Figure 5. Fluorescence spectrum of NNDMP vapor (0.5 Torr) excited at: 210 nm (------); 244 nm (——); and 244 nm plus 50 Torr of *n*-hexane (· · · · · ·). Each spectrum is maximum normalized.

a possible model for the relaxed excited state of NNDMP.

Radicals and Scavengers. III. The Cage Effect in the Decomposition of *tert*-Butyl Diphenylperacetate

John P. Lorand*[1] and Robert W. Wallace

Contribution from the Converse Memorial Laboratories, Department of Chemistry, Harvard University, Cambridge, Massachusetts 02138, and the Department of Chemistry, Boston University, Boston, Massachusetts 02215. Received June 21, 1973

Abstract: The title perester, I, on thermal decomposition in cumene at 60°, affords CO_2 quantitatively when allowance is made for the presence of the impurities benzophenone and *tert*-butyl benzhydryl ether (II). The cage effect resulting in the formation of II is found by both scavenger and product isolation methods to be $16.5 \pm 2\%$, not 35% as implied by previously reported yields of II from I now known to have been impure. Decomposition of I in 88% mineral oil–12% chlorobenzene gives a much reduced yield of *tert*-butyl alcohol and an increase in the yield of II, further supporting the postulated cage effect. In addition, a "phantom" *ca.* 10% cage effect, probably involving p coupling of *tert*-butoxy and benzhydryl radicals, is postulated to explain the deficient material balance.

Studies of *tert*-butyl perester decomposition in these laboratories[2] have progressed from kinetics to cage effects,[3] as the possibility of obtaining information

about radical combination has become evident. A few such studies,[3,4] as well as of cage effects in photolytic perester decompositions,[5] have now been reported. Our own studies faltered for a considerable time on *tert*-butyl diphenylperacetate, I,[6] which alone among reac-

(1) Department of Chemistry, Central Michigan University, Mount Pleasant, Mich. 48859; part II in this series: J. P. Lorand, R. W. Grant, P. A. Samuel, E. M. O'Connell, J. Zaro, J. Pilotte, and R. W. Wallace, *J. Org. Chem.*, **38**, 1813 (1973).

(2) J. P. Lorand and P. D. Bartlett, *J. Amer. Chem. Soc.*, **88**, 3294 (1966).

(3) F. E. Herkes, J. Friedman, and P. D. Bartlett, *Int. J. Chem. Kinet.*, **1**, 193 (1969).

(4) J. P. Lorand, "Inorganic Reaction Mechanisms," Vol. 2, J. O. Edwards, Ed., Wiley-Interscience, New York, N. Y., 1972, pp 207–325.

(5) R. A. Sheldon and J. K. Kochi, *J. Amer. Chem. Soc.*, **92**, 5175 (1970).

(6) P. D. Bartlett and L. B. Gortler, *J. Amer. Chem. Soc.*, **85**, 1864 (1963).

tive peresters resisted purification beyond 90%, thus complicating the determination of cage effect. We have now obtained samples of I of purity approaching 95% and have determined the cage effect in its decomposition at 60° by several methods. We report these results here, and in succeeding papers, results of studies of several additional peresters by similar methods, as well as a discussion of perester cage effects.

Results and Discussion

Preparation and Purification of I. Perester I was previously[6] prepared in ca. 60% yield from the acid chloride, tert-butyl hydroperoxide, and pyridine in pentane; we prepared it from the acid chloride and sodium tert-butyl peroxide (anhydrous), eq 1, in

$$Ph_2CH-COCl + t\text{-}BuOO^-Na^+ \xrightarrow[CH_2Cl_2]{0°} Ph_2CH-CO_3\text{-}t\text{-}Bu + NaCl$$

