J. Org. Chem. 1989, 54, 131-135 131

4e: δ 1.12 (d, 6 H) $(CH_3)_2$, 1.34 (s, 9 H) $C(CH_3)_3$, 2.23 (m, 1 H) CH, 5.25 (br s, 1 H) NH.

2f: δ 1.22 (s, 9 H) $C(CH_3)_3$, 4.33 (s, 1 H) $CH{=}N$, 7.43–7.56, 7.89–7.96 (m, 5 H) Ph.

4f: δ 1.32 (s, 9 H) $C(CH_3)_3$, under aryl peaks (1 H) NH, 7.27–7.36, 7.50–7.55 (m, 5 H) Ph.

The mass spectra of the nitrones show all M^+ for the molecular ion and then $M^+ - 16$ followed by further decomposition.

Oxidation in Organic Solvents. First, 2.5 mmol of **1a** was dissolved in 4 mL of organic solvent (acetone, acetonitrile, or methanol); 5 mmol of $KMnO_4$ was then added. The reaction was stopped after 24 h and worked up as above. The products were identified by ^1H NMR spectroscopy. When water was present **1a** was dissolved in 2 mL of organic solvent and 2 mL of H_2O otherwise as above.

Oxidation with Different Phase-Transfer Catalysts. The general procedure was used but with the different PTC's in the same molar amount as above.

Oxidation under Acidic and Basic Conditions in the Water Phase. The pH in the water phase was adjusted to the appropriate pH (see Table III) with HCl or NaOH, and the general procedure was used.

Calculations. The extended Hückel calculations[17] were used for the calculation of the frontier orbitals, interaction schemes, and overlap population analysis. The geometries for **5a**, **5a′**, and **9** were approximated to the osmium tetraoxide–alkene system.[10] The calculations for **1** were performed for an imine (C=N, 1.27 Å; C—H, 1.09 Å; N—H, 1.05 Å and all angles involving C—H or N—H 120°) to which the permanganate ion (T_d symmetry, Mn—O, 1.64 Å) approaches with an oxygen to the imine nitrogen in the imine plane. The geometry of **9** was optimized with the INDO procedure.[18]

Acknowledgment. Thanks are expressed to Professor Kurt Torssell for fruitful discussions, to Lise Ravn-Petersen for technical assistance, to Hanne Kirkegaard for typing the manuscript, and to Arne Lindahl for the draft work.

Registry No. **1a**, 6852-58-0; **1b**, 538-51-2; **1c**, 718-36-5; **1d**, 15875-74-8; **1e**, 6852-60-4; **1f**, 26029-60-7; **2a**, 3376-24-7; **2b**, 1137-96-8; **2c**, 3585-88-4; **2d**, 40117-28-0; **2e**, 85664-55-7; **2f**, 75351-06-3; **3a**, 43052-01-3; **4a**, 5894-65-5; **4b**, 93-98-1; **4c**, 42498-30-6; **4d**, 19486-73-8; **4e**, 7472-49-3; $KMnO_4$, 7722-64-7; $(CH_3CH_2CH_2CH_2)_4N^+Cl^-$, 1112-67-0; $[CH_3(CH_2)_7]_4N^+Br^-$, 14866-33-2; $(CH_3)_4N^+Cl^-$, 75-57-0; $C_6H_5CH_2(CH_3CH_2)_3N^+Cl^-$, 56-37-1; $C_6H_5CH_2(CH_3)_3N^+BF_4^-$, 35820-01-0; $(C_6H_5CH_2)_2(CH_3)_2N^+Cl^-$, 100-94-7; $C_6H_5(CH_3)_3N^+IO_3^-$, 117678-56-5; $(C_6H_5)_3CH_3P^+I^-$, 2065-66-9; p-$CH_3OC_6H_4CHO$, 123-11-5; C_6H_5CHO, 100-52-7; $(CH_3)_3CCHO$, 630-19-3.

Thermal and Photochemical Reactions of Triarylmethyl Peroxides[1]

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The thermal and photochemical decomposition products of p-benzoyltriphenylmethyl peroxide (I), of m-benzoyltriphenylmethyl peroxide (II), and of isotopically labeled analogues indicate rapid radical 1,2-migrations precluding other radical processes such as β-elimination from the incipient radical. The mechanism of these processes is interpreted in terms of these rearrangements as well as reversible elimination of O_2 from the starting peroxide. Differences in the two isomeric peroxides are assessed.

