7.64 (t, J = 7.63 Hz, 1 H, Py H4).

Anal. Calcd for $C_{23}H_{42}N_2O$: C, 76.19; H, 11.68; N, 7.72. Found: C, 75.88; H, 12.04; N, 7.63.

6-((*n*-Dodecylamino)methyl)-2-((methyloxy)methyl)pyridine (2b). The amino alcohol **2a** (320 mg, 1.04 mmol) was dissolved in dry dioxane (10 mL) containing triethylamine (106 mg, 1.1 mmol). Di-*tert*-butyl dicarbonate (260 mg, 1.1 mmol) was subsequently added and the solution stirred for 3 h at room temperature. The dioxane was rotary-evaporated and the crude material obtained was taken up with slightly basic water (50 mL) and extracted with chloroform (3 × 80 mL). Evaporation of the dried (Na_2SO_4) organic solution gave quantitatively the protected derivative, which was used without any further purification. This was slowly added to a suspension of NaH (1.5 mmol) in dry THF to which CH_3I (1.5 mmol) was subsequently added. The reaction mixture was kept in a nitrogen atmosphere at 40 °C for 1 h and then stirred overnight at room temperature. The slurry was next quenched (cautiously!) with water and extracted with $CHCl_3$. Evaporation of the dried chloroform yielded the methylated alcohol, which was purified by column chromatography (SiO_2, $CHCl_3/CH_3OH$ 20:1). After purification 300 mg of material was collected. Deprotection was achieved by following standard treatment with HBr/CH_3COOH (15 min, room temperature), yielding, after workup, 210 mg of pure **1b** as an oil.

NMR δ_{CDCl_3}: 0.87 (br t, 3 H, $(CH_2)CH_3$), 1.25 (m, 18 H, $(CH_2)_9$), 1.52 (m, 2 H, NCH_2CH_2), 1.98 (br s, 1 H, NH), 2.64 (t, J = 7.32 Hz, 2 H, $NCH_2(CH_2)_n$), 3.47 (s, 3 H, OCH_3), 3.88 (s, 2 H, NCH_2Py), 4.57 (s, 2 H, OCH_2Py), 7.20 and 7.28 (2d, J = 7.63 Hz, 2 H, Py H3 and H5), 7.65 (t, J = 7.63 Hz, 1 H, Py H4).

Anal. Calcd for $C_{20}H_{36}N_2O$: C, 74.95; H, 11.32; N, 8.74. Found: C, 74.81; H, 11.40; N, 8.60.

2-((*n*-Dodecylamino)methyl)pyridine (4). 2-Formylpyridine (563 mg, 5.2 mmol) and *n*-dodecylamine (952 mg, 5.2 mmol) were dissolved in benzene (50 mL) and refluxed under Dean–Stark conditions for 2 h. The solvent was then rotary-evaporated and the crude imine dissolved in ethanol (20 mL). $NaBH_4$ (400 mg, 10.5 mmol) was added in portions and the solution stirred at room temperature for 4 h. Excess hydride was destroyed by addition (caution!) of water. Ethanol was evaporated and the milky water solution extracted with chloroform (3 × 50 mL). Evaporation of the dried (Na_2SO_4) organic layer gave the crude amine as a greasy material (1.2 g, 87% yield). Pure **4** was obtained after column chromatography (SiO_2, $CHCl_3/CH_3OH$, 20:1).

NMR δ_{CDCl_3}: 0.88 (br t, 3 H, CH_3), 1.27 (m, 18 H, $(CH_2)_9$), 1.54 (m, 2 H, NCH_2CH_2), 1.95 (br s, 1 H, NH), 2.65 (t, J = 7.32 Hz, 2 H, NCH_2CH_2), 3.91 (s, 1 H, NCH_2Py), 7.16 (ddd, J = 7.63, 4.88, 1.83 Hz, 1 H, Py H5), 7.31 (ddd, J = 7.63, 1.83, 1.22 1 H, Py H3), 7.64 (td, J = 7.63, 1.83 Hz, 1 H, Py H4), 8.56 (ddd, J = 4.88, 1.83, 1.22 Hz, 1 H, Py H6).

Anal. Calcd for $C_{18}H_{32}N_2$: C, 78.28; H, 11.67; N, 10.13. Found: C, 78.02, H, 11.52; N, 10.24.

Kinetic Studies. Solutions were prepared in the proper buffer (0.05 M) at 35 °C. Reaction temperature was maintained at 35 ± 1 °C. Release of *p*-nitrophenol[26] was followed at 317 nm. Each kinetic run was initiated by injecting a 20–40-μL portion of substrate (1 × 10^{-3} M in CH_3CN) into the cuvette containing 2 mL of the buffer solution. Rate constants were obtained either by linear plots of log ($A_\infty - A_t$) vs time or nonlinear regression analysis[27] of the absorbance data vs time. Calculations in aggregate solutions were made by assuming, in each case, that the reaction medium is a homogeneous solution.

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Registry No. **2a**, 130496-97-8; **2a** *O-t*-Bu derivative, 130496-98-9; **2b**, 130496-99-0; **3**, 130497-00-6; **4**, 130497-01-7; PNPA, 830-03-5; PNPH, 956-75-2; PNPD, 1956-11-2; PNPDPP, 10359-36-1; 6-formyl-2-(carboxymethyl)pyridine, 130497-02-8; *n*-dodecylamine, 124-22-1; *n*-hexadecylamine, 143-27-1; 2-formylpyridine, 1121-60-4.

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[26] Breslow (see ref 6c) has shown that the cleavage of PNPDPP yields *p*-nitrophenol as the principal product though some alternative hydrolysis with loss of phenol may also occur. This is probably true in our case too, though we did not investigate the products composition. The rate constants evaluated from the spectrophotometric appearance of *p*-nitrophenol are, however, not affected by the possibly competing hydrolysis to liberate phenol (see ref 14).

[27] Using the software package ENZFITTER by Leatherbarrow, R. J., Elsivier: Amsterdam, 1987.

Reactions of Thermally Generated *tert*-Butyl and Di(*tert*-alkyl)ketyl Radicals in Toluene: Cage Effects and Hydrogen Transfer

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Thermolysis of di(1-adamantyl)-*tert*-butylmethanol (**2a**) in toluene at 145–185 °C gives mainly bibenzyl, di(1-adamantyl) ketone, di(1-adamantyl)methanol, and the cross-product, 1,1-di(1-adamantyl)-2-phenylethanol. In the presence of benzophenone (BP) or benzenethiols as hydrogen-accepting and hydrogen-donating radical scavengers, respectively, the di(1-adamantyl)methanol/di(1-adamantyl) ketone ratio tends to steady values as the scavenger/**2a** ratio is increased, while the cross-product disappears. At 165 °C the secondary alcohol minimum is 8% (BP) and the ketone minimum 11% (thiol). These represent the contributions of geminate hydrogen atom transfer reactions to the overall yields, i.e., the cage effects. With BP the major cross-product is 1,1,2-triphenylethanol. Products from the self- and cross-reactions of benzyl and thiyl radicals are found when thiol is present, the diaryl disulfide predominating at high thiol concentration. In both cases, cross-products resulting from reaction of the *tert*-butyl radical with the scavenger-derived radical are detected in small amounts, being of greater importance in deuteriated toluene. The *tert*-butyl radical is considered, therefore, to be less reactive in hydrogen atom abstraction than the 1-adamantyl radical. Cage effects for other di(*tert*-alkyl)-*tert*-butylmethanols that thermolyze with exclusive *t*-Bu–C bond fission have also been measured and the product composition of the scavenger-free reaction interpreted by kinetic simulation based on the steady state approximation. Rate constants for hydrogen abstraction by the *tert*-butyl radical from toluene are not accurately determined by this procedure but seem, nevertheless, to indicate that the literature value (14.4 M^{-1} s^{-1} at 48 °C) is an overestimate. Solvent hydrogen abstraction by the ketyl radical shows a small but well-defined steric effect.