(1)
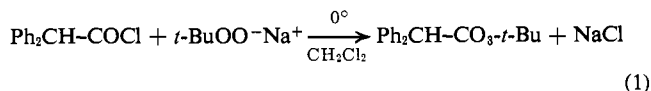
dichloromethane in yields ranging from 45 to 67%. Both methods gave samples of mp 57–60°, showing strong infrared absorption at 5.61 μ. Elemental analyses were, however, not satisfactory; moreover, yields of CO_2 on thermal decomposition in degassed cumene of twice recrystallized samples were usually 85–90%, rather than 100%; and the decomposition products usually contained some 3% of benzophenone. These facts caused concern about the incursion of decomposition mechanisms such as carboxyl inversion and radical-induced decomposition, possibly also giving the polyester of benzilic acid.

The above problems proved to be due to impurities. Infrared analysis at 6.02 μ of concentrated solutions of I disclosed benzophenone, while nmr analysis revealed benzhydryl tert-butyl ether, II, the logical cage product, in amounts ranging from 2 to 13 mol % of the perester present. In one case the estimated benzophenone content was 3%, and approximately that amount was isolated after decomposition. Three recrystallizations from pentane reduced the benzophenone content below 0.6%, and the product of decomposition then contained no benzophenone. Repeated recrystallization also decreased the ether content but never removed it entirely; to this end, use of benzene–pentane might have been more successful. The CO_2 yield from a sample recrystallized three times from purified ligroin was 97.5%, while the analyses for ketone and ether suggested a purity of 93.5%. Considering probable errors, these values are in good agreement. Henceforth, the CO_2 yield has been used as the best index of purity, and yields of II have been corrected according to the nmr assay.

The presence of benzophenone in samples of I may be explained by eq 2 and 3. Wright first proposed[7] such a base-catalyzed oxidative degradation of perester in order to explain the failure to obtain more than trace amounts of the tert-butyl perester of fluorene-9-carboxylic acid. This mechanism, in which presumably pyridine may play the same role as the tert-butyl peroxide anion, also explains the appearance of considerable CO_2 during preparation, even at 0°, and the mediocre yield of I. The reason for the presence of the ether, II, is probably that some homolytic decomposition takes place during preparation and purification,

(7) J. M. Wright, Ph.D. Thesis, Harvard University, 1967.

$$Ph_2C=O + CO_2 + {}^-O\text{-}t\text{-}Bu \quad (3)$$
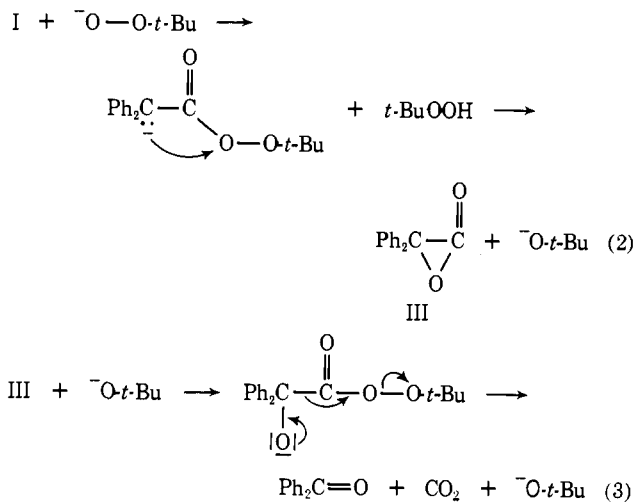
that the cage effect is larger at low temperatures, and that II crystallizes with the perester.

