Photochemistry of Perester Initiators

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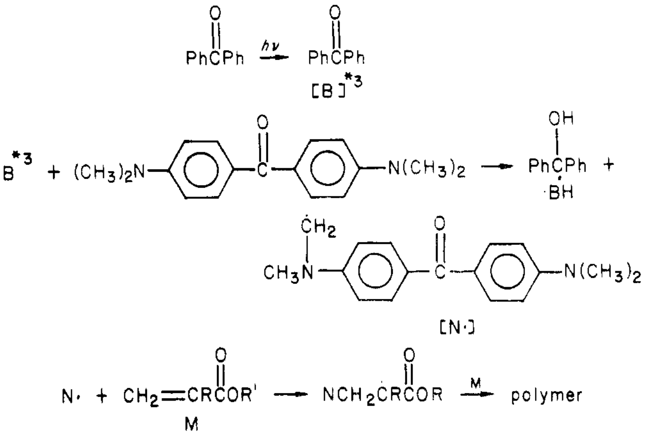
The synthesis and decomposition parameters of several peresters containing the benzophenone chromophore are reported. The thermal decomposition of these peresters is normal, but their photodecomposition is highly efficient, and the quantum yields of perester decomposition at 366 nm approach unity. The peresters are excellent initiators for vinyl polymerization.

Photoinitiators are free-radical sources which decompose photochemically and have various uses in the printing ink, paints, and coatings industry. Among typical commercial initiators are three general types: mixtures of aryl ketones, benzoin ethers, or substituted acetophenones.[1] In past years, highly halogenated aryl hydrocarbons were also used for initiators, but their use is now precluded because they are so highly toxic.

Among the more important commercially used photoinitiators for acrylate polymerization is the so-called "Hammond initiator", benzophenone–Michler's ketone (8:1),[2,3] which likely initiates radical chains as in Scheme I.

Scheme I



[BH·] probably ends up in the polymer as a coupling product.

A major advantage of the Hammond initiator is the rate by which it initiates radical chain reactions; two important disadvantages are the rather large amount of initiator needed to make the rate of polymerization sufficiently rapid for printing applications and the potential toxicity of one of the initiator partners—Michler's ketone (4,4′-bis(*N*,*N*-dimethylamino)benzophenone).

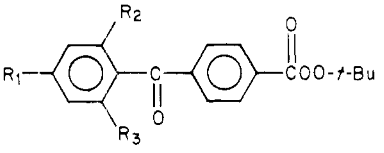
In a continuation of our interest in photochemical reactions of polymer systems,[4] we set out to design initiators of relatively good thermal stability but which were labile when irradiated with wavelengths of UV or visible light.

The photochemical efficiency of triplet benzophenone sensitized decompositions of peroxides in solution is low.[5] We reasoned that by building an absorbing chromophore (triplet sensitizer) and a radical source, such as a perester, into the same molecule an efficiently photodecomposable radical source might be produced. Though Leffler and Miley[6] had studied various benzophenone derivatives of benzoyl peroxide, we reasoned peresters would be more stable thermally and therefore of better practical potential.

In the present article we describe the preparation and photochemical properties of a series of *tert*-butylperbenzoates containing the benzophenone functionality.

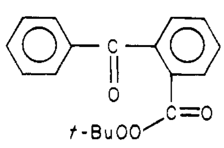
Results

Synthesis. Synthesis of the peresters Ia–d is straightforward, starting from the corresponding carboxylic acids. Refluxing the latter with thionyl chloride and treatment of the resulting acid chlorides with *tert*-butyl hydroperoxide in the presence of triethylamine produced the *tert*-butyl peresters in good yield.

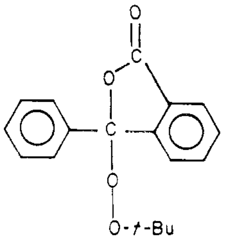


Ia, $R_1 = R_2 = R_3 = H$
b, $R_1 = R_2 = R_3 = CH_3$
c, $R_1 = CH_3O$; $R_2 = R_3 = H$
d, $R_1 = CH_3$; $R_2 = R_3 = H$

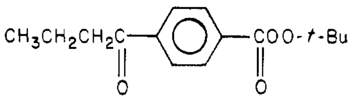
Perester II was particularly attractive from a practical viewpoint, since the corresponding acid was cheap and available in large quantities. This acid chloride exists however primarily in a pseudoconfiguration.[7] Thus formation of II was accompanied by formation of the pseudoperester III, the latter having no aromatic ketone chromophore and hence no UV absorption above 300 nm. Perester IV was prepared to compare the rate of its decomposition with that of the Norrish type II reaction in a system where both were possible. We wondered if the excited carbonyl group would abstract hydrogens from the alkyl side chain more or less rapidly than the perester decomposed.



II



III



IV

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(1) Oster, G; Yang, N. C. *Chem. Rev.* **1968**, *68*, 125.

