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Thermolysis of Model Compounds for Coal. 3. Radical Chain Decomposition of 1,3-Diphenylpropane and 1,4-Diphenylbutane[1-3]

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Cracking of 1,3-diphenylpropane (1) at 345–425 °C to give toluene and styrene proceeded much more rapidly than expected from the strength of its weakest C–C bond. Styrene was rapidly consumed in secondary reactions, one of which was addition to 1 to form 1,3,5-triphenylpentane. The kinetic order at low conversion over a 10^3 variation in initial concentration from neat liquid through solutions in biphenyl to gas at 20 kPa was 1.59 ± 0.03. The activation energy for the neat liquid was 52.3 ± 1.3 kcal mol^{-1}. Toluene product from 1-*1,1,3,3-d*$_4$ contained no detectable deuterium in the aromatic ring. Combination of these experimental data with thermochemical kinetic estimation procedures demonstrates that the rate "acceleration" results from a free-radical chain decomposition mechanism involving steps 5 and 6, in which $k_6 \gg k_5[1]$, rather than from a concerted retro-ene cleavage. The failure of such a chain to develop for 1,2-diphenylethane is a consequence of the dependence of $\Delta H°$ for radical β scission on structure. Cracking of 1,4-diphenylbutane (2) gave both toluene plus allylbenzene and ethylbenzene plus styrene. The ratio between these competitive pathways increased nonlinearly with concentration from 0.18_5 at 100–110 kPa to 0.82 in the neat liquid. This behavior is interpreted in terms of chain reaction steps 22–26. The key step is the interconversion of 1,4-diphenyl-1-butyl radical (6) and its 2-isomer (7) by hydrogen abstraction from 2, a process which is competitive with β scission. Thermochemical kinetic estimates lead to a set of rate constants which are consistent with the observed product ratio behavior. Use of the hydrogen atom donor tetralin as the solvent had only minor effects on the rates of thermolysis of 1 and 2 but dampened the product ratio dependence from 2. Tetralyl radicals are too reactive as hydrogen abstractors at 350–400 °C to serve as chain-inhibiting species. These α,ω-diphenylalkanes, Ph(CH$_2$)$_n$Ph, serve as models for aliphatic bridges between aromatic units in coal. The implications of the demonstrated chain character of their thermolysis when $n \geq 3$ for modeling the thermal decomposition of coal are discussed.

Pyrolysis[4a] and direct liquefaction[4b] processes for conversion of coal to liquid fuels and/or chemical feedstocks rely on the fact that coal begins to decompose thermally at 350–400 °C. On the basis of accumulated evidence from spectroscopic examination and chemical degradation, coal is currently viewed as a three-dimensional network of polycyclic aromatic building blocks joined together by short aliphatic bridges.[4c,5] Pictorial representations have been given by Wiser[5a] and by Heredy and Wender.[5b] Examination of these structural representations reveals both linear polymethylene bridges, Ar(CH$_2$)$_n$Ar, and substituted polymethylene bridges disguised as part of partially hydrogenated aromatic building blocks. These aliphatic bridges (and their less prevalent ether-containing analogues) are the most likely sites of thermally induced bond breaking by processes generally considered to be free-radical in nature.[6] The α,ω-diphenylalkanes, Ph(CH$_2$)$_n$Ph, form the simplest set of model compounds for this structural feature of coal. Elementary considerations of bond strengths suggest that the weakest C–C bond in this series occurs for $n = 2$ because only for this structure can both radicals formed by simple homolysis be resonance stabilized by the phenyl groups. Hence, it is no surprise that most discussions of coal liquefaction focus on dimethylene bridges and that considerable attention has been given recently to mechanistic features of the thermolysis of the model compound 1,2-diphenylethane which indeed proceeds smoothly at 400 °C.[7-9] Kinetic studies have given Arrhenius parameters for liquid-phase decomposition of log A (s^{-1}), E_a (kcal mol^{-1}): 14.4, 61.5;[8a] 16.0, 64.8;[8b] 15.5, 63;[8c] 16.4, 66.3.[8d] A gas-phase determination[8a] gave 14.8 and 60.4, respectively. The bond dissociation energy, $D°$, for the central C–C bond in 1,2-diphenylethane is estimated as ~62 kcal mol^{-1} based on $\Delta H_f°_{298}$ values for 1,2-diphenylethane and the benzyl radical of 34.3[10] and 48.0 kcal mol^{-1},[11] respectively. Hence the observed Arrhenius parameters are indeed consistent with unimolecular homolysis (step 1) as the rate-controlling reaction.

$$PhCH_2CH_2Ph \rightarrow 2PhCH_2\cdot \tag{1}$$

$$PhCH_2\cdot + PhCH_2CH_2Ph \rightarrow PhCH_3 + Ph\dot{C}HCH_2Ph \tag{2}$$

$$PhCH_2\cdot + Ph\dot{C}HCH_2Ph \rightarrow PhCH_2CHPhCHPhCH_2Ph + PhCH_2CHPhCH_2Ph + PhCH{=}CHPh + PhCH_3 \tag{3}$$

Additional product[7] and ESR evidence[9] substantiates the occurrence of hydrogen abstraction (step 2) and radical combination–disproportionation (step 3) as the dominant

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follow-up product-forming steps. Note that steps 1–3 do not constitute a chain process.[12]

Homolysis of the higher homologues ($n \geq 3$) can produce only one resonance-stabilized benzyl radical, e.g., step 4.

$$\underset{\mathbf{1}}{\mathrm{PhCH_2CH_2CH_2Ph}} \rightarrow \mathrm{PhCH_2\cdot} + \mathrm{\cdot CH_2CH_2Ph} \qquad (4)$$

Hence $D°_{\mathrm{C-C}}$ can be estimated as ~72 kcal mol^{-1}, midway between that for 1,2-diphenylethane and *n*-butane (82 kcal mol^{-1} [10]).[13] For experimental calibration, an aniline-carrier study[14] has given $k = 10^{14.9} \exp(-68\,600/RT)$ s^{-1} for unimolecular homolysis of 1-phenylpropane and $k = 10^{14.5} \exp(-67\,200/RT)$ s^{-1} for 1-phenylbutane. At 400 °C, this difference of 10 kcal mol^{-1} in $D°$ would predict a rate depression of $>10^3$ in going from $n = 2$ to $n = 3$. Yet in a comparative study[15] of thermolysis of α,ω-diphenylalkanes in tetralin solution,[16] the extents of conversion after 1 h at 400 °C for n = 2–4 were <5%, 56%, and 10%, respectively. A more recent study[17] gave conversion values in tetralin at 400 °C of 8% each for $n = 2$ and $n = 4$ after 4 h and 25% for $n = 3$ after 0.5 h. This observation of "accelerated" thermolysis for n = 3 and 4 over that predicted from $n = 2$ on the basis of $D°_{\mathrm{C-C}}$ values suggests the incursion of an additional mechanistic pathway for $n \geq 3$ which is not available for $n = 2$.

An earlier study[18] of the thermolysis of 1,3-diphenylpropane (**1**) in the gas phase at 550–700 °C showed the dominant initial products to be toluene (PhMe) and styrene (PhVi). The ultimate products derived from **1** in tetralin at 400 °C at higher conversion were PhMe, ethylbenzene (PhEt), and 1- and 2-methylnaphthalene.[15,17] Secondary reactions of PhVi with tetralin most likely account for these more complex products.[17,19] In the gas phase at low conversion,[18] 1,4-diphenylbutane (**2**) gave largely symmetrical cracking to form PhEt and PhVi with a lesser amount of PhMe. In tetralin at higher conversion,[15,17] the major products from **2** were PhMe, PhEt, and 1-phenylpropane.

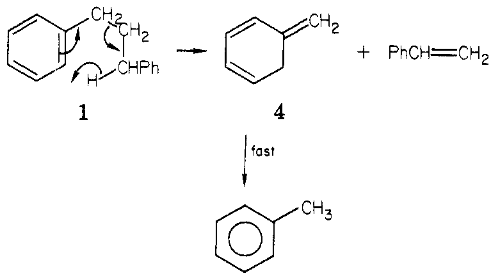
The first mechanistic hypothesis to rationalize the thermolysis for $n \geq 3$ is that these hydrocarbons have available a facile *chain* decomposition route consisting of steps such as 5 and 6 for which homolysis step 4 only serves as the initiating event. Such a route does not occur at 400 °C for 1,2-diphenylethane as evidenced by the failure to observe benzene and PhVi as significant products.[7] Since hydrogen-abstraction steps 2 and 5 are virtually identical, the barrier to chain propagation when $n = 2$ would need to lie in β-scission step 7 (see below for a thermochemical elaboration of this point). Chain decomposition routes based on β scission of alkyl radicals have extensive analogy in cracking of paraffins[20] and were first suggested specifically for the cases of **1** and **2** by Sweeting and Wilshire.[18] Acceleration of the thermolysis of **1** in tetralin solution by added benzyl phenyl sulfide was recently suggested[17] as evidence for chain character.

$$\mathrm{PhCH_2\cdot} + \underset{\mathbf{1}}{\mathrm{PhCH_2CH_2CH_2Ph}} \rightarrow \mathrm{PhCH_3} + \underset{\mathbf{3}}{\mathrm{Ph\dot{C}HCH_2CH_2Ph}} \qquad (5)$$

$$\mathbf{3} \rightarrow \mathrm{PhCH{=}CH_2} + \mathrm{PhCH_2\cdot} \qquad (6)$$

$$\mathrm{Ph\dot{C}HCH_2Ph} \rightarrow \mathrm{PhCH{=}CH_2} + \mathrm{Ph\cdot} \qquad (7)$$

The second hypothesis[21] is that thermolysis for $n \geq 3$ may proceed by an intramolecular, symmetry-allowed hydrogen transfer–bond reorganization as depicted in step 8. Such retro-ene decomposition has been well documented as a contributor, along with radical processes, to the thermolysis of terminal olefins[22] and acetylenes.[23] It has recently been suggested[21a] also for an oxa analogue of **1** where the required π electrons are part of an aromatic system, i.e., 2-phenylethyl ethyl ether.



(8)

For the key case of **1**, these two mechanisms are, of course, not distinguishable on the basis of products because 5-methylene-1,3-cyclohexadiene (**4**) is known to isomerize very rapidly to PhMe.[24–26] However, they should be distinguishable by other criteria such as deuterium labeling. Only the retro-ene process allows transfer of aliphatic hydrogens into aromatic positions in PhMe product. For the case of **2**, Hung and Stock[27] decomposed the *2,2,3,3-d*$_4$ derivative at 400–425 °C in tetralin solution and found the PhMe product to be free from deuterium, a result consistent with the radical chain but not the retro-ene mechanism.

In this paper we focus on thermolysis of **1** and **2** as neat liquids, in solution in nonreactive solvents and hydrogen donor solvents,[16] and in the gas phase. For emphasis of primary reactions and initial kinetic behavior, data are stressed from runs limited to low conversion levels.