The Yield of II. Yields of benzhydryl tert-butyl ether, II, from thermal decompositions of I could be determined with a precision which we estimate as ±2%, using column chromatography. Although yield values generally ranged from 19 to 31%, subtraction of the nmr estimate of ether content gave net yield values which were essentially equal, for cumene solution at 60°, as shown in Table I. Based on the CO_2 yield as the

Table I. Product Yields from Thermal Decomposition of I in Cumene at 60°

Product	—Yield, mol/mol CO_2—		
	Run 1	Run 2	Run 3
Carbon dioxide	0.845[a]	0.890[a]	0.893[a]
tert-Butyl alcohol	0.635	0.755	b
Acetone	Tr	Tr	b
tert-Butyl benzhydryl ether, II			
Found	0.312	0.216	0.245
Contaminant	0.135[c]	0.060[c]	0.080 ± 0.027[d]
Net	0.177	0.156	0.165 ± 0.027
Dicumyl (2,3-dimethyl-2,3-diphenylbutane)	0.122	0.188	b
Cumylbenzhydryl (1,1,2-triphenyl-2-methylpropane)	0.298	0.284	b
sym-Tetraphenylethane	0.202[e]	0.241	b

[a] Moles per mole of perester. [b] Not determined. [c] Moles per mole of perester present, by nmr; assumed equivalent to moles per mole of CO_2 evolved. [d] Not assayed; assuming 50–100% of deficit in CO_2 yield due to II. [e] Chromatogram terminated before material completely eluted.

index of purity, then, thermal decomposition of I under these conditions yields 16.5 ± 2% of II, not 35% as earlier reported.[6]

The Cage Effect in Thermal Decomposition of I. Two methods were applied to nmr-assayed I and a third has been employed previously.[8] First, the yield of II in the presence of scavengers was determined; second, using oxygen as a scavenger, the number of moles of oxygen consumed per mole of I in the presence of an inhibitor of autooxidation was measured; third, zero-order rates of fading of the colored free radical galvinoxyl were measured,[8] the perester being in large excess.[4] In the third case, the reasonable assumption that the perester was only 85% pure gave a cage effect

(8) L. B. Gortler, Ph.D. Thesis, Harvard University, 1961.

estimate for cumene solution at 40°, which was consistent with the yield of II corrected similarly. These data and estimates appear in Tables II and III.

Table II. Kinetics of Reaction of Galvinoxyl and I at 40.4°

Solvent	[Perester]$_0$, M, assuming purity of 100%	85%	$10^5(1 - f)k_1$, sec$^{-1 a,b}$ Obsd^c	Corr^d	Cage effect, f, % Obsd^c	Corr^d
Cumene	0.0605	0.0515	1.71	2.01	37.8	26.8
	0.0510	0.0434	1.68	1.98	38.9	28.0
	0.0590	0.0501	1.76	2.07	36.0	24.7
				Mean	37.6	26.5
Toluene	0.0572	0.0486	1.88	2.21	34.0	22.5
	0.0506	0.0430	1.83	2.15	35.8	24.5
	0.0563	0.0479	1.92	2.26	32.6	20.6
				Mean	34.1	22.5

^{a} k_1(cumene) = 2.75 × 10^{-5} sec^{-1}; k_1(toluene) = 2.85 × 10^{-5} sec^{-1}; both determined by infrared method; cf. ref 6. ^{b} From equation $-d$[scavenger]/dt = 2(1 $- f)k_1$[perester]$_0$; (1 $- f$) = efficiency of radical production; f = cage effect. ^{c} Assuming perester 100% pure. ^{d} Assuming perester 85% pure.

Table III. Comparison of Yield of II with Kinetic Estimate, from Unassayed I, at 40°

Solvent	CO$_2$, mol/ mol I	II, mol/ mol CO$_2$	Net yield of II, —if II =— ΔCO$_2^a$	$^1/_2\Delta$CO$_2^a$	Mean cage effect, f, corr, Table II
Cumene	0.850	0.405	0.255	0.330	0.265
Toluene	0.846	0.363	0.209	0.287	0.225

^{a} ΔCO$_2$ = 1.00 $-$ yield of CO$_2$ in moles per mole of I.

the ether yields were measured and found within experimental error to be the same as in the absence of scavengers.

Table IV also shows the amount of oxygen absorbed by decomposing I to be about 72% of the CO$_2$ evolved, somewhat less than 83.5% as would be consistent with the ether yields. An explanation for this discrepancy in terms of a second, competing cage process is presented below. This result appears to represent the *total* cage effect.

