BRP lamp under continuous oxygen agitation. The disappearance of the dienes were monitored by using a Sigma 3B analytical gas chromatograph. (Conditions: injector, 180 °C; detector, 180 °C; oven programming 93 °C, 30 min; ramp rate, 5 °C/min, final temperature, 110 °C, 10 min, He flow rate 35 cm^3/min.) The peak areas were determined using a Hewlett-packard integrator and are the average of two to four injections. The irradiation times were adjusted for a minimum conversion of 5% for 1 and a maximum conversion of 98% for 3 (Table VI).

($k_{TME}/k_{Z,Z}$). This ratio was determined as described above. In this case the appearance of the allylic hydroperoxide from the ene reaction of 2,3-dimethyl-2-butene (TME) was monitored rather than the disappearance of starting material. The allylic hydroperoxide was monitored by gas chromatography after conversion to the allylic alcohol (TMEOH) with triphenylphosphine.[40] Its concentration was determined by reference to a calibration curve (Table VII).

Acknowledgment. We thank the National Science Foundation (CHE-8418603) and the donors of the Petroleum Research Fund, administered by the American Chemical Society, for their generous support of this research.

Registry No. 1, 86528-14-5; 2, 86528-15-6; 3, 79989-51-8; 6, 101347-18-6; 7, 52752-58-6; 8, 52752-57-5; 9, 101314-72-1; t-BuOCH$_2$C≡CCH$_2$OBu-t, 79989-39-2; (E)-t-BuOCH$_2$CH═CHCH$_2$OBu-t, 52752-63-3; O$_2$, 7782-44-7.

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Reactions of the 2-Allylbenzyl Radical: Relative and Absolute Rate Constants for Abstraction of Hydrogen Atom from Thiophenol, Dicyclohexylphosphine, Phenols, and Arylalkyl Donors[1]

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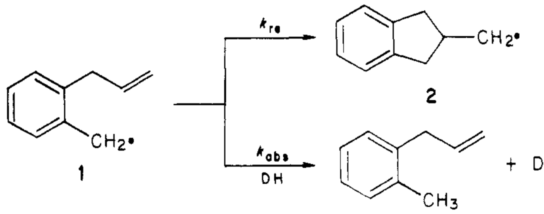
Relative and absolute rate expressions for hydrogen atom abstraction (k_{abs}) by the 2-allylbenzyl radical from thiophenol, dicyclohexylphosphine, and a series of alkyl-substituted aromatic hydrogen donors relative to exo cyclization to the 2-indanylmethyl radical (k_{re}) are presented. The Arrhenius parameters for the competition of the rearrangement of 2-allylbenzyl with abstraction from arylalkyl and heteroatom donors were as follows (donor, log $((A_{re}/A_{abs})/M)$, $E_{abs} - E_{re}$, kcal/mol): p-xylene, 4.007, −2.881; p-xylene-d_6, 3.470, +0.0792; m-xylene, 4.038, −2.881; diphenylmethane, 3.977, −5.267; diphenylmethane-d_2, 3.501, −2.694; fluorene, 3.059, −5.644; fluorene-d_2, 3.101, −4.227; dicyclohexylphosphine, 3.197, −9.895; thiophenol, 2.983, −12.832. From the expression for k_{re} for the 2-allylbenzyl to 2-indanylmethyl cyclization, $\log (k_{re}/s^{-1}) = (11.14 \pm 0.30) - (16.28 \pm 0.53)/\theta$, rate expressions for abstraction (A_{abs}, E_{abs}) are derived. Individual rate constants at 160 and 170 °C for other arylalkyl and phenolic donors are also presented. Evidence for a contribution of hydrogen atom tunneling to the rate of abstraction from diphenylmethane and xylene is presented.

Relative rates of hydrogen atom abstraction by the benzyl and 2-allylbenzyl radicals from a wide variety of aromatic hydrocarbon and heteroatom hydrogen donors have recently been reported by Bockrath[2] and by this laboratory.[3] By contrast, absolute rate expressions for most donors of interest are lacking. Although Jackson and O'Neill have reported rate expressions for hydrogen abstraction by benzyl radical from substituted toluenes and have reported evidence of tunneling in the reaction of benzyl with toluene,[4] the unusually high Arrhenius parameters reported have been questioned.[5] Chain transfer constants for the abstraction of hydrogen atom by polystyryl radical have been reported for a variety of donors,[6] but in general, reliable rate expressions for hydrogen atom transfer to benzylic radicals are not available. A number of mechanistic studies[7,8] of thermal decomposition mechanisms of hydrocarbons related to coal chemistry would benefit from absolute rate expressions for hydrogen atom transfer. Up to the present, rate expressions for hydrogen atom transfer steps in such studies depended on estimates.[7] Our recent development[9,10] of an absolute rate expression for the cyclization of the 2-allylbenzyl radical (1) to the 2-indanylmethyl radical (2) (eq 1) ($\log (k_{re}/s^{-1}) = (11.14 \pm 0.30) - (16.28 \pm 0.53)/\theta$, $\theta = 2.3RT$/kcal/mol), using some of the data presented in this paper, allows the competition of this radical "clock"[11] reaction, k_{re}, with abstraction (k_{abs}) by 1 from donors to provide relative and absolute rates of atom abstraction. We now report relative and absolute rate expressions and isotope effects for the abstraction of hydrogen from a series of hydrocarbon, thiol, and phosphine donors and provide evidence suggesting the



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participation of hydrogen atom tunneling[12] in the reactions of 1 and aralkyl hydrogen donors.

Experimental Section

General Methods. NMR spectra were determined with a Varian FT-80 instrument. Gas chromatography (GC) and GC–mass spectrometry (GCMS) were accomplished with Hewlett-Packard Models 5880A and 5985 systems with 30-m J&W Scientific DB-5 columns. Elemental analyses were determined by Schwarzkopf Microanalytical Laboratory, Woodside, NY, or by Galbraith Laboratories, Knoxville, TN.

Reagents. Tributylstannane (Bu_3SnH), dicyclohexylphosphine (DCPH), and phenyl ether were obtained from Alfa and distilled under inert atmosphere. Bu_3SnD (Alfa) was used as received. 2-Allyltoluene, 2-methylindan, and 2-allylbenzyl alcohol were available from previous work.[10]

Hydrocarbon donors of Table II were available from Aldrich. Allylbenzene, tetralin, and *m*-xylene were >99% purity and were used as received. *p*-Xylene, diphenylmethane, 9,10-dihydroanthracene, fluorene, and 9,10-dihydrophenanthrene were recrystallized several times from methanol to give >99.9% purity. Phenol, cresols, and hydroquinones of Table II were distilled, sublimed, or recrystallized to give material of high purity. A sample of *tert*-butyl 2-indanperacetate was available from a previous study.[13]

2-Allylbenzaldehyde was prepared by pyridine–chlorochromate oxidation[14] of 2-allylbenzyl alcohol. NMR and mass spectral parameters matched those of Kampmeier.[15]

2-Allylbenzaldazine was prepared from 2-allylbenzaldehyde, hydrazine sulfate, and NH_4OH (to pH 10) in aqueous heterogeneous media:[16] ^1H NMR ($CDCl_3$) δ 8.94 (2 H, imine CH), 8.25–8.05 (2 H, Ar H ortho to C=N), 7.6–7.2 (6 H, Ar H), 6.4–5.5 (m, 2 H, $CH{=}CH_2$), 5.2–4.8 (overlapping m, 4 H, $CH{=}CH_2$), 3.64 (d of t, 4 H, $CH_2CH{=}CH_2$); ^{13}C NMR (with off-resonance decoupled multiplicities) ($CDCl_3$) δ 160.16 (d, CH=N), 140.07 (s, Ar C-1), 136.87 (d, $CH{=}CH_2$), 132.16 (s, Ar C-2), 130.92, 130.34 (two d, Ar C-3 and C-6), 127.85, 126.66 (d, Ar C-4 and C-5), 116.25 (t, $CH{=}CH_2$), 36.96 (t, $CH_2CH{=}CH_2$); mp 41–42 °C. Anal. Calcd for $C_{20}H_{20}N_2$: C, 83.3; H, 6.99; N, 9.71. Found: C, 83.2; H, 7.05; N, 9.62.

The precursor aldehyde is regenerated by shaking a $CHCl_3$ solution of the azine with 25% aqueous H_2SO_4.

***N,N'*-Di-2-allylbenzylhydrazine** was prepared by adding excess 5% Na/Hg amalgam to a methanol solution of the azine. Instantaneous loss of the pale yellow color and the imine NMR peak at δ 8.94 resulted. Workup gave a yellow oil which was not further characterized.

Azo-2-allyltoluene (3) was immediately prepared from the hydrazine compound by treatment with boiling aqueous H_2O_2[17] for ca. 3 min to give crude azo-2-allyltoluene. Filtration of a pentane solution of the crude azo-2-allyltoluene through silica gel followed by crystallization from hexane at −25 °C gave the pure product, 40% yield based on aldehyde. This compound may be stored for up to a year or longer at −25 °C in the dark without detectable decomposition: ^1H NMR ($CDCl_3$) δ 7.33–7.20 (m, 8 H, Ar H), 6.25–5.75 and 5.15–4.8 (m, 6 H, olefinic H), 4.96 (s, 4 H, $ArCH_2N$, superimposed on vinyl region), 3.48 (d of t, 4 H, J = 6.2, 1.5 Hz); ^{13}C NMR δ 138.25 (Ar C-1), 136.21 ($CH{=}CH_2$), 133.34 (Ar C-2), 129.71, 129.34 (Ar C-3 and C-6), 127.42, 126.08 (Ar C-4 and C-5), 115.45 ($CH{=}CH_2$), 71.25 (CH_2N), 37.36 ($CH_2CH{=}CH_2$); mp 47.5–49 °C. Anal. Calcd for $C_{20}H_{22}N_2$: C, 82.72; H, 7.64; N, 9.64. Found: C, 82.6; H, 7.33; N, 9.58.

Bi-2-allylbenzyl was prepared by Grignard coupling following a standard procedure.[18] This compound was produced in all reactions of azo-2-allyltoluene and was prepared as a GC standard for material balance determinations. After reaction of 2-allylbenzyl chloride with Mg/ether, the reaction was quenched with CO_2. GC revealed about 20% product along with the major product, 2-allylphenylacetic acid. Preparative gel permeation chromatography on a Waters Association 100-Å μStyragel column (tetrahydrofuran eluent) provided 20 mg of a clear oil: ^1H NMR ($CDCl_3$) δ 7.17 (s, 8 H, Ar H), 6.25–6.15 (m, 2 H, $CH{=}CH_2$), 5.04 (2 H, cis $CH{=}CH_2$, J = 8.9, 1.7 Hz), 4.98 (2 H, trans $CH{=}CH_2$, J = 18.1, 1.8 Hz), 3.39 (overlapping d of d of d appearing as d of t, 4 H, J = 6.2, 1.5, 1.5 Hz), 2.87 (s, 4 H, $ArCH_2CH_2Ar$); ^{13}C NMR ($CDCl_3$) 139.94, 137.54 (Ar C-1 and C-2), 137.23 ($CH{=}CH_2$), 129.61, 129.19 (Ar C-3 and C-5), 126.39, 126.19 (Ar C-4 and C-5), 115.59 ($CH{=}CH_2$), 36.90 ($CH_2CH{=}CH_2$), 34.10 ($ArCH_2CH_2Ar$); 70-eV GCMS, m/e (relative abundance) 77 (7.9), 91 (63.2), 115.1 (28), 116 (28), 117 (10), 129 (39), 130 (9.2), 131 (100), 132 (11.3), 233 (15.8), 262 (M, 5.6), 263 (M + 1, 1.2). Anal. Calcd for $C_{20}H_{22}$: C, 91.55; H, 8.45. Found: C, 90.2; H, 8.56.

