of 2t (8t) (5:22:73) were obtained and isolated by the similar treatment of a mixture of **2t** and **3t** (19:81) in 81% yield. **6r**: mp 90.8–91.3 °C (hexane); IR (KBr disk) 1630 (s), 1590 (m), 1485 (m), 1440 (m), 1130 (s), 1090 (m), 1050 (m), 1010 (m), 975 (w), 950 (w), 920 (w), 910 (m), 850 (w), 840 (w), 810 (w), 780 (w), 765 (m), 745 (m), 695 (m) cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.50 (d, J = 7.1 Hz, 3 H), 2.01–2.44 (m, 1 H, coalescing to a dd, J = 5.7, 14.0 Hz, by irradiation at 5.36), 2.62–2.95 (m, 1 H, coalescing to a d, J = 14.0 Hz, by irradiation at 5.36), 3.46 (dq, J = 5.5, 7.1 Hz, 1 H), 4.71 (t, J = 5.5 Hz, 1 H), 5.10 (t, J = 6.0 Hz, 1 H), 5.36 (dd, J = 5.9, 9.3 Hz, 1 H), 6.83–7.41 (m, 10 H). Anal. Calcd for $C_{19}H_{19}NO_2S$: C, 70.13; H, 5.88; N, 4.30; O, 9.83. Found: C, 70.13; H, 5.90; N, 4.60; O, 10.06. **7r**: mp 219.0–219.5 °C (benzene–hexane); IR (KBr disk) 1490 (m), 1460 (m), 1440 (s), 1200 (s), 1150 (m), 1050 (m), 950 (w), 935 (w), 865 (w), 830 (w), 780 (m), 765 (m), 750 (m), 700 (m) cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.17 (d, J = 6.8 Hz, 3 H), 2.22 (ddd, J = 4.4, 10.0, 13.9 Hz, 1 H), 2.94 (dd, J = 5.6, 13.9 Hz, 1 H), 4.11 (dq, J = 2.7, 6.8 Hz, 1 H), 4.68 (dd, J = 2.7, 4.4 Hz, 1 H), 5.21 (t, J = 4.4 Hz, 1 H), 5.42 (dd, J = 5.6, 10.0 Hz, 1 H), 7.36 (m, 10 H); ^{13}C NMR ($CDCl_3$) δ 17.1 (Me), 42.9 (C_9), 55.0 (C_5), 78.8, 80.6, 82.1, 125.5, 127.9, 128.2, 128.3, 125.5, 141.0, 141.8, 188.5. Anal. Calcd for $C_{19}H_{19}NO_2S$: C, 70.13; H, 5.88; N, 4.30; O, 9.83. Found: C, 70.24; H, 5.83; N, 4.40; O, 9.97. **6t**: mp 116.0–117.0 °C (hexane); IR (KBr disk) 1640 (s), 1590 (m), 1120 (s), 1050 (m), 1015 (m), 970 (m), 905 (m), 750 (s), 690 (s) cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.40 (d, J = 6.8 Hz, 3 H), 2.20 (ddd, J = 5.9, 10.5, 13.9 Hz, 1 H), 2.76 (dd, J = 4.6, 13.9 Hz, 1 H), 3.39 (dq, J = 6.8, 9.5 Hz, 1 H), 4.45 (dd, J = 5.1, 9.5 Hz, 1 H), 5.00 (dd, J = 5.1, 5.9 Hz, 1 H), 5.22 (dd, J = 4.6, 10.5 Hz, 1 H), 6.82–7.4 (m, 10 H); mass spectrum, m/z (relative intensity) 325 (M, 70), 173 (48), 146 (43), 145 (46), 135 (43), 119 (66), 117 (77), 105 (100), 104 (95), 93 (67), 91 (52). **7t**: mp 201–202 °C (benzene–hexane); IR (KBr disk) 1490 (m), 1460 (m), 1195 (s), 1160 (m), 1070 (m), 765 (m), 750 (m), 700 (m) cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.42 (d, J = 7.0 Hz, 3 H), 2.21 (ddd, J = 3.9, 10.3, 14.2 Hz, 1 H), 2.96 (dd, J = 5.6, 14.2 Hz, 1 H), 4.00 (dq, J = 2.5, 7.0 Hz, 1 H), 4.60 (dd, J = 2.5, 4.2 Hz, 1 H), 5.28 (dd, J = 3.9, 4.2 Hz, 1 H), 5.45 (dd, J = 5.6, 10.3 Hz, 1 H), 7.35 (s, 10 H); ^{13}C NMR ($CDCl_3$) δ 16.4 (M), 43.2 (C_9), 58.5 (C_5), 78.7, 80.5, 80.9, 125.4, 127.3, 127.8, 128.0, 128.5, 129.4, 140.8, 144.5, 186.0; high-resolution mass spectrum, calcd for $C_{19}H_{19}NO_2S$ 325.1136, found m/z (relative intensity) 325.1120 (M, 39), 302 (71), 244 (18), 220 (60), 173 (30), 146 (31), 135 (22), 119 (23), 117 (28), 105 (100). **8t**: mp 126.0–127.0 °C (benzene–hexane); IR (KBr disk) 3200 (m), 1595 (m), 1550 (s), 1490 (m), 1200 (s), 1170 (m), 1115 (m), 1080 (m), 1040 (m), 1010 (m), 740 (s), 695 (m), 680 (m) cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.01 (d, J = 7.1 Hz, 3 H), 2.41 (m, 2 H), 3.75 (dd, J = 2.2, 2.9 Hz, 1 H), 4.08 (dq, J = 2.9, 7.1 Hz, 1 H), 5.09 (t, J = 8.1 Hz, 1 H), 5.75 (m, 1 H, coalescing to a dd, J = 2.7, 3.4 Hz, by irradiation at 3.75), 7.35 (m, 10 H), 8.5 (s, 1 H). Anal. Calcd for $C_{19}H_{20}INO_2S$: C, 50.34; H, 4.45; N, 3.09; O, 7.06. Found: C, 50.49; H, 4.34; N, 2.79; O, 7.00.

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Supplementary Material Available: X-ray data for **5w**, including stereoscopic view and tables of non-hydrogen atom coordinates, non-hydrogen thermal parameters, and bond distances and angles (2 pages). Ordering information is given on any current masthead page.

Consecutive Ring Closure and Neophyl Rearrangement of Some Alkenylaryl Radicals

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The endo cyclization products **4a**, **18a**, **18b**, **25b**, and **25c** obtained from the reaction of tributylstannane with the bromoarenes **1a**, **12a**, **12b**, **22b**, and **22c**, respectively, are formed, at least in part, by exo cyclization of the corresponding substituted aryl radicals followed by neophyl rearrangement of the initial products. Kinetic data show that the rearrangement is more rapid for the radicals **15a** and **15b** containing the naphthalene nucleus than it is for the benzenoid radicals **24b** and **24c** and is facilitated by the presence of the electron-attracting substituent in **3a**.

