6, 4.7 Hz), 3.11 (1 H, dd, J = 15.0, 6.9 Hz), 4.03 (1 H, dq, J = 15.6, 6.3 Hz), 4.04 (1 H, dq, J = 15.6, 6.3 Hz), 7.08−7.25 (4 H, m); ^{13}C NMR (125.7 MHz) δ 14.1, 21.9, 23.2, 27.8, 32.7, 37.0, 43.4, 43.5, 48.6, 59.9, 122.7, 125.5, 126.0, 126.4, 142.5, 148.4, 171.7. HRMS: calcd for $C_{17}H_{22}O_2$, 258.1620; found, 258.1625.

Radical Cyclization of 11. Following the general procedure, compound **11** (89.0 mg, 0.31 mmol) was treated with Bu_3SnH (120 mg, 0.41 mmol) in the presence of AIBN (8.6 mg, 0.052 mmol) in benzene (47 mL). After workup, the crude material was chromatographed on alumina (hexane/AcOEt, 20:1) to give *cis*-1,2,3,4,4a,9a-hexahydrofluorene-4a-acetonitrile (**17**) (52.5 mg, 81%) as a colorless oil: IR ($CHCl_3$) ν 2250 cm^{-1}; ^{1}H NMR (500 MHz) δ 1.16−1.45 (3 H, m), 1.45−1.59 (2 H, m), 1.67−1.80 (2 H, m), 2.05−2.12 (1 H, m), 2.26−2.33 (1 H, m), 2.48 (1 H, d, J = 16.6 Hz), 2.52 (1 H, d, J = 16.6 Hz), 2.59 (1 H, dd, J = 15.6, 3.8 Hz), 3.02 (1 H, dd, J = 15.6, 6.3 Hz), 7.15−7.32 (4 H, m); ^{13}C NMR (125.7 MHz) δ 21.7, 23.2, 27.9, 28.4, 32.0, 36.1, 43.9, 47.8, 118.3, 122.3, 125.8, 126.7, 127.4, 142.1, 146.2. Anal. Calcd for $C_{15}H_{17}N$: C, 85.26; H, 8.11; N, 6.63. Found: C, 84.93; H, 8.24; N, 6.45.

***cis*-1,2,3,4,4a,9a-Hexahydro-4a-methylfluorene (18).** To a solution of **15** (105 mg, 0.357 mmol) in EtOH (10 mL) was added Raney Ni, and the mixture was heated under reflux for 2 h. Raney Ni was filtered off, and the filtrate was concentrated to give **18**[9] (65.3 mg, 98%) as a colorless oil: ^{1}H NMR (500 MHz) δ 1.23 (3 H, s), 1.23−1.50 (6 H, m), 1.60−1.74 (2 H, m), 2.08 (1 H, br quintet, J = 6.4 Hz), 2.66 (1 H, dd, J = 15.1, 7.3 Hz), 2.89 (1 H, dd, J = 15.1, 7.3 Hz), 7.10 (1 H, br d, J = 7.3 Hz), 7.12 (1 H, br t, J = 7.3 Hz), 7.16 (1 H, br t, J = 7.3 Hz), 7.22 (1 H, br d, J = 7.3 Hz); ^{13}C NMR (125.7 MHz) δ 22.2, 22.8, 25.7, 26.8, 35.4, 35.6, 45.3, 46.3, 121.6, 125.2, 125.9, 126.1, 142.4, 152.6.