Cited as evidence for the intervention of the free triphenylmethyl radical in the reaction of triphenylmethyl halides with mercury and silver,[2,3] the observation of triphenylmethyl peroxide contributed enormously to early mechanistic and structural theory. Triphenylmethyl peroxide decomposes at the melting point[4] to benzpinacol diphenyl ether, benzophenone, and tetraphenylethylene,[5] a result claimed as evidence for 1,2-migration of phenyl[6] to give α-hydroxy(*O*-phenyl)diphenylmethyl. Benzophenone derives in this context it is said from β-cleavage of phenyl, though diphenylphenoxymethyl cannot be isolated and gives no peroxide in the presence of oxygen.[4] Schmidlin and Hodgson were the first to observe this product, along with the formation of phenol from the "distillate" of triphenylmethyl peroxide at 240 °C. Tetraphenylethylene may result either by α-cleavage of the rearranged radical to the carbene followed by dimerization or by elimination of two phenoxy radicals from benzpinacol diphenyl ether. Though Gomberg also reported that many triarylmethyl radicals such as α-naphthyldiphenylmethyl[7] and β-naphthyldiphenylmethyl[8] are unstable to light, the products as such were identified in these early papers, and there have been no reported studies of the photochemistry of triarylmethyl peroxides containing absorbing chromophores. Product studies were limited to thermolysis reactions.[4,5]

As part of a program established to search for more efficient UV photoinitiators, we have investigated the thermal and photodecomposition of the benzoyltriphenylmethyl peroxides p-benzoyltriphenylmethyl peroxide (I), and m-benzoyltriphenylmethyl peroxide (II). In view of the thermal decomposition results,[4,5] and our own results with *tert*-butyl per-4-benzoylbenzoate,[9] efficient radical formation by O–O cleavage was anticipated when the compounds were irradiated at, or near, the n-π* maximum. The resulting triarylakoxy radical is a masked bis(benzophenone) if the β-cleavage expected to predom-

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(1) Contribution no. 36 from the Center for Photochemical Sciences.

(2) Gomberg, M. *Chem. Ber.* **1900**, *33*, 3150.

(3) Marvel, C. S.; Kaplan, J. F.; Himel, M. M. *J. Am. Chem. Soc.* **1941**, *63*, 1892.

(4) Wieland, H. *Chem. Ber.* **1911**, *44*, 2250.

(5) Schmidlin, J.; Hodgson, P. *Chem. Ber.* **1910**, *43*, 1152.

(6) Walling, C. *Free Radicals in Solution*; Wiley: New York, 1957; p 473.

(7) Gomberg, M.; Schoepfle, C. S. *J. Am. Chem. Soc.* **1919**, *41*, 1655.

(8) Gomberg, M.; Sullivan, F. W. *J. Am. Chem. Soc.* **1922**, *44*, 1810.

(9) Gupta, S. N.; Gupta, I.; Neckers, D. C. *J. Polym. Sci., Chem. Ed.* **1981**, *19*, 103.

0022-3263/89/1954-0131$01.50/0

Table I. Major Products from Decomposition of I (Thermolysis; Photolysis/Air; Photolysis/Degassed)[a,b]

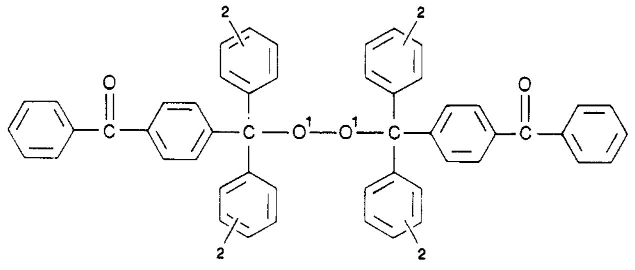
	Ib,[c] %			Ic,[d] %		
	Δ	*hν* (air)	*hν*	Δ	*hν* (air)	*hν*
phenol[e]	1	4	2	6	5	10
benzophenone[e]	40	41	10	34	34	21
p-hydroxybenzophenone[f]	46	52	43	22	50	52
tetraphenylethylene[e,g]	<1	8	35	1	8	22
p-benzoylbenzophenone[e,f]	32	9	3	24	9	9
9,10-diphenylphenanthrene[e,g]	trace	12	26	trace	12	20
p-benzoyltriphenylmethane[e,f]	13	5	5	21	5	6
p-benzoyltriphenylmethanol[e,f]	trace	5	4	trace	4	2