Results

1,3-Diphenylpropane (1). Liquid Phase. Thermolysis of degassed **1** in Pyrex tubes proceeded at a convenient rate for static studies at 365 °C. A series of runs with ~85% of **1** present in the liquid phase, in equilibrium with vapor at ~385 kPa (see Experimental Section), is summarized in Table I. At the lowest conversion studied (~1%), the only significant products were PhMe and PhVi in equimolar amounts. A trace product was tentatively

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[12] The isomerization to form 1,1-diphenylethane[7] which accompanies decomposition is a chain sequence but contributes only a small fraction to total consumption of 1,2-diphenylethane.

[13] To obtain $D° = 72$ kcal mol^{-1} for **1**, the pertinent $\Delta H_f{}°_{298}$ values are 29.4 kcal mol^{-1} for **1**, 48 kcal mol^{-1} for PhCH$_2$·, and 53.4 kcal mol^{-1} for PhCH$_2$CH$_2$·. The latter corresponds to a group contribution of −4.4 kcal mol^{-1} for $\mathrm{C(C\cdot)(C_B)(H)_2}$ which is used herein.

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Table I. Thermolysis of Liquid-Phase[a] 1,3-Diphenylpropane (1) at 365 °C

time, min	source of 1[b]	tube	conv to PhMe, %	rate,[c] % h^{-1}	moles of product/moles of PhMe: PhVi	PhEt	$(PhCH_2CH_2)_2CHPh$	$(PhCH_2)_2$[d]
5	A1	P[e,f]	0.65	11.1	1.14	<0.009	j	j
15	A1	P	2.64	11.7	0.88	<0.006	0.020	0.011
15[g]	A1	P	2.09	9.3				
22.5	A1	P	3.07	8.8	0.78	0.007	0.028	0.009
25	A3	P	4.10	10.5	0.87			
30	A1	P	5.73	12.1	0.70	0.008	0.050	0.009
30	B	P	7.20	15.2	0.62			
30	A2	P	6.14	12.9				
30	A1	P[h]	4.74	10.0	0.79	0.015	0.060	0.007
30	A1	SS[i]	5.45	11.5	0.48	0.034	0.099	
45	A1	P	7.92	10.9	0.52	0.013	0.087	0.009
45	A1	SS	9.38	12.9	0.39	0.041	0.131	
60	A1	P	11.8	12.1	0.36	0.015	0.074	0.009
100	A1	P	21.1	12.9	0.28	0.036	0.121	0.015
150	A1	P	30.4	12.3	0.17	0.063	0.089	0.018

[a] Percent liquid = 85 ± 2% (see Experimental Section). [b] A1 and A2 ≡ synthesis from 1,3-diphenyl-2-propen-1-one; A3 ≡ repeat of A1 with additional purification of starting material; B ≡ synthesis from 1,3-diphenyl-2-propanone (see Experimental Section). [c] Corrected by subtracting a heat-up time of 1.5 min. [d] See the Experimental Section for the estimation procedure. [e] P ≡ Pyrex combustion tube. [f] Typical run: 3.06 mmol of 1 in a 6.5-mL tube. [g] PhVi ($x = 0.117$) added initially to 1. [h] About 1 mL of finely ground Pyrex added. [i] SS ≡ 316 stainless steel tube flushed with argon before being capped. [j] Below detection limits.

Table II. Thermolysis of Liquid-Phase 1,3-Diphenylpropane (1) at Varying Temperatures[a]

temp, °C	% liquid[b]	[1],[c] M	time, min	conv to PhMe, %	rate,[d] % h^{-1}	rate$_{liq}$,[e] M s^{-1}	moles of product/moles of PhMe: PhVi	PhEt	$(PhCH_2CH_2)_2$-CHPh	$(PhCH_2)_2$[f]
343	90	3.75	130	4.80	2.23	2.58×10^{-5}	0.47	0.014	0.12	0.009
365	85	3.65	30-60[g]	5.7-11.8[g]	11.3[g]	1.35×10^{-4}				
385	79	3.50	25	12.4	31.7	3.90×10^{-4}	0.64	0.015	0.068	0.022
400	73	3.40	10	11.9	84	1.09×10^{-3}	0.73	0.011	0.037	0.009
425	62	3.23	5	15.6	267	3.87×10^{-3}	0.87	0.013	0.025	0.011

[a] Source A1 in Pyrex tubes. [b] See the Experimental Section for vapor pressure estimates. [c] See the Experimental Section for density estimates. [d] Corrected by subtracting a heat-up time of 1.5 min. [e] Corrected for "% liquid" by multiplying the "rate" by (100/% liquid). [f] See the Experimental Section for estimation procedure. [g] Average from Table I.

assigned as 1,2-diphenylethane, but its quantitation (~1% of PhMe) was only approximate (see Experimental Section). As conversion increased with increasing reaction time, the ratio PhVi/PhMe decreased rapidly below unity, presumably because of secondary reactions of PhVi. Simultaneously, several secondary products grew in, two of which were identified as PhEt and 1,3,5-triphenylpentane. These two accounted for only a portion of the deficiency of PhVi. The progress of the reaction was monitored by the accumulation of PhMe. The "rate", calculated at each time point with correction for a short heat-up time estimated in blank runs, was independent of conversion within the experimental variability up to at least 30% conversion.

The bulk of the data in Table I were obtained with a sample of 1 (labeled A1) prepared by hydrogenation–dehydration–hydrogenation of 1,3-diphenyl-2-propen-1-one and found to be 99.75% pure by GLC analysis. Parallel preparations (labeled A2 and A3) gave indistinguishable results. Sample B (only 96% pure) derived by a different synthetic scheme from 1,3-diphenyl-2-propanone gave a rate barely outside the scatter of the "A" samples. Added styrene had no significant effect on the initial rate of PhMe formation. Neither increasing the surface/volume ratio of Pyrex nor switching to stainless steel tubes gave significant perturbations. Hence the data shown in Table I appear inherent to substrate 1 and not seriously disturbed by extraneous variables.

A series of runs at varying temperatures are listed in Table II. Reaction time was adjusted to maintain a relatively constant, low conversion level. Expression of initial liquid-phase rates in concentration units (rate$_{liq}$, M s^{-1}) requires two approximations. Because the conversion in the gas phase was so much lower than in the liquid (see below), the reaction was approximated as occurring only in the liquid phase, and the rates were therefore slightly corrected to account for the decreasing percentage of 1 confined to the liquid phase as the temperature (and therefore vapor pressure of 1) increased. Second, use of molar units requires estimates of the density of liquid-phase 1 as a function of temperature (see Experimental Section).

Dilution studies carried out at 365 °C in biphenyl as an inert solvent are compiled in Table III. Amounts of 1 and biphenyl were chosen such as to keep the total liquid volume approximately constant, and reaction times were again adjusted to maintain a relatively constant, low conversion level. Concentration calculations were based on the assumption of ideal mixing. In a parallel run with 0.31 mmol of 1 and 2.76 mmol of the hydrogen-donor solvent tetralin (estimated $[1] \simeq 0.53$ M) for 70 min, conversion to PhMe was 4.71%, corresponding to rate$_{liq}$ = 7.15×10^{-6} M s^{-1}. A correlation of the biphenyl dilution data (see Discussion) predicts rate$_{liq}$ = 5.5×10^{-6} M s^{-1} for [1] = 0.53 M; thus tetralin affected the rate of decomposition of 1 only slightly.

1,3-Diphenylpropane (1). Gas Phase. Results from thermolyses at 365 °C in Pyrex tubes charged with much smaller amounts of 1 such that its vapor pressure was not exceeded are shown in Table IV. Conversion to PhMe increased smoothly with increased reaction time at a given pressure (compare entries 8–12 at 96–98 kPa), but the conversion level at a given time was much less than that for liquid-phase runs. Product compositions were simpler in that the PhVi/PhMe ratio deviated much less from

Table III. Thermolysis of Liquid-Phase 1,3-Diphenylpropane (1) in Biphenyl Diluent at 365 °C[a]

1		PhPh,			conv to	rate$_{liq}$,[c]	PhVi/PhMe
source	mmol	mmol	[1],[b] M	time, min	PhMe, %	M s^{-1}	molar ratio
A1			3.65[d]	15	2.64	1.40×10^{-4}	0.88
A1			3.65[d]	22.5	3.07	1.05×10^{-4}	0.78
A1			3.65[d]	30	5.73	1.44×10^{-4}	0.70
A3			3.65[d]	25	4.10	1.25×10^{-4}	0.87
A1	1.34	2.00	1.70	30	2.94	3.44×10^{-5}	1.01
A3	0.57	2.91	0.75	30	2.47	1.27×10^{-5}	1.01
A1	0.47	2.86	0.64	70	4.45	8.15×10^{-6}	0.87
A1	0.157	2.92	0.240	140	2.29	8.07×10^{-7}	1.03
A1	0.095	3.07	0.142	300	2.88	2.69×10^{-7}	1.00
A3	0.149	4.83	0.142	180	2.64	4.12×10^{-7}	1.02

[a] Pyrex tubes. [b] See the Experimental Section for density estimates. [c] Corrected by subtracting a heat-up time of 1.5 min. [d] Neat liquid; data are from Table I.

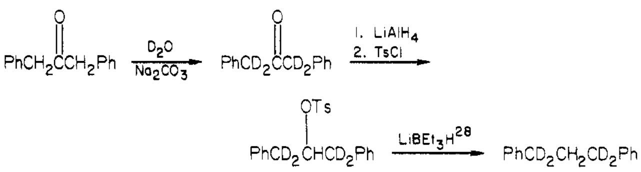
Table IV. Thermolysis of Gas-Phase 1,3-Diphenylpropane (1) at 365 °C

entry	10^2[1],[a] M	P,[b] kPa	time, min	conv to PhMe, %	rate,[c] M s^{-1}	PhVi/PhMe molar ratio
1	5.76	306	150	3.37	2.18×10^{-7}	0.89
2	5.76	305	30	0.72	2.43×10^{-7}	0.93
3[d]	5.57	295	43.5	0.73	1.61×10^{-7}	1.33
4	5.33	283	45	0.88	1.80×10^{-7}	1.02
5[d]	3.93	209	43.5	0.54	8.42×10^{-8}	1.00
6	3.68	194	50	0.92	1.16×10^{-7}	1.06
7	1.96	104	50	0.57	3.84×10^{-8}	0.88
8	1.83	97	150	1.25	2.57×10^{-8}	0.99
9	1.81	96	385	3.51	2.76×10^{-8}	0.93
10	1.86	98	960	8.52	2.76×10^{-8}	1.00
11	1.81	96	2390	18.8	2.37×10^{-8}	0.93
12	1.81	96	6780	85.7	3.83×10^{-8}	0.09
13[d]	1.79	93	15	0.64	1.41×10^{-7}	1.17
14	1.38	73	100	5.94	1.39×10^{-7}	1.70
15	1.34	71	150	0.66	9.93×10^{-9}	1.01
16	1.31	69	110	6.35	1.28×10^{-7}	1.36
17	1.29	68	150	1.26	1.82×10^{-8}	0.85
18	0.76	40	150	12.1	1.03×10^{-7}	1.53
19	0.68	35	150	4.64	3.53×10^{-8}	1.62
20	0.40	21	240	6.54	1.83×10^{-8}	2.17
21	0.38	20	150	0.49	2.09×10^{-9}	0.99
22	0.34	18	300	0.83	1.58×10^{-9}	0.96

[a] [1] = moles of 1 charged (source A1)/Pyrex tube volume. [b] Estimated pressure from ideal gas law. [c] Corrected by subtracting a heat-up time of 1.5 min. [d] Tube washed with chromic acid solution and rinsed with ammonium hydroxide solution before proceeding with the usual rinsing and drying procedure.

unity as the conversion level increased (except see below), and much smaller amounts of secondary products were detected. However, occasionally, and in no apparent pattern, the PhVi/PhMe ratio exceeded the stoichiometric expectation of unity. Invariably, such a run also proceeded at a rate greater than anticipated from the bulk of the runs for which the PhVi/PhMe ratio was ≤1. Although the reasons for this aberrant behavior are not understood, these runs could be "rejected" on the *dual* basis of "fast" rates and incorrect stoichiometry.

