4:1) for elution to yield 35 mg (8%) of (+)-(*R*)-**13** [$[\alpha]^{24}_{\mathrm{Hg}}$ +21° (*c* 0.3, $CHCl_3$, optically pure)] and 13 mg (2%) of 1-fluoro-1-(phenylseleno)-2,2-diphenylcyclopropane [mp 91–3 °C; $[\alpha]^{24}_{\mathrm{Hg}}$ +221° (*c* 0.12, $CHCl_3$); ^1H NMR ($CDCl_3$) δ 2.12 (1 H, dd, *J* = 7.2, 8.4), 2.16 (1 H, dd, *J* = 7.2, 14.4), 7.2–7.35 (11 H, m), 7.4–7.55 (4 H, m)].

Anal. Calcd for $C_{21}H_{17}FSe$: C, 68.66; H, 4.66. Found: C, 68.49; H, 4.68.

Phenyl (+)-(*R*)-1-fluoro-2,2-diphenylcyclopropaneselenocarboxylate was isolated in 48% yield (0.38 g): mp 114–5°, $[\alpha]^{24}_{\mathrm{Hg}}$ +339° (*c* 1.2, $CHCl_3$); ^1H NMR ($CDCl_3$) δ 2.25 (1 H, dd, *J* = 6.6, 18.3), 2.47 (1 H, dd, *J* = 6.6, 9.3), 7.1–7.5 (15 H, m); IR (Nujol) 1710, 1500, 9.55 cm^{-1}.

Anal. Calcd for $C_{22}H_{17}FOSe$: C, 66.84; H, 4.33. Found: C, 66.73; H, 4.38.

E. A 10-mL benzene solution of ester **3** (2 mmol prepared as in **D** above) and 1 mL of thiophenol were refluxed for 0.5 h. The usual workup procedure afforded phenyl disulfide (0.35 g) (mp 57–8 °C; (+)-(*R*)-**13** (0.16 g, 38%) [$[\alpha]^{24}_{\mathrm{Hg}}$ +21.0° (*c* 1.5, $CHCl_3$, optically pure)]; and phenyl (+)-(*R*)-1-fluoro-2,2-diphenylcyclopropanethiocarboxylate (0.115 g, 18‰) [mp 103–4 °C (from hexane); $[\alpha]^{24}_{\mathrm{Hg}}$ +402° (*c* 0.5, $CHCl_3$); ^1H NMR ($CDCl_3$) δ 2.21 (1 H, dd, *J* = 6.9, 18.3), 2.50 (1 H, dd, *J* = 6.9, 9.6), 7.1–7.4 (13 H, m), 7.52 (2 H, d, *J* = 8); IR (Nujol) 1700, 1500, 970 cm^{-1}.

Anal. Calcd for $C_{22}H_{17}FOS$: C, 75.84; H, 4.92. Found: C, 75.82; H, 4.97.

Absolute Rate Constants for the β-Scission Reaction of the 1-Phenyl-2-phenoxypropyl Radical: A Model for Radical Reactions of Lignin[1]

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Absolute rate expressions for β-scission of the phenoxy radical from the 1-phenyl-2-phenoxypropyl radical, forming *cis*- and *trans*-β-methylstyrene, were determined by competition of β-scission (k_β) with abstraction of hydrogen from trimethylstannane (k_{abs}). Relative rates (k_β/k_{abs}) were converted to absolute rates (k_β) by using a rate expression determined for abstraction of hydrogen atom from tributylstannane by the phenylethyl radical: $\log [k_{\mathrm{abs}}/(\mathrm{M^{-1}\,s^{-1}})] = (9.31 \pm 0.30) - (7.11 \pm 0.49)/\theta$, where $\theta = 2.303RT$ kcal/mol (errors are 2σ). The resulting expressions for β-scission are $\log (k_{\beta,\mathrm{trans}}/\mathrm{s^{-1}}) = (13.45 \pm 0.26) - (16.94 \pm 0.52)/\theta$ and $\log (k_{\beta,\mathrm{cis}}/\mathrm{s^{-1}}) = (13.41 \pm 0.3) - (19.3 \pm 0.75)/\theta$. The basis rate expression for abstraction of hydrogen from tributylstannane by the phenylethyl radical was determined in a competition of abstraction (k_{abs}) with self-termination (k_t), using the Smoluchowski expression for self-reaction of phenylethyl radical: $\log [2k_t/(\mathrm{M^{-1}\,s^{-1}})] = 11.93 - 3.112/\theta$. Combining the Arrhenius parameters with the enthalpy change for β-scission leads to activation barriers for addition of phenoxy radical to *trans*- and *cis*-β-methylstyrene of 5.2 and 6.6 kcal/mol, respectively.

Introduction

A predominate structural cross-link in the macromolecular network of lignin is the aryl β-aryl ether linkage, –(ArOCCAr)–.[2] Solid-state NMR studies suggest that alkyl aryl ether linkages may be present in modest extent in low-rank coals.[3] A detailed understanding of the free-radical[4] and radical cation[5] chemistry of lignin is necessary for the design of new processes of pulp preparation,[5] the understanding of pathways of hydrothermal conversion of biomass and coal to useful products,[6] and understanding the process of coalification of lignocellulosic structure.[7] The thermal decomposition of model compounds[6] and polymers[7] containing known structural units of lignin or proposed structural links in coal under hydroliquefaction conditions is a valuable exercise since direct observation of structurally distinct reactions remains nearly impossible for coal and difficult for lignin. Under ideal circumstances, the global kinetics and kinetic reaction order of thermal decomposition reactions of model compounds containing linkages of relevance to lignin and coal structure can be reduced to the contributing individual stepwise rate constants. The careful studies by Poutsma and Dyer[8] and Gilbert and Gajewski[9] of the homogeneous thermal decomposition of 1,*n*-diphenylalkanes (*n* = 2–4) and the studies of Buchanan and co-workers of heterogeneous decomposition of similar structures bonded to silica surfaces[10] provide examples of successful reduction of global rates to individual contributing rates. However, even the early stages of thermal decompositions of nominally simple systems may involve multiple initiation and propagation steps and early participation of secondary reactions. For these cases, design of experiments to directly determine individual reaction steps is desirable. A recent model compound study[9] examined radical chain decomposition pathways for cleavage of the C–O bond in phenyl 2-phenylethyl ether, as a model of reactions of similar structures presumably in low-rank coals. A free-