[a] Product yields were measured by GLC and are calibrated against an internal standard; average of at least three runs. [b] The thermolysis time was 10 min at the melting point of the peroxide; the photolyses were carried out in benzene for 2.5 h. [Peroxide] = (4~7) × 10^{-3} M. The Rayonet reactor was equipped with eight lamps. The temperature in the reactor was 35 ± 2 °C. [c] Entirely labeled with benzene-d_5 as indicated in Ib. [d] O^{18}/O^{16} ratio in the starting peroxide, Ic = 80/20. [e] This product derives only from the diphenylmethyl component of the peroxide. [f] This product derives from the *p*-benzoylphenyl component of the peroxide. [g] Percent calculated based on the relationship of 1 mol of peroxide yields 1 mol of product. The percentage of all other products are based on 1 mol peroxide producing 2 mol of product.

inate produces benzophenone and a *p*-benzoylphenyl radical. Compound I should thus result in four benzophenone moieties from one photochemical event.

Results and Discussion

Red *p*-benzoyltriphenylmethyl (III) forms easily from *p*-benzoyltriphenylmethyl chloride and copper.[8] It is infinitely stable in the absence of oxygen and is about 67% dimeric in a saturated solution in benzene at 25 °C. When exposed to oxygen III is converted to the stable peroxide (in the presence of oxygen gas enriched in O^{18} to the labeled analogue), which decomposes upon melting (164-5 °C) to a red melt highly reminiscent of the color of the original radical. (*p*-Benzoylphenyl)decadeuteriodiphenylmethyl chloride is synthesized from the precursor benzotrichloride[10] and deuteriobenzene. Its red radical is similarly converted to the peroxide.

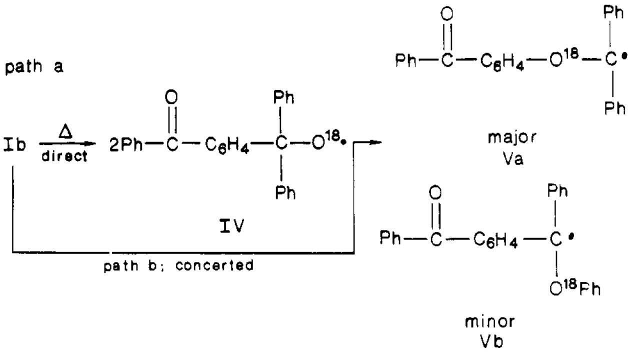


I (*p*,*p*) a: 1 = O^{16}; 2 = 5H
b: 1 = O^{16}; 2 = 5D
c: 1 = O^{18}; 2 = 5H

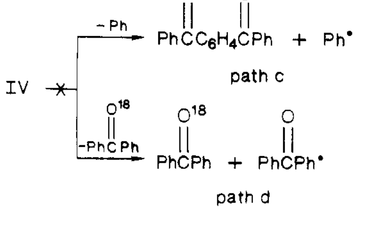
II (*m*,*m*) a: 1 = O^{16}; 2 = 5H
b: 1 = O^{16}; 2 = 5D

The principal thermolysis products isolated from the melt of I are benzophenone, *p*-hydroxybenzophenone, *p*-benzoylbenzophenone, and *p*-benzoyltriphenylmethane (Table I).[11] The yield of the latter two products is less in the photolysis, and the yield of benzophenone decreases as well especially when the photolysis is carried out in the absence of oxygen. Photolysis produces two additional products, tetraphenylethylene and 9,10-diphenylphenanthrene. Control experiments indicate that 50% of the latter derives from the former under aerobic conditions, but[12] there is virtually no interconversion of tetraphenylethylene to 9,10-diphenylphenanthrene in the absence of oxygen. No significant change occurs in product distribution when samples are irradiated for 1.5 h or longer; however, shorter irradiation times produce greater percentages of *p*-benzoylbenzophenone and *p*-benzoyltriphenylmethane. This indicates that on incomplete photolysis thermal products contribute to the product analysis. It would appear therefore that reversible loss of oxygen from I is important during the early stages of the photodecomposition since triarylmethanes are known to form from triarylmethyl thermally and photochemically.[13] Phenol and biphenyl are minor products in every case.

O^{18} peroxide Ic (80% O_2^{18}) produces both phenol (2.5%; 77/23 ± 5% O^{18}/O^{16}) and *p*-hydroxybenzophenone (13.5%; 75/25 ± 5% O^{18}/O^{16}) when heated in melting point tube for 10 min. Since both these products show little detectable loss of the oxygen label, they must derive from rearrangement (aryl from C to O) occurring either very rapidly in the free triarylmethyl alkoxy radical (IV) (path a) or in concert with bond homolysis (path b).



