Synthesis and Calibration of Two Radical Timing Devices: 2-Methyl-2-(1-naphthyl)- and 2-Methyl-2-(2-naphthyl)-1-bromopropane

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Radical reactions have gained increasing importance over the past decades in several fields of chemistry and biology, and the measurement of their rates is of great importance both for theoretical and practical purposes.[1] Several direct and indirect methods have been devised for the determination of radical kinetic parameters. Although, in principle, experimental techniques based on the time-resolved detection of the reacting species are more reliable, indirect measurements may become the method of choice in several cases either for the lack of suitable direct techniques or simply because they allow accurate measurements to be made even when expensive and sophisticated instrumentation is not available.

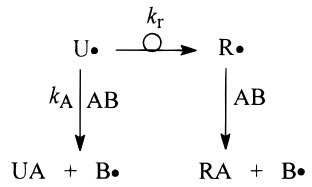
A very popular indirect method makes use of competing unimolecular radical reactions as timing devices to investigate the rates of radical−molecule reactions. In this method, called the "radical clock" technique,[2] a unimolecular rearrangement whose kinetic parameters are well-known is set to compete with the bimolecular reaction to be calibrated, as shown in Scheme 1.

The ratio, k_A/k_r, of the rate for reaction of the unrearranged radical U$^\bullet$ with the atom donating substrate AB over the known rate for rearrangement to R$^\bullet$ can be easily obtained from the analysis of the reaction products ([UA]/[RA]). This method has proven to be especially valuable in the case of the hydrogen atom abstraction by alkyl radicals from any hydrogen-donating substrate (eq 1).

$$R^\bullet + XH \rightarrow RH + X^\bullet \qquad (1)$$

A convenient timing device should satisfy the following requirements: (i) the alkyl radical should be easily generated from a suitable precursor directly in the reaction mixture; (ii) the rate of radical rearrangement should be accurately known and comparable to the pseudo-first-order rate of the bimolecular reaction to be timed, to simultaneously detect products arising from both competing reactions; (iii) the overall system should be sufficiently simple to be represented by Scheme 1; that is, no reaction other than hydrogen abstraction and the unimolecular rearrangement should take place in the same time scale; and (iv) the reaction products should be stable and detectable by means of a simple analytical method such as gas chromatography. Several radical

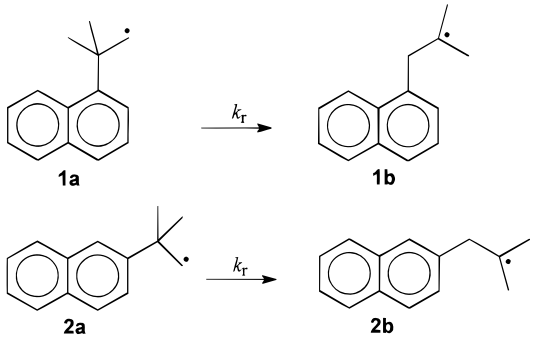
Scheme 1



rearrangements, complying with the above requirements, have been studied over the past few years. The slower ones, for which accurate calibrations have been reported over a wide range of temperatures, are collected in Chart 1.

It can be seen that no radical clock, rearranging at room temperature with a rate constant in the range between 10^3 s^{-1} (neophyl and cyclobutylmethyl radicals) and 10^5 s^{-1} (1-hexenyl radical), is available for common laboratory practice, thus leaving uncovered a gap of 2 orders of magnitude. Incidentally, several substrates of wide interest, such as phenols, react with alkyl radicals with rates that, to be accurately measured, would require a unimolecular competing process falling in this range.[6]