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[1] This work was supported by the Office of Basic Energy Sciences, U.S. Department of Energy (DOE), under contract DE-AC06-76RLO-1830 with Battelle Memorial Institute, which operates the Pacific Northwest Laboratory for DOE.

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radical chain decomposition pathway was suggested for the thermal decomposition of phenyl 2-phenylethyl ether (eqs 1–4). The decomposition of this ether is initiated in the early stage of decomposition by unimolecular cleavage of the ether to form phenoxyl and phenylethyl radicals (eqs 1 and 2). Chain-propagation steps include abstraction of the benzylic hydrogen of the ether and β-scission of the resulting 1-phenyl-2-phenoxyethyl radical to form styrene and phenoxy radical (eq 3), followed by termination reactions (eq 4). A global activation barrier of 50.3 kcal/mol

$$\mathrm{PhCH_2CH_2OPh \rightarrow PhCH_2CH_2^{\bullet} + {}^{\bullet}OPh} \tag{1}$$

$$\mathrm{PhCH_2CH_2OPh + PhO^{\bullet} \rightarrow PhCH(^{\bullet})CH_2OPh + PhOH} \tag{2}$$

$$\mathrm{PhCH(^{\bullet})CH_2OPh \rightarrow PhCH{=}CH_2 + {}^{\bullet}OPh} \tag{3}$$

$$\left.\begin{array}{l}\mathrm{2PhO^{\bullet} \rightarrow} \\ \mathrm{PhO^{\bullet} + PhCH(^{\bullet})CH_2OPh \rightarrow}\end{array}\right\}\text{nonradical products} \tag{4}$$

was reported for the decomposition of the ether, compared to 65 kcal/mol for unimolecular scission of the C–O bond (eq 1), reflecting a chain process. A barrier for β-scission (eq 3) was reported to be 28 kcal/mol,[9] although details of how this value was obtained were not given. This value matches the barrier for β-scission of 1,3-diphenylpropyl radical,[8] for which Poutsma and Dyer estimate $\log (k_5/\mathrm{s}^{-1}) = 14.8 - 28.3/\theta$, $\theta = 2.3RT$ kcal/mol:

$$\mathrm{PhCH(^{\bullet})CH_2CH_2Ph \rightarrow PhCH{=}CH_2 + PhCH_2^{\bullet}} \tag{5}$$

The value of 28 kcal/mol for eq 3 is in significant disagreement with a recent investigation of substituent effects in the β-scission of $\mathrm{PhCH(^{\bullet})CH(CH_3)OPh}$ in competition with hydrogen abstraction from trimethylstannane.[11] That study estimated a barrier of no more than 19 kcal/mol for the β-scission reaction of the structurally similar radical. The discrepancy may reflect the incursion of a variety of second-generation reactions in addition to those of eqs 1–4, making analysis of initial rates of reaction and the overall reaction order difficult and ambiguous. Thus, to provide an accurate value for the β-scission reaction, and to provide a kinetic basis for prediction of radical-based degradation pathways for lignin or low-rank coal structure, we have determined an absolute rate expression for the β-scission of the 1-phenyl-2-phenoxypropyl radical. Arrhenius parameters for scission of this model of the ArCCOAr linkage in lignin by a free-radical pathway and estimates for the reverse reaction, addition of phenoxy radical to β-methylstyrene, are presented.

Results and Discussion

Abstraction of Hydrogen from Tributylstannane by Phenylethyl Radical. Although a rate expression for abstraction of hydrogen atom from $\mathrm{Bu_3SnH}$ by benzyl radical has been published,[12] rate constants for the reaction of alkyl-substituted benzylic radicals with $\mathrm{Bu_3SnH}$ or $\mathrm{Me_3SnH}$, suitable for use as basis rate constants for conversion of relative rates of β-scission vs abstraction (k_β/k_{abs}) to absolute rates (k_β), have not appeared. Thus, an Arrhenius expression for abstraction of hydrogen by the phenylethyl radical from $\mathrm{Bu_3SnH}$ (k_{abs}) was determined by a competition of self-termination of the phenylethyl radical with abstraction. The self-termination rates were in turn calculated by using the Smoluchowski equation (eq 6), which predicts rates of self-reaction of small, carbon-centered radicals in nonassociating solvents of low viscosity with typically less than 15% error:[13-16]

$$2k_t = (8\pi/1000)\sigma\rho D_{\mathrm{AB}}N \tag{6}$$

Table I. Arrhenius Parameters and Rate Constants for Abstraction of Hydrogen by Alkyl and Benzylic Radicals from Tributylstannane[a]

radical	log A	E_a	k(25 °C) × 10^4	solvent
phenylethyl[b]	9.24 ± 0.30	7.11 ± 0.49	1.1	benzene
benzyl[c]	8.65 ± 0.17	5.58 ± 0.24	3.6	c-C_6H_{12}
methyl[d]	9.39 ± 0.28	3.23 ± 0.34	1050	isooctane
isopropyl[d]	8.71 ± 0.37	3.47 ± 0.49	146	isooctane

[a] Errors are 2σ. [b] This work. [c] Reference 12. [d] Reference 20.