In the thermolysis of tri(*tert*-alkyl)methanols in toluene, one of the key products is the secondary alcohol, resulting from hydrogen atom transfer to the ketyl radical intermediate. If all the *tert*-alkyl groups are bridgehead, then

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Table I. Relative Molar Product Composition (Percent) from Thermolysis of Di(*tert*-alkyl)-*tert*-butylmethanols 2a–e in Toluene-l_8 (Ad = 1-adamantyl; Oc = 1-bicyclo[2.2.2]octyl) (Absolute Values in Parentheses)

							cage effects			
R^1	R^2	temp (°C)-*l*	bibenzyl (S_2)	ketone	sec alc	cross-prod.	ketone	sec alc	neopentyl-benzene	sec alc–cage alc–S_2
Ad	Ad	145-*h*	40.0[a] (41)	32.4 (32)	55.1 (54)	12.5 (12)	12.0[b,c]	9.9		5.2
		165-*h*	33.0[a] (33)	36.7 (35)	47.8 (47)	15.5 (15)	10.6[b,c]	7.9		6.9
		185-*h*	27.6[a] (28)	41.0 (39)	41.8 (40)	17.3 (17)	9.8[b,c]	6.8		7.4
		145-*d*	12.0[a]	50.7	32.5	16.8	13.3[c]	10.2		10.3
		165-*d*	9.3[a]	52.8	30.8	16.4	11.6[c]	8.1		13.2
		185-*d*	6.4[a]	55.2	30.1	14.7	10.5[c]	7.0		16.7
Ad	Oc	155-*h*	48.9 (49)	26.8 (27)	63.0 (63)	10.2 (10)	11.2	9.7[d]		4.4
		175-*h*	43.0 (42)	30.9 (31)	55.7 (55)	13.4 (13)	9.6	7.5[d]		5.2
		195-*h*	36.3 (35)	36.1 (35)	48.2 (47)	15.7 (15)	8.7	6.3[d]		5.6
Oc	Oc	160-*h*	55.1 (55)	22.9 (23)	69.5 (69)	7.6 (8)	10.6	8.6		5.8
		185-*h*	48.6 (47)	28.2 (28)	60.8 (59)	11.0 (11)	8.9	6.7		5.5
		205-*h*	41.5 (41)	32.5 (32)	53.5 (52)	13.9 (14)	8.4	5.5		6.5
Ad	t-Bu	160-*h*	58.7 (58)	22.3 (22)	70.3 (69)	7.4 (7)	10.4[c]	8.9[d]		2.7
		180-*h*	52.8 (52)	25.6 (25)	63.5 (62)	10.9 (11)	9.3[c]	7.0[d]		3.7
		205-*h*	43.9 (44)	30.9 (31)	54.4 (54)	14.6 (14)	8.3[c]	5.5[d]		5.1
t-Bu	t-Bu	175-*h*	68.7 (71)	15.0 (15)	80.2 (82)	4.8 (5)	8.2[c]	7.3[d]	1.1	4.2
		200-*h*	64.5 (66)	17.6 (18)	73.8 (76)	8.7 (9)	7.0[c]	5.9[d]	2.0	3.4
		220-*h*	57.0 (59)	21.3 (22)	67.3 (70)	11.4 (12)	6.0[c]	5.1[d]	3.4	5.2
		175-*d*	40.3	28.4	56.8	14.8			4.5	9.2
		200-*d*	32.6	33.1	48.3	18.7			6.8	9.8
		220-*d*	25.3	37.3	42.7	20.0			8.4	12.3

[a] Corrected for contribution from Ad–C fission. [b] 4-Methylbenzenethiol. [c] 4-Chlorobenzenethiol. [d] 4-Chlorobenzophenone.

the bibenzyl (formed by the self-reaction of benzyl radicals) and the secondary alcohol yields are theoretically, and experimentally, the same.[1,2] In a study of five such alcohols, at temperatures chosen so that their thermolysis rates were about the same, the secondary alcohol yield increased from about 26% at 165 °C for the most reactive alcohol to 52% at 245 °C for the least reactive.[1] However, for a *given* alcohol the secondary alcohol yield *falls* as the temperature rises;[2] for example, 37 and 28% at 145 and 185 °C, respectively, for tri(1-adamantyl)methanol (1). This paradox has yet to be explained.

In a first step toward understanding what happens after the rate-determining C–C fission in thermolysis, we examined in detail the products of the reaction of 1 in normal and deuteriated toluene.[2] This is an ideal case insofar as the 1-adamantyl radical formed cannot transfer hydrogen to any other species without forming a prohibited bridgehead olefin and, moreover, was observed neither to self-react, to give biadamantyl, nor to react with the solvent-derived benzyl radical. Furthermore, the di(1-adamantyl)ketyl radical does not rearrange. This reduces the number of potential reactions to a point where it is possible to make a kinetic model of the system which, by the inclusion of suitably chosen rate constants, can be used to simulate the product composition.

Almost any other system is more complicated to analyze. Consider di(1-adamantyl)-*tert*-butylmethanol (**2a**): it is the *t*-Bu–C bond that cleaves, to the extent of about 97%,[1] in preference to the Ad–C bond, but there are, nevertheless, a number of problems in extending our approach to this situation. The *tert*-butyl radical can react by hydrogen transfer to the ketyl radical, by self-coupling, by self-disproportionation, and by cross-reaction with the benzyl radical. The analogous processes cannot or do not occur in the case of the 1-adamantyl radical. However, these complications are resolved to a certain extent by the fact that the self-reactions of the *tert*-butyl radical have been studied kinetically in several solvents.[3] The rate constant of the cross-reaction can be estimated from those of the self-reactions of the *tert*-butyl and benzyl[4] radicals. Analysis of the possible reaction processes indicates that the most important unknowns are the rate constants for hydrogen abstraction by the *tert*-butyl and ketyl radicals from the solvent. Prior information about these reactivities is limited to one measurement on the *tert*-butyl radical[5] and our own work on the di(1-adamantyl)ketyl radical.[2]

We previously[2] found that the cage effect[6] (determined by deuterium analysis of the adamantane formed in toluene-d_8) on the thermolysis of 1 was large, about 40%, and varied little with the temperature. When, however, the alkyl radical is *tert*-butyl, the isotope technique is not applicable (because of the self- and cross-reactions of the radical), but classical scavenger methods prove to be successful. In this paper we shall first present a detailed study of the thermolysis of **2a** in toluene, the cage effects being determined by means of radical scavengers of two types, a hydrogen donor and a hydrogen acceptor. This procedure is then applied to four other alcohols, **2b–e** (Ad = 1-adamantyl; Oc = 1-bicyclo[2.2.2]octyl), where *t*-Bu–C fission is the rate-determining process. Since the reactions are quantitative and the product compositions can be determined with a fair degree of precision, it is possible to account for each intermediate by mass balancing and to model the system of several competing processes by kinetic simulation, thus providing new information about the relative or absolute rate constants of certain radical–radical and radical–molecule reactions.

Results and Discussion

Thermolysis of Di(*tert*-alkyl)-*tert*-butylmethanols in Neat Toluene. It is interesting to compare the product composition for thermolysis of di(1-adamantyl)-*tert*-butylmethanol (**2a**) (Table I) with that of tri(1-adamantyl)methanol (1) previously reported.[2] The salient feature is that at the same temperature the former is always associated with higher yields of secondary alcohol and cross-

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[1] Lomas, J. S. *J. Org. Chem.* **1985**, *50*, 4291.

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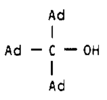
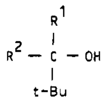
[6] (a) Lorand, J. P. Doctoral Thesis, University of Harvard, 1964; *Diss. Abs.* **1965**, *26*, 701. (b) Koenig, T.; Fischer, H. In *Free Radicals*; Kochi, J. K., Ed.; Wiley: New York, 1973; Vol. I, Chapter 4. (c) See also: Turro, J.; Weed, G. C. *J. Am. Chem. Soc.* **1983**, *105*, 1861.



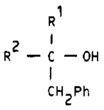
$$Ad-\underset{Ad}{\overset{Ad}{C}}-OH$$

1



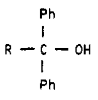
$$R^2-\underset{t\text{-}Bu}{\overset{R^1}{C}}-OH$$

2



$$R^2-\underset{CH_2Ph}{\overset{R^1}{C}}-OH$$

3



$$R-\underset{Ph}{\overset{Ph}{C}}-OH$$

4

a : $R^1 = R^2 =$ Ad

b : $R^1 =$ Ad ; $R^2 =$ Oc

c : $R^1 = R^2 =$ Oc

d : $R^1 =$ Ad ; $R^2 =$ t-Bu

e : $R^1 = R^2 =$ t-Bu

a : R = $PhCH_2$

b : R = t-Bu

c : R = Ad

product, **3a**. The bibenzyl yield is also slightly greater but the difference tends to fall with increasing temperature so that the yields are almost the same at 185 °C (28 and 27%, respectively). Replacement of normal toluene (SL, where L = H) by toluene-d_8 (L = D) has, as before, the effect of decreasing the secondary alcohol and bibenzyl yields. In the case of **1**, where these are virtually identical, there is a uniform reduction by a factor of about 2 at all temperatures. However, for **2a** the effect on secondary alcohol is smaller and decreases with increasing temperature, while that on bibenzyl is greater and rises with increasing temperature.

Clearly, the di(1-adamantyl)ketyl/*tert*-butyl radical pair formed in the thermolysis of **2a** behaves quite differently from the ketyl/1-adamantyl radical pair from **1**. The obvious source of this difference is that, unlike 1-Ad$^•$, the *tert*-butyl radical can transfer a hydrogen atom to another radical species. This may occur within the solvent cage, giving rise to secondary alcohol even when there is a hydrogen atom scavenger in the bulk solution. Recall that, in the presence of excess benzophenone, tri(1-adamantyl)methanol thermolysis gives only di(1-adamantyl) ketone.[2] Conversely, the *tert*-butyl radical can, like 1-Ad$^•$, accept a hydrogen atom from the solvent or another radical. Again, cage reaction may, as for **1**, be responsible for part of the ketone yield.

The general scheme (Scheme I) for the thermolysis of tertiary alcohols with *t*-Bu–C bond fission differs from that proposed for **1**, insofar as we are unable to assign a priori a fraction to the process involving hydrogen abstraction by the *tert*-butyl radical from the solvent (process 6). In addition, it is necessary to include the self-reactions of *tert*-butyl radicals (processes 14 and 15) and the reactions of *tert*-butyl and benzyl radicals (processes 12 and 13). Suffixes e and g denote encounter and geminate reactions, respectively. When a given pair of radicals can lead to more than one product or set of products, numerical suffixes are used.

