

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 $2.5 \pm 0.5\%$ 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 benzoic 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 noncondensable 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.

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Radicals and Scavengers. IV. Cage Effects in the Decomposition of *tert*-Butyl Peresters Which Generate the Stable Radicals Triphenylmethyl and 1,1-Diphenylneopentyl¹

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 $k = 2.39 \times 10^{-5} \text{ sec}^{-1}$ 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

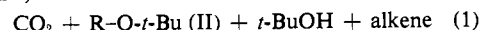
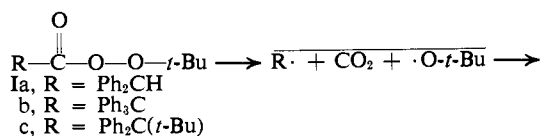




Figure 1. Epr spectrum of the 1,1-diphenylneopentyl radical in toluene at *ca.* 25° from thermal decomposition of *tert*-butyl 2,2-diphenyl-3,3-dimethylperbutanoate (Ic); *cf.* text.

nonviscous solvents.^{1,3} The radical-radical reactions involved thus have essentially diffusion-controlled rates.

The previous paper in this series¹ presented results of a study of the cage effect of Ia by product isolation and scavenger methods. The benzhydryl radical produced by the concerted thermal two-bond cleavage of Ia is not observed by epr during the decomposition, since it is unstable with respect to its dimer. The triphenylmethyl radical, however, is well known to exist in equilibrium with its dimer,⁴ and measures of its reactivity are rare. The cage effect of *tert*-butyl triphenylperacetate, Ib,⁵ has therefore been of interest to us. Previous experiments did not make clear whether or not this cage effect was significantly different from zero; estimates ranging from 6 to 13% had large probable errors.

We have now applied to Ib a diagnostic test for cage effects,^{3a} the observation of an increase as the solvent viscosity is increased,^{3c} and wish to report that the cage effect of Ib, as well as of Ia, is real. In addition, we have prepared and studied the new perester, *tert*-butyl 2,2-diphenyl-3,3-dimethylperbutanoate, Ic, decomposition of which should produce the stable 1,1-diphenylneopentyl radical.⁶ We find the cage effect in decomposition of Ic to be similar to that of Ib.

Results and Discussion

Preparation of Peresters. Perester Ib was prepared by the reported method^{1,5} (treatment of the acid chloride with anhydrous sodium *tert*-butyl peroxide suspended in dichloromethane at 0°) and assayed by its CO₂ yield on thermal decomposition in cumene. For the latter purpose a micro method was developed utilizing a modified Warburg manometer.

Perester Ic was prepared as shown in Chart I and described in the Experimental Section. The new perester, mp 34–36°, was purified by recrystallization, characterized spectrophotometrically, and assayed by its CO₂ yield on thermal decomposition in cumene. As with Ia and Ib, combustion analysis was not attempted, since reactive peresters usually give misleading results.⁵

Kinetics of Decomposition of Ic. Thermolysis of Ic was monitored by gas evolution, using the modified Warburg manometer in three runs at 26 to 39.7°,

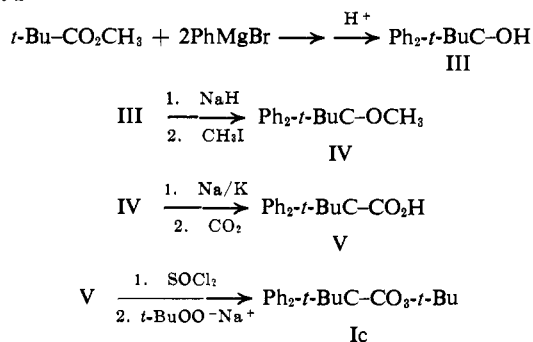
(3) (a) F. E. Herkes, J. Friedman, and P. D. Bartlett, *Int. J. Chem. Kinet.*, **1**, 193 (1969); (b) R. A. Sheldon and J. K. Kochi, *J. Amer. Chem. Soc.*, **92**, 5175 (1970); (c) J. P. Lorand, "Inorganic Reaction Mechanisms," Vol. 2, J. O. Edwards, Ed., Wiley-Interscience, New York, N. Y., 1972, pp 207–325; (d) J. P. Lorand, *J. Amer. Chem. Soc.*, in press.

(4) C. Walling, "Free Radicals in Solution," Wiley, New York, N. Y., 1957.