(2) Wamser, C. C.; Hammond, G. S.; Chang, C. T.; Baylor, C. *J. Am. Chem. Soc.*, **1970**, *92*, 6362.

(3) Koch, T. H.; Jones, A. H. *J. Am. Chem. Soc.* **1970**, *92*, 7503.

(4) Neckers, D. C. *CHEMTECH.* **1978**, *8*, 108.

(5) Walling, C.; Gibian, M. J. *J. Am. Chem. Soc.*, **1965**, *87*, 3413.

(6) Leffler, J. E.; Miley, J. W. *J. Am. Chem. Soc.* **1971**, *93*, 7005.

(7) Newman, M. S.; Courduvelis, C. *J. Am. Chem. Soc.* **1966**, *88*, 781.

Table I. Physical Properties of the Peresters[a]

			IR absorption, cm^{-1}, in CCl$_4$			
perester	yield, %	mp, °C	$\nu_{C=O}$ (ketone)	$\nu_{C=O}$ (adjacent to perester)	UV n-π^*, nm	triplet energy E_T, kcal/mol
Ia	75	62-64	1665	1770	347	67.7
Ib	70	75-77	1665	1770	349	67.4
Ic	63	93-95	1665	1770	325	
Id	78	80-81	1665	1770		
II	mixture	oil	1680	1775 (neat)	327	
III		126-128		1790 (KBr)	none > 300	
IV	52	oil	1700	1775 (neat)	tail > 300	

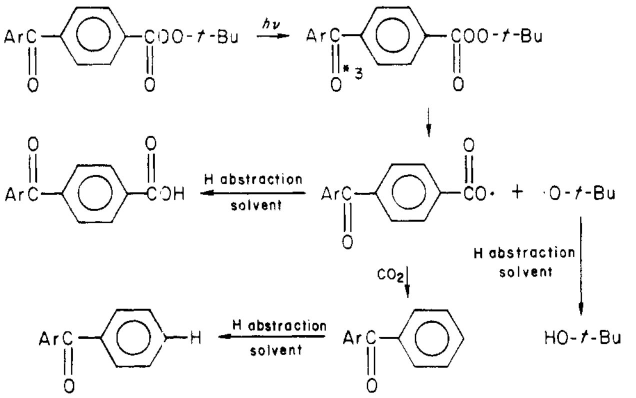
[a] Satisfactory combustion analytical data for C, H (±0.4%) were obtained for these compounds.

Table II. The Products of Photolysis from Different Peresters[e]

				products, mol %		
perester	solvent	concn, M × 10^2	period of irradiation, h	unreacted perester	benzoylbenzoic acid	benzophenone
Ia	cyclohexane	2.4	6	0	55	36[a]
	methanol	2.4	1	0	60	29[b]
Ib	cyclohexane	2.0	2.5	29	27	20
		2.2	4	0	46	43
	methanol	4.2	1	61	13	19
	CH$_3$OD[d]	4.4	1	57	21	16
IV	methanol	3.3	1.5	0	52[c]	10[c]

[a] Minor byproducts were bicyclohexyl and C_6H_5CO-*p*-C_6H_4COO-*c*-C_6H_{11}. [b] Further irradiation gave pinacols and C_6H_5CHOH-*p*-C_6H_4COOH. [c] In addition to the acid, 25% methyl ester of the acid was also found. [d] Decomposition of Ib in CH$_2$OD produced no deuterated mesitoyl phenyl ketone nor was there any deuterium in the recovered Ib. [e] Irradiation light source 300 nm; Pyrex reactors purged with nitrogen.

Scheme II



The overall yield and some physical properties of the synthesized peresters are given in Table I.

Photochemical Decomposition Products. All the peresters photodecomposed with nearly unit quantum efficiency in both polar and nonpolar solvents when irradiated at the wavelength of carbonyl group absorption. In general, the photodecompositions occurred as shown in Scheme II.

The main products from the benzophenone moiety were the parent aryl ketone and the appropriate aroylbenzoic acid, though secondary photoproducts such as pinacols and other solvent-derived products were also formed, the quantity depending on the nature of the solvent. The fate of the *tert*-butoxy radicals was not followed in detail, but acetone and *tert*-butyl alcohol formation could be detected by gas chromatography.

The main products and reaction conditions of the photolysis experiments for some typical peresters are given in Table II.

The decomposition of most of the peresters was faster in methanol than in cyclohexane. In the case of the mesitoyl perester, Ib, the effect of methanol is to slow the rate of decomposition, and it was this which caused us to search for deuterium incorporation in the methyl groups of the recovered perester, Ib.