Balancing radical formation and consumption gives

$$\text{for } t\text{-Bu}^•\text{: } 1 - a_g - a_e - b_g - b_e = c + h + 2i \quad (1)$$

$$\text{for } R_2C^•OH\text{: } 1 - a_g - a_e - b_g - b_e = d + 2e + f_1 + f_2 \quad (2)$$

$$\text{for } S^•\text{: } c + d = f_1 + f_2 + 2g + h \quad (3)$$

$$\text{hence: } d + e = g + h + i \quad (4)$$

While *g* corresponds to the bibenzyl yield, the total secondary alcohol yield is not $d + e$ but $d + e + b_g + b_e$, where the extra terms are due to the geminate and the encounter reactions of the *tert*-butyl and ketyl radicals. This means that the secondary alcohol yield will exceed that of bibenzyl by an amount at least equivalent to the extent of the *tert*-butyl reaction with either benzyl radical or itself. As can be seen from the data in Table I, the difference ranges from 10 to 15%, decreasing with increasing temperature for all compounds. For **2a** in toluene-d_8, however, it rises from 20 to 23% on going from 145 to 185 °C.

Scheme I

Process	Fraction	Rate const.	
$R_2t\text{-}BuCOH \longrightarrow R_2C^•CH + t\text{-}Bu^•$	1.0	k_1	(1)
$R_2C^•OH + t\text{-}Bu^• \longrightarrow R_2C{=}O + C_4H_{10}$	a_g	in cage	(2)
$R_2C^•OH + t\text{-}Bu^• \longrightarrow R_2CHOH + C_4H_8$	b_g		(3)
$R_2C^•OH + t\text{-}Bu^• \longrightarrow R_2C{=}O + C_4H_{10}$	a_e	k_2	(4)
$R_2C^•OH + t\text{-}Bu^• \longrightarrow R_2CHOH + C_4H_8$	b_e		(5)
$SL + t\text{-}Bu^• \longrightarrow S^• + C_4H_9L$	c	k_3	(6)
$SL + R_2C^•OH \longrightarrow S^• + R_2CLOH$	d	k_4	(7)
$2\ R_2C^•OH \longrightarrow R_2C{=}O + R_2CHOH$	e	k_5	(8)
$S^• + R_2C^•OH \longrightarrow SH + R_2C{=}O$	f_1	k_6	(9)
$S^• + R_2C^•OH \longrightarrow R_2SCOH$	f_2	k_7	(10)
$2\ S^• \longrightarrow S_2$	g	k_8	(11)
$S^• + t\text{-}Bu^• \longrightarrow SH + C_4H_8$	h	k_9	(12)
$S^• + t\text{-}Bu^• \longrightarrow t\text{-}BuS$			(13)
$2\ t\text{-}Bu^• \longrightarrow C_8H_{18}$	i	k_{10}	(14)
$2\ t\text{-}Bu^• \longrightarrow C_4H_8 + C_4H_{10}$			(15)

In the case of tri(*tert*-butyl)methanol (**2e**), the product of the reaction (process 13) of benzyl and *tert*-butyl radicals, neopentylbenzene, has a GC retention time similar to that of the ketone and secondary alcohol and is easily determined. Its yield increases from 1.1 to 3.4% in toluene-h_8 to 4.5–8.4% in toluene-d_8. This shows clearly that it is formed in a process that competes with another or others, this or these latter being subject to a kinetic isotope effect, KIE. It seems obvious that the prime candidate for this role is hydrogen abstraction by the *tert*-butyl radical from the solvent (process 6); when this is slowed by the KIE, the *tert*-butyl radical reacts to a greater extent with the benzyl radical.

The temperature dependence of the product composition is generally much the same as before:[2] the secondary alcohol yield tends to decrease and that of the cross-product to increase (but not for **2a** in toluene-d_8) as the temperature rises. It is noteworthy, however, that the least reactive compounds have the highest secondary alcohol and the lowest cross-product yields at a given temperature (Table I). Compare, for example, **2e** and **2b** at 175 °C or **2a** and **2c** at 185 °C. The interpretation of such variations is, in principle, possible by kinetic simulation of the system of competing processes, but first we require more information about cage effects in this reaction (processes 2 and 3).

Radical Scavenging by a Hydrogen Acceptor. When tri(*tert*-alkyl)methanols are thermolyzed in the presence of benzophenone, BP, or other aryl ketones, the reactions of the di(*tert*-alkyl)ketyl radical are to a large extent suppressed, only that fraction which reacts within the cage eluding the ketone.[2] All ketyl radical that leaves the cage suffers fast hydrogen transfer to the aryl ketone[7] with

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Table II. Relative Molar Product Composition (Percent) from Thermolysis of Di(1-adamantyl)-*tert*-butylmethanol (2a) in Toluene-*l*$_8$ in the Presence of Benzophenone

temp (°C)-*l*	[BP]/[2a]	bibenzyl	BPt-BuH (4b)	BPSH (4a)	ketone	sec alc	cross-prod. (3a)
145-*h*	0.8	6.6	1.3	38.2	89.9	10.1	0.0
	1.6	6.6	1.4	38.2	90.1	9.9	0.0
165-*h*	0.1	29.5	0.5	8.3	46.8	41.9	11.2
	0.2	24.9	1.0	16.3	57.4	35.3	7.3
	0.3	19.8	1.6	24.4	68.0	27.7	4.3
	0.4	12.0	2.0	31.6	80.5	18.0	1.5
	0.5	7.4	2.3	37.3	89.8	10.2	0.0
	0.6	7.0	2.4	37.0	91.2	8.8	0.0
	1.0	6.3	2.5	37.2	91.7	8.3	0.0
	1.5	6.3	2.3	37.2	92.1	7.9	0.0
185-*h*	0.8	7.1	3.8	38.5	92.3	7.7	0.0
	1.6	7.1	4.0	38.7	93.1	6.8	0.0
145-*d*	1.07	2.7	7.0	27.3	89.8	10.2	0.0
165-*d*	0.09	8.5	1.9	5.1	60.8	27.5	11.9
	0.19	7.2	4.0	10.0	67.4	24.3	8.3
	0.28	6.5	6.1	14.8	76.1	19.4	4.5
	0.37	4.7	8.6	19.8	84.0	14.4	1.6
	0.47	2.7	9.7	23.2	90.7	9.3	0.0
	0.56	2.6	9.7	23.7	91.7	8.3	0.0
	0.75	2.6	9.8	23.8	92.0	8.0	0.0
	0.93	2.7	9.7	23.7	91.9	8.1	0.0
185-*d*	1.07	1.4	12.3	20.8	93.0	7.0	0.0

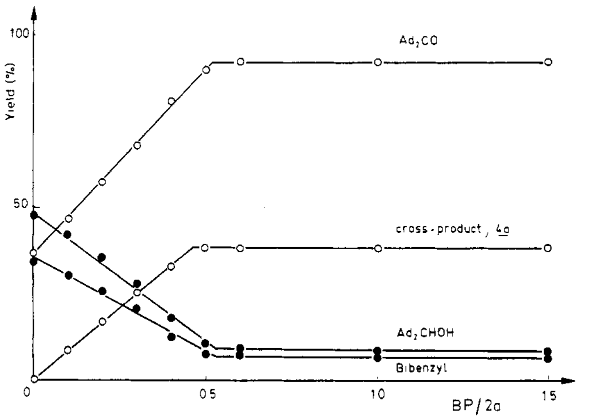

Figure 1. Thermolysis of di(1-adamantyl)-*tert*-butylmethanol (**2a**) at 165 °C in toluene-h_8: dependence of product composition on the benzophenone/alcohol ratio.

formation of the stabler hydroxybenzhydryl radical, BPH$^\bullet$. In the case of 1, since the reaction of the 1-adamantyl radical with the solvent, toluene, is also fast, the subsequent processes concern only S$^\bullet$ and BPH$^\bullet$, the products being bibenzyl, benzhydrol, and the cross-product, 1,1,2-triphenylethanol (**4a**). Inspection of the reaction products of di(1-adamantyl)-*tert*-butylmethanol (**2a**) reveals, however, a somewhat more complicated situation (Table II and Figure 1). The secondary alcohol yield does not go to zero, whatever the BP concentration, but settles at about 8% at 165 °C, regardless of the isotopic nature of the solvent. Moreover, when the reaction is run in toluene-d_8 this residual secondary alcohol is isotopically normal. It is clear that this 8% represents the contribution to the overall secondary alcohol yield of the geminate reaction within the solvent cage. Another important feature of the reaction of **2a** in the presence of BP is that both the bibenzyl and the cross-product, BPSH (**4a**), yields are markedly smaller when the reaction is conducted in toluene-d_8. Furthermore, in addition to **4a** there is a small amount of 2,2-dimethyl-1,1-diphenylpropan-1-ol (BPt-BuH, **4b**), which represents only 2% with respect to the starting alcohol in normal toluene but rises to 10% in toluene-d_8. Not only coupling but also disproportionation of the *tert*-butyl and hydroxybenzhydrol radicals to give benzhydrol or benzophenone (depending on the direction of hydrogen transfer) will be favored in the deuteriated solvent, but these reactions cannot be perceived directly. These observations lead to the same conclusions as those above concerning the formation of neopentylbenzene; they indicate that the *tert*-butyl radical reacts more slowly with the solvent than does 1-Ad$^\bullet$. In this respect our results differ from those of Engel,[8] who considers that these two radicals are of similar reactivity as hydrogen atom abstracting agents. Even in toluene-d_8 the amount of (1-adamantyl)diphenylmethanol (4c) does not exceed 1%.[2]

