

methyl-2,5-bis(hydroperoxy)hexane was purchased from Lucidol under the trade name Luperox-2,5-2,5. It was washed several times with ice water, dried, and recrystallized from benzene, mp 104°. Its purity by iodometric titration was 98.5%.

The reactions at -70° were carried out in a Dry Ice-acetone bath in a 250-ml flask from which the effluent gas was conducted to a graduated cylinder and collected by displacement of water. The reaction mixture was stirred magnetically, and the temperature was read periodically with a low-temperature thermometer. One hour was ordinarily allowed for completion of the low-temperature gas evolution, after which no further oxygen appeared until the temperature was raised by more than 35° .

In expt 3 the gas produced was analyzed mass spectrometrically. It consisted entirely of oxygen except for some nitrogen, which was expected because no precautions were taken to exclude air.

In expt 18 a special apparatus was constructed in which the bottom of the reaction vessel contained a fritted glass filter. The re-

actants were held in the reaction flask by a positive pressure of nitrogen introduced below the fritted glass. After completion of the reaction at -75° , the nitrogen pressure was released, and the solution filtered into a lower vessel, the entire assembly being surrounded by the cooling bath. The upper vessel was then removed, and a precooled solution of 5 ml of *t*-butyl hydroperoxide in 15 ml of methylene chloride was added to the clear filtrate in the lower flask which was magnetically stirred and connected to a gasometer. After this addition was completed without gas evolution, the reaction mixture was warmed up, and the oxygen measured as reported in Table I.

The product analyses were performed by vapor phase chromatography on a 6-ft diisodecyl phthalate column between 45 and 75° without heating the injection port or detector block.

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Peresters. XII. *t*-Butyl Triphenylperacetate

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Abstract: The reactive perester, *t*-butyl triphenylperacetate, decomposes in cumene at 25° with $k = 1.7 \times 10^{-4} \text{ sec}^{-1}$ (more than 40 times faster than the diphenylperacetate), $\Delta H^{\circ} = 24.1 \text{ kcal}$, $\Delta S^{\circ} = 4.9 \text{ eu}$. The yield of carbon dioxide is 95–98% and the solution shows the esr spectrum of the triphenylmethyl radical. There is a cage effect of about 10%; the coupling product of the triphenylmethyl and *t*-butoxy radicals is mono-*p*-*t*-butoxytriphenylmethane (IV); spectral evidence indicates a similar amount of triphenylmethyl *t*-butyl ether (II) in the early product, which is converted during chromatography to triphenylcarbinol. The principal product in styrene is a "one-unit telomer" (VI) produced by addition of *t*-butoxy radical to the primary end of the styrene molecule, followed by coupling of the resulting radical with triphenylmethyl. Although this reaction involves a coupling of the triphenylmethyl radical at its central carbon atom, attempts to synthesize the normal ether II from halide and alkoxide, or the telomer chain of VI from phenylmalonic ester and triphenylmethyl chloride, afforded only further examples of attack at the *para* position of the triphenylmethyl halide.

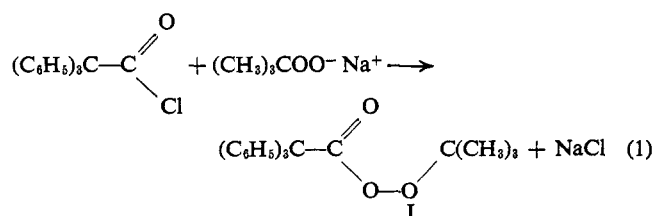
That the decomposition of numerous *t*-butyl peresters proceeds by concerted two-bond cleavage into a pair of free radicals and a molecule of carbon dioxide has been well documented.¹ The rate of decomposition of a perester $\text{RCO}_2\text{C}(\text{CH}_3)_3$ depends in part on the stability of the radical $\text{R}\cdot$. The ultimate products of decomposition result from reactions of the radicals $\text{R}\cdot$ and *t*-butoxy.

Although peresters of most of the simple phenyl- and methyl-substituted acetic acids had been studied, that of triphenylacetic acid had eluded preparation.² We now report its preparation and reactions. Although its rate of decomposition is in accord with expectation, its products are atypical, including an example of the ambident reactivity of triphenylmethyl radical. Proofs of structure of two products of decomposition have led to new examples of the ambident reactivity of triphenylchloromethane.

Results

Preparation and Purification of the Perester. Apparently because of the extreme bulk of the triphenyl-

methyl group, triphenylacetyl chloride had previously been found to be unreactive with *t*-butyl hydroperoxide and pyridine. However, the use of the sodium salt of the hydroperoxide led, in up to 55% yield, to crystalline perester I, mp $61\text{--}64^{\circ}$ (effervescence), $\lambda_{\text{max}} 5.67 \mu$; I,



recrystallized from benzene-pentane at -20° , could be stored at that temperature for 8 months unchanged.

Satisfactory elementary analyses were obtained, but iodometric titration by the method of Silbert and Swern^{3a} gave an apparent purity of only 73%. Such a result is characteristic of the less stable peresters.^{3b} A more positive criterion of purity is the nearly quantitative yield of carbon dioxide from thermal decomposition of the perester in all the solvents used in this study (see below).

(1) (a) P. D. Bartlett and R. R. Hiatt, *J. Am. Chem. Soc.*, **80**, 1398 (1958); (b) P. D. Bartlett and D. M. Simons, *ibid.*, **82**, 1753 (1960); (c) P. D. Bartlett and L. B. Gortler, *ibid.*, **85**, 1864 (1963); (d) P. D. Bartlett and C. Richardt, *ibid.*, **82**, 1756 (1960).

(2) P. D. Bartlett, *Experientia Suppl.*, **7**, 275, 282 (1957).

(3) (a) L. S. Silbert and D. Swern, *Anal. Chem.*, **30**, 385 (1958); (b) J. P. Lorand, Thesis, Harvard University, 1964, p 8.

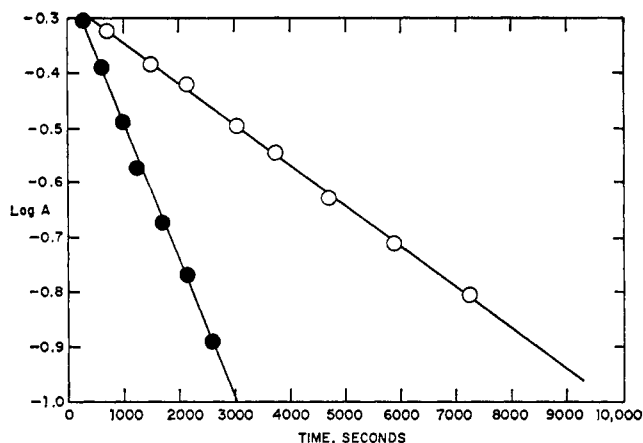


Figure 1. Thermal decomposition of *t*-butyl triphenylperacetate in cumene (infrared method): O, 25.70°, 0.046 *M*, $k_1 = 1.73 \times 10^{-4} \text{ sec}^{-1}$; ●, 34.85°, 0.046 *M*, $k_1 = 5.71 \times 10^{-4} \text{ sec}^{-1}$.

Kinetics of Decomposition of I. Compound I was unstable at room temperature; the intense carbonyl absorption in the infrared was rapidly replaced by absorption at 4.3 μ due to carbon dioxide. Rates of decomposition at 25, 35, and 45° were measured, with the results given in Table I and Figure 1. No dependence of rate constant on perester concentration is evident. The activation parameters as calculated by the Eyring equation⁴ are $\Delta H^* = 24.1 \text{ kcal/mole}$ and $\Delta S^* = +4.9 \text{ cal/deg}$ (see Figure 2). The rate of decomposition and activation parameters of I are compared in Table II with those of related peresters.

Table I. Kinetics of Decomposition of I in Cumene

Temp, °C	Perester concn, <i>M</i>	$10^4 k$, sec^{-1}	Method
25.70	0.0462	1.725	Infrared
	0.0521	1.793	Infrared
	0.192	1.660	Infrared
	0.134	1.88	Mass spectry
	0.0965	1.76	Manometric
34.85	0.140	1.52	Manometric
	0.0462	5.709	Infrared
	0.192	5.857	Infrared
45.45	0.0497	7.76 ^a	Infrared
	0.0384	23.09	Infrared
	0.063	21.88	Infrared
	0.166	23.41	Infrared

^a In chlorobenzene.