Table III. Quantum Yields of Perester Decomposition and Sensitized Decomposition of Benzoyl Peroxide

perester	concn, M × 10^2	solvent	benzophenone concn, M × 10^2	ϕ of dec
Ia	5.90	C_6H_6		0.94
Ib	6.06	C_6H_6		0.80
Ic	5.03	C_6H_6		0.75
Bz_2O_2	4.67	C_6H_6	5.89	0.32
Bz_2O_2	3.50	CCl_4	3.75	0.17

The decarboxylation step of each perester derived carboxyl radical is not effected much by the solvent, but as expected, pinacol products are more prominent in methanol.

The irradiation of the butyrophenone perester, IV, showed no evidence for a competing Norrish type II reaction. Thus, there was no acetophenone, no *p*-acetylbenzoic acid, and no *p*-acetyl *tert*-butylperbenzoate observed among the products from IV. On the other hand, the formation of about 25% of the methyl ester of the expected acid as a photoproduct is somewhat difficult to explain but may come from a solvent-induced decomposition.

Photodecomposition: Kinetics. Kinetic studies were carried out in degassed, sealed tubes by irradiating them with 366 nm light obtained from a Hanovia medium-pressure mercury lamp by combining the Corning Filters 0-52 and 7-60. The decompositions of the peresters were followed by the carbonyl IR absorption adjacent to the peroxide group (O=COO-) (1770 cm^{-1}).[8] Benzophenone–benzhydrol redox actinometry[9] was used throughout the study. Polymerization experiments were

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(8) Byrne, D. R.; Burton, V. S.; Chiu, A.; Kabbe, F.; Green, F. M; Schuetz, R. D. *J. Chem. Eng. Data* **1972**, *17*, 507.

(9) Moore, W. M.; Hammond, G. S.; Foss, R. F. *J. Am. Chem. Soc.* **1961**, *83*, 2789.

Table IV. Decomposition Rates of the Peresters and Sensitized Benzoyl Peroxide[a]

perester	initial concn, M × 10^2	benzophenone concn, M × 10^2	k_d × 10^4 s^{-1}
Ia	5.9		1.84
Ib	6.06		1.34
Ic	5.03		1.45
Bz_2O_2	4.67	5.89	0.64

[a] Light intensity, I = 6.56 × 10^{17} quanta/min; solvent, C_6H_6; temperature 25 °C.

Table V. Quantum Yields of the Peresters in Methanol and CCl_4[a]

perester	concn, M × 10^2	TBP concn, M × 10^2	solvent	ϕ of dec
Ia	7.16		CCl_4	1.05
	4.78	5.01	CCl_4	0.79
	3.56		CCl_4	0.90
	3.56	3.76	CCl_4	0.74
	5.38		methanol	2.77
	5.38	5.08	methanol	0.64
Ib	6.15		methanol	1.30
	6.15	5.08	methanol	0.62
Ic	5.10		methanol	1.54

[a] Radical-induced decomposition of Ia is greater than that of Ic and Ib.

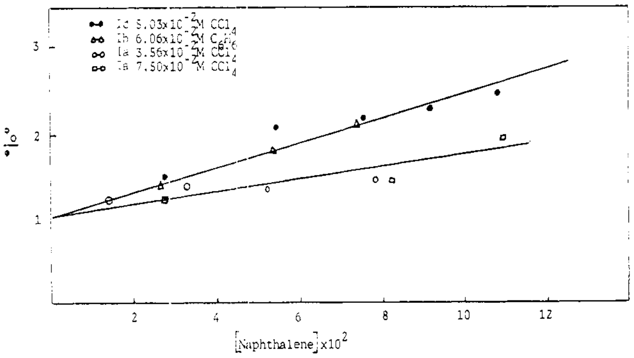

Figure 1. Stern–Volmer plots.

done in sealed degassed ampules, and the yield was followed gravimetrically.

Quantum yields of decomposition of the peresters are shown in Table III and are observed to be near unity in contrast to the low quantum yields of benzophenone-sensitized decomposition of Bz_2O_2.[5] The decomposition rates of the peresters showed first-order reaction kinetics with little or no induced decomposition in benzene solution in the concentration range 0.04 to 0.07 M. The apparent first-order photodecomposition rate constants (k_d) (up to 40% conversion) in C_6H_6 are shown in Table IV.

In methanol the quantum yield was much higher than in cyclohexane and higher than unity, suggesting the possibility of a solvent-induced decomposition.

To test this possibility, a radical scavenger 2,6-di-*tert*-butyl-*p*-cresol (TBP)[10] was included in the reaction mixture; under these conditions the quantum yield in MeOH reduced in value to that found in benzene. The rate of decomposition in benzene did not alter with addition of TBP, and the quantum yields, both in the presence and the absence of TBP, in methanol and CCl_4 are shown in Table V. Thus, under conditions where the solvent-induced decomposition is eliminated by the radical scavenger, the quantum yield is the same in methanol as in nonpolar solvents.