By analogy with the benzyl radical and other small hydrocarbon radicals, the phenylethyl radical will exhibit a spin statistical factor (σ) near $^1/_4$, the fraction of singlet radical pairs, reflecting inefficient intersystem crossing between the singlet and triplet states during the lifetime of the solvent cage. Values of σ near $^1/_4$ have been demonstrated for *tert*-butyl, benzyl, isopropyl, and oxygen-substituted carbon-centered radicals, 2-hydroxyprop-2-yl and hydroxymethyl, in alkane, benzene, acetonitrile, methanol, and tetraethoxysilane solvents, among others.[13,17] The diffusion coefficient of eq 6 is given by $D_{\mathrm{AB}}\eta/T = k/6\pi r_{\mathrm{A}}f$, where f is the microfriction factor of Spernol and Wirtz.[15] To check the accuracy of the Spernol–Wirtz diffusion coefficients, the diffusion coefficients of ethylbenzene, the model for the phenylethyl radical, in benzene at 25 and 60 °C were determined and found to agree within 15% of predicted values. The parameter ρ is the average of the LeBas,[14] van der Waals[16] and Spernol–Wirtz[15] reaction diameters, and N is Avogrado's number.[13] The Smoluchowski expression for total self-termination rate (disproportionation plus combination) for the phenylethyl radical in benzene is given by $\ln [2k_t/(\mathrm{M}^{-1}\ \mathrm{s}^{-1})] = 27.49 - 3112/RT$,[18] or $\log [2k_t/(\mathrm{M}^{-1}\ \mathrm{s}^{-1})] = 11.93 - 3.112/\theta$.

To determine the Arrhenius expression for abstraction by phenylethyl radical, we irradiated 2-phenylpropiophenone in benzene and $\mathrm{Bu_3SnH}$. Low conversion of the ketone photoprecursor and hydride donor produces phenylethyl radicals at constant concentration (eqs 7–10). Abstraction of hydrogen by the phenylethyl radical from the stannane to produce ethylbenzene competes with combination of the phenylethyl radical to yield dimers (1),

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(18) The Smoluchowski equation for self-reaction of phenylethyl radicals in benzene was calculated by using the following data: radical model, ethylbenzene, mp 178.2 K, bp 409.3 K, $\rho = 6.33 \times 10^{-8}$ cm (average of GD (ref 14), van der Waals (ref 16), and Spernol–Wirtz (ref 15) reaction diameters, see ref 13); solvent, benzene MW 78.11, mp 278.7 K, bp 353.3 K; Andrade viscosity of benzene, $\ln (\eta,\mathrm{CP}) = -4.117 + 2093.7/RT$; ethylbenzene density, dens(g/mL) $= 1.134 – 9.0913 \times 10^{-4} \times T(\mathrm{K})$; benzene dens(g/mL) $= 1.192 - 1.059 \times 10^{-3} \times T(\mathrm{K})$. The microfriction factor of Spernol and Wirtz is given by $f = (0.16 + 0.4r_{\mathrm{A}}/r_{\mathrm{B}})(0.9 + 0.4T_{\mathrm{A}}^{\mathrm{r}} - 0.25T_{\mathrm{B}}^{\mathrm{r}})$. Reduced temperatures are given by $T_{\mathrm{X}}^{\mathrm{r}} = (T - T_{\mathrm{X}}^{\mathrm{f}})/(T_{\mathrm{X}}^{\mathrm{b}} - T_{\mathrm{X}}^{\mathrm{f}})$, where $T_{\mathrm{X}}^{\mathrm{f}}$ and $T_{\mathrm{X}}^{\mathrm{b}}$ are freezing and boiling points of species X = phenylethyl (A) or benzene (B). The radii in the microfraction factor term are given by $r_{\mathrm{X}} = (3V_{\mathrm{X}}(\chi)/4\pi N)^{1/3}$, where $\chi = 0.74$, the volume fraction for cubic closest packed spheres. The resulting expression for self-termination of phenylethyl radical is $\ln (2kt/\mathrm{M}^{-1}\ \mathrm{s}^{-1}) = 27.485 - 3112/RT$, or $\log (2kt/\mathrm{M}^{-1}\ \mathrm{s}^{-1}) = 11.93 - 3.112/\theta$.

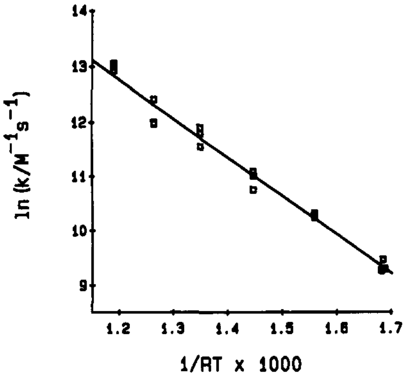

Figure 1. Arrhenius plot for abstraction of hydrogen by the phenylethyl radical from tributylstannane in benzene, 80–160 °C.