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

(6) (a) J. B. Conant and N. M. Bigelow, *J. Amer. Chem. Soc.*, **50**, 2041 (1928); (b) K. Ziegler, *Justus Liebigs Ann. Chem.*, **551**, 127 (1952); (c) K. Ziegler and L. Ewald, *ibid.*, **473**, 163 (1929); (d) for the epr spectrum of the unsubstituted neopentyl radical, *cf.* J. K. Kochi and P. J. Krusic, *J. Amer. Chem. Soc.*, **91**, 3940 (1969), and R. W. Fessenden and R. H. Schuler, *J. Chem. Phys.*, **39**, 2147 (1963).

Chart I



while the more usual infrared method was used at 50°; the data appear in Table I. An Arrhenius plot of the

Table I. Kinetics of Decomposition of *tert*-Butyl 2,2-Diphenyl-3,3-dimethylperbutanoate (Ic)

Initial concn of Ic, <i>M</i>	Temp, °C	10 ⁶ <i>k</i> ₁ , sec ⁻¹	Method ^a
0.183	50.0	56.0	Infrared
0.183	50.0	53.0	Infrared
0.000110	39.7	11.5	Manometric
0.000314	30.0	2.76	Manometric
0.000314	26.0	2.39	Manometric

^a *Cf.* text.

data gives $E_a = 27.4 \pm 2$ kcal/mol, which is in the expected range.⁵ Sufficient quantities of Ic were not prepared to permit more extensive measurements of decomposition rate.

Detection of 1,1-Diphenylneopentyl Radical. Perester Ic was studied principally in the expectation that its decomposition would produce the stable, detectable 1,1-diphenylneopentyl radical.⁶ Decomposition of 0.19 *M* Ic in toluene afforded a very pale yellow solution, the color of which intensified reversibly on warming to 50°. The visible spectrum consisted solely of a tail scarcely extending beyond 400 nm; on cooling to 0°, the tail and yellow color virtually disappeared, in agreement with previous reports.⁶ The thermochromism of the solution is consistent with the existence of an equilibrium, as for triphenylmethyl, between radical and a dimer, but the lack of distinct visible absorption features was unexpected. Triphenylmethyl displays a sharp spike, λ_{max} 515 nm ($\epsilon \sim 656$).^{6c} The radical from Ic was readily detected by epr, Figure 1; it had $g = 2.0022 \pm 0.0002$ and showed more than 150 lines; the maximum number of lines for 1,1-diphenylneopentyl, in the absence of overlaps or coincidences in hyperfine splittings, would be 750. The two outermost lines were separated by 0.24 G, about a fourth to a half of the splitting reported for the γ hydrogens of the neopentyl radical.^{6d} The total span of the spectrum, which should equal the sum of all the hyperfine con-

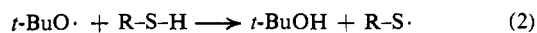
Table II. *tert*-Butyl Alcohol Yields from Decompositions of *tert*-Butyl Triphenylperacetate (Ib) and *tert*-Butyl 2,2-Diphenyl-3,3-dimethylperbutanoate (Ic)

Solvent	Viscosity, η , cP	Perester concn, M	Thiol ^a concn, M	<i>tert</i> -Butyl alcohol yield, ^{b,c} % From Ib	From Ic	
Cumene		0.070	0.0	69.0 (20°)		
		0.030-0.035	0.1-0.2	88.5 (20°)	100 (20°)	
		0.030-0.035	0.1-0.2	93.5 (40°)		
90% Mineral oil-10% chlorobenzene		0.06	0.0	27		
		0.06	0.0	45 (40°)		
		0.03	0.13	38		
		0.03	0.13	64 (40°)		
Toluene (100%)	0.55	0.025	0.000	87.5		
	0.55	0.025	0.015	95.1		
	0.55	0.025	0.030	92.0		
	0.55	0.025	0.060	96.8		
	0.55	0.025	0.120	89.2		
	0.55	0.025	0.240	92.0		
Toluene + 60% mineral oil	3.26	0.025	0.000	32.4		
	3.26	0.025	0.015	77.2		
	3.26	0.025	0.060	75.5		
	3.26	0.025	0.120	77.5		
	3.26	0.025	0.240	79.3		
Toluene-mineral oil mixtures, % mineral oil	0	0.55	0.17-0.19	40	91	
	0	0.55	0.02-0.03	97.5	97	
	20	0.84	0.02-0.03	0.1-0.13	95.0	
	40	1.96	0.02-0.03	0.1-0.13	83	91.5
	60	3.26	0.02-0.03	0.1-0.13	76.5	90.0
	80	11.6	0.02-0.03	0.1-0.13	64	79.5
	85	17.7	0.02-0.03	0.1-0.13	58	
	87	23.0	0.02-0.03	0.1-0.13		58.5
	90	32.3	0.02-0.03	0.1-0.13	51.5	