Table VI. Quenching Constants for the Peresters

peresters	quencher	solvent	$k_q\tau$
Ia	naphthalene	CCl_4	7.5
Ib	naphthalene	C_6H_6	15
Ic	naphthalene	CCl_4	15

Table VII. Thermal Decomposition of the Peresters

perester	initial concn, M × 10^2	1st order dec rate, M × 10^5 s^{-1}	half-life, $t_{1/2}$, h
Ia	5.01	2.88	6.7
Ib	5.15	1.80	10.7
Ic	5.19	3.03	6.4

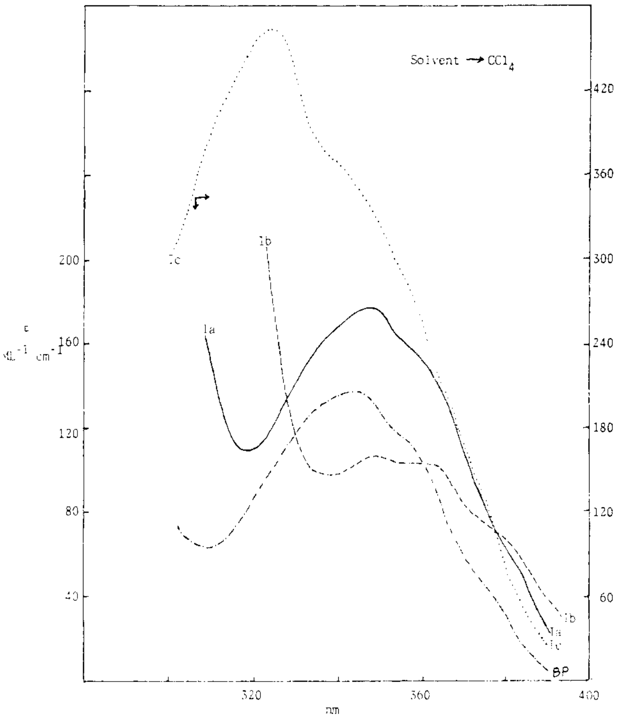

Figure 2. UV absorption spectra of the peresters in CCl_4.

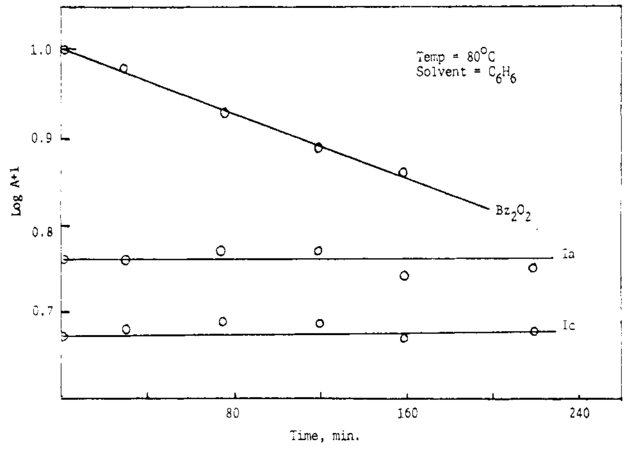

Figure 3. Thermal decomposition of Bz_2O_2, Ia and Ib (decomposition rate constant, K_d, for Bz_2O_2 is 3.35 × 10^{-5} s^{-1}).

All the peresters gave linear Stern-Volmer plots when naphthalene was used as triplet quencher (Figure 1). The values of the slopes ($k_q\tau$) (Table VI) suggest that the triplet lifetimes of the peresters are short when compared to those of benzophenone alone.

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(10) Walling, C. "Free Radicals in Solution"; Wiley: New York, 1957; 430ff.

Scheme III

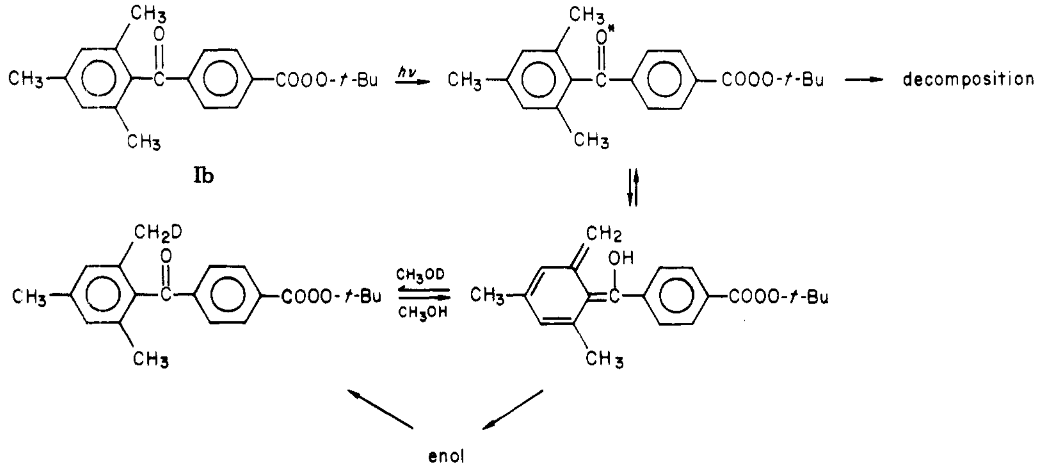

Table VIII. Rate of Polymerization (R_p) of MMA[a]

initiator	benzophenone concn, M × 10^2	$R_p \times 10^5$ mL^{-1} s^{-1}
Ia		8.33
Ib		8.31
Ic		8.16
Bz_2O_2	5.5	2.58

[a] Initiator = 5 × 10^{-2} M, [MMA] = 3.1 M; temperature = 25 °C; benzene.