Interest in the ring closure of suitably constituted *o*-alkenylaryl or *o*-(alkenyloxy)aryl radicals has increased dramatically during recent years. The main thrust of these investigations has been twofold. On the one hand, they have been directed toward the determination of the rates and regiochemistry of such cyclizations and the factors which affect them.[1-5] On the other, there has been some attention given to the utility of aryl radical cyclization for the construction of bi- and polycyclic systems, many of which are related to important naturally occurring compounds.[6-13]

Results obtained in these laboratories[1-7,12,13] and elsewhere[8-11] indicate that most suitably constituted alkenylaryl or (alkenyloxy)aryl radicals, like their alkenyl radical counterparts,[14] undergo ring closure exclusively or pre-

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dominantly in the exo mode. Such behavior conforms to expectation based upon qualitative[1] or semiquantitative[3] estimation of the strain energies of the appropriate transition structures. In a few cases, notably those in which there is a substituent on the terminus of the double bond nearer to the aryl group, significant amounts of endo cyclization products are formed.[4] Kinetic examination of such systems in these laboratories has revealed that the endo products are formed mainly by direct endo cyclization of the substituted aryl radical.[4]

Virtually all of the previous work in this area has been concerned with intramolecular additions of substituted phenyl radicals. In order to realize the full synthetic potential of radical cyclization, kinetic and mechanistic investigation of suitably constituted heteroaromatic and polycyclic aromatic systems is desirable. In the present paper we compare the behavior of the substituted naphthyl radicals **13a** and **13b** with the corresponding phenyl radicals **23a** and **23b** and show that the former, unlike the latter, can give rise under suitable conditions to significant yields of endo products by an indirect route involving ring closure followed by neophyl rearrangement of the initial products **15a** and **15b** to the ring-expanded radicals **16a** and **16b**.

After completion of this work, Parker and co-workers[11] reported that aryl radicals of the type **2** bearing an electron-withdrawing substituent give rise to substantial amounts of endo cyclization products **4**, the formation of which occurs mainly by neophyl rearrangement of the initially formed exo radical **3** to give the ring-expanded radical **5**. Evidence for the hypothesis that **2** initially undergoes exo cyclization was adduced from the observation that the radical **7** gives only the dihydrobenzofuran derivative **9**. Products, e.g., **11**, arising from the radical **10** could not be detected. It was suggested that in the case of the radical **8**, the neophyl rearrangement to give **10** is not sufficiently fast to compete with β-elimination of phenylthiyl radical, a reaction known to be very rapid.[15]

In our view such evidence is inconclusive because the radical **7** is not an appropriate model for investigating the behavior of **2**. The rate of intramolecular addition of an aryl radical to an olefinic bond is known to be retarded by substitution at the point of attack.[4,14] Consequently, by comparison with **2**, the radical **7** is heavily weighted in favor of exo cyclization, not only by the lack of the methyl substituent at the position of exo attack but also by the presence of the phenylthio substituent at the position of endo attack.

In view of these ambiguities we have reexamined the reaction of **1a** with tributylstannane and have found, contrary to the previous report,[11] that **6a** is the major product under the usual conditions. We have also confirmed that the radical **3a**, like **15a** and **15b**, can undergo ring expansion to **5a**, albeit slowly. Finally, we report some other authentic cases of consecutive ring closure and neophyl rearrangement.

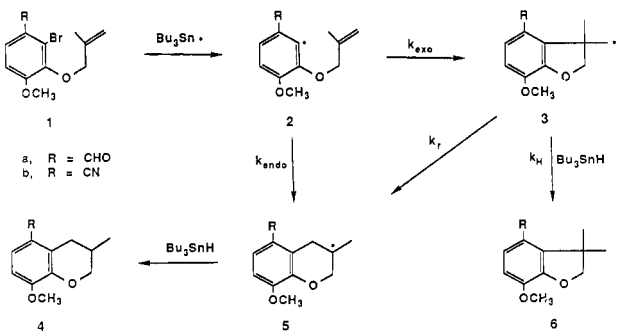
Results and Discussion

Cyclization of Substituted Naphthyl Radicals. When 1-bromo-2-(prop-2-enyloxy)naphthalene (**12a**) was refluxed with a slight excess of 0.06 M tributylstannane in benzene containing a little AIBN as initiator, it gave only two products detectable by GC in the approximate ratio of 10:1. After separation by preparative GC they were identified by ^1H and ^{13}C NMR spectroscopy and by comparison with an authentic sample as the exo (**17a**) and endo (**18a**) cyclization products with the former predominant. No uncyclized product **14a** was detected, indicating that intermolecular hydrogen atom transfer from Bu_3SnH to **13a** under these conditions cannot compete with the rapid cyclization of the latter.

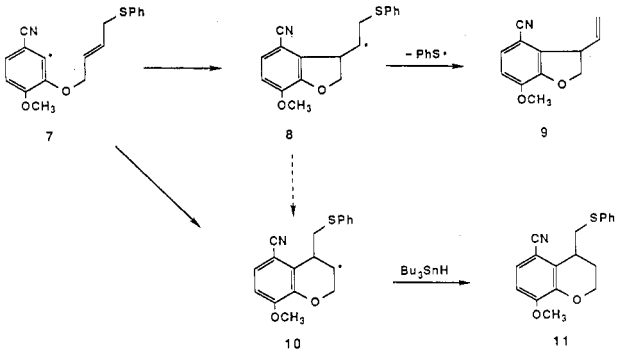
In light of our previous observations[4] that cyclization of the substituted phenyl radical **23a** under similar experimental conditions gives only the exo product, the formation of **18a** from **12a** was unexpected. A possible explanation for the difference in behavior of the two radicals, **13a** and **23a**, is that steric interaction between the proton at C-8 in the former and the terminal vinyl methylene in the side chain might destabilize the transition structure for 1,5-cyclization. However, when this hypothesis was tested by molecular mechanics calculations as previously described,[3] it was found that these interactions are unimportant because of the relatively large nonbonded distances involved.

Further information about the route to the endo product was obtained by carrying out a series of experiments in

Scheme I



Scheme II



Scheme III

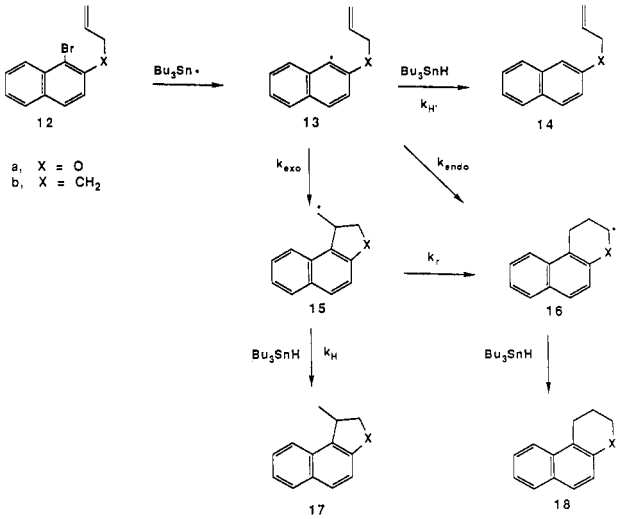


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Table I. Data for Neophyl Rearrangement of 15a[a]

temp, °C	S_0[b], M	17a/18a[c]	k_r/k_H, 10^4M
25	0.01	7.9	3.2
25	0.02	17.8	2.4
25	0.06	28.4	4.1
25	0.10	29.9	6.4
50	0.01	3.3	9.6
50	0.02	8.5	5.9
50	0.06	16.8	7.7
50	0.10	29.2	6.6
80	0.01	1.38	27.4
80	0.02	4.0	15.4
80	0.06	7.5	20.9
80	0.10	12.2	18.9
110	0.01	0.77	53.8
110	0.02	1.95	36.1
110	0.06	3.6	52.0
110	0.10	5.5	50.9
140	0.01	0.46	95.9
140	0.02	0.88	92.1
140	0.06	1.71	127
140	0.10	3.42	91