Radical Cyclization of 12. Following the general procedure, compound **12** (106 mg, 0.36 mmol) was treated with Bu_3SnH (133 mg, 0.46 mmol) in the presence of AIBN (10.5 mg, 0.064 mmol) in benzene (54 mL). After workup, the crude material was chromatographed on silica gel (hexane/AcOEt, 50:1). The first fraction gave 1,2,3,4,4a,10-hexahydroanthracene (**21**) (10.2 mg, 15%), which crystallized on standing: mp 32−34 °C (lit.[10] an oil); ^{1}H NMR (500 MHz) δ 1.15−1.95 (5

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(20) The *exo* selective aryl radical cyclizations onto the corresponding oxime ethers have been reported.[8]

H, m), 1.95−2.25 (2 H, m), 2.35−2.55 (2 H, m), 2.56 (1 H, dd, J = 15.5, 12.2 Hz), 2.90 (1 H, dd, J = 15.5, 7.3 Hz), 6.12 (1 H, t, J = 2.0 Hz), 6.93 (1 H, d, J = 7.3 Hz), 7.00−7.30 (3 H, m). The second fraction gave *cis*-1,2,3,4,4a,9a-hexahydro-4a-(methoxymethyl)fluorene (**19**) (42.6 mg, 55%) as a colorless oil: ^{1}H NMR (500 MHz) δ 1.17−1.93 (8 H, m), 2.32−2.38 (1 H, m), 2.55 (1 H, dd, J = 15.5, 4.6 Hz), 2.98 (1 H, dd, J = 15.5, 6.8 Hz), 3.23 (1 H, d, J = 9.3 Hz), 3.30 (3 H, s), 3.34 (1 H, d, J = 9.3 Hz), 7.10−7.25 (4 H, m); ^{13}C NMR (125.7 MHz) δ 22.3, 23.6, 28.3, 30.2, 36.7, 40.7, 50.7, 59.6, 78.6, 123.2, 125.6, 126.3, 126.7, 143.5, 148.4. Anal. Calcd for $C_{15}H_{20}O$: C, 83.29; H, 9.32. Found: C, 82.92; 9.49.

Radical Cyclization of 13. Following the general procedure, compound **13** (57.0 mg, 0.19 mmol) was treated with Bu_3SnH (76.9 mg, 0.26 mmol) in the presence of AIBN (5.2 mg, 0.032 mmol) in benzene (28 mL). After workup, the crude material was chromatographed on alumina (hexane) to give a ca. 2:1 mixture of *cis*-4a-(chloromethyl)-1,2,3,4,4a,9a-hexahydrofluorene (**20**) and 2-(phenylmethyl)-1-(chloromethylene)-cyclohexane (**22**) (23.2 mg, 55%) as a colorless oil. A ^{1}H NMR spectrum of the mixture showed it to contain a trace amount of **21**.

An analytical sample of **20** was prepared as follows. To a solution of the above mixture (44.0 mg) in *t*-BuOH/H_2O (5:4) (1.8 mL) was added $KMnO_4$ (31.5 mg), and the mixture was stirred at room temperature for 2 h. After the inorganic materials had been filtered off, the filtrate was diluted with water (20 mL) and the whole mixture was extracted with AcOEt. The extract was washed with aqueous $Na_2S_2O_3$ solution (20 mL), dried ($MgSO_4$), and concentrated. The crude material was chromatographed on alumina (hexane) to give **20** (9.6 mg) as a colorless oil: ^{1}H NMR (500 MHz) δ 1.10−1.24 (2 H, m), 1.25−1.37 (1 H, m), 1.45−1.57 (2 H, m), 1.66−1.74 (1 H, m), 1.85 (1 H, ddd, J = 14.7, 10.7, 3.9 Hz), 1.93−2.00 (1 H, m), 2.42−2.49 (1 H, m), 2.52 (1 H, dd, J = 15.4, 3.7 Hz), 3.04 (1 H, dd, J = 15.4, 6.6 Hz), 3.48 (1 H, d, J = 11.0 Hz), 3.56 (1 H, d, J = 11.0 Hz), 7.16−7.27 (4 H, m); ^{13}C NMR (125.7 MHz) δ 21.9, 23.6, 28.5, 30.0, 36.4, 41.4, 51.2, 52.3, 123.2, 125.9, 126.3, 127.2, 143.1, 146.2. HRMS: calcd for $C_{14}H_{17}{}^{35}Cl$, 220.1019; found, 220.1014.