The UV absorption spectra of the peresters are shown in Figure 2. While Ia and benzophenone (BP) have similar spectra, Ic and Ib showed somewhat different shapes, reflecting the substituents in the aryl portion of the perester.

To test the thermal stability of the perester, attempts were made to measure decomposition rates at 80 °C in benzene. While Bz_2O_2 showed a decomposition rate comparable to the literature value,[11a] the peresters did not decompose at all at 80 °C, Figure 3. The thermal rates of decomposition in the dark were measured at 110 °C in chlorobenzene (Table VII) and were comparable in value to the rates of decomposition of substituted *tert*-butyl perbenzoates.[11b]

Some polymerization studies were carried out using the perester initiators under comparable photolytic conditions with methyl methacrylate (MMA) as monomer. Under these conditions, MMA did not polymerize photochemically in the absence of any initiator, but the synthesized initiators facilitated its polymerization. The results are shown in Table VIII.

As expected, the rate of polymerization with the peresters is much higher than that of benzophenone-sensitized Bz_2O_2 initiation.

Discussion

The peresters all provide efficient photochemical sources of free radicals. Important from a practical view is that their photodecomposition is controllable (effectively it can be tuned) by the absorption characteristics of the absorbing chromophore. Thus *p*-benzoyl *tert*-butylperbenzoate decomposes smoothly at room temperature with 360-nm radiation; at this wavelength benzoyl peroxide is photostable. In hydrocarbon solvents where the likelihood of solvent-induced decomposition is minimized, the decomposition quantum yields approach unity (Table III). The quantum efficiency of photodecomposition of the aroyl *tert*-butylperbenzoates is at least three times that of the benzophenone-sensitized decomposition of benzoyl peroxide, clearly indicating the efficacy of the intramolecular process in contrast to bimolecular energy transfer. In fact, all of the peresters decompose with higher quantum yields (by at least a factor of 3) than does benzoyl peroxide in the presence of benzophenone (Table III). The decomposition rates are also 2–3 times higher compared to benzophenone-sensitized benozyl peroxide decomposition (Table IV). In methanol all of the perester decomposition quantum yields are enhanced, the result of induced decompositions which are chain reactions (Table V).

The potential for an intramolecular reaction in the mesitoyl perester (Ib) was suggested by its apparently slower rate of decomposition in methanol than either that of Ia or Ic under identical conditions. This suggested an intramolecular hydrogen abstraction leading to a photoenol, the latter being stabilized by the alcohol solvent. *o*-Alkylbenzophenones give photoenols when the n–π* triplet state abstracts hydrogen from the ortho substituent.[12] Though this process is reported to be inefficient for mesitoyl aryl ketones[13] because the excited state is disrupted from planarity by the excessive *o*-methyls, there was reason to believe[14] the latter theory was based on incomplete experimental evidence.

Photoenolization in the mesitoyl perester (Ib) would be indicated by deuterium incorporation if the reverse reaction is slow compared with intermolecular exchange (Scheme III). Only if the exchange with solvent is slow compared to reversion (a reaction expected to have a rate constant comparable to that of the reverse Norrish type II reaction in *t*-BuOH[12]) would no deuterium incorporation be observed in the starting material recovered or in the products.

The experiments (Table II) indicate that no deuterium incorporation is observed either in the starting perester **Ib** or the products. This result suggests that photochemical perester decomposition from Ib is faster than is the intramolecular hydrogen abstraction from the methyl groups.

The result with the butyrophenone perester IV is similar in that it too indicates that photolytic perester decomposition proceeds much more rapidly than formation of acetophenone derivatives which would be expected from a competitive Norrish type II reaction. The latter reaction is one in which abstraction from the alkyl chain would have

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(11) (a) Nozaki, K.; Bartlett, P. D. *J. Am. Chem. Soc.* **1946**, *68*, 1686. (b) Blomquist, A. T.; Berstein, I. A. *J. Am. Chem. Soc.* 1951, 73, 5546.

