6a·HBr as an oil: ¹H NMR (CDCl₃) δ 1.20-1.80 (8 H), 2.62 (s, CH₃, 3 H), 4.70 (m, CHN, 1 H), 5.50 (m, CHO, 1 H).

Compound 6a-HBr was dissolved in 95:5 MeCN/H₂O, and the solution was allowed to stand at room temperature for 30 min. Evaporation of the solvent gave 5a.

Conversion of Compounds 5 to 7. A solution of 5 (0.8 mmol) in dichloromethane was shaken with 0.1 N aqueous NaOH. The two liquid layers were separated, and the organic layer was dried (MgSO₄). Evaporation of the solvent gave, in quantitative yield, the following: 7a, mp 144-146 °C (benzene) (lit.²⁶ mp 145-146 °C). 7b, recrystallized from CHCl₃. 7c, recrystallized from CHCl₃. 7e, mp 122-123 °C (CHCl₃) (lit.²⁶ mp 123-124 °C).

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Dissociation and Aromatization of a Semibenzene. Reactions of Triphenylmethyl and Methyl Isobutyryl Radicals

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Semibenzene 4, which can be regarded as the recombination product of triphenylmethyl and methyl isobutyryl radicals (5), affords exactly these intermediates on thermolysis or inefficiently on direct photolysis. Recombination and disproportionation of these dissimilar radicals proceeds with a much lower barrier than the dimerization of triphenylmethyl. Whereas thiophenol or triplet 9-fluorenone aromatize 4, thermolysis in the presence of 1,4-cyclohexadiene allows trapping of 5 and oligomeric radical 13. From the measured heat of aromatization (22.0 kcal/mol), the C-H bond dissociation enthalpy of 4 and its analogue lacking the side chain ("p-isotriphenylmethane") is calculated to be 54 kcal/mol, the lowest value known for any closed-shell, neutral hydrocarbon. Exposure of 4 to the atmosphere causes rapid autoxidation to hydroperoxide 19, which thermolyzes in the GC to aromatic ketones and phenols instead of undergoing a 1,2-aryl shift.

In 1953, McElvain and Aldridge reported the following reaction in the absence of solvent:¹ As in the case of



hexaphenylethane itself,² the actual structure of starting material 1 was later found to be the semibenzene methyl 7,7-diphenyl-p-mentha-1(7),2,5-triene-8-carboxylate, 4.3



McElvain and Aldridge tried to deduce the decomposition mechanism by thermolyzing 4 in various solvents thought to be capable of trapping any intermediate radicals or ions. For example, heating 4 in methyl methacrylate failed to initiate polymerization, and toluene as solvent left the product composition unchanged except that 3 was supposedly absent. On the basis of such trapping reactions (and the wrong structure 1), these early workers proposed an unlikely looking concerted cleavage of 1 to Ph₃CH plus

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2. Another dubious concerted process via a "six-membered cyclic complex" of 1 and 2 was offered to account for 3.

Since 4 can be regarded as a recombination product of triphenylmethyl (trityl) and methyl isobutyryl radicals (5), our interest in compounds containing weak bonds⁴⁻⁶ and the paucity of data on radical cross reactions⁷⁻⁹ prompted us to reexamine its decomposition. The comment that



4 was sensitive to light¹⁰ further suggested to us that it might be a photochemical source of free radicals. The present knowledge about semibenzenes coupled with the results to be presented here provide overwhelming evidence that thermolysis of 4 is also a radical reaction. Kinetic and thermodynamic measurements on 4 have allowed us to construct an energy diagram for its thermolysis and to demonstrate that its allylic C-H bond is the weakest on record for this type of compound.

Kinetics and Thermochemistry of 4. A sample of 4 was prepared in our laboratory from triphenylmethyl fluoroborate and dimethylketene methyl trimethylsilyl

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species	$\Delta H_{\rm f}$, kcal/mol	method	ref	
Ph ₃ CH	64.8	combustion, vaporization, calorimetry	15	
Ph ₃ CH	67.4	MM2	this work	
6 [°]	164.4	$2\Delta H_{\rm f}({\rm Ph}_{\rm 3}{\rm CH})(64.8) - \Delta H_{\rm hydrog}(6)(-34.8)$	16	
6	176.8	MM2	this work	
Ph ₃ COO	78.1	$\Delta H_{f}(Ph_{3}CH)(64.8) - [C - (C)_{3}(H)](-1.9) + [C - (C)_{3}(O)](-6.6) + [O - (O)(C)](18)$	17	
Ph ₃ C [•]	87.6	$(\Delta H_{\rm f}(6)(164.4) + {\rm BDH}(6)(10.7))/2$	15, 17	
Ph ₃ C [•]	87.1	$\Delta H(Ph_3COO^* \rightarrow Ph_3C^* + O_2)(9.0) + \Delta H_t(Ph_3COO^*)(78.1)$	18	
Ph ₃ C [•]	93.5	$BDH(Ph_{3}CH)(80.8) + \Delta H_{f}(Ph_{3}CH)(64.8) - \Delta H_{f}(H^{\bullet})(52.1)$	15, 19	
Ph ₃ C [•]	89.5	$BDH(t-Bu-H)(95.8) - RSE(Ph_{3}C^{\bullet})(19) - \Delta H_{f}(H^{\bullet})(52.1) + \Delta H_{f}(Ph_{3}CH)(64.8)$	13, 15	
Ph ₃ C•	87.7	$BDH(Ph_3CH)(75) + \Delta H_f(Ph_3CH)(64.8) - \Delta H(H^*)(52.1)$	20	
<i>p</i> -isotoluene	35. 9	ion cyclotron resonance	21	
<i>p</i> -isotoluene	39.0	MM2	this work	
4	-15.6	solution calorimetry, group additivity	see text	
4	-13.2	MM2	this work	
5	-78	$BCH(8)(85) + \Delta H_{f}(8)(-111.0) - \Delta H_{f}(H^{\bullet})(52.1)$	see text	
7	-32.6	MM2	this work	
7	-37.6	group additivity	see text	