Scheme I



1,3-Diphenylpropane-*1,1,3,3*-d_4. A sample of 1 deuterated in the benzylic positions was prepared as shown in Scheme I; this synthesis corresponds to that used for Sample B of unlabeled material. The chemical purity was 98.6%, and the fraction of residual protium in the benzylic positions, $[H/(H + D)]_\alpha$, was determined from ^{1}H NMR to be 0.050. Thermolysis in the liquid phase at 365 °C was carried out under the same conditions as for unlabeled 1 (Table I). Runs for 30, 60, 75, and 80 min gave initial rates of PhMe formation of 3.6%, 4.2%, 5.1%, and 4.8% h^{-1}, respectively, and PhVi:PhMe ratios of 0.94, 0.71, 0.41, and 0.40, respectively. Hence the rate (4.4% h^{-1} average) was depressed by a factor of 2.5–3.5 dependent on whether the base of comparison from Table I is taken as the bulk of the data with source A (11.3% h^{-1}) or specifically source B (15.2% h^{-1}). The PhMe product from the 75-min run (conversion = 6.3%) was isolated by preparative GLC. No deuterium could be detected in the aromatic position in the ^{2}H NMR spectrum; comparison with the intensity of the benzylic signal gave a detection limit of <0.025 mol of D/mol of PhMe. Examination by ^{1}H NMR revealed a small amount of protium in the benzylic position, split into a pentet (J = 2.2 Hz) by two deuterons; an intensity comparison with the aromatic signal gave $[H/(H + D)]_\alpha$ = 0.13.

1,4-Diphenylbutane (2). Thermolysis of 2 in the liquid phase proceeded somewhat more slowly than that of 1 and was conveniently studied at 400 °C. Results are compiled in Table V. The dominant initial products were PhMe, PhEt, PhVi, and allylbenzene (PhAll) in comparable amounts. In contrast to the behavior of 1, the rates of formation of the alkylbenzene products PhMe and PhEt,

Table V. Thermolysis of Liquid-Phase[a] 1,4-Diphenylbutane (2) at 400 °C

	PhMe product		PhEt product		molar ratio		
time, min	conv, %	rate, % h^{-1} [b]	conv, %	rate, % h^{-1} [b]	PhVi/PhEt	PhAll/PhMe	PhMe/PhEt
10	0.09	0.64	0.11	0.78	0.81	0.92	0.82
20	0.25	0.81	0.28	0.91	0.79	0.92	0.88
35	0.85	1.5	0.91	1.6	0.65	0.78	0.94
65	2.60	2.5	2.26	2.1	0.36	0.47	1.15
120	10.3	5.2	7.3	3.7	0.19	0.16	1.40
240	25.1	6.3	15.6	3.9	0.06	0.04	1.61

[a] >85% in liquid phase in Pyrex tubes (see Experimental Section). [b] Corrected by subtracting a heat-up time of 1.5 min.

Table VI. Thermolysis of Liquid-Phase 1,4-Diphenylbutane (2) in *m*-Terphenyl Diluent at 400 °C for 20 min

[2],[a] *x*	PhMe product conv, %	PhMe product 10^6(rate), $M\ s^{-1}$ [b]	PhEt product conv, %	PhEt product 10^6(rate), $M\ s^{-1}$ [b]	PhMe/PhEt molar ratio
1.00[c]	0.25	7.2	0.28	8.1	0.88[d]
0.704	0.36	7.3	0.47	9.5	0.75
0.399	0.33	3.8	0.59	6.8	0.56
0.241	0.24	1.7	0.51	3.5	0.48
0.199	0.29	1.7	0.74	4.2	0.40

[a] $x = 1$ corresponds to 3.2 M with the density assumption used. [b] Corrected by subtracting a heat-up time of 1.5 min. [c] From Table V. [d] Value extrapolated to $t = 0$ is 0.82.

Table VII. Thermolysis of Liquid-Phase 1,4-Diphenylbutane (2) in *m*-Terphenyl and Tetralin Diluents at 400 °C for 20 min

diluent	[2],[c] *x*	conv, % PhMe	conv, % PhEt	conv, % total	PhMe/PhEt molar ratio
none[a]	1.00	0.25	0.28	0.53	0.88
m-terphenyl[b]	0.40	0.33	0.59	0.92	0.56
tetralin	0.37	0.32	0.29	0.61	1.11
m-terphenyl[b]	0.20	0.29	0.74	1.03	0.40
tetralin	0.15	0.29	0.22	0.51	1.27

[a] From Table V. [b] From Table VI. [c] See footnote *a* of Table VI.

calculated at each time point, steadily increased with increasing conversion level, behavior indicative of mild autoacceleration. As conversion increased, the ratios PhVi/PhEt and PhAll/PhMe decreased from initial values near unity, behavior again indicative of secondary consumption of olefinic products. Although secondary products were not investigated in detail, materials with m/z 314 and 328 were detected by mass spectroscopy, and, by analogy to the secondary conversion of PhVi to 1,3,5-triphenylpentane in the presence of **1**, these are probably triphenylhexane and triphenylheptane. The ratio of the alkylbenzene products, PhMe/PhEt, gradually increased with increasing conversion; extrapolation to zero conversion gave an inherent initial ratio between the PhMe plus PhAll pathway and the PhEt plus PhVi pathway of 0.82.

Dilution studies performed in *m*-terphenyl are described in Table VI. Since the gas-phase conversion level for **2** at a given reaction time was comparable to that in the liquid phase (see below), no rate correction for "% liquid" was made. In the absence of density values of **2** and *m*-terphenyl, conversion of raw data to molarity units was made on the assumptions that the density of **2** at 400 °C was the same as that estimated for **1** and that molarities of the diluted solutions were proportional to the mole fractions (x). Although these runs were limited to only 0.5–1.0% conversion, the rates calculated may still not be as good an approximation to initial behavior as are the corresponding data for **1** (Table III) because of the autoacceleration phenomenon observed in Table V. The PhMe/PhEt ratio decreased smoothly with decreasing [**2**], although the exact values are probably mildly perturbed by the conversion dependence of this ratio (Table V).

A comparison of tetralin and *m*-terphenyl as diluents is shown in Table VII. At equivalent concentrations of **2**, the overall thermolysis rate was slightly depressed in tetralin. The PhMe/PhEt ratio did not decrease with increasing dilution in tetralin, as it did for *m*-terphenyl, but, if anything, slightly increased.

Gas-phase thermolyses of **2** are summarized in Table VIII. At a constant pressure of 102–109 kPa (entries 3–8) both the rates and the PhMe/PhEt ratio tended again to increase with increasing conversion level as they did in the liquid phase. The PhMe/PhEt ratio extrapolated to zero conversion was 0.18_5, over 4-fold lower than that in the liquid phase. The PhVi/PhEt and PhAll/PhMe ratios fell off more slowly than in the liquid phase, behavior analogous to that of **1**.

At 365 °C, a liquid-phase run gave 0.53% conversion to PhMe and 0.34% conversion to PhEt after 4 h for a PhMe/PhEt ratio of 1.56, greater than the corresponding value of ~0.85 at this conversion level at 400 °C (Table V). A 4-h run at 365 °C at 68 kPa gave 0.20% conversion to PhMe and 0.98% conversion to PhEt for a PhMe/PhEt ratio of 0.20_4, not significantly different from the corresponding gas-phase value at 400 °C (Table VIII).

Discussion

1,3-Diphenylpropane (1). Mechanistic Criteria. Exact comparisons of the relative rates of thermolysis of the α,ω-diphenylalkanes, $Ph(CH_2)_nPh$, for $n = 2$–4 depend on the concentration and temperature chosen as the reference point because they show differing kinetic orders and activation energies. For the neat liquids at 365 °C, the experimentally observed times necessary to achieve 1% decomposition for $n = 2$–4 were 2.7,[7a] 0.09 (Table I), and 4.6 h (1.0:0.03:1.7), respectively. For the neat liquids at 400 °C, the corresponding times were 10,[7a] 0.7 (Table II), and 25–30 min (Table V; 1.0:0.07:2.5–3.0). For the gaseous state at 68 kPa at 365 °C, the corresponding times were 2.3,[7a] 2 (Table IV), and 3.4 h (1.0:0.9:1.5). Nevertheless, the "accelerated" decomposition for $n = 3$ and 4 when compared with $n = 2$ in the context of their $D°_{C-C}$ values is clearly an inherent feature and not the result of a major perturbation induced by the tetralin solvent[15] in which the phenomenon was first observed.

Table VIII. Thermolysis of Gas-Phase 1,4-Diphenylbutane (2) at 400 °C[a]

entry	10^2[2], M	*P*, kPa	time, min	PhMe product conv, %	PhMe product rate, $M\ s^{-1}$	PhEt product conv, %	PhEt product rate, $M\ s^{-1}$	molar ratio PhVi/PhEt	molar ratio PhAll/PhMe	molar ratio PhMe/PhEt
1	7.43	415	20	0.21	1.41×10^{-7}	0.86	5.76×10^{-7}	0.88	0.82	0.24_4
2	4.21	236	20	0.18	6.83×10^{-8}	0.82	3.11×10^{-7}	0.87	*b*	0.21_9
3	1.89	105	10	0.081	3.0×10^{-8}	0.43	1.59×10^{-7}	0.89	0.79	0.18_5
4	1.82	102	20	0.14	2.3×10^{-8}	0.80	1.31×10^{-7}	0.91	0.80	0.19
5	1.82	102	45	0.54	3.8×10^{-8}	2.63	1.83×10^{-7}	0.91	0.91	0.20_5
6	1.90	106	75	1.24	5.3×10^{-8}	5.60	2.41×10^{-7}	0.91	0.87	0.22
7	1.90	106	123	1.11	2.9×10^{-8}	5.13	1.33×10^{-7}	0.92	0.84	0.21_5
8	1.95	109	300	7.2	7.8×10^{-8}	19.6	2.13×10^{-7}	0.83	0.54	0.37
9	0.76	43	20	0.23	1.6×10^{-8}	1.26	8.62×10^{-8}	0.92	0.85	0.18_2
10	0.31	17	20	0.21	5.9×10^{-9}	1.18	3.29×10^{-8}	0.94	*b*	0.17_5

[a] Data treatment as in Table IV. [b] No data.

