J. Org. Chem. **1991**, *56*, 5535–5539

the Fonds der Chemischen Industrie. F.W. thanks Professors Mann and Hauptmann, Leipzig, for advice and support.

Registry No. **2a**, 74708-10-4; **2b**, 135029-00-4; **2c**, 74645-05-9; **3a**, 113379-32-1; **4a**, 135029-03-7; **5a**, 127524-18-9; **5b**, 135029-04-8; **5c**, 135029-01-5; **6a**, 74410-61-0; **6c**, 74378-21-5; **7a**, 130915-15-0; **7c**, 130981-63-4; **8a**, 130915-14-9; **8c**, 130981-62-3; **9c**, 135029-02-6; **10a**, 130915-20-7; **10c**, 130981-67-8; A, 612-00-0; B1, 134938-95-7; B2, 134938-96-8; resorcinol, 108-46-3; 3-methoxyphenol, 150-19-6; paraldehyde, 123-63-7; 1,2,3-trihydroxybenzoic acid, 87-66-1; 2,6-dihydroxybenzoic acid, 303-07-1; acetaldehyde, 75-07-0; benzaldehyde, 100-52-7; 2-hydroxybenzaldehyde, 90-02-8; 4-hydroxybenzaldehyde, 123-08-0; 4-methylbenzaldehyde, 104-87-0; 2,4,6-trimethylbenzaldehyde, 487-68-3; 3-nitrobenzaldehyde, 99-61-6.

Supplementary Material Available: A listing of six tables (I*, melting points and C, H, N analyses; II*, ^{1}H NMR data for condensation products from aromatic aldehydes; III*, ^{1}H and ^{13}C NMR data of the new stereoisomer *rcct*; IV*, contribution of higher oligomers (C, D, E) during buildup; V*, energy contributions from CHARMm calculations for T1–T9 (of Table 4); VI*, bond and "gable" angles for T1–T9 tetramers; graphic representations of one tetramer) (7 pages). Ordering information is given on any current masthead page.

Studies of the Formation and Stability of Pentadienyl and 3-Substituted Pentadienyl Radicals

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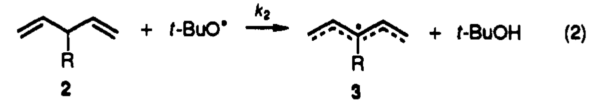
Received August 20, 1990

Pentadienyl radicals and their 3-methyl and 3-hydroxy derivatives were generated from the corresponding 1,4-pentadienes. The rates of hydrogen abstraction were studied by laser flash photolysis, and the bisallylic C–H bond dissociation energies were determined by photoacoustic calorimetry. Pentadienyl radicals were also generated by monoenergetic electron bombardment of 3-*tert*-butyl-1,4-pentadiene, and the radical's enthalpy of formation was deduced from the appearance energy of the *tert*-butyl cation. Evaluation of all recent data leads to recommended values of $\Delta H_f°$(pentadienyl) = 49.8 ± 1.0 kcal mol^{-1} and DH°($(CH_2{=}CH)_2CH$) = 76.6 ± 1.0 kcal mol^{-1}. The EPR spectra of 3-methylpentadienyl and several other radicals were also examined. The effect of substituents on the stabilization energy of pentadienyl radicals was assessed, and pentadienyl radicals were compared with other delocalized polyenyl radicals.

Alkenes, $RCH_2CH{=}CH_2$, frequently undergo scission of the allyl C–H bond in homolytic reactions. These bonds are weaker than the secondary C–H bonds in alkanes because the allylic radicals $R\dot{C}H\dot{C}H\dot{C}H_2$ are thermodynamically stabilized by delocalization of the unpaired electron over three carbon centers. The enthalpy of formation of the allyl radical is known to good precision, and there is considerable information about the effects of substituents.[1] Hydrogen abstraction from "skipped" dienes, e.g., 1,4-pentadiene, by free radicals leads to the formation of pentadienyl radicals, **1**, in which the unpaired electron is delocalized over five carbon centers. These types of intermediate are important in many processes including hydrocarbon combustion and unsaturated fatty acid (and lipid) autoxidation. Because of the greater extent of electron delocalization, **1** is more thermodynamically stabilized than allyl. In spite of several attempts to quantify the difference[1–4] in stabilization energies, the enthalpy of formation of **1**, $\Delta H_f°$(PD•), is known with rather poor precision and practically nothing is known about the effect of substituents on this quantity or on the closely related stabilization energy (SE) of this type of radical.