[a] All reactions in benzene solvent. [b] Initial concentration of Bu_3SnH; the final concentration of Bu_3SnH was zero in each case. [c] As determined by GC.

which the concentration of Bu_3SnH was varied tenfold from 0.01 M to 0.1 M. The usual steady state approach to the kinetics of the steps in Scheme III shows that if the exo and endo products are generated solely by unimolecular 1,5 and 1,6 cyclizations, respectively, then the ratio of those products, **17a/18a**, at any fixed temperature should be independent of stannane concentration. On the other hand, if the endo product **18a** comes exclusively from the exo cyclized radical **15a** via its ring expansion to **16a**, then the amount of endo product formed should conform to the expression $[C]_f = r \ln[(S_0 + r)/(S_f + r)]$ where $[C]_f$ is the normalized final concentration of the endo product, S_0 and S_f are the initial and final concentrations, respectively, of Bu_3SnH, and r is the ratio (k_r/k_H) of k_r, the rate constant for ring expansion, to k_H, the rate constant for transfer of a hydrogen atom from Bu_3SnH to the primary radical **15a**.

The data presented in Table I for the reaction of the naphthalene derivative **12a** with Bu_3SnH clearly show that the ratio of the products **17a/18a** at a fixed temperature is not independent of stannane concentration. We conclude that the endo product **18a** does not arise solely via direct endo ring closure of **13a**. Fitting of the data to the rate equation given above affords apparent values of k_r/k_H. If all of the endo product arises via the pathway **15a** → **16a** → **18a**, then k_r/k_H should have a constant value at any fixed temperature. In fact the values of k_r/k_H show considerable variation. One possible explanation is that **18a** is formed partly via direct endo cyclization of **13a** and partly via rearrangement of **15a**. If this were so, the apparent values of k_r/k_H should show a consistent trend, varying from large to small with decreasing stannane concentration. In fact the variations of k_r/k_H are erratic. We conclude, therefore, that they arise from experimental errors, which are expected to be large under these circumstances when S_0 and **17a/18a** are respectively rather small and rather large.

The behavior of the butenylnaphthyl radical **13b** was similarly studied. Treatment of the bromo compound **12b** with Bu_3SnH in benzene gave both exo and endo products **17b** and **18b**, respectively, together with the uncyclized hydrocarbon **14b**. The relative yields varied with stannane concentration. When $[Bu_3SnH]_0$ was <0.15 M the yield of uncyclized product was negligibly small, and it was then possible to fit the data for the relative yields of cyclized products to the rate equation given above. The results summarized in Table II show that there is fair agreement between the values of k_r/k_H obtained at each temperature for the two concentrations of stannane employed.

Table II. Kinetic Data for the Neophyl Rearrangement of 13b[a]

temp, °C	S_0,[b] M	17b/18b[c]	k_r/k_H, 10^3M
4	0.07	10.6	1.58
4	0.15	16.9	1.42
20	0.07	6.9	2.7
20	0.15	11.6	3.0
50	0.07	3.97	5.3
50	0.15	5.36	7.9
80	0.07	2.03	12.0
80	0.15	3.72	12.3
110	0.07	0.97	28.9
110	0.15	1.93	27.5

[a] All reactions in benzene solvent. [b] Initial concentration of Bu_3SnH; the final concentration of Bu_3SnH was zero in each case. [c] As determined by GC.

Table III. Kinetic Data for Cyclization of 13b[a]

temp, °C	$[Bu_3SnH]$,[b] M	(17b + 18)/14b[c]	k_c/k_H, M
20	0.95	2.2	2.1
20	1.18	1.9	2.2
20	1.42	1.7	2.4
50	0.92	2.4	2.2
50	1.16	2.0	2.3
80	0.89	2.5	2.2
80	1.13	2.1	2.4
80	1.35	1.8	2.4
110	0.86	3.0	2.6
110	1.09	2.5	2.7
110	1.31	2.1	2.8
140	0.84	3.5	2.9
140	1.06	2.8	2.9
140	1.27	2.3	2.9

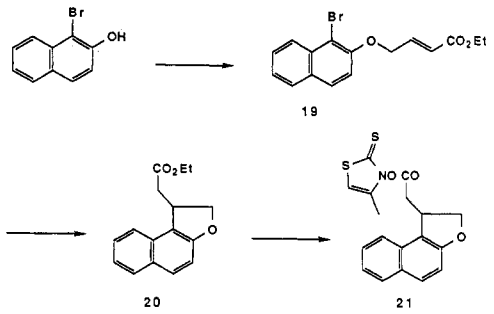
[a] All reactions in benzene solvent. [b] Average concentration of Bu_3SnH which is used in 10-fold excess. [c] As determined by GC.

Application of the usual steady state approximation to the reactions of Scheme III shows that when $[Bu_3SnH]$ is effectively constant, $k_c/k_{H'} = C[Bu_3SnH]/U$, where U is the final concentration of uncyclized product and C is the final total concentration of cyclized products. Table III gives data for reactions conducted with a tenfold excess of stannane at relatively high concentration. Application of the above rate equation where $[Bu_3SnH]$ is the mean stannane concentration during the course of the reaction gives values of $k_c/k_{H'}$ where k_c is the rate constant for ring closure of **13b** and $k_{H'}$ is the rate constant for hydrogen atom transfer from Bu_3SnH to **13b**.

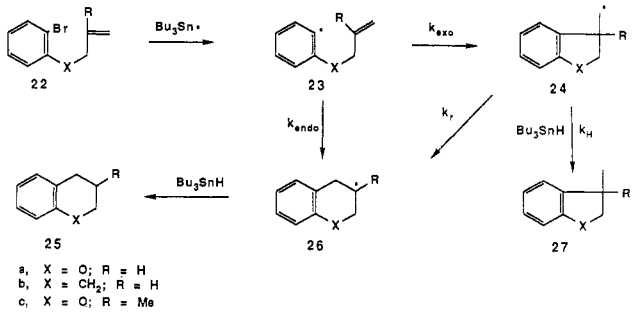
When similar experiments were conducted with the (allyloxy)bromonaphthalene **12a** and Bu_3SnH at relatively high concentration (1.0 M), only the exo cyclization product **17a** was obtained. If we accept that the limit of detectability of the uncyclized product is 2%, it follows that $k_c/k_{H'}$ for **13a** at 80 °C is >50 M and that ring closure of the all-carbon system **13b** is at least 20 times slower at this temperature than that of its oxygen-containing analogue **13a**. A similar enhancement of the rates of cyclization of alkenyl[14] and alkenylaryl[1,4] radicals upon substitution of a chain methylene by an oxygen atom has been previously noted and attributed to relevant changes in the strain energies of the various transition structures.[3]

In order to test further our conclusion that the endo product **18a** arises mainly via rearrangement of the exo radical **15a**, we decided to examine the behavior of **15a** when it was directly generated by a different route. The required precursor **21** was prepared by the route shown in Scheme IV. Treatment with Bu_3SnH of the compound

Scheme IV



Scheme V



19 formed by alkylation of 1-bromo-2-naphthol with bromocrotonic ester gave the cyclized product in excellent yield. Presumably[6] the presence of the carboxylate substituent enhances the rate of cyclization.[16] Hydrolysis of **20** gave the corresponding acid which was converted into the hydroxamic ester **21** in the usual way.[17]

When **21** was treated without purification with 1 molar equiv of tributylstannane (0.05 M) in benzene, the only two products identified by GC of the crude mixture were **17a** and **18a**. Presumably their formation involves generation of the radical **15a** from **21** by the mechanism previously described[17] followed by its conversion into the final products according to the pathways given in Scheme III. In support of this view, the value of k_r/k_H ($\sim 2 \times 10^{-3}$ M) at 80 °C calculated from the observed ratio of products (**17**/**18** = 11) and the average stannane concentration (0.025 M) is in satisfactory agreement with values obtained when **12a** was used as the radical precursor (Table I).