meso- and *d,l*-2,3-diphenylbutane, and disproportionation to yield both $PhCH{=}CH_2$ and $PhCH_2CH_3$. To determine

$$PhCOCH(CH_3)Ph \xrightarrow{h\nu} PhCO^{\bullet} + PhCH(^{\bullet})CH_3 \quad (7)$$

$$PhCH(^{\bullet})CH_3 + Bu_3SnH \xrightarrow{k_{abs}} PhCH_2CH_3 \quad (8)$$

$$2PhCH(^{\bullet})CH_3 \rightarrow PhCH{=}CH_2 + PhCH_2CH_3 \quad (9)$$

$$2PhCH(^{\bullet})CH_3 \rightarrow \underset{\text{1, meso + } d,l}{PhCH(CH_3)CH(CH_3)Ph} \quad (10)$$

the fraction of the total yield of ethylbenzene produced by abstraction from tributylstannane (k_{abs}), the total yield of ethylbenzene must be corrected for ethylbenzene formed during the disproportionation step (eq 9). The temperature dependence of the ratio of disproportionation to combination, k_9/k_{10}, for phenylethyl radical in benzene has been determined in a careful study: $k_9/k_{10} = \exp(1.47/RT + 8.43/R)$.[19] Thus, the yield of ethylbenzene produced in the disproportionation step can be calculated at each temperature from the yield of meso and *d,l* dimers (1). The rate of abstraction, k_{abs}, is given by eq 11, and the rate of total termination, $k_t = k_9 + k_{10}$, calculated from the Smoluchowski equation, is given in eq 12. Under conditions of short (<1%) extent of conversion of ketone and stannane, $[PhCH(^{\bullet})CH_3]$ is constant, and eqs 11 and 12 can be integrated separately. Dividing the integral of eq 11 by the square root of the integral of eq 12 and rearranging gives eq 13. Thus, analysis of the products

$$d[PhCH_2CH_3(abs)/dt = k_{abs}[Bu_3SnH][PhCH(^{\bullet})CH_3] \quad (11)$$

$$d([1] + (k_9/k_{10})[1])/dt = k_t[PhCH(^{\bullet})CH_3]^2 \quad (12)$$

$$k_{abs} = \frac{k_t^{1/2}\{[PhCH_2CH_3]_{total} - (k_9/k_{10})[1]\}}{\{[1] + (k_9/k_{10})[1]\}^{1/2}[Bu_3SnH]\Delta t^{1/2}} \quad (13)$$

(ethylbenzene and 1) after photolysis of 2-phenylpropiophenone and the use of values of k_t from the Smoluchowski equation provide the rate constants for abstraction according to eq 13. Figure 1 shows an Arrhenius plot for the abstraction of hydrogen from Bu_3SnH by the phenylethyl radical. Table I presents rate expressions for abstraction by phenylethyl, alkyl,[20] and benzyl[12] radicals from tributylstannane. The phenylethyl radical abstracts hydrogen from tributylstannane only 3 times more slowly than benzyl at room temperature.[12] The enthalpy changes for reaction of benzyl and phenylethyl radical with the stannane, $\Delta H° = -15$ and -17 kcal/mol,[21-23] respectively, account for the small differences in selectivity of the stannane toward benzyl vs phenylethyl radical.

Table II. Arrhenius Expressions for β-Scission Reactions[a]

$PhCH(^{\bullet})CH(CH_3)OPh \rightarrow PhCH{=}CHCH_3$ (cis + trans) + $PhO(^{\bullet})$

reaction	log (A/s^{-1})	E_a, kcal/mol	k(298K,s^{-1})
trans-β-scission	13.45 ± 0.26	16.94 ± 0.52	10.7
cis-β-scission	13.41 ± 0.3	19.3 ± 0.75	0.18

[a] Errors are 2σ.

β-Scission of Phenoxy Radical from 1-Phenyl-2-phenoxypropyl Radical (2). 1-Phenyl-2-phenoxypropyl radical 2 was generated over a temperature range of 80–160 °C from the chain reaction of 1-phenyl-2-phenoxy-1-chloropropane, trimethylstannane (Me_3SnH), and an appropriate initiator. β-Scission of 2 formed *trans*- and *cis*-β-methylstyrene (3) in a ratio of about 20:1 at the mean reaction temperature in competition with abstraction to yield the reduction product 1-phenyl-2-phenoxypropane (4) (eqs 14–17). The relative rate of β-scission to reduction

$$Me_3SnH + In(^{\bullet}) \rightarrow Me_3Sn(^{\bullet}) \quad (14)$$

$$Me_3Sn(^{\bullet}) + PhCHClCH(CH_3)OPh \rightarrow Me_3SnCl + \underset{2}{PhCH(^{\bullet})CH(CH_3)OPh} \quad (15)$$

$$PhCH(^{\bullet})CH(CH_3)OPh \xrightarrow{k_\beta} \underset{3}{\beta\text{-methylstyrene}} + PhO(^{\bullet}) \quad (16)$$

$$PhCH(^{\bullet})CH(CH_3)OPh + Me_3SnH \rightarrow \underset{4}{PhCH_2CH(CH_3)OPh} \quad (17)$$

by the stannane can be determined from eq 18 or, for cases of significant (>10%) consumption of the stannane, by using the integrated rate equation (eq 19),

$$k_{\beta,trans}/k_{abs} = [\mathit{trans}\text{-}3][Me_3SnH]/[4] \quad (18)$$

$$[3 + 4] = (B_0 + r)[1 - \exp(-[3]/r)] \quad (19)$$

where $r = k_\beta(\text{cis + trans})/k_{abs}$, B_0 = initial stannane concentration, and $k_{\beta,trans}/k_{abs} = r\{[\mathit{trans}\text{-}3]/([\mathit{trans}\text{-}3] + [\mathit{cis}\text{-}3])\}$. The product ratios were analyzed with an iterative computer program which solves eq 19. For trans-β-scission, the relative rate expression from a linear least-squares regression is given by $\log[(k_{\beta,trans}/k_{abs})/M] = (4.162 \pm 0.26) - (9.705 \pm 0.27)/\theta$. Combining this expression with the rate expression for abstraction $\log[k_{abs}/(M^{-1}\,s^{-1})] = 9.24 - 7.11/\theta$ yields the absolute rate expression for trans-β-scission, $\log(k_{\beta,trans}/s^{-1}) = 13.45 - 16.94/\theta$. Data for the minor product, *cis*-β-methylstyrene, formed to the extent of about 5% of the trans product yield, exhibited more scatter than the trans product, so that direct linear least-squares analysis of $\log(k_{\beta,cis}/k_{abs})$ vs $1/T$ gave unsatisfactory results in the form of a low A factor and a low activation barrier: $\log[(k_{\beta,cis}/k_{abs})/M] = (2.18 \pm 1.3) - (8.56 \pm 2.3)/\theta$. The higher scatter may perhaps be due to occasional isomerization of a small fraction (1–2%) of the