Table II. Relative Rates of Decomposition of Several Peresters Compared at 25°

R in $\text{RCO}_2\text{-}t\text{-Bu}$	k , sec^{-1} ^a	Relative k	ΔH^* , kcal/mole	ΔS^* , eu
CH_3^b	2.1×10^{-11}	1.0	39	20
$\text{C}_6\text{H}_5\text{CH}_2^c$	6.3×10^{-8}	3.0×10^3	27.9	2.0
$(\text{C}_6\text{H}_5)_2\text{CH}^d$	3.7×10^{-8}	1.8×10^5	25.0	0.5
$(\text{C}_6\text{H}_5)_3\text{C}$	1.7×10^{-4}	8.1×10^8	24.1	4.9

^a Extrapolated to 25°, except for I. ^b See ref 1. ^c See ref 1d. ^d See ref 1c.

The rate of decomposition was also measured at 25° using the mass spectrometric method of Traylor,⁵

(4) A. A. Frost and R. G. Pearson, "Kinetics and Mechanism," 2nd ed, John Wiley and Sons, Inc., New York, N. Y., 1961, p 99.
(5) T. G. Traylor, *J. Am. Chem. Soc.*, **85**, 2411 (1963).

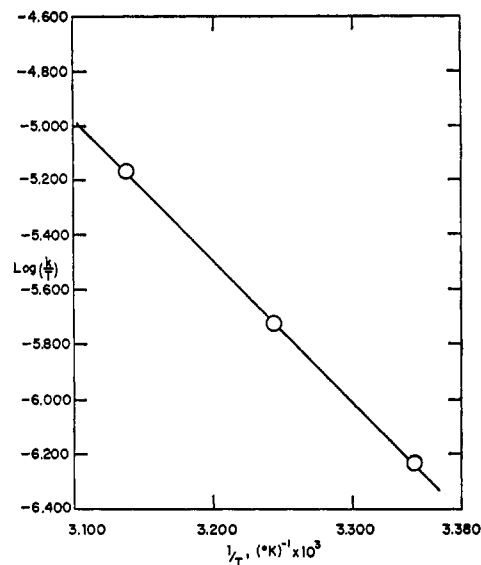


Figure 2. Activation parameters for the thermal decomposition of *t*-butyl triphenylperacetate in cumene: $\Delta H = 24.1 \text{ kcal/mole}$, $\Delta S = +4.9 \text{ cal/deg}$.

which allowed observation of $^{13}\text{CO}_2$ at its 1.2% natural abundance, as well as $^{12}\text{CO}_2$. The ^{12}C rate constant is included in Table I; the carbon isotope effect, k_{13}/k_{12} , calculated as the slope of a plot of $\log ([^{13}\text{CO}_2]_\infty - [^{13}\text{CO}_2]_t)$ against $\log ([^{12}\text{CO}_2]_\infty - [^{12}\text{CO}_2]_t)$, was 0.964.

Observation of Triphenylmethyl Radical. Decomposition of perester I in degassed cumene solution in an esr spectrometer gave rise to an intense signal, identified as that of the triphenylmethyl radical by comparison with published spectra.⁶ In particular, the hyperfine splitting of two lines on opposite sides of the central line was $2.82 \pm 0.05 \text{ gauss}$ (lit.⁶ 2.77 gauss); the interaction is attributed by Chesnut and Sloan to the *para* protons. The concentration of radicals in the present experiment was estimated as between 10^{-4} and 10^{-3} M . This concentration was reached early in the first half-life and varied by much less than an order of magnitude over 4 half-lives.

The visible spectrum of a solution of I in cumene at 14° developed a sharp maximum at 515 $m\mu$, absorbance = 0.5; triphenylmethyl radical is reported⁷ to have λ_{max} 515 $m\mu$ (ϵ 656) in benzene. The radical concentration was thus about $7.5 \times 10^{-4} \text{ M}$. Exposure to air extinguished the absorption, as expected because of the known rapid oxidation of the radical to the colorless peroxide.

Products of Thermal Decomposition in Cumene and Chlorobenzene. Perester samples were decomposed *in vacuo* in degassed solutions and the products were fractionated as previously described;⁸ typical product balances are given in Table III. The nonvolatile products were isolated by elution chromatography on Florisil or silical gel. The carbon dioxide yield, as noted above, was nearly quantitative; the yields of *t*-butyl alcohol and acetone were unusually low in both solvents.

(6) D. B. Chesnut and G. J. Sloan, *J. Chem. Phys.*, **33**, 637 (1960).
(7) K. Ziegler and L. Ewald, *Ann.*, **473**, 163 (1929).
(8) P. D. Bartlett, E. P. Benzing, and R. E. Pincock, *J. Am. Chem. Soc.*, **82**, 1766 (1960).

Table III. Products of Decomposition of I in Cumene, Chlorobenzene, Styrene, and Vinyl Acetate

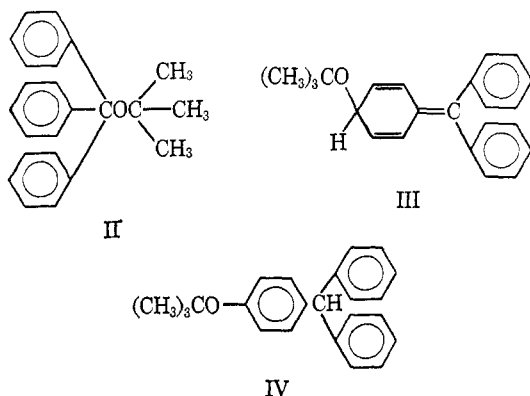
Product	Yield, moles per mole of CO ₂ , in—			
	Cumene	Chlorobenzene	Styrene	Vinyl acetate
CO ₂ ^a	0.95	0.94	0.95	1.01
<i>t</i> -Butyl alcohol	0.42	0.17	0.09	0.23
Acetone	0.000	0.005	0.003	<i>b</i>
α -Methylstyrene	0.13	...	...	...
Triphenylmethane	0.36	0.16	0.06	0.15
<i>p</i> - <i>t</i> -Butoxytriphenylmethane (IV)	0.16	0.16	0.15	0.10
Triphenylcarbinol	0.20	0.15	0.06	0.11
Benzophenone	0.14	0.10	0.13	0.085
<i>t</i> -Butyl 2,3,3,3-tetra-phenylpropyl ether (VI)	...	...	0.50	...

^a Moles per mole of perester taken. ^b Not determined.

With cumene as solvent, the distribution of nonvolatile products was highly unusual, the coupling product dicumyl being entirely absent. Cumyl radicals were instead found as α -methylstyrene, identified by vpc retention time. Bistriphenylmethyl peroxide, expected to be formed from triphenylmethyl radicals on exposure of the residue to air, was absent. Triphenylmethane appeared in high yield: this contrasts strongly with the decomposition of *t*-butyl diphenylperacetate in cumene,⁹ which produces no diphenylmethane.

The *t*-Butyl Ethers from *t*-Butyl Triphenylperacetate. At least two isomeric *t*-butyl ethers were formed during the decomposition of I, corresponding to "normal" and "abnormal" coupling of the radicals *t*-butoxy and triphenylmethyl. Formation of these products affords new illustration of the ambident reactivity of triphenylmethyl radical.

The triphenylcarbinol isolated is difficult to explain as a primary product of decomposition, since it would need to originate from triphenylmethoxy radical and cumene, or from triphenylcarbonium ion and adventitious moisture. Indeed, triphenylcarbinol could not be detected in the infrared spectrum of the mixture prior to chromatography. It is therefore considered to be the product of cleavage during chromatography of the as yet unknown¹⁰ triphenylmethyl *t*-butyl ether (II).



The presence of II is inferred from the nmr spectrum of the crude mixture: this shows a sharp singlet at τ 9.0 which does not appear in the spectrum of any of the chromatographic fractions. That II should be cleaved

under conditions which do not affect benzhydryl *t*-butyl ether is consistent with the facts that triphenylcarbinol and methanol yield triphenylmethyl methyl ether on alumina (grade 1), but benzhydrol and methanol do not react on alumina.¹¹

The unusual ether, *p*-*t*-butoxytriphenylmethane (IV), was originally mistaken for II. However, its structure was revealed by a one-proton nmr signal at τ 4.6, shown also by triphenylmethane, and by the resemblance of its very characteristic infrared spectrum to those of phenol and phenyl *t*-butyl ether (intense $\lambda_{\max}$ 8.1 and 8.5 μ). Degradation by benzoyl chloride and stannic chloride¹² afforded the benzoate of *p*-hydroxytriphenylmethane, mp 117.5–119.5°, identical with an authentic sample. Therefore, IV is *p*-*t*-butoxytriphenylmethane. It must arise by *para* attack of *t*-butoxy radical on triphenylmethyl, a process competing about equally with central atom attack.