On the basis of EPR measurements, Maillard and Ingold[7] estimated that the neophyl-like rearrangement of the 2-methyl-2-(2-naphthyl)-1-propyl radical (**2a**) would have a log *A* value of 11.75 and an activation energy, E_a, of 11.3 kcal/mol, which yield a rate of rearrangement $k_r = 2.9 \times 10^3$ s^{-1} at 25 °C. Since in the same paper the rate constant for the neophyl rearrangement was given as $k_r = 59$ s^{-1} at 25 °C, which has proven to be much lower than the currently accepted value of 1.1×10^3 s^{-1},[3] a value of ca. 5×10^4 s^{-1} would be expected for radical **2a** if relative measurements were correct. This would fall between neophyl and 1-hexenyl radicals in the scale of unimolecular reactivity. As an additional advantage, this radical clock does not contain olefinic double bonds that could easily undergo homolytic addition either in the unrearranged or in the rearranged forms. Nevertheless, this radical rearrangement has not been fully experimentally calibrated and a suitable precursor has been devised. Actually, in the above-mentioned paper, radical **2a** was generated by hydrogen abstraction with *tert*-



butoxyl radicals from the corresponding hydrocarbon,

(1) Newcomb, M. *Tetrahedron* **1993**, *49*, 1151−1176.
(2) Griller, D.; Ingold, K. U. *Acc. Chem. Res.* **1980**, *13*, 317−323.
(3) (a) Franz, J. A.; Barrows, R. D.; Camaioni, D. M. *J. Am. Chem. Soc.* **1984**, *106*, 3964−3967. (b) Burton, A.; Ingold, K. U.; Walton, J. C. *J. Org. Chem.* **1996**, *61*, 3778−3782.
(4) Walton, J. C. *J. Chem. Soc., Perkin Trans. 2* **1989**, 173−177.
(5) Chatgilialoglu, C.; Ingold, K. U.; Scaiano, J. C. *J. Am. Chem. Soc.* **1981**, *103*, 7739.
(6) Franchi, P.; Lucarini, M.; Pedulli, G. F.; Valgimigli, L.; Lunelli, B. *J. Am. Chem. Soc.* **1999**, *121*, 507−514.
(7) Maillard, B.; Ingold, K. U. *J. Am. Chem. Soc.* **1976**, *98*, 1224−1226, 4692.

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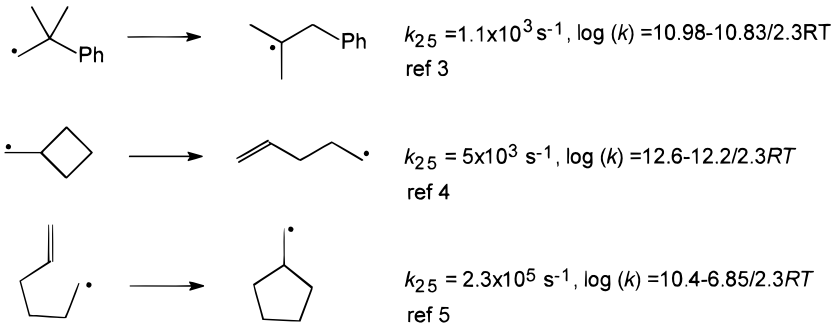
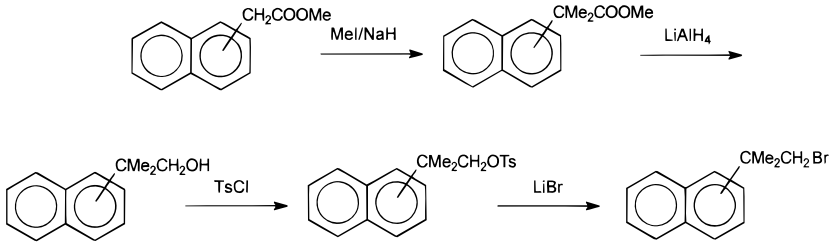
Chart 1



Scheme 2



which, however, does not represent a convenient source of radicals for competitive kinetic experiments.

In this paper, we report the synthesis of 2-methyl-2-(1-naphthyl)-1-bromopropane (**1**) and of 2-methyl-2-(2-naphthyl)-1-bromopropane (**2**) that, upon halogen abstraction (eq 2), can generate radicals **1a** and **2a**, respectively, as well as an accurate kinetic investigation, carried out over a wide range of temperatures, of the rearrangements of these radicals. The usefulness of bromides **1** and **2** as precursors of radical timing devices is also shown in one case.