The kinetic data discussed above are consistent with *any* process that results in the conversion of the exo radicals **15a** and **15b** into their endo counterparts. There are precedents for two such processes: (i) the neophyl rearrangement and (ii) ring opening followed by recyclization in the endo mode. However, of the two possible modes of ring opening of **15a** and **15b**, the more exothermic is that which affords radicals of the general type $ArXCH_2^{\bullet}$, and if such species were formed they would certainly be trapped by Bu_3SnH under our conditions to give $ArXCH_3$. Since these products could not be detected we conclude that ring expansion of **15a** and **15b** and of the radicals discussed below occurs by the neophyl rearrangement.

Cyclization of Substituted Phenyl Radicals. Having established that ring closures of the substituted naphthyl radicals **13a** and **13b** do occur initially in the exo mode and that the subsequent neophyl rearrangements of the primary species occur too slowly to lead to substantial yields of endo products under normal conditions, we decided to reexamine the behavior of the radical **2a**, for which, as noted above, the mechanistic information is ambiguous. When a suitable substrate, **1a**, was prepared by standard methods[11] and heated with Bu_3SnH (0.2 M) and a catalytic amount of AIBN in benzene under reflux, it was slowly converted into a mixture of two products which were separated and unambiguously identified as **4a** and **6a** by ^{13}C and ^1H NMR spectroscopy. Contrary to the earlier report,[11] the major product (42%) was that (**6a**) formed by exo ring closure, while the minor (12%) was the endo product **4a**.

Table IV. Relative Yields of Products from Cyclization of 2a at 80 °C in Benzene

$[Bu_3SnH]$,[a] M	yield of **6a**,[b] %	yield of **4a**,[b] %
0.5	90.4	9.6
0.05	66.2	33.8
0.02	43.5	56.5

[a] Bu_3SnH was present in large excess. [b] Determined by GC and based on the assumption that the total yield of **4a** and **6a** was 100%.

A series of quantitative experiments with differing concentrations of Bu_3SnH was then conducted in the usual way,[4] and the mixtures were analysed by GC. The dependence of the exo/endo product ratio with stannane concentration (Table IV clearly shows that at least some of the endo product arises via rearrangement of the initially formed exo radical.

If the endo product arises by both the direct and indirect routes shown in Scheme I, k_r/k_H will be given by $S([\mathbf{4a}] - x[\mathbf{6a}])/\{[\mathbf{6a}](1 + x)\}$, where [**4a**] and [**6a**] are the final concentrations of the products, S is the effective concentrations of Bu_3SnH during the reaction, and x is the ratio of rate constants k_{endo}/k_{exo}. Fitting of the data of Table IV to this expression gives $k_{endo}/k_{exo} = 0.059$ and $k_r/k_H = 0.022$ M. Substitution for k_H by the value at 80 °C of the rate constant for hydrogen atom abstraction from stannane by neopentyl radical (7.0×10^6 M^{-1} s^{-1})[18] gives a value for k_r at this temperature of 1.4×10^5 s^{-1}.

In view of this demonstration that the substituted phenyl radical **2a** undergoes consecutive ring closure and neophyl rearrangement, we decided to study the behavior of the simple radicals under conditions likely to favor rearrangement. Thus treatment of the bromide **22b** with 0.05 M Bu_3SnH in benzene at 115 °C gave an exo/endo ratio of 14.1. Repetition of the experiment with 1.0 M Bu_3SnH gave a ratio of 15.5. If one assumes that all of the endo product, **25b**, formed in the latter case arises by direct closure, it follows from the former result that k_r/k_H for the radical **23b** is about 2.9×10^{-4} M. In view of the obvious approximations involved, the agreement of this value with that ($k_r/k_H = 2.2 \times 10^{-4}$ M) calculated for this temperature from the data given by Franz and his co-workers[19] is reassuring.

In the case of the radical **24c**, the difference between the exo/endo ratio observed when the $[Bu_3SnH]$ is 1.0 M (exo/endo = 18.6) and when it is 0.05 M (exo/endo = 8.2) is much greater than that for radical **24b**. Similar reasoning gives k_r/k_H of 3.1×10^{-3} M.

Kinetics of Rearrangement. Linear regression analysis of the data in Tables I and II gives the Arrhenius expressions for the temperature dependence of k_r/k_H, where k_r is the rate constant for neophyl rearrangement

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Table V. Arrhenius Coefficients and Rate Constants for Radical Rearrangements[a]

reaction	log A, s^{-1}	E, kcal/mol	k_r, s^{-1}
15a → 16a	11.0 ± 0.4	11.1 ± 0.6	1.3×10^4 (80 °C)
15b → 16b	10.6 ± 0.4	9.1 ± 0.6	9.3×10^4 (80 °C)
3a → 5a			1.4×10^5 (80 °C)
24b → 26b			2.9×10^3 (115 °C)
24c → 26c			3.1×10^4 (115 °C)
13b → 15b	10.3	2.2	9×10^8 (80 °C)
23a → 24a[b]	11.7	3.2	5.2×10^9 (80 °C)
23b → 24b[b]	10.8	3.6	3.7×10^8 (80 °C)

[a] Errors in this table and in the text represent 95% confidence limits but include only random errors. [b] Reference 4, but corrected in the light of the new data for the reaction of aryl radicals with stannane (see text).

of the radical **15a** (eq 1) or **15b** (eq 2), k_H is the rate constant for hydrogen atom transfer from stannane, $\theta = 2.3RT$ (kcal/mol), and uncertainties are at the 95% confidence level.

for **15a**

$$\log k_r/k_H\ (M) = (1.93 \pm 0.35) - (7.46 \pm 0.60)/\theta \quad (1)$$

for **15b**

$$\log k_r/k_H\ (M) = (1.48 \pm 0.34) - (5.41 \pm 0.53)/\theta \quad (2)$$

It is reasonable to assume that k_H in these reactions has Arrhenius parameters very similar to those for typical primary alkyl radicals [$\log k_H = (9.1 \pm 0.2) - (3.7 \pm 0.3)/\theta$].[18] By combining this expression with eq 1 and 2, the Arrhenius coefficients listed in Table V for the reactions **15a → 16a** and **15b → 16b** were obtained.