The reactions of the scavengers used are depicted by eq 4–6. The disappearance of oxygen, observed both

$$Ar-OH + t\text{-}Bu\text{-}O \cdot \longrightarrow Ar\text{-}O \cdot + t\text{-}Bu\text{-}OH \qquad (4)$$
$$(Ar-OH = \text{pyrogallol, } 1,2,3\text{-}C_6H_3(OH)_3)$$

$$O_2 + Ph_2CH \cdot \longrightarrow Ph_2CH\text{-}O\text{-}O \cdot \xrightarrow{ArOH}$$
$$Ph_2CH\text{-}O\text{-}O\text{-}H + ArO \cdot \qquad (5)$$

$$t\text{-}C_{12}H_{25}\text{-}SH + t\text{-}Bu\text{-}O \cdot \longrightarrow t\text{-}C_{12}H_{25}\text{-}S \cdot + t\text{-}Bu\text{-}OH \qquad (6)$$

manometrically and mass spectrometrically, supports eq 5; oxygen and pyrogallol had been used by Ziegler and coworkers in their classic studies of the kinetics of dissociation of highly substituted ethanes (actually the isomeric methylenecyclohexadienes).[9] For reactions 4 and 6 in our study we have no direct evidence, since the yields of II in the presence and absence of the scavengers were the same. Reaction 6 probably takes place, since *tert*-dodecanethiol greatly increases the yield of *tert*-butyl alcohol from the decomposition of *tert*-butyl triphenylperacetate.[2,11] A reason for expecting reaction 4 is that *tert*-alkoxy radicals appear to be more reactive even than peroxy radicals.

Table IV. Yields of II from I in the Presence of Scavengers in Cumene at 59.5°

Scavenger	—CO$_2$, mol/mol I— With scav	No scav	—II, mol/mol CO$_2$, with scav— Gross	Contaminant	Net	O$_2$ absorbed, mol/mol CO$_2$	*tert*-Butyl alcohol, mol/mol CO$_2$
tert-Dodecanethiol	0.915	0.935	0.235	0.045	0.190	a	0.727
n-Octanethiol	0.790	0.935				a	
Thio-*p*-cresol	0.572	0.881				a	
Pyrogallol	0.873		0.237	0.060	0.177	a	
Pyrogallol + O$_2$	0.870		0.288	0.135	0.153	0.710^b	0.82
Pyrogallol + O$_2$	0.880		0.274	0.135	0.139	0.730^b	0.69
Pyrogallol + O$_2$	0.895		0.188	0.050	0.138	0.695^b	
Pyrogallol + O$_2^c$	0.900^d		0.293	0.100	0.193	0.525^e	

^{a} Decomposition conducted in degassed solution *in vacuo*. ^{b} O$_2$ absorption and CO$_2$ evolution monitored mass spectrometrically; mean values of 10$^4k_1$, sec^{-1}, for these three runs: CO$_2$ evolution, 3.57; O$_2$ absorption, 3.37; from ref 6a (infrared), 10$^4k_1$ = 3.37 sec^{-1}. ^{c} At 50.2°; CO$_2$ removed continuously with ascarite. ^{d} Determined in separate experiment. ^{e} O$_2$ absorption monitored manometrically.

As scavengers for the first two methods we used pyrogallol (a good scavenger of peroxy radicals[9]), three thiols, and oxygen in the presence of pyrogallol[2] to prevent autoxidation of cumene. Oxygen absorption was measured *via* the mass spectrometric technique of Traylor.[10] All CO$_2$ and ether yields are presented in Table IV. CO$_2$ yields were the same as for similar samples of I in the absence of scavengers, except for thio-*p*-cresol and *n*-octanethiol. These thiols presumably transesterified the perester to the corresponding thiol esters, so no effort was made to determine the yield of II. In the presence of *tert*-dodecanethiol, however, as well as pyrogallol, with or without oxygen,