2-Allylbenzyl phenyl sulfide was prepared to confirm its identity as the cross-termination product from the reaction of the 2-allylbenzyl radical with thiophenoxy radical. A solution of 0.34 g of KOH, 16 mmol of thiophenol, and 1 g of 2-allylbenzyl chloride in 75 mL of ethanol was refluxed under N_2. Approximately 50 mg were isolated by HPLC (Waters 10μm silica radical compression module column, isooctane eluent), ca. 95% purity, sufficient for GC calibration. Insufficient material remained for elemental analysis: NMR ($CDCl_3$) δ 7.4–7.2 (m, 5 H, Ar H of SC_6H_5), 7.17 (s, 4 H, Ar H of $C_6H_4(CH_2CH{=}CH_2)$), 6.25–5.7 (m, 1 H, $CH{=}CH_2$), 5.2–4.05 (m, two of g overlapping, 2 H, CH_2CH_2), 4.12 (s, 2 H, $ArCH_2SPh$), 3.50 (d of t, 2 H, J = 6.1, 1.6 Hz, $CH_2CH{=}CH_2$); GCMS, (m/e, relative abundance) 91 (49), 103 (11.6), 109 (10.4), 115 (26.4), 116 (16.4), 128 (13.6), 129 (51.2), 130 (100), 131 (34.8), 240 (M^+, 9.5).

(*E*)-1-(2-Methylphenyl)propene was prepared for use as a GC standard to detect isomerization of 2-allyltoluene in the kinetic experiments by treatment of the Grignard reagent from 2-bromotoluene with propionaldehyde: the alcohol was dehydrated by distillation from $KHSO_4$ following a standard procedure[19] to give ca. 90% *E* isomer: the ^1H NMR matched a published spectrum,[20] ^{13}C NMR 137.17, 134.66 (Ar C-1 and C-2), 130.19, 129.26, 126.82, 126.62, 126.10, 125.62 (Ar and olefinic C), 19.74, 18.71 (methyls).

Diphenylmethane-d_2 and fluorene-d_2 were prepared by exchange reactions of the hydrocarbon in $Me_2SO\text{-}d_6$/$NaCD_2SOCD_3$. The hydrocarbons were dissolved in $Me_2SO\text{-}d_6$ under N_2, NaH was added (ca. 1g/100g $Me_2SO\text{-}d_6$), and the reaction was heated rapidly to 130 °C and allowed to cool over a period of 15 min to ~50 °C. The mixture was quenched with D_2O (or for fluorene, DCl/D_2O) extracted with water and hexane, dried over $MgSO_4$, distilled or sublimed (fluorene), and recrystallized from methanol. *p*-Xylene-d_6 (Aldrich) was recrystallized 4 times from CH_3OH at −25 °C and distilled. Label levels were determined by careful integration of the total aromatic region relative to the residual proton signal in the ^1H NMR spectrum: fluorene, 96.64 ± 0.1% d_2; diphenylmethane, 99.1 ± 0.1% d_2; and xylene, 99.17 ± 0.05% d_6.

Kinetic Experiments. Kinetics of the Decomposition of Azo-2-allyltoluene. The temperature dependence of the decomposition of azo-2-allyltoluene was determined in *m*-xylene by monitoring the disappearance of the azo compound as a function of time and temperature by quantitative HPLC. Freeze–thaw degassed samples of 100 μL of a solution of 3×10^{-2} M 3 were heated at temperatures between 120 and 190 °C in a thermostated oil bath for varying times and opened, and 100 μL of a solution of acetophenone were added as internal HPLC standard. Analysis of the solution on a Water's 10 μm silica radial compression module column programming from 0.7% THF in isooctane to 100% THF gave convenient quantitation of unreacted 3. The disappearance of 3 followed the expression $\log (k_d/s^{-1}) = (13.96 \pm 1) - (33.28 \pm 1.5)/\theta$, $\theta = 2.303RT$ (kcal/mol).

Decomposition of Azo-2-allyltoluene (3) in the Presence of Hydrogen Atom Donors. General Methods. For reactive donors such as thiophenol and dicyclohexylphosphine, the donor,

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[12] For a related paper which examines isotope effects in the reaction of benzyl radical with aralkyl hydrogen donors, see: Bockrath, B.; Bittner, E.; McGrew, J. *J. Org. Chem.* **1986**, *51*, 15–19.

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azo-2-allyltoluene (**3**), and internal GC standard were dissolved in phenyl ether or dodecane. For the less reactive arylalkyl donors which are liquids at room temperature, the azo compound and internal GC standard were dissolved in the neat donor, freeze–thaw degassed in Pyrex tubes, and sealed. For solid donors such as fluorene, phenols, and 9,10-dihydroanthracene, a degassed solution of **3** in phenyl ether and internal GC standard was added to the solid donor under inert atmosphere and sealed on a vacuum line. Densities of the binary liquid mixtures were determined for these cases. All other liquid densities were measured or calculated as necessary.[21] Reaction times of 15 min, 30 min, 1 h, 2 h, 8 h, and 24 h were required at 190, 180, 170, 160, 140, and 120 °C for >99% consumption of **3** for direct analysis by GC. Occasionally at 120 °C, the long reaction time led to spurious results, due probably to loss of the product 2-allyltoluene. To circumvent this problem, 120 °C reactions were terminated at 2–4 h, and the hydrocarbon products were separated by preparative HPLC before GC analysis. Material balances were determined by GC quantitation of 2-allyltoluene, 2-methylindan, and tetralin, the cross-termination product of the reaction of 2-allylbenzyl and the donor radical, and the self-termination product of 2-alkylbenzyl, bi-2-allylbenzyl. The C_{10} hydrocarbons were easily quantitated with less than 1% relative error for a wide variety of reaction media. The cross-termination products and bi-2-allylbenzyl were difficult to quantitate with less than about 10% error due to nonlinear GC injector discrimination effects caused by injecting large amounts of compounds such as fluorene or diphenylmethane in the splitless/direct injection mode. Since allyltoluene, the azo precursor, and product bi-2-allylbenzyl are themselves donors, an upper limit of ca. 10^{-2} M azo compound **3** was necessary to prevent significant radical reaction with these species. In order to prevent undesirable side reactions, concentrations of **3** at $<10^{-3}$ M were required for most donors. Low concentrations of **3** were necessary to prevent formation of 2-allyltoluene in disproportionation reactions and to prevent loss of 2-indanylmethyl radical in ring addition/termination reactions (see below). Detailed results for individual donors follow.

Test for Linear Dependence of [2AT]/[2MI] on Donor Hydrogen Concentration for 9,10-Dihydroanthracene. Solutions of 9,10-dihydroanthracene varying from 0.4 to 18 M (donor hydrogen concentration, [DHC] = 4[9,10-DHA]) in phenyl ether were prepared, containing 1×10^{-3} M **3**. These solutions were freeze–thaw degassed, sealed, and heated for 2 h at 160.0 °C. A least-squares regression of [2AT]/[2MI] vs. [DHC] gave $[2AT]/[2MI] = (2.082 \pm 0.05)[DHC] - (0.04 \pm 0.04)$, $r = 0.997$. The slope of this expression is k_{abs}/k_{re}. The near-zero intercept of this expression confirmed that values of k_{abs}/k_{re} could be calculated accurately from single-concentration experiments using eq 3, below, for aralkyl donors. The percent of phenyl ether varied from 98% to 20% in these experiments. This variation in the polarity of the medium caused no detectable difference in values of k_{abs}/k_{re} within experimental error.

***p*-Xylene and *p*-Xylene-d_6.** Decomposition of **3** at 2.2×10^{-2} M in *p*-xylene-d_6 revealed only 38, 27, and 16% d_1 in 2AT at 190, 160, and 130 °C, and material balances averaged 75%. Lowering the concentration of **3** to 2×10^{-4} M led to satisfactory label incorporation (84–95% d_1) and >95% average material balances. Kinetic experiments with **3** at 1×10^{-4} M in *p*-xylene gave slightly (5–7%) higher material balances and about 6–8% alteration in k_{re}/k_{abs} values from experiments with 8×10^{-3} M **3** in *p*-xylene.

***m*-Xylene.** Decomposition of **3** (5×10^{-3} M in *m*-xylene) gave small yields of C_{18} and C_{20} products whose GCMS spectra revealed them to be dimers of 2-indanylmethyl and 2-tetralyl or adducts of 2-indanylmethyl to xylene. Reducing the concentration of **3** to 1×10^{-4} M reduced these products to trace levels and gave bixylyl, 2-allylbenzylxylyl, and bi-2-allylbenzyl as the only significant C_{16}, C_{20}, and C_{18} products for a 96% average material balance.

Diphenylmethane and Diphenylmethane-d_2. For diphenylmethane, concentrations of **3** or 1.6×10^{-4} M and 3.4×10^{-3} M gave identical kinetic results. However, for the slower donor diphenylmethane-d_2 (99.1% *d*), a concentration of **3** of 3.4×10^{-3} M gave evidence of formation of 2-allyltoluene by reaction with extraneous hydrogen sources: at 190, 180, 160, 140, 120 °C, the 2-allyltoluene contained 78, 76, 68, 60, and 38% d_1 label (remainder d_0). Lowering the azo concentration to 2.8×10^{-4} M gave >96% d_1, at all temperatures, (Table II) indicating that alternate sources of abstractable hydrogen were insignificant. The GCMS values are about 3–4% higher than possible with even conventional isotope effects and a small systematic GCMS error is suspected for this case. Material balances averaged 95% for the three sets.

Fluorene and Fluorene-d_2. Fluorene and fluorene-d_2 samples were prepared by adding 20 μL of 3.96–4.2×10^{-3} M azo-2-allyltoluene in phenyl ether to 100 mg of fluorene or fluorene-d_2. Material balances averaged 94%.

Dicyclohexylphosphine (DCPH). The reaction of DCPH by thermal decomposition of **3** in phenyl ether led to material balances of greater than 90% above 170 °C. Between 160 and 130 °C, however, material balances fell from 60% at 160 °C to 20% at 130 °C. To thwart the apparent slow consumption of 2-allyltoluene and bi-2-allylbenzyl by CDPH at the longer reaction times, **3**, DCPH, and internal GC standard were dissolved in dodecane, sealed in quartz tubes, thermostatted at 90 to 190 °C in an octadecane bath, and illuminated with the light from a 1000-W Hanovia Model 977B0010 Hg/Xe lamp. Complete photolysis of **3**, as determined by HPLC, occurred in 20 min at all temperatures (compared to thermal reaction times of 4–24 h below 170 °C). This procedure gave a 97% average material balance, excellent precision, and permitted a 100° temperature range. It is the method of choice for donors compatible with photolysis.