^a *tert*-Dodecanethiol. ^b Based on CO₂ yield. ^c At 25° unless otherwise noted.

stants, was found to be 22.0 G; the expected span, using the hyperfine constants for triphenylmethyl and the value just noted for the γ hydrogens, is 22.3 G.

Determination of *tert*-Butyl Alcohol Yields. Ia. The method by which the cage effect of Ia had previously been determined, isolation of cage product, IIa,¹ was tedious; it would be troublesome if applied to Ib, which affords at least two recombination products.⁵ A more attractive method would be the scavenging of *tert*-butoxy radicals by an efficient H-atom donor, e.g., a thiol, eq 2, and determination of the resulting *tert*-



butyl alcohol by glpc. The cage effect would be given by eq 3.

$$\% \text{ cage effect} = 100 - \% \text{ } t\text{-butyl alcohol} \quad (3)$$

Application of this method to Ia had shown that the yields of alcohol, with a precision of ca. $\pm 3\%$, were essentially unaffected by 0.2 M *tert*-dodecanethiol, in accord with the previous conclusion that cumene efficiently scavenges *tert*-butoxy radicals in this system. Repetition of these experiments in 85% mineral oil gave, as we hoped, drastically lower alcohol yields, again independent of the presence or absence of thiol, corresponding to a cage effect of 70% at 60° and ca. 77% at 40°.

***tert*-Butyl Alcohol Yields. Ib and Ic.** Ib has previously been found to produce much more *tert*-butyl alcohol in the presence of thiol than in its absence, 94% vs. 40% in cumene alone.⁵ The discrepancy was ascribed to scavenging of free *tert*-butoxy radicals by

triphenylmethyl, which was detected spectrophotometrically at a high concentration. Repetition of these experiments (cf. Table II) gave similar results, except that the yields in the presence and absence of thiol were respectively lower and higher than previously. In this work we have compared glpc integrals with those of standard solutions, while previously, *neat* alcohol was the standard. Furthermore, as shown in a succeeding paper,^{3d} the yield of alcohol in the absence of thiol depends on initial perester concentration, since this should also determine the concentration of triphenylmethyl radicals. The lower perester concentration used in the present experiments leads as expected to more alcohol.

We assume that the thiol scavenges *tert*-butoxy radicals, rather than triphenylmethyl radicals, because the reaction of the latter with thiols has been shown to be very slow. Thus, the disappearance of the absorbance of triphenylmethyl radical at 515 nm required several minutes at ambient temperature in the presence of several different thiols.⁷ The reaction of triphenylmethyl and *tert*-butoxy radicals, however, is fast enough to compete with the reaction of *tert*-butoxy radicals with cumene and is probably nearly diffusion controlled.

To show that the thiol was scavenging free *tert*-butoxy radicals with 100% efficiency, we varied the thiol concentration in toluene as solvent, obtaining the alcohol yields shown in Table II. The yields are higher than that in the absence of thiol and essentially constant from 0.015 to 0.24 M thiol. (The complete scavenging

(7) J. P. Lorand, Ph.D. Thesis, Harvard University, 1964.

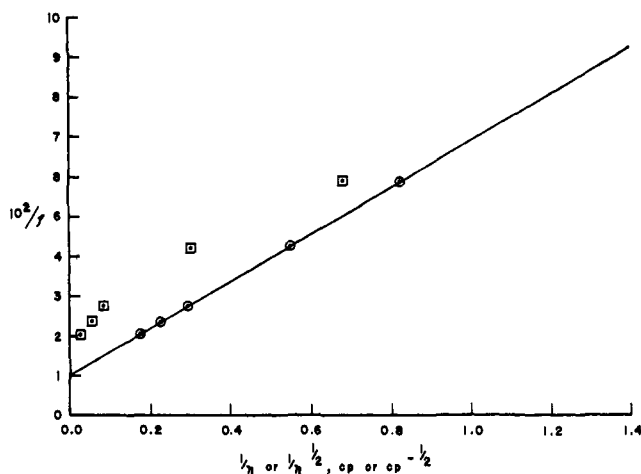


Figure 2. Relation between cage effect (f) and viscosity for Ib in toluene–mineral oil mixtures at 25°; data from Table II: (○) $1/f$ vs. $(1/\eta)^{1/2}$; (□) $1/f$ vs. $1/\eta$.

of radicals in the presence of insufficient thiol (0.015 M) probably means that the solvent and the thiol scavenge competitively at that concentration.)