We have studied the formation of radical **1** and several 3-substituted pentadienyl radicals. In order to obtain data that were as reliable as possible, we used three independent methods to determine the enthalpies of formation. Firstly, pentadienyl radicals were generated by hydrogen abstraction from the corresponding 1,4-pentadiene, and the C(3)-H BDE was then measured using photoacoustic calorimetry.[4] Secondly, pentadienyl radicals were generated by electron bombardment of the 3-*tert*-butyldiene **2d** in a mass spectrometer.[5] $\Delta H_f°$(PD•) was then deduced from

$$t\text{-BuOOBu-}t \xrightarrow{k_1} 2t\text{-BuO}^\bullet \qquad (1)$$



2

3

R
a H
b CH_3
c *i*-Pr

R
d *t*-Bu
e OH
f $OSiMe_3$

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0022-3263/91/1956-5535$02.50/0 Published 1991 by the American Chemical Society

Table I. Kinetic and Thermodynamic Values for the Reaction of Di-*tert*-butyl Peroxide and 3-Substituted 1,4-Pentadienes, RH, and Bond Dissociation Energies, DH°(RH)

RH	$10^{-6}k_R$ (M^{-1} s^{-1})	ΔH_{rctn} (kcal mol^{-1})	DH°(RH) this work (kcal mol^{-1})
2a	4.5 ± 0.8	−17.4 ± 0.8	76.6 ± 0.6
2b	3.5 ± 0.1	−16.9 ± 0.8	76.6 ± 0.6
2e	15.0 ± 1.0	−32.2 ± 0.9	69.0 ± 0.6
1,4-cyclohexadiene	53.0[a]	−26.2 ± 1.0[b]	73.0 ± 2.0[b]

[a] Reference 10. [b] Reference 4.

the appearance energy (AE) of the accompanying *tert*-butyl cation. Thirdly, several 3-substituted pentadienyl radicals were generated in an EPR spectrometer, and attempts were made to determine the barrier to rotation about the C(2)–C(3) bond, which is related to the radical SE.[6]

There are two main planar conformations of pentadienyl radicals **1a** and **1b**. The third possible planar form, i.e., the *Z,Z*, or "U" conformation, is not significantly populated at room temperature.[7] The difference in the enthalpies of formation of **1a** and **1b** is only about[6,7] 1 kcal mol^{-1} so that **1a** and **1b** are usually formed in equilibrium at ambient temperatures and above. On generation from the dienes **2**, the measured $\Delta H_f°(PD^•)$ refers to the equilibrium mixture of planar conformers. It has been shown by EPR spectroscopy that the *E,E* conformer **1a** predominates by a factor of about 25 at 370 K.[6]

Results and Discussion

Kinetics of Hydrogen Abstraction. An accurate knowledge of the rates of H abstraction from the 1,4-pentadienes by *tert*-butoxyl radicals is extremely important for the photoacoustic experiments (vide infra). Values of k_2 for **2a**, **2b**, and **2e** are summarized in Table I along with that for 1,4-cyclohexadiene, a rather well-studied substrate. The rate constants reported represent the overall reactivity of diene toward *tert*-butoxyl radicals, and no effort was made to separate the relative importance of abstraction versus addition reactions. *tert*-Butoxyl radicals tend toward abstraction over addition where allylic systems are concerned.[8] Only in cases where geometrical or stereoelectronic effects dominate does addition to olefins occur, as in the case of norbornadiene.[9] Even in cases such as cyclopentadiene, abstraction is more important than addition,[9] and in 1,4-cyclohexadiene addition is unimportant.[10] EPR spectroscopy showed only radicals formed by H abstraction for **2** and none of the adduct radicals (vide infra). On this basis, we assumed that the *tert*-butoxyl radical addition was unimportant in the case of the unconjugated 1,4-pentadienes studied here.

Photoacoustic Calorimetry. The net enthalpy change associated with reactions 1 and 2, ΔH_{rctn}, is given by eq 3, where the energy provided by a 337.1-nm photon is 84.8 kcal mol^{-1}, ϕ is the quantum yield for photolysis of di-*tert*-butyl peroxide in benzene (ϕ = 0.85), and a_R and a_S are the slopes obtained from the plots of the "normalized photoacoustic response" (vide infra), *N*, versus (1/*T*) for the sample and calibration runs, respectively, at 22 °C.

$$\Delta H_{rctn} = 84.8(1 - a_R/a_S)/\phi \qquad (3)$$

The experimental results are related to the enthalpies of formation of the reactants and the products by eq 4 and to the C–H bond dissociation enthalpy by eq 5. These

$$\Delta H_{rctn} = 2\Delta H_f°(t\text{-BuOH}) + 2\Delta H_f°(R^•) - \Delta H_f°(t\text{-BuOOBu-}t) - 2\Delta H_f°(RH) \qquad (4)$$

$$DH°(RH) = \Delta H_f°(R^•) + \Delta H_f°(H^•) - \Delta H_f°(RH) \qquad (5)$$

results, when combined with literature values[11] for the enthalpies of formation of gaseous *t*-BuOH, *t*-BuOOBu-*t*,[11,12] and H$^•$, give the BDE as shown in eq 6.