Thiophenol. In the presence of this donor, nearly all 2-allylbenzyl radicals dimerize or are scavenged to form 2-allyltoluene. To observe rearrangement, low concentrations of thiophenol were necessitated. Since a significant (e.g., 30%) fraction of thiophenol is consumed, an integrated rate expression account for changing donor concentration was used (see below). Material balances averaged about 85%, independent of reaction temperature. A small amount (~5%) of each, 2-allyltoluene and, presumably, bi-2-allylbenzyl, was consumed in secondary reactions, as evidenced by the detection of (*E*)-1-(2-methylphenyl)propene. The diversion of this amount of product introduced a small (≲5%) error in k_{re}/k_{abs} and was neglected. Isomerized 2-allyltoluene was not observed in any other reactions of **3**.

Isotopic Analysis of 2-Allyltoluene. Mass spectra were determined for 2-allyltoluene and 2-allyltoluene-α-d_1 prepared from 99.9% label tributylstannane-*d* and 2-allylbenzyl chloride. From an average of several 70 eV spectra the molecular ion cluster of 2-allyltoluene gave *m*/*e*, relative abundance) 128 (11.3), 129 (11.3), 130 (2.2), 131 (30.3), 132 (100), 133 (11.2), 134 (0.57), 135 (0). 2-Allyltoluene-α-d_1 gave 128 (6.3), 129 (9.2), 130 (7.5), 131 (2.8), 132 (35.7), 133 (100), 134 (10.5), 135 (0.3). Similar spectra were obtained for 2-(methyl-d_1)indan and tetralin-2-d_1. The SIMS procedure for the Hewlett-Packard Model 5985 system was used to provide a weighted average of the ion cluster abundances over the GC peak of interest. A computer program was used to generate normalized linear combinations of the molecular ion clusters were compared of the d_1 and d_0 isomers, with which the experimental mass clusters were compared to determine the percent d_1 for 2-allyltoluene (2AT), 2-methylindane (2MI), and tetralin (TET) from reactions with deuterated donors.

Test for Reversibility of the 2-Allylbenzyl → 2-Indanylmethyl Rearrangement. A freeze–thaw degassed, 0.05 M solution of *tert*-butyl-2-indanperacetate[13] in toluene was heated at 160 °C for 15 min. GC analysis showed 2-methylindan to be the major product and revealed no detectable 2-allyltoluene. Higher temperatures were not feasible since the rate of decomposition of the perester would have been fast[22] relative to the sample heatup time.

Phenol, Cresols, and Hydroquinones. The phenolic donors were examined by adding 20 μL of a solution of **3** in phenyl ether or dodecane to 100 mg of the solid donor to give 8 ± 0.1 M

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Table I. Relative Rate Expressions log (k_{re}/k_{abs}) and Absolute Rate Expressions log (k_{abs}) for Reactions of 2-Allylbenzyl with Donors

donor	log $[(A_{re}/A_{abs})/M]$[a]	$E_{abs} - E_{re}$ (kcal/mol)[a]	log ($A_{abs}/M^{-1}\ s^{-1}$)[b]	E_{abs} (kcal/mol)[b]	k_{abs} ($M^{-1}\ s^{-1}$) (160 °C)
dicyclohexylphosphine	3.197 ± 0.038	-9.895 ± 0.071	(8.001)[c]	(6.278)[c]	6.82×10^4
thiophenol	2.983 ± 0.133	-12.832 ± 0.263	(8.273)[c]	(3.790)[c]	2.30×10^6
Bu_3SnH	2.320 ± 0.160	-10.470 ± 0.360	(8.647)[c]	(5.584)[c]	6.76×10^5
p-xylene	4.007 ± 0.036	-2.881 ± 0.071	7.133 ± 0.38	13.399 ± 0.67	2.36
p-xylene-d_6[d]	3.470 ± 0.033	+0.0792 ± 0.007	7.673 ± 0.37	16.359 ± 0.54	0.26
m-xylene	4.038 ± 0.037	-2.881 ± 0.073	7.102 ± 0.37	13.398 ± 0.68	2.20
diphenylmethane	3.977 ± 0.050	-5.267 ± 0.098	7.163 ± 0.40	11.013 ± 0.73	40.49
diphenylmethane-d_2[e]	3.501 ± 0.052	-2.694 ± 0.104	7.639 ± 0.40	13.586 ± 0.74	6.10
fluorene	3.059 ± 0.067	-5.644 ± 0.058	8.081 ± 0.43	10.636 ± 0.65	519.5
fluorene-d_2[d]	3.101 ± 0.068	-4.227 ± 0.133	8.039 ± 0.44	12.053 ± 0.79	90.94

[a] Errors are one standard deviation (σ). [b] Errors are 95% confidence interval (2σ). [c] log A_{abs} and E_{abs} values obtained from reaction of benzyl radical with the donor (ref 9). Combining these values with log (A_{re}/A_{abs}) and $E_{abs} - E_{re}$ produces log $k_{re}/s^{-1} = (11.14 \pm 0.30) - (16.28 \pm 0.53)/\theta$ (an average of three expressions for log k_{re}). The average expression for log k_{re} was used to calculate the Arrhenius parameters for the remaining arylalkyl donors. [d] Method B. [e] Method A.

Table II. Relative and Absolute Rates of Abstraction of Hydrogen Atom by 2-Allylbenzyl per Hydrogen Atom

donor	k_{abs}[b] ($M^{-1}\ s^{-1}$) (160 °C)	k_{abs}/k_{re} (M) 160 °C	k_{abs}/k_{re} (M) 170 °C	relative rates 160 °C	relative rates 170 °C	relative rates 170 °C[a]
		Hydrocarbon Donors				
m-xylene	2.20	2.60×10^{-3}	2.41×10^{-3}	(1)	(1)	
p-xylene	2.36	2.79×10^{-3}	2.59×10^{-3}	1.07	1.07	
p-xylene-d_6	0.261	3.09×10^{-4}	3.10×10^{-4}	0.119	0.129	
mesitylene						(1)[a]
diphenylmethane-d_2	6.10	7.21×10^{-3}	6.72×10^{-3}	2.77	2.79	2.92[a,c]
diphenylmethane	40.49	4.79×10^{-2}	4.1×10^{-2}	18.2	17.3	20.7[a]
fluorene-d_2[j]	90.94	1.07×10^{-1}	9.63×10^{-2}	41.15	39.96	21.7[d]
fluorene[j]	519.5	0.614	0.530	236.2	219.9	169.2[a]
tetralin	43.15	0.0516		19.62		21.54[a]
9,10-dihydrophenanthrene	81.23	0.096		36.9		33.8[a]
1,2-diphenylethane	10.07	1.19×10^{-2}		4.58		4.5[a]
allylbenzene	2.56×10^2	0.303		116.5		
9,10-dihydroanthracene	1.53×10^3	2.08	1.98	798	820.2	715.4[a]
		OH, SnH, PH, and SH Donors				
phenol[e,j]	1.18×10^2	0.14[g]		53.8		
phenol[g]		0.14[i,j]		53.8		
phenol[g,k]		0.287[k]		109[k]		
p-cresol[e,j]	3.34×10^2	0.395[f,i,j]		152		
m-cresol[e,j]	1.95×10^2	0.230[f,i,j]		88.5		
o-cresol[e,j]	3.06×10^2	0.362[f,i,j]		139		
p-hydroquinone[e,j]	4.00×10^2	0.473[j]		182		
m-hydroquinone[e,j]	2.21×10^2	0.261[j]		100		
o-hydroquinone[i,j]	2.59×10^2	0.306[j]		117.7		
dicyclohexylphosphine[g]	6.82×10^4	62.32	48.08	2.40×10^4	2.00×10^4	
tributylstannane[h]	6.76×10^5	9.16×10^2	6.96×10^2	3.52×10^5	2.89×10^5	
thiophenol[i]	2.30×10^6	3.09×10^3	2.21×10^3	1.19×10^6	9.17×10^5	

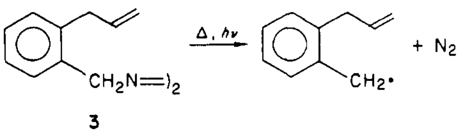
[a] Reference 2. [b] k_{abs} values converted from k_{abs}/k_{re} values by using the expression log $(k_{re}/s^{-1}) = 11.14 - 16.28/\theta$. [c] From $k_H/k_D = 7.1$ (ref 2 and 12). [d] From $k_H/k_D = 7.8$ (ref 12). [e] Not corrected for hydrogen bonding. [f] Methyl hydrogens neglected, number of abstractable hydrogens set to one per molecule. [g] Solvent, dodecane. [h] Solvent, phenyl ether (data from ref 10). [i] Solvent, phenyl ether. [j] Reactions of 100 mg of reagent and 20 μL of a phenyl ether solution of azo-2-allyltoluene. Donor concentration was 8.1 ± 0.2 M for the phenolic donors. [k] Corrected for hydrogen bonding, assuming monomer–trimer equilibrium with $K_3 = 0.0175\ M^{-2}$ at 160 °C.

solutions of the phenolic donor at 160 °C, which were freeze–thaw degassed and sealed. Following reaction, the phenolic donor (which interfered with C_{10} hydrocarbon GC analysis) was removed by passing the reaction mixture through a Water's Associates silica HPLC column eluting with 0.7% THF in hexane. GC analysis of the nonpolar HPLC fraction provided quantitation of 2-methylindan, 2-allyltoluene, *tert*-butylbenzene (GC standard), and bi-2-allylbenzyl.

Effect of Phenol Concentrations on [2AT]/[2MI]. Solutions of phenol at 0.313, 1.27, 5.81, and 8.05 M in dodecane containing 5×10^{-4} M **3** were heated at 160 °C for 2 h. After workup (as with phenol above), ratios of [2AT]/[2MI] were found to be 0.12, 0.37, 1.04, and 1.21, for nominal values of k_{abs}/k_{re} of 0.38, 0.29, 0.18, and 0.14, respectively, calculated from eq 3 below by using the total phenol concentration without correction for hydrogen bonding. The cited concentrations are at 160 °C. At ambient temperature the mixutres of phenol and dodecane were heterogeneous, but became quickly homogeneous at 160 °C. It did not appear practicable to utilize phenol concentrations below about 0.1 M without incurring side reactions with the solvent and formation of 2AT in disproportionation reactions.