Table I Heats of Formation

acetal,¹¹ and its thermolysis kinetics in degassed benzene were monitored by NMR, leading to the following rate constants: $(T, {}^{\circ}C, 10^{4}k, s^{-1})$ (109.46, 1.97), (117.25, 4.25), $(123.69, 6.63), (127.72, 10.4), (130.80, 13.6), \Delta H^* = 26.6 \pm$ 2.3 kcal/mol, $\Delta S^* = -6.4 \pm 5.8$ eu. The rate was relatively insensitive to solvent polarity, as shown by $k = 2.28 \times 10^{-4}$ s⁻¹ in acetonitrile at 109.3 °C. Comparing 4 with trityl dimer 6 ($\Delta H^* = 18.4 \text{ kcal/mol}, \Delta S^* = -3 \text{ eu}$),¹² we see that



the additional resonance energy (RSE) and steric repulsion of trityl compared to methyl isobutyryl radical decreases ΔH^* by only 26.6-18.4 = 8.2 kcal/mol. This value is surprisingly small considering that the RSE difference alone would surely exceed 8 kcal/mol.¹³ As described below, we have analyzed this problem in detail and conclude that the discrepancy arises not from any anomaly in 4 but from the higher barrier to dimerization of Ph₃C.

Thermochemical calculations also predict that the difference between the bond dissociation enthalpy (BDH) of 4 and 6 will be much greater than the observed $\Delta \Delta H^*$ of 8.2 kcal/mol. The BDH of 6 is 10.7 kcal/mol according to ESR equilibrium studies.¹⁴ but the same method cannot succeed with 4 on account of radical disproportionation. In order to obtain BDH (4), we require the heat of formation (ΔH_t) of 4, 5, and Ph₃C[•]. However, none of these $\Delta H_{\rm f}$'s is known precisely, as shown by the data in Table I. We carried out a MM2 calculation on 4, but the rather poor result obtained for 6 by this method prompted us to undertake an experimental determination of $\Delta H_f(4)$. In view of its lability toward oxygen, combustion calorimetry is not feasible; however, solution calorimetry offered an appealing alternative. The experimentally determined¹⁵

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 $\Delta H_{\rm f}$ of triphenylmethane could be corrected using group additivity to obtain ΔH_f of 7, the known¹⁰ aromatic isomer of 4. If the isomerization enthalpy (ΔH_i) of 4 to 7 could be determined, $\Delta H_{\rm f}(4)$ would be easily calculable from $\Delta H_{\rm i}$



= $\Delta H_f(7) - \Delta H_f(4)$. Semibenzenes can be aromatized by acid^{2,22,23} or base¹⁰ but only certain reagents will allow survival of the ester group of 4. We were pleased to discover that 0.023 M DBN in DMSO would isomerize 4 to 7 in 5 min. GC analysis revealed no methanol and both GC and NMR (DMSO- d_6) showed exclusively 7. After correction for the heat of solution of DBN, we found ΔH_i to be -22.0 kcal/mol. ΔH_f of 7 can be calculated using Benson's group equivalents²⁴ as $\Delta H_f(Ph_3CH)-[C_B - (H)]$ + $[C_B - (\tilde{C})] + [C - (C_B)(C)_2(CO)] + 3[C - (\tilde{H})_3] + [CO]$ -(C)(O)] + [O - (CO)(C)] = 64.8 - 3.30 + 5.51 + (2.5) - 64.8 - 3.50 + 5.51 + (2.5) - 64.8 - 5.50 + 5.530.24 - 33.4 - 41.3 = -35.4 kcal/mol. However, use of these group increments with aliphatic esters of known ΔH_f gives values that are consistently too positive. As shown by the following examples, the method of Pedley, Naylor, and Kirby¹⁵ is more reliable (compound, experimental $\Delta H_{\rm f}$, Benson $\Delta H_{\rm f}$, Pedley $\Delta H_{\rm f}$, kcal/mol): methyl 2-methylbutyrate, -117.7, -114.9, -116.1; ethyl propionate, -110.8, -108.4, -110.9; dimethyl tetramethylsuccinate, -211.5,25 -203.1,²⁶-212.7.²⁶ Since the newer additivity scheme does not yet include aromatic compounds, we employed an indirect method: equating the heat evolved in the hypothetical conversion of Ph₃CH to 7 to the heat of the analogous conversion of benzene to methyl 2-methyl-2phenylpropionate (MMPP). We can estimate ΔH_f of MMPP from $\Delta H_{\rm f}(tert$ -butylbenzene)¹⁵ by assuming that introduction of -COO- does not affect the contribution of the attached groups. Thus $\Delta H_f(MMPP) = \Delta H_f(tert$ butylbenzene) + K2(O2 4) + O2(K2 1) = -5.42 - 44.2 -35.1 = -84.7 kcal/mol. Since this value is 104.5 kcal/mol more negative than $\Delta H_{\rm f}$ (benzene) (19.8), it follows that