Scheme II

Process	Fraction	
$SL + t\text{-}Bu^\bullet \longrightarrow S^\bullet + C_4H_9L$	c = 0.73 (0.43)	(6)
$R_2C^\bullet OH + BP \longrightarrow BPH^\bullet + R_2C{=}O$	j_1 = 0.82 (0.82)	(16)
$t\text{-}Bu^\bullet + BP \longrightarrow BPH^\bullet + C_4H_8$	j_2 = 0.01 (0.04)	(17)
$t\text{-}Bu^\bullet + BPH^\bullet \dashrightarrow BPt\text{-}BuH$	m_1 = 0.02 (0.10)	(18)
$t\text{-}Bu^\bullet + BPH^\bullet \longrightarrow BP + C_4H_{10}$	m_2 = 0.04 (0.20)	(19)
$t\text{-}Bu^\bullet + BPH^\bullet \longrightarrow BPH_2 + C_4H_8$	m_3 = 0.02 (0.05)	(20)
$S^\bullet + BPH^\bullet \longrightarrow BPSH$	n_1 = 0.38 (0.24)	(21)
$S^\bullet + BPH^\bullet \longrightarrow BP + SH$	n_2 = 0.21 (0.13)	(22)
$2\ BPH^\bullet \longrightarrow BP + BPH_2$	p = 0.08 (0.08)	(23)
$2\ S^\bullet \longrightarrow S_2$	g = 0.07 (0.03)	(11)

The scheme for the reactions of the ketyl/*tert*-butyl radical pair in the presence of benzophenone is then as shown (Scheme II). For convenience we have repeated the reaction of the *tert*-butyl radical with the solvent (6) and the self-reaction of benzyl radicals (11), but have assumed that the reactions of the *tert*-butyl radical with itself or with benzyl (processes 12–15) can be neglected.

Balancing radical formation and consumption gives four equations. To these we can add the fact that there is a limiting value of the initial BP/alcohol ratio, beyond which the product composition stagnates. This is the total BP consumption, to give benzhydrol and the two cross-products, and is about 0.50 and 0.47 in toluene-h_8 and -d_8,

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[8] Engel, P. S.; Chae, W. K.; Baughman, S. A.; Marschke, G. E.; Lewis, E. S.; Timberlake, J. W.; Luedtke, A. E. *J. Am. Chem. Soc.* **1983**, *105*, 5030.

Table III. Relative Molar Product Composition (Percent) from Thermolysis of Di(1-adamantyl)-*tert*-butylmethanol (2a) in Toluene-l_8 in the Presence of 4-Methylbenzenethiol (Aryl = 4-Methylphenyl)

temp (°C)-*l*	[thiol]/ [**2a**]	*tert*-butyl aryl sulfide	bibenzyl	benzyl aryl sulfide	diaryl disulfide	ketone	sec alc	cross-prod.	total sulfides	sec alc–cage alc
145-*h*	1.56	0.5	0.4	7.1	64.8	13.0	87.0	0.0		
	2.07	0.0	0.0	1.4	73.8	12.2	87.8	0.0	75.2	77.9
165-*h*	0.26	2.8	24.8	9.1	5.1	32.9	56.5	10.6		
	0.65	5.1	15.7	15.7	19.1	25.6	70.6	3.8		
	1.04	4.2	8.0	16.0	38.5	17.3	81.8	0.9		
	1.43	1.2	1.9	11.1	60.1	12.0	88.0	0.0		
	1.81	0.0	0.0	3.3	72.9	11.1	88.9	0.0		
	2.20	0.0	0.0	2.2	76.6	10.5	89.5	0.0	78.8	81.6
185-*h*	1.56	0.9	1.4	10.9	63.2	11.2	88.8	0.0		
	2.07	0.0	0.0	4.2	76.2	9.9	90.1	0.0	80.4	83.3
145-*d*	2.05	0.0	0.0	0.0	77.3	13.3	86.7	0.0	77.3	76.8
165-*d*	0.51	12.2	3.1	8.9	13.7	40.6	57.4	2.0		
	1.03	7.7	0.7	5.9	43.9	27.5	72.5	0.0		
	2.06	0.0	0.0	0.0	75.6	11.6	88.4	0.0	75.6	80.6
185-*d*	2.05	0.0	0.0	0.7	77.1	10.5	89.5	0.0	77.8	82.7

respectively. Solution of these equations (see supplementary material) leads to the values in Scheme II; the first is that for toluene-h_8, the second (in parentheses) referring to toluene-d_8. These figures indicate that the principal reaction of the *tert*-butyl radical is hydrogen atom abstraction from the solvent, reactions with benzophenone or the hydroxybenzhydryl radical being relatively unimportant in toluene-h_8 (0.09) but rising to 0.39 in toluene-d_8. Hydrogen transfer from the *tert*-butyl radical to benzophenone (process 17) or to the hydroxybenzhydryl radical (process 20) is a minor reaction even in the deuteriated solvent.

The fraction of secondary alcohol formed within the solvent cage, b_g, was determined for alcohols **2b–e** by use of benzophenone or suitably substituted benzophenones at an initial BP/2 ratio of 2.0; results are listed in Table I. We can now reexamine the relationship between the total secondary alcohol and bibenzyl yields (eq 4). Subtracting the alcohol component of the cage effect from the total leaves us with $d + e + b_e$, which is greater than the bibenzyl yield, g, by an average of 5% (or 0.05, if we work with fractional yields). By eq 4 this is equivalent to $h + i + b_e$, i.e., all the encounter reactions of the *tert*-butyl radical with other radicals, including its self-reaction. The data for tri(*tert*-butyl)methanol (**2e**) in toluene-h_8 are particularly revealing; by eq 4, $h + i + b_e$ is only 4% and this is almost completely accounted for by the neopentylbenzene alone, i.e., one component of h. The contributions from processes 5, 12, 14, and 15 must therefore be insignificantly small. Even in toluene-d_8, where the competing hydrogen transfer is slower, these processes represent only about 4% of the overall reaction of the *tert*-butyl radical.

Radical Scavenging by a Hydrogen Donor. While scavenging the ketyl radical with benzophenone tells us how much secondary alcohol is formed by hydrogen transfer from *tert*-butyl to ketyl within the cage, we should like to know also how much ketone arises by transfer in the opposite direction, ketyl to *tert*-butyl. We require a donor more efficient than toluene. Thiols have long been used for this purpose,[9,10] and, in the present case, benzenethiols (denoted TH) prove to be suitable, as is shown by the data for **2a** (Table III and Figure 2). The reaction (Scheme III) is somewhat more complicated than that of benzophenone, insofar as both the initially formed radicals can accept hydrogen and that there is competition with toluene. Nevertheless, since the thiol transfers hydrogen much faster than the solvent, when the molar ratio of thiol to tertiary alcohol reaches about 2, disulfide (T_2) is formed to the complete exclusion of bibenzyl, there remaining a trace of benzyl phenyl sulfide (TS).

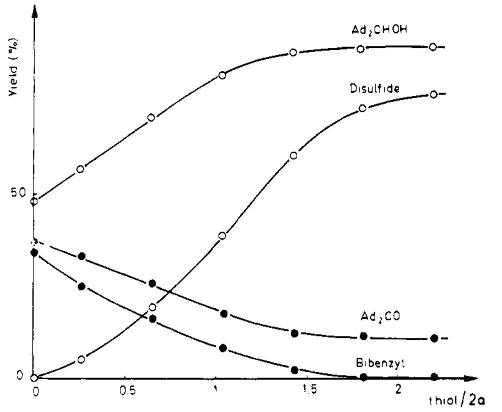

Figure 2. Thermolysis of di(1-adamantyl)-*tert*-butylmethanol, (**2a**) at 165 °C in toluene-h_8: dependence of product composition on the 4-methylbenzenethiol/alcohol ratio.

Scheme III

Process	Fraction	
$R_2C^{\bullet}OH + TH \rightarrow T^{\bullet} + R_2CHOH$	q	(24)
$t\text{-}Bu^{\bullet} + TH \rightarrow T^{\bullet} + C_4H_{10}$	r	(25)
$t\text{-}Bu^{\bullet} + T^{\bullet} \rightarrow t\text{-}BuT$	s	(26)
$t\text{-}Bu^{\bullet} + T^{\bullet} \rightarrow TH + C_4H_8$		(27)
$S^{\bullet} + T^{\bullet} \rightarrow TS$	t	(28)
$2\ T^{\bullet} \rightarrow T_2$	u	(29)
$t\text{-}Bu^{\bullet} + T_2 \rightarrow t\text{-}BuT + T^{\bullet}$	v	(30)
$T^{\bullet} + C_4H_8 \rightarrow T\text{-}C_4H_8^{\bullet}$	w	(31)
$T\text{-}C_4H_8^{\bullet} + TH \rightarrow t\text{-}BuT + T^{\bullet}$	x	(32)

In addition to the above products there is also *tert*-butyl phenyl sulfide (t-BuT); in toluene-h_8 the yield goes through a shallow maximum as the initial thiol/**2a** ratio increases. In toluene-d_8 this product, analogous to neopentylbenzene

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(10) For rates of hydrogen transfer from thiols, see: Newcomb, M.; Glenn, A. G.; Manek, M. B. *J. Org. Chem.* **1989**, *54*, 4603.