Benzophenone formed in the thermolysis of Ic in a melt loses over half its label (O^{18}/O^{16} = 35/65 ± 5%). This we attribute to oxidation of the stable rearranged radical Va during GC/MS analysis (see the Experimental Section). This result is consistent with the extremely rapid rearrangement during thermolysis (path a or path b) to radicals Va and Vb, respectively, thus essentially, though not entirely, precluding β-elimination steps, (path c and path d). Path d is precluded by the observation that peroxide Ib produces only perdeuteriated benzophenone.



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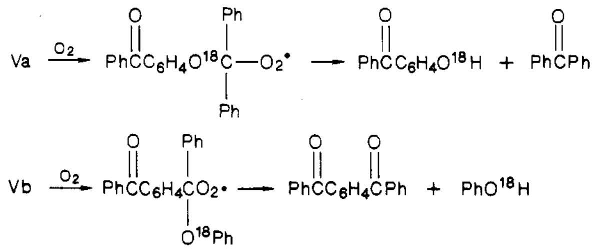
(10) Zarkadis, A. K.; Neumann, W. P. Uzick, W. *Chem. Ber.* **1984**, *118*, 1183.

(11) Photolysis experiments reported in Table I were carried out both in the presence and in the absence of air. Experiments in the presence of oxygen show similar products and trends of product formation but are complicated by oxidation steps.

(12) Sargent, M. V.; Timmons, C. J. *J. Chem. Soc.* **1964**, 5544.

(13) Letsinger, R. L.; Collat, R.; Magnusson, M. *J. Am. Chem. Soc.* **1954**, *76*, 4185.

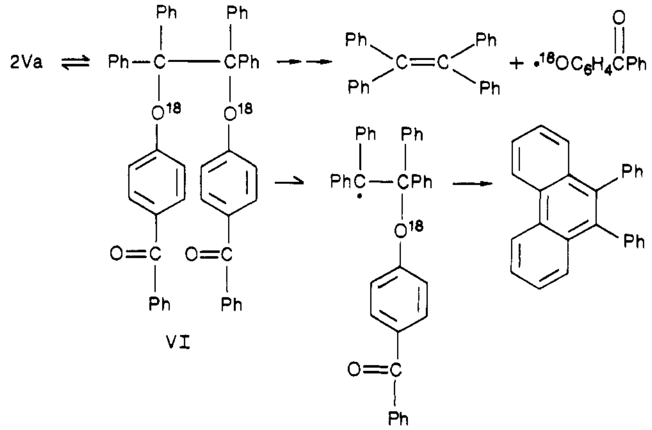
Oxidation of radical Va represents a significant source of the benzophenone in the thermal process; oxidation of Vb is a significant source of *p*-benzoylbenzophenone. Another process is also evident in the thermal reaction; namely reversible loss of oxygen to reform radical III. This is evidenced by the formation of *p*-benzoyltriphenylmethane[13] (13%) and is also suggested by the red color of the melt.



$$\mathrm{Va} \xrightarrow{O_2} \mathrm{Ph\overset{O}{\overset{\|}{C}}C_6H_4O^{18}\underset{Ph}{\overset{Ph}{C}}{-}O_2^{\bullet}} \longrightarrow \mathrm{Ph\overset{O}{\overset{\|}{C}}C_6H_4O^{18}H} + \mathrm{Ph\overset{O}{\overset{\|}{C}}Ph}$$

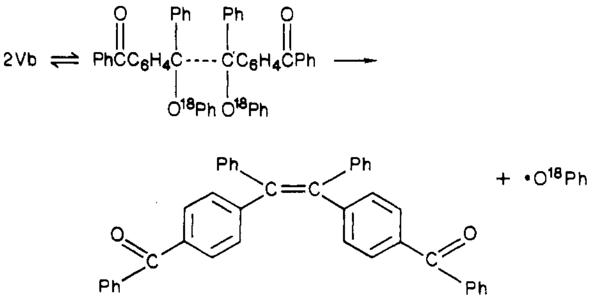
$$\mathrm{Vb} \xrightarrow{O_2} \mathrm{Ph\overset{O}{\overset{\|}{C}}C_6H_4\underset{O^{18}Ph}{\overset{Ph}{C}}O_2^{\bullet}} \longrightarrow \mathrm{Ph\overset{O}{\overset{\|}{C}}C_6H_4\overset{O}{\overset{\|}{C}}Ph} + \mathrm{PhO^{18}H}$$