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Figure 1. Enthalpy diagram for dissociation and recombination.

 $\Delta H_{\rm f}(7)$ lies the same amount below $\Delta H_{\rm f}(\rm Ph_3CH)$ (64.8 kcal/mol). The resulting $\Delta H_f(7)$ is -39.7 kcal/mol, which is less than the Benson value of -35.4 kcal/mol. Since both of these methods involve assumptions, we shall simply take $\Delta H_{\rm f}(7)$ to be -37.6 ± 2.5 kcal/mol. Adding this figure to our measured ΔH_i yields $\Delta H_f(4) = -15.6 \pm 2.5$ kcal/mol, a value not far from the -13.2 kcal/mol calculated by MM2 (cf. Table I).

 $\Delta H_{\rm f}$ of the methyl isobutyryl radical (5) and of methyl isobutyrate (8) can be estimated by three different approaches: thermolysis of azoalkanes, thermolysis of dimethyl tetramethylsuccinate (9), and ESR determination of carboalkoxyalkyl radical rotational barriers. We showed in 1980 that a Polanyi plot of azoalkane activation energy versus BDH of the corresponding alkane approximates a straight line with a slope of unity.²⁷ Using more recent BDH data^{28,29} (10 points) and azoalkane ΔG^* (100°) values gave a line ΔG^* (100°) = 0.885(BDH) + 46.9, with a correlation coefficient of 0.97. Ethyl azoisobutyrate and methyl azoisobutyrate exhibit ΔG^* (100°) = 27.1 kcal/ mol_{27}^{27} corresponding to BDH(8) = 83.6 kcal/mol.



In the second method, Rüchardt and Rausch^{13,25} have measured both $\Delta H_{\rm f}(g)$ (-211.5 kcal/mol) and the activation parameters for central C-C bond homolysis of dimer 9 $(\Delta H^* = 55.0 \pm 3.1, \Delta S^* = 12.0 \pm 5.0 \text{ eu})$. Making the reasonable assumption that there is no barrier to radical recombination³⁰ allows us to calculate that $\Delta H_f(5) = -78.3$ kcal/mol. The sum of this figure and $\Delta H_{\rm f}({\rm H}^{\bullet})$ minus $\Delta H_{\rm f}(8)$ calculated by Pedley's scheme¹⁵ (-111.0 kcal/mol) gives BDH(8) = 84.8 kcal/mol.

The last approach to estimating BDH(8) relies on the observed linear correlation between the rotational barrier of RCH₂[•] and BDH (RCH₂ - H).^{31,32} Placing the 11 kcal/mol rotational activation energy for CH₃CHCOOEt³³ and 5^{34} on this line and ignoring steric contributions to the barrier yields BDH (ROOCCH₂ – H) = 90 kcal/mol. Since methyl groups on a radical center decrease BDH of the corresponding hydrocarbon by 2-3 kcal/mol even when the radical is resonance stabilized,²⁸ we can estimate BDH(8) as 85 kcal/mol. Fischer has stated that the delocalization energy for CH₃CHCOOEt is about 9.6 kcal/

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mol.³³ Assuming that this value equals the C-H BDH difference between isobutane (95.8 kcal/mol)²⁹ and 8, we obtain BDH(8) = 86.2 kcal/mol. The average (85 kcal/ mol) of the four BDH's just deduced (83.6, 84.8, 85, 86.2) will be taken as BDH(8), leading to $\Delta H_{\rm f}(5) = -78 \pm 2$ kcal/mol. Combining this value with the average ΔH_f of 4 and Ph_3C^{\bullet} as shown in the equations below, we calculate



 $BDH_2 = 26.7 \pm kcal/mol$

 $\Delta H_{\rm f}(4) = -15.6 \pm 2.5$ $\Delta H_{\rm f}(5) = -78 \pm 2$ $\Delta H_{\rm f}({\rm Ph}_3{\rm C}^{\bullet}) = -89.1 \pm 2.6$

BDH(4) to be 26.7 ± 4 kcal/mol, which is much greater than the corresponding figure of 10.7 kcal/mol for 6. Although better precision in BDH(4) would be desirable, it must be remembered that bond dissociation enthalpies are not easily determined. We shall present evidence below favoring a value near 27 kcal/mol, thus placing a constraint on $\Delta H_{\rm f}$ of 5 and Ph₃C[•]. If these radicals were of higher energy than our estimates and the C-H bonds of 8 and Ph₃CH were correspondingly stronger, BDH(4) would exceed $\Delta H^*(4)$ by more than the combined error. In that case, ΔH^* for cross recombination would have to be negative, which would require the existence of a complex in rapid equilibrium with the radicals. Such situations are known,²⁹ but we have no reason to include this complication in our mechanism.