Results

Synthesis of the Radical Precursors 1 and 2. The synthesis of bromides **1** and **2** was achieved by starting from the commercially available methyl 1-naphthyl acetate and 2-naphthylacetic acid, respectively. The latter was converted into the corresponding methyl ester by reaction with MeI in DMF in the presence of K_2CO_3 at room temperature. According to Hixson and Tausta,[8] the two esters were first dimethylated with MeI/NaH and then reduced to the corresponding propanol with $LiAlH_4$. These alcohols were converted into the tosylates, which were eventually transformed into bromides **1** and **2** by reaction with LiBr in anhydrous HMPA in the presence of some drops of water (Scheme 2).

Calibration of the Radical Clocks. To check the reactivity of bromides **1** and **2** under free-radical conditions, their quantitative reduction was carried out at 20 °C by photolyzing a 0.1 M benzene solution containing 0.6 M tris(trimethylsilyl)silane, $(TMS)_3SiH$, and *tert*-butylbenzene as internal standard in the presence of di-*tert*-butyl peroxide. The only detectable reaction products were 1-*tert*-butylnaphthalene and 2-*tert*-butylnaphthalene, respectively, obtained with 96% and 98% yields and 97% conversions, arising from the unrearranged radicals **1a** and **2a** by hydrogen abstraction from the silane. By reducing the concentration of the hydrogen donor (0.1 M), small amounts of a second product, identified on the basis of the mass spectrum as 1- and 2-isobutylnaphthalene, respectively, were also dectected. This is consistent with the fact that a fraction of radicals **1a** and **2a** undergoes an intramolecular 1,2-aryl migration, similar to the well-known neophyl rearrangement, giving the rearranged radicals **1b** and **2b**, which are quenched to the corresponding hydrocarbons by reaction with the silane.

Since by using $(TMS)_3SiH$ as the reducing agent the rearranged hydrocarbons are only formed at low silane concentrations, i.e., far from the pseudo-first-order conditions under which competitive kinetic experiments are more conveniently carried out, we preferred to investigate the rearrangement of radicals **1a** and **2a** using 2,4,6-trimethylphenol (TMP) as hydrogen donor. The competition with the hydrogen abstraction from TMP was chosen because the kinetic parameters for this reaction (log $A = 7.26$; $E_a = 3.34$ kcal/mol) have been recently measured with the same technique using the 5-exo cyclization of 1-hexenyl radicals as a competing unimolecular process.[6]

Analysis of the reaction products obtained from the reaction of the photochemically generated radicals with 2,4,6-trimethylphenol, according to eqs 2−6, was carried out by means of GC.

$$Bu_3Sn{-}SnBu_3 \xrightarrow{h\nu} 2Bu_3Sn^{\bullet} \qquad (2)$$

$$U{-}Br + Bu_3Sn^{\bullet} \rightarrow U^{\bullet} + Bu_3SnBr \qquad (3)$$

$$U^{\bullet} \xrightarrow{k_r} R^{\bullet} \qquad (4)$$

$$U^{\bullet} + ArOH \xrightarrow{k_H} U{-}H + ArO^{\bullet} \qquad (5)$$

$$R^{\bullet} + ArOH \rightarrow R{-}H + ArO^{\bullet} \qquad (6)$$

In all cases, 1-*tert*-butylnaphthalene and 1-isobutylnaphthalene were obtained from bromide **1** (and the corresponding hydrocarbons from bromide **2**) in variable ratios depending on the concentration of the hydrogen donor employed. Very minor side products, identified on the basis of their mass spectra as 1-(1-naphthyl)-2-

(8) Hixson, S. S.; Tausta, J. C. *J. Org. Chem.* **1977**, *42*, 2191.