Results

Table I provides relative Arrhenius parameters for the rearrangement of 2-allylbenzyl vs. abstraction from donors and absolute rate expressions for the abstraction reactions. Table II provides absolute and relative rate constants for the abstraction from a variety of donors at 160 and 170 °C. For the donors with high concentrations of abstractable hydrogen (for all cases but PhSH and Bu_3SnH in Tables I and II), reaction with radicals from the thermal or photolytic decomposition of **3** (eq 2) leads to negligible



3

(2)

change in abstractable hydrogen concentration, and the relative rate of rearrangement (k_{re}) to abstraction (k_{abs}) in eq 1 is given by eq 3, where DHC is the abstractable donor

$$k_{re}/k_{abs} = [2MI][DHC]/[2AT] \qquad (3)$$

hydrogen concentration. For thiophenol, an integrated rate expression[23] (eq 4) was applied to correct for changing

$$2AT + 2MI + TET = (DHC + r)(1 - e^{-(2MI + TET)/r}) \qquad (4)$$

donor concentration, since an appreciable amount of PhSH was consumed during the reaction. In eq 4, 2AT = 2-allyltoluene, 2MI = 2-methylindan, TET = tetralin, and $r = (k_{re} + k_{re'})/k_{abs}$, where $k_{re'}$ is the rate constant for the 2-allylbenzyl to 2-tetralyl endo cyclization, and DHC is the initial abstractable hydrogen concentration. A computer guesses values of r until the right side of eq 4 converges to the experimental value of 2AT + 2MI + TET. From the resulting value of r, $k_{re}/k_{abs} = r(2MI/(2MI + TET))$.

Correction of Relative Rates for Partial Deuterium Labeling in the Hydrogen Donor. The label levels (f_D) in *p*-xylene-d_6, diphenylmethane-d_2, and fluorene-d_2 were 99.17 ± 0.05, 99.10 ± 0.10, and 96.64 ± 0.10%. Two methods were used to correct for the partial label in the total 2AT values determined by GC.

Method A. It can be shown in straightforward fashion that the observed value of k_{abs}/k_{re}, which is equal to the experimental value 2AT/2MI[DHC], is given by eq 5a,

$$\left(\frac{k_{abs}}{k_{re}}\right)_{obsd} = \frac{1}{[DHC]}\left(\frac{2AT}{2MI}\right)_{obsd} = \frac{k_{abs(D)}f_D + k_{abs(H)}(1 - f_D)(g) + E/[DHC]}{k_{re}} \qquad (5a)$$

where $k_{abs(D)}$ is the rate constant for abstraction of deuterium from a carbon atom substituted with one or two additional deuterium atoms, g is the secondary isotope effect correcting for abstraction of hydrogen from a carbon atom substituted by one or two deuterium atoms, $k_{abs(H)}/k_{re}$ is the relative rate of hydrogen abstraction vs. rearrangement determined in the spearate experiments with the *totally protonated* donor, f_D is the percent of deuterium in the donor at the site of abstraction, and E corresponds to protonated 2-allyltoluene formed by abstraction of hydrogen by 2-allylbenzyl from impurities or in disproportionation reactions ($E = k'[RH] + k_d[R\cdot]$). The small value of g (ca. 0.9 per deuterium) causes less than a 1% reduction in the value of eq 5a and can be set to one with negligible error. For cases with negligible participation of disproportionation or abstraction from extraneous sources as revealed by GCMS analysis of the 2-allyltoluene and high material balances, the term $E/[DHC]$ can be neglected. Thus, eq 5a simplifies to eq 5b, where $(k_{abs(D)}/k_{re})_{obsd}$ is the

$$\frac{k_{re}}{k_{abs(D)}} = \frac{f_D}{\left(\frac{k_{abs(D)}}{k_{re}}\right)_{obsd} - (g)\left(\frac{k_{abs(H)}}{k_{re}}\right)(1 - f_D)} \qquad (5b)$$

observed GC ratio [2AT]/[2MI][DHC]. Dividing eq 5b by $k_{re}/k_{abs(H)}$ determined from the Arrhenius expression for the protonated donor (Table I) gives $k_{abs(H)}/k_{abs(D)}$ for hydrogen vs. deuterium abstraction by 2-allylbenzyl. Method A was used for diphenylmethane-d_2 to correct observed values of k_{re}/k_{abs} and to calculate $k_{abs(H)}/k_{abs(D)}$ values, with the value of g set to one in eq 5b.

Method B. For a known label level in the donor, f_D, and a known percent of 2-allyltoluene-d_1 in the total 2-allyltoluene, % d_1, eq 3 can be modified to give corrected $k_{re}/k_{abs(D)}$ values (eq 6a). Values of $k_{re}/k_{abs(D)}$ from eq 5b

$$\frac{k_{re}}{k_{abs(D)}} = \left(\frac{[2MI][DHC]}{[2AT]}\right)\left(\frac{f_D}{\%\ d_1}\right) \qquad (6a)$$

or eq 6a are converted to $k_{abs(H)}/k_{abs(D)}$ according to eq 6b.

$$\frac{k_{abs(H)}}{k_{abs(D)}} = \frac{(k_{re}/k_{abs(D)})}{(k_{re}/k_{abs(H)})} \qquad (6b)$$

Note that $k_{abs(D)}$ retains α-secondary isotope effects retarding deuterium abstraction due to one or two deuterium atoms. It can be shown from eq 6a that % d_1 in 2-allyltoluene is given by eq 6c, where $E' = E/(k_{abs(D)})([DHC])$.

$$\%\ d_1 = \frac{f_D}{(f_D + (g)(1 - f_D)(k_{abs(H)}/k_{abs(D)}) + E')} \qquad (6c)$$

Since % d_1, f_D, and $k_{abs(H)}/k_{abs(D)}$ in eq 6c are known and g can be estimated (see below), E' can be evaluated at each temperature, providing the percent of 2-allyltoluene formed by abstraction of residual hydrogen label, % $d_{0(res)}$, in eq 6d and an estimate of the percent of 2-allyltoluene

$$\%\ d_{0,res} = \frac{(g)\{(1 - f_D)(k_{abs(H)}/k_{abs(D)})\}}{(f_D + (g)(1 - f_D)(k_{abs(H)}/k_{abs(D)}) + E')} \qquad (6d)$$

formed by abstraction from extraneous impurities and disproportionation, % $d_{0,E}$, eq 6e.

$$\%\ d_{0,E} = \frac{E'}{(f_D + (g)(1 - f_D)(k_{abs(H)}/k_{abs(D)}) + E')} \qquad (6e)$$

Methods A and B give identical results if adventitious sources of hydrogen are negligible [E and E' in eq 5a and 6c–e are small]. Thus, for the reactions of fluorene-d_2, less than 3% of 2AT is formed in abstraction reactions involving impurities or disproportionation (Table VI, supplementary material) resulting in less than 2% differences in $k_{abs(H)}/k_{abs(D)}$ between method A and method B. For diphenylmethane-d_2, the small (3–4%) systematic GCMS error precluded by using method B. However, the excellent material balances and apparently satisfactory label allow application of method A with probably less than ca. 2% error in $k_{abs(D)}$.

While method A could be used for diphenylmethane-d_2 or fluorene-d_2, method B was required for correction of $k_{abs(D)}$ values for *p*-xylene-d_6, since 1–7% of 2AT was formed in reactions with adventitious sources of hydrogen (Table IV). Since excellent average material balances were achieved for *p*-xylene-d_6 reactions, protonated 2AT probably was not formed in disproportionation reactions with adducts of the 2-indanylmethyl radical to available aromatic systems. However, material balances, while averaging >95%, usually displayed ±8–10% errors for individual kinetic points. Thus, a small contribution of disproportionation, in addition to the incursion of adventitious impurities, while not important, cannot be completely ruled out.

Corrections for Secondary Isotope Effects in Methods A and B. Equations 5a, 5b, and 6c–e require a correction factor, g, for the α-secondary isotope effects[24] for abstraction of hydrogen from a carbon center substituted with one (fluorene-d_1 or diphenylmethane-d_1) or two

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[23] Rüchardt, C. *Ber. Dtsch. Chem. Ges.* **1961**, *94*, 1599.

[24] Streitwieser, A., Jr.; Jagow, R. H.; Fahey, R. C.; Suzuki, S. *J. Am. Chem. Soc.* **1958**, *80*, 2326.

Table III. Rate Constants for the Reaction of Benzyl Radical with Donors[a]

donor	log (A/M^{-1} s^{-1})	E_a, kcal/mol	k_{abs}, M^{-1} s^{-1} (298 K)
BuSnH	8.647 ± 0.086	5.584 ± 0.119	3.586×10^4
$(C_6H_{11})_2PH$	8.001 ± 0.092	6.278 ± 0.130	2.512×10^3
PhSH	8.273 ± 0.090	3.790 ± 0.12	3.129×10^5

[a] Reference 9. Indicated errors are one standard deviation (σ).

(p-xylene-d_5) deuterium atoms. The transition states for atom transfer for these systems are expected to involve less planarization of the donor carbon[25] center than in solvolysis reactions, which may display typical α-secondary isotope effects of 1.15 per deuterium and maximum values of 1.26 for limiting solvolyses.[26,27] For hydrogen atom abstraction reactions, the isotope effects would be expected to be comparable to or smaller than those found for radical forming reactions such as the decomposition of α-(phenylethyl)azopropane-α-d (k_H/k_D = 1.15 at 143.2 °C),[28] azobis(α-phenylethane) (k_H/k_D = 1.13 per deuterium at 103 °C),[29] the concerted decomposition of *tert*-butyl peresters of phenylacetic acid (k_H/k_D = 1.06 per deuterium at 84.78 °C),[30] or 2-phenylpropionic acid (k_H/k_D = 1.046 at 73.99 °C),[30] and the β-scission of *tert*-butoxy radical forming methyl or methyl-d_3 (k_H/k_D varies from 1.17 at −9 °C to 1.12 at 75 °C.[31] In eq 5b, applying an isotope effect of 1.20 (g = 1/1.20), which is higher than most experimental data, leads to less than 1% change in $k_{re}/k_{abs(D)}$ and thus was neglected in method A calculations. In eq 6c–e, neglect of the secondary isotope effets will lead to significant differences in the estimates of the percent of 2AT formed from residual hydrogen abstraction vs. 2AT formed from extraneous hydrogen sources. Thus, for method B calculations (eq 5a–d and 6c–e), Koenig's[30] and Seltzer's[28,29] values of isotope effects for azobis(α-phenylethane) and *tert*-butyl 2-phenylperpropionate were scaled and averaged to give the expression $g = 1/(k_H/k_D) \simeq 1/\exp(0.1875(204)/T)$ for an estimated α-secondary isotope effect of 1.092 and 1.19 for one and two deuterium atoms, respectively, at 160 °C. The expression for g retains the form[24] $\exp(0.1875(204)/T)$ to emphasize the small (204 cm^{-1}) frequency changes contributing to the corresponding small changes in transition state and reactant partition functions with deuterium substitution, which are attributed mainly to the out-of-plane CH wagging mode.[24] Tables IV and VI show the resulting estimates of 2AT formed from extraneous sources compared to estimates which neglect the isotope effect (g = 1).