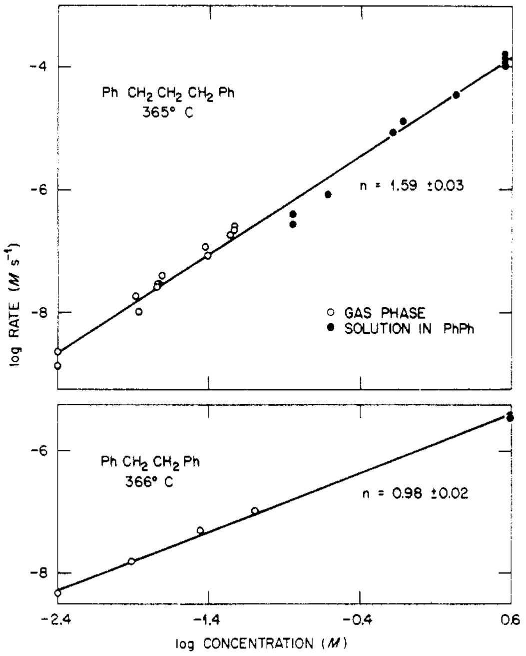


Figure 1. Differential kinetic-order plots for low-conversion thermolysis of 1,3-diphenylpropane (**1**) and 1,2-diphenylethane: (○) gas-phase runs; (●) liquid-phase runs, neat and in biphenyl diluent.

In contrast to the rather complex mixture of cracking, dehydrogenation, and dehydrocondensation products derived from thermolysis of 1,2-diphenylethane ($n = 2$),[7] the initial products from both **1** and **2** are those of simple cracking. Application of group additivity[10,29] allows estimation of the thermochemical parameters for cracking reaction 9. Simple cracking of neat **1** at 365 °C (~3.65

$$\underset{\mathbf{1}}{PhCH_2CH_2CH_2Ph} \rightleftarrows PhCH_3 + PhCH{=}CH_2 \quad (9)$$

$$\Delta H^\circ_{298} \simeq 17.7 \text{ kcal mol}^{-1}$$

$$\Delta S^\circ_{298} \simeq 35.4 \text{ cal mol}^{-1} \text{ K}^{-1}$$

$$\Delta C_p^\circ \simeq -1.4 \text{ cal mol}^{-1} \text{ K}^{-1}\,[30]$$

$$\Delta G^\circ_{638} \simeq 17.2 - (638)(0.0343) \simeq -4.7 \text{ kcal mol}^{-1}$$

$$K_{638} \simeq 41 \text{ atm} \simeq 0.8 \text{ M}$$

M) is equilibrium-limited to only 35–40% conversion, and higher observed conversions to PhMe product must in fact be driven by thermodynamically favorable secondary reactions of PhVi. Thus, by whatever mechanism the reaction occurs, it is not surprising on thermodynamic grounds to find some addition of **1** to PhVi to form 1,3,5-triphenylpentane by a reaction which is essentially the reverse of reaction 9. In fact, the greater survival of PhVi as temperature increased (Table II) and as concentration decreased (Tables III and IV compared with Table I) is also understandable from thermodynamic considerations.

Although they do not differ in the ultimate products formed, the radical chain (steps 5 and 6) and retro-ene mechanisms (step 8) for cracking of **1** should differ in kinetic behavior. Because of the prevalence of secondary reactions and the potential for autoacceleration and autoinhibition in high-conversion runs, we chose to evaluate kinetic order by a differential treatment of initial rates, estimated from observed conversions to PhMe at low conversion levels, as a function of varying initial concentration. In this format (Figure 1), the slope of a log–log plot of initial rate vs. initial concentration is the kinetic-order, n. The ten solid points portray the data in Table III, for liquid **1** and its dilution with biphenyl, all conversions being limited to ≲5%. The 13 open points portray the data points in Table IV for gas-phase **1** which meet the joint criteria of conversion being ≤10% and the PhVi/PhMe ratio being ≤1.1. A linear least-squares correlation of all points gave $n = 1.59 \pm 0.03$ ($r^2 = 0.991$). (Our corresponding previous data for 1,2-diphenylethane[7a] are plotted for comparison and demonstrate clearly the first-order character for this case.) If instead the data for **1** are treated as two sets, we obtain $n = 1.82 \pm 0.07$ ($r^2 = 0.990$) for the liquid-phase set and $n = 1.74 \pm 0.07$ ($r^2 = 0.986$) for the gas-phase set, and the two correlation lines fail to meet at the gas–liquid boundary by a rate factor of only 2.7.

The kinetic order of the retro-ene mechanism must be unity. The usual steady-state treatment of the radical chain mechanism as specified by steps 4–6 and 10–13 gives

$$\underset{\mathbf{1}}{PhCH_2CH_2CH_2Ph} \rightarrow PhCH_2\cdot + \cdot CH_2CH_2Ph \quad (4)$$

$$PhCH_2CH_2\cdot + \mathbf{1} \rightarrow PhCH_2CH_3 + \underset{\mathbf{3}}{Ph\dot{C}HCH_2CH_2Ph} \quad (10)$$

$$PhCH_2\cdot + \mathbf{1} \rightarrow PhCH_3 + \mathbf{3} \quad (5)$$

$$\mathbf{3} \rightarrow PhCH{=}CH_2 + PhCH_2\cdot \quad (6)$$

$$2PhCH_2\cdot \rightarrow \text{nonradical products} \quad (11)$$

$$PhCH_2\cdot + \mathbf{3} \rightarrow \text{nonradical products} \quad (12)$$

$$2\ \mathbf{3} \rightarrow \text{nonradical products} \quad (13)$$

$$\text{rate} = \frac{k_4^{1/2}k_5k_6[1]^{3/2}}{(k_6^2k_{11} + k_5k_6k_{12}[1] + k_5^2k_{13}[1]^2)^{1/2}} \quad (14)$$

rate expression 14. This expression simplifies to expression 15 if $k_6 \gg k_5$ [1] since $k_{11} \approx k_{12} \approx k_{13}$ for radical termination.

$$\text{rate} = (k_4/k_{11})^{1/2}k_5[1]^{3/2} \quad (15)$$

The resulting prediction of $n = 1.5$ is in reasonable accord with the results portrayed in Figure 1. But is this inequality in accord with thermochemical kinetic precedents? Following Miller and Stein's suggested modification[7b] of Jackson and O'Neill's data,[31] we take k (per H) $\simeq 10^{8.0} \exp(-16\,100/RT)$ M^{-1} s^{-1} for the symmetrical hydrogen transfer reaction between benzyl radical and toluene. We estimate[10] the analogous reaction 5 which produces 1,3-diphenyl-1-propyl radical (**3**) to have $\Delta H^\circ_{298} \simeq -3.7$ kcal mol^{-1} and $\Delta S^\circ_{298} \simeq -0.2$ cal mol^{-1} K^{-1}.[32] Since such hydrogen transfer is a relatively symmetrical process, we next assume an Evans–Polanyi $\alpha = 0.5$[33] and therefore "split" this ΔH° between the forward and reverse reactions; we also "split" the ΔS° term; since $\Delta H^\circ = E_f - E_r$ and $\Delta S^\circ = R \ln (A_f/A_r)$, we estimate k_5 (per H) $\simeq 10^{8.0} \exp(-14\,200/RT)$ M^{-1} s^{-1} and k_{-5} (per H) $\simeq 10^{8.1} \exp(-17\,900/RT)$ M^{-1} s^{-1}. We estimate[10] β-scission step 6 to have ΔH°_{298}

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[29] To maintain internal consistency, we have used group additivity estimates for $\Delta H_f^\circ{}_{298}$ and S°_{298} values even when measured values are available, although these differ slightly.

[30] $\overline{\Delta C_p}^\circ$ values were averaged between 300 and 800 K.

[31] Jackson, R. A.; O'Neill, D. W. *Chem. Commun.* **1969**, 1210.

[32] Estimated ΔH°_{298} and ΔS°_{298} values were not corrected to reaction temperatures because these small ΔC_p° corrections are within the range of accuracy of the thermochemical kinetic estimation procedures being used.

[33] Russell, G. A. In "Free Radicals"; Kochi, J. K., Ed.; Wiley-Interscience: New York, 1973; Vol. I, p 283.

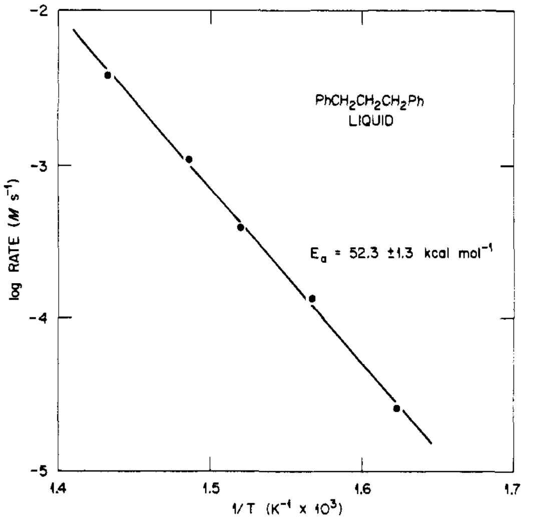


Figure 2. Arrhenius plot for low-conversion thermolysis of liquid-phase 1,3-diphenylpropane (1).

$\simeq$ 21.3 kcal mol^{-1} and $\Delta S°_{298} \simeq$ 35.6 cal mol^{-1} K^{-1}. We estimate the intrinsic activation parameters for the reverse reaction in step 6 as log A (M^{-1} s^{-1}) $\simeq$ 7.0 and $E_a \simeq$ 7 kcal mol^{-1} on the basis of values for the polymerization of styrene;[34] thus $k_6 \simeq 10^{14.8} \exp(-28\,300/RT)$ s^{-1}. Over the concentration range [1] = 0.0035–3.65 M covered in Figure 1, these estimates give $(k_6/k_5[1])_{365°C} \simeq$ 6000–6. Indeed then, the observed kinetic behavior of the thermolysis of 1 is in much better agreement with the radical chain than the retro-ene mechanism.

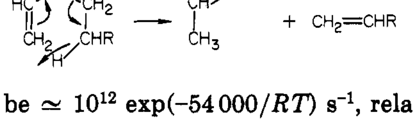
An accurate determination of the amount of PhEt produced from step 10 or of 1,2-diphenylethane produced from step 11 among the *initial* products would give a measure of the kinetic chain length. Only a lower limit of >100 can be set from the present data because of the experimental realities that PhEt is also a secondary product and that 1,2-diphenylethane could be only semiquantitatively estimated.

An Arrhenius plot (Figure 2) of the data in Table II gave E_a = 52.3 ± 1.3 kcal mol^{-1} (r^2 = 0.998) for thermolysis of 1 in the liquid phase. Because the heat-up time correction involved a significant fraction of the reaction time for the highest temperature run, the least-squares correlation was repeated without this point, but the result (E_a = 53.5 ± 2.1 kcal mol^{-1}; r^2 = 0.997) was not significantly different.