The structure of **22** was confirmed by the following independent synthesis. Using a procedure similar to that described above for the preparation of **13**, a suspension of (chloromethyl)-triphenylphosphonium chloride (732 mg, 2.11 mmol) in Et_2O (3 mL) was treated with PhLi (0.88 M cyclohexane/diethyl ether solution) (2.40 mL, 2.11 mmol) and then with 2-(phenylmethyl)cyclohexanone[21] (132 mg, 0.70 mmol). After workup, the crude material was chromatographed on alumina (hexane) to give **22** (146 mg, 94%) as a colorless oil: ^{1}H NMR (500 MHz) δ 1.32−1.40 (1 H, m), 1.40−1.50 (1 H, m), 1.50−1.76 (4 H, m), 2.29 (1 H, ddd, J = 13.3, 7.5, 4.7 Hz), 2.38−2.45 (1 H, m), 2.51 (1 H, ddd, J = 13.3, 8.0, 4.7 Hz), 2.61 (1 H, dd, J = 13.2, 8.8 Hz), 2.89 (1 H, dd, J = 13.2, 6.3 Hz), 5.70 (1 H, s), 7.11 (2 H, br d, J = 7.0 Hz), 7.19 (1 H, br t, J = 7.0 Hz), 7.28 (2 H, br t, J = 7.0 Hz). HRMS: calcd for $C_{14}H_{17}{}^{35}Cl$, 220.1019; found, 220.1018.

Radical Cyclization of 14. Following the general procedure, compound **14** (123 mg, 0.44 mmol) was treated with Bu_3SnH (194 mg, 0.67 mmol) in the presence of AIBN (10.4 mg, 0.063 mmol) in benzene (66 mL). After workup, the crude material was chromatographed on alumina (hexane) to give a mixture of (4a*S**,9*R**,9a*R**)-**23a**,[11] (4a*S**,9*S**,9a*R**)-**23b**,[11] and (4a*R**,9*S**,9a*R**)-1,2,3,4,4a,9,9a,10-octahydro-9-methylanthracene (**23c**)[11] (70.0 mg, 79%) as a colorless oil: ^{1}H NMR (270 MHz) δ 0.80−2.00 (m), 1.10 (d, J = 7.3 Hz, Me for **23a**), 1.31 (d, J = 6.9 Hz, Me for **23b**), 1.32 (d, J = 6.9 Hz, Me for **23c**), 2.00−3.10 (m), 6.98−7.30 (4 H, m). The ^{1}H NMR spectrum of this mixture showed it to contain a trace amount of *cis*-4a-ethyl-1,2,3,4,4a,9a-hexahydrofluorene (**24**) (δ 0.76 (t, J = 7.4 Hz, *Me*CH_2)), whose structure was confirmed by the following independent synthesis.

Preparation of 24 from 16. $LiAlH_4$ (19.0 mg, 0.500 mmol) was added to a solution of **16** (64.6 mg, 0.250 mmol) in THF (2 mL) at 0 °C, and the mixture was stirred at the same temperature for 6 h. After completion of the reaction, Celite, AcOEt (1 mL), EtOH (1 mL), and water (1 mL) were added successively to the reaction mixture, and the mixture was stirred for 1 h. The inorganic materials were filtered off, and the filtrate was washed with brine, dried ($MgSO_4$), and concentrated. The residue was chromatographed on silica gel (hexane/AcOEt, 2:1) to give *cis*-1,2,3,4,4a,9a-hexahydro-4a-(2-hydroxyethyl)fluorene (**25**) (49.9 mg, 92%) as a colorless oil: IR ($CHCl_3$) ν 3620 cm^{-1}; ^{1}H NMR (500 MHz) δ 1.15 (1 H, br), 1.18−1.28 (2 H, m), 1.29−1.40 (1 H, m), 1.40−1.53 (3 H, m), 1.61−1.70 (1 H, m), 1.80 (1 H, ddd, J = 13.9, 8.8, 5.9 Hz), 1.80−1.89 (1 H, m), 1.98 (1 H, ddd, J = 13.7, 8.8, 5.9 Hz), 2.20 (1 H, br quintet, J = 6.3 Hz), 2.56 (1 H, dd, J = 15.3, 5.1 Hz), 2.99 (1 H, dd, J = 15.3, 6.6 Hz), 3.56 (1 H, ddd, J = 10.3, 8.8, 5.9 Hz), 3.65 (1 H, ddd, J = 10.3, 8.8, 5.9 Hz), 7.07−7.18 (3 H, m), 7.22 (1 H, br d, J = 6.4 Hz). This compound was used immediately in the next step.