The rate constant for the reaction **24b → 26b** was similarly obtained from the value of k_r/k_H (2.9×10^{-4} M) by substitution of the value for k_H (1.0×10^7 M^{-1} s^{-1}) for a primary radical at 80 °C.[18] In the case of the reactions **3a → 5a** ($k_r/k_H = 2.1 \times 10^{-2}$ M) and **24c → 26c** ($k_r/k_H = 3.1 \times 10^{-3}$ M), the appropriate model for the hydrogen atom abstraction from Bu_3SnH is the neopentyl radical which has $k_H = 7.0 \times 10^6$ M^{-1} s^{-1} at 80 °C and $k_H = 1.0 \times 10^7$ M^{-1} s^{-1} at 115 °C.[18]

Determination of the absolute kinetics for the cyclization of the substituted aryl radicals **13b**, **23a**, and **23b** requires substitution for $k_{H'}$ in the experimental values of $k_c/k_{H'}$. Unfortunately, the previously published data[18] for the reaction of phenyl radicals with Bu_3SnH now appear to be in error.[20] However, separate experiments in these laboratories[21] based on the assumption that aryl radicals will react with a nitroxide radical at the same rate as primary alkyl radicals[21,22] give the following Arrhenius equation for the abstraction of hydrogen atom from Bu_3SnH by aryl radicals: $k_{H'} = 9.6 - 1.7/\theta$. The Arrhenius coefficients presented in Table V were then obtained by combining the equation for $k_{H'}$ with the appropriate relative rate expressions obtained by linear regression of the data in Table III available from earlier work:[4]

for **13b**

$$\log k_c/k_{H'} = (0.73 \pm 0.11) - (0.54 \pm 0.18)/\theta$$

for **23a**

$$\log k_c/k_{H'} = (2.06 \pm 0.04) - (1.47 \pm 0.05)/\theta$$

for **23b**

$$\log k_c/k_{H'} = (1.20 \pm 0.04) - (1.91 \pm 0.05)/\theta$$

In view of the assumptions involved in their derivation, the absolute kinetic data for cyclization of the aryl radicals **3a**, **23a**, and **23b** must be regarded as tentative. However, since they are all related to the same values of $k_{H'}$, the data for the various radicals can be validly and confidently compared with each other.

Turning first to the kinetic data for neophyl rearrangements[23] (Table V, entries 1–5), we note that the reaction is considerably faster for the radicals **15a** and **15b** containing a naphthalene nucleus than it is for the benzenoid radicals **24b** and **24c**. Presumably this reflects the fact that naphthalene at the 1-position is more reactive than benzene toward homolytic attack.[24] The high reactivity of **15b** by comparison with **15a** and of **3a** by comparison with **24b** or **24c** is consistent with the view that alkyl radicals are essentially nucleophilic in character.[14,16] Thus the neophyl rearrangement will be facilitated by the presence of electron-attracting substituents (e.g., CN, CHO) on the aromatic nucleus and may be weakly disfavored by electron-donating substituents (e.g., OR). However, it is noteworthy from the data for **24b** and **24c** that the effect of the extra methyl group in **24c** which facilitates the reaction both by the Thorpe–Ingold effect and by increasing the thermodynamic driving force since **26c** is a *tertiary* radical, outweighs the rate-retarding effect of the oxygen substituent.

Comparison of the data in Table V for ring closures shows the substituted 1-naphthyl radical **13b** to be more reactive than its phenyl analogue **23b**. The fact that the rate of ring closure of **13a** was too fast to be determined whereas that of its phenyl analogue **23a**, though fast, was measurable also supports the conclusion that 1-naphthyl radicals undergo ring closure more rapidly than equivalent phenyl radicals. The other possible explanation is that $k_{H'}$ for 1-naphthyl radicals is not, as we have assumed above, identical with $k_{H'}$ for phenyl radicals but is in fact less. Experiments designed to test this possibility are in hand.

Conclusions. The experiments discussed above give the first unequivocal evidence that ring closure of suitably substituted aryl radicals generated by the reaction of bromoarenes with Bu_3SnH may afford endo products both by direct endo cyclization and by consecutive exo cyclization and neophyl rearrangement. The neophyl rearrangement is faster for radicals containing the naphthalene nucleus than it is for benzenoid radicals and is facilitated by electron-withdrawing substitutents. Nevertheless, in most cases it is a relatively slow process, and the formation of endo products by this route will only become predominant when the experimental conditions are such (e.g., very low concentrations of Bu_3SnH and high temperatures) as to disfavor competing intermolecular reactions.

Experimental Section

^1H and ^{13}C NMR were recorded on a JEOL FX-200 spectrometer operating at 199.50 and 50.10 MHz, respectively. All chemical shifts are in ppm relative to internal Me_4Si. Gas chromatography was performed on Varian 3400 and 6000 chromatographs equipped with flame ionization detectors and coupled to Hewlett-Packard 3390A recorder/integrators. Vitreous silica capillary columns (25 m) (25QCa/BP1 1.0 or 25QC2/BP5 1.0) were employed with helium as the carrier gas. Infrared spectra were measured on a Perkin-Elmer 683 infrared spectrophotometer. Thermostatted baths accurate to ±0.3 °C were used for temperature control. Elemental analyses were performed by the ANU

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Analytical Service unit. Melting points were determined on a Reichert hot stage microscope. Melting and boiling points are uncorrected.

Kinetic Experiments. Solutions in benzene of the halide and tributylstannane, accurately weighed to afford the desired concentrations, were kept frozen under a nitrogen atmosphere. Where possible, the concentration of stannane was chosen so as to give comparable amounts of cyclized and direct reduction products. For kinetic experiments, 200 μL of each solution was carefully syringed into a glass ampule and 1–2 μL of 0.2 M solution of azobis(isobutyronitrile) (AIBN) or di-*tert*-butyl peroxide (BOOB) in benzene was added as initiator such that its concentration was 1–2% of the halide. After being degassed by the freeze–thaw technique, the ampules were sealed under vacuum and immediately transferred to a constant temperature bath until the reaction was complete. After addition of CCl_4 to quench any excess Bu_3SnH, the mixtures were then analyzed by GC on a capillary column. For experiments conducted at <50 °C the reaction was initiated by UV irradiation. For those carried out at temperatures above 100 °C, BOOB was used as initiator instead of AIBN.

For reactions conducted with Bu_3SnH in large excess, the value of k_c/k_H was determined by means of the appropriate first-order integrated rate equation from the relative yields of cyclized and uncyclized products and the mean value of [Bu_3SnH]. For ring expansions a slight deficiency of stannane was employed. In these cases the final concentration of cyclized product was determined from the analytical results and values of k_c/k_H were obtained from the appropriate integrated rate equation by an iterative technique.

1-Bromo-2-(prop-2-enyloxy)naphthalene (12a). A mixture of 1-bromo-2-hydroxynaphthalene (6.0 g, 27 mmol), allyl bromide (4.56 g, 38 mmol), and K_2CO_3 (5.94 g, 43 mmol) in dry acetone (50 mL) was refluxed under nitrogen overnight. After removal of the solvent under reduced pressure, the residue was diluted with H_2O and extracted with ether. The extracts were washed with 5% NaOH solution and H_2O, dried ($MgSO_4$), and evaporated to afford crude product, recrystallization of which from pentane gave white crystalline **12a** (6.0 g, 84.5%); mp 41–42 °C; ^1H NMR ($CDCl_3$) δ 4.75 (d, 2 H, J = 4.9 Hz, OCH_2), 5.23–5.56 (m, 2 H, $=CH_2$), 6.05–6.13 (m, 1 H, CH=), 7.21–7.79 (m, 5 H, Ar H), 8.23 (d, 1 H, J = 8.6 Hz, Ar H); ^{13}C NMR ($CDCl_3$) δ 70.43 (t), 109.58 (s), 115.25 (t), 117.67 (d), 124.39 (d), 126.08 (d), 127.51 (d), 127.95 (d), 128.62 (d), 129.88 (s), 132.79 (d), 132.89 (s), 152.48 (s). Anal. Calcd for $C_{13}H_{11}BrO$: C, 59.34; H, 4.21. Found: C, 58.97; H, 4.23.