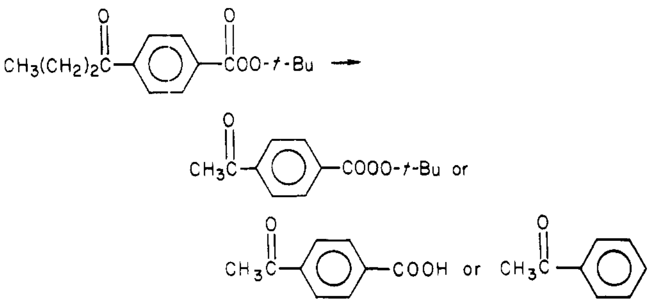
(12) For a review see: Tammes, P. G. *Tetrahedron* **1976**, *32*, 405.

(13) Matsuura, T.; Kitaura, Y. *Tetrahedron* **1969**, *25*, 4487.

(14) Neckers, D. C. Ph.D. Thesis, University of Kansas, 1963.

(15) Wagner, P. J. *Acc. Chem. Res.* **1971**, *4*, 168.

Scheme IV



to occur more rapidly than perester bond homolysis. This process would be indicated by acetyl products—either in the form of acetophenone, *p*-acetylbenzoic acid, or even perhaps *p*-acetyl *tert*-butylperbenzoate (Scheme IV). None of these are observed.

The point is that few of the typical photochemical reactions of aryl ketones seem to compete with light absorption and perester decomposition—in that order in the case of the UV active peresters. None of the typical n-π^* triplet ketone reactions of the aryl ketone systems we have tested are viable in competition with the homolysis of the -O-O- bond of the perester unit.

Vinyl polymerization was studied with methyl methacrylate as the monomer and with the three specific initiators, Table VIII. These initiators are each more efficient than is benzophenone-sensitized initiation using benzoyl peroxide or when benzophenone alone is used as an initiator. They are also comparable to the Hammond initiator in rate and have several obvious advantages—by design. The thermal decompositions of the synthesized peresters are slow, also as was expected. In a thermal reaction, these peresters are quite similar to *tert*-butylperbenzoates.

Experimental Section

Melting points were determined on a Thomas-Hoover capillary melting point apparatus and are uncorrected. Infrared spectra were recorded in KBr disks or neat, using a Perkin-Elmer 337 infrared spectrophotometer (when other conditions were used they are given at the appropriate place). NMR spectra were recorded either on a Varian A-60 or CFT-20 spectrometer with deuteriochloroform as the solvent and tetramethylsilane as the internal reference.

UV spectra were determined using a Beckman Acta MIV spectrophotometer. Mass spectra were obtained using a Varian MAT Model CH-7 mass spectrometer. GLC measurements were made on a Hewlett Packard 5710 A TD or 5710 FID chromatograph. High-pressure LC chromatograms were run on a Waters Associates instrument with UV detection and a Porasil column. Photolysis experiments except those of the kinetic measurements were carried out in a Rayonet RPR-100 reactor fitted with 300-nm fluorescence lamps.

p-Benzoylbenzoic acid was commercially available; 4-(2′,4′,6′-trimethylbenzoyl)benzoic acid[16] and 4-(4′-methylbenzoyl)benzoic acid[17] were prepared by the Friedel–Crafts reaction of 4-(carbomethoxy)benzoyl chloride[18] with the appropriate aromatic hydrocarbon followed by saponification and acidification.

4-(4′-Methoxybenzoyl)methylbenzoate (mp 158 °C) was obtained in 62% yield: IR 1650 (C=O ketone), 1730 cm^{-1} (C=O ester); NMR δ 3.93 (s, 3 H, ArOCH$_3$), 4.00 (s, 3 H, COOCH$_3$), 6.93–8.35 (2 AB quartets, 8 H, aromatic protons).

All acid chlorides were prepared by boiling the corresponding acids with a large excess of thionyl chloride until no more HCl was produced. Adding a few drops of pyridine often proved advantageous. Before use, the acid chlorides were purified by crystallization from cyclohexane or ether–pentane.

Preparation of the Peresters Ia–d. General Procedure. Typically, the acid chloride (10 mmol) was dissolved in 50 mL of ether. If the acid chloride did not dissolve well in ether, some dichloromethane was added. The solution was stirred magnetically and cooled in an ice-water bath while a solution of *tert*-butyl hydroperoxide (11 mmol) and triethylamine (12 mmol) in 20 mL of ether was added over a period of 5 min. After the addition, the reaction mixture was stirred for another hour at ice-water bath temperatures. Filtration and evaporation gave the desired perester. Chromatography over silica gel (Merck, mesh 60–200) with CH$_2$Cl$_2$ as eluent and recrystallization from ether–pentane gave the pure peresters (Table I).

p-Butyrylbenzoic acid was prepared from *p*-bromobutyrophenone[19] by treatment with cuprous cyanide[20] and hydrolysis.