Table IV. Absolute Molar Product Composition (Percent) for the Thermolysis of Tri(1-adamantyl)methanol (1) in the Presence of 4-Methylbenzenethiol (in Toluene-h_8 at 165 °C) (Aryl = 4-Methylphenyl)[a]

[thiol]/[1]	AdH	bibenzyl	benzyl aryl sulfide	diaryl disulfide	adamantyl aryl sulfide	ketone	sec alc	cross-prod.	total Ad•[c]	total $Ad_2C^{\bullet}OH$[d]
0.22	93	23	10	3	3	51	46	5	96	102
0.43	96	17	15	9	5	46	54	2	101	102
0.75	94	8	17	23	4	40 (39.6)[b]	62	0	98	102
1.07	98	1	11	39	2	40 (38.7)[b]	63	0	99	103
1.61	98	0	6	50	1	40 (38.2)[b]	64	0	98	104
2.15	101	0	4	52	0	39 (38.4)[b]	63	0	101	102

[a] Individual and summed yields are rounded off to the nearest 1%. [b] Relative ketone yield based on exact data. [c] Adamantane + adamantyl aryl sulfide. [d] Ketone + secondary alcohol + cross-product.

and to **4b** in that it arises from the reaction of *tert*-butyl radical with another radical (process 26), is clearly more abundant. There are, however, at least two other processes that can lead to this same product: attack of *tert*-butyl on disulfide[11] (30) and thiol addition to olefin (31–32).[12] Nonetheless, since these processes are all competing with hydrogen transfer from the solvent and their resultant increases when the solvent is deuteriated, this result is consistent with the idea that the *tert*-butyl radical reacts relatively slowly with the solvent.

Once again, radical balancing (see supplementary material) indicates a relationship between the secondary alcohol yield (short of that part which is formed by reaction of ketyl with *tert*-butyl) and those of the products of the various radical–radical reactions. At high thiol concentration reaction of the *tert*-butyl radical with any species other than the thiol should be negligible. This expectation is approximately satisfied, as can be seen by subtracting the alcohol cage effect from the total alcohol yield and comparing the result with the sum of the sulfide and disulfide yields (Table III, last two columns). The average difference of 3% (ranging from −0.5 to 5%) must be attributed to other reactions of the *tert*-butyl radical or to desulfurization.[13]

The ceiling concentration is not well defined and the relative yields of bibenzyl, sulfide, and disulfide continue to evolve even when the secondary alcohol/ketone ratio is close to its terminal value. Nevertheless, it seems reasonable to assume that the amount of ketone remaining when the molar ratio exceeds about unity, in toluene-h_8, corresponds to that which is formed within the solvent cage. This was confirmed by thermolyzing **1** at 165 °C with benzenethiol, whereupon the ketone yield fell to 39% (average of the last four data, Table IV), in close agreement with the value of 40% obtained by measuring the deuterium content of the adamantane produced when **1** is thermolyzed in toluene-d_8. It will be noted that adamantane and adamantyl phenyl sulfide account for 99% of the adamantyl radical, while ketone, secondary alcohol, and cross-product **3a** correspond to slightly more than 100% of the ketyl radical, the excess being, however, within the experimental error. On the other hand, the sum total of the bibenzyl, sulfide, and disulfide yields, which should be equal to that of secondary alcohol when there is excess thiol, ranges from 52 to 57% only, as against the expected 61%.

Adamantyl phenyl sulfide can only be formed in reactions analogous to (26) and (30). The feasibility of this latter process was confirmed by thermolyzing **1** in toluene in the presence of diphenyl disulfide (Table S-V); both benzyl and adamantyl phenyl sulfide are obtained in yields of 39 and 31%, respectively (disulfide/**1** = 2.0). The bibenzyl and ketone yields decrease but not so much as for the same thiol concentration. Clearly, disulfide can compete with toluene for the 1-Ad• radical, though it is much less effective than thiol. Again, the sulfide yields fall somewhat short of what is expected, it being possible to account for only 91–93% of the original disulfide.

These experiments drew our attention to the fact that, while there are several procedures for the synthesis of aryl *tert*-butyl sulfides,[14] analogous derivatives with bridgehead *tert*-alkyl groups do not appear to have been described. In order to check the ITD identification of the 1-adamantyl derivative, we sought to synthesize it. Attempts to do so by the acid-catalyzed reaction of 1-adamantanol with thiol failed. A rather different approach has been reported by Davis,[15] who reacted disulfides with *tert*-butyllithium. Although the bridgehead organolithium compound is accessible,[16] its preparation is not very convenient and it is often found that the Barbier procedure, where 1-adamantyl halide and the substrate, e.g., a ketone, react on the lithium surface, gives better yields.[17] When this procedure was applied to the synthesis of 1-adamantyl phenyl sulfide from 1-bromoadamantane and diphenyl sulfide, a yield of 75% was achieved. Other bridgehead alkyl thioethers can be prepared in the same way.[18]

Radical scavenging by means of thiols constitutes a much simpler and more general method than alkane labeling for measuring the ketone component of the cage effect in thermolysis. Benzenethiol or suitably substituted benzenethiols were used to determine the cage effect for the thermolysis of **2b–e** in toluene; results are listed in Table I.

Cage Effects in Alcohol Thermolysis. Two radicals formed in a solvent cage, very often in the presence of a third, nonradical, species may come together inside the cage in a geminate reaction or diffuse out of the cage and come together again in an encounter reaction. The early work has been surveyed by Lorand,[6a] with particular attention to peresters, and somewhat more recently, by Koenig and Fischer.[6b] A particular point of interest is the dependence of the cage reaction on solvent viscosity and/or

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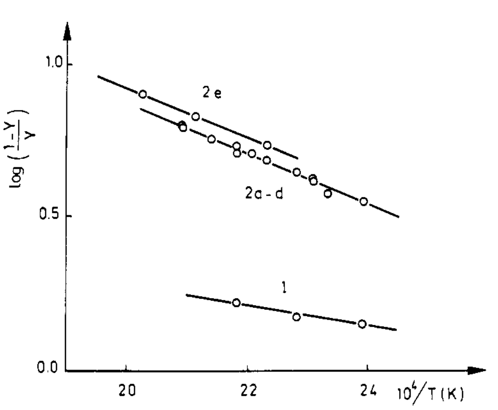

Figure 3. Thermolysis of tri(1-adamantyl)methanol (**1**) and di(*tert*-alkyl)-*tert*-butylmethanols **2a–e** in toluene-h_8: Arrhenius plot of the cage effect (Y = total cage effect).

temperature. The common approach is to take a series of solvents at a given temperature and to plot $1/Y$ or, better, $(1 - Y)/Y$, where Y is the cage yield, against $\eta^{-\alpha}$. The exponent α has been ascribed values of $^{1}/_{2}$, $^{3}/_{4}$, and 1.[19-21] The fact that most theoretical developments tend to favor $^{1}/_{2}$[22] and that there is some experimental support for this value[19] has not prevented other authors correlating their data, often in the form of $1/Y$, against η^{-1}.[21] Pryor's remark[23] that α may be "dependent on the solvent series, the temperature and the size and shape of the geminate radicals" has found no translation in theory so far.

In the few cases where the temperature dependence of the cage effect has been considered, it is standard practice to estimate $E_{\text{escape}} - E_{\text{cage}}$, the difference between the activation energies of the two competing processes, escape from the cage and reaction within the cage, from the Arrhenius plot of $(1 - Y)/Y$.[8,24,25] The resulting differences are generally about 2 ± 1 kcal mol^{-1}, i.e., of the same order of magnitude as the activation energy for diffusion-controlled reactions and, in agreement with the Smoluchowski equation, as the analogous parameter for the temperature dependence of the viscosity, E_η ($\eta = A\exp(-E_\eta/RT)$). This implies that $\alpha = 1$ and that escape and diffusion have the same viscosity dependence. However, in the general case we can write: $(1 - Y)/Y = A\exp(-(\alpha E_\eta - E_{\text{cage}})/RT)$. The Arrhenius slope therefore depends on both α and E_{cage}. If E_{cage} is close to zero,[26] the limiting acceptable slope is E_η or, in most theories, $0.5E_\eta$. A greater apparent activation energy difference implies an excessively high α or a negative activation energy for the cage reaction.[27] Such is the case in the present study (Figure 3) where the Arrhenius slope corresponds to 3.8 kcal mol^{-1}, E_η for toluene in the range 75–225 °C being 2.4 kcal mol^{-1} at 50 bar and 2.3 kcal mol^{-1} at 100 bar.[28,29] It will be noted that the cage effects for tri(*tert*-butyl)methanol (**2e**) are systematically smaller than those for the other alcohols but that the "activation energy" is the same, the difference being in the preexponential factor. Engel et al.[8] claim that their value for 1-adamantyl radicals in benzene is similar to that of Nelsen and Bartlett[25] for cumyl radicals in toluene, 1.5 and 1.3 kcal mol^{-1}, respectively. Upon recalculation, however, this proves to be not 1.5 but 3.2 kcal mol^{-1}, which raises the same possibility of a negative activation energy for the geminate reaction.[31]

An interesting finding is that the cage effects for $Ad_2C^{\bullet}OH/Ad^{\bullet}$ (38–41%)[2] are about twice those for $Ad_2C^{\bullet}OH/t\text{-}Bu^{\bullet}$ (17–22%) at the same temperatures, but that the temperature dependence is much smaller, the Arrhenius slope corresponding to 1.4 kcal mol^{-1}. Since diffusion rates are not very sensitive to molecular size,[26] it seems reasonable to exclude the possibility that there is a large difference in E_{escape} for $Ad^{\bullet}$ and $t\text{-}Bu^{\bullet}$. The geminate reaction of the adamantyl radical must, therefore, have a higher activation energy and a higher preexponential term than that of *tert*-butyl. These differences may correspond in some way to the distance between and the relative orientations of the radicals in the solvent cage, as they are formed and as they must be for hydrogen transfer to occur, but further consideration is beyond the scope of this paper.