If simplified rate expression 15 correctly represents the chain reaction, then the experimentally determined E_a can be expressed in eq 16. Use of the estimates of E_4, E_5, and

$$E_a = 0.5E_4 + E_5 - 0.5E_{11} \simeq 0.5(72) + 14.2 - 0 \simeq 50.2 \text{ kcal mol}^{-1} \quad (16)$$

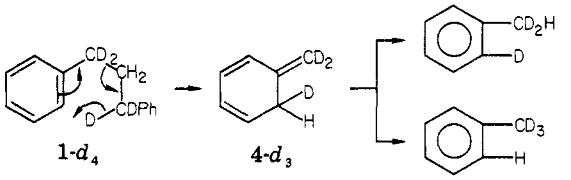
E_{11} already discussed gives a predicted E_a in agreement with our observation within the accuracy of the estimation procedures being used. To attempt to estimate a priori E_a for the retro-ene mechanism, we begin with the analogous process 17 for terminal olefins for which k has been



(17)

found[22] to be $\simeq 10^{12} \exp(-54\,000/RT)$ s^{-1}, relatively insensitive to aliphatic structure. Carrying out this process for 1 (step 8) in which the requisite π bond is part of an aromatic system must entail a significant additional energy barrier. On the other hand, the observation[35] that retro-ene cleavage of 1,6-heptadiene (R = Vi) has an E_a some 7 kcal mol^{-1} less than when R = H or alkyl suggests that the second phenyl group in 1 (but incidentally not in 2) may have a stabilizing influence on the transition state for step 8. Hence it is difficult on this qualitative basis to make a prediction. However, a more quantitative prediction can be made by noting that E_8 is made up of three additive terms: (1) $\Delta H°_9$, the enthalpy of overall reaction; (2) $\Delta H°_{\text{isom}}$, the difference in enthalpy between PhMe and tautomer 4; and E_{-8}, the activation energy for the reverse reaction between 4 and PhVi. We have already estimated $\Delta H°_9 \simeq$ 18 kcal mol^{-1}. A recent determination[36] of the gas-phase acidity of 4 compared to PhMe gave $\Delta H°_{\text{isom}}$ = 23 ± 3 kcal mol^{-1}. The ene reaction between 3 and PhVi to generate 1 (and a larger amount of 1,2-diphenylpropane) has indeed been observed,[25] and $k_{-8,60°C} = 1.15 \times 10^{-5}$ M^{-1} s^{-1}. If we then assume that the A factor will fall in the range $10^{6.5}$–$10^{8.0}$ M^{-1} s^{-1}, typical of ene reactions of olefins,[37] E_{-8} would fall into the range 17–19 kcal mol^{-1}. Hence we crudely estimate $E_8 \simeq$ 59 kcal mol^{-1}. Thus the observed activation energy for thermolysis of 1 is also in better agreement with the radical chain than the retro-ene mechanism.

The radical chain mechanism operating on 1-d_4 offers *no opportunity for migration of deuterium from the benzylic positions into the aromatic ring of PhMe product.* On the other hand, such migration is demanded by the retro-ene mechanism as shown in eq 1. To the extent that



1-d_4 4-d_3 (18)

kinetic isotope effects during aromatization of 4-d_3, by whatever mechanism, favor net migration of protium into the side chain, we predict the PhMe product to have >0.5 aromatic D/molecule. Thus our experimental value of <0.025 *is a third point of evidence against the retro-ene mechanism.*

By purely statistical considerations, the PhMe derived from 1-d_4 by the radical chain route should have $[\text{H}/(\text{H} + \text{D})]_\alpha$ = 0.050 for the benzylic position, the same value as 1-d_4. The observed value was 0.13. Ignoring secondary isotope effects which are expected to be small, we note two possible sources of this enrichment of protium in the benzylic position: (1) a primary kinetic isotope effect in hydrogen abstraction step 5, $k_\alpha^{\text{H}}/k_\alpha^{\text{D}}$; (2) a minor amount of abstraction from C-2 (k_β^{H}) via step 19 (written for

$$\text{PhCH}_2\cdot + 1 \rightarrow \text{PhCH}_3 + \underset{5}{\text{PhCH}_2\dot{\text{C}}\text{HCH}_2\text{Ph}} \quad (19)$$

$$5 + 1 \rightarrow 1 + 3 \quad (20)$$

convenience here for unlabeled 1). (Much more direct evidence for formation of such nonbenzylic radicals will be presented below for the case of 2.) Since the 1,3-diphenyl-2-propyl radical (5) so formed has no energetically accessible β-scission pathway (see below), it would be expected ultimately to revert back to radical 3 via step 20 and hence not affect the overall stoichiometry. (Steps 19 and 20 predict H–D scrambling in 1-d_4 but at a level below our experimental detection at low conversion levels.) We

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(34) Ingold, K. U. In "Free Radicals"; Kochi, J. K., Ed.; Wiley-Interscience: New York, 1973; Vol. I, p 92.

(35) Egger, K. W.; Vitins, P. *J. Am. Chem. Soc.* **1974**, *96*, 2714.

(36) Bartmess, J. E. *J. Am. Chem. Soc.* **1982**, *104*, 335.

(37) Richard, C.; Back, M. H. *Int. J. Chem. Kinet.* **1978**, *10*, 389.

now assume that *small* amounts of residual protium in 1-d_4 can be represented only as 1-d_3 in a fractional ratio of q:(1 − q) (0.80:0.20 for the particular batch of 1-d_4 at issue) and define $k_\alpha^{\mathrm{H}}:k_\alpha^{\mathrm{D}}:k_\beta^{\mathrm{H}} = m:p:l$ (per H). Then straightforward, albeit cumbersome, manipulation of the radical chain mechanism at low conversion shows that for the benzylic position of PhMe product

$$\left(\frac{\mathrm{H}}{\mathrm{H}+\mathrm{D}}\right)_\alpha = \frac{(2-R)(m-mq+2)+p(1-R)(q+3)}{3[(m-mq+2)+p(q+3)]}$$

where

$$R = \frac{(\mathrm{PhCD_2\cdot})}{(\mathrm{PhCDH\cdot}+\mathrm{PhCD_2\cdot})} = \frac{4pq+(m+p)(1-q)}{4pq+(m+3p)(1-q)}$$

For $q = 0.80$, typical paired values of the isotope effect $k_\alpha^{\mathrm{H}}/k_\alpha^{\mathrm{D}}$ ($\equiv m/p$) and the positional selectivity $k_\alpha^{\mathrm{H}}/k_\beta^{\mathrm{H}}$ ($\equiv m$) which will reproduce the observed result are as follows: 2.5, 4.4; 3.25, 6.5; 3.75, 8.2; 4.25, 10.5; 5.0, 15.

To the extent that the global kinetic isotope effect for thermolysis of 1 vs. 1-d_4 is controlled by $k_\alpha^{\mathrm{H}}/k_\alpha^{\mathrm{D}}$ (see eq 15), our low-conversion rate data suggest a value for $k_\alpha^{\mathrm{H}}/k_\alpha^{\mathrm{D}}$ of 2.5–3.5. The reported[31] isotope effect for the symmetrical reaction of benzyl radical with toluene is 6.8 at 168 °C; attenuation by an $\exp(1/T)$ dependence gives 3.8 at 365 °C.[38] The reported[39] isotope effect even for the rather unsymmetrical reaction of methyl radical with toluene is $\exp(-1800/RT)$ over the range 100–300 °C, which corresponds to $k^{\mathrm{H}}/k^{\mathrm{D}} = 4.1$ at 400 °C.[38] These inputs regarding isotope effects would then suggest a positional selectivity, $k_\alpha^{\mathrm{H}}/k_\beta^{\mathrm{H}} \equiv k_5/k_{19}$ (per H), value in the range 5–10. We will have more occasion below to estimate rate constants for processes such as step 19. For now we simply note that these estimates give $(k_5/k_{19})_{365\,°\mathrm{C}}$ (per H) $\simeq 9$. Hence the observed $[\mathrm{H}/(\mathrm{H}+\mathrm{D})]_\alpha$ in the PhMe product is consistent with the radical chain mechanism and does not indicate any contribution from the retro-ene mechanism.

Finally, note that the contrast in thermolysis pathways between 1 (long chain) and 1,2-diphenylethane (nonchain) results from the comparative enthalpies of β-scission steps 6 and 7. Whereas step 6 is endothermic by only ~21 kcal mol^{-1}, ejection of phenyl radical in step 7 would require an additional ~27 kcal mol^{-1}.[7b,40] Thus 1,2-diphenylethyl radical has no energetically feasible unimolecular decay pathways available at 400 °C in competition with radical–radical reactions, and a chain cannot develop.[12]

1,4-Diphenylbutane (2). Cracking of 2 proceeds by two competitive channels to give PhMe plus PhAll and PhEt plus PhVi whose ratio depends on both concentration and temperature. As the concentration of 2 increased from 0.018–0.019 (gas at ~100 kPa) to 3.2 M (neat liquid) at 400 °C, the PhMe/PhEt ratio extrapolated to zero conversion increased from 0.18$_5$ to 0.82 (Tables V and VIII) in a nonlinear fashion. At 365 °C the corresponding increase was from ~0.2 to ~1.5. The conversion dependence of this product ratio is not understood, but it is significant enough that only data at very low conversion levels are reliable quantitative indicators of mechanism.