The fact that the yield of II is independent of scavengers means that the solvent, cumene, is an efficient scavenger of *tert*-butoxy radicals. (Cumene does not scavenge benzhydryl radicals, for no diphenylmethane has been detected as a product.) Although benzhydryl radicals couple with each other and with solvent-derived cumyl radicals, which also couple with each other, the lifetime of *tert*-butoxy radicals is reduced to the point that their bulk coupling reactions cannot compete with their reaction with cumene. This observation has also been made by Sheldon and Kochi,[5] from their study of the photolyses of aliphatic *tert*-alkyl peresters, mixtures of which afforded no detectable amounts of "crossed over" ethers. It is consistent with
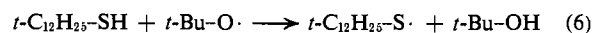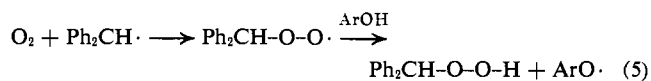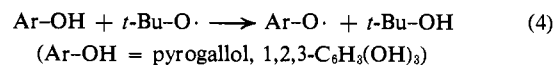
(9) (a) K. Ziegler and L. Ewald, *Justus Liebigs Ann. Chem.*, **473**, 163 (1929); (b) K. Ziegler, P. Orth, and K. Weber, *ibid.*, **504**, 131 (1933).
(10) T. G. Traylor, *J. Amer. Chem. Soc.*, **85**, 2411 (1963).

(11) J. P. Lorand and R. W. Wallace, *J. Amer. Chem. Soc.*, **96**, 1402 (1974).

the very high lower limit which Zavitsas and Blank have determined[12] for the rate constant of reaction of tert-butoxy radicals with toluene, viz., $6 \times 10^4 \ M^{-1}$ sec^{-1}. From this it can be estimated that the ratio of scavenging to coupling exceeds 10^4, if $(t\text{-BuO}\cdot) = 10^{-8} \ M$.

The Effect of Viscosity on Yields. Increasing viscosity has been found to increase a variety of cage effects;[4] accordingly, the search for this effect has been advocated as a "diagnostic test of a cage effect."[3] Decomposition of I in 88% mineral oil-12% chlorobenzene drastically reduced the yield of tert-butyl alcohol, as shown in Table V; again, the yield of alcohol

Table V. Yields of tert-Butyl Alcohol and II from Decomposition of I

| Solvent	Thiol[a] concn, M	tert-Butyl —alcohol[b]— 40°	60°	—II[c]— 40°	60°
Cumene	0.0	73	70	30	25
	0.2	74	75		
	1.0	73.5	77	24.5	22.5
75% Mineral oil– 25% C₆H₅Cl	0.0	51		43	
88% Mineral oil– 12% C₆H₅Cl	0.0	22	30		
	0.2	24			

[a] tert-Dodecanethiol. [b] Based on yield of CO_2, by glpc, referred to standard solutions. [c] By pmr, referred to anisole as integration standard.

was not significantly changed by adding tert-dodecanethiol. The yields in cumene at 40 and 60° in both the presence and absence of thiol ranged from 70 to 75%. The yields in mineral oil correspond to total cage effects of 70–78%, those in cumene to 25–30%. These results are nearly identical with those of Sheldon and Kochi[5] for photolysis of aliphatic tert-butyl peresters at 30° in pentane and mineral oil. In both systems, we feel, operation of cage effects is conclusively demonstrated. In further support we cite the 43% yield of II at 40° in 75% mineral oil–25% chlorobenzene, Table V, a value markedly higher than those in cumene. Since the result of the pmr method used exceeds that of direct isolation by 6–9% (at 60°), the true yield of II in 75% mineral oil is probably about 34–37%. Considering the 51% of tert-butyl alcohol found, some 12–15% of tert-butyl groups is not accounted for, slightly more than in cumene (vide infra).