Decomposition of Ib in 90% mineral oil–10% chlorobenzene gave much lower alcohol yields, even in the presence of thiol. Use of a series of toluene–mineral oil mixtures gave smoothly decreasing yields in the presence of 0.1 M thiol. Finally, variation of the thiol concentration in 60% mineral oil–40% toluene over the same range as in pure toluene again gave a constant yield of alcohol, considerably greater than that in the absence of thiol. These experiments make clear that a cage effect accompanies the homolysis of Ib, increasing dramatically in viscous solutions.

Decomposition of Ic in the presence and absence of thiol gave results closely similar to those for Ib, as shown in Table II. In this case also a cage effect must operate even in nonviscous media.

Cage Effects of Ib and Ic. The actual values of the cage effects of Ib and Ic in cumene and toluene are uncertain because of the closeness of the alcohol yields to 100%. Therefore, the apparent cage effects, eq 3, for Ib in mineral oil–toluene mixtures were plotted, as their reciprocals, against $1/\eta$ and $(1/\eta)^{1/2}$, as has been attempted previously for other systems;^{3c} these plots appear in Figure 2. As noted in other studies employing mineral oil, the square root plot was more nearly linear. Figure 3 shows the square root plot for Ic. The cage effects were estimated by extrapolation to the $(1/\eta)^{1/2}$ value of toluene and found to be 11% for Ib and 4–5% for Ic, both at 25°. These values are regarded as upper limits because plots of $1/(\text{cage effect})$ vs. $(1/\eta)^{1/2}$ tend to curve upward at low viscosities. Thus, the measured value of 3% for Ic may be fairly accurate.

The observation of cage effects for Ib and Ic shows that the reactivity of *tert*-butoxy radical toward triphenylmethyl and 1,1-diphenylneopentyl radicals is very great, although less than that of *tert*-butoxy with diphenylmethyl. It is significant that these stable radicals are reactive enough to be involved in cage effects. Precedent for such behavior is found in the Meisenheimer rearrangement of *N*-benzyl-*N*-methylaniline *N*-oxide to *N*-benzyloxy-*N*-methylaniline. In aqueous ethanol at 70°, a cage effect of 40% is opera-

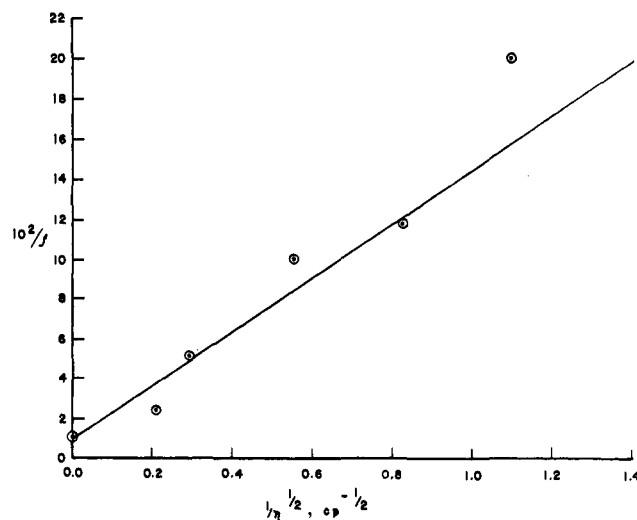


Figure 3. Relation between cage effect (f) and viscosity for Ic in toluene–mineral oil mixtures at 25°; data from Table II.

tive,⁸ involving the “stable” radical methylphenylnitroxyl, $\text{CH}_3\text{-N}(\text{O}\cdot)\text{-Ph}$.

We are aware of few other measures of the reactivity of triphenylmethyl radical.

(1) Solutions of triphenylmethyl in toluene are stable,⁹ hence H-atom abstractions from C–H bonds are very slow indeed. Additions to quinones are also slow.