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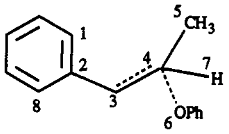
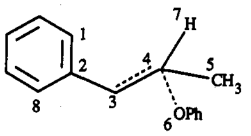
Table III. AM1/UHF Transition-State Geometries for Trans- and Cis-β-Scission of PhCH($^{\bullet}$)CH(CH_3)OPh

A. Cis-β-Scission Transition-State Geometry[a]



dihedral angles, deg	bond angles, deg	bond distances, Å
5–4–3–2, 20.5	5–4–3, 123.8	4–6, 1.92
6–4–3–2, −91.4	7–4–3, 116.1	2–3, 1.40
7–4–3–2, 173.8	6–4–3, 96.6	5–4, 1.48
4–3–2–8, −160.9		

B. Trans-β-Scission Transition-State Geometry[b]



dihedral angles, deg	bond angles, deg	bond distances, Å
1–2–3–4, −0.9	1–2–3, 123.0	4–6, 1.93
5–4–3–2, −166.2	2–3–4, 125.6	4–5, 1.48
6–4–3–2, 89.4	3–4–5, 119.9	
8–2–3–4, 178.7	6–4–2, 97.3	
	7–4–3, 119.7	
	6–4–5, 98.8	

[a] MM2 methyl rotational barrier: 3.00 kcal/mol. [b] MM2 methyl rotational barrier: 2.21 kcal/mol.

major product, *trans*-β-methylstyrene. Since the A factors for cis- and trans-β-scission will be very similar (see analysis below), the experimental ratio of trans/cis isomers of ca. 20:1 at the mean temperature dictates a relative activation barrier of about 2.4 kcal/mol. Thus, the Arrhenius parameters for cis-β-scission were calculated from the ratio *trans*-**3**/*cis*-**3** for each kinetic experiment using an estimated value of $A_{\mathrm{trans}}/A_{\mathrm{cis}}$ (see below) in eq 20.

$$E_{\mathrm{cis}} - E_{\mathrm{trans}} = -RT \ln \{([cis\text{-}\mathbf{3}]/[trans\text{-}\mathbf{3}])(A_{\mathrm{trans}}/A_{\mathrm{cis}})\} \qquad (20)$$

Using the calculated ratio of A factors, $A_{\mathrm{trans}}/A_{\mathrm{cis}} = 1.17$, individual $E_{\mathrm{cis}} - E_{\mathrm{trans}}$ values were averaged to give $\langle E_{\mathrm{cis}} - E_{\mathrm{trans}} \rangle = 2.4 \pm 0.3$ kcal/mol, giving the relative rate expression $\log (k_{\beta,\mathrm{trans}}/k_{\beta,\mathrm{cis}}) = 0.04 + 2.4/\theta$. Combining this expression with the Arrhenius expression for trans-β-scission results in the Arrhenius expression for cis-β-scission: $\log (k_{\beta,\mathrm{cis}}/\mathrm{s}^{-1}) = (13.41 \pm 0.3) - (19.3 \pm 0.75)/\theta$. Table II presents Arrhenius expressions for the β-scission reactions.

Estimation of Relative A Factors for Cis- vs Trans-β-Scission. Transition-state geometries were modeled by using AM1/UHF[24] semiempirical molecular orbital calculations. Entropy changes caused by changes in internal group rotational barriers were determined by using molecular mechanics calculations.[25] Although the absolute enthalpies calculated by using AM1 for the cis and trans transition structures are appreciably higher than the experimental values, the relative energetics of cis- vs trans-β-scission predicted by AM1 are in good agreement with experiment. AM1 predicts the activation barrier for cis-β-scission to be greater than that for trans-β-scission by 3.1 kcal/mol, compared with the experimental difference, 2.4 kcal/mol. Table III provides selected bond lengths and angles. Steric repulsion between the methyl group and the ortho hydrogen in the cis transition structure results in partial localization of the benzylic spin density, as shown by the dihedral angle 4–3–2–8 of −160.9°, in the cis structure. In the trans structure the dihedral angle 4–3–2–1 is less than 1°, indicating that the radical geometry retains the optimum angle for overlap with the phenyl π-system. In both structures, the phenoxyl group departs in the manner of a trans-peri elimination: dihedral angles 6–4–3–2 are 91.4° and 89.4°, respectively, for the cis and trans structures. The relative entropy changes between cis and trans pathways will be dominated by the methyl interactions. In the trans case, the methyl rotates against the evolving adjacent olefinic hydrogen, while in the cis structure, the methyl rotation is hindered by interaction with the ortho hydrogen of the aromatic ring. All other relative changes in rotational barriers and vibrational frequencies are negligible for the two transition structures. The A factors for the scission pathways are thus very similar as expected; the difference reflects the relative change in the entropy of rotation of the methyl group. (The small reduction in the cis phenyl torsional potential due to localization of spin density on the benzylic carbon will be small and compensated by an increase in the same torsional barrier due to the methyl/ortho-hydrogen interaction). To estimate the increase in the methyl rotational barrier, MM2 calculations were carried out on the AM1 transition structures with bond lengths and angles locked at the values listed in Table III. The rotational energy barriers for methyl rotation were 2.12 kcal/mol for the trans and 3.00 kcal/mol for the cis structure. These barriers correspond to a loss of 0.44 and 0.77 eu, respectively, from a free methyl rotor.[23] These results lead to a value of $A_{\mathrm{trans}}/A_{\mathrm{cis}} = \exp(0.33/R) = 1.17$, thereby providing a reliable estimate for conversion of *cis*-**3**/*trans*-**3** ratios to $E_{\mathrm{cis}} - E_{\mathrm{trans}}$ values.