Simple homologation of chain steps 5 and 6 from structure 1 to structure 2 leads only to the PhEt plus PhVi channel whereas the retro-ene mechanism is constrained to the PhMe plus PhAll channel. However, the latter possibility is inconsistent with the results of Hung and Stock[27] for 2-d_4. Rather, we consider the consequences of a more complex chain reaction. There is strong precedent in this temperature range for hydrogen abstraction being a relatively unselective process. For example, in the various thermal reactions of tetralin, the presence of the less stable 2-tetralyl radical, along with the more stable 1-isomer, has been revealed by skeletal isomerization and isotopic exchange.[41] Hence we formulate a reasonable chain decomposition route for 2 as steps 21–25 in which β scission

$$\underset{\mathbf{2}}{\mathrm{PhCH_2CH_2CH_2CH_2Ph}} \longrightarrow \mathrm{PhCH_2\bullet} + \bullet\mathrm{CH_2CH_2CH_2Ph} \longrightarrow \mathrm{C_2H_4} + \mathrm{PhCH_2\bullet} \tag{21}$$

$$\mathrm{PhCH_2\bullet} + \mathbf{2} \longrightarrow \mathrm{PhCH_3} + \underset{\mathbf{6}}{\mathrm{Ph\overset{\bullet}{C}HCH_2CH_2CH_2Ph}} \tag{22a}$$

$$\mathrm{PhCH_2\bullet} + \mathbf{2} \longrightarrow \mathrm{PhCH_3} + \underset{\mathbf{7}}{\mathrm{PhCH_2\overset{\bullet}{C}HCH_2CH_2Ph}} \tag{22b}$$

$$\mathbf{6} \rightarrow \mathrm{PhCH{=}CH_2} + \mathrm{PhCH_2CH_2\cdot} \tag{23}$$

$$\mathbf{7} \rightarrow \mathrm{PhCH_2CH{=}CH_2} + \mathrm{PhCH_2\cdot} \tag{24}$$

$$\mathrm{PhCH_2CH_2\bullet} + \mathbf{2} \longrightarrow \mathrm{PhCH_2CH_3} + \mathbf{6} \tag{25a}$$

$$\mathrm{PhCH_2CH_2\bullet} + \mathbf{2} \longrightarrow \mathrm{PhCH_2CH_3} + \mathbf{7} \tag{25b}$$

of 1,4-diphenyl-1-butyl radical (6) leads to PhEt and that of 1,4-diphenyl-2-butyl radical (7) leads to PhMe. We estimate[10] radical 6 to be more stable than isomer 7 by ~10.3 kcal mol^{-1}. Hence, surely in the intramolecular competitions involved in hydrogen abstraction steps 22 and 25, radical 6 will be formed preferentially; i.e., $k_{22a} > k_{22b}$ and $k_{25a} > k_{25b}$. In this case the ratio PhMe/PhEt cannot exceed unity whereas in the liquid phase at 365 °C it clearly does, and at 400 °C it approaches very closely. Nor does the set of chain steps 22–25 predict a product ratio dependence on [2]. Accommodation of these observations requires an additional step which interconverts radicals 6 and 7 in a substrate-dependent fashion. The most probable candidate is hydrogen-abstraction step 26.[42]

$$\underset{\mathbf{6}}{\mathrm{Ph\dot{C}HCH_2CH_2CH_2Ph}} + \underset{\mathbf{2}}{\mathrm{PhCH_2CH_2CH_2CH_2Ph}} \rightleftarrows \underset{\mathbf{2}}{\mathrm{PhCH_2CH_2CH_2CH_2Ph}} + \underset{\mathbf{7}}{\mathrm{PhCH_2\dot{C}HCH_2CH_2Ph}} \tag{26}$$

Steady-state treatment of chain steps 22–26 leads to expression 27 for the dependence of the PhMe/PhEt ratio

$$\frac{\mathrm{PhMe}}{\mathrm{PhEt}} = \frac{\left(\dfrac{k_{25b}}{k_{25}}\right) + \dfrac{k_{26}}{k_{23}}[\mathbf{2}]}{\left(\dfrac{k_{22a}}{k_{22}}\right) + \dfrac{k_{-26}}{k_{24}}[\mathbf{2}]} \tag{27}$$

on [2] where $k_{22} = k_{22a} + k_{22b}$ and $k_{25} = k_{25a} + k_{25b}$. Data for this product ratio as a function of [2] at low conversions (20-min reaction times from Tables VI and VII) are plotted in Figure 3 (the insert for gas-phase data is on the same

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[38] The value of 6.8 at 168 °C exceeds that expected for loss of C–H stretching zero-point energy (Melander, L. "Isotope Effects on Reaction Rates"; Ronald Press: New York, 1960, p 22), and the authors[31] suggested tunneling. Hence the expected value at 365 °C may be somewhat lower. The transition state for step 5, exothermic by only ~4 kcal mol^{-1}, should be quite symmetrical with regard to the C···H···C coordinate and hence should have a nearly maximal isotope effect (Lewis, E. S.; Butler, M. M. *Chem. Commun.* **1971**, 941. Pryor, W. A.; Kneipp, K. G. *J. Am. Chem. Soc.* 1971, *93*, 5584).

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

[40] In fact, the more likely β-scission process for the 1,2-diphenylethyl radical is expulsion of a hydrogen atom.

[41] Franz, J. A.; Camaioni, D. M. *J. Org. Chem.* **1980**, *45*, 5247; *Fuel* **1980**, *59*, 803. Benjamin, B. M.; Hagaman, E. W.; Raaen, V. F.; Collins, C. J. *Ibid.* **1979**, *58*, 386.

[42] For discussion of a similar "isomerization" process for alkyl radicals during cracking of alkanes, cf.: Niclause, M.; Baronnet, F.; Scacchi, G.; Muller, J.; Jezequel, J. V. *ACS Symp. Ser.* **1976**, *No. 32*, 17.

Table IX. Thermochemical Kinetic Estimates for Rate Constants for Hydrogen Abstraction

step	$\sim\Delta H^\circ_{298}$, kcal mol^{-1}	$\sim\Delta S^\circ_{298}$, cal mol^{-1} K^{-1}	k_f (per H), M^{-1} s^{-1}	k_r (per H), M^{-1} s^{-1}
		Case I: Both Centers Benzylic		
a	0	0	$10^{8.0}$ exp(−16 100/RT)	$10^{8.0}$ exp(−16 100/RT)
5	−3.7	−0.2	$10^{8.0}$ exp(−14 200/RT)	$10^{8.1}$ exp(−17 900/RT)
22a	−3.6	−0.2	$10^{8.0}$ exp(−14 300/RT)	$10^{8.1}$ exp(−17 900/RT)
		Case II: One Center Benzylic and One Aliphatic		
b	−10.0	−5.2	$10^{7.6}$ exp(−10 000/RT)^b	$10^{8.7}$ exp(−20 000/RT)
19	7.1	2.9	$10^{8.5}$ exp(−18 500/RT)	$10^{7.8}$ exp(−11 400/RT)
22b	6.7	4.1	$10^{8.6}$ exp(−18 300/RT)	$10^{7.7}$ exp(−11 600/RT)
25a	−13.9	−4.2	$10^{7.7}$ exp(−8000/RT)	$10^{8.6}$ exp(−21 900/RT)
26	10.3	4.3	$10^{8.6}$ exp(−20 100/RT)	$10^{7.7}$ exp(−9800/RT)
		Case III: Both Centers Aliphatic		
c	0	0	$10^{7.8}$ exp(−12 600/RT)	$10^{7.8}$ exp(−12 600/RT)
25b	−3.6	0.1	$10^{7.8}$ exp(−10 800/RT)	$10^{7.8}$ exp(−14 400/RT)

[a] Base case is $PhCH_2\cdot + PhCH_3$; $k = 10^{8.5}$ exp(−16 100/RT).[7b] [b] Base case is $CH_3CH_2\cdot + PhCH_3$; $k = 10^{8.1}$ exp(−10 000/RT).[43] [c] Base case is $CH_3CH_2\cdot + CH_3CH_3$; $k = 10^{8.3}$ exp(−12 600/RT).[44a]

relative scale as the total plot so the slopes can be compared). Note, however, that these data are only an approximation to inherent behavior since, even at these low conversions, they already vary somewhat from the extrapolation to zero conversion in the two cases where this was done. The data fall on a curve whose slope decreases from ~1 in the dilute gas to <0.15 for the neat liquid. Although the data are not numerous enough to validate rigorously the form of expression 27 or to assign accurately the four rate constant ratios involved, semiquantitative correspondence to the postulated chain scheme can be demonstrated.

To do this, we will first estimate rate constants for the several hydrogen abstraction steps involved as shown in Table IX. We have already discussed our protocol for the case where both centers involved in the hydrogen transfer are benzylic. For the cases where one is benzylic and the other aliphatic, we have anchored the estimates to a reported value[43] of $k = 10^{8.1}$ exp(−10000/RT) M^{-1} s^{-1} for the reaction between ethyl radical and toluene. For two aliphatic centers, we have used $k = 10^{8.3}$ exp(−12600/RT) M^{-1} s^{-1} for the reaction between ethyl radical and ethane.[44a] In all cases the estimated ΔH°_{298} and ΔS°_{298} values were "split" equally between the forward and reverse Arrhenius parameters.

The intercept of Figure 3, $(PhMe/PhEt)_{[2]\to 0}$ = 0.17–0.18, assigns $(k_{25b}/k_{25})/(k_{22a}/k_{22})$. Since surely $k_{22a} > k_{22b}$ and $k_{25a} > k_{25b}$ (see above), the algebraic form of this ratio is such that it is less sensitive to the choice of k_{22b}/k_{22a} than of k_{25b}/k_{25a}. From Table IX, we estimate $k_{22a}/k_{22b} \simeq 5$, a not unreasonable value for the benzyl radical selectivity in favor of abstracting a benzylic hydrogen from 2; hence, $k_{22a}/k_{22} \simeq 0.83$. Then $k_{25b}/k_{25} \simeq (0.83)(0.17–0.18) \simeq 0.14–0.15$, and $k_{25a}/k_{25b} \simeq 6$. From Table IX we would have estimated $k_{25a}/k_{25b} \simeq 6.4$. Hence, with minor readjustments to reflect the presupposition that benzyl radical will be somewhat *more* selective than 2-phenylethyl radical in choosing between benzylic and aliphatic hydrogens, the agreement between experiment and thermochemical estimation is excellent.

To attempt next to interpret the slope and negative curvature in Figure 3 and subject to subsequent quantitative revision, we will take $k_{22a}/k_{22b} = 9$, $k_{22a}/k_{22} = 0.9$, $k_{25a}/k_{25b} = 5.25$, and $k_{25b}/k_{25} = 0.16$ to reproduce the intercept of 0.17–0.18. The form of Figure 3 constrains the k_{26}/k_{23} and k_{-26}/k_{24} ratios to be not far from unity, with the former being slightly larger. For example, the solid line in Figure 3 was drawn for

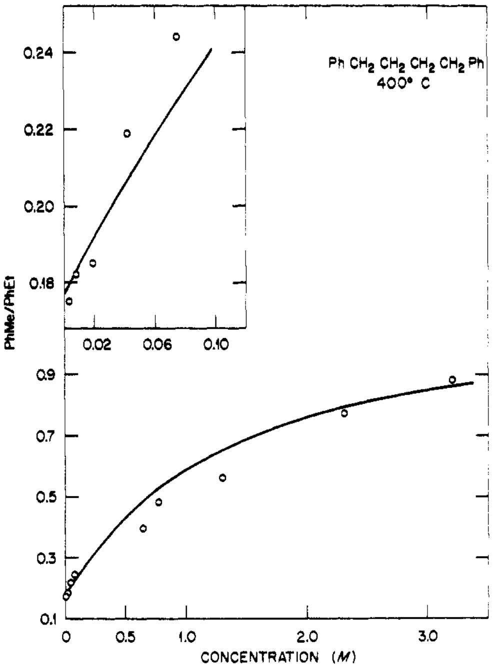

Figure 3. Toluene/ethylbenzene product ratio from low-conversion thermolysis of 1,4-diphenylbutane (2) as a function of concentration. Insert scale is expanded 12.5-fold. For information on the correlation curve, see the text.

$$\frac{PhMe}{PhEt} = \frac{0.16 + 0.75[2]}{0.90 + 0.65[2]}$$

Hence the hydrogen abstraction from substrate and the β-scission decay pathways are competitive for *both* radicals 6 and 7. From Table IX, we estimate $k_{26,400^\circ C} \simeq 4.7 \times 10^2$ M^{-1} s^{-1} and $k_{-26,400^\circ C} \simeq 1.3 \times 10^5$ M^{-1} s^{-1}. Hence, realizing the potential for piling up errors, we can crudely estimate $k_{23,400^\circ C} \simeq 6.3 \times 10^2$ s^{-1} and $k_{24,400^\circ C} \simeq 2.0 \times 10^5$ s^{-1}. For β-scission step 6 with $\Delta S^\circ_{298} \simeq 35.6$ cal mol^{-1} K^{-1}, we earlier estimated $A_6 \simeq 10^{14.8}$ s^{-1}. We similarly estimate[10] ΔS°_{298} for β-scission steps 23 and 24 to be 39.4 and 33.7 cal mol^{-1} K^{-1}, respectively. If again half of these entropy differences are manifested at the transition state, we can then estimate $A_{23} \simeq 10^{15.2}$ s^{-1} and $A_{24} \simeq 10^{14.6}$ s^{-1}. Then

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[43] Paputa, M. C.; Price, S. J. W. *Can. J. Chem.* **1979**, *57*, 3178. Daly, M.; Price, S. J. W. *Can. J. Chem.* **1976**, *54*, 1814. Koski, A. A.; Price, S. J. W.; Trudell, B. C. *Ibid.* **1976**, *54*, 482.