Combining the above thermochemical data with the enthalpies of activation allows us to construct the energy diagrams shown in Figure 1. $\Delta H^*(4) - \Delta H^*(6)$ is unexpectedly small because ΔH^* of 6 is raised by the high barrier to recombination of two Ph₃C[•] radicals while ΔH^* of 4 equals its true BDH. The BDH difference (Δ BDH) is (26.6 - 10.7) = 15.9 kcal/mol, which is close to one determination of the RSE difference between Ph₂C[•] and 5 (15.5 kcal/mol).¹⁴ However, if we ascribe the entire Δ BDH to resonance effects, the steric strain of 4 and 6 would have to be the same. In that case, it would be hard to understand why Ph₃C[•] dimerization exhibits such a large barrier. Most likely, the BDH of 6 is lowered by both its elevated ground-state energy due to steric strain, and some fraction of the additional resonance energy of Ph₃C[•] relative to 5.13,16

The large exothermicity found for $4 \rightarrow 7$ rationalizes why a base as weak as DBN was able to catalyze aromatization. The pK_a of Ph₃CH in DMSO is 30.6,³⁵ which should be

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Table II. Decomposition Products of 4. % Yield^a (GC Condition 1 and 2)

7 8 9 10	21
1 trace trace	
4.1 trace trace	
1 35 trace 16	
2.3	
1 9.1 2.2 1.5	16
5	
1	
1 2 1 5 1	35 trace 16 .3 9.1 2.2 1.5

^a Yield of 3, 9, and 10 = 2 (moles product/moles starting 4). No entry indicates that the product was not detected by GC. ^bResidual 4, measured by NMR 'Reference 1 ${}^{d}F$ = 9-fluorenone irradiated at 435 nm. 'Toluene-d₈.

very close to the pK_a of 7. Since both 4 and 7 afford the same triarylmethide, heterolysis is 22 kcal/mol easier from 4 than 7. Simple free energy considerations show that this energy gap corresponds to 16.1 pK, units, leading to a pK, value for 4 of 14.5. This figure is sufficiently low that DBN $(pK_a \sim 12)^{36}$ can produce triarylmethide fast enough to effect aromatization under our experimental conditions. Among compounds containing C-H bonds but lacking electronegative atoms, there are few more acidic than 4.37 (The ester functionality of 4 would of course have a negligible effect.) Since 4 lies 22 kcal/mol above 7, homolytic C-H bond scission should also be facilitated by this amount, so that BDH(4) = (76 - 22) = 54 kcal/mol. Ignoring the ester side chain, this BDH is the lowest one known for any neutral closed-shell hydrocarbon. Isotoluene, for example, exhibits a C-H BDH of 64 kcal/ mol.²¹

Product Studies of 4. On heating a benzene solution of 4 to 110 °C, we found the same products as McElvain and Aldridge but without their "yellow oil" (cf. Table II). This oil, which proved to be a hydroperoxide (see below), was avoided in our study by careful exclusion of oxygen. It is gratifying that the yield of methyl isobutyryl groups (66 + 12 + 4) = 82% is close to that of trityl groups (93%)and that the product balance is high.

The ratio of 3 to 2 obtained in our solution-phase thermolysis is considerably less than that reported¹ for pyrolysis of neat 4. This observation is consistent with the notion that 3 arises by attack of 5 on 2, whose concentration is lower in solution (cf. Scheme I). Product 3 is formed via this same radical addition in the thermolysis of methyl azoisobutyrate.38

In the early stages of this work, thiophenol was added to 4 in hopes of trapping trityl and methyl isobutyryl radicals. However, thiophenol isomerized 4 to the 1,5hydrogen shift product 7, presumably by a well-precedented radical chain reaction.³⁹⁻⁴¹ This aromatization has been seen as a side reaction in the trityl dimer³⁹ but did not occur in the dimer of 1,1-diphenyl-2-methylpropyl radicals,42 which underwent the expected dissociation and thiophenol trapping. Chain propagation via thiyl radical hydrogen abstraction is favored in 4 by steric accessibility of the ring hydrogen as well as by its very low BDH (see above).

Radical trapping was successful with 1,4-cyclohexadiene (1,4-CHD) as scavenger, causing formation of two new

Scheme I. Radical Reactions of 4



products 8 and 10, which were identified by comparison with authentic samples (cf. Table II).