2-(Prop-2-enyloxy)naphthalene (14a). 2-Naphthol (3.0 g, 20.8 mmol), allyl bromide (3.53 g, 29.2 mmol), and K_2CO_3 (4.6 g, 33.3 mmol) in dry acetone (30 mL) were refluxed under nitrogen overnight and worked up as described above to afford crude product, distillation of which under vacuum through a short path distillation apparatus afforded 2-(prop-2-enyloxy)naphthalene as a clear oil, 2.8 g, (74%): bp 108–110 °C (2 mmHg); ^1H NMR ($CDCl_3$) δ 4.54 (d, 2 H, J = 5.4 Hz, OCH_2), 5.20–5.45 (m, 2 H, $=CH_2$), 5.91–6.13 (m, 1 H, CH=), 7.06–7.75 (m, 7 H, Ar H); ^{13}C NMR ($CDCl_3$) δ 68.73 (t), 107.04 (t), 117.56 (d), 118.86 (d), 123.60 (d), 126.29 (d), 126.72 (d), 129.00 (s), 133.18 (d), 134.49 (s), 156.51 (s). Anal. Calcd for $C_{13}H_{12}O$: C, 84.75; H, 6.56. Found: C, 84.58; H, 6.67.

Cyclization of 1-Bromo-2-(prop-2-enyloxy)naphthalene (12a). A solution of **12a** (500 mg, 1.9 mmol), Bu_3SnH (664 mg, 2.28 mmol), and AIBN (31 mg, 0.1 mol) in dry benzene (38 mL) was degassed and refluxed under nitrogen for 16 h. The solvent was removed (rotary evaporator) and the residue was dissolved in ether and stirred with an excess of 10% aqueous KF solution for 4 h. The precipitate was then removed by filtration and the two layers were separated. The aqueous layer was extracted with ether and the extracts were washed with brine and dried ($MgSO_4$), filtered, and stripped to afford crude product. MPLC with ethyl acetate–hexane (10% v/v) as elutant gave 184 mg (71% overall yield) of a mixture of **17a** and **18a** (10:1 GC) which was separated by preparative GC. Pure **17a** was an oil: ^1H NMR ($CDCl_3$ δ 1.45 (d, 3 H, J = 6.8 Hz, CH_3), 3.92 (m, 1 H, CH), 4.32–4.85 (m, 2 H, OCH_2), 7.10–7.85 (m, 6 H, ArH); ^{13}C NMR ($CDCl_3$) δ 20.35 (q), 36.18 (d), 79.30 (t), 112.27 (d), 122.23 (d), 122.64 (d), 123.51 (s), 126.52 (d), 128.97 (d), 129.18 (d), 129.51 (s), 130.52 (s), 156.97 (s). Anal. Calcd for $C_{13}H_{12}O$: C, 84.75; H, 6.56. Found: C, 84.75; H, 6.24.

The endo cyclization product 2,3,4-trihydronaphthopyran (**18a**) was identical with a sample prepared[25] from 2-[3-hydroxypropyl)oxy]naphthalene by treatment with P_2O_5. It formed colorless crystals from ethanol: mp 40–42 °C (lit.[25] mp 41–42 °C); ^1H NMR ($CDCl_3$) δ 2.15–2.30 (m, 2 H, CH_2), 3.10 (t, 2 H, J = 6.1 Hz, CH_2), 4.3 (t, 2 H, J = 5.1 Hz, OCH_2), 7.05–7.9 (m, 6 H, Ar H); ^{13}C NMR ($CDCl_3$) δ 21.32 (t), 22.31 (t), 66.14 (t), 113.79 (s), 119.07 (d), 121.76 (d), 123.16 (d), 126.26 (d), 127.57 (d), 128.39 (d), 128.91 (s), 133.27 (s), 152.57 (s).

Ethyl 4-Bromobut-2-enoate. Treatment of ethyl crotonate with *N*-bromosuccinimide gave the required bromo compound: bp 72–76 °C (3 mmHg); (lit.[26] bp 78–82 °C, 2 mmHg); ^1H NMR ($CDCl_3$) δ 1.28 (t, 3 H, CH_3), 4.00 (d, 2 H, $BrCH_2$), 4.20 (q, 2 H, OCH_2), 6.03 (d, 1 H, $=CHCO_2$), 7.02 (m, 1 H, $BrCH_2CH=$).

Ethyl 4-(1-Bromo-2-naphthyl)but-2-enoate (19). 1-Bromo-2-hydroxynaphthalene (6 g, 26.9 mmol), ethyl 4-bromocrotonate (6.23 g, 32.28 mmol), and K_2CO_3 (5.2 g, 37.68 mmol) in dry acetone (50 mL) were refluxed under nitrogen overnight. The mixture was then worked up as described above and the crude product was subjected to column chromatography with ethyl acetate–hexane (15% v/v) as elutant to afford **19** as a light yellow oil (3.3 g, 37%): ^1H NMR ($CDCl_3$) δ 1.28 (t, 3 H, J = 6.9 Hz, CH_3), 4.20 (q, 2 H, J = 6.7 Hz OCH_2CH_3), 4.75 (m, 2 H, OCH_2), 6.34 (m, 1 H, =CH—), 7.00–7.75 (m, 7 H, CH= and Ar H), 8.18 (d, 1 H, J = 7.8 Hz, Ar H); ^{13}C NMR ($CDCl_3$) δ 14.19 (q), 60.50 (t), 68.21 (t), 109.67 (s), 114.69 (d), 122.34 (d), 124.62 (d), 126.17 (d), 127.78 (d), 127.98 (d), 128.91 (d), 130.05 (s), 133.06 (s), 141.73 (d), 152.27 (s), 165.94 (s); IR ν_{max} (neat) 1720 cm^{-1} (C=O). Anal. Calcd for $C_{16}H_{15}BrO_3$: C, 57.33, H, 4.51. Found: C, 57.20; H, 4.41.

Ethyl 1,2-Dihydronaphtho[2,1-*b*]furan-1-acetate (20). Bu_3SnH (1.91 g, 6.57 mmol) in dry benzene (20 mL) was added dropwise over a periof of 1 h to a mixture of **19** (2.0 g, 5.97 mmol) and AIBN (20 mg) in refluxing dry benzene (60 mL) under nitrogen. The mixture was refluxed for an additional 30 min, then cooled, and evaporated. The residue was dissolved in ether and stirred with excess KF solution (60%) for 4 h. The precipitate was removed by filtration and the two layers of the filtrate were separated. The aqueous layer was extracted with ether and the combined extracts washed with brine and dried ($MgSO_4$), filtered, and stripped to afford crude product which was subjected to column chromatography with ethyl acetate–hexane (15% v/v) as elutant to afford **20** (1.49 g, 97%) as a thick yellow oil which solidified on long standing at room temperature. Pure **20** formed crystals from hexane; mp 55–57 °C; ^1H NMR ($CDCl_3$) δ 1.27 (t, 3 H, J = 6.9 Hz, CH_3), 2.78 (m, 2 H, CH_2CO_2), 4.1–4.3 (m, 3 H, OCH_2CH_3 and CH), 4.5–4.8 (m, 2 H, OCH_2), 7.2–7.8 (m, 6 H, Ar H); ^{13}C NMR ($CDCl_3$) δ 14.13 (q), 38.10 (d), 38.51 (t), 60.62 (t), 77.31 (t), 112.18 (d), 120.18 (s), 121.82 (d), 122.78 (d), 126.81 (d), 128.97 (d), 129.43 (s), 129.79 (d), 130.11 (s), 157.23 (s), 171.66 (s); IR ν_{max} (Nujol) 1740 cm^{-1} (C=O). Anal. Calcd for $C_{16}H_{16}O_3$: C, 74.98; H, 6.29. Found: C, 74.67; H, 6.25.