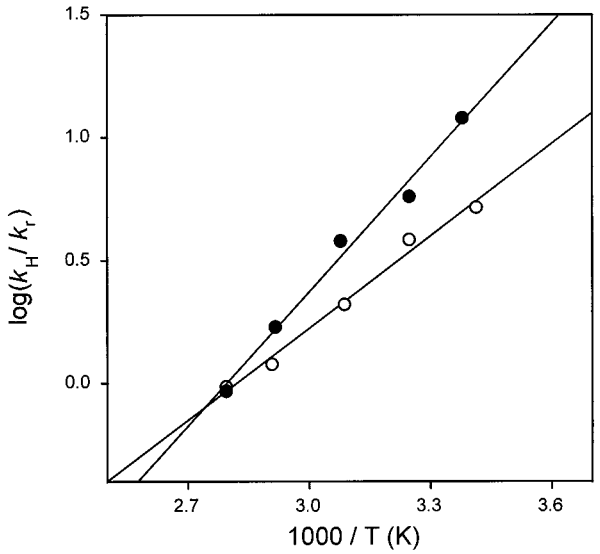


Figure 1. Arrhenius plots of the ratios between the rate constants for hydrogen abstraction from 2,4,6-trimethylphenol and the rearrangements of radicals **1a** (full symbols) and **2a** (empty symbols).

methylpropene and 1-(2-naphthyl)-2-methylpropene, respectively, were also detected. These most likely arise from disproportionation of the rearranged radicals **1b** and **2b**, similarly to what reported for the related neophyl radical.[3b]

$$\frac{[ArCMe_3]}{[ArCH_2CHMe_2] + [ArCH=CMe_2]} = \frac{k_H}{k_r}[ArOH] \quad (7)$$

The first-order rate constant k_r for the rearrangement of radicals **1a** and **2a** was determined over the temperature range 293−358 K and was obtained by plotting the measured product ratio $[ArCMe_3]/([ArCH_2CHMe_2] + [ArCH{=}CMe_2])$ against the phenol concentration, according to eq 7. The plots had a nonzero intercept, whose actual value depended on temperature, falling in the range 1.3−0.5 for clock **1a** and 0.4−0.07 for **2a** (see the Supporting Information). This indicates that radicals **1a** and **2a**, in addition to rearranging and reacting with TMP, also abstract an hydrogen atom from some different substrate. To check the importance of this side reaction under our experimental conditions, we performed a set of experiments using 2,4,6-trimethylphenol deuterated at the hydroxylic position (*d*-TMP) and measured the relative amount of deuterated over nondeuterated *tert*-butylnaphthalene in the reaction products by GC−MS. From the fact that only about 15% and 10% nondeuterated product was obtained with clocks **1a** and **2a**, respectively, it can be inferred that the hydrogen abstraction reaction by alkyl radicals from TMP takes place essentially at the hydroxylic group.[9]

From the Arrhenius plot (see Figure 1) of the measured rate ratio k_H/k_r it was found E_a(TMP) − E_a(**1a**) = 8.28 kcal/mol, log *A* (TMP) − log *A*(**1a**) = −5.07, and E_a(TMP) − E_a(**2a**) = 5.72, log *A*(TMP) − log *A*(**2a**) = −3.54, which afforded the Arrhenius parameters for the rearrangement reactions reported in Table 1.

(9) When using the nondeuterated phenol, the amount of hydrogen coming from the OH group should be larger because of the isotope effect normally found in hydrogen-transfer reactions from phenols.[10]

Table 1. Room-Temperature Rate Constants and Arrhenius Parameters for the Intramolecular Rearrangement of 1a and 2a in Benzene[b]

radical	log A/s^{-1}	E_a/kcal mol^{-1}	k_r (298 K)/s^{-1}
1a	12.33 ± 0.84	11.62 ± 0.54	6.4×10^3
2a	10.80 ± 0.49	9.06 ± 0.32	1.4×10^4
neophyl	10.98	10.83	1.1×10^3

[a] Errors correspond to twice standard deviations on the relative measurements and do not incorporate the errors for the rate of H-abstraction from 2,4,6-trimethylphenol by alkyl radicals.[6] [b] Data for neophyl radical (ref 3) have been added for comparison.

The reported data indicate that the rearrangement of radicals **1a** and **2a** is 6 and 12 times, respectively, faster than that of the neophyl radical, thus falling in a range of reactivity that is strategic for the measurement of the rate of hydrogen abstraction by primary alkyl radicals from many substrates of wide interest.