Mixture of *tert*-Butyl 2-Benzoylperbenzoate (II) and the Pseudoperester III. *o*-Benzoylbenzoic acid (5.0 g, 22 mmol) was heated for 4 h, with 10 mL of thionyl chloride. After evaporation of the thionyl chloride, the remaining oil proved to be almost pure pseudoacid chloride (no C=O absorption around 1650 cm^{-1}, a strong C=O absorption at 1790 cm^{-1}).[7]

The oil was dissolved in 100 mL of ether and the solution cooled in an ice–salt bath. Over a period of 15 min a solution of 2.0 g of *tert*-butyl hydroperoxide (23 mmol) and 2.4 g of Et$_3$N (24 mmole) in 25 mL of ether was added. A yellow color developed on addition of the first drops. After the addition, stirring was continued for 1 h. Filtration and evaporation gave a yellow oil which was chromatographed over silica gel (CH$_2$Cl$_2$ as eluent). An oil (4.5 g) was obtained which gave some solid on trituration with ether. The solid appeared to be the pseudoperester III which could be crystallized from dichloromethane–ether giving a colorless compound: mp 126–128 °C; IR $\nu_{C=O}$ 1790 cm^{-1} (no C=O of benzoyl group); NMR δ 1.23 (s, 9 H, CH$_3$), 7.2–8.7 (m, 9 H, aromatic protons). The oil was chromatographed again and freed from pseudoperester by dissolving it in ether–pentane mixtures, cooling, and filtrating. The purified oil II gave one spot on TLC (CH$_2$Cl$_2$) and showed only a minute amount of pseudoperester (III) by high-pressure LC: IR ν 1680 (C=O ketone), 1775 cm^{-1} (C=O perester); NMR δ 1.21 (s, 9 H, CH$_3$), 7.2–8.1 (m, 9 H, aromatic protons)

***tert*-Butyl *p*-Butyrylperbenzoate (IV).** This perester was made by the general procedure. Purification was best done by chromatography over neutral aluminum oxide with dichloromethane–ether (5:1) as eluent. The perester was obtained as a yellow oil, which solidified after several months in the refrigerator: IR ν 1700 (C=O ketone), 1775 cm^{-1} (C=O perester); NMR δ 7.04 (i, 3 H, CH$_3$), 1.46 (s, 9 H, CH$_3$), 1.83 (m, 2 H, CH$_2$), 3.06 (i, 2 H, CH$_2$), 8.17 (s, 4 H, aromatic protons).

Product Analysis of Perester Decompositions in Cyclohexane and Methanol. The peresters were dissolved in concentrations as given in Table II. The amount of perester used was in the range of 300–500 mg. The solutions were placed in Pyrex tubes, flushed with nitrogen for 10 min, and sealed with a rubber cap.

After the irradiation, the yield of CO$_2$ was measured by applying N$_2$ pressure and trapping the CO$_2$ with a Ba(OH)$_2$ solution. The photolyzed solutions were evaporated (in the case of perester Ia treatment with excess diazomethane gave the best separation procedure) and again evaporated. Chromatography over 2 mm silica gel plates (E. Merck) with dichloromethane as the developing solvent separated the products. Extraction of the silica gel was done with ether. The identity of the samples was confirmed by GLC or high-pressure LC by comparison with authentic samples or by melting points of the solids.

Byproducts. Irradiation of Ia in cyclohexane gave bicyclohexyl as a secondary photolysis product. This was proved by comparison with an authentic sample and combination of spectroscopic techniques. GLC indicated that minor fractions of C$_6$H$_5$-CO-*p*-C$_6$H$_4$COO-*c*-C$_6$H$_{11}$ were present in cyclohexane while in MeOH a secondary photoproduct was C$_6$H$_5$CHOH-*p*-C$_6$H$_4$COOH. The same product was formed when 4-benzoylbenzoic acid was irradiated for 2 h in MeOH in 26% yield. The structure of this secondary photoproduct was proven by independent synthesis

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(reduction of methyl 4-benzoylbenzoate by $NaBH_4$). Among other secondary photoproducts found in small amounts was a mixture of pinacols. These were confirmed by synthesis of a similar pinacol mixture upon irradiation of methyl 4-benzoylbenzoate in isopropyl alcohol.

Photolysis of *tert*-Butyl 4-(2′,4′,6′-Trimethylbenzoyl)perbenzoate (Ib) in CH_3OD. After photolysis of the perester (300 mg in 20 mL of CH_3OD) for 1 h, the following products were found: 14.1% of CO_2, 15.6% of phenyl mesityl ketone, 56.6% of starting perester, and 21.8% of the corresponding acid.

The phenyl mesityl ketone showed no deuterium incorporation (mass spectrometry). The perester showed no deuterium incorporation (NMR).

The recovered perester was irradiated again in cyclohexane solution (25 mL) for 4 h. The following products were found: carbon dioxide, 44%; bicyclohexyl (21 mg); mesityl phenyl ketone (52%); and the corresponding acid, 46%. No deuterium incorporation in the mesityl phenyl ketone was found.

