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Arrhenius Parameters for Rearrangements of the Neophyl, 1-Indanylmethyl, 2-Allylbenzyl, and 2-(2-Vinylphenyl)ethyl Radicals Relative to Hydrogen Abstraction from Tributylstannane[1]

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Abstract: The temperature dependence of rates of several radical rearrangements relative to abstraction of hydrogen atom from tributylstannane has been determined. The rearrangement of 2-phenyl-2-methylpropyl to 1-phenyl-2-methylprop-2-yl (neophyl rearrangement) relative to hydrogen abstraction is represented by $\log (r/\mathrm{M}) = (2.48 \pm 0.08) - (8.13 \pm 0.16)/\theta$, $\theta = 2.3RT$ kcal/mol. The rearrangement of 2-allylbenzyl to 2-indanylmethyl exhibited $\log (r/\mathrm{M}) = (2.32 \pm 0.16) - (10.47 \pm 0.36/\theta$, and the rearrangement of 2-allylbenzyl to 2-tetralyl is represented by $\log (r/\mathrm{M}) = (2.18 \pm 0.28) - (12.47 \pm 0.60)/\theta$. The rearrangement of 1-indanylmethyl to 2-tetralyl is represented by $\log (r/\mathrm{M}) = (2.65 \pm 0.12) - (11.21 \pm 0.24)/\theta$. Closure of 2-(2-vinylphenyl)ethyl to the five-member ring occurs with a 7.3 ± 0.6 kcal/mol barrier and was preferred over closure to the six-member ring by 2.1 ± 1 kcal/mol. From known or estimated rates of abstraction of hydrogen from tributylstannane, rates of rearrangement of the radicals are estimated.

The recent availability of absolute rates of reaction of primary, secondary, and tertiary alkyl radicals with tributylstannane[2] has made possible the determination of absolute rates of radical rearrangements by competition of the rearrangement with hydrogen abstraction from tributylstannane ($\mathrm{Bu_3SnH}$). Our interest in the thermochemistry of radical-mediated ring opening and isomerization reactions of hydroaromatic radicals[3] related to coal dissolution[4] prompted the present investigation, whose purpose was to determine forward (exothermic) cyclization and aryl migration rates, which, when combined with radical thermochemical data, provide estimates of the corresponding reverse (endothermic) radical reactions. Thus, we present relative Arrhenius parameters for the 1,2-aryl migration of 1-indanylmethyl to 2-tetralyl, refined values for the neophyl rearrangement, and relative Arrhenius parameters for the five- and six-member ring cyclization of 2-allylbenzyl as well as the five- and six-member ring cyclization reactions of 2-(2-vinylphenyl)ethyl in competition with hydrogen abstraction from $\mathrm{Bu_3SnH}$.

Experimental Section

General. NMR spectra were determined with a Varian FT-80 spectrometer. Gas chromatography (GC) was carried out on a Hewlett-Packard Model 5880A instrument equipped with flame ionization detection and 30-m J&W Scientific SE-52 or DB-5 capillary columns, and GC-mass spectrometry was carried out on a Hewlett-Packard Model 5985 system. Oxygen- or water-sensitive manipulations were carried out in a Vacuum Atmospheres Dri-lab system. Elemental analyses were determined by Schwarzkopf Microanalytical Laboratory, Woodside, NY.

Reagents. Tributylstannane ($\mathrm{Bu_3SnH}$) and $\mathrm{Bu_3SnD}$ were obtained from Alfa Products, stored, and used under inert atmosphere. A quantitative assay of $\mathrm{Bu_3SnH}$ at the end of this study by complete consumption in excess neophyl chloride revealed 99.7 ± 1% purity. 1-Methylindan and 2-methylindan were available from previous studies.[3]

Neophyl chloride (1) was prepared according to Rüchardt.[5a]

2-Ethylstyrene was prepared by treatment of 2-ethylbenzonitrile with methylmagnesium bromide to form 2-ethylacetophenone, which was reduced with $\mathrm{LiAlH_4}$ to the alcohol and dehydrated by distillation of the alcohol from $\mathrm{KHSO_4}$ at 80 °C and ~10 torr pressure.[5b]

2-Allyltoluene was prepared by treatment of the Grignard of 2-bromotoluene with allyl bromide:[5c] $^{13}\mathrm{C}$ NMR ($\mathrm{CDCl_3}$) (with off-resonance decoupled multiplicities) δ 138.06 (s, C-1 or C-2), 136.65 (d, $\mathrm{CH_2}\mathit{C}\mathrm{H{=}CH_2}$), 136.27 (s, C-1 or C-2), 130.16, 129.18 (d, C-3 and C-6), 126.34, 126.07 (d, C-4 and C-5), 115.56 (t, $\mathrm{CH_2CH{=}}\mathit{C}\mathrm{H_2}$), 37.73 (t, $\mathit{C}\mathrm{H_2CH{=}CH_2}$), 19.25; $^1\mathrm{H}$ NMR ($\mathrm{CDCl_3}$) δ 7.13 (s, 4 H, Ar H), 6.25–5.65 (m, 1 H, $\mathrm{CH_2\,C}\mathit{H}\mathrm{{=}CH_2}$), 5.15–4.75 (two overlapping doublets of quartets, 2 H, $\mathrm{CH_2CH{=}C}\mathit{H}_2$), 3.36 (d of t, 2 H, $\mathrm{C}\mathit{H}_2\mathrm{CH{=}CH_2}$, J = 6.3, 1.5 Hz), 2.28 (5, 3 H, Ar $\mathrm{CH_3}$).