Errors correspond to twice standard deviations on the relative measurements and do not incorporate the errors for the rate of H-abstraction from 2,4,6-trimethylphenol by alkyl radicals.[6]

A useful application of these results was that to measure the rate constant for hydrogen abstraction by primary alkyl radicals from triphenylsilane at 298 K. In the literature two values determined by using the neophyl radical rearrangement are reported, both at high temperatures ($k_H^{363} = 3.0 \times 10^4$ M^{-1} s^{-1},[11] $k_H^{393} = 4.6 \times 10^4$ M^{-1} s^{-1})[12] since this clock is too slow to calibrate that reaction at room temperature. Radicals **1a** and **2a** instead rearrange at 298 K with rates comparable to that of hydrogen transfer from Ph_3SiH when this silane is used in appropriate concentrations (0.2−1 M). The values of k_H measured in benzene at 298 K were 4.7×10^3 when using **1a** and 4.3×10^3 M^{-1} s^{-1} when using **2a**. This value can be checked by using the Arrhenius equation[13] log$(k_H/M^{-1}\ s^{-1}) = 8.7 - 7.0/2.3RT$, derived by assuming that the log *A* value (8.7) is identical to that of many other hydrogen abstraction reactions and by calculating the activation energy from the two experimental values given above.[11,12] The rate constant estimated at 298 K from this equation is 3.6×10^3 M^{-1} s^{-1}, in very good agreement with the experimental value measured in the present study.

Discussion

The 1,2-aryl migrations in hydrocarbon radicals are well-documented reactions, and their mechanism has been extensively investigated. In the past, there has been plenty of discussion in the literature concerning whether the rearrangement proceeds through an intermediate bridged radical,[14] which in the present case would have structures **1c** and **2c** for the rearrangement of **1a** and **2a**, respectively, or by migration of the aryl group concerted with the bond cleavage of the Ar−C bond

(10) (a) Howard, J. A.; Furimsky, E. *Can. J. Chem.* **1973**, *51*, 3738. (b) Burton, G. W.; Doba, T.; Gabe, E. J.; Hughes, L.; Lee, F. L.; Prasad, L.; Ingold, K. U. *J. Am. Chem. Soc.* **1985**, *107*, 7053−7065.

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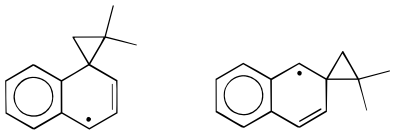
without formation of any intermediate. Since direct evidence that bridged-radical intermediates are formed in the rearrangement of β-anthrylethyl radicals[15] and in that of neophyl-like alkoxy radicals,[16] it seems safe to assume that other 1,2-aryl migrations also proceed through bridged spiro intermediates.



1c **2c**

An examination of the activation parameters reported in Table 1 shows that the log *A* value for the rearrangement of **2a** is very similar to that of the neophyl radical while the corresponding activation energy is lower by 1.6 kcal/mol. This is entirely consistent with expectations if it is assumed that the transition state for rearrangement has a structure very close to that of the cyclic spiro intermediates, since in **2c** the resonance stabilization energy should be larger than in the analogous species formed during the neophyl radical isomerization. At the same time, steric factors are expected to be quite similar in both radicals at any stage of the rearrangement process.

Somewhat unexpected are instead the values of the activation parameters for the rearrangement of **1a**, as the preexponential factor, i.e., $10^{12.33}$, is 22 times higher than that for the neophyl radical and the activation energy is larger than that of both **2a** and neophyl. One might note that differences in logA and E_a between the rearrangements of radicals **1a** and **2a** go in the opposite direction so that, at about 90 °C, the corresponding Arrhenius plots intersect. This feature is sometimes referred to as a "compensation effect" and might be artifactual, since an error in the value of E_a (slope of the plot) would reflect in an error, in the opposite direction, in the value of log *A* (intercept). Nevertheless, the errors extimated for the Arrhenius parameters of the above rearrangement reactions (see Table 1) are small enough to make the measured differences significant at higher than 85% confidence interval (2σ). Thus, a plot of $\log(k_r(\mathbf{2a})/k_r(\mathbf{1a}))$, where $k_r(\mathbf{2a})$ and $k_r(\mathbf{1a})$ are the rate constants for the rearrangement of **1a** and **2a**, versus $1000/T$ has a slope = 0.46 (σ = 0.18) and an intercept = −1.31 (σ = 0.57), showing that the temperature dependence of the rearrangements of radical **1a** and **2a** are significantly different within twice standard deviation (see Supporting Information).[17]