As shown in Scheme I, these compounds must arise when radicals 5 and 13 abstract hydrogen from 1,4-CHD. However, 1,4-CHD is not a particularly efficient scavenger of 5, as evidenced by continued attack of 5 on primary product 2. Since the propagation rate constant for polymerization of methyl methacrylate (2) is 2.5×10^3 M⁻¹ s⁻¹ at 110 °C,⁴³ and since the concentration of 1,4-CHD is at least 5 times greater than that of 2, we may conclude that the rate constant of 5 with 1,4-CHD is below 2.2 \times $10^3 \text{ M}^{-1} \text{ s}^{-1}$. This figure is entirely reasonable in light of slow hydrogen transfer rate (k < 100) from 1,4-CHD to allyl or benzyl radicals at 25 °C.44 It is of interest that 1,4-CHD does manage to decrease the yield of 2 4-fold, showing that the formation of 2 without scavenger occurs mostly outside the solvent cage.

Though the scavenging results strongly support a radical mechanism, additional evidence was sought by ESR

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spectroscopy. Thus heating a hexadecane solution of 4 at 25-106 °C in the ESR spectrometer gave rise to the spectrum of triphenylmethyl radical,45 uncontaminated by 5.³³ The same spectrum was produced by heating ditert-butyl peroxide with triphenylmethane to 140 °C. It was shown by computer simulation⁴⁶ that 12 was not the carrier of the observed spectrum, since its coupling constants would surely resemble those of 4-tert-butyltrityl radical.14

The reason why McElvain and Aldridge found 4 to be a poor initiator of methyl methacrylate polymerization is no doubt the powerful radical scavenging ability of Ph₃C^{•.47} These authors expected 5 to attack toluene and, based on the literature of the time,⁴⁸ might have expected the same of Ph_3C^{\bullet} . However, we obtained no evidence for participation of toluene in the reaction since neither 8 nor bibenzyl were found and any GC peaks which might have been 1,1,1,2-tetraphenylethane constituted less than 3% of the product. Since the BDH of toluene is much greater than that of 1,4-CHD, the absence of 8 in toluene is easily understood. The failure of Ph₃C[•] from 4 to attack toluene probably derives from its low steady-state concentration relative to that from triarylmethyl dimers.⁴⁸ Not only is the dissociation equilibrium constant 10⁹ smaller for 4 than 6, but the radical pair from 4 will disproportionate rapidly.

Independent Generation of Ph₃C[•] and 5 from an Azoalkane. Since the reaction of radical pairs containing structurally different partners has been little studied,^{7-9,49} we sought to determine the disproportionation to recombination ratio, k_d/k_r , of Ph₃C[•] and 5. Triene 4 is obviously not an appropriate precursor because it is the recombination product; however, an unsymmetrical azoalkane that affords Ph₃C[•] and 5 would be ideal. We therefore generated the unstable azoalkane 14 using Baldwin's procedure⁵⁰ and allowed it to decompose to Ph₃CH, 2, and 4. Because

4 is not stable enough for GC analysis, it was aromatized quantitatively to 7 with thiophenol. The yield of Ph₃CH and 4 was 33% and 54%, respectively, using biphenyl as an external GC standard. HPLC analysis of decomposed 14 without addition of thiophenol gave the same ratio of Ph₃CH to 4. Additionally, 11% of triphenylcarbinol was found, of which some arose during the synthesis of 14, and the rest is attributed to adventitious oxygen. The yield of 2, the other disproportionation product, was only 9%, suggesting that it undergoes secondary reactions.³⁶

From the yield of Ph₃CH and 4, we conclude that k_d/k_r = 0.61, a lower value than the 0.79 found for methyl isobutyryl radical.³⁸ Since Ph_3C^{\bullet} is an unlikely hydrogen atom donor, statistics alone predict less disproportionation from the heterogeneous pair Ph₃C[•], 5. Recombination is clearly an important pathway for Ph₃C[•] and 5; hence, the observed rate constants for thermolysis of 4 should be corrected for "radical return". Thus $k_{obs} = k_l k_d / (k_d + k_r)$

= $0.38k_1$ so that C-C bond homolysis of 4 is actually 2.6 times faster than the observed rate constant. Though this correction would lower $\Delta H^*(4)$ in Figure 1 by 0.6 kcal/mol, the experimental error in ΔH^* and BDH(4) is large enough that our conclusions remain unchanged. It is important to note that the large fraction of radical return supports the notion of a negligible barrier to this process as shown in Figure 1. Since disproportionation should be much less sensitive than recombination to any steric barrier, the predominance of recombination implies that it involves virtually no barrier. We further note that radical return will be less important in solvents of lower vicosity, thus rationalizing the $\sim 20\%$ faster rate in MeCN than benzene.

In light of the results with 14, we should reconsider a related observation⁵⁰ about thermolysis of 15. Inclusion of ethanethiol gave mostly the desired product 16, along with some 17 that probably arose by disproportionation in the solvent cage. Without thiophenol, the reaction is analogous to our study of 14 so formation of triene 18 would be expected. This triene may have gone undetected on account of its lability but may be responsible for the lower overall yield of 16 and 17 in the absence of thiol. Moreover, the alkyl radical from 15 could be less prone to recombine than our more delocalized 5.