[2-(2-Ethylphenyl)ethyl]tributylstannane was prepared by heating a degassed mixture of 2-ethylstyrene (0.44 mmol) and tributylstannane (0.6 mmol) and 10 μL of di-*tert*-butyl peroxide at 130 °C for 40 min, similar to a standard procedure.[5d] Preparative GC isolation gave 30 mg of product: $^1\mathrm{H}$ NMR ($\mathrm{CDCl_3}$) δ 7.13 (s, 4 H, Ar H), 2.79 (overlapping m, 2 H, Ar $\mathrm{C}\mathit{H}_2\mathrm{CH_2Sn}$), 2.65 (q, J = 7.5, 2 H, Ar $\mathrm{C}\mathit{H}_2\mathrm{CH_3}$), 1.8–0.75 (m, 32 H, $\mathrm{C}\mathit{H}_2\mathrm{SnC}\mathit{H}_2\mathrm{C_3H_7}$ and Ar $\mathrm{CH_2C}\mathit{H}_3$). The EI mass spectrum gave no $\mathrm{M}^{+\cdot}$ but gave characteristic Sn clusters at M − 57 (loss of *n*-butyl), M − 133 (loss of 2-(2-ethylphenyl)ethyl), M − 144 (loss of two butyls), M − 190 (loss of butyl and 2-(2-ethylphenyl)ethyl). The CI mass spectrum gave M − 1 for $^{120}\mathrm{Sn}$ at m/e 423 (0.9%) and M − 1 for $^{118}\mathrm{Sn}$ at 421 (0.7%).

1-(Chloromethyl)indan (2). A mixture of 1-indenecarboxylic and 3-indenecarboxylic acids, prepared from indenyllithium and $\mathrm{CO_2}$, was hydrogenated in acetic acid/tetrahydrofuran (90 psi $\mathrm{H_2}$, 25 °C, 10% Pd/C, 1.5 h) to give 1-indancarboxylic acid: $^1\mathrm{H}$ NMR ($\mathrm{CDCl_3}$) δ 10.4 (br s, 1 H, COOH), 7.5–7.1 (m, Ar H, 4 H), 3.97 (J = 7.5 Hz, t, Ar $\mathrm{C}\mathit{H}\mathrm{(CO_2H)}$, 1 H), 3.2–2.8 (m, 2 H, Ar $\mathrm{CH_2}$), 2.6–2.45 (m, Ar $\mathrm{CH_2C}\mathit{H}_2$, 2 H). Reduction with $\mathrm{LiAlH_4}$ gave 1-(hydroxymethyl)indan: $^1\mathrm{H}$ NMR ($\mathrm{CDCl_3}$) δ 7.25 (m, Ar H, 4 H), 3.8 (d, $\mathrm{CH_2O}$, 2 H), 3.5 (m, $\mathrm{C}\mathit{H}\mathrm{CH_2OH}$), 2.9 (t, Ar $\mathrm{CH_2}$, 2 H), 2.6–1.8 (m, Ar $\mathrm{CH_2C}\mathit{H}_2$, 2 H), 1.7 (s, 1 H, OH). The alcohol, 1.5 g (10 mmol), was treated with 5.3 g (20 mmol) of triphenylphosphine and 1.5 g of $\mathrm{Cl_2}$ in dimethylformamide at −10 °C. After extraction with water, a pentane solution of the reaction mixture was dried ($\mathrm{Na_2SO_4}$) and filtered through neutral alumina to give 1.2 g (7 mmol, 72%) of 1-(chloromethyl)indan. Anal. Calcd for $\mathrm{C_{10}H_{11}Cl}$: C, 72.03; H, 6.66; Cl, 21.31. Found: C, 71.90, 72.19; H, 6.74, 6.75; Cl, 21.48. $^1\mathrm{H}$ NMR ($\mathrm{CDCl_3}$) δ 7.4–7.1 (Ar H, m, 4 H), 3.95–3.45 (m, Ar $\mathrm{C}\mathit{H}\mathrm{C}\mathit{H}_2\mathrm{Cl}$, 3 H), 3.1 (crude t, Ar $\mathrm{CH_2}$, 2 H), 2.7–1.75 (m, Ar $\mathrm{CH_2C}\mathit{H}_2$, 2H); $^{13}\mathrm{C}$ NMR ($\mathrm{CDCl_3}$) 144.39, 143.39 (quaternary aromatic carbons), 127.39, 126.35, 124.81, 124.08 (protonated aromatic carbons), 48.25 ($\mathrm{CH_2Cl}$, triplet from off-resonance decoupled spectrum), 47.59 (Ar $\mathit{C}\mathrm{HCH_2Cl}$, doublet from off-resonance decoupled spectrum), 30.98, 30.16 (Ar $\mathit{C}\mathrm{H_2}\mathit{C}\mathrm{H_2}$).