An explanation of the high *A* value for clock **1a** may be given as follows: in 1,2-aryl migrations the intermediate and conceivably the transition state are characterized by a lower motional freedom than the rearranging radicals due to the formation of the spiro cyclopropane ring, with a consequent reduction of log *A* to ca. 11 from the value of 13.2, which is considered to be "normal" for a unimolecular reaction.[18] We attribute the larger than usual value of *A* (12.33) for the rearrangement of **1a** to the fact that the strong steric hindrance to the internal rotation of the aliphatic chain reduces the rotational freedom also in the ground-state radical, thus decreasing the entropy difference with respect to the transition state.

With regard to the activation energy, one should expect for **1a** a value lower than for **2a**, since the ground state of **1a** should have a larger energy content due to the steric interaction of the peri hydrogen with the aliphatic substituent, while the cyclic intermediates **1c** should be conjugatively stabilized more than **2c**. The fact that E_a is larger for **1a** than for **2a** and for neophyl can be interpreted by considering that the cyclic radicals **1c** and **2c** are not transition-state structures but real intermediates that, as mentioned above, in a couple of cases have been observed experimentally.[15,16] Presumably, with radicals where the rotation of the aliphatic chain is not subject to a large energy barrier, as in **2a** or in the neophyl radical, both geometry and enthalpic content of the transition state and of the intermediate are quite similar, while in the rearrangement of **1a** the transition state is reached during the rotation of the bond connecting the naphthalene ring to the CMe_2CH_2 group while trying to adopt the conformation where the radical can cyclize. This higher than usual rotational barrier might be responsible for the observed high activation energy as suggested also by semiempirical calculations indicating that the rotation of the aliphatic substituent in 1-*tert*-butylnaphthalene is characterized by an energy barrier from three to six times higher than in the analogous 2-substituted hydrocarbon.

Conclusion

A convenient synthesis of the bromide precursors of the two radical clocks 2-methyl-2-(1-naphthyl)-1-propyl (**1a**) and 2-methyl-2-(2-naphthyl)-1-propyl (**2a**) and the calibration of their rearrangement reactions to the corresponding 2-methyl-1-(1-naphthyl)-2-propyl and 2-methyl-1-(2-naphthyl)-2-propyl radical, in the range of temperatures 293−358 K, has been described. Since **1a** and **2a** rearrange at room temperature with rate constants of 6.4×10^3 and 1.4×10^4 M^{-1} s^{-1}, respectively, they can be of valuable use in the determination of rate constants for hydrogen abstraction by primary alkyl radicals from substrates whose reactivity is intermediate between those measurable with the neophyl and the 1-hexenyl radical clocks.

Experimental Section

General Procedures. Melting points were determined on an Electrothermal capillary apparatus and are uncorrected. ^1H (200 MHz) and ^{13}C NMR spectra were recorded in $CDCl_3$ using tetramethylsilane as an internal standard. Mass spectra and high-resolution mass spectra (HRMS) were performed by electron impact with a beam energy of 70 eV. IR spectra were recorded in $CHCl_3$. Column chromatography was carried out on silica gel (ICN Silica, 63−200, 60 Å) using light petroleum (40−70 °C) as eluant.

Starting Materials. 2-Methyl-2-(1-naphthyl)-1-propanol[19] and methyl 2-naphthyl acetate[20] were prepared according to the literature.

2-Methyl-2-(1-naphthyl)-1-propyl *p*-Toluensulfonate. According to the procedure of Hixson and Tausta,[8] the title tosylate

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(17) We thank a reviewer for suggesting this correlation.

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was obtained in 91% yield: mp = 75−7 °C (from methanol); ^{1}H NMR δ 1.50 (6H, s), 2.35 (3H, s), 4.45 (2H, s), 7.07 (2H, bd, J = 8.1 Hz, A part of AA′BB′), 7.26−7.45 (4H, m), 7.49 (2H, bd, J = 8.1 Hz, B part of AA′BB′), 7.73 (1H, bd, J = 8.0 Hz), 7.84 (1H, dd, J_1 = 8.2 Hz, J_2 = 1.5 Hz), 7.95 (1H, bd, J = 8.8 Hz); MS *m/z* (rel inten) 354 (M^+, 13), 182 (15), 169 (100), 141 (20), 91 (10); HRMS calcd for $C_{21}H_{22}O_3S$ 354.1290, found 354.1286. Anal. Calcd for $C_{21}H_{22}O_3S$: C, 71.16; H, 6.26; S, 9.04. Found: C, 71.20; H, 6.23; S, 9.07.