Kinetic Simulation of Thermolysis in Neat Toluene. The main problem in attempting kinetic simulation of this system is that for each tertiary alcohol the number of independent data is less than that of the rate constants, some of which, however, can be estimated from the literature. Nevertheless, one of the unknowns, k_3, proves to be very sensitive not only to small uncertainties in the experimental data but also to the other constants.

In previous work[2] we took the initial alcohol concentration as that at ambient temperature; in the following calculations we have taken account of the expansion of toluene, by extrapolating Massart's empirical equation,[32] and correcting the alcohol and toluene concentrations accordingly.

We assume, as before, that the rate of appearance of ketyl and *tert*-butyl radicals in solution is governed by the overall thermolysis rate constant corrected for reaction inside the cage. The rate constants for the self-reactions of the *tert*-butyl (k_{10}) and benzyl (k_8) radicals are obtained by extrapolation of Fischer's data.[3,4] The rate of the self-reaction of *tert*-butyl in toluene has not been determined but the viscosity of toluene lies between those of n-octane and benzene; we therefore take the mean of data (differing by no more than 5% at any temperature in our range) for these two solvents. For the cross-reaction of *tert*-butyl and benzyl radicals (k_9), we use twice the geometric mean of the rates for the corresponding self-reactions,[33] which differ by no more than 10% at any temperature. Rate constants k_4, k_5, and $k_6 + k_7$ (but not k_3) are linked in that, for a given $(k_6 + k_7)/k_4$ ratio, the same product output can be obtained with values of k_5 varying

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[27] For a discussion of negative activation energies, see: Seetula, J. A.; Russell, J. J.; Gutman, D. *J. Am. Chem. Soc.* **1990**, *112*, 1347.

[28] Akhundov, T. S.; Taurov, A. D. *Izv. Vyssh. Uchebn. Zaved. Neft. Gaz* **1978**, *21*, 67.

[29] Viscosities at 1 bar, calculated by extrapolating the Vogel equation,[30] are smaller and suggest, probably incorrectly, E_η = 1.5 kcal mol^{-1}.

[30] Fieggen, W.; Gerding, H. *Recl. Trav. Chim. Pays-Bas* **1970**, *89*, 236.

[31] For a semiempirical correlation with macroscopic solvent parameters other than viscosity, see: Nodelman, N.; Martin, J. C. *J. Am. Chem. Soc.* **1976**, *98*, 6597.

[32] Massart, L. *Bull. Soc. Chim. Belg.* **1936**, *45*, 76.

[33] Paul, H.; Segaud, C. *Int. J. Chem. Kinet.* **1980**, *12*, 637.

as the square of either $k_6 + k_7$ or k_4.[2] As before, $k_6 + k_7$ is set equal to k_8. In the thermolysis of 1 the self-reaction of ketyl radicals was relatively unimportant and appeared to have a slightly negative temperature dependence;[2] k_5 is therefore set arbitrarily at 0.45×10^9 M^{-1} s^{-1} in all calculations. In fact, it has very little effect upon the two principal unknowns.

The interdependence of the other rate constants and their sensitivity to experimental error (see Experimental Section) were investigated in preliminary calculations. Constants k_3 and k_4 were optimized for various values of k_2, it being assumed that processes 4 and 5 make equal contributions to the ketone and secondary alcohol yields. This is a reasonable hypothesis insofar as the disproportionation/combination ratio of two alkyl radicals is the same for geminate and encounter reactions;[6b] we should expect the same to be true for two competing disproportionations. Up to $k_2 = 10^9$ M^{-1} s^{-1}, processes 4 and 5 have a negligible impact on k_3 and k_4. As k_2 is increased further, k_3 starts to rise and is typically about 30% above its base value when k_2 is 3×10^{10} M^{-1} s^{-1}, while k_4 is less than 2% higher than before.

Increasing k_2 naturally enhances the contribution of process 5 to the overall scheme, but the calculations based on eq 4, described above, leave little scope for this or the *tert*-butyl self-reactions. Process 5 can, moreover, be investigated directly by determining the isotopic labeling of the secondary alcohol produced in the thermolysis of **2a** in toluene-d_8. Isotopically normal secondary alcohol arises from the cage reaction 3, encounter reaction 5, and ketyl self-reaction 8, while deuteriated secondary alcohol can only come from solvent deuterium abstraction by the ketyl radical (process 7). If k_2 is zero, the calculated deuterium content is 43, 41, and 35 at 145, 165, and 185 °C, respectively, while the corresponding experimental values (±3%) are 45, 41, and 38%. There is, consequently, no case whatsoever for including either process 5 or 4.

In what follows, therefore, k_2 is assumed to be below the level at which encounter reactions contribute significantly, and k_3 and k_4 are calculated by optimizing the fit with the bibenzyl and secondary alcohol yields for the five alcohols, **2a–e**, each one at three temperatures (Table S-VI). In the case of tri(*tert*-butyl)methanol (**2e**), the neopentylbenzene yield was used as a further constraint, but with a smaller weighting since the disproportionation/combination ratio for benzyl and *tert*-butyl is unknown. The value, assumed temperature independent, that gave the best overall fit for the six data for this alcohol was 0.43. The calculated breakdown of the reaction of each alcohol in terms of the various product-forming processes is given in Table S-VII.

Though one would like to use the cross-product, **3**, yield also, this introduces the disproportionation/combination ratio for ketyl and benzyl radicals as a further unknown. The calculated average ratio for **2a** is 1.79, in fair agreement with that (2.0) found before,[2] while for the other ketyl radicals the average ranges from 1.35 to 1.65, with no obvious temperature dependence. When the appropriate ratios for each alcohol were used with the cross-product yields as a further constraint (also with a smaller weighting), the effect on k_4 was negligible and that on k_3 averaged 2%, the greatest difference being 9% for **2a** at 185 °C in toluene-d_8 for which the cross-product yield appears anomalously low. The small changes in the calculated rate constants do not appear to justify the extra assumption required by the use of cross-product as a constraint; nevertheless, the results are consistent with the idea that the disproportionation/combination ratio is approximately temperature and solvent isotope independent and varies little, from 1.35 to 1.79 on average, with the ketyl radical substituents (Table S-VII).

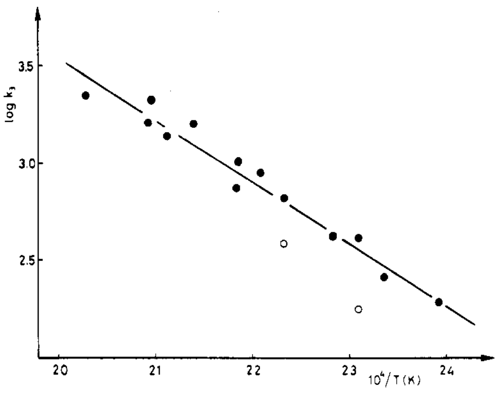

Figure 4. Thermolysis of di(*tert*-alkyl)-*tert*-butylmethanols **2a–e**: Arrhenius plot of the rate constant, k_3, for hydrogen transfer from toluene-h_8 to the *tert*-butyl radical.

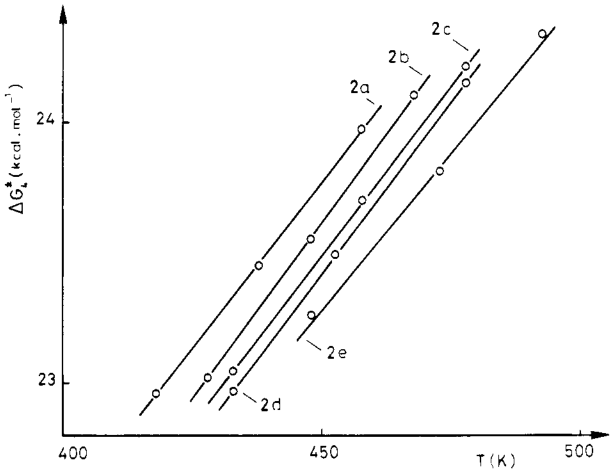

Figure 5. Thermolysis of di(*tert*-alkyl)-*tert*-butylmethanols **2a–e**: Eyring plots of the rate constant, k_4, for hydrogen transfer from toluene-h_8 to di(*tert*-alkyl)ketyl radicals.