1,2-Dihydronaphtho[2,1-*b*]furan-1-acetic Acid. A solution of **20** (1.0 g, 3.9 mmol) and KOH (0.26 g, 4.6 mmol) in 10 mL of water–ethanol (1:1 v/v) was stirred at room temperature for 2 h. Ethanol was then removed under reduced pressure, and the residue was acidified with dilute H_2SO_4. Extraction with ether and with dichloromethane gave crude product, recrystallization of which from dichloromethane–hexane afforded the required acid (0.88 g, 99%): mp 143–145 °C: ^1H NMR ($CDCl_3$) δ 2.8 (m, 2 H, CH_2CO_2), 4.22 (m, 1 H, CH), 4.6–4.8 (m, 2 H, OCH_2), 7.1–7.8 (m, 6 H, ArH); ^{13}C NMR ($CDCl_3$ δ 38.02 (d), 38.31 (t), 77.32 (t), 112.36 (d), 119.86 (s), 121.76 (d), 123.05 (d), 127.13 (d), 129.24 (d), 129.70 (s), 130.17 (d), 157.30 (s), 178.38 (s); IR ν_{max} (Nujol) 1685 cm^{-1} (C=O). Anal. Calcd for $C_{14}H_{12}O_3$: C, 73.67; H, 5.30. Found: C, 73.99; H, 5.29.

Formation of the Thiohydroxamate 21 and Its Treatment with Bu_3SnH. A mixture of the foregoing acid (100 mg, 0.438 mmol) and oxalyl chloride (133 mg, 1.0 mmol) in benzene (5 mL) was refluxed for 2 h and then concentrated under reduced pressure. The residue, without further purification, was dissolved in dry ether (5 mL), 3-hydroxy-4-methylthiazole-2(3*H*)-thione[17] (68 mg, 0.461 mmol), pyridine (80 μL), and DMAP (4 mg, 0.03

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mmol) were added, and the mixture was stirred at room temperature for 20 min. The precipitated pyridinium hydrochloride was removed by filtration and the ether layer was washed with dilute H_2SO_4 (1 N) and H_2O, dried ($MgSO_4$), filtered, and evaporated under reduced pressure. Without purification the residual thiohydroxamate **21** was mixed with Bu_3SnH (153 mg, 0.562 mmol) and AIBN (2 mg) in dry benzene (10.5 mL) and the solution was degassed and refluxed for 40 min, then cooled, and analyzed by GC. The GC analysis revealed the presence of **17a** and **18a** in the ratio of 11:1. Column chromatography of the crude product in ethyl acetate–hexane afforded a mixture of **17a** and **18a** (23 mg, 29%).

1-Bromo-2-(bromomethyl)naphthalene. Treatment of 1-bromo-2-methylnaphthalene with *N*-bromosuccinimide gave the required bromo compound as light yellow crystals (8.0 g, 59%) from ether: mp 107–108 °C (lit.[27] mp 107–108 °C); ^1H NMR ($CDCl_3$) δ 4.83 (s, 2 H, CH_2Br), 7.45–7.80 (m, 5 H, Ar H), 8.30 (d, 1 H, J = 8.3 Hz, ArH).

1-Bromo-2-but-3-enylnaphthalene (12b). A solution of 1-bromo-2-(bromomethyl)naphthalene (3.0 g, 10 mmol) was added dropwise to a filtered Grignard solution prepared from allyl bromide (2.42 g, 20 mmol) in dry ether (100 mL), and the mixture was stirred at room temperature. After 2 days it was poured onto a mixture of 2 N HCl and ice (1:1) and stirred until it became clear. The organic layer was then separated and the aqueous layer was extracted with ether. The ether extracts were washed with saturated $NaHCO_3$ solution and H_2O, dried ($MgSO_4$), filtered, and concentrated to give crude product, which was subjected to flash column chromatography with ethyl acetate–hexane (3% v/v) as elutant to afford **12b** as a clear oil (1.67 g, 64%): ^1H NMR ($CDCl_3$) δ 2.39–2.55 (m, 2 H, CH_2CH=), 3.1 (t, 2 H, J = 7.5 Hz, $ArCH_2$), 4.98–5.18 (m, 2 H, =CH_2), 5.84–6.08 (m, 1 H, —CH=), 7.31–7.84 (m, 5 H, ArH), 8.35 (d, 1 H, J = 8.3 Hz, Ar H); ^{13}C NMR ($CDCl_3$) δ 34.01 (t), 36.85 (t), 115.22 (t), 123.66 (s), 125.79 (d), 127.22 (d, 2C), 127.43 (d), 127.95 (d), 128.10 (d), 133.21 (s), 137.57 (d), 139.25 (s); one quaternary carbon was not detected. Anal. Calcd for $C_{14}H_{13}Br$: C, 64.39; H, 5.02. Found: C, 64.29; H, 4.98.

Cyclization of 1-Bromo-2-but-3-enylnaphthalene (12b). A solution of **12b** (300 mg, 1.15 mmol), Bu_3SnH (368 mg, 1.26 mmol), and AIBN (19 mg) in dry benzene (21 mL) was degassed and refluxed under N_2 for 16 h. The solvent was then removed under reduced pressure and the residue was chromatographed with hexane as elutant to give a clear oil (200 mg, 96%) containing **14b**, **17b**, and **18b** in the ratio 1:36.6:16.8, respectively (GC). Preparative GC of the mixture gave pure **17b** as an oil: ^1H NMR ($CDCl_3$) δ 1.30 (d, 3 H, J = 6.1 Hz, CH_3), 1.9–2.5 (m, 2 H, —CH_2—), 2.9–3.3 (m, 2 H, $ArCH_2$), 3.70–3.86 (m, 1 H, CH), 7.30–7.90 (m, 6 H, ArH); ^{13}C NMR ($CDCl_3$) δ 20.44 (q), 31.62 (t), 33.64 (t), 38.22 (d), 123.45 (d), 124.04 (d), 124.48 (d), 125.76 (d), 126.96 (d), 128.65 (d), 129.94 (s), 132.94 (s), 139.92 (s), 144.10 (s). Anal. Calcd for $C_{14}H_{14}$: C, 92.26; H, 7.74. Found: C, 92.14; H, 7.61. A sample of pure **18b** was similarly obtained as an oil: ^1H NMR ($CDCl_3$) δ 1.90 (m, 4 H, —$(CH_2)_2$—), 2.88 (t, 2 H, J = 5.3 Hz, —CH_2—), 3.10 (t, 2 H, J = 5.3 Hz, —CH_2—), 7.15–8.00 (m, 6 H, Ar H); ^{13}C NMR ($CDCl_3$) δ 22.98 (t), 23.27 (t), 25.70 (t), 30.48 (t), 122.75 (d), 124.65 (d), 125.61 (d), 125.73 (d), 128.27 (d), 128.36 (d), 131.48 (s), 132.10 (s), 132.59 (s), 134.32 (s). Anal. Calcd for $C_{14}H_{14}$: C, 92.26; H, 7.74. Found: C, 92.06; H, 7.88.