When Ic is irradiated (eight 300-nm lamps; Rayonet reactor; in benzene) the rearrangement prior to product formation becomes exclusive, and products *p*-hydroxybenzophenone and phenol retain their O^{18} label entirely. *No O^{18} label* is retained whatsoever in the benzophenone produced. Neither is any label retained in the *p*-benzoylbenzophenone. Paths c and d (vide supra) for product formation from IV are thus precluded, and oxidation of Va and Vb becomes responsible for all of the benzophenone and *p*-benzoylbenzophenone observed in the process. The actual yields of benzophenone and *p*-benzoylbenzophenone decrease dramatically in the photochemical process relative to the thermal reaction. Produced in their stead are major quantities of tetraphenylethylene and 9,10-diphenylphenanthrene.[12] In view of this we conclude that the actual products of the initial photochemical event are Va and Vb or their respective dimers (eq 1 and 2). These dimers, being benzophenones, are readily converted in a subsequent photochemical step to tetraphenylethylene and/or 9,10-diphenylphenanthrene. *p*-Hydroxylbenzoyl serves as the hydrogen abstracting agent in this process. A second, minor event (2) produces VII. Its observation in trace quantities reflects the relative migratory aptitudes of *p*-benzoylphenyl and phenyl. In the latter case phenoxyl is the hydrogen abstracting agent.



(1)

This mechanistic analysis is consistent with the results obtained with the deuteriated peroxide Ib. Thus Ib produces perdeuteriobenzophenone (>97% D), *p*-hydroxybenzophenone (>97% containing no deuterium in the phenyls), *p*-benzoylbenzophenone containing >97% C_6D_5 in only one of the phenyl rings, and *p*-benzoyltriphenylmethane with >97% C_6D_5 in two of the three phenyl rings of the triphenylmethyl group. The tetraphenylethylene and 9,10-diphenylphenanthrene are entirely deuteriated



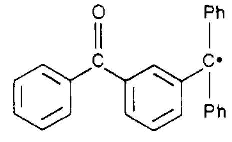
$$2\mathrm{Vb} \rightleftharpoons \mathrm{Ph\overset{O}{\overset{\|}{C}}C_6H_4\underset{O^{18}Ph}{\overset{Ph}{C}}{\cdots\cdots}\underset{O^{18}Ph}{\overset{Ph}{C}}C_6H_4\overset{O}{\overset{\|}{C}}Ph} \longrightarrow$$

(2)

VII

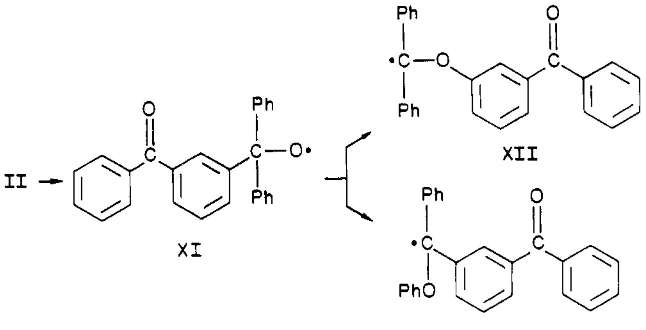
in the product. α-Elimination of *p*-benzoylphenyl from III to form diphenylcarbene is precluded by a control experiment in which the red radical III was irradiated under identical experimental conditions to those used in the irradiation of the peroxides.[14]

m-Peroxide II is synthesized in a route identical with that used for I. The orangish radical VIII is similarly converted to IIa and the deuterated analogue IIb. The

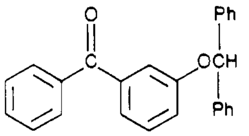


VIII

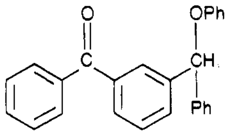
products of thermolysis of II are benzophenone, *m*-benzoylbenzophenone, *m*-benzoyltriphenylmethane, and *m*-benzoyltetraphenylethylene (Table II). Alternative



products IX and X are observed in the case of II with X being the major product. The benzophenone, *m*-benzoylbenzophenone, *m*-hydroxybenzophenone, and *m*-benzoyltriphenylmethane observed in the thermal process remain in the photochemical process but are formed in much lesser amounts under degassed conditions.