$$DH°(RH) = \Delta H_{rctn}/2 + 85.1 \text{ kcal mol}^{-1} \qquad (6)$$

The technique requires that the heat of reactions 1 and 2 be completely released in a time that is short compared to the response of the instrument. Since the rate constants were determined for reaction 2 we were able to adjust the diene concentrations (3–5.5 M) so that reaction 2 was complete in a time that was short (<62 ns) compared to the response of the microphone (ca. 2 μs). The results obtained for 1,4-pentadienes, **2a**, **2b**, and **2e** compare well with those previously determined for 1,4-cyclohexadiene (see Table I).

Appearance Energy Measurements. $\Delta H_f°$ values for free radicals, which agree well with those obtained via conventional kinetic measurements, can be obtained from appearance energies, AE, of ionic dissociations:[13]

$$RY + e^- \rightarrow Y^+ + R^• + 2e^-$$

$$\Delta E = \Delta H_{rctn} = \Delta H_f°[Y^+] + \Delta H_f°[R^•] - \Delta H_f°[RY]$$

The criteria for this method to be successful have recently been summarized.[14] We found that the dissociation of 3-*tert*-butyl-1,4-pentadiene (**2d**) was a suitable process for measurement of $\Delta H_f°(PD^•)$. The main dissociation path on bombardment with monoenergetic electrons gave radical **1** together with the *tert*-butyl cation, which has a well-established enthalpy of formation.[15] The AE for this process was determined as 9.41 ± 0.01 eV. The final quantity needed was therefore the enthalpy of formation of **2d**. In principle, this could be quite accurately derived from the Benson group equivalents,[16] but the group equivalent for C(Cd$_2$)(C)(H) was unknown; it was estimated in the following way. The difference between the two group equivalents C(Cd)(C)(H$_2$) and C(Cd)(C$_2$)(H) is 3.28 kcal mol^{-1}. Assuming that the difference for C(Cd$_2$)(H$_2$) and C(Cd$_2$)(C)(H) is the *same*, we obtain −1.0 kcal mol^{-1} for the C(Cd$_2$)(C)(H) group equivalent, and

2d

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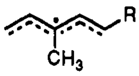
Table II. EPR Parameters of 1,3-Disubstituted Pentadienyl Radicals[a]



		hfs[b] (G)					
radical (R)	T (K)	H_1^{anti}	H_1^{syn}	$H_{2,4}$	H_4^{anti}	H_5^{syn}	H^{other}
H	450	9.8	9.3	3.8	9.8	9.3	10.9 (CH_3)
H	289	9.7	9.3	3.2	9.7	9.3	10.2 (CH_3)
OH	239		9.2	3.0	9.2	9.2	9.3 (CH_3), 0.8 (OH)
$OSiMe_3$	239		9.1	3.1	9.6	9.6	9.3 (CH_3)

[a] All g factors 2.003 ± 0.001. [b] All hfs checked by computer simulation.

hence $\Delta H_f°(\mathbf{2d}) = -1.4$ kcal mol^{-1}. This agrees well with a different derivation by Trenwith.[2] Confirmation of these values was obtained from work with the 3-isopropyl-1,4-pentadiene **2c**. The main dissociation pathway in this case gave 1,3-pentadienyl ions and propene. Because the isopropyl cation and **1** were formed in a minor pathway the AE is untrustworthy. However, from the main process, the AE of the 1,3-pentadienyl radical cation was found to be 9.28 eV; hence

$$9.28\text{ eV} = \Delta H_f°(C_5H_8^{\bullet+}) + \Delta H_f°(\text{propene}) - \Delta H_f°(\mathbf{2c})$$

and $\Delta H_f°(\mathbf{2c}) = 6.87$ kcal mol^{-1}. Using the group equivalent derived above we find $\Delta H_f°(\mathbf{2c}) = 6.9$ kcal mol^{-1}, in perfect agreement. Our calculation of $\Delta H_f°(\mathbf{2d})$ is likely to be very good, therefore, and it follows that

$$9.41\text{ eV} = \Delta H_f°(t\text{-Bu}^+) + \Delta H_f°(\text{PD}^\bullet) + (-1.4)$$

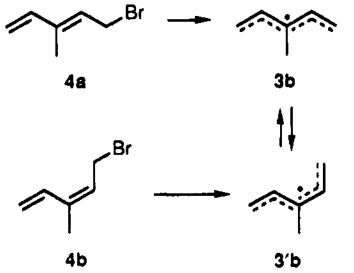
Since $\Delta H_f°(t\text{-Bu}^+) = 166$ kcal mol^{-1}[15] we obtain $\Delta H_f°(\text{PD}^\bullet) = 49.6$ kcal mol^{-1}, and the corresponding BDE (RH) in **2a** is 76.5 kcal mol^{-1}.