2-Allylbenzyl Chloride (3). 2-Bromobenzyl alcohol was converted to the tetrahydropyranyl (THP) ether:[6] $^1\mathrm{H}$ NMR ($\mathrm{CDCl_3}$) δ 7.65–7.0 (m, 4 H, Ar H), 4.8 (br s, 1 H, OCHO), 4.86 (Ar CH, 1 H, d, J = 13.9 Hz),

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4.56 (Ar CH, 1 H, d, J = 13.9 Hz), 4.2–3.3 (m, 2 H, pyran OCH_2), 2.15–1.25 (m, 6 H, $CH_2CH_2CH_2CH_2O$). A Grignard reagent from the protected alcohol in THF was treated with allyl bromide to give THP-protected 2-allylbenzyl alcohol: ^1H NMR ($CDCl_3$) δ 7.55–7.1 (m, 4 H, Ar H), 6.4–5.8 (m, 1 H, $CH_2CH{=}CH_2$), 5.2–4.85 (m, cis and trans $=CH_2$), 4.83 (d, J_{gem} = 12 Hz, 1 H, Ar CHO), 4.69 (br s, 1 H, OCHO), 4.49 (d, J_{gem} = 12 Hz, 1 H, Ar CHO), 4.15–3.3 (m, 2 H, pyran OCH_2), 3.44 (d of t, J = 6.3, 1.5 Hz, 2 H, allyl CH_2), 2.0–1.4 (m, 6 H, pyran $OCH_2CH_2CH_2CH_2$). Note the diastereotopic, geminally coupled methylene protons (Ar CH_2OTHP). Deprotection[6] and distillation gave 2-allylbenzyl alcohol: ^1H NMR ($CDCl_3$) δ 7.6–7.1 (m, 4 H, Ar H), 6.02 (d of d of t, 1 H, J = 10.5, 16.6, 6.1 Hz, $CH_2CH{=}CH_2$), 5.05 (m, 1 H, $=CH_2$ (cis H)), 5.0 (m, 1 H, $=CH_2$ (trans)), 4.70 (Ar CH_2OH, s, 2 H), 3.47 (d of t, 2 H, Ar $CH_2CH{=}CH_2$), 1.6 (s, 1 H, OH). A sample of 11 g (74 mmol) of alcohol in CH_2Cl_2 was treated with 20 g of $SOCl_2$, extracted (aqueous $NaHCO_3$), dried (Na_2SO_4), concentrated, dissolved in pentane (cloudiness), and filtered through neutral alumina to give 2-allylbenzyl chloride, white liquid, 8.5 g (0.051 mol, 69%): ^1H NMR ($CDCl_3$) δ 7.6–7.1 (m, 4 H, Ar H), 6.0 (d of d of t, 1 H, J = 10.5, 16.4, 6.1 Hz, $CH_2CH{=}CH_2$), 5.09 (m, J = 1.5, 10.5, 1.8 Hz, 1 H, cis $=CH_2$), 5.03 (m, J = 1.5, 16.4, 1.8 Hz, 1 H, trans $=CH_2$), 4.61 (s, 2 H, CH_2Cl), 3.52 (d of m, J = 1.5, 6.1 Hz, 2 H, $CH_2CH{=}CH_2$). Anal. Calcd for $C_{10}H_{11}Cl$: C, 72.03; H, 6.66. Found: C, 72.06; H, 6.63.