The direct product of *para* attack of *t*-butoxy radical on triphenylmethyl would be III, which could lead to IV by transfer of either a proton or a hydrogen atom. No III could be detected in the crude product mixture, although concentrations comparable to that of II or IV should have given a substantial nmr signal in the ethylenic region. Heating with *n*-propylamine at reflux in chlorobenzene failed to affect the relative amounts of IV and triphenylcarbinol in the product. It seems probable that III is a very active H donor to the *t*-butoxy radical, yielding *p*-*t*-butoxytriphenylmethyl, which leads to IV in a final step like that in which the triphenylmethane is produced.

Recently Nelsen and Bartlett¹³ have detected an analog of III, quinoid isodicumyl, as a minor coupling product of cumyl radicals in solution. The prevailing mode of disappearance of this substance was not hydrogen shift at all, but redissociation into cumyl radicals. Compared with it, III would be expected to be less prone to redissociate and more prone to transfer a hydrogen atom.

An attempt to prepare II by the reaction of triphenylchloromethane with potassium *t*-butoxide in *t*-butyl alcohol-benzene solution gave instead the isomer IV in 70% yield. The product was in all respects identical with the decomposition product. Only minor amounts of triphenylcarbinol appeared after chromatography; ring attack therefore predominates heavily. Under those conditions III probably goes to IV through proton removal by the strong base.¹⁴

Geminate Recombination of the Radicals from I. The total yield of IV and triphenylcarbinol was at least 35%, while the low *t*-butyl alcohol yield suggested that the total yield of ethers might approach 60%. Such a large "cage effect" would not be expected of a radical as stable as triphenylmethyl. Indeed the cage effect of *t*-butyl diphenylperacetate in cumene has been shown to be only about 25% at 40°. Attempts to estimate the cage effect of I in cumene solution were therefore carried out, using several scavenger systems. These are summarized in Table IV.

(11) C.-H. Wang, *J. Org. Chem.*, **28**, 2914 (1963).

(12) H. Meerwein and H. Maier-Hüser, *J. Prakt. Chem.*, **134**, 51 (1932); see R. L. Burwell, Jr., *Chem. Rev.*, **54**, 615 (1954).

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

(14) D. J. Cram, F. Willey, H. P. Fischer, and D. A. Scott, *ibid.*, **86**, 5370 (1964).

(15) (a) See ref 9; (b) J. P. Lorand, Thesis, Harvard University, 1964.

(9) See ref. 1c.

(10) H. A. Smith and R. J. Smith, *J. Am. Chem. Soc.*, **70**, 2400 (1948).

Table IV. Cage Effect in Thermal Decomposition of *t*-Butyl Triphenylperacetate in Cumene

Temp, °C	Scavenger	Cage effect	How determined
25.5	<i>t</i> -Dodecanethiol	0.06	Total CO ₂ , <i>t</i> -BuOH
25.5	Pyrogallol + O ₂	0.11	Total CO ₂ , O ₂ , and control using DBPO
14.0	Galvinoxyl + O ₂	0.13	Disappearance rates of perester and scavenger

(1) **Thiols.** Addition of 0.5M *t*-dodecanethiol raised the yield of *t*-butyl alcohol to 94%. That is, those *t*-butoxy radicals which escaped coupling with triphenylmethyl in the solvent cage were converted to alcohol by reaction with thiol.

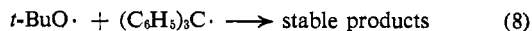
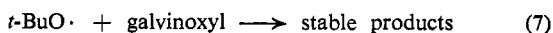
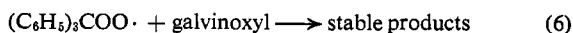
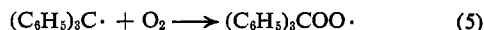
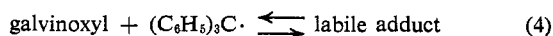


(2) **Galvinoxyl.** Kinetic experiments using this colored stable radical in degassed solutions were carried out, as described previously.^{16,17} Typically, an initiator in large excess over galvinoxyl produces radicals at a constant rate and causes the scavenger to fade at a constant rate, from which the efficiency of radical production (*f*), and hence the cage effect (1 - *f*), is calculable by eq 3.

$$\text{rate} = \text{constant} = 2fk_1[P]_{av} \quad (3)$$

where $[P]_{av}$ is the average perester concentration; k_1 is the first-order constant for perester decomposition. Excess I faded galvinoxyl, but zero-order kinetics was not observed, in contrast to the behavior of *t*-butyl diphenylperacetate,⁹ *t*-butyl α,α -diphenylperpropionate,^{15b} AIBN,¹⁷ DBPO di-*t*-butyl diperoxyoxalate,¹⁷ and di-*t*-butyl monoperoxyoxalate.¹⁸ The rate of fading of I was clearly dependent on the galvinoxyl concentration, plots of absorbance against time being strongly concave upward. With galvinoxyl in the presence of oxygen, however, good zero-order kinetics was observed, and the derived rate constants were 87% of k_1 extrapolated from the values of Table I. The cage effect is thus estimated to be 13%.

Galvinoxyl does not react with oxygen under the conditions used. In these experiments, the very sterically hindered triphenylmethyl radical reacts rapidly with oxygen, forming a less hindered peroxy radical which can be rapidly and irreversibly trapped by galvinoxyl. In the absence of oxygen, the reaction of galvinoxyl and triphenylmethyl may well be reversible,



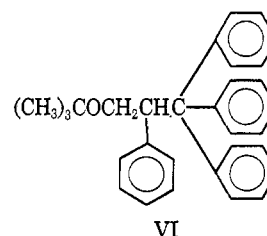
and triphenylmethyl may effectively reduce the efficiency of galvinoxyl by competing with it as a scavenger of *t*-butoxy radicals (eq 8).

(3) **Oxygen and Pyrogallol.** The perester was allowed to decompose in the presence of this scavenger-inhibitor system, which had been employed by Ziegler, *et al.*,¹⁹ to measure the rate of dissociation of highly substituted ethanes. It was anticipated that 1 mole of oxygen per mole of kinetically free triphenylmethyl radicals would be absorbed.²⁰ As measured, 1.01 moles of O₂ per mole of perester was absorbed, while 0.12 mole of O₂ per mole of DBPO (see above) was absorbed in a control experiment. If the latter amount represents O₂ absorption by the inhibitor and the solvent, then I absorbed 0.89 mole of oxygen per mole. The cage effect at 25° is thus 11%.

The three scavenger systems yield an average value of about 10% for the "cage effect" of I at 20 ± 6°. The agreement is rough, but the value is clearly different from zero.

Decomposition of I in Styrene. A "One-Unit Telomer." The behavior of I in polymerizable olefins as solvents was of interest because of the efficacy of triphenylmethyl as a polymerization inhibitor.²¹ In degassed, purified styrene at 25° no polymerization took place, and most of the styrene could be distilled out *in vacuo*. The products are shown in Table III; they include smaller amounts of all the products (except α -methylstyrene) isolated from decompositions in cumene or chlorobenzene, as well as carbon dioxide in quantitative yield.

In addition to the above, there was isolated in 50% yield an oily ether (VI) which is considered to be *t*-butyl 2,3,3,3-tetraphenylpropyl ether. Its nmr spectrum showed a sharp singlet at τ 9.1 (*t*-butyl protons), two



doublets and a triplet, each with $J = 8.5$ to 9.0 cps, at 5.50, 6.05, and 6.75 (aliphatic protons of the styrene residue), and intense absorption at 3 (aromatic protons). The methylene protons have different chemical shifts because they are adjacent to an asymmetric center.²²

Treatment of the oil with benzoyl chloride and stannic chloride in benzene afforded a benzoate (VII) in 70% yield, mp 164.0–166.5°, yielding an elementary analysis consistent with its formation. Its nmr spectrum lacked the *t*-butoxy signals, retained the triplet due to the methine proton, and showed a complex multiplet in place of the pair of doublets for the methylene protons.

Attempts to synthesize the ether, or at least the benzoate, *via* the unreported 2,3,3,3-tetraphenylpropionic acid were unsuccessful. Although triphenyl-

(19) K. Ziegler, L. Ewald, and A. Seib, *Ann.*, **504**, 182 (1933).

(20) N. N. Lichtin and G. R. Thomas, *J. Am. Chem. Soc.*, **76**, 3020 (1954).