EPR Study of Pentadienyls. The SE of a pentadienyl radical is related to the barrier to rotation about the C(2)–C(3) bond, E_i, by eq 7[7,17] where V_2 is the small, but

$$E_i = V_2 + \text{SE}(\text{PD}^\bullet) - \text{SE}(\text{allyl}) \tag{7}$$

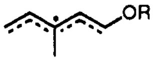
experimentally inaccessible, barrier to rotation about the C(2)–C(3) *single* bond in the *absence* of delocalization and SE(allyl) is the stabilization energy of the allyl radical. In favorable cases, the rotation barriers in delocalized radicals can be determined by the EPR exchange line-broadening method.[6] For the parent pentadienyl **1**, exchange broadening was observed in the EPR spectrum in the temperature range 320–430 K, with coalescence at 370K. The measured rotation barriers were 11.7 and 9.3 kcal mol^{-1} for **1a** → **1b** and **1b** → **1a**, respectively.[6]

We examined the EPR spectra of several 3-substituted pentadienyl radicals in an attempt to observe the exchange broadening and hence derive their SEs. The 3-methyl radical **3b** was generated by bromine abstraction from 5-bromo-3-methyl-1,3-pentadiene (E-(**4a**) + Z-(**4b**)) with photochemically generated trimethyltin radicals, and spectra were observed in the range 290–450 K.



The major radical conformer **3b** was readily distinguished at 289 K with hyperfine splittings (hfs) essentially the same as those reported previously[7] (Table II). However, the spectrum of the minor conformer **3'b**, though visible, was too weak for definitive analysis. As T was increased exchange broadening was observed with coalescence at ca. 370 K. The final average spectrum at 450 K was easily analyzed (Table II). Because the proportion of the minor conformer and its hfs could not be determined, the exchange broadening could not be matched to computer-simulated spectra. It is probable, however, that the hfs of the minor conformer are virtually the same as those of the analogous conformer of the parent radical **1b**. Because the coalescence temperature is also the same, it follows that the barrier to rotation about the C(2)–C(3) bond in the 3-methyl radical **3b** is virtually the same as that of the parent, and hence SE$^{\text{EPR}}$ (**3b**) is also the same, i.e., 25 kcal mol^{-1}.

The 3-hydroxy- **3e**, 1-hydroxy-3-methyl **5a**, and 1-[(trimethylsilyl)oxy]-3-methyl radicals **5b** were generated by H abstraction from the corresponding dienes. Good



5

a, R = H
b, R = $SiMe_3$

EPR spectra were obtained at ca. 240 K (Table II), but only the major E,E conformers could be distinguished and the spectra weakened so rapidly at higher temperatures that the exchange broadening could not be observed. No EPR signals were obtained on H abstraction from either the 3-isopropyl **2c** or the 3-*tert*-butyl diene **2d** by *tert*-butoxyl radicals in the accessible temperature range.

Stability of Pentadienyl and Related Radicals. The $\Delta H_f°(\text{PD}^\bullet)$ values and the BDE of the bisallylic hydrogens in 1,4-pentadiene from recent work are collected in Table III. There is excellent agreement between the values obtained by gas-phase pyrolysis of pentadiene derivatives[2] and our gas-phase AE determinations. In addition, the photoacoustic calorimetric measurements made in hydrocarbon solution also give closely similar results. The averages of these four values are $\Delta H_f°(\text{PD}^\bullet) = 49.8 \pm 1.0$ kcal mol^{-1} and DH°[$(CH_2{=}CH)_2CHH$] = 76.6 ± 1.0 kcal mol^{-1}; we believe this data can be recommended as being very reliable.

The SE of a radical R$^\bullet$ is usually defined[1] as the difference between the BDE of RH and that of a nonstabilized model compound MH, i.e., eq 8

$$\text{SE}^{\text{MH}}(\text{R}^\bullet) = \text{DH}°(\text{MH}) - \text{DH}°(\text{RH}) \tag{8}$$

For odd conjugated systems, such as polyenyl radicals, there is no unambiguous way to choose a model compound. The SE contains contributions from the "resonance energy" (RE) and from other hyperconjugative, inductive, steric, etc. effects that can also lead to stabilization.