1-Chloro-2-(2-vinylphenyl)ethane (4). 2-Bromobenzaldehyde (10 g, 0.054 mol) was refluxed with ethylene glycol, toluene, and *p*-toluenesulfonic acid followed by vacuum distillation to give the ketal (9.9 g, 80%): ^1H NMR ($CDCl_3$) δ 7.7–7.1 (m, 4 H, Ar H), 6.10 (s, 1 H, OCHO (ketal H)), 4.18–4.06 (m, 4 H, OCH_2CH_2O). The ketal, 30 g (130 mmol), was treated with 1.1 equiv of *n*-butyllithium in ethyl ether followed by 13 mL (11.4 g) ethylene oxide introduced from a calibrated cold trap in a stream of dry nitrogen. To this mixture was added excess acetic anhydride. The reaction mixture was stirred overnight and diluted with ethyl ether, extracted, dried (Na_2SO_4), and chromatographed on 250 g of neutral alumina (pentane–ether) to yield the pure ethylene glycol ketal of 2-(2-formylphenyl)ethyl acetate (8.5 g, 36 mmol, 28%): ^1H NMR ($CDCl_3$) δ 7.7–7.4 (m, 4 H, Ar H), 5.98 (s, 1 H, OCHO (ketal H)), 4.30 (t, J = 7.3 Hz, 2 H, Ar CH_2CH_2O), 4.3–4.0 (m, 4 H, OCH_2CH_2O (ketal ethylene)), 3.06 (t, J = 7.3 Hz, 2 H, Ar CH_2CH_2O), 2.02 (s, 3 H, O_2CCH_3). Anal. Calcd for $C_{13}H_{16}O_4$: C, 66.01; H, 6.83. Found: C, 65.88; H, 6.97. IR (thin film) 1743 cm^{-1} (ester C=O). The material was deketalized with 10% aqueous HCl. The aldehyde (6.2 g, 30 mmol) in ethyl ether was added to a Wittig reaction mixture formed from $(C_6H_5)_3PCH_3Br$ (60 mmol) and 61 mmol of *n*-butyllithium. NMR and IR spectra showed the desired styrene olefin, the absence of aldehyde, and about 75% cleavage of the acetyl group. The remaining ester was cleaved with $LiAlH_4$ to give 1.4 g (10 mmol) of 2-(2-vinylphenyl)ethanol of about 90% purity (GC), which was converted to **4** by reaction with tri-*n*-butylphosphine in CCl_4.[7] The mixture was chromatographed on neutral alumina (pentane) to yield a total of 0.7 g (4 mmol, 45%) of **4** (ca. 95% purity): ^1H NMR ($CDCl_3$) δ 7.65–7.2 (m, 4 H, Ar H), 6.99 (d of d, J_{cis} = 10.8, J_{trans} = 17.3 Hz, 1 H, Ar $CH{=}CH_2$), 5.60 (d of d, J_{trans} = 17.3, J_{gem} = 1.5 Hz, 1 H, Ar $CH{=}CH_2$ (trans H)), 5.34 (d of d, J_{cis} = 10.8, J_{gem} = 1.5 Hz, Ar $CH{=}CH_2$ (cis H)), 3.65 (center line of multiplet, 2 H, Ar CH_2CH_2Cl), 3.13 (center line of multiplet, 2 H, Ar CH_2CH_2Cl).

Kinetic Experiments. Samples of halides **1**–**4**, initiator (azo-1,1-dimethylethane or di-*tert*-butyl peroxide), internal standard (*n*-butyl or *tert*-butylbenzene), and Bu_3SnH were mixed in phenyl ether or benzene under argon and sealed in Pyrex tubes under vacuum after three freeze–thaw cycles. The samples were heated in a Braun Thermomix 1480 oil bath or in a Tecam SBS-4 fluidized sand bath. Concentrations of hydrocarbon products were determined by GC. The values of ln r ($r = k_{re}/k_{abs}$) were determined from the expression described by Rüchardt[5a] (eq 1) where E is the concentration of unrearranged hydrocarbon (RH in eq 3) and D is the sum of concentrations of rearranged products (R′H and R″H in eq 4 and 5).

$$E + D = (B_0 + r)(1 - e^{-D/r}) \tag{1}$$

$$RCl + Bu_3Sn\cdot \rightarrow R\cdot + Bu_3SnCl \tag{2}$$

$$R\cdot + Bu_3SnH \xrightarrow{k_{abs}} RH + Bu_3Sn\cdot \tag{3}$$

$$R\cdot \xrightarrow{k_{re}} R'\cdot \xrightarrow{Bu_3SnH} R'H \tag{4}$$

$$R\cdot \xrightarrow{k'_{re}} R''\cdot \xrightarrow{Bu_3SnH} R''H \tag{5}$$

The value of r that causes the right side of eq 1 to agree with experimental values of $E + D$ was determined with a programmable desk calculator. The method assumes that the concentration of Bu_3SnH at time t, $B(t)$, follows the relationship $B(t) = B_0 - E(t) - D(t)$ and that formation of unrearranged hydrocarbon occurs only by abstraction from Bu_3SnH (eq 3). Radical consumption through termination and side reactions must be negligible, and the method requires irreversibility in eq 4 and 5. These conditions held in all of the experiments. Average yields of hydrocarbon based on halide or hydride in benzene or phenyl ether were >95% in all cases. For example, **1** gave a 97.6 ± 3.8% average hydride yield and a 100.4 ± 1.4% halide yield.