The results for **2a–e** give two rough Arrhenius plots; that for k_3 is displayed in Figure 4. Inspection of the k_4 plot reveals that it consists in reality of 5 parallel three-point lines. This is seen more clearly when activation free energies are plotted against T (Figure 5); the lines span about 0.5 kcal mol^{-1} and $\Delta G^\ddagger$ at a given temperature increases roughly in the order of the combined steric size of R^1 and R^2. Sums of the revised[34] Taft steric parameters, E_s' for the ketyl radicals corresponding to **2a–e** are (in order) −3.28, −3.17, −3.06, −3.07, −2.86. Hydrogen abstraction from the solvent is clearly subject to steric effects, even though the reactivity range spans a factor of less than 2 (1.75 at 175 °C). The corresponding activation parameters are (R^1, R^2, $\Delta H^\ddagger$ in kcal mol^{-1}, $\Delta S^\ddagger$ in cal mol^{-1} deg^{-1}): t-Bu, t-Bu, 12.7, −23.6; t-Bu, Ad, 11.7, −26.1; Oc, Oc, 11.8, −25.9; Ad, Oc, 11.7, −26.4; Ad, Ad, 11.7, −26.7. Again, the real activation entropies depend on the magnitude of $k_6 + k_7$.[2]

When two outliers are eliminated from the k_3 plot (Figure 4), the activation enthalpy and entropy are 13.4 kcal mol^{-1} and −16.5 cal mol^{-1} deg^{-1}, respectively. The extrapolated rate constant at 48 °C is 1.04 M^{-1} s^{-1}, whereas that determined by time-resolved ESR spectroscopy of photochemically generated *tert*-butyl radicals at this temperature[5] is 14.4 M^{-1} s^{-1}. While k_3 is tied to k_8, k_9, and k_{10},

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(34) MacPhee, J. A.; Panaye, A.; Dubois, J. E. *Tetrahedron* **1978**, *34*, 3553. Panaye, A.; MacPhee, J. A.; Dubois, J. E. *Tetrahedron Lett.* **1980**, *21*, 3485.

all of which are derived from Fischer's work on self-reactions,[3,4] it is conceiveable that part of this difference is due to extrapolation errors. Another possibility is that the small perturbation of the kinetic trace observed in the reaction of t-Bu$^\bullet$ in toluene[5] was not entirely due to reaction with the solvent, despite the detection of benzyl radicals, but to other processes. This would perhaps explain the discrepancy between Fischer's work and Pryor's competition experiments[35] when electron-donating substituents are present.

For comparison with the present work, we recalculated the previous data[2] on Ad_3COH (1) thermolysis, allowing for solvent expansion and the k_3 term; all other constants were as for **2a**. Values of k_4[tol] fell by about 5% on average (Table S-VI). Those of k_3, which depend critically on the very small difference between the bibenzyl and secondary alcohol yields (less than 2%), are all higher than the corresponding values for t-Bu$^\bullet$, but show considerable scatter ($k_3^{Ad}/k_3^{t\text{-}Bu}$ ranges from 2.4 to 16.9), the most anomalous values being for toluene-d_8. For toluene-h_8 the average reactivity factor is 3.

The activation parameters for k_4 are $\Delta H^\ddagger = 12.3$ kcal mol^{-1} and $\Delta S^\ddagger = -25.5$ cal mol^{-1} deg^{-1}, similar to those above. Although the agreement between individual rate constants is reasonably good, considering the different origins of the data, the kinetic isotope effects resulting from these two series differ somewhat (T in °C, k_H/k_D from 1 after recalculation, k_H/k_D from **2a**): 145, 7.3, 9.3; 165, 6.8, 7.6; 185, 6.0, 7.3. They nevertheless agree as to the order of magnitude and show roughly the expected temperature dependence.

Kinetic isotope effects for hydrogen abstraction by the *tert*-butyl radical are altogether less satisfactory than those for the ketyl radical in that they suggest an anomalous temperature dependence (T, k_H/k_D): 145, 3.7; 165, 4.6; 185, 4.5 (from **2a**); and 175, 3.8; 200, 4.9; 220, 4.1 (from **2e**). This must probably be attributed to the acute sensitivity of k_3 to small errors in the experimental data. Clearly, this is not a practical method for determining isotope effects upon hydrogen abstraction; the more direct approach[36] will be the subject of a forthcoming study.

Conclusion

Analysis of literature data on the viscosity and temperature dependence of cage effects reveals a confusing situation as regards the former, theory being in conflict with a large fraction of the experimental work. There is a penury of convincing data and arguments concerning what happens when both factors change simultaneously, the only somewhat complete study, on azomethane decomposition, going back almost 30 years.[37] The calculation of $E_{escape} - E_{cage}$ from the Arrhenius plot is rather uninformative and seems to beg more questions than it answers.

The extent of the two competing geminate disproportionation reactions occurring when ketyl/*tert*-butyl radical pairs are generated by thermolyzing di(*tert*-alkyl)-*tert*-butylmethanols can be accurately determined by scavenging, by means of hydrogen donors or acceptors, those ketyl radicals that escape from the cage. The temperature dependence of this cage effect is greater than current theory accepts.

In the absence of scavengers the ketyl and *tert*-butyl radicals either self-terminate or react with the solvent, toluene, to give benzyl radicals that may self-react or react with the initially formed radicals. The *tert*-butyl radical survives long enough to react with the benzyl radical, and the yield of the resulting neopentylbenzene increases 3–4-fold when hydrogen abstraction is slowed by using toluene-d_8. In the same way, in the presence of benzophenone the *tert*-butyl radical reacts with the hydroxybenzhydryl radical. The *tert*-butyl radical is, therefore, a poorer hydrogen abstractor than the 1-adamantyl radical, which reacts almost exclusively with the solvent. However, our calculations show that a factor of 3 would accommodate most of the data, at least in toluene-h_8. This conclusion differs slightly from that of Engel,[8] who finds these radicals to be of similar reactivity when generated by azoalkane photolysis at much lower temperatures than our thermolyses. Though we cannot explain this contradiction, in the light of previous work it seems reasonable that 1-adamantyl should be the more reactive. Despite some evidence to the contrary,[38] thermolysis/MM2[1] and PES[39] studies have shown Ad$^\bullet$ to be 2.4 or 3.7 kcal mol^{-1}, respectively, more strained than t-Bu$^\bullet$ (relative to the corresponding alkanes) and can be expected to be more reactive, therefore, on purely energetic grounds.

Kinetic simulation of the product data, with the key values for the self- and cross-reactions of *tert*-butyl and benzyl radicals extrapolated from Fischer's work, leads to a rate constant for hydrogen abstraction by t-Bu$^\bullet$ from toluene, k_3, somewhat smaller than Fischer's own value.[5] The real rates of hydrogen abstraction from the solvent by ketyl radicals, k_4, are unknown because the necessary "fixed point", the rate constant for the reaction of benzyl with ketyl radical, has not been measured. Nevertheless, relative rates, approximate kinetic isotope effects and the temperature dependence can be calculated. This reaction shows a small but quite definite and well-ordered response to steric factors, isotope effects for $Ad_2C^\bullet OH$ in much the same range as those found in tri(1-adamantyl)methanol (1) thermolysis, and activation enthalpies close to 12 kcal mol^{-1}. Activation entropies are −24 to −26 cal mol^{-1} deg^{-1} or less, in absolute terms, depending on the fixed point.

One of the aims of this work was to seek an understanding of the way in which the products of alcohol thermolysis depend on structure and temperature. This is achieved by means of the kinetic simulation program, which is a highly satisfactory rationalization of the product data; when smoothed values of k_3 and k_4 are calculated from the Arrhenius plots and reinserted into the program, the mean errors on the bibenzyl and secondary alcohol yields are 0.8 and 0.2%, respectively. It is, finally, fairly easy to explain qualitatively the results referred to in the Introduction.[1,2] When k_1 is small the principal reaction of the ketyl and *tert*-alkyl radicals is hydrogen transfer from the solvent, the radical concentrations being low. As k_1 and the radical concentrations increase, however, radical–radical reactions, particularly those involving the solvent-derived radical, become more important. This means that the secondary alcohol, formed in process 7, will give way to cross-product and ketone, arising from processes 9 and 10. Consequently, at a given temperature the more reactive alcohol will be associated with the lowest secondary alcohol and bibenzyl yields. For a given alcohol, because thermolysis and hydrogen transfer have positive and negative activation entropies, respectively, k_1 increases with temperature much faster than k_3 and k_4, hence the observed temperature dependence of the yields.

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(35) Pryor, W. A.; Tang, Y.; Tang, R. H.; Church, D. F. *J. Am. Chem. Soc.* **1982**, *104*, 2885.

(36) Lomas, J. S.; Briand, S. *Tetrahedron Lett.* **1989**, *30*, 707.

(37) Kodama, S. *Bull. Soc. Chem. Jpn.* **1962**, *35*, 652, 658, 824, and 827.