Calculation of Absolute Rate Expressions for Abstraction. Absolute rate expressions for abstraction from the donors of Tables I and II were calculated by combining the absolute rate expression for exo rearrangement (k_{re}) of the 2-allylbenzyl radical with the relative rates, k_{re}/k_{abs}, determined for the various donors. The expression for the exo rearrangement was estimated by combining rate expressions for the abstraction of hydrogen by the benzyl radical from Bu_3SnH, PhSH, and DCPH[9] with the relative rates of rearrangement of the 2-allylbenzyl radical determined in the present work (DCPH and PhSH) and in previous work (Bu_3SnH).[10] Thus, the first three relative rate expressions of Table I were combined with the rate expressions for abstraction in Table III to give three independent estimates of the Arrhenius expression for k_{re}. The average of the three expressions is $\log (k_{re}/s^{-1} = (11.14 \pm 0.30) - (16.28 \pm 0.53)/\theta$. The errors are twice the average deviation in log A and E_a. The sources of error in this procedure have been discussed in a companion paper.[9] The only significant potential source of error derives from extrapolation of data of Table I, determined at a mean temperature of 150 °C to the mean temperature of data of Table III, 35 °C. The final seven hydrocarbon entries of Table I were calculated by using the average expression for k_{re}.

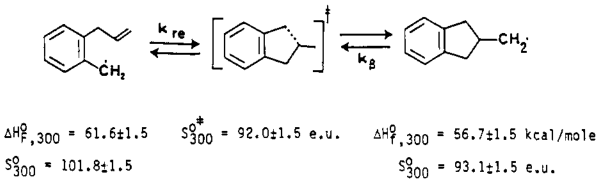

Figure 1. Thermochemical parameters for the 2-allylbenzyl → 2-indanylmethyl interconversion.

Irreversibility of the 2-Allylbenzyl → 2-Indanylmethyl Rearrangement. The absence of detectable 2-allyltoluene from the decomposition of the *tert*-butyl perester of 2-indanylacetic acid is consistent with the irreversibility of the exo rearrangement under the present experimental conditions. Irreversibility is determined by the relative rate of the 2-indanylmethyl → 2-allylbenzyl ring opening reaction (k_β) vs. the much faster abstraction of hydrogen by the 2-indanylmethyl radical from the donor trapping it as 2-methylindan. The thermochemistry of the 2-allylbenzyl → 2-indanylmethyl rearrangement is shown in Figure 1 (see Discussion for details). The entropy of activation for k_{re} is estimated[33] by correction of $S_{300}{}^0$ of 2-indanylmethyl by $R\ln 2$ (1.4 eu) for optical isomerism of the transition state, −2.4 eu for conversion of the hindered (2.4 kcal/mol) methylene rotation to a 500-cm^{-1} olefinic torsion, and −0.1 eu for loss of the 1000-cm^{-1} C–C stretch to the reaction coordinate. Other vibrational corrections to the 2-indanylmethyl radical model of the transition state structure are negligible. thus, $\Delta S_{re}{}^{\ddagger} = 92 - 101.8 = -9.8$ eu, and $\log A_{re} \simeq 11.25$ at 160 °C, assuming $\Delta(\Delta C_{p,T}{}^{\ddagger})$ (300 → 433) $\simeq$ 0.

Benson calculations[33] predict the exo cyclization of 2-allylbenzyl to be exothermic by 4.9 kcal/mol.[34,35] Using this value and the experimental activation barrier, E_{re} = 16.28, allows the estimate of E_β = 21.2 kcal/mol. The use of the experimental barrier, of course, implicitly assumes irreversibility. Fortunately, the validity of this assumption

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(25) The H–C–H angle of the hydrogen of methane undergoing abstraction by methyl radical is predicted to change from 109.47° to 107.4° in the transition state. Rayez-Meaume, M. T.; Dannenberg, J. J.; Whitten, J. L. *J. Am. Chem. Soc.* **1978**, *100*, 747. For the benzyl–toluene reaction, a slightly greater angle change might be expected, but the C–H tetrahedral bending mode will fall substantially short of being converted to the sp^2 out-of-plane bending mode of a fully trigonal center required for the maximum α-secondary isotope effect (ref 24).

(26) Harris, J. Milton; Hall, Robert E.; Schleyer; P. R. *J. Am. Chem. Soc.* **1971**, *93*, 2551.

(27) Dafforn, G. A.; Streitwieser, A., *Jr. Tetrahedron Lett.* **1970**, 3159. Shiner, Jr., V. J.; Buddenbaum, W. E.; Murr, B. L.; Lamaty, G. *J. Am. Chem. Soc.* **1968**, *90*, 418.

(28) Seltzer, S. *J. Am. Chem. Soc.* **1963**, *85*, 14.

(29) Seltzer, S. *J. Am. Chem. Soc.* **1961**, *83*, 2625.

(30) Koenig, T.; Wolf, R. *J. Am. Chem. Soc.* **1969**, *91*, 2574.

(31) Zavitsas, A. A.; Seltzer, S. *J. Am. Chem. Soc.* **1964**, *86*, 3836.

(32) Wiberg, K. B. *Chem. Rev.* **1955**, *55*, 713. Westheimer, F. H. *Ibid.* **1961**, *61*, 265 and references therein.

(33) Benson, Sidney W. "Thermochemical Kinetics. Methods for the Estimation of Thermochemical Data and Rate Parameters", 2nd ed.; Wiley-Interscience: New York, 1976. To estimate $\Delta H°$ for 2-allylbenzyl → 2-indanylmethyl, the enthalpies were calculated for the parent hydrocarbons and BDE's for toluene (88.5 kcal/mol) (ref 34) and primary radicals (100.5 kcal/mol) (ref 35) were applied.

(34) Rossi, M.; Golden, D. M. *J. Am. Chem. Soc.* **1979**, *101*, 1230.

(35) Tsang, W. *J. Am. Chem. Soc.* **1985**, 2872–2880, and references therein. See: Tsang, W. In "Shock Waves in Chemistry"; Lifshitz, A., Ed.; Marcel Dekker: New York, 1981; Chapter 2.

can be checked by comparison with the barrier for β-scission of the cyclopentylmethyl radical to give 5-hexenyl, 22.4 kcal/mol, estimated from the known Arrhenius barrier for the 5-hexenyl cyclization (E_a = 6.85 kcal/mol)[36] and the calculated enthalpy change of the reaction ($\Delta H°$ = −15.6 kcal/mol).[33] Since an MNDO calculation has shown[9] that no benzylic resonance stabilization has developed at the transition state of β-scission of 2-indanylmethyl, the two systems are unlikely to differ by more than about 2 kcal/mol in activation barrier for β-scission. Thus, the reverse reaction, k_β, can be estimated to be $\log (k_\beta/\mathrm{s}^{-1}) = (12.98 \pm 2) - (21.2 \pm 0.6)/\theta$. The rate expression for the abstraction of hydrogen from toluene by methyl radical can be used as an estimate of the rate expression for abstraction of hydrogen by the 2-indanylmethyl radical from xylene: $\log (k_{\mathrm{abs}}/\mathrm{M}^{-1}\,\mathrm{s}^{-1}) = 8.1 - 9.5/\theta$.[37] From these two expressions, the relative rate of ring opening of 2-indanylmethyl vs. abstraction from xylene (43 M abstractable hydrogen concentration) is given by $k_\beta/(k_{\mathrm{abs}}(43\ \mathrm{M}))$. Calculation of $k_\beta/(k_{\mathrm{abs}}(43))$ shows the reverse ring opening reaction to be between 1800 and 200 times slower than abstraction between 120 and 190 °C. Thus, for the decomposition of the perester precursor to 2-indanylmethyl, ring opening of the 2-indanylmethyl radical is predicted to be 230 times slower than abstraction at 160 °C. Substitution of rate constants and donor concentrations for primary radical abstraction from the heteroatom donors of Table I yields similar results. Reversibility of the 2-allylbenzyl → 2-indanylmethyl rearrangement within the temperature range of this study can be confidently ruled out.

Phenolic Donors. Rate constants for phenol, the cresols, and the isomeric hydroquinones (Table II) were determined by adding a solution of **3** in phenylether to the neat donor. The concentrations of the resulting mixture were about 8 M in phenolic donor. Phenol itself was examined both in phenyl ether and dodecane and at the high (8 M) concentrations; relative rates were identical within experimental error, since the added dodecane or phenyl ether comprised only about 15% of the mixture, and in both cases the phenol would be ($\gtrsim$50%) hydrogen bonded at 160 °C. The relationship of the [2AT]/[2MI] ratio to the concentration of phenol in dodecane (Figure 2) revealed a nonlinear dependence with a higher reactivity per total phenol concentration as the total phenol concentration was reduced, showing that hydrogen bonding reduces the reactivity of the phenol at 160 °C. Figure 2 also shows the linear correlation between [2AT]/[2MI] and the nonhydrogen-bonded phenol concentration [PF], obtained by assuming that only free phenol reacts with the radical and that free phenol is in equilibrium with only one other species, the (inert) cyclic trimer, with an equilibrium constant K_3 = 0.175 M^{-2}. Phenol was not sufficiently reactive to permit lowering its concentration to much below 0.1 M, without incurring undesirable side reactions forming 2AT by disproportionation pathways.

Thus, conditions were determined allowing the successful application of the benzylic radical clock to the least reactive phenols and benzylic donors with isolated aromatic ring systems and to heteroatom donors covering seven orders of magnitude in relative rate. However, attempts to extend this study to methylanthracenes and methylquinolines failed. These donors gave very poor material balances, probably due to addition of the 2-indanylmethyl radical to the aromatic systems, followed by trapping of the adducts.

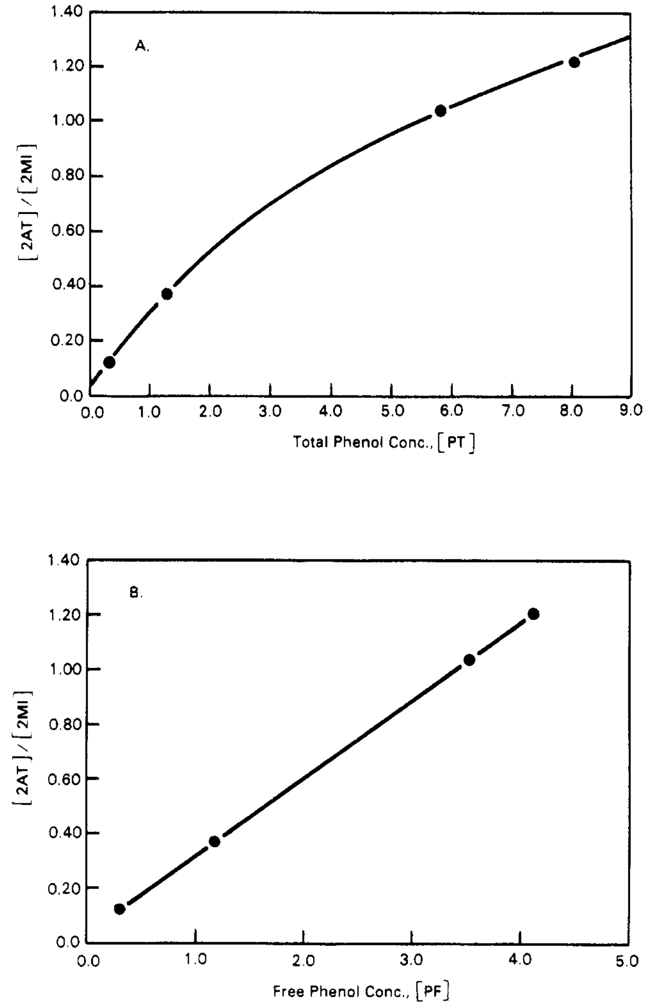

Figure 2. (A) Plot of 2MI/2AT vs. total phenol concentration (M) shows decreasing slope with increasing total phenol, indicating reduced reactivity due to hydrogen bonding. (B) In this plot of nonhydrogen-bonded phenol (M), phenol is assumed to exist as free monomer in equilibrium with a cyclic trimer which is inert to abstraction. For PT = total phenol and PF = free monomer, PT = PF + $3K_3[\mathrm{PF}]^3$. For known values of total phenol, PF was determined by varying K_3 until the best fit of [2AT]/[2MI] vs. PF was obtained for the four experimental concentrations. Each point is the average of three experimental determinations. For K_3 = 0.175 M^{-2}, 2AT/2MI = (0.2865 ± 0.0004)[PF] + (0.031 ± 0.0004).