(2) As shown by Pryor and Smith, triphenylmethyl undergoes cage coupling with *p*-nitrophenyldiazonyl radical ($p\text{-O}_2\text{NC}_6\text{H}_4\text{N}=\text{N}\cdot$) during thermal decomposition of *p*-nitrophenylazotriphenylmethane.¹⁰ A cage effect involving phenyl radical is absent from the decomposition of phenylazotriphenylmethane, presumably because fragmentation of phenyldiazonyl is too slow.¹¹

(3) The capture of O_2 by triphenylmethyl in a crystal of triphenylacetic acid is very rapid and has $\Delta H^\ddagger < 1$ kcal/mol.¹²

(4) As noted above, triphenylmethyl reacts relatively slowly with thiols at ambient temperature.⁷

(5) In spectacular contrast to 2, 3, and our cage effects is the slow coupling of triphenylmethyl pairs, which from the data of Ziegler, *et al.*,¹³ have $k \approx 3600 M^{-1} \text{sec}^{-1}$ at ambient temperature and $E_a = 19$ kcal/mol, about 10^5 slower than for coupling of other radicals. Steric hindrance is probably responsible for the rate decrease. The role of steric hindrance in determining the reactivity of radical pairs will be discussed in detail in a later paper.^{3d}

Experimental Section

Materials. Cumene was purified by extraction with 95% sulfuric acid, followed by washing with aqueous sodium carbonate solution, water, and brine, drying over MgSO_4 , and distilling from sodium;

(8) 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).

(9) R. W. Wallace, Ph.D. Thesis, Boston University, 1973.

(10) W. A. Pryor and K. Smith, *J. Amer. Chem. Soc.*, **92**, 5403 (1970).

(11) (a) R. G. Kryger, Ph.D. Thesis, Boston University, 1973; (b) R. G. Kryger and J. P. Lorand, paper presented at the 159th National Meeting of the American Chemical Society, Houston, Texas, Feb. 1970, Abstracts ORGN 21.

(12) E. G. Janzen, F. J. Johnston, and C. L. Ayers, *J. Amer. Chem. Soc.*, **89**, 1176 (1967).

(13) Cited by C. Walling, ref 4, p 533.

the fraction which distilled at 150.9–151.4° was stored under nitrogen in the dark. Toluene was treated in the same manner, bp 109.8–110.1°. Chlorobenzene was also treated as above except that it was distilled without sodium, bp 131.6–132.0°. Mineral oil ("Nujol," Plough, Inc.) was used as received. *tert*-Butyl triphenylperacetate (1b) was prepared as described in the literature;⁵ samples were assayed by measuring the yield of CO₂ on complete decomposition in degassed cumene *in vacuo*.

1,1-Diphenyl-2,2-dimethyl-1-propanol. In a 2 l, 3-necked flask with mechanical stirrer, condenser, and dropping funnel, a solution of phenylmagnesium bromide from 45 g, 1.85 mol, of magnesium turnings and 200 ml, 1.91 mol, of bromobenzene in 300 ml of anhydrous ether was prepared. To this solution at 10° was added 120 ml, 1.08 mol, of methyl pivalate in 200 ml of ether, the temperature being maintained below 15°. Addition of excess 4 *N* sulfuric acid was accomplished while keeping the temperature below 15°. The ether layer was washed with dilute sodium bicarbonate solution, 2% sodium thiosulfate solution, and brine and dried over anhydrous MgSO₄ for 12 hr. The ether was stripped *in vacuo* and the oily carbinol distilled: bp 156–159° (4.1 Torr) (lit.¹⁴ 140–142° (0.3 Torr)); yield 155 g, 0.65 mol, 70% of theory. On standing for 2 days in the freezer in twice its volume of petroleum ether, the carbinol formed white prisms: mp 29–30.5° (lit.¹⁵ 28.5–29.5°); infrared (CCl₄) O–H, 3570 cm⁻¹; nmr (CCl₄ + TMS) δ 1.10 (9 H, s, *tert*-butyl), 1.98 (1 H, s, OH), 7.0–7.6 ppm (10 H, m, phenyl).