A "Phantom" Cage Effect. One troublesome matter remains, namely the material balances in the decomposition of I. In run 2, Table I, about 7% of the benzhydryl radicals are not accounted for; the sum of the mean yields of II, 17%, and tert-butyl alcohol, 72%, altogether 89%, fall 11% short of 100%; finally, the sum of the mean yield of II and of oxygen absorbed, 72%, likewise is only 89%, again 11% short of quantitative. There is ample reason for confidence in the individual figures. Studies of II (cf. Experimental Section) show that it can be recovered essentially quantitatively by column chromatography on Florisil, while the hydrocarbons "cumylbenzhydryl" and sym-tetraphenylethane are expected to be stable and ap-

(12) A. A. Zavitsas and J. D. Blank, J. Amer. Chem. Soc., **94**, 4603 (1972).

peared to be eluted completely. Yields of tert-butyl alcohol as determined by glpc should be accurate; despite the wide variation reported in Tables I and IV, those of Table V, referred to standard solutions of alcohol rather than the pure material, give the same mean value, 72%, with much smaller variation. The extent of oxygen absorption by decomposing tert-butyl triphenylperacetate in cumene at 25° was found by the same method as used in the present paper to be 90%,[2] in good agreement with both the tert-butyl alcohol yield and the efficiency of radical production from a zero-order galvinoxyl experiment.

The discrepancies of 7–11% suggest a "phantom" cage effect, competing with the formation of II and leading to a product which was not isolated. By analogy with the triphenylperacetate,[2] as well as cumyl radicals from azocumene,[13] we assume that the competing process involves p coupling, eq 7. There is a

$$Ph_2CH\cdot \ + \ \cdot O\text{-}t\text{-Bu} \ \longrightarrow$$

$$(7)$$
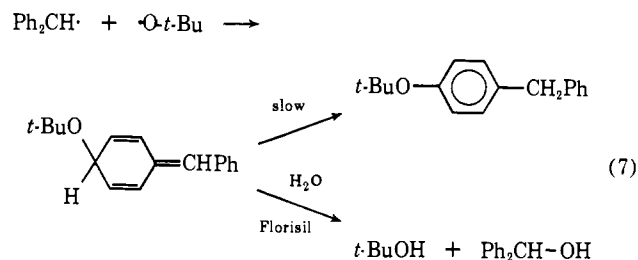
plausible reason why the product was not found. If it survives radical induced rearrangement, it may decompose on the chromatographic column, perhaps to tert-butyl alcohol and benzhydrol, the latter expected to be eluted much later than the hydrocarbons or ether. In the decomposition of the triphenylperacetate, rearrangment was evidently induced by triphenylmethyl radicals, observed at ca. $10^{-4} \ M$; benzhydryl radicals from I, however, were not detected.

Experimental Section

tert-Butyl Diphenylperacetate (I). Sodium tert-butyl peroxide of neutralization equivalent ca. 125, 7.85 g or 0.063 mol, was ground in a mortar and suspended under magnetic stirring in 150 ml of dichloromethane at 0°. Diphenylacetyl chloride, 11.6 g or 0.0503 mol, in 50 ml of dichloromethane was added within a few minutes. Transient pink and yellow-green colors appeared, the more intensely the more rapid the addition. The reaction was mildly exothermic, the temperature rising from about 0–4 to over 10°. Stirring was continued for over 2 hr at 0°.

The infrared spectrum of the supernatant 5 min after mixing showed that the acid chloride had largely disappeared. There remained in the carbonyl region a weak shoulder at 5.50 μ (acid chloride), a strong band at 5.61 μ (perester), and a medium band at 6.02 μ, assigned to benzophenone. In addition, absorption by carbon dioxide at 4.3 μ in the cold solution was much greater than in a freshly prepared solution of perester at room temperature, absorbance of 0.11 vs. 0.01. During the purification of residues from several preparations of perester, vide infra, one 100-mg fraction showed the entire infrared spectrum of benzophenone.