Photolysis of Perester IV in MeOH. Perester IV (1.0 mmol) was irradiated for 85 min in 30 mL of MeOH. The following products were obtained: carbon dioxide, 11%; butyrophenone, 10% (confirmed by high-pressure LC); methyl *p*-butyrylbenzoate (25%) (mp 83–85 °C from hexane) (confirmed by independent synthesis); and *p*-butyrylbenzoic acid (52%) (confirmed by preparation of the methyl ester. No products of a Norrish type II reaction could be found.

Determination of Photodecomposition Rate and Quantum Yields. A solution of perester (2 mL) in the appropriate solvent was placed in Pyrex tubes (12-mm diameter), degassed, and sealed under vacuum. Three cycles of freeze–thaw removed dissolved oxygen. The tubes were placed in a merry-go-round around a water-cooled light source, removed at different predetermined intervals, and kept frozen in liquid nitrogen in the dark until analysis was done. The estimation of perester was done by quantitative IR, monitoring the carbonyl peak at 1770 cm^{-1}. None of the products of decomposition or the solvent interfered at this wavelength. Absorbance was measured with a 0.1-mm NaCl cell against solvent reference. With every run, two tubes containing actinometric solutions (benzophenone (0.1 M) and benzhydrol (0.05 M) in benzene) were also irradiated. The light intensity and quantum yield of benzophenone loss were measured by measuring the decrease in benzophenone content spectrophotometrically (using the benzophenone peak at 345 nm).

Polymerization Studies. Commercial methyl methacrylate monomer was washed three times with 2% NaOH solution to remove stabilizer. It was then washed with distilled water three times, dried with molecular sieves, and distilled under vacuum before use. Polymerization solutions were prepared in cylindrical tubes which were degassed and sealed. The amount of polymer formed was determined by precipitating the polymer with an excess of methanol, washing with methanol, and filtering through fine sintered crucibles (previously weighed) followed by drying in a vacuum oven. The irradiation condition was the same as that in the decomposition rate studies.

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Registry No. Ia, 71616-77-8; Ib, 71616-78-9; Ic, 71616-79-0; Id, 71616-80-3; II, 24546-34-7; III, 25251-51-8; IV, 71616-81-4; *p*-benzoylbenzoic acid, 611-95-0; benzophenone, 119-61-9; 4-(2′,4′,6′-trimethylbenzoyl)benzoic acid, 65414-32-6; mesityl phenyl ketone, 954-16-5; *p*-butyrylbenzoic acid, 71616-82-5; methyl *p*-butyrylbenzoate, 71616-83-6; butyrophenone, 495-40-9; Bz_2O_2, 94-36-0; 4-(4′-methoxybenzoyl)methylbenzoate, 71616-84-7; *tert*-butyl hydroperoxide, 75-91-2; *o*-benzoylbenzoic acid, 85-52-9; bicyclohexyl, 92-51-3.

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Stereochemistry of Ring Enlargement by [2,3] Sigmatropic Rearrangement of Cyclic Sulfonium Ylides. Synthesis of 5-Methylthiacycloalk-4-enes

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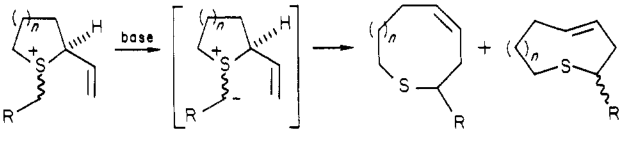
Sulfonium ylides generated in situ from *r*-1,*t*-2-dimethyl-2-vinylthiolanium (**1b**), *r*-1,*t*-2-dimethyl-2-vinylthianium (**2b**), and *r*-1,*c*-2-dimethyl-2-vinylthianium (**2c**) hexafluorophosphates undergo highly stereoselective but nonstereospecific [2,3] sigmatropic ring enlargement. The six-membered methylide from **2b**, where the carbanionic and vinyl moieties are on the same side of the ring, reacts faster than the ylide from **2c**; however, both give (*E*)-5-methylthiacyclonon-4-ene as the exclusive product. The five-membered methylide from **1b** ring expands, giving a ca. 17:1 mixture of (*Z*)- and (*E*)-5-methylthiacyclooct-4-ene. The isomeric methylide from **1c**, where the carbanionic and vinyl moieties are on opposite sides of the ring, does not appreciably react in the [2,3] sigmatropic fashion but undergoes *β*-elimination, probably by the *α′*,*β* mechanism. The results are rationalized in terms of ground-state conformational effects, in accord with an early transition state for the [2,3] sigmatropic rearrangement of allylic sulfonium ylides.

The well-known [2,3] sigmatropic rearrangement of allylic sulfonium ylides to homoallylic sulfides[1] has been recently exploited[2] for a three-carbon ring enlargement involving stabilized (R = COPh, COOEt)[3] as well as unstabilized (R = H, CH_3, Ph)[4] sulfonium ylides.



When R = CH=CH_2, the reaction may be especially useful for a ring-growing sequence since the expanded product has the 2-vinyl moiety already built in and may be further expanded in three carbon unit steps.[5,3b]

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