(21) F. R. Mayo and R. A. Gregg, *ibid.*, **70**, 1284 (1948).

(16) See ref 1d.
(17) P. D. Bartlett and T. Funahashi, *J. Am. Chem. Soc.*, **84**, 2596 (1962).

(18) P. D. Bartlett, B. A. Gontarev, and H. Sakurai, *ibid.*, **84**, 3101 (1962).

(22) (a) J. A. Pople, W. G. Schneider, and H. J. Bernstein, "High-Resolution Nuclear Magnetic Resonance," McGraw-Hill Book Co., Inc., New York, N. Y., 1959, pp 377–381; (b) P. M. Nair and J. D. Roberts, *J. Am. Chem. Soc.*, **79**, 4565 (1957); (c) G. M. Whitesides, D. Holtz, and J. D. Roberts, *ibid.*, **86**, 2628 (1964).

carbinol and malonic acid react at 160° to afford 3,3,3-triphenylpropionic acid in good yield,²³ triphenylcarbinol and phenylmalonic acid gave only phenylacetic acid and recovered carbinol.

Reaction took place between triphenylchloromethane and the sodium salt of diethyl phenylmalonate (from the ester and sodamide) in ether. The acid IX, mp 201°, was isolated in high yield after saponification and decarboxylation. Its acid chloride (X) showed two nonaromatic one-proton nmr signals (τ 4.60 and 4.75), the former similarly located to that of triphenylmethane. Since the desired product should show but a single such signal, the observed product must be its isomer, mono-*p*-(diphenylmethyl)diphenylacetic acid. Lithium aluminum hydride converted X to an alcohol (XI), the benzoate (XII) of which had mp 108.0–110.5°, and was by analysis an isomer of VII. The nmr spectrum of XII showed four nonaromatic protons, rather than three; one of these occurred at τ 4.6. The structures of VI, VII, and XII and their reaction products are then as shown in Chart I.

t-Butyl triphenylperacetate thus forms a "one-unit telomer," or addition compound, in styrene. By contrast, the decomposition of *t*-butyl diphenylperacetate in styrene at 60° caused considerable polymerization; most of the product was precipitated by methanol from hot benzene, and the soluble material appeared from its infrared and nmr spectra to be telomeric. A crystalline benzoate could not be obtained from it by reaction with benzoyl chloride and stannic chloride.

The decomposition of I in freshly distilled vinyl acetate likewise proceeded without polymerization; the carbon dioxide yield was again quantitative, and very little monomer was chemically bound in the product.

Relative Reactivities of Cumene and Styrene toward *t*-Butoxy Radical. The reactivity ratio $k_{\text{cumene}}/k_{\text{styrene}}$, or k_c/k_s , was determined in order to elucidate the manner of formation of the addition compound (VI) (cf. Discussion). An efficient source of *t*-butoxy radicals, di-*t*-butyl diperoxyoxalate (DBPO), was allowed to decompose in a mixture of cumene and styrene, as well as in each pure solvent. Benzoquinone was added in all experiments to inhibit polymerization. The yield of *t*-butyl alcohol was the indicator of the extent of reaction with cumene; these values are given, together with the yields of carbon dioxide, in Table V.

Table V. Decomposition of DBPO in Cumene and Styrene

Solvent	Yield	
	CO ₂ ^a	<i>t</i> -Butyl alcohol ^b
Cumene	0.975	1.05
Cumene + styrene (equal vol.)	0.985	0.56
Cumene + styrene (equal vol.)	1.000	0.60
Cumene + benzene (equal vol.)	1.013	0.99
Styrene	1.013	0.37

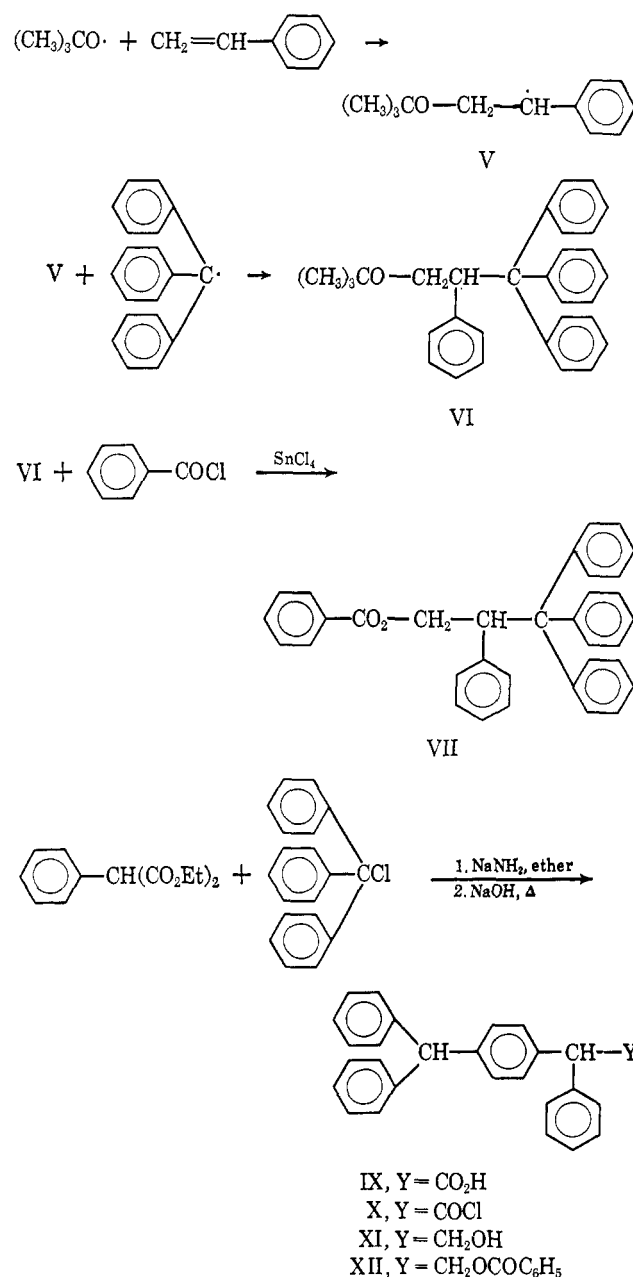
^a Moles per half mole of DBPO (di-*t*-butyl peroxyoxalate).

^b Moles per mole of CO₂.

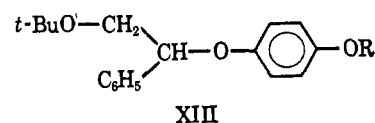
Since the competition experiment results in a yield of alcohol (58%) intermediate between zero and 100%,

(23) (a) L. Hellerman, *J. Am. Chem. Soc.*, **49**, 1737 (1927); (b) D. B. Denney, R. L. Ellsworth, and D. Z. Denney, *ibid.*, **86**, 1116 (1964).

Chart I. The 1:1 Telomer from I and Styrene



the relative reactivities of the substrates are similar. The calculation of the relative reactivity, described in the Experimental Section, must take into consideration the appreciable yield of alcohol in pure styrene. This must be due to the accumulation of a reactive hydrogen atom donor, probably of the type XIII. The tertiary benzylic ether hydrogen atom is expected to be more



labile than the tertiary hydrogen atom of cumene. The resulting value of k_c/k_s is 0.96. Walling and Thaler,²⁴ using *t*-butyl hypochlorite in a fluorocarbon solvent, found the value 0.66.

(24) C. Walling and W. Thaler, *ibid.*, **83**, 3877 (1961).

Discussion

The rate of decomposition of *t*-butyl triphenylperacetate presents a straightforward extrapolation of the behavior of less highly substituted peracetates. All of its chemistry after the rate-determining step is, however, atypical because of the intermediacy of the stable triphenylmethyl radical.