The mixture after standing overnight at −20° had set to a gel. After warming to 0°, it was cut with 100 ml of dichloromethane and stirred for 30 min with an additional 1.5 g (0.012 mol) of sodium tert-butyl peroxide. The suspension was filtered in 10 min on Supercel (Fisher) on a sintered glass suction funnel and the solvent removed on a rotary evaporator below room temperature. The

(13) S. F. Nelsen and P. D. Bartlett, J. Amer. Chem. Soc., **88**, 137 (1966).

oil crystallized from ligroin in two crops of long needles, total yield 9.6 g, 0.034 mol, 67% of theory. The yield was generally 45-50%.

The product was recrystallized from 300 ml of petroleum ether after filtering from amorphous or gummy insoluble matter. The first crop, 6.0 g, of long, white needles, had a melting point of 57.5-60°; a second crop of 1.2 g had a melting point of 52-60.5°. *Anal.* Calcd for $C_{18}H_{20}O_3$: C, 76.02, H, 7.09. Found (crop 1): C, 73.92, H, 7.18. Found (crop 2): C, 77.29, H, 7.47. The second crop contained benzophenone, as shown by infrared analysis (6.02 μ). Both crops showed nmr signals for benzhydryl *tert*-butyl ether, II, δ 5.50 ppm, and perester, δ 4.88 ppm; integration showed crops 1 and 2 to contain respectively 5.0 and 2.5 ± 0.5% of II, based on perester. Decomposition of crop 1 in cumene in the presence of O_2 and pyrogallol gave 89.5% CO_2 (measured mass spectrometrically), regarded as equal to the purity of the sample. Since all of the conceivable impurities (ether, benzophenone, acid chloride, acid, or polyester of benzilic acid) contain more carbon than I, it must be inferred that either the analyst's method contains a systematic error or I intrinsically gives a misleading result.

Three recrystallizations from ligroin of a different sample of I gave the following. *Anal.* Calcd for $C_{18}H_{20}O_3$: C, 76.02, H, 7.09. Found: C, 73.33, H, 6.87. Infrared analysis of the sample in CCl_4, 105 mg/ml, compared with benzophenone (3 mg/ml), showed it to contain 0.3-0.6% of ketone; nmr analysis gave 4.5% II. Decomposition in degassed cumene gave 97.5% CO_2 and in degassed styrene 92% CO_2. The products of decomposition in degassed cumene included a trace of benzophenone and 18 mg of a compound absorbing at 5.72 μ in the infrared (*ca.* 2% yield). It is concluded that the purity of the sample of I was 93.5%, a value consistent with the CO_2 yields.

Benzhydryl *tert*-Butyl Ether (II). Oily crystals, 3.6 g, residues from perester preparations, were chromatographed on 60 g of Florisil with ligroin as eluent. Recovery in several fractions afforded 3.08 g of II, mp 53-55°: nmr δ 7.2 (s, 10 H, aromatic), 5.5 (s, 1 H, benzylic), and 1.2 ppm (s, 9 H, *tert*-butyl). *Anal.* Calcd for $C_{17}H_{20}O$: C, 84.95, H, 8.39. Found: C, 84.64, H, 8.20.

Stability of II toward *tert*-Butoxy Radicals. A degassed solution of II, 0.7431 g, 3.09 mmol, and di-*tert*-butyl peroxyoxalate (DBPO), 0.3547 g, 1.515 mmol, in 15 ml of cumene was heated for 19 hr at 46°, at which DBPO had $t_{1/2} \cong 1$ hr. The yield of CO_2 was 3.07 mmol (101%), determined manometrically, or 3.10 mmol (102%), by absorption on ascarite *in vacuo*. No noncondensible gas was found. The distillate contained *tert*-butyl alcohol, 2.66 mmol, and acetone, 0.013 mmol, with a total yield of 87% of the gravimetric value of CO_2.