Methyl 1,1-Diphenyl-2,2-dimethyl-1-propyl Ether. Method A. In a 2 l, 3-necked flask fitted with a dropping funnel, drying tube, and mechanical stirrer, 100 g, 0.41 mol, of 1,1-diphenyl-2,2-dimethyl-1-propanol was allowed to react with 30 g, 0.63 mol, of sodium hydride (52% in mineral oil) in 200 ml of DMF, with stirring overnight. A solution of 96 g, 0.67 mol, of methyl iodide in 200 ml of DMF was slowly added with cooling and stirring and the mixture let stand overnight. After cautious dilution with an equal volume of water, the mixture was extracted with five 100-ml portions of dichloromethane. The combined extracts were washed with two 50-ml portions of 10% sodium thiosulfate and with distilled water, then dried over MgSO₄ and the solvent stripped *in vacuo*. The residual clear oil was distilled from sodium hydride: bp 171–174° (10 Torr) (lit.¹⁶ 174° (13 Torr)); yield, 45 g, 0.18 mol, 44% of theory; nmr (CCl₄) δ 1.00 (9 H, s, *tert*-butyl), 2.93 (3 H, s, methyl), 7.0–7.6 ppm (10 H, m, phenyl).

Method B. To a solution of 1.5 ml of 95% H₂SO₄ in 100 ml of absolute methanol at room temperature was added 20 g, 0.083 mol, of 1,1-diphenyl-2,2-dimethyl-1-propanol. After 24 hr, the solution was neutralized with 10% aqueous Na₂CO₃, diluted with water, extracted with two 50-ml portions of dichloromethane, and further worked up as in Method A; bp 173–176° (10 Torr); yield, 10 g, 0.039 mol, 47%. Contrary to the report by Ziegler, *et al.*,¹⁶ two layers did not form during the reaction. Several unsuccessful attempts were made to recrystallize the ether from petroleum ether (lit.¹⁶ mp 45°).

3,3-Dimethyl-2,2-diphenylbutanoic Acid. In a 3-necked flask equipped with magnetic stirring bar, condenser with drying tube, gas inlet tube, and stopper was prepared alloy from 30 g of potassium and 6 g of sodium and a small volume of toluene, the flask being continuously purged with nitrogen and heated above the melting point of the metals. The toluene was distilled out and the alloy washed with anhydrous ether, then covered with 400 ml of ether.

A solution of 45 g, 0.18 mol of methyl 1,1-diphenyl-2,2-dimethyl-1-propyl ether in 100 ml of anhydrous ether was slowly dripped into the flask, initially producing a blue color which became almost black and finally turned to dark red. The addition required 90 min, after which 100 ml of ether was added, and the mixture was allowed to reflux overnight. After cooling the mixture, CO₂ ("bone dry") was bubbled in at a moderate pace; after 90 min the solution had changed from a dark red to a pale tan, and an off-white solid had formed; CO₂ was added for an additional 30 min. The alloy was destroyed by cautious addition of 80 ml of 2-propanol in 200 ml of ether, and the reaction mixture was slowly added to 500 ml of water. After transfer to a separatory funnel, the mixture was made acidic with 6 *N* hydrochloric acid. The ether layer was washed with 3 *N* hydrochloric acid, distilled water, and brine, dried 12 hr over MgSO₄, filtered, and stripped of solvent *in vacuo*. The

residual pale yellow solid, 30.5 g, was crystallized from benzene (40 ml) and hexane: white crystals, 18.9 g, 0.071 mol, 40%; mp 157.5–159° (lit.^{6a} 160°). Additional acid was obtained from the mother liquor: 7 g, 0.025 mol, 15%; mp 157–158.5°; infrared (CH₂Cl₂) O–H, 2600 (b), C=O, 1700 cm⁻¹.

3,3-Dimethyl-2,2-diphenylbutanoyl Chloride. To a solution of 10 g, 37.5 mmol, of 3,3-dimethyl-2,2-diphenylbutanoic acid and 6 drops of pyridine in 100 ml of benzene in a 200-ml flask fitted with reflux condenser was added 5.5 ml, 76.5 mmol, of thionyl chloride. Bubbles began forming soon, and the solid acid had disappeared within 2 hr; the solution was refluxed for 1 hr. The solution was cooled and stripped of solvent and thionyl chloride *in vacuo*. Petroleum ether, 40 ml, was added, and the mixture was heated to dissolve the product; sometimes a few milliliters of benzene was added to aid the process. On cooling, the solution deposited white prisms: 8.5 g, 30 mmol, 80%; mp 82.5–83.5°; infrared C=O, 1789 cm⁻¹.