Discussion

Trends in Relative Rates. Relative rates of abstraction from aralkyl donors (Table II) were found to vary over a factor of 800 from xylene to 9,10-dihydroanthracene. The results presented here are in excellent overall agreement with recent work of Bockrath.[12] The trend generally follows the expected correlation of reactivity the exothermicity modified by differing requirements of entropy in the transition states of abstraction. A notable exception is fluorene. Fluorene is predicted by Stein and Golden's modification of the Herndon resonance theory for radicals[38] to exhibit a BDE 5.3 kcal/mol lower than 9,10-dihydroanthracene (DHA) and, other factors aside, should be significantly more reactive than DHA. Since no differences in A-factors are expected between DHA and fluorene, the

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[36] Chatgilialglu, C.; Ingold, K. U.; Scaiano, J. C. *J. Am. Chem. Soc.* **1981**, *103*, 7739–7742, and references therein.

[37] Cher, M.; Hollingsworth, C. S.; Sicillio, F. *J. Phys. Chem.* **1966**, *70*, 877.

[38] Stein, S. E.; Golden, D. M. *J. Org. Chem.* **1977**, *42*, 839. Equation 5 of this reference predicts E_{RSE} = 23.8 kcal/mol for fluorenyl and 18.5 kcal/mol for 9,10-dihydroanthracen-9-yl radical.

differences in relative rates must be enthalpic in nature: DHA exists in a boat conformation with two pseudoaxial and two pseudoequatorial hydrogens, whereas the central ring of fluorene is nearly planar, with the methylene H–C–H angle bisected by the plane of the aromatic system, leaving the methylene CH tilted by about 20° from the vector normal to the aromatic ring. Thus, in the transition state for abstraction strain energy must be invested to distort the central ring geometry to allow the breaking CH bond to be fully stabilized by resonance with the ring. By contrast, the pseudoaxial hydrogens of DHA are optimally situated for stabilization of the forming radical center by the aromatic rings. This familiar structural effect causes tetralin to be slightly more reactive than indan in hydrogen abstraction reactions.[39]

The familiar effects of entropy in abstraction reactions are also apparent in Tables I and II. The higher reactivity of tetralin compared to 1,2-diphenylmethane is due to the necessity of freezing the phenyl rotation during abstraction from 1,2-diphenylethane, since similar BDE's are expected for the two donors. The effect of rotational entropy is also seen by comparing log A for fluorene-d_2 with that of diphenylmethane-d_2 (Table I). [The deuterated donors should be compared to avoid possible variable effects of tunneling on A-factors with changing exothermicity of the reaction (see below)]. For diphenylmethane-d_2, abstraction requires freezing the rotation of both phenyl rings, involving conversion of one hindered phenyl rotor from a 2 kcal/mol to a 12 kcal/mol barrier and the second phenyl to a ca. 6 kcal/mol barrier.[40] This accounts for most of the difference in log A between fluorene and diphenylmethane. The entropy requirement for freezing out the two hindered phenyl rotations of diphenylmethane is close to that predicted for imposing a 12–13 kcal/mol barrier on the free methyl rotor of toluene. This results in a similar A-factor for xylene-d_6 and diphenylmethane-d_2.

Arrhenius Parameters. The Arrhenius parameters of Table I reveal A-factors for abstraction for aralkyl donors which appear to be somewhat low. Most normal (i.e., gas phase) abstraction reactions of carbon-centered radicals from hydrocarbons are suggested to lie in the range log $(A/\mathrm{M}^{-1}\ \mathrm{s}^{-1}) = 8.5 \pm 0.5$.[33] For the reaction benzyl + toluene, Benson's guidelines for estimating a lower limit of the entropy of activation call for correction of the entropy of a suitable model, bibenzyl, for symmetry, spin, moment of inertia, and significant rotational and vibrational changes. Thus, correction of the model bibenzyl for spin

$PhCH_2CH_2Ph$	$PhCH_2\cdots H\cdots CH_2Ph$
$S_{\mathrm{int}}{}^0 = 117.2$ eu	$S^\ddagger = 120.7$ eu
$\sigma_{\mathrm{ext}} = 2$	$\sigma_{\mathrm{ext}} = 2$

(+1.4 eu), conversion of two hindered benzyl rotations to free rotations (+2.8 eu), conversion of two hindered phenyl rotational barriers from 2 to 12 kcal/mol (−4.4 eu), and correction for an increase in the moments of inertia (1.7 eu) result in $S^\ddagger = 120.7$ eu. Subtracting the entropy of toluene (76.6 eu) and benzyl (75.3 eu) and converting to concentration units by adding 6.4 eu ($R\ln R'T$)[33] provides $\Delta S_{\mathrm{c}}{}^\ddagger \geq -26.6$ eu and $A_{\mathrm{c}}(300\ \mathrm{K}) \geq \frac{e^2kT}{h}e^{-26.6/R} = 7.1 \times 10^7$ $\mathrm{M}^{-1}\ \mathrm{s}^{-1}$. Thus, log $A_{\mathrm{c}} \geq 7.85$ at 300 K. Further correction of the bibenzyl model by replacement of 2 C–C–C bends with two C·H·C–C bends ($400 \rightarrow 280$ (?) cm^{-1}) and replacement of a 1000-cm^{-1} C–C stretch with a symmetric C·H·C stretch at 700 (?) cm^{-1} will contribute an additional 1.4 eu to give log $A_{\mathrm{c}} = 8.16$. On this basis, Jackson and O'Neill's Arrhenius parameters for benzyl + toluene, log $(k_{\mathrm{abs}}/\mathrm{M}^{-1}\ \mathrm{s}^{-1}) = 10.5 \pm 3.5 - 19.9 \pm 2.0/\theta$, have been criticized for being unusually large. Stein[41] and Poutsma[7] have assumed Jackson and O'Neill's rate constant at their mean temperature to be correct and assigned log $(A/\mathrm{M}^{-1}\ \mathrm{s}^{-1}) = 8.0$ to give the estimated rate expression log $(k_{\mathrm{abs}}/\mathrm{M}^{-1}\ \mathrm{s}^{-1}) = 8.0 - 16.1/\theta$. Gilbert and Gajewski[8] assigned log $(A/\mathrm{M}^{-1}\ \mathrm{s}^{-1}) = 8.5$ for the benzyl and toluene reaction. It is somewhat typical of kinetic determinations of this type that although our Arrhenius parameters for the xylenes (Table I) are in gross disagreement with Jackson and O'Neill's[4] results, our rate constants for m-xylene (2.2 $\mathrm{M}^{-1}\ \mathrm{s}^{-1}$) and p-xylene (2.36 $\mathrm{M}^{-1}\ \mathrm{s}^{-1}$) are in agreement with their results (2.89 $\mathrm{M}^{-1}\ \mathrm{s}^{-1}$) at approximately the mean temperature of both studies. We now can compare the present A-factors (Table I) with the A-factors predicted by the simple model discussed above for a tight transition state. Since tunneling may lower the observed Arrhenius parameters for abstraction (see below), the A-factors for deuterium abstraction, which do not involve tunneling, should be compared to the predicted A-factors. It is customarily assumed that in the absence of tunneling, $A_{\mathrm{H}}/A_{\mathrm{D}} = 1$.[42,43] Although few examples of temperature dependent studies are available for radical abstractions, Zavitsas' competition of methyl vs. methyl-d_3 formation from the β-scission of the *tert*-butoxy radical gives $A_{\mathrm{H}}/A_{\mathrm{D}} = 0.98$.[25] Thus, while log $(A_{\mathrm{H}}/\mathrm{M}^{-1}\ \mathrm{s}^{-1})$ for m-xylene and p-xylene, 7.10 and 7.13, definitely appear low, log $(A_{\mathrm{D}}/\mathrm{M}^{-1}\ \mathrm{s}^{-1}) = 7.67 \pm 0.37$ for p-xylene-d_6 is only low by perhaps 0.4 in log A units, i.e., within statistical experimental error of the roughly estimated lower limit of the gas phase log A value for benzyl + toluene. Most of this error, if it is error, would derive from error in Arrhenius expression for the 2-allylbenzyl → 2-indanylmethyl rearrangement, since the statistical errors in log $(A_{\mathrm{re}}/A_{\mathrm{abs}})$ values (Table I) are quite low, as is typical for relative rate expressions, and there are no apparent sources of systematic errors in the relative rate determinations. Fortunately, the structural similarity of the transition state structure (Figure 1) of the rearrangement of **1** → **2** to the structure of the 2-indanylmethyl radical allows a reasonably reliable estimate of the A-factor for the rearrangement by applying corrections to the 2-indanylmethyl radical. Errors in the estimated entropies (Figure 1) are probably not greater than ±1.5 eu. Thus, $\Delta S_{300}{}^\ddagger = 9.8 \pm 2.1$ eu for the 2-allylbenzyl → 2-indanylmethyl reaction, and log $A_{\mathrm{re}} = 11.09 \pm 0.46$ at 300 K and log $A_{\mathrm{re}} \simeq 11.3 \pm 0.5$ at 433 K, the mean temperature of this work, assuming $\Delta(\Delta C_{p,T}{}^\ddagger) \simeq 0$ over this temperature range. The experimental value, log $A_{\mathrm{re}} = 11.18 \pm 0.3$ thus lies well within the expected range. These considerations lead us to suspect that log A_{re} is not low by more than ca. 0.3 and that the measured log A_{abs} values (Table I) for p-xylene, m-xylene, and diphenylmethane are within 0.3 of the true values, and we are probably justified in looking beyond systematic experimental error for the source of the low A-factors.

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[39] Russell, G. In "Free Radicals"; Kochi, J. K., Ed.; Wiley-Interscience: New York, 1973; Vol. I, p 302.

[40] Rossi, M. J.; McMillen, D. F.; Golden, D. M. *J. Phys. Chem.* **1984**, *88*, 5031–5039.

[41] Stein, S. E. *ACS Symp. Ser.* **1981**, No. 169, p 97. Robaugh, D. A. Ph.D. Thesis, West Virginia University, Morgantown, WV, 1983.

[42] A theoretical study of a variety of systems involving hydrogen transfer between carbon centers revealed all values of $A_{\mathrm{H}}/A_{\mathrm{D}}$ to lie between 0.7 and 1.2, with $A_{\mathrm{H}}/A_{\mathrm{D}}$ usually close to 1, see: ref 43a, Chapter 4, and Schneider, M. E.; Stern, M. J. *J. Am. Chem. Soc.* **1972**, *94*, 1517.