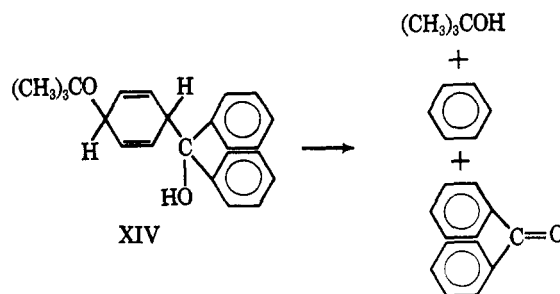
Kinetics of Decomposition. The relative decomposition rates of several *t*-butyl peresters were presented in Table II. Rate constants for I were independent of perester concentration. The kinetic order of any induced decomposition depends upon the nature of the terminating step which here consists chiefly of reaction between dissimilar radicals, making $(t\text{-BuO}\cdot)$ proportional to $(\text{I})/((\text{C}_6\text{H}_5)_3\cdot)$. Since we know that the triphenylmethyl radical concentration rises during reaction, the most probable induced decomposition (*para* attack of *t*-butoxy radical on I) must be of order greater than 2. Induced decomposition is therefore very probably absent. For the triphenylperacetate (I) and for the α,α -diphenylperpropionate^{3b} this mechanism is supported by the carbon isotope effects of 0.964 and 0.945, respectively, consistent with a bond to the carboxyl carbon atom being broken in the rate-determining step.²⁵

Although ΔH^* for the peresters of Table II shows a decline from monophenyl- to triphenylperacetate, the value of ΔS^* has a minimum at the diphenylperacetate, rising again markedly for the triphenylperacetate. In line with the general observations previously made about activation parameters in concerted perester decomposition, this suggests that the new perester has appreciable steric restrictions on its phenyl groups. This crowding is partially relieved at the transition state for decomposition, with a resulting positive contribution to ΔS^* . At the same time, as a result of the obstacle to coplanarity in the radical, the lowering of ΔH^* *per phenyl group* declines steadily as the number of these increases.

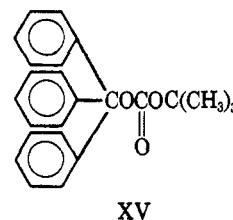
Products. Products isolated account for the triphenylmethyl radical to the extent of 86% in cumene, 57% in chlorobenzene, and 90% in styrene. Despite the limited number of recognized possible products of the tertiary butoxy radical, it is directly accounted for only to 58, 33.5, and 74.3%, respectively, in the three solvents. If we assume that the triphenylcarbinol arose from "normal" ether undergoing late cleavage, the *t*-butyl part being lost at that time, the *t*-butoxy balances are raised 78, 48.5, and 80.3%.

There remains benzophenone to be accounted for; we may speculate on a possible way of forming benzophenone with an additional lost *t*-butoxy group. The quinoid coupling product III which escapes hydrogen capture may readily undergo hydration to the dihydroaromatic ether alcohol XIV, which may suffer rapid concerted decomposition to benzene, benzophenone, and *t*-butyl alcohol. This assumption would account in the three solvents for 92, 58.5, and 93.3% of the tertiary butoxy radical. We have not attempted to recover the extra *t*-butyl alcohol which may be formed during column chromatography.

(25) An example of a reaction *not* involving labeled carbon in the rate-determining step is the acid-catalyzed decarbonylation of triphenylacetic acid-2-¹⁴C (G. A. Ropp, *J. Am. Chem. Soc.*, **82**, 842 (1960)) which shows no isotope effect.



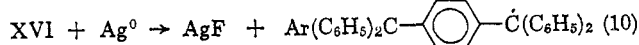
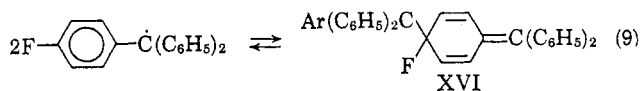
The possibility that the observed "cage effect" is actually a carboxyl inversion²⁶ such as has been observed in the decomposition of diacyl peroxides seems unlikely in view of the high yields of carbon dioxide. The product of carboxyl inversion would be triphenylmethyl *t*-butyl carbonate, XV, and might be readily hydrolyzed but probably would not lose carbon



dioxide spontaneously at the temperatures of these reactions. But the carbon dioxide appears (95, 94, and 95%) before hydrolysis of any reaction product is possible.

Ambident Reactivity of the Triphenylmethyl Species. Several examples of the ambident reactivity of triphenylmethyl radical and triphenylcarbonium ion appeared in course of the study of I. Coupling of triphenylmethyl with *t*-butoxy radical led to a pair of isomeric ethers, while its coupling with 2-*t*-butoxy-1-phenylethyl radical (from I and styrene) led exclusively to the product containing the triphenylmethyl group. Reaction of triphenylchloromethane with either *t*-butoxide ion or diethyl phenylmalonate ion afforded solely the "abnormal" product of ring attack.

Reported examples of *para* attack on triphenylmethyl or related radicals include the copolymerization of 1,1-diphenylethylene with methyl methacrylate,²⁷ the Chichibabin rearrangement of hexaphenylethane to *p*-(diphenylmethyl)tetraphenylmethane,²⁸ the removal of fluorine from *p*-fluorotriphenylmethyl radical²⁹ and of bromine from *p*-bromotriphenylmethyl radical³⁰ by elemental silver.



Cases of *para* coupling involving ions include the reactions of triphenylchloromethane with mono- and

(26) (a) J. E. Leffler, *ibid.*, **72**, 67 (1950); (b) P. D. Bartlett and F. D. Greene, *ibid.*, **76**, 1088 (1954); (c) F. D. Greene, H. P. Stein, C. C. Chu, and F. M. Vane, *ibid.*, **86**, 2080 (1964).

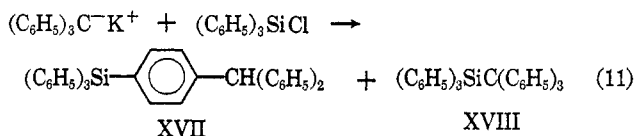
(27) J. L. Kice and F. Taymoorian, *ibid.*, **81**, 3405 (1959).

(28) F. Ullmann and W. Borsum, *Ber.*, **35**, 2877 (1902).

(29) S. T. Bowden and T. F. Watkins, *J. Chem. Soc.*, 1249 (1940).

(30) M. Gomberg and F. F. Blicke, *J. Am. Chem. Soc.*, **45**, 1765 (1923).

dimethylketene dimethyl acetals³¹ and with phenylmagnesium bromide,³² of diphenyldichloromethane with 2 moles of diethyl malonate in the presence of base,³³ and the isomerization of tris(*p*-bromophenyl)chloromethane in liquid sulfur dioxide to *p*-chlorophenylbis(*p*-bromophenyl)bromomethane.³⁴ Potassium triphenylmethide reacts with triphenylchlorosilane to give the *para*-coupling product XVII, 8–15%, and the "normal" product XVIII, 60% yield.³⁵



The position of attack in these reactions is probably controlled by steric factors, so that the bulkier species give *para* coupling. It is instructive to compare *t*-butoxy radical with potassium *t*-butoxide. While the radical is considerably hindered by the three methyl groups, and gives roughly equal amounts of the two possible products, the anion is further encumbered by hydrogen-bonded alcohol molecules and by the counterion. The anion gives only *para* coupling. *t*-Butylthiyl radical and *t*-butyl sulfide ion, on the other hand, both give predominantly normal coupling.³⁶ As suggested by Kampmeier, the greater size and polarizability of sulfur, as well as its lower basicity, is probably responsible. Crowding in the anion of diethyl phenylmalonate is probably quite severe, so that only *para* coupling is observed.

The exclusive observed central attack of 2-*t*-butoxy-1-phenylethyl radical is ambiguous because thermodynamic rather than kinetic control may be operating. *para* coupling may be so readily reversible that only the stable "normal" product is observed. A recent example of redissociation of a *para*-coupling product into free radicals has been observed in the case of the quinoid isodicumyl.¹³

Experimental Section

Detailed descriptions of the procedures used in this work are contained in the thesis of J. P. Lorand, Harvard University, May 1964, available through University Microfilms, Ann Arbor, Mich.

***t*-Butyl Triphenylperacetate.** Triphenylacetyl chloride, mp 118–123°, (8.0 g 26.1 mmoles), and ground freshly prepared anhydrous sodium *t*-butylperoxide (7.05 g, 47.0 mmoles) were stirred together in 200 ml of methylene chloride cooled by an ice bath, for 3 hr. The solution was filtered in 15 min on Supercel, the filtrate being cooled in ice. Following removal of solvent on the rotary evaporator, the oily residue was taken up in 80 ml of petroleum ether (bp 30–60°) and cooled to –20°. The first crop of crystals (5.25 g, 14.6 mmoles, 56%) had mp 61–64°, unchanged after 8 months at –20°.

Anal. Calcd for $\text{C}_{24}\text{H}_{24}\text{O}_3$: C, 79.97; H, 6.71. Found: C, 78.56; H, 6.63.

Despite the low carbon analysis, the CO_2 yields were 95–98% on decomposition. Many peresters and many compounds with quaternary carbon present special analytical difficulties.