Reaction of 4 with Oxygen. Two groups have attested to the reactivity of 4 toward oxygen^{1,10} though the product was not identified. In our hands, brief exposure of 4 to air afforded a yellow, viscous oil whose structure was found to be hydroperoxide 19. ¹³C NMR comparison of 19 with



authentic trityl hydroperoxide was particularly revealing, but neither compound showed a signal for OOH in the ¹H NMR. The IR spectrum, however, exhibited a distinct OOH band at 3510 cm⁻¹ for both 4 and trityl hydroperoxide. Oxidation of 4 no doubt proceeds via radical chain autoxidation as in the case of other semibenzenes.^{42,51}

In the course of analyzing the thermolysis products of 4, we injected 19 into the GC and noticed that it decomposed to a mixture of phenols and ketones in the mole ratio shown below. Although this reaction can be viewed as an

19
$$\xrightarrow{200 \text{ C}}$$
 PhOH + PhCOPh + ArOH + PhCOAr + Ph₂ArCOH
3.8 2.4 1.2 2.0 1.0
Ar = $\xrightarrow{}$ COOMe

ordinary β -scission of an alkoxyl radical, triarylmethoxy radicals generated from peroxide thermolysis do not cleave but rather rearrange via a 1,2-aryl shift to 1-phenoxy-benzhydryl radicals. 52,53 On the other hand, there are

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reports that cobalt-catalyzed decomposition of trityl hydroperoxide leads to cleavage products such as ours.⁵⁴ Since rearrangement is exothermic while β -scission is endothermic, it is not surprising that higher temperatures favor cleavage.⁵⁵ Thus the high temperature of our GC injection port (220 °C) may have been responsible for the observed reaction. Alternately, we note that ketones and phenols are typical products of acid-catalyzed hydroper-oxide heterolysis.⁵⁶ Perhaps a small amount of phenol is produced by radical rearrangement followed by decomposition of the benzhydryl hemiketal, and this phenol is sufficiently acidic at 220 °C to catalyze heterolytic decomposition of 17.

Photochemistry of 4. The reported photolability of 4^{10} and the photolytic dissociation of 20^{57} prompted us to expose a sample of 4 to UV light. The UV spectrum of



4 ($\lambda_{max} = 310 \text{ nm}, \epsilon = 25200$) permitted irradiation through a Pyrex NMR tube but we found the photoreaction to be inefficient ($\phi = 0.0015$). This low quantum yield must be due to radiationless decay, not to radical recombination since we know that $k_d/k_r = 0.61$. Despite the lower product balance than thermolysis, most of the products were the same (Table II), suggesting the same C-C dissociation as the primary step. The major new product was 9-phenylfluorene (21), which surely arose by secondary photolysis



of $Ph_3C^{\bullet,58-62}$ This process, coupled with the much lower temperature in the photolysis, produces a lower steady state concentration of Ph_3C^* , allowing formation of 8, 9, and 10. The dissociation of 4 most likely occurs on the singlet surface⁶³ because olefins do not intersystem cross rapidly.

Finally, the triplet-sensitized photolysis of 4 was investigated using 9-fluorenone (F) and 435-nm irradiation to prevent 4 from competing for light. We expected that the 53 kcal/mol triplet energy of F would suffice to populate triplet 4, which would then decay radiationlessly by twisting of the flexible exocyclic double bond.⁶⁴ Surprisingly, the quantum yield for destruction of 4 was 0.5, with aromatization being the major process (Table II).

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This result is in accord with the excellent hydrogen-donating ability of 447 and the known photoreducibility of F.65 Hydrogen transfer affords triarylmethyl radical 12,

$$4 + F^{*3} \longrightarrow 0 + 12$$

which picks up a second hydrogen either from 22 or from starting 4.66 The latter is not likely, however, since it amounts to a chain reaction that should have also occurred on direct irradiation, where 7 was formed with low quantum yield. It is also conceivable that 22 transfers hydrogen to 4 and that the resulting 23 gives up a ring hydrogen to some other radical. Energy transfer from F^{*3} to 4 followed

4 + 22
$$\longrightarrow$$
 Ph \xrightarrow{H} COOMe + F
Ph 23

by dissociation of 4^{*3} may be responsible for the observed Ph₃CH (Table I) but we were unable to detect the expected products from 5. In view of the much lower product balance than in the other reactions, formation of high molecular weight materials is likely.

In summary, we have found that in contrast to McElvain and Aldridge's conclusion, 4 undergoes C-C homolysis with heat or inefficiently with UV light to produce trityl and methyl isobutyryl radicals. Thermochemical considerations and independent generation of these radicals show that they competitively disproportionate and recombine with little activation energy. From the enthalpy of aromatization of 4, we calculate its pK_a to be 14.5 and its C-H bond dissociation enthalpy to be only 54 kcal/mol. Autoxidation of 4 affords the hydroperoxide, which fragments at high temperatures to ketones and phenols.