Table I. Arrhenius Expressions for Radical Rearrangements[a]

rearrangement	relative rate expression, log r (M)[b,c]	absolute rate expression, log k_{re} (s^{-1})
1-indanylmethyl → 2-tetralyl	$(2.65 \pm 0.12) - (11.21 \pm 0.42)/\theta$	$(11.72 \pm 0.36) - (14.90 \pm 0.74)/\theta$[e]
2-methyl-2-phenylpropyl (neophyl) → 2-methyl-1-phenylprop-2-yl	$(2.48 \pm 0.08) - (8.13 \pm 0.16)/\theta$	$(11.55 \pm 0.32) - (11.82 \pm 0.48)/\theta$[e]
2-allylbenzyl → 2-indanylmethyl	$(2.32 \pm 0.16) - (10.47 \pm 0.36)/\theta$	*d*
2-allylbenzyl → 2-tetralyl	$(2.18 \pm 0.28) - (12.47 \pm 0.60)/\theta$	*d*
2-(2-vinylphenyl)ethyl → 1-indanylmethyl	$(1.51 \pm 0.14) - (3.60 \pm 0.28)/\theta$	$(10.58 \pm 0.38) - (7.29 \pm 0.60)/\theta$[e]
2-(2-vinylphenyl)ethyl → 1-tetralyl	$(2.18 \pm 0.32) - (5.67 \pm 0.68)/\theta$	$(11.25 \pm 0.6) - (9.36 \pm 1.0)/\theta$[e]

[a] $\theta = 2.303RT$ kcal/mol. [b] $r = k_{re}/k_{abs}$, the ratio of rearrangement (k_{re}) to hydrogen abstraction (k_{abs}) from Bu_3SnH. [c] Uncertainties are 95% confidence (2σ). [d] Not available, see text. [e] Calculated by combining the relative rate expression (log r) with expression log k_{abs} = $(9.07 \pm 0.24) - (3.69 \pm 0.32)/\theta$; see ref 2.

Decomposition of 1 in Bu_3SnD. Reduction of **1** at 192.5 °C in phenyl ether by Bu_3SnD gave ln r = −2.58. By comparison with the reaction of **1** in Bu_3SnH (ln r = −3.08), a kinetic isotope effect of k_H/k_D = 1.64 for abstraction of hydrogen by neophyl from $Bu_3SnH(D)$ is obtained. For *tert*-butylbenzene produced from the reaction of **1** and Bu_3SnD, GCMS (15 eV) analysis gave m/e (relative intensity) 134 (0.5), 135 (100), 136 (12.0), and 137 (0.6). For isobutylbenzene produced from Bu_3SnD, GCMS gave m/e (relative intensity) 134 (0.3), 135 (100), 136 (12.4), and 137 (0.6). Unlabeled *tert*-butylbenzene gave 133 (0), 134 (100), 135 (10.2), and 136 (0.3), and unlabeled isobutylbenzene gave 133 (0), 134 (100), 135 (10.1), and 136 (0.5).

Decomposition of 3 in Bu_3SnD. Reaction of **3** at 236 °C with Bu_3SnD in phenyl ether gave ln r_1 = −4.36. From the Arrhenius expression for reaction of **3** with Bu_3SnH, Table I, ln r_1 = −5.01 and k_H/k_D = 1.91 for the kinetic isotope effect in the abstraction of hydrogen by 2-allylbenzyl from $Bu_3SnH(D)$. GCMS analysis (15 eV) of 2-allyltoluene from the Bu_3SnD reaction of **3** gave m/e (relative intensity) 131 (2.2), 132 (21.3), 133 (100), 134 (10.5), and 135 (0.3). Unlabeled 2-allyltoluene gave 131 (22.5), 132 (100), 133 (10.3), and 134 (0.5). GCMS analysis of 2-methylindan from the reaction of **3** and Bu_3SnD gave 131 (3), 132 (35.7), 133 (100), 134 (9.7), and 135 (0.3) compared to unlabeled 2-methylindan, which gave 130 (2.2), 131 (31.4), 132 (100), 133 (10.4), and 134 (0.5). The tetralin product gave similar results.

Results and Discussion

Relative Arrhenius expressions for the temperature dependence of the radical rearrangements in competition with hydrogen abstraction ($r = k_{re}/k_{abs}$) from Bu_3SnH are presented in Table I for 1-indanylmethyl, 2-methyl-2-phenylpropyl, 2-allylbenzyl, and 2-(2-vinylphenyl)ethyl. Kinetic data for the least-squares analyses of log r vs. $1/RT$ providing $E_{abs} - E_{re}$ and A_{re}/A_{abs} are provided in the supplementary material.

The reactions of **1** and **3** in Bu_3SnD demonstrated, from the absence of nondeuterated hydrocarbon products, that Bu_3SnD is the species with which the intermediate radicals exclusively react. Greater than 99% d_1 content in the products was observed, consistent with the course of reaction depicted in eq 2–4.

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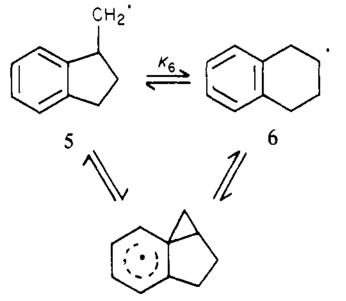
[7] Hooz, J.; Gilam, S. H. *Can. J. Chem.* **1968**, *40*, 86. This procedure gave very poor results in attempts to apply it to produce **2** and **4**. Triphenylphosphine is the preferred reagent.