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Table III. Thermodynamic Data for Pentadienyl Radicals[a]

radical	method	DH°(RH)	$\Delta H_f°(R^•)$	SE^{MeH} [j]	SE^{MH} [k]	SE^{EPR}	ref
PD	GPP[b]	(76.8)	49.9[g]	28.3	19.5		2
PD	GPP[c]	76.6	49.7	28.5	19.6		2
PD	PAC[d]	76.6	(49.9)[h]	28.5	19.6		this work
PD	AE[e]	(76.5)	49.6	28.6	19.7		this work
PD	EPR[f]					25.0	this work
3-MePD	PAC[d]	76.6	(43.6)[i]	28.5			this work
3-MePD	EPR[f]					25.0	this work
3-HOPD	PAC[d]	69.0		36.1			this work

[a] Primary values in plain text; parenthesis indicates derived data; all in kcal mol^{-1}. [b] Gas-phase pyrolysis of 1,3-hexadiene. [c] Gas-phase pyrolysis of 3-methyl-1,4-pentadiene. [d] Photoacoustic calorimetry. [e] Appearance energy (see text). [f] EPR study of internal rotation (see text). [g] Including 4 kcal mol^{-1} for conjugation in 1,3-hexadiene. [h] $\Delta H_f°$(1,4-pentadiene) taken as[11] 25.2 kcal mol^{-1}. [i] $\Delta H_f°$(3-methyl-1,4-pentadiene) taken as 19.1 kcal mol^{-1}. [j] Assuming DH°(CH_3H) = 105.1 kcal mol^{-1}. [k] Assuming DH°(sec-H) = 96 kcal mol^{-1}; increase SE^{MH} values by 2 kcal mol^{-1} if the recent[19] DH°(sec-H) value of 98 kcal mol^{-1} is preferred.

Ideally, MH is chosen to factor out these terms leaving only the RE due to electron delocalization. Thus, the RE of allyl radicals has often been assessed by using primary alkyl radicals as the model, while secondary alkyl radicals have been used for pentadienyl radicals. Of course, the hyperconjugative, inductive, etc. effects in a primary radical are *not* the same as they would be in an allyl radical in the absence of electron delocalization. A second drawback of this procedure is that as MH is changed from one radical to another so the basis of the RE values changes and a nonuniform set of energies is obtained. The alternative therefore is to use methane and the methyl radical as the model.[7,18] With this model the impossible attempt to subtract out hyperconjugative etc. effects is given up and the data reflect the total SE, but with the great advantage of having a uniform basis for all radicals.

SE's for pentadienyl radicals using both secondary radicals and methyl radicals as the model are given in Table III. The average of the four results from above gives $SE^{MeH}(PD^•)$ = 28.5 kcal mol^{-1}, $SE^{secH}(PD^•)$ = 19.6 kcal mol^{-1} where the recently recommended[1,19] values of DH°(CH_3H) = 105.1 kcal mol^{-1} and DH°(sec-H) = 96 kcal mol^{-1} have been used (see, however, ref 19). Hyperconjugation does not contribute to the internal rotation barrier measured by EPR,[3] and therefore the stabilization energy determined in this way, i.e., SE^{EPR}, should lie between SE^{MeH}, which contains the full contribution from hyperconjugative, inductive, steric, etc. effects and SE^{MH}, which almost certainly overcompensates for them. Table III shows that the measured SE^{EPR} for pentadienyl radicals does indeed fall between these two limits.

The experimental results in Table III indicate that a 3-methyl substituent has very little effect on the SE of pentadienyl radicals. The 3-hydroxy substituent causes a decrease in DH°(RH) of about 7 kcal mol^{-1} and an equivalent increase in SE($PD^•$) (Table III). This seems quite reasonable when compared with the known stabilizing influence of the OH group in alkyl radicals.[1] For example, DH°(CH) in methane is some 11 kcal mol^{-1} higher than in methanol.[1] Trenwith found a similar effect on the allyl radical stabilization energy by the OH substituent.[20] However, comparisons with allyl are not straightforward because the steric situation at C_3 in $PD^•$ differs from that of the terminal C atoms of allyl radicals. In particular, there can be no single choice of model radical, in the pentadienyl case, that would factor out steric, hyperconjugative, etc. effects. For this reason, the values of SE^{MH} (Table III) are not given for substituted pentadienyl radicals.

Experimental Section

EPR spectra were recorded with a Bruker ER 200D spectrometer on degassed solutions in Spectrosil tubes irradiated with light from a 500-W super-pressure Hg arc. ^1H and ^{13}C NMR spectra were obtained at 300 and 75 MHz, respectively, on a Bruker AM 300 spectrometer utilizing $CDCl_3$ solutions at ambient temperature with $SiMe_4$ as an internal standard. GC/MS analyses were carried out with a Finnegan Incos instrument fitted with an HP1 capillary column. Preparative GLC employed a Pye-Unicam 105 chromatograph. The purity of all title compounds was judged to be >95% by ^1H NMR spectral determinations.