The general methods of product analysis have been described.^{1a}

(31) R. J. Heck, P. S. Magee, and S. Winstein, *Tetrahedron Letters*, No. 30, 2033 (1964).

(32) (a) H. Gilman and H. L. Jones, *J. Am. Chem. Soc.*, **51**, 2840 (1929); (b) C. S. Schoepfle and S. G. Trepp, *ibid.*, **58**, 791 (1936).

(33) T. C. Bruice and W. C. Bradbury, *J. Org. Chem.*, **28**, 3403 (1963).

(34) M. Gomberg and L. H. Cone, *Ann.*, **376**, 183 (1910).

(35) A. G. Brook, H. Gilman, and L. S. Miller, *J. Am. Chem. Soc.*, **75**, 4759 (1953).

(36) J. A. Kampmeier and R. P. Geer, private communication.

***p*-*t*-Butoxytriphenylmethane.** Potassium metal (0.6 g, ca. 15 g-atoms) was cut under kerosene and allowed to dissolve (in 90 min) in 13 ml of *t*-butyl alcohol and 25 ml of benzene in a 100-ml, round-bottomed flask fitted with a drying tube. Triphenylchloromethane (4.2 g, 15 mmoles) was dissolved in the basic solution. After 5 months of standing at 25°, the solution was filtered from 1.30 g of solid. The solvent was stripped, the residual oil taken up in hexane and filtered, and the hexane was stripped, leaving 3.70 g of oil (11.7 mmoles, 78% yield (assuming $\text{C}_{23}\text{H}_{24}\text{O}$)) which crystallized on standing, mp 55–65°. The infrared spectrum was superposable upon that of the ether isolated from decomposition of the perester I. The product could be recrystallized only from *n*-hexane at –78°, but a yellow impurity separated as well. Chromatography on Florisil (with hexane as eluent) gave 2.1 g of crystals (6.6 mmoles, 44% of theory) and two further chromatograms gave white needles, mp 81–83.5°.

Anal. Calcd. for $\text{C}_{23}\text{H}_{24}\text{O}$: C, 87.29; H, 7.64. Found: C, 87.29; H, 7.61.

The nmr spectrum showed τ 2.9 (10 H), 3.1 (4 H), 4.6 (1 H), and 8.7 (9 H).

When a similar reaction mixture was worked up after 1 week, the yield of *p*-butoxytriphenylmethane after chromatography was less than 10%.

Benzoate of *p*-Hydroxytriphenylmethane from the *t*-Butyl Ether. The ether (0.677 g, 2.14 mmoles) from the second chromatogram was dissolved in 10 ml of benzene, and benzoyl chloride (ca. 1 ml, ca. 6 mmoles) and stannic chloride (6 drops) were added, the latter producing a yellow color on contact. After standing overnight, the solution was stripped of benzene, dissolved in 10 ml of boiling 95% ethanol, and cooled, when white needles formed. Collected by suction filtration and washed with fresh ethanol, the needles had 117.5–119.5° corr (lit.³⁷ mp 125°). The over-all yield was 0.71 g, 2.0 mmoles, 91%.

Anal. Calcd for $\text{C}_{26}\text{H}_{20}\text{O}_2$ (material recrystallized from EtOH): C, 85.49; H, 5.53; Found: C, 85.12; H, 5.44.

***p*-*t*-Butoxytriphenylmethane from Decomposition of I.** A solution of I (0.962 g, 2.67 mmoles) in 25.0 ml of cumene in a break-seal flask was degassed and the flask was sealed off and allowed to stand for 43 hr at 25°. The contents were worked up by the usual vacuum-line technique,^{1a} and the nonvolatile residue (0.85 g) was chromatographed on Florisil. Elution with hexane produced triphenylmethane, mp 94–97° uncorr (lit.³⁸ mp 92°), 0.249 g, 1.02 mmoles, 0.421 mole per mole of CO_2 (the yield of CO_2 was 90.5% of theory). Elution with 10% benzene in hexane produced an oil which solidified, mp 75–80.5°, with infrared and nmr spectra superposable upon those of synthetic *p*-*t*-butoxytriphenylmethane, 0.124 g, 0.39 mmole, 16% yield based upon the CO_2 yield.

Attempts to convert samples of *p*-*t*-butoxytriphenylmethane, obtained as above, to the benzoate of *p*-hydroxytriphenylmethane by reaction with benzoyl chloride and stannic chloride in benzene always led to separation of a dark red oil and failure to isolate crystalline product. The infrared spectra of ether samples usually showed the presence of ca. 10% of benzophenone, eluted from Florisil after the ether.

***p*-Hydroxytriphenylmethane from Phenol and Benzhydrol.** Phenol (47 g, 0.50 mole) and 96% sulfuric acid (3.1 g, 0.030 mole) were mixed in a 250-ml, round-bottomed flask and benzhydrol (55.2 g, 0.30 mole) was added through a powder funnel. The mixture turned yellow and then red during the addition and the temperature rose well above 60°, necessitating cooling. The mixture again became hot at the close of the addition and was thereafter heated for 1 hr on the steam bath. The mixture was neutralized with 200 ml of 10% sodium bicarbonate solution and 400 ml of water. The gummy residue was taken up in ether, and the ether layer was washed with water, dried over magnesium sulfate, filtered, and stripped of solvent. The residue was taken up in 150 ml of hot benzene, and 150 ml of hexane was added. The crystals which formed on cooling (53.4 g) were recrystallized five times from benzene, affording white crystals free of the odor of phenol and with an infrared spectrum free of a band at 9.7 to 9.9 μ due to benzhydrol (35 g, 0.135 mole, 65% of theory), mp 112–117° uncorr (lit.³⁷ mp 81–82°), with 1 mole of benzene of crystallization, or 111° without solvent. The product repeatedly turned yellow or green in solution, especially if exposed to air, and its melting point behavior was not

(37) R. C. Huston, W. C. Lewis, and W. H. Grotemut, *J. Am. Chem. Soc.*, **49**, 1367 (1927).

(38) R. L. Shriner, R. C. Fuson, and D. Y. Curtin, "The Systematic Identification of Organic Compounds," 4th ed, John Wiley and Sons, Inc., New York, N. Y., 1956.

reproducible. The nmr spectrum (in CS_2) showed τ 2.9 (10 H), 3.3, quartet ($J = 9$ cps) (4 H), 4.6 (1 H), and 5.0 (1 H).

Benzoate of *p*-Hydroxytriphenylmethane. Benzoic acid (1.42 g, 12 mmoles) and *p*-hydroxytriphenylmethane (1.3 g, 5 mmoles) were ground together in a 50-ml erlenmeyer flask and 3.0 ml of trifluoroacetic anhydride was added. Trituration gradually brought about solution; the mixture was heated to about 50° for a few minutes, cooled, and poured into 50 ml of 10% sodium bicarbonate solution. The yellow color vanished and a white precipitate appeared; this was collected and recrystallized from 95% ethanol. The product (1.30 g, 3.6 mmoles, 72% yield) had mp $121\text{--}124.5^\circ$ and mmp (with benzoate from *p*-*t*-butoxytriphenylmethane) $121\text{--}124.5^\circ$ (resolidification and melting at 127.5° ; all values uncorrected).

***t*-Butyl 2,3,3,3-Tetraphenylpropyl Ether.** A solution of I (2.004 g, 5.57 mmoles) in 25 ml of purified styrene was degassed and allowed to stand for 24 hr at 25° . The yield of CO_2 was 5.30 mmoles, 95.2% of theory; the yields of *t*-butyl alcohol and acetone were 9.5 and 0.3%, respectively.

The nonvolatile residue was separated fairly cleanly on 80 g of Florisil, material weighing 2.352 g being recovered. Triphenylmethane occurred in early fractions, ca. 100 mg, 0.41 mmole, 8%. *p*-*t*-Butoxytriphenylmethane occurred in several fractions, total 210 mg, 0.67 mmole, 12.5%. There next occurred, in ten consecutive fractions, *t*-butyl 2,3,3,3-tetraphenylpropyl ether (1.125 g, 2.70 mmoles, 50.5%), a viscous, colorless oil which did not solidify even after many months of standing. Nmr spectra disclosed the presence of other compounds in some of these fractions; their signals appeared from τ 7.0 to 9.0; none of these or later fractions showed any benzylic triphenylmethane proton absorption at τ 4.6. The infrared spectrum (CCl_4) showed 3.2, 3.3, 6.25 (w), 6.7, 6.9, 7.2, 7.3, 8.1 (w), 8.35 (s), 9.25 (s), 9.6, 11.2 (w), 14.1–14.2 (vs), and 14.0 (sh) μ . The nmr spectrum (in CCl_4) showed 2.6–3.4, complex multiplet (20 H); 5.50, doublet ($J = 8.5$ cps) (1 H); 6.05, doublet ($J = 8.5$ cps) (1 H); 6.75, triplet ($J = 9.0$ cps) (1 H); 9.12, sharp singlet (9 H). The doublets had width at half-height of 4 cps; the triplet, 2 cps.