Neophyl and 1-Indanylmethyl Rearrangements. Chatgilialoglu, Ingold, and Scaiano[2] suggested the use of the Arrhenius expression $\log (k_{abs}/M^{-1}\,s^{-1}) = (9.07 \pm 0.24) - (3.69 \pm 0.32)/\theta$, $\theta = 2.3\,RT$, to represent the absolute rate of hydrogen abstraction by primary radicals from Bu_3SnH. Thus, combining the relative rate expression determined here (Table I) for the primary 1-indanylmethyl radical with the absolute rate expression for hydrogen abstraction extrapolated to the temperature of this work provides the Arrhenius expression for rearrangement, $\log (k_6/s^{-1}) = (11.72 \pm 0.36) - (14.90 \pm 0.74)/\theta$, where the errors are the composite of the absolute and relative rates at the 95% confidence level. From this result, the Arrhenius parameters for the reverse reaction can be estimated. From the estimated[8,9] heats of formation of **5** and **6**, $\Delta H°_{443}$ (**5** → **6**) = -6.5 kcal/mol. From $E_6 = 14.9$ kcal/mol (this work), $E_{-6} = E_6 - \Delta H°_{433}$ (**5** → **6**) = 21.4 kcal/mol.[8] Similarly, from $\Delta S_6{}^{\ddagger}{}_{433} = -7.9$ eu (this work) combined with $\Delta S°_{443}$ (**5** → **6**) from thermochemical estimates,[8b] we find $\Delta S_{-6}{}^{\ddagger} = \Delta S_6{}^{\ddagger} - \Delta S° = -6.3$ eu. From appropriate thermodynamic relationships[8c] we estimate that the reverse neophyl-like rearrangement **6** → **5** will follow the Arrhenius relationship $\log (k_6/s^{-1}) = (12 \pm 1.5) - (21.4 \pm 2.5)/\theta$. The entropy loss ($\Delta S_{-6}{}^{\ddagger} = -6.3$ eu) predicted for the rearrangement **6** → **5** is similar to the ring tightening undergone by cyclohexane on conversion to bicyclo[3.1.0]hexane (**8**) (eq 7) ($\Delta S° \cong -5.8$ eu)[8a]



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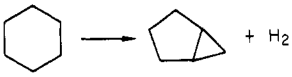
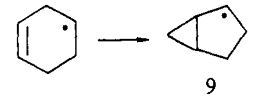


8 (7)

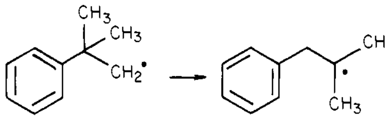
or the internal cyclization of 4-cyclohexenyl to give bicyclo[3.1.0]hexyl-2 (**9**) ($\Delta S° \cong -6.4$ eu) (eq 8).[8a] Both examples



9 (8)

suggest that significant entropy loss is to be expected from ring tightening in the reverse neophyl-like rearrangement of the 2-tetralyl system, and that the estimate of $\Delta S_{-6}{}^{\ddagger}$ is of the right order of magnitude.

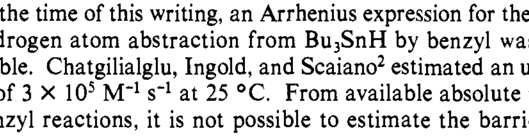
For the neophyl rearrangement (eq 9), Maillard and Ingold[10] determined the Arrhenius expression $\log (k_9/s^{-1}) = (11.7 \pm 1) - (13.6 \pm 1.0)/\theta$ from rotating-sector EPR experiments over the range 283–307 K. The neophyl-like rearrangements are the slowest isomerizations that can be conveniently studied by this method.[10] The absolute rate expression for the neophyl rearrangement obtained by combining the relative rate expression of this work (Table I) with the absolute rate expression of abstraction by primary radicals from Bu_3SnH[2] predicts a rate constant of $k_9 = 764$ s^{-1} at 298 K compared to 59 s^{-1} by the EPR method. The data of this work were gathered over a fourfold greater temperature range and the overall precision is better than that of the EPR technique. It is assumed that the neophyl radical abstracts at the same rate as *n*-butyl or ethyl, i.e., that there is no steric hindrance that slows the abstraction rate and that the absolute abstraction rate data[2] can be extrapolated from a mean temperature of 300 K to the temperature range of this work. Hamilton and Fischer[11] reported an earlier EPR value of $E_a = 10 \pm 2$ kcal/mol for this rearrangement, compared with 13.6 (Ingold)[10] and 11.82 (this work) kcal/mol.