Materials. Benzene, used as received (Aldrich spectrophotometric grade, 99+%, as well as Fisher Spectroanalyzed), was the solvent of choice in the laser flash photolysis (LFP) and photoacoustic calorimetry (PAC) experiments. 1,4-Pentadiene (**2a**) and 3-methyl-1,4-pentadiene (**2b**) were obtained from Aldrich and used as received. 3-Hydroxy-1,4-pentadiene (**2c**; Aldrich) was distilled in vacuo (ca. 1 mmHg) before use. 2-Hydroxybenzophenone was recrystallized twice from ethanol. Di-*tert*-butyl peroxide (Aldrich) was passed through a column of neutral alumina at least three times before use.

3-Isopropyl-1,4-pentadiene (2c). To a solution of 1,4-pentadiene (1.0 g) in dry THF (2.6 mL) at −78 °C under N_2 was added *n*-BuLi (9.2 mL of 1.6 M solution in hexane). The mixture was warmed to room temperature over 1 h and was stirred for a further 2 h. The lower, deep orange layer, which separated on standing, was removed by syringe and added dropwise to a solution of isopropyl methanesulfonate (2.02 g) in dry THF (2.6 mL) at −78 °C under N_2. The mixture was allowed to warm to room temperature, stirred overnight, briefly warmed to 50 °C, and then poured into 1 M NaOH (18 mL) and extracted with pentane (2 × 50 mL). The pentane extracts were washed with saturated $NaHCO_3$ and water, dried over $MgSO_4$ and distilled. The product distilled as a mixture with pentane and was purified by preparative GLC on a 20% Carbowax 20 M column (12-ft) at 60 °C: δ_H 0.87 (6 H, d, CH_3), 1.66 (1 H, m), 2.50 (1 H, dd) 4.97–5.07 (4 H, m, CH_2), 5.71–5.84 (2 H, m, CH); δ_C 19.82, 31.70, 55.10, 114.88, 139.76; *m/z* 110 (M^+, 1), 95 (21), 68 (60), 67 (100), 54 (15), 43 (37), 41 (47), 39 (27); M^+ obsd 110.1091, C_8H_{14} requires 110.1095. Apart from diene **2c**, several $C_{11}H_{16}$ tetraenes were observed to form. Two of these tetraenes were isolated by preparative GLC (20% Carbowax 20 M; 12 ft; 120 °C) and identified as 3,5-divinyl-1,6-heptadiene (δ_H 1.47 (2 H, t, CH_2), 2.80 (2 H, quintet, CH), 5.0 (8 H, m, CH_2), 5.69 (4 H, m, CH_2); δ_C 38.45, 44.93, 114.39, 140.86; *m/z* 147 $(M - 1)^+$ (1), 133 (5), 119 (8) 105 (12), 91 (15), 81 (31), 79 (80), 67 (100), 65 (27), 53 (31)) and 3-vinyl-1,6,8-nonatriene (δ_H 1.50 (2 H, q), 2.10 (2 H, q), 2.76 (1 H, quintet), 5.03 (6 H, m), 5.72 (3 H, m), 6.05 (1 H, m), 6.32 (1 H, m); δ_C 12.28, 35.59, 43.74, 114.06, 116.42, 129.79, 133.60, 136.47, 140.32; *m/z* 148 (M^+) (1), 133 (5), 119 (9), 106 (30), 91 (20), 81 (33), 79 (100), 67 (49), 53 (31).

3-*tert*-Butyl-1,5-dibromopentane. $MeSO_2Cl$ (23.6 g) was added dropwise to a solution of 3-*tert*-butylpentane-1,5-diol[21,22] (15.0 g) and Et_3N (19.0 g) in dry CH_2Cl_2 cooled to 0 °C under

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N_2. The solution was stirred for 1 h then washed with water, 2 M HCl, and saturated NaCl solution, dried over Na_2SO_4, and evaporated. The crude dimesylate was added to a solution of LiBr (32.7 g) in dry acetone (350 mL), which was refluxed for 15 h. This solution was cooled, filtered, and evaporated. Water was added to the residue, which was then extracted several times with ether. The ether layers were washed with water, dried (Na_2SO_4), and evaporated. The residue was distilled at 139 °C (1 mm) to give the dibromide (70%): δ_H 0.90 (9 H, s, CH_3), 1.25 (1 H, m, CH), 1.63 (2 H, m), 2.09 (2 H, m), 3.44 (4 H, m, CH_2); δ_C 24.93, 27.90, 33.21, 34.95, 46.47; M^+ obsd 270.9539, $C_9H_{18}Br_2$ requires 270.9522.