2-Methyl-2-(1-naphthyl)-1-bromopropane. The tosylate prepared above (8 g, 22.6 mmol), lithium bromide (1.9 g, 22.0 mmol), anhydrous hexamethylphosphorictriamide (20 mL), and water (25 drops) were heated at 90 °C under stirring for 5 h. After cooling, the reaction mixture was poured into water and extracted three times with 50 mL portions of diethyl ether. The combined organic layers were dried ($MgSO_4$) and concentrated under vacuum to give an oily residue that was chromatographed on silica gel. Elution with light petroleum furnished an oil that was distilled under vacuum to give 5.10 g (85%) of the title compound: bp = 114−5 °C (0.019 mbar); ^{1}H NMR δ 1.85 (6H, s), 4.15 (2H, s), 7.48−7.70 (4H, m), 7.85 (1H, bd, J = 8.3 Hz), 7.86−8.06 (1H, m), 8.43 (1H, m); ^{13}C NMR (50 MHz) δ 29.4, 41.2, 46.2, 125.5, 125.8, 125.9, 126.1, 129.1, 130.6, 131.9, 135.7, 141.5; MS *m/z* (rel inten) 264 (M^+ + 2, 15), 262 (M^+, 15), 183 (5), 169 (100), 141 (25), 127 (8); HRMS calcd for $C_{14}H_{15}Br$ 263.0357, found 263.0354. Anal. Calcd for $C_{14}H_{15}Br$: C, 63.89; H, 5.74; Br, 30.36. Found: C, 63.87; H, 5.77; Br, 30.31.

Methyl 2-methyl-2-(2-naphthyl)-propanoate. A 10.4 g portion of a 60% NaH (260 mmol) dispersion in mineral oil was added to 200 mL of anhydrous dimethylformamide. The mixture was kept under N_2, stirred, and cooled at ca. 10 °C, and 37.0 g (260 mmol) of MeI and subsequently 13.0 g (65 mmol) of methyl 2-naphthyl acetate[20] were added dropwise. The mixture was warmed at room temperature, stirred for 10 h, and then poured into ice-cooled diluted HCl and extracted three times with 80 mL portions of diethyl ether. The combined organic phases were dried ($MgSO_4$), and the solvent was removed under reduced pressure. The oily residue was distilled under vacuum to give 12.1 g (80%) of the desired ester: bp = 100−2 °C (0.04 mbar); ^{1}H NMR δ 1.7 (6H, s), 6.68 (3H, s), 7.44−7.56 (3H, m), 7.78−7.90 (4H, m); ν_{max} 1730 cm^{-1}; MS *m/z* (rel inten) 228 (M^+, 33), 169 (100), 153 (9), 152 (9), 141 (40); HRMS calcd for $C_{15}H_{16}O_2$ 228.1150, found 228.1153. Anal. Calcd for $C_{15}H_{16}O_2$: C, 78.92; H, 7.06. Found: C, 78.97; H, 7.08.

2-Methyl-2-(2-naphthyl)-1-propanol. A solution of methyl 2-methyl-2-(2-naphthyl)propanoate (11.85 g, 51.9 mmol) in anhydrous diethyl ether (20 mL) was added dropwise to a suspension of $LiAlH_4$ (1.98 g, 51.9 mmol) in anhydrous diethyl ether (100 mL) with stirring at room temperature under N_2 atmosphere. After the reaction was complete (ca. 2 h), the mixture was hydrolyzed with ethyl acetate and subsequently with dilute HCl. The organic layer was separated and dried ($MgSO_4$), and the solvent was removed under vacuum to give the title propanol as an oil that solidified upon standing: 9.9 g (95%); mp = 56−8 °C (from light petroleum); ^{1}H NMR δ 1.40 (6H, s), 1.70 (1H, bs), 3.63 (2H, s), 7.48−7.61 (3H, m), 7.81−7.93 (4H, m); ν_{max} 3600 cm^{-1}; MS *m/z* (rel inten) 200 (M^+, 20), 169 (100), 153 (8), 152 (8), 141 (25); HRMS calcd for $C_{14}H_{16}O$ 200.1201, found 200.1205. Anal. Calcd for $C_{14}H_{16}O$: C, 83.96; H, 8.05. Found: C, 83.94; H, 8.02.