IX



X

Deuterium labeling results in the expected products from the thermal decomposition: perdeuteriophenol, perdeuteriobenzophenone, *m*-hydroxybenzophenone, *m*-benzoylbenzophenone (C_6D_5), and *m*-benzoyltriphenylmethane $(C_6D_5)_2$. In contrast to peroxide I, radicals XII and XIII produced by rearrangement either formed directly from II or from radical XI behave differently from

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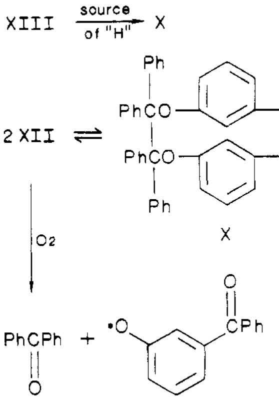
[14] Photodecomposition of III at both 588 and 360 nm produces greater than 50% *p*-benzoyltriphenylmethane. D. C. Neckers and S. Rajaduran, unpublished.

Table II. Products from the Decomposition of II (Thermolysis; Photolysis/Air; Photolysis/Degassed)[a,b]

	IIa, %			IIb,[c] %		
	Δ	hν (air)	hν	Δ	hν (air)	hν
phenol[d]	1	14	3	5	5	3
benzophenone[d]	8	12	3	13	14	3
m-hydroxybenzophenone[e]	2	11	7	4	11	11
m-benzoylbenzophenone[d,e]	25	34	8	28	35	8
m-benzoyltriphenylmethane[d,e]	10	2	4	16	2	6
phenyl(*m*-benzoylphenyl)diphenylmethyl ether (X)[d-f]	2	2	24	1	3	27
m-benzoylphenyl diphenylmethyl ether (IX)[d-f]	trace	trace	6	trace	3	4
m-benzoyltriphenylmethanol	5	3	3	1	trace	2
m-benzoyltetraphenyl ethylene[d-g]	30	18	24	18	14	18
higher molecular weight product	trace	trace	trace	trace	trace	trace

[a-f] Same as footnotes *a–f*, Table I. [g] Uncalibrated.

one another. XII produces no olefin but instead produces X.[15] Compound XIII either forms a dimer that is oxidatively dissociated upon GC/MS analysis or resides as the monomeric radical that leads to the same result.



In conclusion both I and II undergo rapid, smooth photochemical decomposition leading both to O–O bond homolysis and some apparent O–C cleavage. Labeling experiments (Ib,c) confirm an extremely rapid migration of aryl from C to O with *p*-benzoylphenyl the preferred migrating group relative to phenyl. Either rearrangement is concerted with oxygen–oxygen bond homolysis or radical IV has an extremely short lifetime. Tetraphenylethylene and 9,10-diphenylphenanthrene are predominant products after rearrangement. Both I and II also undergo elimination of O_2 with said elimination being more important in II than in I.

Compound II rearranges to XII and XIII in a fashion that is more equivocal than is the case of I. Products from the rearrangement indicate hydrogen abstraction (disproportionation) by XIII is preferred over olefin formation leading to ether X as a significant product.

Photochemical experiments on the stable radicals III and VIII are continuing in our laboratories.

Experimental Section

p-Methylbenzophenone, *m*-trifluorobenzophenone, benzene-d_6, and flavone were purchased from Aldrich. Oxygen gas (98% O^{18}) was obtained from MDS Isotopes. Benzene was purified according to known methods.[16] Infrared spectra were recorded on a Nicolet 20DX FT infrared spectrometer, and the NMR spectra were taken with a Varian XL-200 nuclear magnetic resonance spectrometer. GLC analyses were performed on a Hewlett-Packard 5800 gas chromatograph equipped with a J & W fused silica capillary column (15 m) containing a 5% phenylmethylsilicon film (0.25 mm thickness) and a flame-ionization detector. Mass spectra were obtained from a Hewlett-Packard 5987A GC–mass system either by utilizing a direct insertion probe method or after passing the sample through the HP 5800 gas chromatograph. Thermolyses were conducted in an open tube immersed in a constant-temperature oil bath with the temperature ranging from 185 to 187 °C. Photolyses were performed inside a Rayonet RPR-100 photoreactor equipped with eight RPR-3000A° lamps. Anerobic samples were degassed by using three consecutive freeze–thaw cycles. All the product yields were measured by GLC analyses of the samples with the addition of the standard compound (flavone) after the thermolysis or photolysis had taken place. The conversion factors for the GLC analysis were calculated from the GLC results of the mixture containing known concentrations of the standard and the products.