2,3,3,3-Tetraphenylpropyl Benzoate. *t*-Butyl 2,3,3,3-tetraphenylpropyl ether, fraction 9 of the above chromatogram (0.172 g, ca. 0.36 mmole), was dissolved in 12 ml of benzene with 0.2 ml (1.2 mmoles) of benzoyl chloride. Addition of 5 μ l of stannic chloride *via* a syringe immediately produced a permanent orange color. A drying tube was attached, and after 1 hr 3 drops of stannic chloride was added. After 1 day of standing the solution was washed with two 20-ml portions of 7.5% sodium bicarbonate solution and the benzene was removed *in vacuo*. The residual oil, taken up in 10 ml of 95% ethanol, crystallized at -20° . The product, isolated by suction filtration, weighed 0.117 g, 0.25 mole, 70% yield, mp $142\text{--}146.5^\circ$. Recrystallization from 95% ethanol gave 0.097 g of crystals, mp $164\text{--}166^\circ$.

Anal. Calcd for $\text{C}_{34}\text{H}_{28}\text{O}_2$: C, 87.15; H, 6.02; Found: C, 87.15; H, 6.33.

The infrared spectrum (in CCl_4) showed 3.25, 5.80 (vs), 7.85 (vs), 9.0 (s), and 14.0–14.2 (vs) μ as the most conspicuous peaks. The nmr spectrum (in CS_2) showed τ 2.3–3.5, complex multiplet (25 H); 4.8–5.1, multiplet (2 H); 5.9, triplet ($J = 11$ cps) (1 H). The integrated intensity ratio of the first group to the other two groups was 8.8 (calcd, 8.33).

Mono-*p*-diphenylmethylphenylacetic Acid. Sodamide (5.1 g, 0.13 mole) was placed in a 1-l., three-necked, round-bottomed flask fitted with trubore stirrer and reflux condenser; it was covered with ether and the flask was purged with dry nitrogen. Diethyl phenylmalonate (Eastman Yellow Label, 26.8 g, 0.113 mole) in 100 ml of ether was added to form the colorless enolate, when the sodamide was seen to go into solution. Following removal of most of the ammonia, triphenylchloromethane (30.6 g, 0.11 mole, in 200 ml of ether) was added, without noticeable heat evolution. Following hydrolysis with 200 ml of water and separation of layers, the ether was removed on the steam bath. The residue, which showed no infrared hydroxyl absorption, was saponified with 50 g of sodium hydroxide in 100 ml of water, 200 ml of 95% ethanol, and 100 ml of benzene, at reflux for 12 hr. This solution was filtered from 11 g of precipitated sodium bicarbonate (0.13 mole) and stripped of solvents on the rotary evaporator. The solid was recrystallized from benzene, yield 39.0 g after air drying. Solution in 500 ml of hot water on the steam bath and addition of 30 ml of concentrated hydrochloric acid precipitated a viscous mass which hardened on digestion at 100° for 2 hr. Recrystallization from benzene–ethanol afforded a first crop of 18 g of white crystals, mp $196\text{--}202^\circ$ cor. In all, about 30 g of solid was isolated and another

10 g obtained from the organic liquors was not purified. The estimated yield of 40 g is almost quantitative (theoretical, 41.5 g).

Mono-*p*-diphenylmethylphenylacetyl Chloride. The acid (5.0 g, 13.2 mmoles) was refluxed with thionyl chloride (16.5 g, 139 mmoles) in 40 ml of benzene overnight, with vigorous foaming. Most of the solvent and volatile materials were distilled out on the steam bath, the remainder on the rotary evaporator. The product was a viscous straw-colored oil, $\lambda_{\text{max}}^{\text{CHCl}_3}$ 5.56 μ . The dichloromethane used in obtaining the infrared spectrum was carefully removed *in vacuo*, with heating on the rotary evaporator. The nmr spectrum (in CS_2) showed τ 2.9–3.0, broad (ca. 20 H), 4.60, singlet (1 H), and 4.75, singlet (1 H). Addition of 4 drops of dichloromethane to the carbon disulfide solution (ca. 0.5 ml) resulted in appearance of a signal at τ 5.05; therefore, neither one-proton signal was due to residual dichloromethane, but both signals originated from the acid chloride.

2-*p*-Diphenylmethylphenyl-2-phenylethanol. To the acid chloride (above, 5.4 g, 13.5 mmoles, in 50 ml of absolute ether) was added lithium aluminum hydride (0.50 g, 13 mmoles); the lumps were crushed with a stirring rod, and the mixture was refluxed 3 hr. The hydride was destroyed with 5 ml of ethyl acetate and then 30 ml of 10% hydrochloric acid, the layers being separated and the ether layer being dried over magnesium sulfate and filtered. Removal of the ether left 4.51 g of colorless oil showing strong hydroxyl absorption in the infrared. The nmr spectrum (in CCl_4) showed τ 3.0 and 3.1, unsymmetrical doublet (19 H), 4.6, singlet (1 H), 6.15, broad singlet (3 H), and 7.75, singlet (1 H).

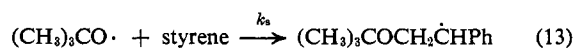
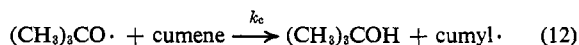
2-*p*-Diphenylmethylphenyl-2-phenylethyl Benzoate. Treatment of the alcohol with benzoic acid and trifluoroacetic anhydride led to recovery of the alcohol. Mixing 3.2 g (9 mmoles) of alcohol with benzoyl chloride (2.0 g, 14 mmoles) and pyridine (1.0 g, 12.5 mmoles) in 50 ml of ether led to precipitation of pyridine hydrochloride in a few minutes. The solution was washed with excess 10% aqueous hydrochloric acid followed by water, dried over magnesium sulfate, filtered, and stripped of solvent. The oil was taken up in hot 95% ethanol, decanted from some yellow-brown gummy oil, and allowed to cool; the oil which separated solidified in several days. Seed crystals were reserved and the remainder taken up in hot ethanol and allowed to stand at 50° in contact with the seed, when white needles formed. Three recrystallizations afforded 1.4 g of product, mp $108\text{--}110.5^\circ$ uncor.

Anal. Calcd for $\text{C}_{34}\text{H}_{28}\text{O}_2$: C, 87.15; H, 6.02. Found: C, 86.90, 86.93; H, 5.75, 5.65.

The infrared spectrum of the product was very similar to that of 2,3,3,3-tetraphenylpropyl benzoate, from the I-styrene telomer. Each of the sharp aromatic bands at 6.7 and 6.9 μ , however, had a shoulder, and a peak appeared at 3.50 μ , due to the aliphatic C–H bond of the diphenylmethyl group. The nmr spectrum (in CCl_4) showed τ 2.2 and ca. 3.0, complex (24 H); 4.6, singlet (1 H); and 5.4, multiplet (3 H).

Relative Rates of Reaction of *t*-Butoxy Radicals with Cumene and Styrene. Di-*t*-butyl diperoxyoxalate (DBPO, 2.0 mmoles) was allowed to decompose for 6 hr or more at 50° , in the presence of 4.0 mmoles of benzoquinone, in degassed solutions in 20 ml each of cumene, styrene, and mixtures of equal volumes of cumene and styrene, and of cumene and benzene. Polymerization was suppressed, as shown by the low viscosity of the resulting solutions and the fact that the styrene could be distilled out almost quantitatively. The CO_2 yield was determined gravimetrically (Ascarite), and the *t*-butyl alcohol yield was determined by vpc. The data are summarized in Table V.