***tert*-Butyl 3,3-Dimethyl-2,2-diphenylperbutanoate.** Powdered sodium *tert*-butyl peroxide,⁵ 8.0 g, 67 mmol, was suspended with magnetic stirring in 150 ml of dichloromethane in a 500-ml flask fitted with pressure-equalized dropping funnel and drying tube and cooled in ice. A solution of 3,3-dimethyl-2,2-diphenylbutanoyl chloride, 6.0 g, 21 mmol, in 100 ml of dichloromethane was slowly added over 45 min to the vigorously stirred suspension; stirring was continued for 3 hr. The progress of the reaction was monitored by the infrared absorption in the carbonyl region of 0.5-ml aliquots, rapidly filtered, and diluted with 1 ml of dichloromethane. Unless the absorbance of the perester exceeded by tenfold that of the chloride, an additional 3 g of sodium *tert*-butyl peroxide was added, stirring continued 3 hr, and the infrared spectrum again scanned. After at least 90% conversion the mixture was filtered by suction in the cold room (4°), the solvent was stripped at 0° *in vacuo*, and traces of volatiles were removed under high vacuum.

The residual oil, dissolved in 4 ml of benzene followed by 80 ml of petroleum ether, was chromatographed on a column of 60–100 mesh Florisil prepared in petroleum ether in a 50-ml buret (to the 10-ml mark). Elution was accomplished with petroleum ether in fractions of 50, 100, 100, and 100 ml, followed by 150 ml of benzene, all of which were kept at 0° during removal of solvent. Infrared analysis showed the second and third fractions to contain perester, an oil; crystallization was achieved by adding a few milliliters of petroleum ether and cooling to –25°. In a few cases, crystallization began within 30 min and was complete in 2 hr; seed crystals were used in other cases. The mother liquor was removed by pipet and the crystals were washed with fresh solvent at –25°. The wash solvent was removed by pipet, and traces of solvent were removed *in vacuo*: yield, 2.3 g, 6.8 mmol, 31% of theory; mp 34–36°. The purity of the product was 100 ± 2% as determined by the yield of CO₂ from thermal decomposition in the modified Warburg apparatus described below: infrared (CCl₄) C=O, 1758 cm⁻¹; nmr (CCl₄) δ 1.00 (9 H, s, *C-*t*-Bu*), 1.26 (9 H, s, *O-*t*-Bu*), 7.0–7.6 ppm (10 H, m, aromatic).

Yields of *tert*-Butyl Alcohol. These were determined by glpc using an F & M Model 700 instrument equipped with Brown recorder and Disc chart integrator. Columns used were a 6 ft 10% UCON 50HB 550X and 10 ft 5% Carbowax 20M, both on 60–80 mesh Haloport F. Duplicate or triplicate 10-μl aliquots of the standard and of each decomposition solution were injected; mean values are reported. Standards were prepared in the same solvent used for decomposition and were within 50% of the theoretical yield of alcohol in order to ensure equivalent sensitivity of the instrument to both sample and standard.

Kinetics of Perester Decomposition. Infrared Method. Essentially the same method was used as has been reported.¹⁷ Aliquots of a perester solution were syringed into ampoules and sealed. They were placed in a constant temperature bath and at desired intervals removed, quenched in Dry Ice–acetone, and stored in the freezer (–25°) until analysis *via* a Perkin–Elmer Model 21 spectrometer, locked at the carbonyl maximum of the perester. Plots of log (*A*/*A*₀) vs. time were linear over 5 half-lives.

Kinetics and Determination of Perester Purity. Manometric Method. An improved Warburg syringe manometer from Roger Gilmont Instruments was employed to measure the rate of CO₂ evolution; the final volume was used as a measure of perester purity. The manometer was equipped with a micrometer syringe with a capacity of 200 μl in 0.2-μl divisions, an adjustable screw to

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raise and lower the level of manometer fluid, a three-way stopcock, and a 25-ml vessel with a septum cap. The entire volume of the manometer was submersible. The temperature of the constant temperature bath used had to be maintained within $\pm 0.05^\circ$, since the reading sensitivity of the meniscus line of the manometer was $\pm 0.15 \mu\text{l}$.

Before immersing the apparatus in the bath, it was flushed with nitrogen for 30 min. During this time the manometer fluid was added and the stopcock opened to the nitrogen reservoir. The perester decomposition was used as the manometer fluid, in place of mercury, because of the increased sensitivity of less dense liquids to pressure change. Thermal equilibrium was attained only about 12 hr after immersion.