Chromatography of the residue on Florisil, eluting the first six 100-ml fractions with ligroin and the balance with 15% benzene in ligroin, gave six nearly pure fractions of II, mp 51-55°, 625 mg, following fraction 3, a mixture of II, *ca.* 100 mg, with dicumyl and unidentified material absorbing at δ 1.53 ppm in the nmr. The total recovery of II is 725 mg, 98% of that taken.

Stability of II toward Pyrogallol. A degassed mixture of purified II, 0.274 g, 1.14 mmol, and pyrogallol, 1.398 g, 11.10 mmol, in 15 ml of cumene was heated at 60° for 11 hr with vigorous magnetic stirring. No gases were found; the distillate contained less than 0.008 mmol of *tert*-butyl alcohol; chromatography of the benzene-soluble part of the residue gave 265 mg of oil, which crystallized while the cumene was being evaporated in an air steam (recovery, 97%).

Search for Benzhydryl *tert*-Butyl Carbonate as Decomposition Product from I. Decomposition of I, 1.0824 g, 3.815 mmol, in 15 ml of cumene for 28 hr at 50° *in vacuo* gave 89% CO_2 (gravimetric) and 68% *tert*-butyl alcohol (distillate, glpc). A solution of 1.0 ml of trifluoroacetic acid and 2.2 ml of water in 16 ml of dioxane was distilled into the nonvolatile residue attached to the vacuum manifold. After standing at 25° for 30 hr, the contents were distilled into the Dry Ice-acetone and liquid nitrogen traps. The latter contained no gas whatever.

Radicals and Scavengers. IV. Cage Effects in the Decomposition of *tert*-Butyl Peresters Which Generate the Stable Radicals Triphenylmethyl and 1,1-Diphenylneopentyl[1]

John P. Lorand*[2] and Robert W. Wallace

Contribution from the Department of Chemistry, Boston University, Boston, Massachusetts 02215. Received June 21, 1973

Abstract: The new perester, *tert*-butyl 2,2-diphenyl-3,3-dimethylperbutanoate, Ic, has been prepared and found to undergo first order homolysis with $k = 2.39 \times 10^{-5}$ sec^{-1} at 26°, about eightfold more slowly than the previously prepared triphenylperacetate (Ib). The 1,1-diphenylneopentyl radical, readily detected by epr during and after decomposition, displays only end absorption in the visible, in contrast to triphenylmethyl. Decomposition of peresters Ib and Ic in toluene produces higher yields of *tert*-butyl alcohol in the presence of *tert*-dodecanethiol than in its absence; these yields are independent of thiol concentration at and above 0.015 M. Addition of mineral oil up to 90% again lowers the yields, supporting operation of cage effects estimated to be 11 and 4-5% for Ib and Ic, respectively, in toluene.

Thermal and photochemical decompositions of *tert*-butyl peresters, I, eq 1, show substantial cage effects,

(1) (a) Previous paper in the series: J. P. Lorand and R. W. Wallace, *J. Amer. Chem. Soc.*, **96**, 1398 (1974); (b) portions of this work were presented at the 2nd Northeast Regional Meeting of the American Chemical Society, Providence, R. I., Oct. 1970, Abstract No. 182.

(2) Department of Chemistry, Central Michigan University, Mount Pleasant, Mich. 48859.

typically 30% or more near ambient temperature in

$$R-\overset{\overset{\displaystyle O}{\|}}{C}-O-O-t\text{-Bu} \longrightarrow \overline{R\cdot + CO_2 + \cdot O\text{-}t\text{-Bu}} \longrightarrow$$

Ia, R = Ph_2CH
b, R = Ph_3C
c, R = $Ph_2C(t\text{-Bu})$

$$CO_2 + R\text{-}O\text{-}t\text{-Bu} (II) + t\text{-BuOH} + \text{alkene} \quad (1)$$