Compound **25** (49.9 mg, 0.231 mmol) was dissolved in pyridine (1 mL), *p*-toluenesulfonyl chloride (52.8 mg, 0.277 mmol) was added to the solution at room temperature, and the mixture was stirred at the same temperature for 18 h. The reaction mixture was diluted with AcOEt (30 mL), and the whole mixture was washed successively with 1 *N* HCl (30 mL) and brine, dried ($MgSO_4$), and concentrated. The residue was chromatographed on silica gel (hexane/AcOEt, 7:1) to give *cis*-1,2,3,4,4a,9a-hexahydro-4a-[2-(*p*-toluenesulfonyloxy)ethyl]fluorene (**26**) (52.4 mg, 61%) as a colorless oil: IR ($CHCl_3$) ν 1360, 1175 cm^{-1}; ^{1}H NMR (500 MHz) δ 1.13−1.35 (3 H, m), 1.38−1.47 (3 H, m), 1.57−1.65 (1 H, m), 1.73−1.80 (1 H, m), 1.87 (1 H, ddd, J = 15.1, 8.8, 6.3 Hz), 2.01 (1 H, ddd, J = 15.1, 8.8, 5.8 Hz), 2.08 (1 H, br quintet, J = 6.9 Hz), 2.44 (3 H, s), 2.53 (1 H, dd, J = 15.6, 5.8 Hz), 2.87 (1 H, dd, J = 15.6, 6.3 Hz), 3.93 (1 H, ddd, J = 10.0, 9.4, 5.9 Hz), 4.03 (1 H, ddd, J = 10.0, 9.4, 6.3 Hz), 6.91 (1 H, br d, J = 6.9 Hz), 7.09 (1 H, br t, J = 6.9 Hz), 7.12 (1 H, td, J = 6.9, 1.9 Hz), 7.19 (1 H, br d, J = 6.9 Hz), 7.30 (2 H, d, J = 7.8 Hz), 7.70 (1 H, d, J = 7.8 Hz). This compound was used immediately in the next step.

Compound **26** (52.4 mg, 0.141 mmol) was dissolved in THF (2 mL), $LiAlH_4$ (10.7 mg, 0.283 mmol) was added to the solution at room temperature, and the mixture was heated under reflux for 2 h. After workup as described above for the preparation of **25**, the crude material was chromatographed on silica gel (hexane/AcOEt, 2:1) to give **24** (22.9 mg, 81%) as a colorless oil: ^{1}H NMR (500 MHz) δ 0.76 (3 H, t, J = 7.4 Hz), 1.14−1.36 (3 H, m), 1.38−1.54 (2 H, m), 1.59−1.72 (2 H, m), 1.81−1.89 (1 H, m), 2.19 (1 H, quintet, J = 6.6 Hz), 2.52 (1 H, dd, J = 15.1, 4.9 Hz), 2.98 (1 H, dd, J = 15.1, 6.8 Hz), 7.06 (1 H, br d, J = 6.4 Hz), 7.10−7.17 (4 H, m), 7.22 (1 H, br d, J = 6.4 Hz); ^{13}C NMR (67.9 MHz) δ 8.7, 22.1, 23.5, 28.0, 30.9, 32.8, 36.3, 43.3, 49.4, 122.8, 125.5, 125.6, 125.9, 143.2, 149.2. Anal. Calcd for $C_{15}H_{20}$: C, 89.94; H, 10.06. Found: C, 89.77; H, 10.29.