Experimental Section

General. The following instruments were employed in this work: NMR, JEOL FX-90Q and IBM AF 300; UV, Cary 17 and Hewlett-Packard 8452A; mass spectroscopy, Finnigan 3300; gas chromatography, Antek 300, HP 5890 (computer interfaced); IR, Beckman 4230. NMR samples were degassed to 10⁻⁴ Torr on a vacuum line using NMR tubes equipped with 10/30 standard taper joints. Benzene- d_6 and toluene- d_8 from Cambridge Isotope Laboratory were used as received. The NMR samples were thermolyzed by total submersion in a DC-200 silicone oil bath contained in a 4-L Dewar flask. The bath temperature was regulated with a Bayley Model 123 temperature controller and was measured with a platinum thermometer connected to a HP 3456 6 1/2 digit voltmeter. An Oriel 500-W high-pressure mercury lamp was employed in all photochemical work. Authentic samples of 9³⁸ and 10⁶⁷ were prepared according to the literature, and 10 was purified by preparative GC. These compounds were inseparable on all GC columns tried except for the capillary FFAP (cf. Table VI, supplementary material). The NMR spectra of 9 and 10 were in good agreement with those reported. 38,68 All other authentic compounds were purchased from Aldrich. Molecular mechanics calculations were carried out using PCMODEL-PI v. 3.2 from Serena Software.

Synthesis and Oxidation of 4. Compound 4 was synthesized following Reetz's procedure¹¹ and was oxidized to hydroperoxide 19 by exposure to air. The hydroperoxide was a slightly yellow, viscous oil, whose identification was based on iodometric titration

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and on its NMR and IR spectra. A 68.2-mg sample of 19 purified by SiO₂ chromatography with 5% EtOAc-95% hexane eluent was reacted with 2 mL of saturated aqueous NaI in 5 mL of CHCl₃ and 5 mL of CH₃COOH with FeCl₃ catalysis.⁶⁹ Titration of the liberated I_2 with standard $Na_2S_2O_3$ indicated that 19 was 91.4% pure: ¹H NMR (C_6D_6) δ 1.46 (6 H, s), 3.20 (3 H, s), 7.2 (14 H, m); ¹³C NMR (C_6D_6) δ 26.59, 46.32, 51.64, 93.97, 125.45, 127.57, 128.00, 129.30, 129.63, 141.60, 143.28, 144.37, 176.51; IR (CHCl₃, cm⁻¹) 3510 (OOH), 3000 (Ar-H), 1725 (-COOMe). For comparison, the ¹³C NMR and IR spectra of authentic triphenylmethyl hydroperoxide (Aldrich) were determined: ¹³C NMR (C_6D_6) δ 93.80, 127.62, 128.00, 129.35, 143.23; IR (CHCl₃, cm⁻¹) 3510 (-OOH), 3000 (Ar-H). Neither hydroperoxide showed the -OOH group in the ¹H NMR spectrum.

Studies with 2-[(Triphenylmethyl)azo]-2-carbomethoxypropane (14). To a three-neck flask was added 0.18 g of degassed acetone tritylhydrazone.⁵⁰ The solid was then placed under a blanket of nitrogen. Dry THF (3 mL) was added, the mixture was cooled to -78 °C, 0.39 mL of MeLi (1.42 M) was transferred into the flask under nitrogen, and the mixture was stirred for 20 min. Methyl chloroformate (53 mg) was added, and the solution was stirred for 3 h.

To analyze the decomposition products of 14, an aliquot was warmed to room temperature for 15 min. A 0.2-mL portion of this solution and 10 μ L of PhSH were placed into a tube fitted with a 10/30 standard taper joint and the mixture was freeze-thaw degassed three times under vacuum. The tube was sealed and allowed to stand at room temperature for 1-2 days until the pale yellow color had disappeared. The solution was filtered, and the products were analyzed by GC with biphenyl as external standard using a SE-54 capillary column, inj. 200 °C, det. 250 °C; initial temperature 40 °C, initial time 5 min, rate 20 °C/min, final temperature 250 °C, final time 20 min.

For HPLC analysis, the reaction solution was warmed to room temperature for 15 min and filtered, and a known weight of anthracene was added as external standard. A 5- μ L aliquot was then injected into a 4.6 mm \times 25 cm silica gel column. The eluent was initially pure hexane, but the percentage of ethyl acetate was increased to 15% over the course of 15 min.

Solution Calorimetry. The glass Dewar flask was the one used much earlier for determining heats of hydrogenation.⁷⁰ Temperature was monitored by a thermistor connected to a 61/2digit voltmeter set to take a reading every second. The data were transferred to an IBM-compatible computer by means of a metrabyte MBC-488 HPIB interface card, and the temperature rise was calculated from a least-squares fit of the pre- and post-reaction periods. Electrical calibration was carried out by passing an accurately known current (145 mA) and voltage (14.95 V) for a carefully measured time (80 s) through a small heating coil immersed in the solution. The reaction mixture was stirred under Ar by means of a glass propeller driven magnetically by a constant speed motor.