[43] (a) Bell, R. P. "The Tunnel Effect in Chemistry"; Chapman and Hall: New York, 1980; Chapter 4. (b) See also "Proton-Transfer Reactions"; Caldin, Edward, Gold, Victor, Eds.; Chapman and Hall: London, Chapters 8 and 10, and references therein.

Table IV. Isotope Effects and Formation Pathways of 2AT in the Reactions of the 2-Allylbenzyl Radical with *p*-Xylene-d_6 (Method B)

temp °C	$k_{abs(H)}/k_{abs(D)}$	contribution to 2AT, %		
		% d_1[a]	% d_0, res[b]	% d_0, E[c]
189.6	7.26	94 (94.36)	5.7 (4.9)[d]	0 (0.8)[d]
180.0	7.77	93 (92.97)	6.0 (5.1)[d]	1.0 (1.9)[d]
170.2	8.35	84 (91.55)	6.4 (5.4)[d]	2.0 (3.1)[d]
160.6	9.00	89 (90.16)	6.8 (5.7)[d]	3.0 (4.1)[d]
149.8	9.82	91 (88.59)	7.3 (6.1)[d]	4.1 (5.3)[d]
140.0	10.68	88 (87.17)	7.8 (6.5)[d]	5.0 (6.3)[d]
130.2	11.66	84 (85.75)	8.4 (6.9)[d]	5.9 (7.3)[d]

[a] Experimental values of % d_1 in 2AT, with least-squares value (fit excludes 170.2 °C point) of % d_1 vs. T (°C) in parentheses. The values in parentheses were used to calculate the Arrhenius expression for $k_{re}/k_{abs(D)}$ (eq 6a) and $k_{abs(H)}/k_{abs(D)}$ from the Arrhenius expression for $k_{re}/k_{abs(H)}$ of *p*-xylene. The value of E' in eq 6c was also evaluated by using the least-squares % d_1 values. [b] Percent of 2-allyltoluene formed by abstraction of residual hydrogen in the donor, calculated from eq 6d, with $g = 1$. [c] Percent of 2-allyltoluene formed by abstraction from impurities or in disproportionation reactions, calculated from eq 6e, with $g = 1$. [d] Calculated from eq 6d and 6e with $g = (1/\exp(0.1875 \times 204/T))^2$.

Isotope Effects and Tunneling. The Westheimer treatment of primary isotope effects[32] predicts a maximum value of k_H/k_D for a transition state in which the hydrogen is symmetrically bonded to the atoms between which it is transferred. For the case in which vibrations in the transition state are isotopically insensitive or cancel those of the reactant, the full zero-point energy differences of the protonated and deuterated reactant will be reflected in k_H/k_D. Theories of tunneling in hydrogen atom transfer also predict a maximum tunnel effect for the symmetrical, thermoneutral transition state,[43] and, thus, maximum tunnel effects are superimposed on maximum conventional isotope effects for the near thermoneutral reactions. In the absence of tunneling, the maximum isotope effect for hydrogen transfer between carbon centers is estimated from the relation $k_H/k_D = \exp[h(\nu_H - \nu_D)/2kT]$, where $h(\nu_H - \nu_D)$ is the difference in reactant zero-point energies. This expression predicts maximum primary isotope effects of 3.3, 4.7, and 7 at 190, 130, and 25 °C for a difference in ground-state zero-point energy corresponding to the CH or CD stretching vibration of 1.1 kcal/mol. Primary isotope effects substantially in excess of these values, accompanied by values of $A_H/A_D < 0.5$ and $E_D - E_H > 1.1$ kcal, are attributed to tunneling or experimental error.[43] For direct comparison of the observed isotope effects with the maximum predicted values, the values of Tables IV–VII must be corrected for α-secondary isotope effects for abstraction of deuterium from carbon-centered radicals substituted with one (diphenylmethane-d_2 or fluorene-d_2) or two (*p*-xylene-d_6) deuterium atoms. A guide to the magnitude of these corrections comes from studies of isotope effects for reactions forming radical centers substituted with deuterium atoms. As discussed above, this correction of k_H/k_D for abstraction of hydrogen from partially labeled residual hydrogen in the donor was applied to convert available rates of abstraction from the fully protonated donors to obtain the slightly retarded rates for the d_1- or d_2-substituted donor compounds. Note that the primary isotope effects of Tables IV–VII retain the effects of multiple deuterium labeling in the deuterated donor. While no measurements of α-secondary isotope effects in abstraction reactions from benzylic donors have been reported, studies of isotope effects on the formation of benzyl, phenethyl, and methyl radicals have reported values of k_H/k_D for radical forming reactions of 1.1 ± 0.1 at 130 °C.[28-32] This range of k_H/k_D values will contribute 0.08 ± 0.08 kcal/mol to $E_D - E_H$ for one deuterium atom substituted at the forming radical center and 0.15 ± 0.08 kcal/mol for two deuterium atoms. Thus, maximum values of $E_D - E_H$ of 1.18 ± 0.1 kcal/mol for diphenylmethane-d_2 and fluorene-d_2 and 1.25 ± 0.1 kcal/mol for *p*-xylene-d_6 are expected in the absence of tunneling. Applying these corrections to $E_D - E_H$ values reveals that fluorene-d_2, diphenylmethane-d_2, and *p*-xylene-d_6 exceed normal $E_D - E_H$ values of 1.18, 1.18, and 1.25 kcal/mol after correction for secondary effects by 0.24, 1.4, and 1.7 kcal/mol, as $\Delta H°$ progresses from the most exothermic reaction (fluorene) to the thermoneutral reaction (*p*-xylene). Similarly, correction of k_H/k_D values by $g = 1/\exp[0.1875(204)/T]$ or g^2 (*p*-xylene) for secondary isotope effects gives k_H/k_D for *p*-xylene of 6.16, 9.64, and 33.7 at 190, 130, and 25 °C. For diphenylmethane, k_H/k_D = 5.99, 8.17, and 23.3 at 190, 120, and 25 °C. For fluorene, k_H/k_D = 4.4, 5.2, and 9.4 at 190, 130, and 25 °C. *p*-Xylene and diphenylmethane, after correction for the expected magnitude of the secondary isotope effect, exhibit isotope effects substantially greater than the maximum conventional values of 3.3, 4.7, and 7 at 190, 130, and 25 °C. Note that the 25 °C values are extrapolations which will be lower than the actual values if concave upward curvature in the Arrhenius plots is occurring. Fluorene is only slightly above the conventional maximum value of k_H/k_D. Finally, A_H/A_D for xylene, diphenylmethane, and fluorene increases from 0.25 to 0.33 to 1.1. This trend is consistent with a decreasing participation of tunneling as the abstraction reaction becomes increasingly exothermic.

Of the three criteria cited as evidence for tunneling,[43] values of $A_H/A_D < 0.5$, $E_D - E_H >$ 1.1–1.3 kcal/mol for the present cases, and concave upward curvature of the Arrhenius plot for hydrogen transfer to the protonated species, the latter effect is rarely observed since it requires large temperature ranges in order to observe modest curvature. The fit of hydrogen transfer data to a small range of mildly concave upward curve of log (k_{abs}) vs. $1/T$ may give an excellent linear correlation but will produce an intercept smaller than that of the high temperature portion of the true temperature dependence, producing a correspondingly low value of log (A_{abs}). The data of this work appear to fulfill these criteria, although accurate rate expressions over a much wider temperature range are needed to observe a failure of the simple Arrhenius formulation. We suggest that tunneling is detectable for xylene and diphenylmethane and low or negligible for the more exothermic reaction of fluorene.

Evidence for Reversible Addition of 2-Indanylmethyl Radical to Aromatic Rings of Donors. The facile addition of alkyl radicals to aromatic rings is well-known.[44] Activation parameters for addition of alkyl radicals to substituted benzenes are comparable to those for addition to olefins: log $A = 8 \pm 1$ and $E_a = 8 \pm 2$ kcal/mol.[45] As pointed out by Zavitsas,[46] a number of studies of hydrogen abstraction by primary and secondary alkyl radicals[47-51] from substituted toluenes have involved

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(44) Reference 5, p 92 and references cited therein.

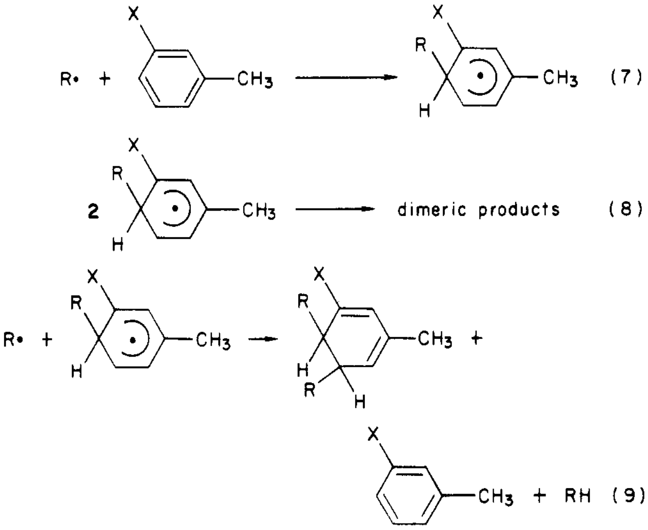
(45) (a) Tedder, J. M.; Walton, I. C. In "Advances in Physical Organic Chemistry"; Gold. V., Bethell, D., Eds.; Academic Press: New York, 1978; Vol. 16. (b) Kerr, J. A. In "Free Radicals"; Kochi, J. K., Ed.; Wiley-Interscience: New York, 1973; Vol. 1.

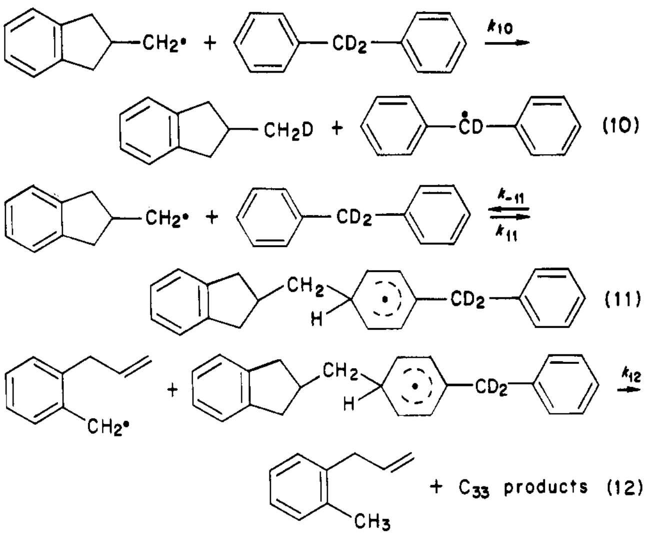
(46) Zavitsas, A. A.; Solademi, A. O.; Arafat, A. M.; Clonmell, M. A.; Matthew, S. K.; Morris, C. D. *J. Am. Chem. Soc.*, submitted for publication.