Addition of Phenoxy Radical to β-Methylstyrene. The enthalpy of reaction for β-scission of the 1-phenyl-2-phenoxypropyl radical (**2**) is estimated to be 12.7 (cis) and 11.7 (trans) kcal/mol (eq 21):[23,26–28]

$$\Delta H^{\circ}(\text{cis-}\beta\text{-scission}) = 12.7 \text{ kcal/mol}$$

$$\Delta H^{\circ}(\text{trans-}\beta\text{-scission}) = 11.7 \text{ kcal/mol}$$

$$\begin{array}{l} \mathrm{PhCH}(^{\bullet})\mathrm{CH}(\mathrm{CH_3})\mathrm{OPh} \rightarrow \\ \mathbf{2},\ \Delta H_f{}^{\circ}{}_{298} = 25.8 \text{ kcal/mol} \\ \qquad \beta\text{-methylstyrene} + \\ \qquad \mathbf{3},\ \Delta H_f{}^{\circ}{}_{298} = 29 \text{ (cis)},\ 28 \text{ (trans) kcal/mol} \\ \qquad\qquad \mathrm{PhO}(^{\bullet}) \qquad (21) \\ \qquad\qquad \Delta H_f{}^{\circ}{}_{298} = 9.7 \text{ kcal/mol} \end{array}$$

From the relation $E_{-21} = E_{\beta} - \Delta H^{\circ}$, $E_{-21}(\text{trans}) = 16.9 - 11.7 = 5.2$ kcal/mol for addition of the phenoxy radical to *trans*-β-methylstyrene, and $E_{-21}(cis) = 19.3 - 12.7 = 6.6$ kcal/mol for addition to *cis*-β-methylstyrene. This value of $E_{-21}(\text{cis}) - E_{-21}(\text{trans}) = 1.4$ kcal/mol matches the relative activation energies determined by Szwarc et al. for the addition of methyl radical to *cis*- vs *trans*-stilbene, reflecting a similar degree of retardation of addition to the cis isomer due to steric inhibition of resonance.[29]

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[24] The MOPAC Molecular Orbital Program Package, QCPE 455 (version 5.0), Quantum Chemistry Program Exchange, Chemistry Department, Indiana University, Bloomington IN. AM1: Dewar, M. J. S.; Zoebisch, E. G.; Healy, D. F.; Stewart, J. P. *J. Am. Chem. Soc.* **1985**, *107*, 3902.

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[27] $\Delta H_f{}^{\circ}{}_{298}$ of the 1-phenyl-2-phenoxypropyl radical: Calculated from $\Delta H_f{}^{\circ}{}_{298} = -7.04$ for phenyl-2-phenoxypropane (ref 23) and a secondary benzylic BDE of 85.5 kcal/mol (ref 22).

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Conclusions. This work has provided a new rate expression for abstraction of hydrogen by a secondary benzylic radical from trialkylstannanes and has provided a new rate expression for β-scission of the phenoxy radical from a parent benzylic radical, a key bond-breaking step in the thermal degradation of lignin. The activation barrier for the β-scission reaction is lower by 11.4 kcal/mol than the corresponding β-scission barrier of a benzyl radical (eq 5) from the 1,3-diphenylpropyl radical, reflecting in part the stronger (by 9.6 kcal/mol) C–C bond in 1,3-diphenylpropyl radical compared to the corresponding C–O bond in $PhCH(^{\bullet})CH(CH_3)OPh$, but apparently not explained by the incursion of a polar transition state.[11]

Experimental Section

General. ^1H NMR spectra were obtained using a Varian VXR 300-MHz spectrometer. Gas chromatography–mass spectrometry (GCMS) was performed on a Hewlett-Packard Model 5890 chromatograph interfaced to a Model 5970 mass-selective detector. Gas chromatography (GC) was carried out with a Hewlett-Packard 5890 instrument equipped with an on-column injector and a flame-ionization detector. Product analyses were performed on 30-m J&W Scientific DB-5 and DB-1 capillary columns.

Reagents. Benzene (Aldrich reagent grade) was washed with concentrated sulfuric acid and water, predried over $CaCl_2$, and distilled from CaH_2. Trimethyltin hydride was prepared from trimethyltin chloride and lithium aluminum hydride by following a literature procedure.[30] 1-Phenyl-2-phenoxypropane was available from a previous study.[11] 1-Chloro-1-phenyl-2-phenoxypropane, available from a previous study,[11] was purified on a Harrison Chromatotron by using 5% ether in pentane on silica gel.

Preparation of (α-Chloroethyl)benzene. (α-Chloroethyl)benzene was prepared by treatment of acetaldehyde with phenylmagnesium bromide and conversion of the resulting alcohol to the chloride by treatment with thionyl chloride: bp 63–65 °C (15 mmHg); ^1H NMR ($CDCl_3$) δ 1.89 (d, 3 H), 5.14 (q, 1 H), 7.3–7.5 (m, 5 H); ^{13}C NMR ($CDCl_3$) δ 26.6, 58.85, 126.57, 128.32, 128.70, 142.86.