Since the perester solution was kept at a temperature 20–30° below that of the bath, in order to avoid decomposition, it was necessary to measure the effect of this temperature differential on the volume. Solvent aliquots at this lower temperature were syringed into the manometer, the stopcock was immediately closed, and the

volume change noted over the expected reaction period. If the volume changes of two consecutive solvent injections were within 5–10 μl of each other, then the perester stock solution was injected. After decomposition was complete, another blank was injected.

Esr Spectra and Uv-Vis Spectra of 1,1-Diphenylneopentyl Radical. Esr spectra were recorded on a Varian V-4502 X-band spectrometer using 100 kc modulation. A solution of Ic was syringed into an apparatus consisting of a quartz esr tube and a pyrex visible spectra sample tube sealed end to end with the aid of graded seals, with a T joint in the middle to a stopcock. The apparatus was flushed with nitrogen and the perester allowed to decompose. The esr spectrum of the resulting pale yellow solution was then recorded. The uv-visible spectrum was recorded on a Cary 14 instrument and found to consist of a tail into the violet region, without any maximum.

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Evidence for Comparable Reactivity of Alkanone Excited Singlet and Triplet States toward Hydrogen Donors¹

David R. Charney,^{2a} J. Christopher Dalton,*^{2b} Richard R. Hautala,^{2a} John J. Snyder,^{2b,3} and Nicholas J. Turro^{2a,4}

Contribution from the Departments of Chemistry, University of Rochester, Rochester, New York 14627, and Columbia University, New York, New York 10027. Received September 26, 1972

Abstract: Studies of solvent effects on the relative fluorescence quantum yield (ϕ_f^{rel}) and fluorescence lifetime (τ_s) of 2-adamantanone are presented. The ability of a given solvent to quench adamantanone fluorescence correlates well with the facility of the solvent as a hydrogen donor, suggesting that the quenching process involves at least partial intermolecular hydrogen abstraction by the adamantanone excited singlet state. Kinetic studies indicate that the alkanone n, π^* singlet is just as reactive as the n, π^* triplet toward quenching by hydrogen donors.

The intermolecular photoreduction of alkyl ketones has been the subject of considerable interest over the past few years.^{5–10} Particular emphasis has been placed on the importance of the multiplicity of the alkanone excited states (S_1 or T_1) and the degree of ring strain present in cyclic alkanones in determining the reactivity toward intermolecular hydrogen abstraction.^{6–9} It has been reported that the alkanone n, π^* singlet state (S_1) is at least two or three orders of magnitude less reactive than the n, π^* triplet state (T_1) toward intermolecular hydrogen abstraction.^{6,8} This result requires significant differences in the effect of excited-state multiplicity on intermolecular hydrogen abstraction and intramolecular hydrogen abstraction, for

which the alkanone S_1 and T_1 states have been shown to have comparable reactivity.¹¹ We would like to present evidence from studies of solvent effects on the quantum yield and lifetimes of fluorescence from 2-adamantanone that demonstrate that several hydrogen donors quench the n, π^* singlet and n, π^* triplet states at equivalent rates. Our results suggest that alkanone S_1 and T_1 states have comparable reactivity (but not necessarily efficiency) toward intermolecular hydrogen abstraction.

Experimental Section

Solvents were at least spectral grade further purified by fractional distillation prior to use. 2-Adamantanone (Aldrich) was twice sublimed prior to use. Tributyltin hydride (TBTH) was prepared by reduction of tributyltin chloride. 2-Propanol-*d*₈ (Merck) was used as received. 2-Propanol-*O-d* was prepared by exchange with D₂O.

Fluorescence and phosphorescence lifetimes were measured using the single photon counting technique. The air spark lamp used had a half-width of 1.8 nsec. Phosphorescence lifetimes were measured on degassed solutions in acetonitrile. Fluorescence yield measurements were carried out using a Hitachi-Perkin-Elmer MPF-2A spectrofluorometer. Minor corrections were made for differences in absorbance at λ_{ex} (310 nm).

Results and Discussion

We have studied solvent effects on the fluorescence lifetime, τ_s , and relative fluorescence quantum yield,

(11) See N. J. Turro, *et al.*, *Accounts Chem. Res.*, **5**, 92 (1972), and references therein.

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(2) (a) Columbia University; (b) University of Rochester.

(3) NSF Trainee, 1970–1971; NDEA Title IV Fellow, 1971–1978.

(4) Alfred P. Sloan Fellow, 1966–1970.

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