***m*-Benzoyltriphenylmethanol.** A dry benzene solution (25 mL) containing 2.5 g of *m*-(trifluoromethyl)benzophenone and 4.0 g of $AlCl_3$ was refluxed for 4 h. A 5% HCl solution (50 mL) was added after the reaction mixture was cooled down. The benzene extracts were combined, and the solvent was removed in vacuo. A 80% acetic acid (50 mL) was added to the residue, and the resulting solution was refluxed for a half hour. After cooling, the solution was poured into 200 mL of water, and the precipitate of *m*-benzoyltriphenylmethanol that formed was collected (1.45 g, 31% yield): mp 138–140 °C; IR (KBr) 1652 (C═O), 3471 cm^{-1} (OH); NMR ($CDCl_3$) δ 7.29 (s, 10 H), 7.36–7.78 (m, 9 H). Anal. Calcd for $C_{26}H_{20}O_2$: C, 85.69; H, 5.53. Found: C, 85.19; H, 5.47.

(*m*-Benzoylphenyl)decadeuteriodiphenylmethanol. This compound was obtained in 35% yield when benzene-d_6 was used to replace regular benzene (vide infra): mp 140–142° °C; IR (KBr) 1652 (C═O), 3471 cm^{-1} (OH); NMR ($CDCl_3$) δ 7.36–7.78 (m, 9 H).

***m*-Benzoyltriphenylmethyl Chloride.** One gram of *m*-benzoyltriphenylmethanol was dissolved in benzene (20 mL), and thionyl chloride (5 mL) was added. The mixture was refluxed for 2 h, the excess of benzene and thionyl chloride was removed in vacuo, and a large quantity of petroleum ether (~100 mL) was added. *m*-Benzoyltriphenylmethyl chloride formed and was collected (0.8 g, 78%): mp 92–93 °C; IR (KBr) 1663 cm^{-1} (C═O); NMR ($CDCl_3$) δ 7.28 (s, 10 H), 7.36–7.78 (m, 9 H).

(*m*-Benzoylphenyl)decadeuteriodiphenylmethyl Chloride. This compound was prepared from (*m*-benzoylphenyl)decadeuteriodiphenylmethanol in 82% yield (vide infra): mp 83–84 °C; IR (KBr) 1663 cm^{-1} (C═O); NMR ($CDCl_3$) δ 7.36–7.81 (m, 9 H).

***p*-Benzoyltriphenylmethyl Peroxide (I).** Para peroxides Ia–c were prepared from *p*-methylbenzophenone.[17,18] *p*-Benzoyltriphenylmethyl peroxide (Ia): mp 175–177 °C (lit.[3] mp 175–177.5 °C); IR (KBr) 1658 (C═O), 976 and 754 cm^{-1} (peroxide). (*p*-Benzoylphenyl)decadeuteriodiphenylmethyl peroxide (Ib): mp 164–165 °C; IR (KBr) 1653 (C═O), 968 and 754 cm^{-1} (O—O).

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(15) Compound X was prepared for comparison in a three-step synthesis. Reduction of *m*-benzoylbenzophenone with sodium borohydride in THF produced *m*-benzoyldiphenylcarbinol. Conversion of the carbinol to the chloride [mp 84–5 °C; IR (KBr) 1652 (C═O), 591 cm^{-1} (C—*cl*); NMR ($CDCl_3$) δ 6.17 (s, 1 H), 7.88–7.25 (m, 14 H)] was followed by reaction with sodium phenoxide [IR (KBr) 1657 (C═O), 1231 cm^{-1} (C—O); NMR δ 6.28 (1 H), 7.88–7.23 (m, 14 H), and 7.20–6.90 (m, 5 H)]. Ether X was, as expected, highly susceptible to hydrolysis.

(16) Vogel, G. *A Textbook of Practical Organic Chemistry*, 3rd ed.; Lowe and Brydone; London, 1972; p 172.

(17) Wittig, G.; Hopf, W. *Chem. Ber.* **1932**, *65*, 760.

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p-Benzoyltriphenylmethyl O^{18} peroxide (Ib): mp 161–162 °C; IR (KBr) 1657 (C=O), 966 and 756 cm^{-1} (peroxide).