2-Methyl-2-(2-naphthyl)-1-propyl *p*-Toluenesulfonate. Following the procedure of Hixson and Tausta,[8] from the corresponding propanol (9.48 g, 47.4 mmol) we obtained the title tosylate: 10.6 g (65%); mp = 102−4 °C (from methanol); ^{1}H NMR δ 1.39 (6H, s), 2.31 (3H, s), 4.07 (2H, s), 7.10 (2H, bd, J = 8.1 Hz, A part of AA′BB′3, 7.32−7.84 (9H, m, B part of AA′BB′ and ArH); MS *m/z* (rel inten) 354 (M^+, 100), 182 (8), 169 (44), 141 (8), 91 (5); HRMS calcd for $C_{21}H_{22}O_3S$ 354.1290, found 354.1293. Anal. Calcd for $C_{21}H_{22}O_3S$: C, 71.16; H, 6.26; S, 9.04. Found: C, 71.14; H, 6.29; S, 9.07.

2-Methyl-2-(2-naphthyl)-1-bromopropane. With the same procedure described above for the 1-naphthyl isomer, starting from the corresponding tosylate (8 g, 22.5 mmol) we obtained the title bromide: 4.1 g (70%); bp = 116−8 °C (0.019 mbar); ^{1}H NMR δ 1.61 (6H, s), 3.70 (2H, s), 7.47−7.59 (3H, m), 7.80−7.92 (4H, m); ^{13}C NMR (50 MHz) δ 27.9, 40.0, 47.2, 124.8, 125.1, 126.4, 126.7, 128.0, 128.6, 128.7, 132.7, 133.9, 143.9; MS *m/z* (rel inten) 264 (M^+ + 2, 15), 262 (M^+, 16), 183 (10), 169 (100), 141 (27), 127 (7); HRMS calcd for $C_{14}H_{15}Br$ 263.0357, found 263.0360. Anal. Calcd for $C_{14}H_{15}Br$: C, 63.89; H, 5.74; Br, 30.36. Found: C, 63.87; H, 5.71; Br, 30.37.

Kinetic Measurements. Competitive kinetic measurements were performed in samples consisting of 300 μL of benzene solutions containing the reactants and the radical initiator. Deoxygenated samples were sealed under nitrogen atmosphere in a quartz tube and irradiated for 30−90 min in a thermostated (±0.2 °C) photoreactor equipped with a 125 W high-pressure mercury lamp. The crude reaction mixture was analyzed by gas chromatography for quantitative measurements and by GC−MS for preliminary experiments and for the identification of reaction products.

Calibration of the Radical Clocks. Measurements were performed in the temperature range 293−358 K on samples containing the radical clock precursor (typically (3−5) × 10^{-2} M), 2,4,6-trimethylphenol (0.15−0.8 M), and bis(tributyltin) (typically (2−3) × 10^{-2} M). Concentrations of the reactants were chosen so as to avoid significative consumption of the phenol during the experiment. At each temperature, five to eight experiments were performed with different phenol concentrations, and the product ratio [UH]/[RH] was plotted against the initial phenol concentration to obtain the rate constant ratio k_H/k_r.

Determination of k_H for Triphenylsilane. Six measurements were performed at 298 K on samples containing the radical clock precursor (typically (4−5) × 10^{-2} M), di-*tert*-butylperoxide (5 × 10^{-2} M), and different concentrations of triphenylsilane in the range 0.3−1.0 M.

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Supporting Information Available: Tables of kinetic data and a detailed Experimental Section describing the kinetic measurements and the data treatment. This material is available free of charge via the Internet at http://pubs.acs.org.

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