[44] Kerr, J. A. In "Free Radicals"; Kochi, J. K., Ed.; Wiley-Interscience: New York, 1973; Vol. I: (a) p 15, (b) pp 26, 31.

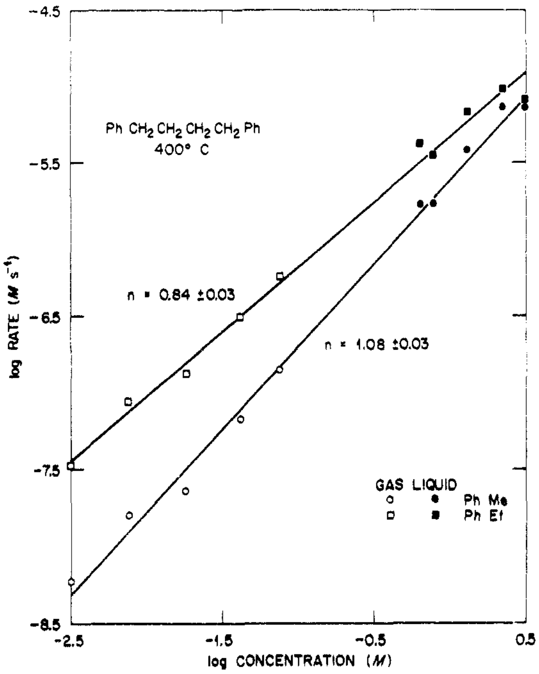
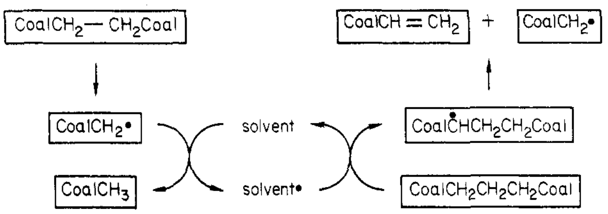


Figure 4. Differential kinetic-order plots for low-conversion thermolysis of 1,4-diphenylbutane (**2**): open symbols, gas-phase runs; solid symbols, liquid-phase runs, neat and in *m*-terphenyl diluent; (○) toluene formation; (□) ethylbenzene formation.

for $k_{23,400°C} \simeq 6.3 \times 10^2$ s^{-1}, $E_{23} \simeq 38.2$ kcal mol^{-1}. Since we estimate $\Delta H°_{23} \simeq 31.5$ kcal mol^{-1}, the inherent activation energy for step 23 is finally estimated on this basis as ~6.7 kcal mol^{-1}, fully consistent with the range (7–8 kcal mol^{-1}) typical for addition of alkyl radicals to olefins.[44b] Similarly, for $k_{24,400°C} \simeq 2 \times 10^5$ s^{-1}, $E_{24} \simeq 28.6$ kcal mol^{-1}. With $\Delta H°_{24} \simeq 13.3$ kcal mol^{-1}, we arrive at an inherent activation energy for step 24 of 15.3 kcal mol^{-1}. For comparison of an energetically equivalent case, the activation energy for addition of allyl radical to propylene has been reported[45] to be 14.5 kcal mol^{-1}. Hence, within the accuracy of the cumulative estimation methods employed, we conclude that the experimental product distributions for thermolysis of **2** are consistent with the expected kinetics of the chain scheme consisting of steps 22–26.

Finally, consider the overall kinetic form. Obviously chain steps 22–26 predict a very complex complete rate law since four chain-carrying radicals and hence 10 possible termination reactions are involved. However, we may look for simplifications if termination proceeds largely through a single, most prevalent radical. For one radical to accumulate, the chain step(s) consuming it must be slower than all others. For benzyl radical consumption, the controlling term is $k_{22}[\mathbf{2}]$, for 2-phenylethyl radical it is $k_{25}[\mathbf{2}]$, for radical **6** it is $k_{23} + k_{26}[\mathbf{2}]$, and for radical **7** it is $k_{24} + k_{-26}[\mathbf{2}]$. Using the rate constant estimates discussed above, we find these four terms at 400 °C with [**2**] = 3.2 M to be 3.5×10^4, 1.9×10^6, 2.1×10^3, and 6.2×10^5 s^{-1}; thus for the neat liquid, radical **6** should be the most prevalent. However, for [**2**] = 0.01 M, these four terms are 1.1×10^2, 5.9×10^3, 6.3×10^2, and 2.0×10^5 s^{-1}, so that now benzyl radical should be the most prevalent. Hence no simplified form of the rate law would be expected over the concentration range studied herein. The rate data for the 20-min runs from Tables VI and VIII are plotted in log–log format in Figure 4 and correlated linearly to give $n_{PhMe} = 1.08 \pm 0.03$ and $n_{PhEt} = 0.84 \pm 0.03$. However, mild curvature in this plot would be difficult to detect with the data in hand.

Scheme II



Effect of Tetralin. Tetralin has been widely used recently as a model hydrogen atom donor[16] in studies of the thermolysis of model coal compounds. Implicit in some of this work appears to be the assumption that capture of substrate-derived radicals by tetralin will inhibit induced decomposition. In another context, a "tetralin carrier" technique,[46a] modeled after the classic toluene carrier technique,[46b] has been used in determinations of $D°_{C-C}$ values in sterically crowded alkanes. Yet in the present study we note that tetralin had very small effects on rates of thermolysis of **1** and **2** when compared with biphenyl or *m*-terphenyl as diluents at equivalent concentrations; clearly it did not serve as an efficient chain inhibitor. In fact, this is not surprising in light of the rapidity of hydrogen transfer at these temperatures. Surely, in mixtures of **1** and tetralin, hydrogen transfer step 28 will compete

$$PhCH_2\cdot + C_{10}H_{12} \rightarrow PhCH_3 + C_{10}H_{11}\cdot \quad (28)$$

$$C_{10}H_{11}\cdot + \mathbf{1} \rightarrow C_{10}H_{12} + \mathbf{3} \quad (29)$$

with step 5. However, it will be quickly followed[17] by step 29 ($C_{10}H_{11}\cdot$ may be partially isomerized),[41] so that the sum of steps 28 and 29 is equivalent to step 5. Such chemically unproductive reactions between radicals derived from $Ph(CH_2)_nPh$ and tetralin have been revealed by hydrogen–deuterium exchange.[27,47] In summary, tetralyl radicals are too reactive as hydrogen abstractors to serve a significant inhibitory function.

However, the falloff in the PhMe/PhEt ratio observed when **2** was diluted with *m*-terphenyl (Figure 3) did not occur in tetralin. This is also understandable if we note that dilution of **2** with the cyclic analogue tetralin does not to a first approximation change the total concentration of reactive hydrogens which govern the dynamics of step 26 and thereby the steady-state **6**/**7** ratio.

Relevance to Coal. The results of the thermolysis studies described herein highlight the fact that future discussions of thermal decomposition and liquefaction of coal will need to consider cleavage not only of two-carbon bridges but also of those containing three or more carbons. (Corresponding ether linkages appear to be even more reactive.) A key distinction, however, is that two-carbon bridges most probably cleave by direct C–C homolysis whereas bridges with three or more carbons cleave by β scission only *after* activation by hydrogen abstraction by another radical center (induced decomposition).

The results also highlight the probability that thermal decomposition of coal may have a significant chain character. In the early stages of decomposition when coal will still be rigid or, for caking coals, highly viscous, radicals formed by direct homolysis of two-carbon bridges may be diffusionally restricted from encountering C–H bonds in nearby three-carbon bridges. However, chain reactions may still make a significant contribution in liquefaction

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(45) Tardy, D. C. *J. Am. Chem. Soc.* **1975**, *97*, 5695.

(46) (a) Rüchardt, C.; Beckhaus, H.-D. *Angew. Chem., Int. Ed. Engl.* **1980**, *19*, 424. Rüchardt, C.; Weiner, S. *Tetrahedron Lett.* **1979**, 1311. (b) Szwarc, M. *Proc. R. Soc. London, Ser. A* **1951**, *207*, 5.

(47) Benjamin, B. M.; Michalczyk, M. J.; Woody, M. C. Reprints of Papers, Fuels and Petrochemical Division AIChE National Meeting, June, 1980, p 366.

because small solvent-derived[4b] radicals should be much more mobile and hence may play the activating role by hydrogen shuttling[6c] in an analogue of steps 28 and 29. Thus we propose the schematic picture shown in Scheme II where species in boxes have their mobility restrained by the three-dimensional matrix of coal but species without boxes do not.

We would note again that *n* carbon bridges do not have to be purely linear chains for the above model to operate, but they may well be part of hydroaromatic units[5a,b] which would be modeled by structures such as 2-benzyltetralin or 9-benzyl-9,10-dihydrophenanthrene. Appropriate structure-reactivity modifications of the chemical steps discussed herein must of course be made for coal itself. For example, the average aromatic ring in coal is not phenyl but rather a three- or four-ring system,[5] and therefore appropriate modifications of the benzylic radical resonance energy[48] would need to be made. Fortunately, the thermochemical kinetic approach[7b,10] used herein offers a very useful semiquantitative method of making such modifications.