Four determinations of the heat equivalent of the calorimeter plus 250 mL of freshly dried and distilled DMSO gave a value of 172.23 ± 0.42 cal/deg. A 0.6467-g portion of 4 was dissolved in the DMSO contained in the calorimeter, the solution was allowed to equilibrate, and 0.7001 g of DBN was injected, causing a temperature rise of $0.227\,65\,$ °C. After the solution had equilibrated again, 1.4656 g of DBN was added, causing a rapid temperature drop of 0.0258 °C. The isomerization enthalpy was calculated (0.240 deg \times 172.23 cal/deg)/1.88 mmol = 22.0 kcal/mol. The error in this figure is determined mainly by the purity of 4, which was at least 95% by NMR.

Decomposition Product Study. The product identification relied mainly on GC and GC/MS analysis. The product yields were obtained from GC relative peak areas (FID detector) using biphenyl as an external standard and the experimentally determined molar response factors. GC and GC/MS conditions are listed in Tables III and IV while the MS fragmentation patterns of selected compounds are shown in Table V (see supplementary material).

Pyrolysis of 19. When injected into the GC (condition 2), hydroperoxide 19 decomposed to the five products shown in the text. Phenol and benzophenone were identified by comparison of retention time with that of authentic materials while the other structures were deduced from GC/MS (conditions 1 and 4); see Table V (supplementary material) for mass spectra. The products were roughly quantified by assuming equal FID weight response factors.

Thermolysis of 4. A C_6D_6 solution of 4 in an NMR tube was degassed and sealed. The sample was thermolyzed for 8 h at 110 °C and monitored by ¹H NMR. Methyl methacrylate and triphenylmethane were identified by both NMR and GC (conditions 1, 2, and 3). Thermolysis kinetics were carried out similarly using degassed, sealed solutions of 4 in NMR tubes immersed completely in a precisely regulated oil bath. Temperature was measured with a platinum thermometer and a HP 3456 6 1/2 digit voltmeter. First-order plots were linear to 2 half-lives, but after this point, the signals became too small for accurate integration.

A 0.5-mL benzene- d_6 solution of 15.5 mg (0.045 mmol) of 4 and 16 μ L of 1,4-cyclohexadiene (0.169 mmol) was degassed and sealed in an NMR tube. The sample was thermolyzed at 110 °C and monitored by ¹H NMR. The completely decomposed product mixture was analyzed by GC (conditions 1, 2, and 3), as shown in Table VI (supplementary material). The ratio of 2 to 8 to triphenylmethane was 1.0:1.4:6.3 by NMR peak integrations. Compound 7 was identified by GC/MS (condition 2).

Thiophenol-Catalyzed Isomerization of 4. A 0.5-mL benzene- d_6 solution of 10 mg (0.029 mmol) of 4 and 20 μ L (0.195 mmol) of thiophenol in an NMR tube was degassed and sealed. After the sample was stored at room temperature overnight, it was completely converted to a new compound, which was assigned as 7 based on ¹H and ¹³C NMR spectra and GC/MS (condition 3): ¹H NMR (C_6D_6) δ 1.50 (6 H, s), 3.23 (3 H, s), 5.39 (1 H, s), 7 (m); ¹³C NMR (C₆D₆) δ 26.69, 46.27, 51.64, 56.75, 125.93, 126.49, 127.22, 128.55, 129.82, 142.70, 143.11, 144.26, 176.55. GC analysis (condition 3) showed only 7 and a trace of diphenyl disulfide with retention times of 8.21 and 14.97 min, respectively.

Irradiation of 4 at 366 nm. A sealed, degassed 0.5-mL benzene solution of 0.05 M 4 in an NMR tube was irradiated through a 2,7-dimethyl-3,6-diazacyclohepta-1,6-diene perchlorate filter solution at 25 °C for 7.8 h. The product mixture was analyzed by GC/MS (condition 3) and by GC (conditions 1, 2, and 3). The retention time of 9-phenylfluorene was 10.19 min under GC condition 3. The type II cleavage of butyrophenone served as an actinometer.⁷¹

9-Fluorenone Photosensitization of 4. A 0.5-mL benzene- d_6 solution of 7.2 mg (0.021 mmol) of 4 and 27.8 mg (0.154 mmol) of 9-fluorenone in an NMR tube was degassed and sealed. The sample was irradiated for 35 min at room temperature with 435-nm light (aqueous sodium nitrite filter) and was monitored by ¹H NMR. The product mixture was analyzed by GC/MS (condition 3) and by GC (conditions 1 and 3). The photoreduction of 9-fluorenone by 0.1 M triethylamine ($\phi = 0.91$)⁶⁵ was used as an actinometer.

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Supplementary Material Available: Table of GC and GC/MS conditions for the product study of 4, mass spectral data of most of the compounds mentioned in the text, the ^{13}C NMR spectrum of 4 and 7, and a table of GC retention times and response factors for the products (5 pages). Ordering information is given on any current masthead page.

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