Radical Cyclization of 6 with Bu_3SnH at a 0.1 M Concentration. To a solution of **6**[6,22] (92.2 mg, 0.360 mmol) in benzene (3.5 mL) were added Bu_3SnH (115 mg, 0.396 mmol) and AIBN (9.7 mg, 0.040 mmol), and the mixture was heated under reflux for 9 h. After workup, the crude material was chromatographed on silica gel (hexane). The first fraction gave an oily mixture of **7**,[6,22] **18**, and the recovered **6** (52.1 mg) in a ratio of ca. 7:1:2: ^{1}H NMR (500 MHz) δ 1.00−1.10 ($^7/_{10}$ × 2 H, m, for **7**), 1.23 ($^1/_{10}$ × 3 H, s, for **18**), 1.23−1.90 [($^2/_{10}$ × 6 + $^7/_{10}$ × 8 + $^1/_{10}$ × 8) H, m], 2.05−2.13 [($^2/_{10}$ + $^1/_{10}$) H, m], 2.35 ($^2/_{10}$ H, dt, J = 13.1, 3.8 Hz, for **6**), 2.40−2.50 [($^2/_{10}$ + $^7/_{10}$) × 2 H, m], 2.66 ($^1/_{10}$ H, dd, J = 15.1, 7.3 Hz, for **18**), 2.72 ($^2/_{10}$ H, dd, J = 14.1, 8.8 Hz, for **6**), 2.78 ($^7/_{10}$ × 2 H, dd, J = 15.5, 4.0 Hz, for **7**), 2.89 ($^1/_{10}$ H, dd, J = 15.1, 7.3 Hz, for **18**), 3.08 ($^2/_{10}$ H, dd, J = 14.1, 5.6 Hz, for **6**), 4.60 ($^2/_{10}$ H, s, for **6**), 4.70 ($^2/_{10}$ H, s, for **6**), 7.00−7.30 [(3 + $^8/_{10}$) H, m], 7.53 ($^2/_{10}$ H, d, J = 6.9 Hz, for **6**). The second fraction gave 1-methylene-2-(phenylmethyl)-

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cyclohexane (**27**)[23] (10.8 mg, 16%) as a colorless oil: ^{1}H NMR (500 MHz) δ 1.10−1.74 (7 H, m), 2.00−2.12 (1H, m), 2.25−2.37 (1 H, m), 2.53 (1 H, dd, J = 13.4, 9.3 Hz), 2.98 (1 H, dd, J = 13.4, 5.4 Hz), 4.60 (1 H, s), 4.68 (1 H, s), 7.16 (1 H, br d, J = 7.3 Hz), 7.18 (1 H, br t, J = 7.3 Hz), 7.27 (1 H, br t, J = 7.3 Hz).