For calculation of the rate constant ratio k_c/k_s for reactions 12 and 13, a correction had to be applied. Since pure styrene affords



a 37% yield of *t*-butyl alcohol from *t*-butoxy radical, an active hydrogen atom donor must be formed in the quinone-inhibited reaction of *t*-butoxy radical with styrene, whose most probable product is a hydroquinone ether of type XIII. Thus our cumene–styrene solutions give rise to a three-way competition for *t*-BuO $\cdot$ by styrene acting as a radical captor, and cumene and XIII acting as hydrogen donors. We assume that all *t*-BuO $\cdot$ not found as alcohol has reacted with styrene, which was 0.63 mmole in pure styrene and 0.42 in the cumene–styrene mixture. Thus the total amounts of XIII formed in the two systems were in the ratio of 3 to 2. If the competition between styrene and XIII remained the same on addition of cumene, then in the mixed solvent $\frac{2}{3} \times 0.37 =$

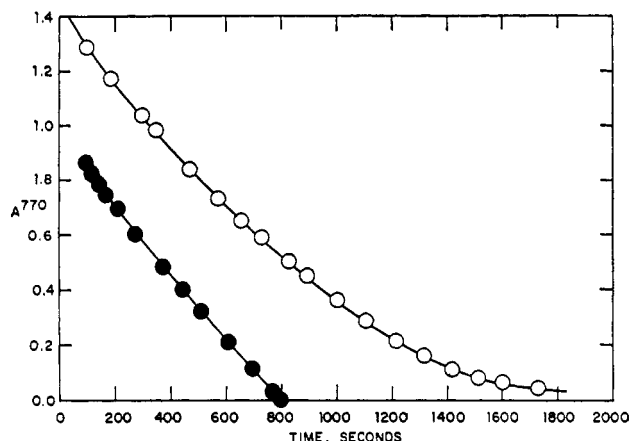


Figure 3. Fading of galvinoxyl by *t*-butyl triphenylperacetate in cumene at 14.0°: O, without O₂, [P]₀ = 0.0730 M; ●, O₂ added, [P]₀ = 0.0370 M.

0.247 mole of *t*-BuOH was from reaction with XIII and the rest, 0.58 - 0.247 = 0.333 mole, came from reaction with cumene. From the known densities of cumene and styrene the equal-volume mixture of the two contained them in the mole ratio

$$\frac{(\text{cumene})}{(\text{styrene})} = \frac{0.86}{0.91} \times \frac{104}{120} = 0.826$$

From these figures we arrive at

$$\frac{k_c}{k_s} = \frac{0.333}{0.42} \times \frac{1}{0.826} = 0.96$$

for the relative rate constants of *hydrogen capture* from cumene and *addition only* to styrene.

I and Galvinoxyl. A typical run, using a degassed cumene solution, is plotted in Figure 3.

I, Galvinoxyl, and Oxygen. A typical run, with the solution under *ca.* 600 mm of oxygen, is plotted in Figure 3, along with the "degassed" run. The rate constant fk_1 at 14.0°, from eq 3, is $2.60 \times 10^{-5} \text{ sec}^{-1}$; $k_1 = 3.05 \times 10^{-6} \text{ sec}^{-1}$, extrapolated from infrared measurements at 25–45°; the cage effect, $100(1 - f)$, is 14.5%.

DBPO, Oxygen, and Inhibitors. Control Experiments. The amount of oxygen absorbed by a solution of inhibitor and decomposing perester was measured by a manometric technique, the carbon dioxide being continuously absorbed on Ascarite. Pyrogallol, 2,6-di-*t*-butyl-*p*-cresol, N,N'-diphenyl-*p*-phenylenediamine, and 4-*t*-butylcatechol (3 to 6 mmoles) were used as inhibitors in cumene or acetophenone (15 ml at 50°). Di-*t*-butyl diperoxyoxalate (DBPO, 1.5 mmoles) was the perester, a compound which produces no radical capable of reacting with oxygen. The gas volume approached a constant value after 10 to 15 half-times of DBPO decomposition. With all the inhibitors except pyrogallol, a volume decrease of 4.9 to 13.4 ml (*i.e.*, 0.28 to 0.56 mmole) was observed. With pyrogallol dissolved in acetophenone, the decrease was 6.5 ml, and with pyrogallol suspended in cumene, 0.0 ml.

Oxygen uptake by DBPO and pyrogallol in cumene, measured by the mass spectrometric method of Traylor,⁵ was 0.12 mole per mole of DBPO.

I, Oxygen, and Pyrogallol in Cumene. I was allowed to decompose at 25° and the gas phase was periodically analyzed mass spectrometrically. Plots of $\log ([O_2]_t - [O_2]_\infty)$ and $\log ([CO_2]_\infty - [CO_2]_t)$ vs. time were made. The yield of CO₂ was 95%. Gross oxygen absorption was 1.01 moles per mole of CO₂, or 0.89 mole (corrected for DBPO control), corresponding to a cage effect of 11%. No cage product was isolated from a run with inhibitor present.

I and *t*-Dodecanethiol. From 2.89 mmoles of I in 10 ml of cumene with 8.2 mmoles of thiol at 25°, the yield of CO₂ was 2.76 mmoles,

95.5% of theory; of *t*-butyl alcohol, 2.59 mmoles, 94% of the CO₂ yield. If the remainder represents the cage effect, this is 6%.

Sodium *t*-Butyl Peroxide. A 5-l., wide-necked, round-bottomed flask was equipped with a rubber stopper bearing a tribore stirrer and gas outlet to a bubbler. In the flask were placed sodium hydride (from Metal Hydrides, Inc., 56% suspension in mineral oil, 22.3 g, 0.52 mole) and 1 l. of absolute ether. *t*-Butyl hydroperoxide (85.5% pure by iodometric analysis,^{3a} 60 g, 0.57 mole) in 1 l. of ether was added, the flask was stoppered, and the contents were stirred for 20 hr at room temperature. Effervescence occurred on mixing, but heat was not evolved. The thick, white suspension was filtered by suction and the product was sucked dry under a rubber dam, yield 53.0 g, neut equiv 131 (theoretical, 112). The product was a hard, brittle white cake, stable at 0° for long periods if cut into 0.5-in. cubes; it lost basicity more rapidly if powdered. The powder is extremely irritating to the mucous membranes, and the material should be handled under the hood. The material is soluble only in hydroxylic solvents; it forms a gelatinous suspension in methylene chloride and in this state is very reactive toward acid chlorides.

Fresh sodium *t*-butyl peroxide was ground many times in a mortar without incident. However, one aged batch suspected of containing rust and bits of aluminum foil from the container ignited during grinding, burning slowly with a yellow flame.

***p*-Hydroxytriphenylmethane.** Bromobenzene (55 g, 0.35 mole) was converted under nitrogen to the Grignard reagent using 8.4 g (0.35 g-atom) of magnesium and 300 ml of ether. To this solution was added over 1 hr with vigorous stirring 18 g (0.10 mole) of *n*-propyl *p*-hydroxybenzoate (Eastman White Label grade; mp 93.5–95.5° cor; lit.³⁹ mp 96.2°) in 150 ml of ether. Precipitation set in after the first 20 ml had been added, and the solution eventually contained a large amount of hard, gummy precipitate. Following hydrolysis with 50 ml of concentrated hydrochloric acid in 150 ml of water, separation of phases, and removal of solvent from the organic phase, there remained 26 g of solid with a medium intensity carbonyl absorption at 5.85 μ , as in the original ester.

Reduction of any *p*-hydroxytriphenylcarbinol present was effected by refluxing the entire product for 3 hr on the steam bath in 100 ml of benzene and 70 ml of 97% formic acid. The mixture was cooled and partitioned between benzene and 200 ml of cold water, and the organic phase was washed repeatedly with water, then with 7.5% aqueous sodium bicarbonate. The solvent was removed on the steam bath and on the rotary evaporator. Crystals which formed on cooling in ice were separated from the tar by adding 10 ml of benzene and filtering, yielding 8 g of yellow solid.

Any ester remaining was saponified at reflux with ethanolic sodium hydroxide, most of the ethanol being boiled off, the solution being neutralized, and the gummy precipitate being taken up in ether. The ether phase was separated, washed with aqueous sodium bicarbonate, dried over magnesium sulfate, filtered, and stripped, leaving 5.3 g of solid, mp 112–117°, showing no carbonyl absorption in the infrared. Its infrared and nmr spectra were identical with those of material prepared from phenol and benzhydrol.

Benzoate of *p*-Hydroxytriphenylmethane. The above product (1.5 g) was converted to its benzoate as previously described, using 1.8 g of benzoic acid and 3 ml of trifluoroacetic anhydride. Two recrystallizations from 95% ethanol gave 1.2 g of ester, mp 122.0–124.0°, with resolidification and melting at 128.5°. The melting point behavior of its mixture with benzoate from *p*-*t*-butoxytriphenylmethane was identical.

Anal. Calcd for C₂₆H₂₀O₂: C, 85.69; H, 5.53. Found: C, 85.15; H, 5.66.

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