Preparation of *d,l*- and *meso*-2,3-Diphenylbutane (1). An ethereal solution of (α-chloroethyl)benzene (50 mmol) was converted to the corresponding Grignard reagent by treatment with magnesium metal. Excess anhydrous $CuCl_2$, obtained by heating the dihydrate $CuCl_2{\cdot}2H_2O$ at 120 °C for 4 h, was slowly added and stirred overnight at room temperature. The mixture was quenched with an aqueous NaOH solution and extracted with ether. The organic portion was dried and concentrated to give an oil, which yielded crystals from pentane at −30 °C of a mixture of *d,l*- and *meso*-2,3-diphenylbutane. Repeated recrystallization from pentane produced exclusively the meso isomer: mp 126–127 °C (lit.[31] mp 126.4–127 °C); ^1H NMR ($CDCl_3$) δ 1.02 (d, 6 H), 2.80 (m, 2 H), 7.21–7.40 (m, 10 H); ^{13}C NMR ($CDCl_3$) δ 21.8, 47.25, 126.06, 127.63, 128.30, 146.50.

Preparation of 2-Phenylpropiophenone. 1,2-Diphenylpropanol was prepared from the reaction of phenylmagnesium bromide and 2-phenylpropionaldehyde in tetrahydrofuran. The alcohol was oxidized with pyridine chlorochromate[32] to the ketone. Vacuum distillation (0.5 mmHg, bp 115–117 °C) and repeated recrystallization from 25% aqueous methanol produced 2-phenylpropiophenone: mp 52–54 °C (lit.[33] mp 53–55 °C); ^1H NMR ($CDCl_3$) δ 1.56 (d, 3 H), 4.71 (q, 1 H), 7.2–7.5 (m, 8 H), 7.98 (d, 2 H); ^{13}C NMR ($CDCl_3$) δ 20.9, 49.2, 128.3, 129.1, 129.8, 130.1, 130.3, 134.2, 137.8, 142.8, 201.7.

Kinetic Experiments: Abstractions of Hydrogen from Bu_3SnH by Phenylethyl Radical. To argon-purged Pyrex tubes were added 100-μL aliquots of a benzene solution containing 2-phenylpropiophenone (5.80 mM), isobutylbenzene (internal GC standard), and tri-*n*-butylstannane (5.95 mM). The tubes were sealed under high vacuum after three freeze–thaw cycles and photolyzed with a defocused 450-W xenon lamp for 15–45 s at 25.5–150 °C, resulting in 1–3% consumption of the ketone. Sealed, but unphotolyzed, tubes were analyzed by GC for background corrections.

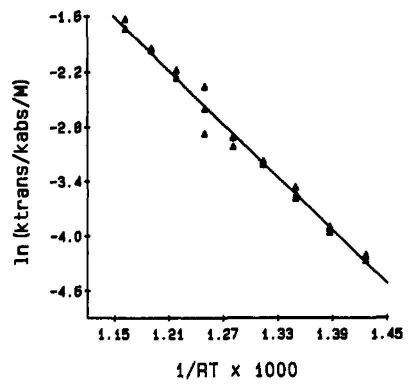

Figure 2. Arrhenius plot of the relative rate constants for trans-β-scission vs abstraction of hydrogen from trimethylstannane, ln ($k_{\beta,\mathrm{trans}}/k_{\mathrm{abs}}$, M) vs $1/RT$.

Diffusion Coefficients. Different coefficients calculated according to Spernol and Wirtz[15] for the phenylethyl radical in benzene were checked by experimental measurement of values of the diffusion coefficient of ethylbenzene in benzene at 23 °C and 60 °C. The diffusion coefficients were determined by the Taylor[34] method following Pratt[35] and Fischer.[36] The instrument consisted of a Water's Associates liquid chromatograph with a 30-cm analytical silica column located between the pump and the injector to dampen residual pressure fluctuations. A 33.22-m, 0.0398 cm internal diameter stainless steel coil (coil diameter 25 cm) was maintained at constant temperature in a Braun Model 1340 Thermomix thermostated oil bath. Samples of ethylbenzene were eluted at a flow rate of 0.1–0.2 mL/min benzene and detected with a Water's Model R401 differential refractometer. The variance (σ^2) of the ethylbenzene peak was determined from the chromatography trace by averaging the measurement of the peak width at half height Γ, where $\Gamma = 2.345\sigma$, and the measurement taken from the half width ($=\sigma$) at 60.65% of peak height. The relationship between the internal radius of the coiled tube r, the retention volume t, σ^2, and the diffusion coefficient D is given by $D = r^2t/24\sigma^2$. The diffusion coefficients were as follows: (units of 10^{-5} cm^2 s^{-1}): 24 °C, 1.84 (calcd 1.81); 60 °C, 3.55 (calcd 3.17). Since the predicted and measured values agreed within 15%, the Spernol–Wirtz diffusion coefficients were used.

Test for Cage Disproportionation of the Phenylethyl Radical. Stock solutions of 2-phenylpropiophenone in benzene were prepared with Bu_3SnH concentrations from 0.3 to 0.6 M. Photolysis of 2-phenylpropiophenone at room temperature produced ethylbenzene and benzaldehyde, but no detectable styrene. The absence of styrene under these reaction conditions indicates that cage disproportionation of the phenylethyl and benzoyl radical pairs does not occur. Thus, a correction of the observed styrene yields in the competition kinetics was unnecessary.