10 11 (9)

The higher barrier for the rearrangement of 1-indanylmethyl ($E_a = 14.9$ kcal/mol) compared to the neophyl rearrangement reflects the greater difficulty in achieving the transition state or intermediate **7**, due to the unfavorable angle between the localized p orbital of the aryl group and the C–CH$_2$· bond of the methylcyclopentane portion of the molecule.[12]

Cyclization of 2-Allylbenzyl and 2-(2-Vinylphenyl)ethyl. Stereoelectronic control of the intramolecular cyclization of the 5-hexenyl radical and related cyclizations has been the subject of much interest.[13] Our interest stemmed from a desire to determine the rate of ring opening of 2-tetralyl (**6** to **12**), relative to the reverse neophyl-like rearrangement (**6** to **5**) (eq 10). In addition, the cyclization of 2-allylbenzyl provides an excellent benzyl radical "clock"[10] for the determination of rate constants for benzyl reactions, providing Arrhenius parameters for the absolute rates of cyclization of 2-allylbenzyl are available.



12 6 5 (10)

At the time of this writing, an Arrhenius expression for the rate of hydrogen atom abstraction from Bu_3SnH by benzyl was not available. Chatgilialglu, Ingold, and Scaiano[2] estimated an upper limit of 3×10^5 M^{-1} s^{-1} at 25 °C. From available absolute rates of benzyl reactions, it is not possible to estimate the barrier to ring closure of 2-allylbenzyl with sufficient accuracy to warrant discussion. Experiments to determine the absolute rates of reaction of benzyl radical with Bu_3SnH and thiophenol are underway to provide 2-allylbenzyl cyclization rates.

The halide 1-chloro-2-(2-vinylphenyl)ethane, **4**, gave a less precise expression of log *r* vs. $(RT)^{-1}$ (Table I), due primarily to greater error in the measurement of 2-ethylstyrene. It was necessary to run halide **4** at low Bu_3SnH concentrations to avoid addition of tributylstannyl radicals to **4** or to 2-ethylstyrene. This, in turn, resulted in a very low concentration of unrearranged hydrocarbon product and is responsible for the reduced precision. Correlation coefficients of only 0.98 and 0.96 for five- and six-member ring closure were obtained. Insignificant amounts of

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(8) (a) Benson, S. W. "Thermochemical Kinetics. Methods for the Estimation of Thermochemical Data and Rate Parameters", 2nd ed.; Wiley-Interscience: New York, 1976. Benson, S. W.; Cruikshank, F. R.; Golden, D. M.; Hanger, G. R.; O'Neal, H. B.; Rodgers, A. S.; Walsh, R. *Chem. Rev.* **1969**, *69*, 125 and ref 9. (b) The thermochemical estimates on which the discussion is based are as follows (structure number, $\Delta H_f{}^\circ{}_{298}$(g), kcal/mol, $\Delta H_f{}^\circ{}_{443}$(g), kcal/mol, $S_{int}{}^\circ{}_{298}$, eu, $S_{int}{}^\circ{}_{443}$, eu): **5**, 55.2, 52.1, 93.8, 110.6; **6**, 48.4, 45.6, 91.1, 109; **12**, 61.3, 59, 100.4, 119.3; **14**, 69, 66.8, 101.6, 121.3; **13**, 54.3, 51.2, 92.4, 109.5; **15**, 38.6, 35.8, 86.8, 104.7. (c) The conversion of Eyring to Arrhenius expressions is accomplished with the relationships $\Delta S^{\ddagger} = R \ln (hA/(ekT))$, $E = \Delta H^{\ddagger} + RT$. See (a) above and: Moore, J. W.; Pearson, R. G. "Kinetics and Mechanism. A Study of Homogeneous Chemical Reactions", 3rd ed.; Wiley-Interscience: New York, 1981; pp 178–179 and ref 9.

(9) McMillen, D. F.; Golden, D. M. *Annu. Rev. Phys. Chem.* **1982**, *33*, 493–532.

(10) (a) Maillard, B.; Ingold, K. U. *J. Am. Chem. Soc.* **1976**, *98*, 1224, 4692. (b) For a discussion of radical rearrangements suitable for competitive studies ("clocks") see: Ingold, K. U. In "Organic Free Radicals"; Pryor, W. A., Ed.; American Chemical Society: Washington, DC, 1978; pp 188–207.

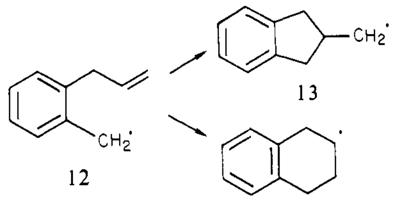
(11) Hamilton, E. J.; Fischer, H. *Helv. Chim. Acta* **1973**, *56*, 795.

(12) Wilt, J. *Free Radicals* **1973**, *1*.

(13) Beckwith, A. L. J.; Ingold, K. U. In "Rearrangements in Ground and Excited States"; Academic Press: New York, 1980; Chapter 4, Vol. 1, pp 170–172.

tributyl[2-(2-ethylphenyl)ethyl]stannane were detected at the concentrations of Bu_3SnH used here.