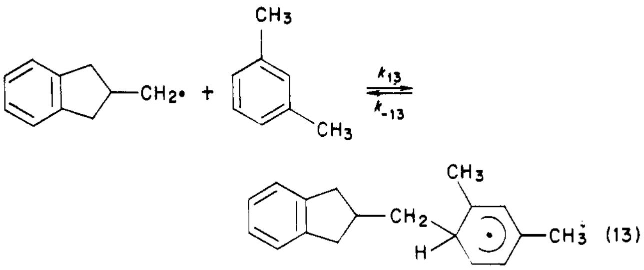
(47) Henderson, R. W.; Ward, R. D. *J. Am. Chem. Soc.* 1974, *96*, 7556–7557.

(48) Pryor, W. A.; Davis, Jr., W. H. *J. Am. Chem. Soc.* 1974, *96*, 7557–7559.

(49) Henderson, R. W. *J. Am. Chem. Soc.* 1975, *97*, 213–215.







addition of a substantial fraction of the alkyl radicals to the aromatic rings of the donors. Under conditions of effectively irreversible addition of R· (eq 7–9) to aromatic rings of substituted toluenes, both adducts and dimers of adducts provide sources of hydrogen formation of RH by abstraction from species other than the intended donor. Zavitsas[46] has suggested that observed reactivities reported in several studies[47–51] of the alkyl radicals "do not pertain exclusively, or even predominantly, to benzyl hydrogen abstraction". The dimers of the adducts to the substituted toluenes as well as the adducts can provide reactive sources of hydrogen. In light of these observations, our first attempts to test for exclusive abstraction by the 2-allylbenzyl radical from the intended donor by using deuterated donors were discouraging, with substantial percentages of the product 2-allyltoluene containing no deuterium, accompanied by material balances occasionally as low as 70%, in experiments which utilized concentrations of ca. 10^{-2} M azo-2-allyltoluene. By lowering the concentration of azo-2-allyltoluene from 10^{-3} to 10^{-4} M, it was found that material balances based on the azo-2-allyltoluene increased to around 95% or higher and deuterium labeling of the azo-2-allyltoluene indicated, after correction for residual hydrogen in the donors, that the donor was the only significant source of hydrogen. These results are consistent with the *reversible* addition of 2-indanylmethyl to available aromatic systems, as depicted in eq (10–12) diphenylmethane-d_2. Trapping of the adduct of 2-indanylmethyl to the aralkyl donor by disproportionation with 2-allylbenzyl will lead to 2AT without deuterium label. Combination with any available radicals will lead to an apparent reduction in yield, since the adducts (C_{33} products in eq 12) in many cases will not survive GC conditions. For the 2-indanylmethyl radical to be trapped quantitatively as 2-methylindan by abstraction from the donor (eq 10) under circumstances that addition to the ring(k_{-11}) of the donor occurs at a rate comparable to abstraction demands that scission (k_{11}) of the aromatic adduct must occur many times for each irreversible termination event (eq 12). Scission should be $\gtrsim 10^2$ faster than termination to avoid adduct trapping. Similarly, for exclusive formation of 2-allyltoluene by abstraction from the donor, the pseudo-first-order abstraction from the donor must be much faster than the second-order termination route (eq 12). This can be illustrated for the donor xylene. The barrier to scission of 2-indanylmethyl radical from its xylene adduct (k_{13}) can be estimated by adding the barrier of addition, $E_{13} = 8 \pm 2$ to $\Delta H_{-13}^0 = 14 \pm 2$ to obtain $E_{-13} = 22 \pm 3$ kcal/mol.[33,35,45] The *A*-factor for scission will be $\geqslant 10^{15}$ s^{-1}, so that log (k_{-13}/s^{-1}) $\simeq$ 15–22/θ. The relative rate of scission vs. termination of 2-indanylmethyl will be given to good approximation by $10^{(15-22/\theta)}/k_t[\mathrm{R}\cdot]$, where [R·] is the total radical concentration. At steady-state conditions, $[\mathrm{R}\cdot] = (k_d[\mathbf{3}]/k_t)^{1/2}$, where k_d is the rate constant for unimolecular decomposition of the radical precursor, **3**, and k_t is the rate constant for termination, $k_t \simeq 10^{10}$ M^{-1} s^{-1}. The ratio of scission to termination, given by $10^{(15-22/\theta)}/k_t(k_d[\mathbf{3}]/k_t)^{1/2}$, will be 100 for [**3**] = 9 × 10^{-4} M at 190 °C and [**3**] = 1.1 × 10^{-4} M at 120 °C. These concentrations correspond to the experimental concentrations of **3** which gave negligible formation of 2-allyltoluene in termination reactions and good material balances. The 2-indanylmethyl radical must also abstract hydrogen much faster than it engages in termination. The rate of abstraction from xylene by 2-indanylmethyl relative to termination is given approximately by $10^{8.5-8.5/\theta}[\mathrm{DHC}]/k_t(k_d[\mathbf{3}]/k_t)^{1/2}$. For [DHC] = 43 M (xylene) and [**3**] = 1 × 10^{-3}, the ratio of abstraction to termination is 3 × 10^3 at 190 °C and 1.3 × 10^4 at 120 °C. Thus, we conclude that concentrations of **3** between 1 × 10^4 M and 1 × 10^{-3} M will lead to complete recovery of the 2-indanylmethyl radical as 2-methylindan, even though it undergoes addition to the arylalkyl rings at a rate comparable to abstraction from the donor. Our observation of poor deuterium incorporation in 2-allyltoluene at concentrations of **3** higher than ca. 5 × 10^{-2} M with some aralkyl donors is fully consistent with trapping of the reversibly formed 2-indanylmethyl adduct by the 2-allylbenzyl radical.

Thus, conditions for the successful application of the radical clock method required identifying temperature limitations of irreversibility of the radical rearrangement, suitable concentrations of donors allowing detection of rearranged or unrearranged hydrocarbon products, and control of the radical concentration by lowering the pre-

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(50) Davis, Jr., W. H.; Pryor, W. A. *J. Am. Chem. Soc.* **1977**, *99*, 6365–6372.

(51) Tanner, D. D.; Henriquez, R.; Reed, D. W. *Can. J. Chem.* **1979**, *57*, 2578–2584.

cursor concentration to the lowest practicable level.

Phenolic Donors. The phenolic donors of Table II contained about 8.1 M of phenolic donor, and, thus, much of the phenolic hydrogen was hydrogen bonded. Studies which have attempted to quantify the equilibrium concentrations of non-hydrogen-bonded phenol by NMR have successfully utilized simple models with typically two equilibrating species (monomer–dimer or monomer–trimer) in solutions of phenol in hydrocarbons.[52,53] At 20–50 °C in cyclohexane, a model of phenol with free phenol in equilibrium with a cyclic trimer is suggested,[52,53] with K_3 values of 17.0, 4.4, and 16 M^{-2} at 20, 35, and 50 °C, corresponding to a hydrogen bond strength of 4.7 kcal/mol. Cresols are suggested to exist in a monomer–trimer equilibrium,[53] while 2-hydroxyphenol exists in a monomer–dimer equilibrium. The trend of K_3 at different temperatures suggests that K_3 will be very small, $<10^{-1}$ M^{-2} at 160 °C. To test the monomer–trimer model for phenol, we assumed the cyclic trimer to be inert to hydrogen abstraction and that only monomeric phenol will undergo abstraction. The equilibrium constant, K_3, was varied, and the concentration of free phenol was calculated for each total value (8.05, 5.81, 1.27, and 0.31 M) until the best least-squares fit of [2AT]/[2MI] vs. corrected phenol concentration was achieved. At $K_3 = 0.175$ M^{-2}, a plot of [2AT]/[2MI] vs. the corrected phenol concentrations gave a linear correlation coefficient $r^2 = 1.0$ and $k_{abs}/k_{re} = 0.287$ M^{-1} as shown in Figure 2. Thus, excellent agreement with the model of a single reactive species, free phenol, and an inert cyclic trimer is apparent. A plot of ln K_3 vs. $1/T$ gave $r = 0.997$ for the three literature values of K_3[52,53] in cyclohexane plus $K_3 = 0.0175$ M^{-2} in dodecane determined here.

Thus, for the phenols of Table II, the monomer–trimer equilibrium model predicts the concentration of free phenol to be 50% for the 8 M solutions and 99% free phenol at 0.3 M total phenol at 160 °C. The values of k_{abs}/k_{re} of Table II for phenolic donors at 8 M should be multiplied by ca. 2 to obtain k_{abs}/k_{re} of the free phenol if the monomer–trimer model is correct. The values for phenol and cresol at 8 M are in good agreement with results of Bockrath for abstraction of hydrogen from 5-hydroxyindan.[2] Arrhenius parameters for the reaction of 2-allylbenzyl with phenols will be presented in a separate study.

Conclusions

The 2-allylbenzyl → 2-indanylmethyl rearrangement provides precise relative rate expressions for hydrogen donors covering a wide range of reactivity for a wide variety of donors. Thermochemical estimates of the *A*-factor for the radical clock reaction indicate that the Arrhenius parameters for the clock reaction are sufficiently accurate to support tunneling for the reactions of **1** with xylene and diphenylmethane, as suggested by the primary isotope effects. More accurate calculations of the thermochemical parameters would be valuable to support this conclusion, and calculation of appropriate vibrational and rotational quantities using semiempirical MO methods are underway for the benzyl–toluene reaction and deuterated analogues as well as for the rearrangement of **1** → **2**.

For single-ring aromatic systems, conditions have been identified for which reversible addition of the rearranged radical may occur without its loss as an adduct to the aromatic system giving the 2-allylbenzyl radical clock the broadest applicability for determination of benzyl radical atom transfer rate expressions.

For phenol, the present results support the monomer–trimer equilibrium associaton model and reveal the concentration dependence of the hydrogen atom donating characteristics of phenols to be a useful measure of hydrogen bonding.

Registry No. *o*-($CH_2{=}CHCH_2$)$C_6H_4CH_2$, 75421-42-0; PhSH, 108-98-5; Bu_3SnH, 16216-29-8; *p*-$Me_2C_6H_4$, 106-42-3; *m*-$Me_2C_6H_4$, 108-38-3; Ph_2CH_2, 101-81-5; $Ph(CH_2)_2Ph$, 103-29-7; $CH_2{=}CHCH_2Ph$, 300-57-2; PhOH, 108-95-2; H_2, 1333-74-0; D_2, 7782-39-0; dicyclohexylphosphene, 829-84-5; fluorene, 86-73-7; mesitylene, 108-67-8; tetralin, 119-64-2; 9,10-dihydrophenanthrene, 776-35-2; 9,10-dihydroanthracene, 613-31-0; *p*-cresol, 106-44-5; *m*-cresol, 108-39-4; *o*-cresol, 95-48-7; *p*-hydroquinone, 123-31-9; *m*-hydroquinone, 108-46-3; *o*-hydroquinone, 120-80-9.

Supplementary Material Available: Tables V–XVI provide detailed kinetic data for the entries of Table I and isotopic analytical data for the deuterated donors. Figures 3–11 provide Arrhenius plots for data of Table I (except Bu_3SnH) (24 pages). Ordering information is given on any current masthead page.

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