Relative Rate of β-Scission vs Reduction. Two stock solutions were prepared in argon-purged benzene containing an internal standard (undecane) for GC analysis with different initiators. Solution A contained azobis(isobutryonitrile) (AIBN, 1.8 mM), trimethylstannane (85.2 mM), and 1-chloro-1-phenyl-2-phenoxypropane (29.9 mM). Solution B contained di-*tert*-butyl hydroperoxide (DTBP, 1.4 mM), trimethylstannane (57.8 mM), and 1-chloro-1-phenyl-2-phenoxypropane (18.4 mM). Pyrex pyrolysis tubes were purged with argon, charged with 50-μL aliquots of the stock solutions, degassed, and sealed under under vacuum with three freeze–pump–thaw cycles. The tubes were heated in a constant-temperature bath for 3–15 min (10–28% conversion of trimethylstannane). Solutions containing AIBN

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were employed between 80 and 120 °C, and solutions containing DTBP were employed between 130 and 160 °C. The relative rate of β-scission to reduction was determined by using the integrated rate equation (eq 19). The Arrhenius parameters for trans-β-scission were calculated from linear least-squares regression analysis of ln $(k_{\text{trans}}/k_{\text{abs}})$ vs $1/RT$ as depicted in Figure 2. The Arrhenius parameters for cis-β-scission were calculated from ratios of *trans*- to *cis*-β-methylstyrene and the estimated ratio $A_{\text{trans}}/A_{\text{cis}} = 1.17$ (see text), yielding the relative rate expression $\log (k_{\beta,\text{trans}}/k_{\beta,\text{cis}}) = 0.04 - 2.4/\theta$. The expression was combined with the absolute rate expression for trans-β-scission to yield $\log (k_{\beta,\text{cis}}/\text{s}^{-1}) = 13.41 - 19.3/\theta$.

Regioselectivity and Solvent Effects in Cyclopropanation of Alkadienes

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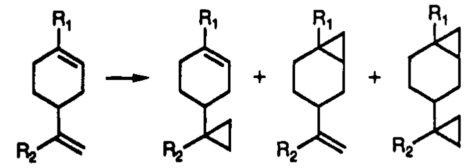
A comparison of the regioselectivities for monocyclopropanation of limonene and 4-vinylcyclohexene using diiodomethane with zinc dust and copper(I) chloride in ether, with diethylzinc in toluene, or with triethylaluminum in toluene–dichloromethane has been carried out. Some studies were also done using dibromomethane with zinc dust and copper(I) chloride in ether. The procedure using diethylzinc in toluene exhibited the least steric hindrance toward cyclopropanation at more highly substituted, electron-rich double bonds. In a study of solvent effects on the diiodomethane, zinc dust, and copper(I) chloride procedure, use of diisopropyl ether as a reaction solvent proved to be a satisfactory method for almost doubling the steric requirements of the cyclopropanating reagent.

In connection with other studies in our laboratory, it became of interest to carry out an investigation of regioselectivities in monocyclopropanation of dienes using organometallic carbenoids generated from diiodomethane or dibromomethane by various methodologies. The methodologies, which were of special interest to us because of their operational simplicity, low cost, and adaptability to larger scale reactions, were those using zinc dust and copper(I) chloride for in situ generation of a zinc–copper couple,[1] diethylzinc[2] and triethylaluminum.[3]

Some studies[4,5] of intermolecular alkene competitions reported for the diiodomethane and zinc–copper couple cyclopropanating system have revealed that the organozinc intermediate is electrophilic but rather sterically hindered. In the few cases of intramolecular competitions using this methodology that have appeared,[6-8] the results are conflicting. With the diiodomethane–diethylzinc system, no intramolecular alkene cyclopropanation competitions have been reported. However, some intermolecular competition studies[9] have suggested that the diethylzinc system, especially in noncoordinating solvents, gives a much less sterically hindered cyclopropanating intermediate than that formed with the zinc–copper couple in ether. Finally, with the only recently reported triethylaluminum method,[3] neither intra- nor intermolecular competition was reported with hydrocarbon dienes. However, with several dienols, cyclopropanation using diiodomethane and triethylaluminum in toluene–dichloromethane took place exclusively at the olefinic site distant from the hydroxyl group. The opposite behavior is observed in cyclopropanation using diiodomethane and diethylzinc in ether.

Results and Discussion

For our initial studies, which are reported in Table I, we investigated the regioselectivities of all of the cyclopropanating systems of interest toward limonene (**1a**).



1a, $R_1 = R_2 = CH_3$ **2** **3** **4**
b, $R_1 = R_2 = H$

The solvent used in each case was that usually associated with the method. Two different mole ratios of reactants were examined in each case. For the zinc dust–copper(I) chloride procedure, we used the acetyl chloride promotion method recently developed in our laboratory[10] to ensure rapid, high-yield reactions. The use of dibromomethane was examined only when the zinc dust–copper(I) chloride procedure was employed because, with diethylzinc or triethylaluminum, dibromomethane has not been reported to react.

It is immediately seen that the diiodomethane–diethylzinc system in toluene exhibits the lowest regioselectivity in monocyclopropanation of limonene, presumably due to use of the noncoordinating toluene solvent. With limonene, the trisubstituted ring double bond is the most electron rich but also the most sterically hindered. Thus, lower regioselectivity in the direction shown in the limonene system should be associated with a cyclopropanating reagent having lower steric requirements. The observation that with use of zinc dust and copper(I) chloride the cyclopropanations involving diiodomethane and dibromomethane in ether exhibited such closely similar regioselectivities toward the double bonds of limonene was unexpected. Also, it is seen that the regioselectivity for cyclopropanation for the triethylaluminum with diiodomethane in toluene–dichloromethane procedure lies between those for the zinc dust–copper(I) chloride and diethylzinc methods.

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