2-But-3-enylnaphthalene (14b). Treatment of 2-(bromomethyl)naphthalene[28] (1.0 g, 4.5 mmol) with allylmagnesium bromide as described above gave **14b** isolated by flash column chromatography (hexane) as a clear oil (300 mg, 38%); ^1H NMR ($CDCl_3$) δ 2.35–2.50 (m, 2 H, —CH_2—), 2.82 (t, 2 H, J = 7.5 Hz, $ArCH_2$), 4.90–5.10 (m, 2 H, =CH_2), 5.77–5.98 (m, 1 H, —CH=), 7.24–7.80 (m, 7 H, ArH); ^{13}C NMR ($CDCl_3$) 35.33 (t), 35.48 (t), 114.96 (t), 125.03 (d), 125.76 (d), 126.34 (d), 127.25 (d), 127.37 (d), 127.51 (d), 127.75 (d), 131.95 (s), 133.56 (s), 137.9 (d), 139.28 (s). Anal. Calcd for $C_{14}H_{14}$: C, 92.26; H, 7.74. Found: C, 92.25; H, 7.67.

2-Bromo-3-[(2-methylprop-2-enyl)oxy]-4-methoxybenzaldehyde (1a). A solution of 2-bromo-3-hydroxy-4-methoxybenzaldehyde (1.15 g, 5 mmol) in dry DMF (8 mL) was added to a suspension of sodium hydride (144 mg, 6 mmol) in dry DMF (2 mL). After the evolution of hydrogen had ceased, a solution of 3-bromo-2-methylprop-1-ene (0.68 g, 7.5 mmol) was added dropwise, and the mixture was stirred at 60 °C for 4 h. The mixture was then cooled, quenched with saturated NaCl solution, and extracted with ether. The extracts were washed with 10% NaOH solution and dried (Na_2SO_4), and the solvent was evaporated. The crude residue was recrystallized from water/ethanol to give colorless needles (0.97 g, 68%): mp 80–80.5 °C; ^1H NMR δ ($CDCl_3$) 1.98 (s, 3 H, CCH_3), 3.98 (s, 3 H, OCH_3), 4.46 (s, 2 H, OCH_2), 5.04 (br s, 1 H, =CH), 5.19 (br s, 1 H, =CH), 6.99 (d, 1 H, Ar H), 7.77 (d, 1 H, ArH), 10.29 (s, 1 H, CHO); ^{13}C NMR δ ($CDCl_3$) 20.01, 56.38, 76.84, 110.94, 113.82, 123.36, 126.40, 127.42, 141.10, 145.32, 158.68, 191.04. Anal. Calcd for $C_{12}H_{13}O_3Br$: C, 50.55; H, 4.60. Found: C, 50.31; H, 4.45.

2,3-Dihydro-3,3-dimethyl-7-methoxybenzofuran-4-carboxaldehyde (6a) and 3,4-Dihydro-3-methyl-8-methoxy-2*H*-1-benzopyran-5-carboxaldehyde (4a). A solution of the bromide **1a** (114 mg, 0.4 mmol), Bu_3SnH (142 mg, 0.48 mmol), and AIBN (5 mg) in degassed benzene (2.4 mL) was heated under reflux for 8 h after which GC analysis indicated ~50% of the starting material to be consumed. A further few milligrams of AIBN were then added, and the solution was heated under reflux for another 16 h during which the reaction proceeded to completion. The solution was cooled, the solvent evaporated under vacuum, and the residue taken up in ether. The solution was stirred vigorously with 10% aqueous KF solution for 3–4 h to remove most of the tin residues from the organic layer. The ether solution was concentrated and then chromatographed on a chromatotron. Compound **6a** (35 mg, 42%) was isolated as an oil: ^1H NMR δ ($CDCl_3$) 1.54 (s, 6 H, CH_3), 3.97 (s, 3 H, OCH_3), 4.35 (s, 2 H, OCH_2), 6.89 (d, 1 H, Ar H), 7.43 (d, 1 H, ArH), 10.01 (s, 1 H, CHO); ^{13}C NMR δ ($CDCl_3$) 25.78, 43.26, 55.10, 84.99, 109.25, 124.95, 125.57, 127.41, 136.08, 148.46; exact mass, $C_{12}H_{14}O_3$ requires M^+ 206.0943, found M^+ 206.0944. Compound **4a** (10 mg, 12%) was isolated as an oil: ^1H NMR δ ($CDCl_3$) 1.10 (d, 3 H, CH_3) 2.17 (m, 1 H, CH), 2.73 (d, 1 H, HCH), 3.44 (dd, 1 H, HCH), 3.77 (dd, 1 H, HCH), 4.32 (dd, 1 H, HCH), 6.87 (d, 1 H, Ar H), 7.38 (d, 1 H, Ar H), 9.98 (s, 1 H, CHO); ^{13}C NMR ($CDCl_3$) 17.67, 27.09, 31.46, 56.63, 72.33, 108.46, 124.70, 128.18, 129.52, 144.62, 153.49, 192.56; exact mass, $C_{12}H_{14}O_3$ requires M^+ 206.0943, found M^+ 206.0944.

Registry No. **1a**, 107345-55-1; **3a**, 109433-12-7; **4a**, 107345-58-4; **5a**, 109433-13-8; **6a**, 109433-14-9; **12a**, 109433-15-0; **12b**, 109433-16-1; **13a**, 109433-17-2; **13b**, 109433-18-3; **14a**, 3698-15-5; **14b**, 2489-89-6; **15a**, 109433-19-4; **15b**, 109433-21-8; **16a**, 109433-21-8; **16b**, 109433-22-9; **17a**, 5665-42-9; **17b**, 37977-36-9; **18a**, 3722-88-1; **18b**, 1013-08-7; **19**, 109433-23-0; **20**, 109433-24-1; **21**, 109433-25-2; **22a**, 60333-75-7; **22b**, 71813-50-8; **22c**, 10178-53-7; **23a**, 56182-32-2; **23b**, 57056-96-9; **24a**, 25154-61-4; **24b**, 75421-36-2; **24c**, 104820-80-6; **25a**, 493-08-3; **25b**, 119-64-2; **25c**, 70401-56-8; **26b**, 75421-37-3; **26c**, 104820-81-7; **27a**, 13524-73-7; **27b**, 767-58-8; **27c**, 13524-78-2; Bu_3SnH, 688-73-3; 1-bromo-2-hydroxynaphthalene, 573-97-7; allyl bromide, 106-95-6; 2-naphthol, 135-19-3; ethyl 4-bromobut-2-enoate, 6065-32-3; ethyl crotonate, 10544-63-5; 1,2-dihydronaphtho[2,1-*b*]furan-1-acetic acid, 109433-26-3; oxalyl chloride, 79-37-8; 3-hydroxy-4-methylthiazole-2(3*H*)-thione, 49762-08-5; 1-bromo-2-(bromomethyl)naphthalene, 37763-43-2; 1-bromo-2-methylnaphthalene, 2586-62-1; 2-(bromomethyl)naphthalene, 939-26-4; 3-bromo-2-methylprop-1-ene, 1458-98-6.

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