Radical Cyclization of 14 with Bu_3SnH−Et_3B at Room Temperature. A 1.06 M solution of Et_3B in hexane (1.10 mL, 1.17 mmol) was added in one portion to a solution of **14** (81.6 mg, 0.29 mmol) and Bu_3SnH (114 mg, 0.39 mmol) in benzene (4 mL) at room temperature, and the mixture was stirred for 12 h under the same conditions. After workup, the crude material was chromatographed on alumina (hexane) to give an oily mixture of **24** and the recovered **14** (54.0 mg) in a ratio of ca. 6:1: ^{1}H NMR (270 MHz) δ 0.76 ($^6/_7$ × 3 H, t, J = 7.4 Hz, for **24**), 1.10−2.15 (10 H, m, for **14** and **24**), 2.19 ($^6/_7$ H, br quintet, J = 6.6 Hz, for **24**), 2.25−2.45 ($^1/_7$ H, m, for **14**), 2.52 ($^6/_7$ H, dd, J = 15.1, 4.9 Hz, for **24**), 2.75−3.15 ($^1/_7$ × 3 H, m, for **14**), 2.98 ($^6/_7$ H, dd, J = 15.1, 6.8 Hz, for **24**), 5.12 ($^1/_7$ H, q, J = 6.4 Hz, for **14**), 6.97−7.30 [($^6/_7$ × 4 + $^1/_7$ × 3) H, m, for **14** and **24**], 7.49 ($^1/_7$ H, dd, J = 7.8, 1.0 Hz, for **14**). The ^{1}H NMR spectrum of this mixture also showed a negligibly small signal due to the methyl protons for **23a** [δ 1.10 (d, J = 7.3 Hz)].

Radical Cyclization of 30. Following the general procedure, compound **30** (250 mg, 0.696 mmol) was treated with Bu_3SnH (243 mg, 0.835 mmol) in the presence of AIBN (13.7 mg, 0.083 mmol) in benzene (105 mL). After workup, the crude material was chromatographed on silica gel (hexane) to give *cis*-1,2,3,3a,8,8a-hexahydro-3a-((phenylthio)methyl)cyclopenta[*a*]indene (**32**) (145 mg, 75%) as a colorless oil: ^{1}H NMR (500 MHz) δ 1.37−1.50 (2 H, m), 1.60−1.70 (1 H, m), 1.91−2.07 (3 H, m), 2.65 (1 H, dd, J = 16.6, 2.0 Hz), 2.74 (1 H, ddt, J = 14.1, 6.3, 2.0 Hz), 3.28 (1 H, d, J = 12.0 Hz), 3.29 (1 H, dd, J = 16.6, 8.8 Hz), 3.33 (1 H, d, J = 12.0 Hz), 7.09−7.14 (1 H, m), 7.15−7.29 (8 H, m); ^{13}C NMR (125.7 MHz) δ 26.1, 35.6, 38.8, 39.6, 45.5, 47.3, 60.8, 123.7, 124.6, 125.5, 126.7, 127.0, 128.7 (2C), 128.8 (2C), 138.1, 143.4, 148.8. Anal. Calcd for $C_{19}H_{20}S$: C, 81.38; H, 7.19. Found: C, 81.30; H, 7.26.

Radical Cyclization of 31. Following the procedure, compound **31** (260 mg, 0.67 mmol) was treated with Bu_3SnH (585 mg, 2.01 mmol) and AIBN (33.0 mg, 0.201 mmol) in benzene (100 mL). After workup, the crude material was chromatographed on silica gel (hexane) to give *cis*- and *trans*-1,2,3,4,5,5a,10,10a-octahydro-5a-(phenylthiomethyl)cyclohepta[*a*]indene (**33**) (168 mg, 82%) as an oily mixture of two stereoisomers in a ratio of ca. 4:1: ^{1}H NMR (270 MHz) δ 1.26−2.16 [($^4/_5$ × 9 + $^1/_5$ × 10) H, m], 2.28 ($^4/_5$ H, dd, J = 14.5, 8.9 Hz), 2.50−2.69 (2 H, m), 2.79−2.94 ($^1/_5$ H, m), 3.09 ($^1/_5$ H, d, J = 11.8 Hz), 3.16 ($^4/_5$ H, d, J = 12.0 Hz), 3.23 ($^4/_5$ H, d, J = 12.0 Hz), 3.32 ($^4/_5$ H, dd, J = 16.5, 8.9 Hz), 3.34 ($^1/_5$ H, d, J = 11.8 Hz), 7.05−7.30 (9 H, m). HRMS: calcd for $C_{21}H_{24}S$, 308.1599; found, 308.1600.