***m*-Benzoyltriphenylmethyl Peroxide (IIa).** A dry benzene solution (100 mL) containing 1 g of *m*-benzoyltriphenylmethyl chloride and 3 mL of mercury was shaken for 2–4 h. The resulting brown solution was separated, and a stream of oxygen was bubbled into this solution until it became colorless. The solvent was removed under reduced pressure, and the wet residue was then washed several times with acetone: yield (1.72 g, 76%): mp 161–162 °C; IR (KBr) 1658 (C=O), 976 and 758 cm^{-1} (peroxide). Anal. Calcd for $C_{52}H_{38}O_4$: C, 85.93; H, 5.27. Found: C, 85.65; H, 5.62.

(*m*-Benzoylphenyl)decadeuteriodiphenylmethyl Peroxide (IIb). This peroxide was obtained in 81% yield from *m*-(benzoylphenyl)decadeuteriodiphenylmethyl chloride (vide supra): mp 161–162 °C; IR (KBr) 1658 (C=O), 978 and 760 cm^{-1} (peroxide).

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Photochemical Reactions of Arenecarboxylic Acid Esters with Electron-Rich Alkenes: 2 + 2 Cycloaddition, Hydrogen Abstraction, and Cycloreversion

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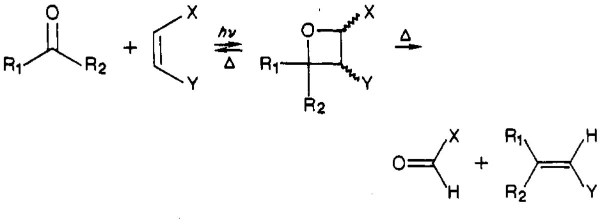
The photochemical reaction of arenecarboxylic acid methyl esters and isopropyl esters with alkenes has been examined and found to afford three types of products: (a) 2-alkoxyoxetanes **3** via a direct 2 + 2 cycloaddition to the substrate alkenes; (b) β,γ-unsaturated ketones **5** via hydrogen abstraction by the carbonyl oxygen of the photoexcited ester from an allylic position of the substrate alkene; and (c) alkoxyalkenes **4**, which arise via 2 + 2 cycloreversion of the oxetanes **3**. The quantum yields for the formation of the various products generally fell in the range 0.005–0.03, approximately 1 order of magnitude less than those of aryl ketones and aldehydes undergoing similar reactions.

Introduction

The photochemical 2 + 2 cycloaddition of ketones and aldehydes to the carbon–carbon double bond of alkenes affording oxetanes is one of the earliest reported organic photochemical reactions.[1,2] The reaction was long neglected, as the product oxetanes seemed to be of little interest or value. However, in the past ten years, this reaction, termed the Paterno–Buchi cycloaddition, has proven to be of considerable synthetic utility. Most of the oxetanes, thereby available, undergo a thermal retro 2 + 2 cleavage at relatively low temperatures. In some cases this thermal 2 + 2 cycloreversion (Carbonyl–Olefin Metathesis, or COM) leads to unsaturated long-chain compounds that are otherwise accessible only with considerably more difficulty, especially in the case of bicyclic oxetanes derived from carbonyl compounds and cyclic alkenes.[3a] Furthermore, aqueous acidic hydrolysis of certain oxetanes, particularly those derived by photochemical addition of carbonyl compounds to furans as olefinic substrates, can provide a convenient and high-yield route to dihydroxy ketones and dihydroxy aldehydes of known relative stereochemistry at three or four contiguous asymmetric centers.[3b]



(1)

Some time ago one of us reported in preliminary fashion that esters of benzoic acid underwent photochemical 2 + 2 cycloaddition to several electron-rich alkenes across the carbonyl group to afford 2-alkoxyoxetanes and their oxetane-derived retro 2 + 2 cleavage (COM) products.[4] These were accompanied by smaller amounts of acyclic ketones formed by an initial hydrogen abstraction, followed by subsequent ground-state free-radical reactions.[4] The details of the various photochemical processes and the results of subsequent studies of the photochemical, thermal, and hydrolytic behavior of the products are reported here.

Results and Discussion

Irradiation through Vycor of hexane solutions of methyl benzoate (or the ethyl or isopropyl esters as well) and excess 2,3-dimethyl-2-butene (**2a**), 2-methyl-2-butene (**2b**), 1,1-dimethyl-2,2-dimethoxyethene (**2c**), 1,2-dimethylcyclohexene (**2d**), and 1,1-diethoxyethene (**2e**) gave oxe-

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