Five- vs. Six-Member Ring Formation by 2-Allylbenzyl and 2-(2-Vinylbenzyl)ethyl. Examination of the Arrhenius parameters of Table I reveals that five-member cyclization of 2-allylbenzyl is favored over six-member cyclization by 2 kcal/mol, reminiscent of 5-hexenyl and its analogues.[13] The less favorable approach by the radical center to the olefin results in predominant formation of the less stable radical, 2-indanylmethyl (**13**).[13]



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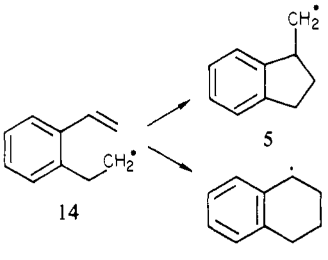
(11)

The 2-(2-vinylphenyl)ethyl radical (**14**) is also favored by 2 kcal/mol to form the five-member ring closure product, 1-indanylmethyl (**5**), over the six-member ring closure product, 1-tetralyl (**15**). The slightly higher barrier for five-member cyclization of 2-(2-vinylphenyl)ethyl (7.29 kcal/mol) compared to 5-hexenyl (6.87 kcal/mol)[2] may indicate that substitution of a double bond into the 5-hexenyl system leads to a less geometrically favorable approach to the olefin by the radical center, and perhaps a small barrier contribution for rotation of the vinyl group out of the aryl ring plane. From the estimated values of $\Delta H_{\mathrm{f}}{}^{\circ}{}_{298}$ for 1-tetralyl (35.6 kcal/mol) and 2-(2-vinylphenyl)ethyl (69 kcal/mol)[8,9] and the 9.4 ± 0.7 kcal/mol barrier for six-member ring formation, we estimate that 1-tetralyl will undergo the reverse-ring-opening reaction with a barrier of 42 ± 2 kcal/mol, only slightly less than the barrier for β-scission of hydrogen atom from 1-tetralyl, about 46 ± 2 kcal/mol,[8,9] estimated by assuming a 2 kcal/mol barrier for the addition of hydrogen atom to 1,2-dihydronaphthalene.[14]



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(12)

In conclusion, the present study has provided a new expression for the neophyl rearrangement and the first experimentally determined expression for the neophyl-like rearrangement of 1-indanylmethyl to 2-tetralyl, as well as the relative rates of five- and six-member ring formation from **12** and **14**. These expressions provide useful rates by which competitive atom transfer rates and other radical reactions may be determined for primary radicals and provide estimates of the ring-opening reactions of the tetralin and indan systems. The 2-allylbenzyl radical cyclization is a particularly useful radical "clock",[10] which we have applied to the determination of relative rates of hydrogen atom abstraction relative to cyclization for various hydrogen donors.[15] Further work to determine the absolute rates of cyclization of 2-allylbenzyl is under way.

Registry No. **1**, 515-40-2; **2**, 90320-62-0; **3**, 89121-39-1; **4**, 90320-63-1; **5**, 75421-36-2; **6**, 75421-37-3; **10**, 25087-41-6; **11**, 31987-29-8; **12**, 75421-42-0; **13**, 75421-38-4; **14**, 90320-64-2; **15**, 69339-77-1; Bu_3SnD, 6180-99-0; D_2, 7782-39-0; 2-ethylstyrene, 7564-63-8; 2-allyltoluene, 1587-04-8; 2-bromotoluene, 95-46-5; allyl bromide, 106-95-6; 1-indenecarboxylic acid, 5020-21-3; 3-indenecarboxylic acid, 14209-41-7; 1-indancarboxylic acid, 14381-42-1; 1-(hydroxymethyl)indan, 1196-17-4; 2-bromobenzyl alcohol, 18982-54-2; 2-bromobenzyl alcohol THP ether, 17100-66-2; 2-allylbenzyl alcohol THP ether, 34708-50-4; 2-allylbenzyl alcohol, 84801-07-0; 2-bromobenzaldehyde, 6630-33-7; ethylene glycol, 107-21-1; 2-bromobenzaldehyde ethylene glycol ketal, 34824-58-3; 2-(2-formylphenyl)ethyl acetate ethylene glycol ketal, 90320-65-3; *tert*-butylbenzene-d_1, 35389-41-4; *iso*-butylbenzene-d_1, 90320-66-4; 2-allyltoluene-d_1, 90320-67-5; 2-methylindan-d_1, 90320-68-6; [2-(2-ethylphenyl)ethyl]tributylstannane, 90320-69-7.

Supplementary Material Available: Data from density measurements of phenyl ether and Tables II–VI of experimental results from the reactions of several alkyl halides with tributylstannane (11 pages). Ordering information is given on any current masthead page.

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(14) (a) Kerr, J. A. *Free Radicals* **1973**, *1*, 28. (b) Perkins, M. J. *Ibid.* **1974**, *2*, 236. (c) James, D. G. L. *Chem. Commun.* **1960**, 484; *Trans. Faraday Soc.* **1968**, *64*, 2735, 2752.

(15) Franz, J. A.; Barrows, R. D.; Camaioni, D. M. *Prepr. Pap.—Am. Chem. Soc., Div. Fuel Chem.* **1983**, *28* (5), 77–80.