3-*tert*-Butyl-1,4-pentadiene (2d). The dibromide (1.7 g) was heated to 195 °C, and a stream of N_2 was bubbled through it. Hexamethylphosphoric triamide (2.3 g) was added dropwise, and the temperature was slowly raised to 210 °C. The diene was trapped out of the N_2 stream in a dry ice/acetone bath. Pure diene was obtained by preparative GLC on a 12-ft column packed with 20% Carbowax 20 M maintained at 60 °C (lit.[23]): δ_H 0.89 (9 H, s, CH_3), 2.45 (1 H, t, CH), 4.97–5.07 (4 H, m, CH_2), 5.86 (2 H, ddd, CH); δ_C 27.16, 32.74, 59.56, 115.60, 138.57; m/z 124 (M^+, 1), 109 (23), 91 (2), 81 (6), 68 (23), 67 (25), 57 (100), 55 (7).

1-[(Trimethylsilyl)oxy]-3-methylpenta-2,4-diene (5b). Trimethylsilyl chloride (1.1 g) in light petroleum (bp 40–60 °C, 20 mL) was added dropwise to **5a**[24–26] (1.0 g) and pyridine (0.80 g) in light petroleum (20 mL). The solution was stirred for 0.5 h, filtered, and distilled at 73 °C (14 mm) to give **5b** (58%) as a mixture of isomers. The ^1H NMR spectrum indicated the E/Z ratio was ca. 2.4:1: δ_H (E isomer) 0.12 (9 H, s, $Si(CH_3)_3$), 1.76 (3 H, s, CH_3), 4.29 (2 H, d, CH_2OSi), 5.12–5.34 (2 H, m, CH_2), 5.52 (1 H, br t, CH), 6.66–6.83 (1 H, m, CH) (the Z isomer considerably overlapped with the E isomer except for δ 1.79 (3 H, s, CH_3), 5.52 (1 H, br t, CH); δ_C (E-isomer −0.24, 11.90, 69.76, 112.50, 131.55, 134.88, 141.19 (the Z isomer was similar except for peaks at δ 11.73, 113.33, 141.07); m/z 170 (M^+, 11), 155 (50), 80 (25), 75 (96), 73 (100), 70 (10), 59 (12), 53 (13); M^+ obsd 170.1132, $C_9H_{18}OSi$ requires 170.1126.

5-Bromo-3-methylpenta-1,3-diene (4). PBr_3 (1.1 g) was added dropwise to a solution of **5a** (1.0 g) and pyridine (0.04 g) in dry ether cooled to −5 °C in an ice/salt bath. The mixture was stirred cold for 20 min and then ice/water (20 mL) was added. The ether was decanted, and the aqueous phase was extracted with more ether. The combined ether layers were washed (water, saturated $NaHCO_3$, saturated NaCl), dried (Na_2SO_4), and evaporated. The product was distilled at 52 °C (14 mm) (lit.[27] 45 °C (10 mm)) to give 0.75 g (45%) of the E/Z isomer mixture. Attempts to separate them by preparative GLC was unsuccessful. The ^1H NMR spectra overlapped considerably. E isomer: δ_H 1.90 (3 H, s, CH_3), 4.12 (2 H, d, CH_2Br), 5.03–5.63 (2 H, m), 5.80 (1 H, br t, CH), 6.40 (1 H, dd, CH). The Z isomer had similar shifts except for δ 1.85 (3 H, s, CH_3), 6.80 (1 H, dd, CH). The E/Z ratio was 2.0:1: δ_C (E isomer) 11.33, 29.03, 114.85, 126.85, 139.64, 140.12, (Z-isomer) 19.82, 27.82, 117.03, 124.79, 131.82, 138.12; m/z 162, 160 (M^+, 5), 81 (100), 79 (32), 66 (10), 53 (37), 41 (49), 39 (28).

Apparatus. The photoacoustic apparatus has been described in full elsewhere.[4] Briefly, pulses from a Molectron UV-24 nitrogen laser (337.1 nm, ca. 8 ns, ca. 10 mJ/pulse, 2–3 Hz) were used to irradiate argon-purged solutions containing di-*tert*-butyl peroxide (2–12% v/v) and diene (3–5.5 M) in benzene. In the case of **2a** and **2b** the solutions were rendered oxygen free by a series of 2–3 freeze–pump–thaw cycles (in vacuo, ca. 5 mmHg). The samples were flowed through standard 6.5 × 10 mm (internal dimensions) quartz luminescence flow cells (Helma 174). The photolysis gave rise to reactions 1 and 2 from which the net heat evolved produced a shock wave in the solution. The photoinitiated acoustic waves were detected by a piezoelectric transducer (Panametrics V101, response 2.0 μs) in contact with the bottom of the sample cuvette. The transducer signals were amplified (Panametrics ultrasonic preamplifiers), and the analogue signals were relayed to a programmable digitizer/oscilloscope (Tetroniks 7D20/7603).