***cis*-1,2,3,3a,8,8a-Tatrahydro-3a-methylcyclopenta[*a*]indene (34).** Using a procedure similar to that described above for the preparation of **18** from **15**, compound **32** (126 mg, 0.448 mmol) was treated with Raney Ni in EtOH (12 mL). Workup gave **34** (77.9 mg, quant.) as a colorless oil: ^{1}H NMR (500 MHz) δ 1.32 (3 H, s), 1.35−1.47 (2H, m), 1.55−1.64 (1 H, m), 1.66−1.74 (1 H, m), 1.86−2.00 (2 H, m), 2.38 (1 H, tdd, J = 8.8, 4.7, 2.7 Hz), 2.61 (1 H, dd, J = 16.1, 2.7 Hz), 3.22 (1 H, dd, J = 16.1, 8.8 Hz), 7.06−7.20 (4 H, m); ^{13}C NMR (125.7 MHz) δ 26.2, 28.4, 35.2, 38.6, 41.9, 50.1, 56.5, 123.1, 124.4, 126.2, 126.6, 142.7, 152.1. HRMS: calcd for $C_{13}H_{16}$, 172.1252; found, 172.1253.

***cis*- and *trans*-1,2,3,4,5,5a,10,10a-Octahydro-5a-methylcyclohepta[*a*]indene (35).** Using a procedure similar to that described above for the preparation of **18** from **15**, compound **33** (204 mg, 0.661 mmol) was treated with Raney Ni in EtOH (20 mL). Workup gave **35** (124 mg, 95%) as an oily mixture of two stereoisomers in the ratio of ca. 4.3:1: ^{1}H NMR (500 MHz) δ 1.03 ($^{10}/_{53}$ × 3 H, s), 1.21 ($^{43}/_{53}$ × 3 H, s), 1.25−1.96 [($^{43}/_{53}$ + 9) H, m], 2.15−2.23 (1 H, m), 2.35−2.45 ($^{10}/_{53}$ H, m), 2.60 (1 H, dd, J = 16.1, 3.9 Hz), 2.80 ($^{10}/_{53}$ H, dd, J = 16.1, 8.3 Hz), 3.23 ($^{43}/_{53}$ H, dd, J = 16.1, 8.3 Hz), 7.09−7.23 (4 H, m); ^{13}C NMR (125.7 MHz) δ 20.1 (*trans*), 24.2 (*cis*), 26.2 (*trans*), 26.6 (*trans*), 26.9 (*trans*), 27.8 (*trans*), 28.5 (*cis*), 30.0 (*cis*), 31.3 (*cis*), 32.8 (*cis*), 38.0 (*trans*), 39.0 (*cis*), 39.2 (*cis*), 40.6 (*trans*), 48.1 (*cis*), 49.0 (*trans*), 50.5 (*trans*), 50.9 (*cis*), 121.9 (*trans*), 122.8 (*cis*), 124.0 (*trans*), 124.2 (*cis*), 125.9 (*trans*), 126.1 (*cis*), 126.2 (*trans*), 126.3 (*cis*), 141.78 (*cis*), 141.84 (*trans*), 152.8 (*cis*), 155.0 (*trans*). HRMS: calcd for $C_{15}H_{20}$, 200.1565; found, 200.1566.