Experimental Section

1,3-Diphenylpropane (1). 1,3-Diphenyl-2-propen-1-one was prepared from base-catalyzed condensation of acetophenone and benzaldehyde[49a] and crystallized twice from 95% ethanol. A suspension in 100% ethanol (25 g/100 mL) was hydrogenated over Raney nickel (W-2)[49b] at ~400 kPa until hydrogen consumption ceased. Since the crude product showed spectral evidence for the presence of some of the saturated alcohol, it was dehydrated by refluxing with 0.2 g of *p*-toluenesulfonic acid in 250 mL of toluene under a Dean-Stark trap. A second catalytic hydrogenation in ethanol then gave the final product which was distilled through a spinning-band column; a center cut [bp 83 °C (~90 Pa)] was retained for use (batch A1). GLC analysis revealed only two impurities in amounts of 0.21% and 0.025%, both with shorter retention times than 1. Batch A2 was a repeat preparation, as was batch A3 except that the 1,3-diphenyl-2-propen-1-one was crystallized four additional times before use. Batch B was prepared from 1,3-diphenyl-2-propanone as outlined below for 1-d_4. Vapor pressures of 1 at various temperatures were estimated by extrapolation of the correlation determined by Gilman,[50] $\log P\ (\mathrm{mm}) = 8.49 - 3211(1/T(\mathrm{K}))$. Densities of liquid 1 were estimated from the Gumm-Yamada correlation coupled with the Lydersen method to estimate critical parameters and the Tyn-Calus method to estimate the density at the boiling point;[51] the values used were 0.735, 0.712, 0.686, 0.667, and 0.633 g/mL at 343, 365, 385, 400, and 425 °C, respectively.

1,4-Diphenylbutane (2). 1,4-Diphenylbutadiene was hydrogenated in ethanol solution at ~400 kPa over Raney nickel (W-2) catalyst[49b] and crystallized twice from ethanol before use. GLC analysis revealed no significant impurities. Extrapolation of handbook data[52] for vapor pressure vs. temperature for $\mathrm{Ph(CH_2)}_n\mathrm{Ph}$ (n = 0-2) and the Gilman correlation[50] for $n = 3$ gave vapor pressure estimates at 400 °C of 1.42, 1.21, 0.83, and 0.69 MPa for n = 0-3, respectively. Hence we estimate the corresponding value for $n = 4$ as ~0.40 MPa.

Diluents. Biphenyl was crystallized twice from ethanol. The density at 365 °C was estimated[51] from reported critical constants to be 0.74 g/mL. *m*-Terphenyl was crystallized three times from ethanol. Tetralin was a center distillation cut passed through activated alumina immediately before use.

Thermolysis and Analytical Procedures. The general procedure for preparing degassed sealed tubes and heating them in a fluidized sand bath has been described previously.[2,7a] Estimations of "% liquid" for liquid-phase runs were made on the basis of the amount of substrate charged, the volume of headspace, the vapor-pressure estimates discussed above, and the ideal gas law. GLC analyses for runs with 1 were made on carbon disulfide solutions with a packed Dexsil 300 column with the use of *n*-propylbenzene or naphthalene as the internal standard. For runs with 2, acetone solutions were analyzed with an OV-101 WCOT column with the use of cumene as the internal standard. Calibration factors were determined from solutions of authentic products. Conversions were calculated by comparing accumulated products with the charge of 1 or 2.

Product Assignments. Assignments of cracked products were made by GLC/MS comparison with authentic products. 1,3,5-Triphenylpentane[53] was identified by GLC/MS comparison with an authentic sample prepared by condensing an excess of 2-phenylethyl Grignard reagent with ethyl benzoate, dehydrating the product alcohol with *p*-toluenesulfonic acid catalyst in refluxing *p*-xylene, and hydrogenating the product olefin over Raney nickel (W-2)[49b] catalyst. It had a boiling point of 160 °C (~10 Pa) and characteristic m/z (relative intensity) values of 300 (P, 27), 196 (P − PhVi, 10), 92 (32), and 91 (100). A trace product with the correct retention time for 1,2-diphenylethane was only partially resolved from the major impurity in 1; its attempted quantitation involved subtracting this impurity from the total peak on the assumption that it was not selectively consumed during thermolysis.

1,3-Diphenylpropane-*1,1,3,3*-d_4. 1,3-Diphenyl-2-propanone (30.4 g) was mixed with 30 mL of D_2O which had been saturated with Na_2CO_3 at 40 °C. The mixture was refluxed with vigorous stirring for 19 h. After the mixture cooled, the organic layer was recovered, and the exchange procedure was repeated with a fresh batch of $D_2O-Na_2CO_3$. The organic product was recovered by extraction with methylene chloride, drying over $CaSO_4$, and evaporation. The crude deuterated ketone (29.1 g) was reduced with $LiAlH_4$ (3.88 g) in refluxing ether for 1.5 h. The organic product was recovered in ether in the usual fashion after basic aqueous quenching of excess hydride. The crude alcohol (28.3 g) was dissolved in 500 mL of pyridine and was converted to the tosylate by treating it with 49.5 g of tosyl chloride and storing it at 0 °C for 21 h. The reaction mixture was quenched by 2.5 L of an ice-H_2O mixture, and the organic product was recovered as rapidly as possible by extraction with ether. The combined cold extracts were washed with cold dilute HCl and H_2O, dried over $CaSO_4$, and evaporated to give, after drying in vacuum, 43.8 g of crude tosylate. NMR comparison of the **H**-C-OTs and **H**-C-OH resonances showed <10% alcohol impurity. An ice-cold solution of the tosylate in dry THF (160 mL) was treated with stirring under argon with 240 mL of a 1 M solution of lithium triethylborohydride in THF;[28] the solution was allowed to warm to room temperature and was stirred for 26 h. The cooled solution was then treated successively with H_2O-THF (1:2) until H_2 evolution ceased and then with a cooled mixture of 125 mL of 3 N NaOH solution and 125 mL of 30% H_2O_2 to destroy triethylborane. After 30 min, the aqueous layer was removed; it was extracted with two 50-mL portions of hexane which were added to the THF layer. This organic phase was then washed with four 75-mL portions of H_2O. The aqueous washes were back-extracted with hexane which was combined with the H_2O-washed THF layer. Drying over $CaSO_4$ and evaporation gave 26.6 g of crude product which was passed through an Al_2O_3 column (neutral, Brockman I) in benzene and then distilled through a 25-cm Vigreaux column to give 16.1 g of final product, bp 81 °C (~80 Pa). NMR integration (60 MHz) of the $PhCH_2$ region compared with the CH_2 region gave an $[H/(H + D)]_\alpha$ value of 0.050. The mass spectrum (70 eV) had the appropriate parent peak at m/z 200 ($C_{15}H_{12}D_4$) and the base peak at m/z 95 ($C_7H_5D_3$).[54]

For isolation and examination of PhMe product, 3.5 g of 1-d_4 was thermolyzed in the usual way for 75 min at 365 °C. A small

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aliquot was removed to determine conversion to PhMe (6.3%). The residual material was treated with 0.5 mL of C_2Cl_4 to serve as a chaser, and ~0.5 mL was distilled off under vacuum and collected in a cold trap. A sample of pure PhMe product was then collected from this distillate by preparative GLC. ^1H NMR spectra in a minimal amount of CCl_4 solvent were taken at 60 and 200 MHz and gave an $[H/(H + D)]_\alpha$ value of 0.13 integrated against the aromatic resonance. The ^2H NMR spectrum was then taken at 30.71 MHz in added $ClCH_2CH_2Cl$ solvent (14 mL), the natural-abundance ^2H in which served as an internal standard. Integration of the (nonobserved) aromatic region against the benzylic resonance after 34 700 accumulations set an upper limit of <0.025 D/mol of PhMe.

Acknowledgment. The synthesis of 1-d_4 was developed by Lawrence A. Zeff, College of Wooster, as a student participant in the Oak Ridge Science Semester of the Great Lakes College Association/Associated Colleges of the Midwest. Some analytical aspects of its thermolysis were performed by Emily C. Douglas. We acknowledge very helpful discussions with and preprints from Professor L. M. Stock. We also acknowledge Professor Gajewski and Dr. Gilbert for a preprint of the companion paper.[55]

Registry No. 1, 1081-75-0; 2, 1083-56-3; 1,2-diphenylethane, 103-29-7.

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Photochemistry of 2-Phenylbenzothiazole with Ethoxyacetylene and Ethoxypropyne. Synthesis of 1,5-Benzothiazepines

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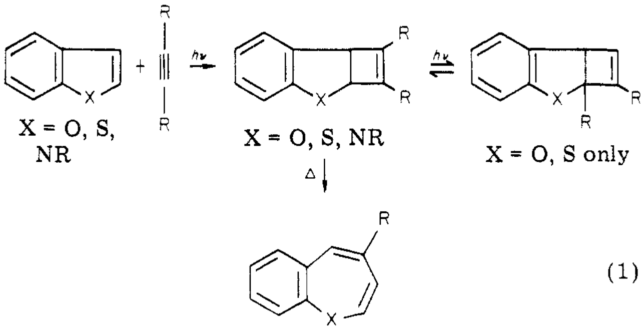
Photocycloaddition reactions of 2-phenylbenzothiazole with electron-rich alkynes, ethoxyacetylene, and ethoxypropyne gave substituted 1,5-benzothiazepines in a one-step processes.

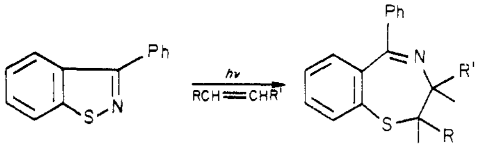
Previous results from our laboratories have shown that $[_{\pi}2_s + _{\pi}2_s]$ cycloaddition reactions of acetylenes and benzo[*b*]thiophenes, benzo[*b*]furans, or indoles, followed by thermal ring-opening rearrangement, generate, in one synthetic step, benzo[*b*]thiepines, benzo[*b*]oxepines, and benzo[*b*]azepines (eq 1).[1]



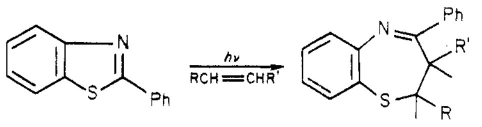
(1)

Recent studies[2-5] have extended this chemistry to condensed heteroaromatic systems containing sulfur and nitrogen in view of the potential of this as a synthetic route to potentially pharmacologically active benzothiazepine derivatives. Thus, 3-phenyl-1,2-benzisothiazole and 2-phenyl-1,3-benzothiazole (eq 2), when irradiated in the presence of alkenes such as ethyl vinyl ether or *cis*- and *trans*-2-butene, gave 2,3-dihydro-1,4- and 2,3-dihydro-1,5-benzothiazepines[4] in a regio- and stereospecific way in the first synthesis of these compounds.

Although saturated 1,4- and 1,5-benzothiazepines have been widely studied,[6] there are only a few known unsaturated 1,5-benzothiazepines.[7-11]



(2a)



(2b)

We report herein the first general one-step photochemical synthesis of substituted 1,5-benzothiazepines and comment on various aspects of their properties, including their NMR characteristics, UV spectral data, thermal stability, and relative aromaticity.

Results

2-Phenylbenzothiazole (**1**), when irradiated in the presence of ethoxyacetylene (**2a**), gave *two* products, **3a** and **6a** (eq 3), in 25% and 13% yield, respectively. In a similar manner, however, **1**, in the presence of 1-ethoxy-1-propyne (**2b**) gave a complex reaction mixture. Five products could be isolated (**3b**–**7b**) in 51%, 29%, 5%, 12%, and 1% yields, respectively, and their structures were determined by spectroscopic and chemical means. The major products in both cases were the previously unknown

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