In order to account for variations in laser intensity during the experiment, a splitter was placed in front of the sample cuvette. A portion of the beam was directed at a second cuvette/transducer/preamplifier arrangement as described above. This "reference" cuvette contained 2-hydroxybenzophenone and acted as the energy monitor for the system. The photostable molecule, 2-hydroxybenzophenone, is particularly suited for this purpose as it returns 100% of the absorbed energy to the solution in the form of heat within a few nanoseconds.[28] Each data point from the sample cuvette was normalized using the signal from the reference cuvette. The ratio of these signal amplitudes defined the normalized acoustic response, N. Each data point was produced from the average of 4 runs of 64–128 shots.

In order to determine ΔH_{rctn} for (1) and (2) the photoacoustic apparatus was calibrated before each experiment. The qualities that make 2-hydroxybenzophenone a good energy monitor, as described above, also make it an excellent calibrant for the photoacoustic experiment. Two methods were used to determine the magnitude of the deposited heat. The magnitude of the heat evolved in the H abstraction reaction was determined using the enthalpic factor, $\alpha = a_R/a_S$, where a_R and a_S are the slopes obtained from the sample and calibration runs, respectively. The first method for determining α involved varying the concentration of di-*tert*-butyl peroxide (or calibrant) over a range of optical densities (0.02–0.16) but keeping the laser intensity constant. The ratio of the slopes ($\alpha = a_R/a_S$) obtained from plots of normalized signal amplitude, N, versus the fraction of light absorbed, $1 - T$, is directly proportional to the enthalpy balance of reactions 1 and 2. In the second method, the concentration of di-*tert*-butyl peroxide (or calibrant) remained constant, the optical densities of the substrate and calibrant solutions being optically matched within ±1%. The laser beam intensity was attenuated over the range 15–100% light transmission by use of a series of neutral density filters.

Laser flash photolysis (LFP) was used to determine the rates of reaction between the *tert*-butoxyl radical and diene. The laser flash photolysis experiments were carried out using pulses from a Molectron UV-24 nitrogen laser (337.1 nm, ca. 8 ns, 10 mJ/pulse). The apparatus has been described elsewhere.[29] All experiments were carried out on deaerated samples under N_2 atmospheres. Since the pentadienyl radicals do not absorb strongly in the visible or in the near-UV, diphenylmethanol (DPM) was used as a probe. The application of DPM as a probe has been fully described elsewhere.[30] Typically, 0.1 M solutions of diphenylmethanol in 1:2 (v/v) benzene/di-*tert*-butyl peroxide and various concentrations of diene (0.001–0.01 M) were used to determine the kinetics of H abstraction for reaction 2.

Acknowledgment. We thank NATO and the Russell Trust for travel grants, which made this research possible, and Dr. Larkin Kerwin for a grant from the President's Fund, which supported J.A.M.S.

Registry No. 1, 3808-35-3; **2a**, 591-93-5; **2b**, 1115-08-8; **2c**, 78395-93-4; **2d**, 49826-91-7; **2e**, 922-65-6; **3b**, 78395-90-1; **3e**, 78395-92-3; (E)-4, 53776-92-4; (Z)-4, 53779-29-6; (E)-**5a**, 1572-08-3; (Z)-**5a**, 40930-20-9; **5a** radical, 135105-97-4; (E)-**5b**, 135106-01-3; (Z)-**5b**, 135106-02-4; **5b** radical, 135105-98-5; *tert*-butoxy, 3141-58-0; 3,5-divinyl-1,6-heptadiene, 135105-99-6; 3-vinyl-1,6,8-nonatriene, 135106-00-2; 3-*tert*-butylpentane-1,5-diol, 50635-65-9; 3-*tert*-butyl-1,5-dibromopentane, 758-75-8; hydrogen, 1333-74-0; ethyl 3-methylpenta–2(E),4-dienoate, 37850-26-3; ethyl 3-methylpenta-2(Z),4-dienoate, 37850-27-4.

Supplementary Material Available: ^1H and ^{13}C NMR spectra of compounds **2c**, **2d**, *trans*-**5b**, and 3-*tert*-butyl-1,5-dibromopentane, ^1H NMR spectrum of *cis*-**5b**, and experimental details of the preparations of **5a**, 3-*tert*-butylpentane-1,5-diol, and ethyl 3-methylpenta-2,4-dienoate (11 pages). Ordering information is given on any current masthead page.

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