Radical Cyclization of 39. Following the general procedure, compound **39** (138 mg, 0.355 mmol) was treated with Bu_3SnH (310 mg, 1.06 mmol) and AIBN (17.5 mg, 0.106 mmol) in benzene (52 mL). After workup, the crude material was chromatographed on silica gel (hexane). The first fraction gave an inseparable mixture of 1,3,4,10,11,11a-hexahydro-2*H*-dibenzo[*a*,*d*]cycloheptene (**41**) and unknown compounds (total 12.7 mg). The mass spectrum of this mixture showed peaks at *m*/*z* 310, 200, and 198 (for **41**). ^{1}H NMR for **41** (500 MHz): δ 1.18−1.65 (5 H, m), 1.75−1.89 (2 H, m), 2.04 (1 H, dddd, J = 14.9, 8.9, 6.6, 1.0 Hz), 2.13−2.23 (1 H, m), 2.33−2.43 (2 H, m), 2.74 (1 H, ddd, J = 14.9, 9.9, 0.5 Hz), 2.81 (1 H, ddd, J = 14.9, 8.9, 1.0 Hz), 6.24 (1 H, s), 7.00−7.05 (2 H, m), 7.09−7.14 (2 H, m). The second fraction gave 2-(2-phenylethyl)-1-((phenylthio)methylene)cyclopentane (**42**) (5.5 mg, 5%) as a colorless oil: ^{1}H NMR (500 MHz) δ 1.45−1.87 (7 H, m), 1.93−2.04 (1 H, m), 2.23−2.34 (1 H, m), 2.40 (2 H, t, J = 6.1 Hz), 2.62 (2 H, t, J = 8.1 Hz), 5.9 (16/17 H, s), 5.97 (1/17 H, s), 7.10−7.34 (5 H, m). Anal. Calcd for $C_{21}H_{24}S$: C, 81.77; H, 7.84. Found: C, 81.97; H, 8.10. The third fraction gave *cis*-1,2,3,4,4a,9,10,10a-octahydro-4a-((phenylthio)methyl)phenanthrene (**40**) (44.1 mg, 40%) as a colorless oil: ^{1}H NMR (500 MHz) δ 1.19−1.46 (3 H, m), 1.48−1.70 (4 H, m), 1.80 (1 H, ddd, J = 14.4, 11.5, 3.4 Hz), 1.96−2.05 (1 H, m), 2.13−2.27 (2 H, m), 2.79 (1 H, ddd, J = 17.6, 6.8, 3.4 Hz), 2.88 (1 H, ddd, J = 17.6, 10.3, 7.3 Hz), 3.12 (1 H, d, J = 12.5 Hz), 3.30 (1 H, d, J = 12.5 Hz), 7.06−7.17 (4 H, m), 7.21 (2 H, br t, J = 6.8 Hz), 7.29 (2 H, br d, J = 6.8 Hz), 7.32 (1 H, br d, J = 6.8 Hz); ^{13}C NMR (125.7 MHz) δ 22.5, 23.7, 25.3, 26.3, 27.8, 34.5, 36.6, 42.1, 47.9, 123.78, 123.80, 125.7, 125.92, 125.94, 126.2, 128.7, 129.4, 129.6, 136.5, 138.1, 141.2. Anal. Calcd for $C_{21}H_{24}S$: C, 81.77; H, 7.84. Found: C, 81.86; H, 7.94.

***cis*-1,2,3,4,4a,9,10,10a-Octahydro-4a-methylphenanthrene (43).** Using a procedure similar to that described above for the preparation of **18** from **15**, compound **40** (47.5 mg, 0.154 mmol) was treated with Raney Ni in EtOH (3 mL). Workup gave **43**[19] (30.1 mg, 98%) as a colorless oil: ^{1}H NMR (500 MHz) δ 1.24 (3 H, s), 1.18−1.74 (9 H, m), 1.98−2.07 (1 H, m), 2.10−2.20 (1 H, m), 2.76 (1 H, ddd, J = 16.4, 6.4, 4.9 Hz), 2.86 (1 H, ddd, J = 16.4, 9.3, 6.4 Hz), 7.02−7.16 (3 H, m), 7.28 (1 H, d, J = 7.8 Hz).

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Supporting Information Available: Text giving experimental procedures for radical precusors **8**−**14**, **28**−**31**, **38**, and **39** and figures giving ^{1}H NMR spectra for **16**, **20**, **22**, **33**−**35**, and **41** and a ^{13}C NMR spectrum for **34**. This material is available free of charge via the Internet at http://pubs.acs.org.

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