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(39) Kruppa, G. H.; Beauchamp, J. L. *J. Am. Chem. Soc.* **1986**, *108*, 2162.

Experimental Section

Thermolysis. Thermolysis and analytical procedures have been described elsewhere.[2] Various linear saturated hydrocarbons were used as internal standards for the determination of the absolute yields. In all cases the integrated absolute yields of ketone, secondary alcohol, and cross-product were close to 100% and the individual absolute yields were close to the relative yields (Tables I and IV). The latter are considered to be the more accurate and were used in the simulation experiments. Cage effects are percentages, with respect to t-Bu–C fission only, of ketone and secondary alcohol remaining at the highest concentrations of benzenethiol and benzophenone, respectively. 4-Substituted benzenethiols and benzophenones were used when necessary to facilitate GC separation (see Table I). Unless stated otherwise the initial scavenger/**2** ratio was 2.0. The tabulated yields are reproducible to ±1%, the cage effects to ±0.3%. For **2a**, only data relating to t-Bu–C homolysis are reported; appropriate corrections for the small contribution of Ad–C fission (2.3, 3.4, and 4.3% of the reaction at 145, 165, and 185 °C, respectively) have been made.

1,1-Di(*tert*-alkyl)-2-phenylethanols 3b–e were prepared by the Barbier reaction[17] of the appropriate ketone and benzyl bromide with lithium in ether at −20 °C. They were isolated in yields of 37–73% after chromatography on alumina and recrystallization (not **3e**, which is a liquid) from hexane. Physical and analytical data are as follows. **3b**: mp 143–4 °C; NMR ($CDCl_3$) δ 1.36 (s, 1 H), 1.6–2.1 (br m, 28 H), 2.94 (q, 2 H), 7.0–7.5 (m, 5 H). Anal. Calcd for $C_{26}H_{36}O$: C, 85.66; H, 9.95. Found: C, 85.58; H, 9.90. **3c**: mp 123 °C; NMR ($CDCl_3$) δ 1.3–1.9 (br m, 27 H), 2.95 (s, 2 H), 7.1–7.5 (br m, 5 H). Anal. Calcd for $C_{24}H_{34}O$: C, 85.15; H, 10.12. Found: C, 84.79; H, 10.04. **3d**: mp 75–6 °C; NMR ($CDCl_3$) δ 1.13 (s, 9 H), 1.42 (s, 1 H), 1.65 (br s, 6 H), 1.8–2.1 (br m, 9 H), 2.98 (q, 2 H), 7.0–7.5 (m, 5 H). Anal. Calcd for $C_{22}H_{32}O$: C, 84.56; H, 10.32. Found: C, 84.64; H, 10.30. **3e**: NMR ($CDCl_3$) δ 1.12 (s, 18 H), 1.46 (s, 1 H), 3.02 (s, 2 H), 7.0–7.4 (m, 5 H). Anal. Calcd for $C_{16}H_{26}O$: C, 82.00; H, 11.18. Found: C, 82.28; H, 11.00.

2,2-Dimethyl-1,1-diphenylpropan-1-ol (4b) was prepared by the reaction of phenyllithium (9 mmol) with *tert*-butyl phenyl ketone (1.0 g, 6 mmol) in ether at room temperature. The crude product (after quenching in water, ether extraction, drying over $MgSO_4$, and removal of the solvent) was chromatographed on alumina in hexane/ether mixtures. The product crystallized slowly from a few drops of pentane at −40 °C to give 1.25 g (84%): mp 29 °C (lit.[40] 28.5–29.5 °C); NMR ($CDCl_3$) δ 1.18 (s, 9 H), 2.21 (br s, 1 H), 7.1–7.35 (br m, 6 H), 7.45–7.6 (br m, 4 H). Anal. Calcd for $C_{17}H_{20}O$: C, 84.95; H, 8.39. Found: C, 84.90; H, 8.41.

1-Adamantyl Phenyl Sulfide. To a vigorously stirred (stainless steel flail) solution of diphenyl disulfide (0.44 g, 2 mmol) and 1-bromoadamantane (2 g, 9 mmol) in dry ether under argon at −2 °C (internal) was added finely chopped lithium metal (1% sodium) (0.21 g, 0.03 g-atom). After 1.5 h at this temperature, the cooling bath was removed and the mixture allowed to warm to room temperature. The crude product (after quenching in water, ether extraction, and drying over $MgSO_4$) contained some residual disulfide, which was reduced by means of $LiAlH_4$. After a second workup and evaporation of the solvent, the sulfide was isolated by chromatography on alumina in hexane/ether mixtures and was recrystallized from hexane (0.37 g, 75%): mp 71 °C; NMR ($CDCl_3$) δ 1.61 and 1.80 (br m, 12 H), 2.00 (br m, 3 H), 7.15–7.6 (m, 5 H). Anal. Calcd for $C_{16}H_{20}S$: C, 78.63; H, 8.25. Found: C, 78.53; H, 8.28. 1-Adamantyl 4-methylphenyl sulfide was prepared in the same way (0.41 g, 82%): mp 76–7 °C; NMR ($CDCl_3$) δ 1.61 and 1.79 (br m, 12 H), 1.99 (br m, 3 H), 2.35 (s, 3 H), 7.0–7.5 (m, 4 H). Anal. Calcd for $C_{17}H_{22}S$: C, 79.01; H, 8.58. Found: C, 79.00; H, 8.60.

Deuterium Determinations on Di(1-adamantyl)methanol were performed as previously[2] by coupled GC/ITD (Finnigan MAT 800B) analysis, but with chemical ionization. As before, the base peak is at *m/e* 135 but M − 1 (*m/e* 299 or 300) is about 15% and M − 17 (*m/e* 283 or 284) about 9%. A calibration plot, based on mixtures of pure Ad_2CHOH and 97% labeled Ad_2CDOH, was used for the analysis of samples from the thermolysis of **2a** in neat toluene-d_8. The deuterium content (±3%) was (*T*, %) 145, 45; 165, 41; 185, 38. Normal secondary alcohol has a M/(M − 1) ratio of 0.22 ± 0.01; that resulting from thermolysis of **2a** with excess benzophenone in toluene-d_8 at 165 °C had M/(M − 1) = 0.23 ± 0.01 and is, therefore, normal within the experimental error.

Kinetic Simulation Experiments. The previously described program,[2] now known as SSAIKS (Steady State Approximation Iteration for Kinetic Simulation), was modified to take into account the reactions of the *tert*-butyl radical, the steady state approximation being applied to the ketyl, *tert*-butyl, and benzyl radicals. The experimental values of the bibenzyl and secondary alcohol yields were used as targets in a simple empirical optimization procedure. Since with only two targets a perfect match can be obtained, constants k_3 and k_4 are thereby calculated with a "precision" which greatly exceeds that experimentally accessible. Introduction of a third constraint, e.g., the neopentylbenzene yield from **2e**, substantially reduces the quality of the fit.

Regardless of k_2, variations of 0.01 (1%) in one or other of the target values modify the optimized log k_3 by 0.1–0.14 l.u., log k_4 by about 0.02 l.u. The effect of adjusting the secondary alcohol cage effect is very similar, but log k_3 and log k_4 change by no more than 0.016 l.u. when the ketone contribution to the cage effect is altered by 0.01.

When our results were put into the KISS program,[41] which solves the differential equations by means of an integration routine especially suited to stiff systems,[42] the output product compositions were the same as ours; the steady state approximation therefore holds for this kinetic system.

Acknowledgment. We are indebted to Professor B. A. Gottwald for making available the KISS program, to J. P. Lomas for programming assistance, and to Dr. W. Smadja for the NMR spectra. Helpful discussions with Professor C. Rüchardt, Dr. H. D. Beckhaus, and Dr. J. Toullec are also gratefully acknowledged.

Registry No. 1, 93754-90-6; **2a**, 80514-85-8; **2b**, 82903-00-2; **2c**, 89849-36-5; **2d**, 66951-98-2; **2e**, 41902-42-5; **3b**, 98395-37-0; **3c**, 98395-39-2; **3d**, 130247-45-9; **3e**, 75501-40-5; **4b**, 1657-60-9; H_2, 1333-74-0; $(H3C)_3C^{\bullet}$, 1605-73-8; *p*-MeC_6H_4SH, 106-45-6; PhCOPh, 119-61-9; $PhCH_2Br$, 100-39-0; $AdCOC(CH_3)_3$, 31482-45-8; $(H_3C)_3CCOC(CH_3)_3$, 815-24-7; PhLi, 591-51-5; *t*-BuCOPh, 938-16-9; PhSSPh, 882-33-7; AdBr, 768-90-1; AdSPh, 88459-01-2; $Ad_2C^{\bullet}OH$, 121862-05-3; 1-adamantyl 1-bicyclo[2.2.2]octyl ketone, 93754-97-3; bis(1-bicyclo[2.2.2]octyl) ketone, 93754-95-1.

Supplementary Material Available: Tables S-V (thermolysis of Ad_3COH in presence of diphenyl disulfide), S-VI (kinetic simulation of product data), and S-VII (calculated breakdown of product-forming processes) and details of radical balancing for breakdown of Schemes II and III (7 pages). Ordering information is given on any current masthead page.

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